GECH-01

B. Sc. Ist Semester

ELEMENTARY CHEMISTRY

SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY

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CONTENTS

UNIT 1: ATOMIC STRUCTURE

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.

$E = h\nu$ ……….. (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.

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

or $E = mv^2$ (for a particle where $v \neq c$) ……….. (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

$$h\nu = mv^2 \ \ldots\ldots\ldots (1.4)$$

or $\frac{hv}{\lambda} = mv^2$

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

or $\lambda = \frac{h}{p}$ or $(\frac{h}{mv})$ …… (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.

$$mvr = n\frac{h}{2\pi} \ \ldots\ldots\ldots.(1.6)$$

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. 2π r = n λ ………(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

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Putting the value of λ in equation 1.7, we get

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

or $mvr = n\frac{h}{2\pi}$ (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)

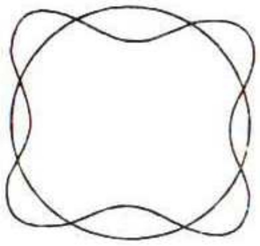


Fig. 1.1 a: in phase

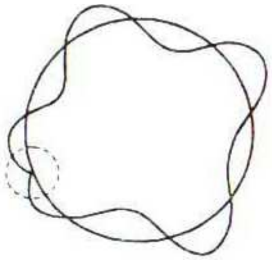


Fig. 1.1 b: out of phase

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:

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

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

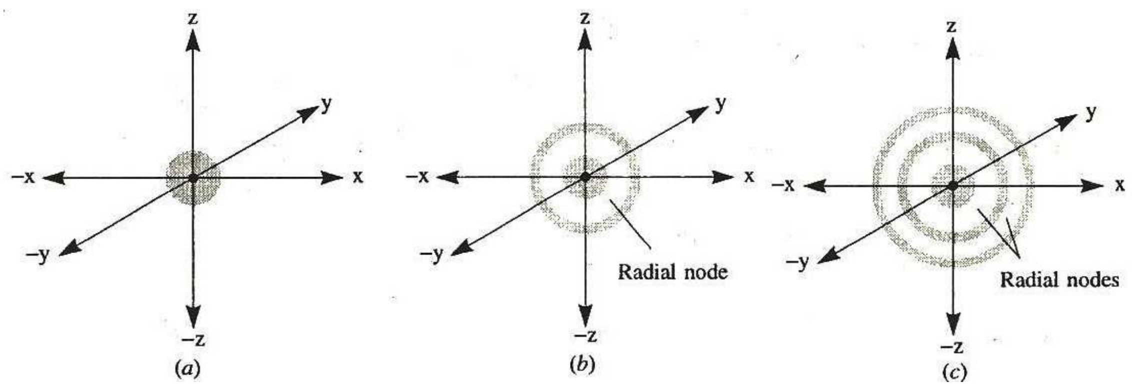
where $\Delta x$is the uncertainty or error in the position of the particle, Δp and Δv are the uncertainties in it's momentum and velocity and h is Planck's constant.

This equation states that the product of Δx and Δp can either be greater than or equal to ($\geq$) 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. 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:



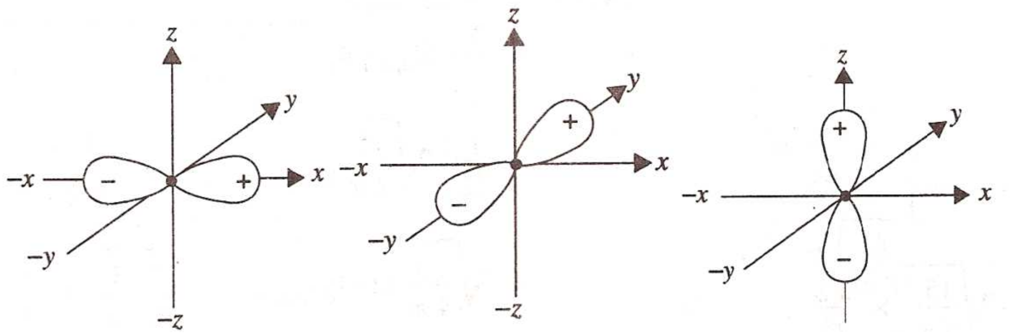
1s-orbital 2s-orbital 3s-orbital

(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. $\Theta_{1,+1} \times \Phi_{+1} - \Theta_{1,-1} \times \Phi_{-1}$ 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 P_y orbital p_z orbital

(a) **(b)** **(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 $\psi(\Theta, \Phi)$ has (+)sign on one lobe and (–)sign on the opposite lobe although $\psi 2 (\Theta, \Phi)$ 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.

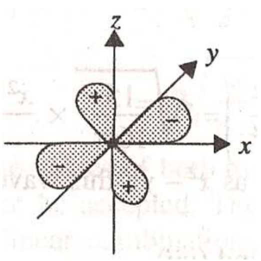
(ii) Each of the three p-orbitals has two lobes on each side of the nucleus which is at the origin of the axes, hence the probability of finding the electron (s) in both lobes is equal. These lobes are separated by nodal planes passing through the nucleus. The electron density on the nodal plane is zero.

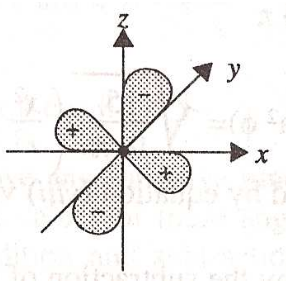
(iii) Greater the value of n (principal quantum number or the shell number), larger is the size of p orbital i.e. 3p orbital is larger in size than 2p orbital though the shapes of both the orbitals are the same.

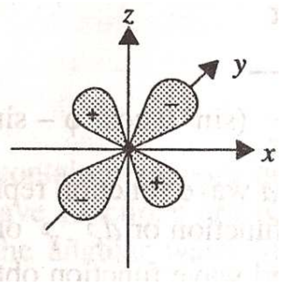
(iv) The energy of the three p-orbitals with the same value of n is same i.e. all the three p-orbitals are degenerate.

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 $\Theta_{2,0}$ x Φ_0 has a real value and corresponds to d_z^2-orbital. For l =2 and m = ±1, we have two angular wave functions, $\Theta_{2,+1}$ x Φ_{+1} and $\Theta_{2,-1}$ x Φ_{-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. $\Theta_{2,+1}$ x Φ_{+1} + $\Theta_{2,-1}$ x Φ_{-1} gives the wave function for d_{zx} (or d_{xz}) orbital and subtraction process, i.e. $\Theta_{2,+1}$ x Φ_{+1} - $\Theta_{2,-1}$ x Φ_{-1}, gives the wave function for dyz, orbital, for l = 2 and m = ±2, we have two wave functions *viz.* $\Theta_{2,+2}$ x Φ_{+2} and $\Theta_{2,-2}$ x Φ_{-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., $\Theta_{2,+2}$ x Φ_{+2} + $\Theta_{2,-2}$ x Φ_{-2}, gives the wave function for d_{x2-y2} orbital and subtraction process i.e., $\Theta_{2,+2}$ x Φ_{+2} - $\Theta_{2,-2}$ x Φ_{-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.

1.6. 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)01234……
Notation for the subshellspdfg……

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.

1.7. 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 ms

For any two electrons in an atomsamesamesamedifferent

orsame samedifferent 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:

nlms

1st electron 100 $+\frac{1}{2}$
For $1s^2$ electrons
2nd electron100 $-\frac{1}{2}$

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:

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

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

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

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

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.

1.8. 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.

1.9. THE AUFBAU PRINCIPLE

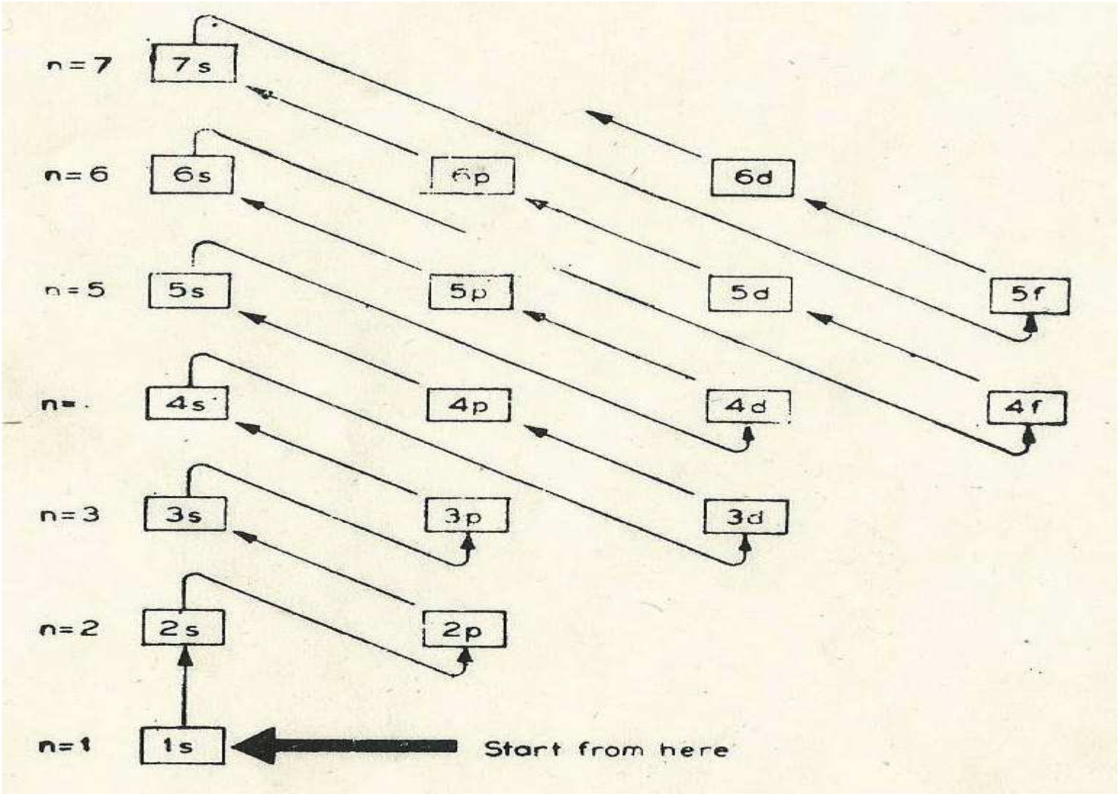
Aufbau is a German word which means building up or construction. The building up of orbitals implies the filling of orbitals with electrons. This principle gives us the sequence in which various orbitals are filled with electrons. The principle can be stated as "**in the ground state of poly electronic 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.

1.10. 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 Electronic Symbol with atomic number Configuration

Scandium Sc (Z = 21) [Ar] $4s^2$ $3d^1$

TitaniumTi (Z = 22) [Ar] $4s^2$ $3d^2$

VanadiumV (Z = 23) [Ar] $4s^2$ $3d^3$

Chromium Cr (Z = 24) [Ar] $4s^1$ $3d^5$

ManganeseMn (Z = 25) [Ar] $4s^2$ $3d^5$

Iron Fe (Z = 26) [Ar] $4s^2$ $3d^6$

Cobalt Co (Z = 27) [Ar] $4s^2$ $3d^7$

Nickel Ni (Z = 28) [Ar] $4s^2$ $3d^8$

Copper Cu (Z = 29) [Ar] $4s^2$ $3d^{10}$

Zinc 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: $4s^2 3d^4 \rightarrow 4s^1 3d^5$ 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 n^{th}s 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.

1.11. 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 ψ2 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.

1.12. 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 $\psi 2$ 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.

ANSWERS

i) Please see de Broglie’s matter waves.

ii) Please see significance of ψ and $\psi 2$.

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 = + or - .

vii) According to Bohr – Burry scheme, the maximum number of electrons in nth shall = 2n2.

∴ In fourth shell, maximum number of electrons = 2x42 = 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 37Rb = [Kr] 5s1 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 5s1 electron. Its quantum numbers are n=5, l= 0, m = 0, s = +

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 = -

xi) 25Mn = $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^5$ $4s^1$

(18) (5) (2)

4s2 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

∴ Zeff = Z – σ = 25- 19.40 = 5-60

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

Z = 46 : 1s2 2s2 2p6 3s2 3p6 4s2 3d10 4p6 5s0 4d10 (observed config.)

Z = 71 : 1s2 2s2 2p6 3s2 3p6 4s2 3d10 4p6 5s2 4d10 5p6 6s2 4f14 5d1

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UNIT 2: PERIODIC PROPERTIES

CONTENTS:

2.1. OBJECTIVES

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.

2.2. 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.

2.3. PERIODIC PROPERTIES

2.3.1Atomic 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:

$$d_{A\text{-}A} = r_A + r_A = 2r_A \ldots\ldots\ldots\ldots\text{(2.1)}$$

$$\text{or } r_A = \frac{dA - A}{2} \ldots\ldots\ldots\ldots \text{(2.2)}$$

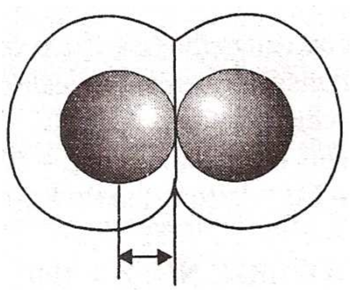
where d_{A-A} is the internuclear distance between two A atoms in A_2 molecules; r_A in equation 3.2 is known as single bond covalent radius of atom A and is used for a gaseous diatomic molecule. For example, internuclear distance (d_{H-H}) in H_2 molecule is 0.74 Å. The covalent radius of H – atom,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

(Å = 10^{-8} cm)

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

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.

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



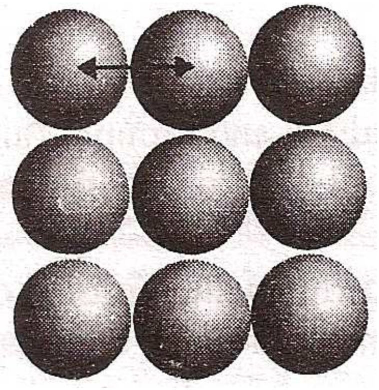


Fig. 2.1 Diatomic molecule Fig. 2.2 Bulk of atoms

(covlalent radius) (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;

$$d_{A-B} = r_A + r_B \text{ (when } \chi_A = \chi_B) \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.3)$$

The internuclear distance, d_{A-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:

$$d_{A\text{-}B} = r_A + r_B - 0.09\,(\chi_B - \chi_A) \quad \ldots\ldots(2.4)$$

(schoemaker and Stevenson)

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

$$d_{A\text{-}B} = r_A + r_B - 0.07\,(\chi_B - \chi_A)^2 \ldots\ldots(2.5)$$

(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 2.1: 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. $r_{cov.} \propto \frac{1}{Zeff}$

(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. $r_{cov.} \propto n$

(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

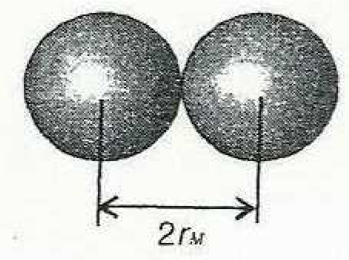


Fig. 2.3 Metallic radius

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 2.2 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 2.2** and **table Table 2.3**

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

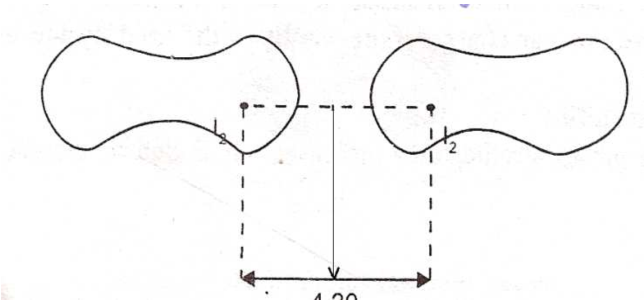


Fig. 2.3 van der Waals' radii

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).

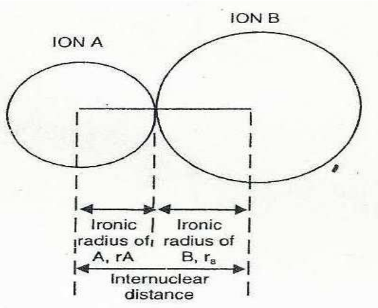


Fig. 2.4 The ionic radius

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.

$d_{C^+ - A^-} = r_{C^+} + r_{A^-}$ …….(2.6)

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^-}

∴ 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. $r_{ion} \alpha \frac{1}{covalent\ character}$.

2.3.2 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:

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

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:

$$(IE)_1 \ll (IE)_2 \ll (IE)_3 \ \ldots\ldots\ldots\ldots\ldots (IE)_{n.}$$

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 2.4: The successive ionization energy values (in kJ/ mole) of the first ten elements

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 $\alpha \frac{1}{n\ or\ r\ atom}$. 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 $\alpha \frac{1}{shielding\ effect}$

(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.

2.3.3 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.

2.3.4 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.

$$A_2 + B_2 = 2\ AB$$

$$\text{Or}\quad \frac{1}{2} A_2 + \frac{1}{2} B_2 = AB \ldots\ldots\ldots (2.8)$$

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)

$$\therefore \Delta = E_{A-B} - \frac{1}{2}(E_{A-A} + E_{B-B}) = 23\,(\chi_B - \chi_A)^2 \text{ (where } \chi_B > \chi_A \text{)} \ldots\ldots.(2.9)$$

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

$$\text{Or}\ \chi_B - \chi_A = 0.208\,\sqrt{\Delta} \ldots\ldots\ldots\ldots\ldots(2.10)$$

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

$$\Delta' = E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2} = 30(\chi_B - \chi_A)^2 \ldots\ldots\ldots(2.11)$$

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

$$\therefore \chi_B - \chi_A = 0.182\,\sqrt{\Delta'} \ldots\ldots\ldots\ldots(2.12)$$

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 2.5: 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:

$$(\chi_A)_{AR} = \frac{0.359\ xZeff}{r^2} + 0.744 \ldots\ldots\ldots\ldots(3.13)$$

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

$$(\chi_A)_{AR} = \frac{0.359\ x(Z-\sigma)}{r^2} + 0.744 \ldots\ldots\ldots\ldots(2.14)$$

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 2.6: 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	Mg	Al	Si	P	S	Cl	Ar

1.01	1.23	1.47	1.74	2.06	2.44	2.83	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 = $\frac{I_E+E_A}{2}$…………(2.15)

He proposed two relations for obtaining the electronegativity:

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

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

$$= 0.187 \frac{(I_E+E_A)}{2} + 0.17 \quad \ldots\ldots\ldots(2.16)$$

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

$$\chi_A = \frac{I_E+E_A}{540} \quad \ldots\ldots\ldots..(2.17)$$

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 = $[1-e^{0.25(\chi_B-\chi_A)}]$ % ………(2.18)

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

Ionic Character in A - B bond = $[\,16\,(\chi_B-\chi_A)+3.5\,(\chi_B-\chi_A)^2]$ % $(\chi_B>\chi_A)$….(2.19)

(ii) To calculate the bond length

In a heterodiatomic molecule of AB type, the bond length $d_{A\text{-}B}$ 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.*

$d_{A-B} = r_A + r_B - 9\,(\chi_B-\chi_A)$ $(\chi_B>\chi_A)$ …………..(2.20)

(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 ($\chi_{Cl} = 3.0$) and $\chi_I = 2.5$ 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.

2.4TRENDS 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.

2.5 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

2.6 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?

2.7. 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.

UNIT 3: CHEMICAL BONDING

CONTENTS:

3.1 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.

3.2 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.

3.3 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:HH-H
Cl:ClCl-Cl$^{\textbf{single bond}}$
H:ClH-Cl
O::OO=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

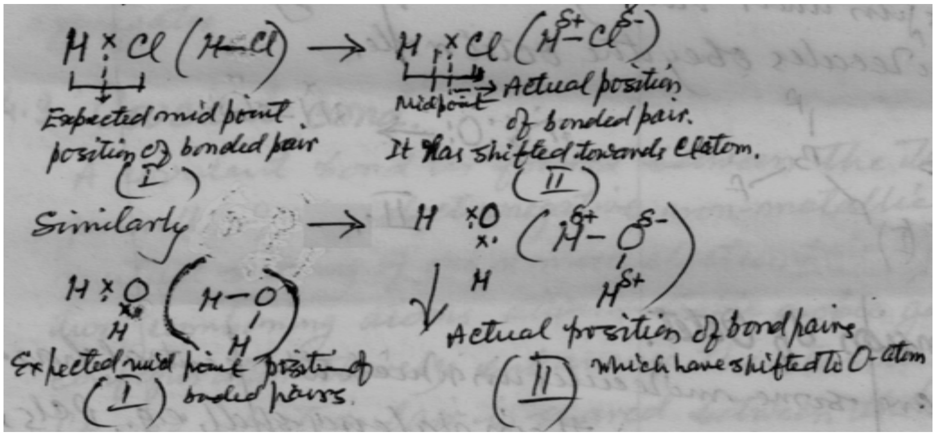
Bond length: triple bond < double bond < single bond

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 midpoint 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,



3.3.1. 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 neutralized. 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.

$\Psi = \Psi_A(1).\ \Psi_B(2)$ ……(3.1)

and the energy of the system by

$E=E_A+E_B$ …….(3.2)

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:

$\Psi = N(C_1\Psi_1+C_2\Psi_2+C_3\Psi_3+\ldots\ldots)$ …..(3.3)

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

$\Psi=\Psi_A(1).\ \Psi_B(2)$ ……(3.1 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:

$\Psi_s= \Psi_A(1).\ \Psi_B(2) + \Psi_A(2).\ \Psi_B(1)$……..(3.4)

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:$\Psi_a= \Psi_A(1).\ \Psi_B(2) - \Psi_A(2).\ \Psi_B(1)$ …….(3.5)

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 3.1)***

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.

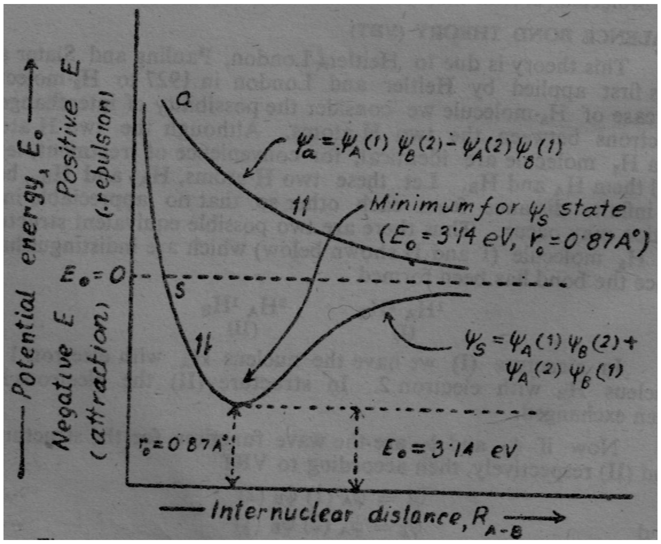


Fig 3.1

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 $\Psi_{(1)} = \Psi_A(1).\ \Psi_A(2)$ …..(3.6)

And $\Psi_{(2)} = \Psi_B(1).\ \Psi_B(2)$ ……(3.7)

The consideration of ionic structures as given above of H_2 molecule converts the equation 3.4 to

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

or $\Psi s = [\Psi_A(1).\ \Psi_B(2) + \Psi_A(2).\ \Psi_A(1)] + \lambda[\Psi_A(1).\ \Psi_A(2) + \Psi_B(1).\ \Psi_B(2)]$ ..(3.8)

or $\Psi s = \Psi cov. + \Psi ionic$ …..(3.9)

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 behavior 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.

3.3.2 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.

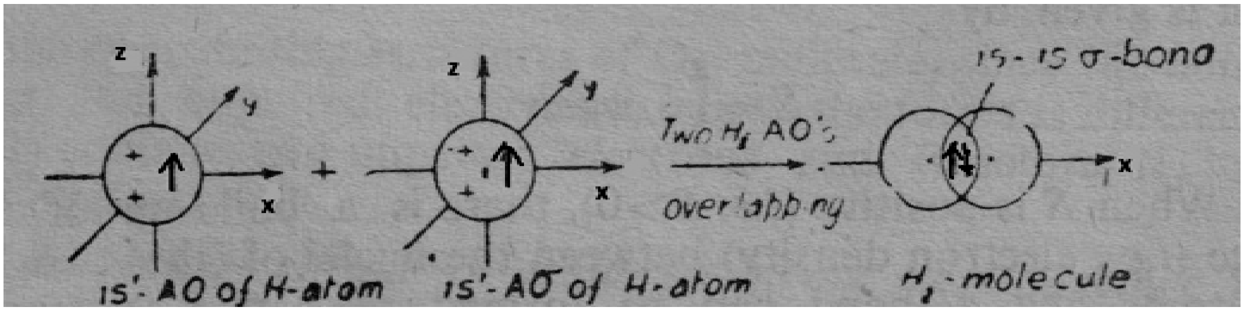


Fig 3.2 ovrelapping of two s-orbitals along molecular axis

(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.

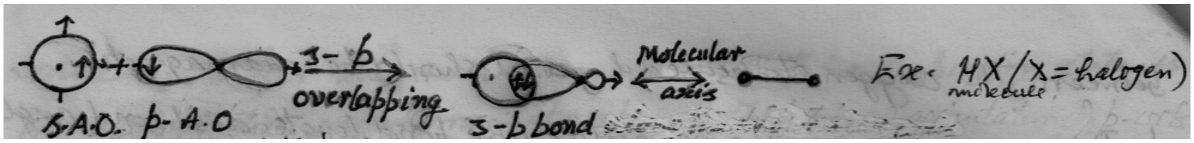


***Fig 3.3** overlapping of s and p orbitals along molecular axis*

(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.

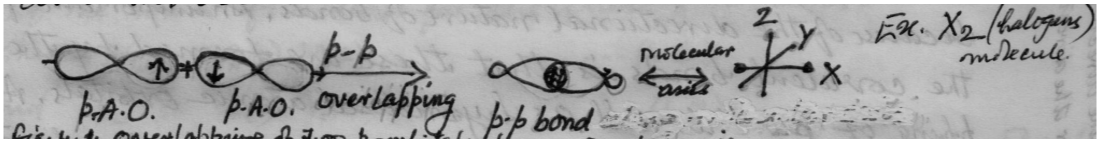


***Fig 3.4** overlapping of two p-orbitals along molecular axis*

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

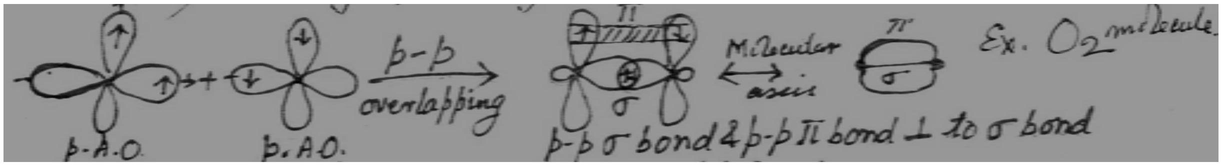


***Fig 4.5** overlapping of orbitals forming σ and πbonds*

(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^{3}d (PCl_5), p-sp^{3}d^2 (SF_6) p-sp^{3}d^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.

3.3.3 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

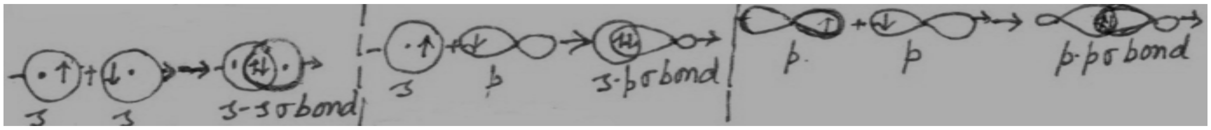


Fig 3.6(a) *formation of σbond by atomic orbitals*

(ii)Hybrid atomic orbital – hybrid atomic orbital overlapping

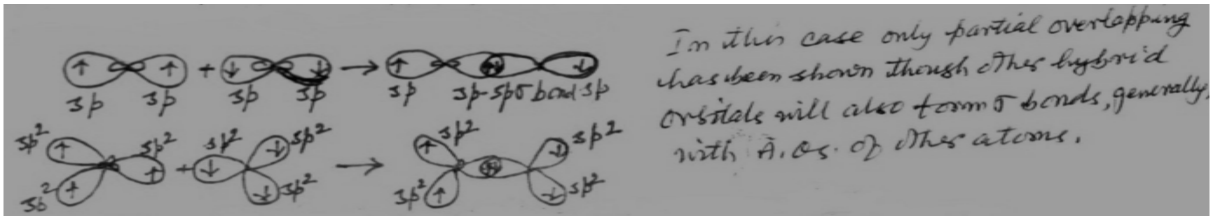


Fig 3.6(b) *formation of σbond by hybrid orbitals*

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.

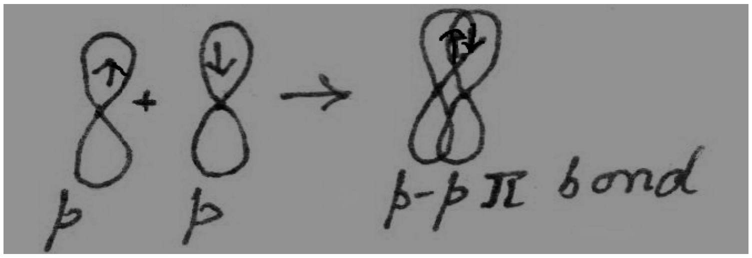


Fig 3.7 *formation of πbond by lateral overlapping of atomic orbitals*

For σ and π bonds, the following points are important:

(i) A σ bond 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 σ bond is stronger than a π bond due to greater extent of overlapping of orbitals along the inter nuclear axis than in lateral overlapping.

(iii) A σ bonds 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 σ bond because the electron cloud overlaps symmetrically along the internuclear axis while this is not possible about a π bond because the electron clouds overlap above and below the plane of the atoms.

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

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

3.4. 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_6 etc.

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.

3.4.1. 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:

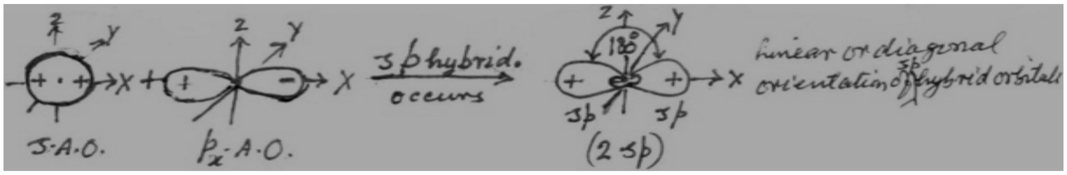


Fig 3.8 (a) *Formation of two collinear sp hybrid orbitals from the mixing of one s and one p atomic orbitals*

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}: $\underline{2s^1p^1}\longrightarrow$

sp

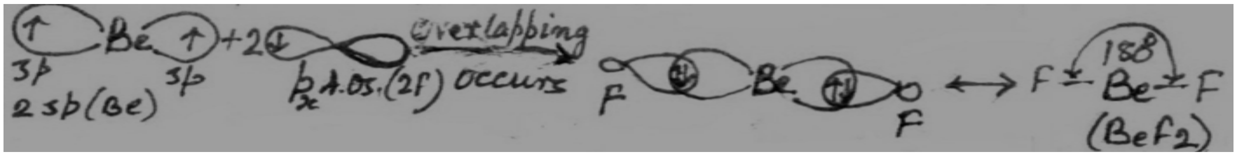


Fig 3.8 (b) *formation of two σ covalent bonds by the overlapping of sp-hybrid orbitals of Be and 2p-orbitals of F-atoms*

(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:

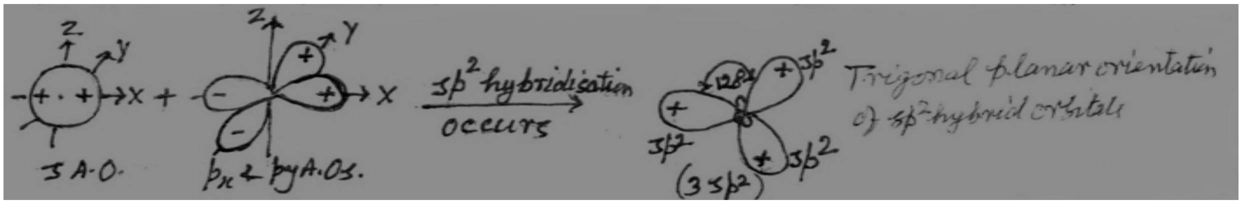


Fig 3.9(a) Formation of three trigonal planar sp^2 hybrid orbitals from the mixing of one s and two p atomic orbitals

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}: $2s^1p_x^1p_y^1 \longrightarrow$ ________ sp^2

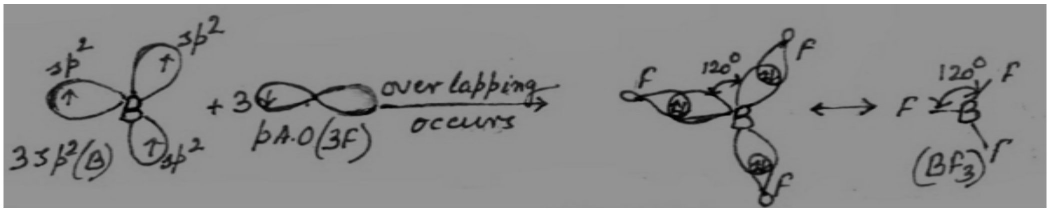


Fig 3.9(b) formation of three σ covalent bonds by the overlapping of sp^2 hybrid orbitals of B-atoms and 2p-orbitals of 3F-atoms

(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:

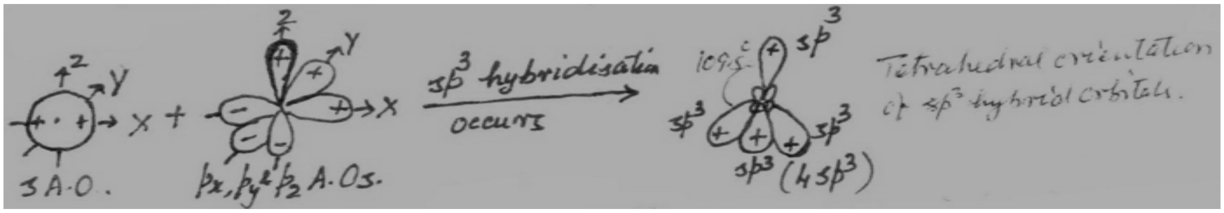


Fig 3.10(a) *formation of four tetrahedral sp*^{3} *hybrid orbitals from the mixing of 1s and 3p atomic orbitals*

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^3hybridisation as follows:

C_g:$2s^2\ p_x^1 p_y^1 p_z^0$ C_{ex}:$2s^1 p_x^1 p_y^1 p_z^1 \rightarrow$ ____________

sp^3

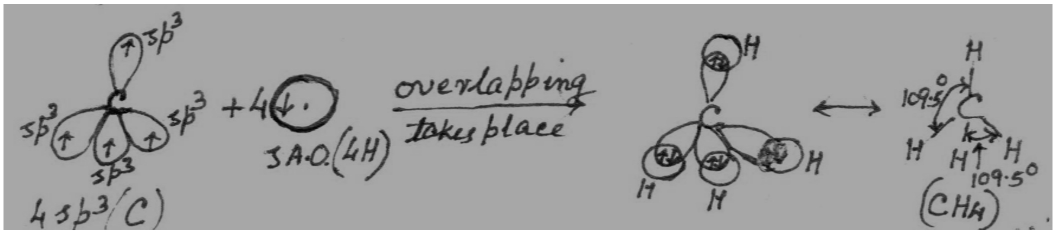


Fig 3.10 (b) *formations of four σ covalent bonds by the overlapping of sp*^{3} *hybrid orbitals of C-atom and 1s orbitals of four H-atoms*

(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:

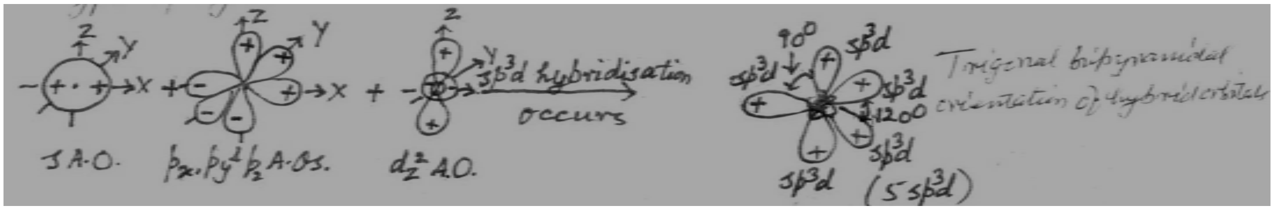


Fig 3.11 (a) formation of five trigonal tripyramidal sp^3d *hybrid orbitals from the mixing of one s, three p and one d* (dz^2) *atomic orbitals*

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: $3s^2\ p_x^1 p_y^1\ p_z^1$ p_{ex}: $3s^1\ p_x^1 p_y^1 p_z^1 \rightarrow d_{z2}^1$ ________________

sp^3d

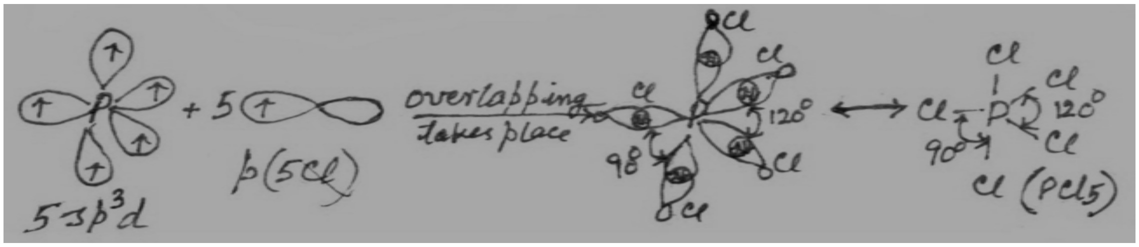


Fig 3.11(b) Formation of five σ covalent bonds by the overlapping of sp^3d *hybrid orbitals of P central atom and p-orbitals of five Cl-atoms*

(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:

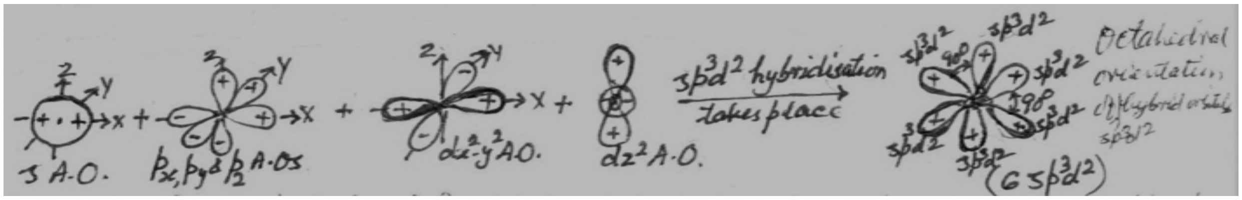


Fig 3.12(a) *Formation of six sp^3d^2 hybrid orbitals from the mixing of one s, three p and two d-atomic orbitals*

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: $3s^2p_x^{\ 2}p_y^{\ 1}p_z^{\ 1}$ $\longrightarrow$ S_x: $s^1p_x^{\ 1}\underline{p_y^{\ 1}p_z^{\ 1}\ d^1_{z2}d^1_{x2-y2}}$

sp^3d^2

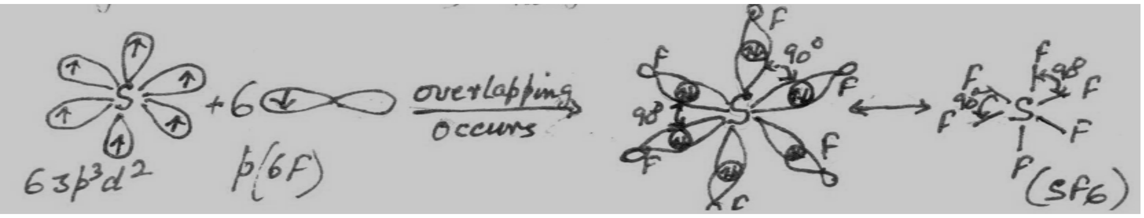


Fig 3.12 (b) *Formation of six σcovalent bonds by the overlapping of sp^3d^2 hybrid orbitals of S central atom with p-orbitals of six F atoms*

(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:

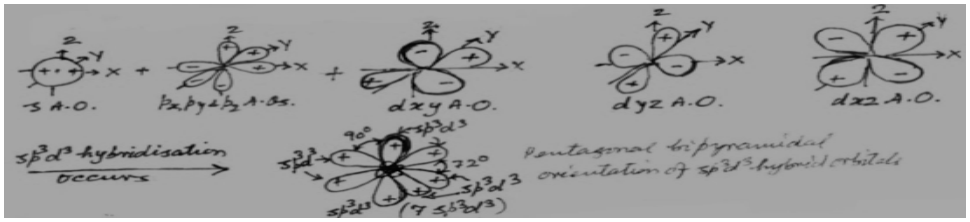


Fig 3.13 (a) *Formation of seven sp^3d^3 hybrid orbitals from the mixing of one s, three p and three d-orbitals of the central atom*

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)

$I_g : 5s^2p_x^2p_y^2p_z^1 \longrightarrow I_{ex} : \underline{5s^1p_x^1p_y^1p_z^1dxy^1dyz^1dzx^1}$

sp^3d^3

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

Fig 3.13(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*

3.4.2 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.

3.5. 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)∠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 ∠HOH and ∠HSH in H_2O and H_2S molecules. It has been observed that∠HOH $(104.5^0) >> $∠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: $5s^2 5p_x^1 p_y^1 p_z^0$ → sp^2 hybridization

This atom undergoes partial hybridisation mixing up together the paired 5s and unpaird $5p_x$ 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:

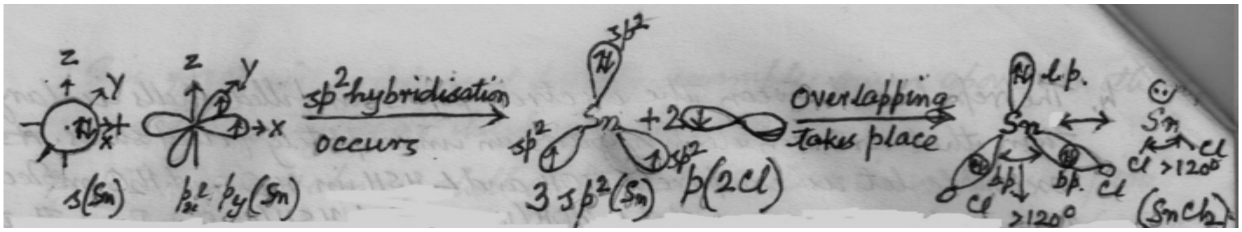


Fig 3.14 *Formation of hybrid orbitals and their overlapping with 3p-orbitals of Cl atoms to give $SnCl_2$ molecule*

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 : $2s^2 p_x^1 p_y^1 p_z^1$ → 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).

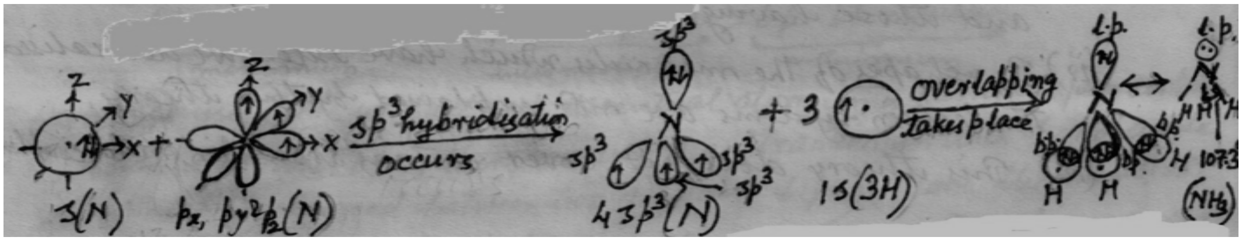


Fig 3.15 *Formation of hybrid orbitals and their overlapping with 1s orbitals of 3H atoms to give NH_3 molecule*

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: $2s^2p_x^2p_y^1p_z^1 \quad \rightarrow \quad sp^3$ 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).

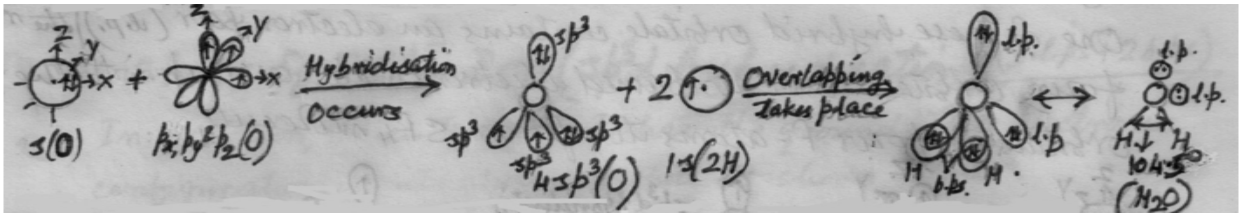


Fig 3.16 *Formation of hybrid orbitals and their overlapping with 1s orbitals of two H-atoms to give H_2O molecule*

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:

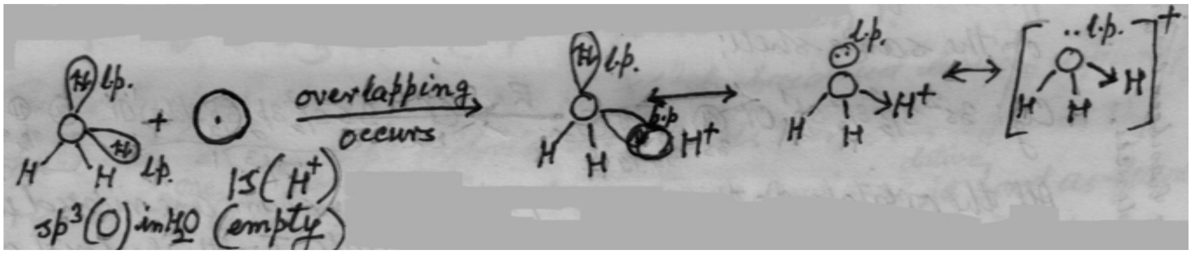


Fig 3.17 Overlapping of filled sp^3 hybrid orbital of O-atom in H_2O and empty 1s orbital of H^+ ion to form H_3O^+ ion

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^{3}d 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^{3}d →

All these atomic orbitals of S_{ex} central atom get hybridised to give five sp^{3}d 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.

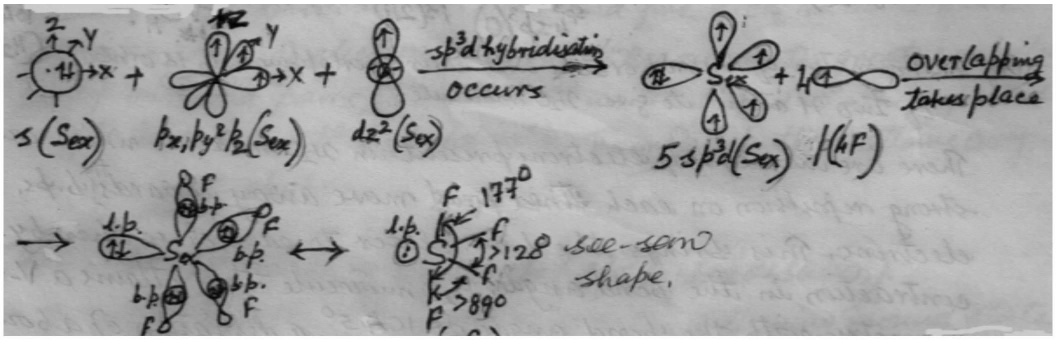


Fig 3.18 Formation of five hybrid orbitals of S_{ex} atom and their overlapping with p-orbitals of four F-atom to give SF_4 molecule

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

All the orbitals of the valence shell of $C_1{}^{st}{}_{ex}$ 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):

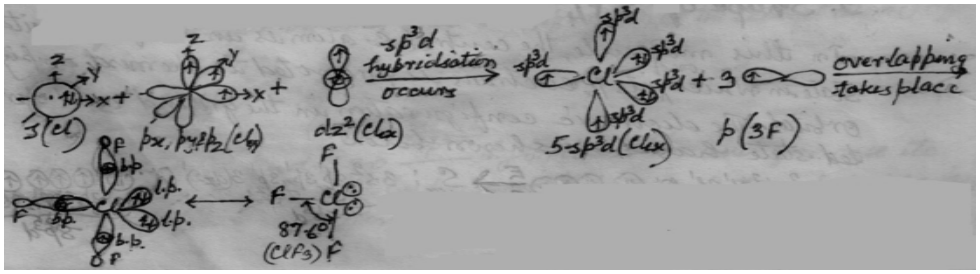


Fig 3.19 *Formation of five hybrid orbitals of Cl atom and their overlapping with p-orbitals of three F-atoms to give ClF_3 molecule*

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:

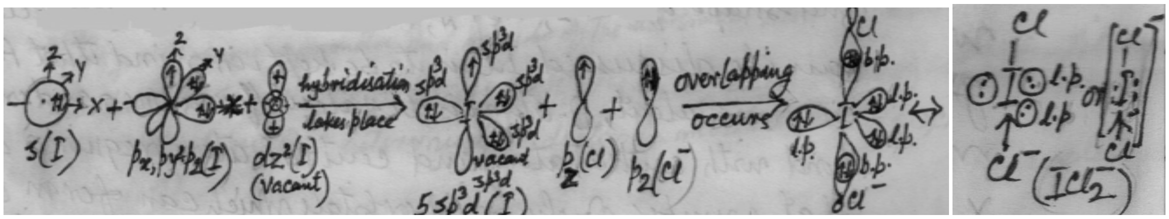


Fig 3.20 Formation of five sp^3d hybrid orbitals of central atom, I and overlapping of one of these hybrid orbitals with p-orbital of Cl atom and that of filled p-orbital of *Cl^- ion with vacant hybrid orbital of I atom*

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:

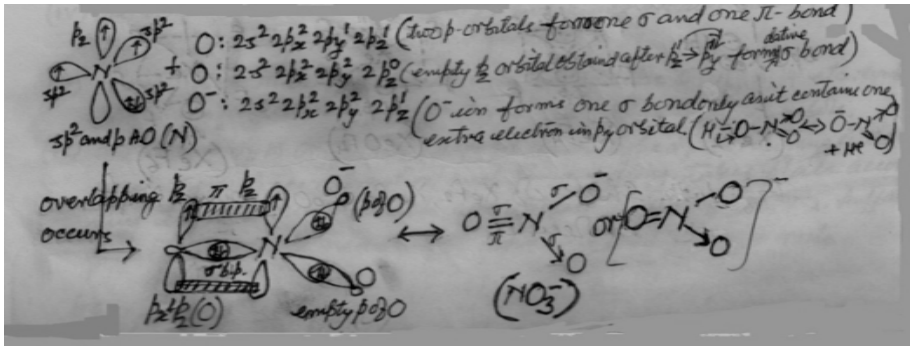
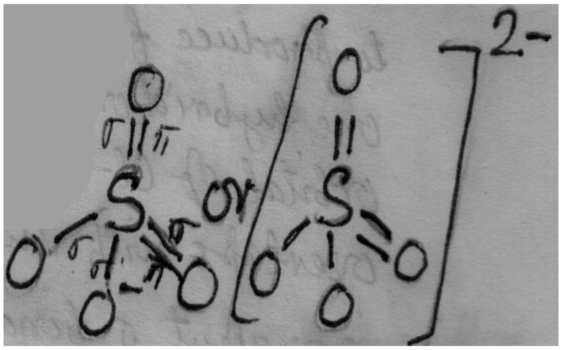


Fig 3.21 Formation of two normal σ bonds, one dative σ bond and one π bond between N central atom and oxygen atoms/ion

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 σ bonds 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 π bond and is square pyramidal

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

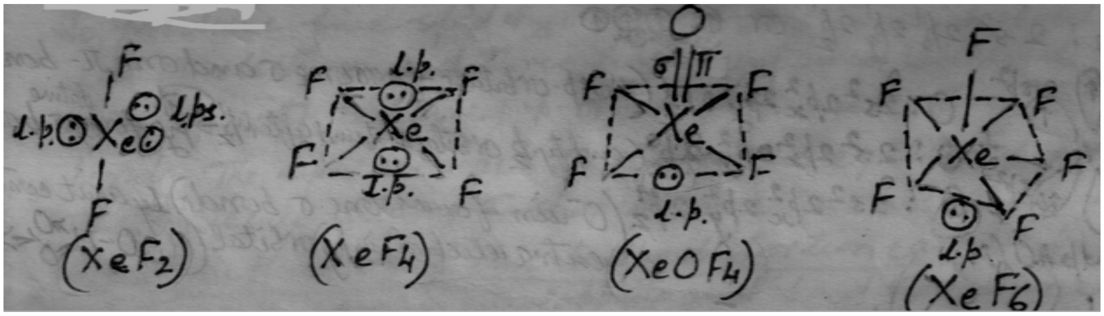


Fig 3.22 *Shapes of* XeF_2, XeF_4, $XeOF_4$ *and* XeF_6 *molecules*

3.6. 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 hybridization has been fruitfully discussed with examples as well as shapes of inorganic molecules and ions based on hybridization 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.

3.7.TERMINAL QUESTIONS

i)The d-orbital involved in sp^3d hybridization 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 hybridized. 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 them electronic configuration of O_2, O_2^+ and O^-_2 and predicts the bond order and magnetic behavior.

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 behavior.

xii) XeF_2 molecule is linear though Xe atom in this molecule undergoes sp^3d hybridization. Explain.

3.8. 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

UNIT 4: COORDINATION COMPOUND

CONTENTS:

4.1 OBJECTIVES

By the end of this Unit, you will be able to define the following terms:

- Coordination compound,
- Ligand,
- Coordination number (CN),
- Complex ion
- Nomenclature of Coordination compounds
- Valence Bond Theory (VBT) and discussion of inner and outer orbit complexes

4.2 INTRODUCTION

The compounds that can easily dissociate into their constituent ions in aqueous medium are called simple salts and double salts such as NaCl, $MgCl_2$, $FeSO_4.(NH_4)_2SO_4.6H_2O$, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, etc. On the other hand, the compounds which do not dissociate into their constituent ions in any solvent are known as coordination or complex compounds such as $[Cu(NH_3)_4]^{2+}$. Transition metals have an ability to form a number of coordination compounds due to their small size, high charge and presence of empty d orbitals on the metal ion. A compound formed from the union of metal ion (an electron deficient species, central metal atom/ion; Lewis acid) and electron rich species (ligand; Lewis base) which can donate one electron pair is called coordination compound or complex compound. The coordination compounds can be represented by the general formula, $[ML_n]^{\pm m}$, where M is a metal ion, L is electron rich species; n is the number of L attached to the metal atom/ion and m is the charge on complex ion.

Some metal complexes were prepared and used in the eighteenth century in the form of metal salts and vegetable extracts as paints. The first well known coordination compound was Prussian blue, $Fe_4[Fe(CN)_6]_3$ in the beginning of eighteenth century. In 1798, $CoCl_3.6NH_3$ was discovered. Werner gave a theory to understand the bonding in such compounds about a century later in 1893. We are studying chemistry of coordination compounds because they have many applications in analytical / environmental chemistry, metallurgy, biological systems, industries and medicine.

4.3 LIGANDS AND THEIR TYPES

The electron rich species, which may be charged species, e.g. Cl^-, CN^-, NO_2^-, etc or neutral species e.g. H_2O, NH_3, $NH_2CH_2C_2NH_2$, CO, NO, etc., that can donate an electron pair to the metal atom/ion are called ligands.

4.3.1 Types of ligands

The ligands can be classified in the following ways:

4.3.1.1 Type I- Based on electron accepter/donor properties of the ligand

- **σ (sigma) donor ligands** are those ligands which can only donate electron pair to the meal ion, e.g. H_2O, NH_3, F^-. These ligands are also known as weak field ligands.
- **σ (sigma) donor and Π (pi) accepter ligands** are those ligands which can donate electron pair and also have a tendency to accept electron in their empty antibonding π molecular orbitals (MO). Such ligands can involve in backbonding (π bond) with the metal ion. For example, CO, CN^-, NO, etc. These ligands are also known as strong field ligands.

- **Π (pi) donor ligands are those ligands** like benzene and ethylene, which do not have lone pair of electrons but only π electrons for donation to the metal atom/ion.

4.3.1.2 Type II- Based on the basis of number of donor atoms in the ligand

- **Monodentate or unidentate ligands**
  The ligands that bound to a metal ion through a single donor atom are called as monodentate or unidentate ligands, e.g. Cl^-, H_2O or NH_3. These ligands can be further divided into the following subclasses on the basis of charge (**Figure 6.1**).
- **Ambidentate ligands**
  Some ligands have two or more than two different donor atoms. These ligands can attach through any of the donor atoms. They are given different names depending upon nature of the donor atom linked to the metal atom. These ligands are known as ambidentate ligands e.g. NO_2 (donor atom may be either N or O), SCN^- (donor atom may be either S or N), CN^- (donor atom may be either C or N), $S_2O_3^{2-}$ (donor atom may be either S or N). These are also monodentate ligands.

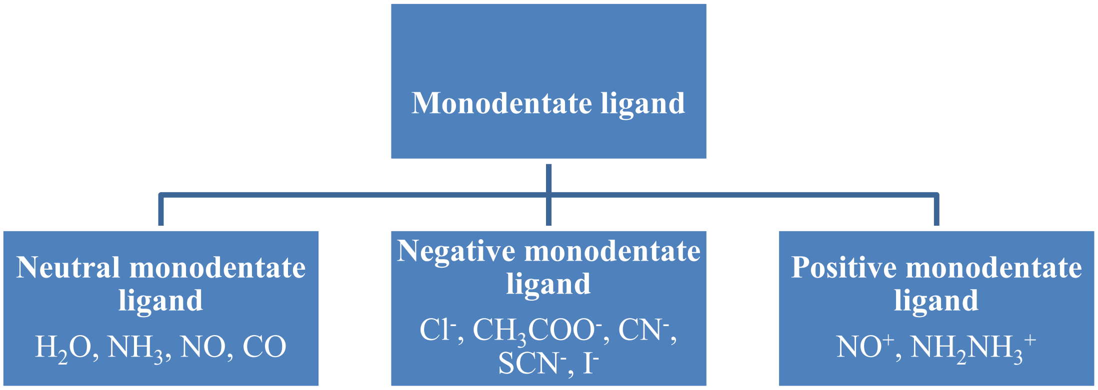
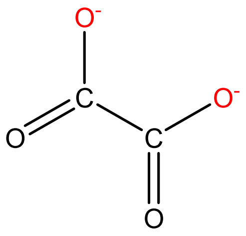
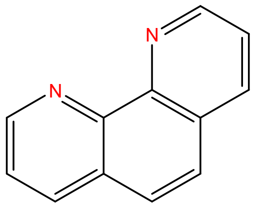
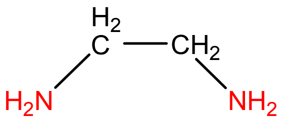


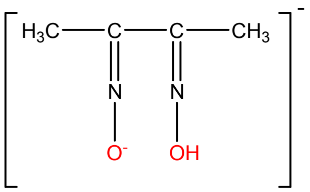
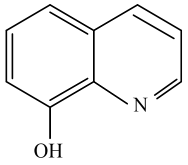
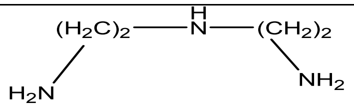
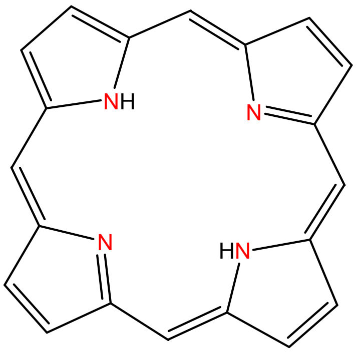
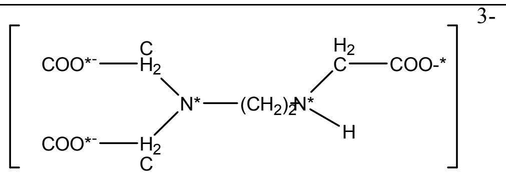
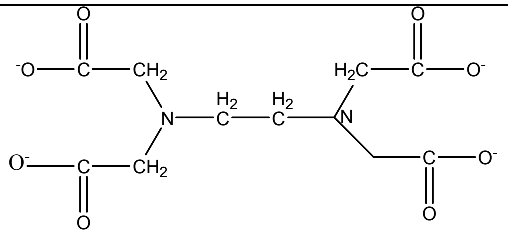
Figure 4.1: Classification of monodentate ligands

- **Polydentate (bidentate, tridentate, tetradentate, pentadentate, hexadentate) ligands**

These ligands bind to a metalatom/ion through two, three, four, five and six donor atoms, respectively. These ligands are also known as chelating ligands. These ligands form ring type (chelates) compounds (**Table 4.1**).

Table 4.1: Polydentate ligands

Ligand type	Ligand name	Ligand formula/structure
Bidentate	oxalate ion	
	1,10-phenanthroline	
	ethylenediamine (en)	
	dimethylglyoxime	
	8-hydroxyquinoline	

		 
Tridentate	diethylenetriamine	
Tetradentate	triethylenetetramine porphyrin ring	$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$ 
Pentadentate	ethylenediaminetriacetato	
Hexadentate	ethylenediaminetetraacetate (EDTA)	

Red colour letter in the structure represents the donor atom of the ligand.

4.3.1.3 Type III- Based on size of ligand

- **Chelating ligands** are those ligands that bind via more than one atom and form chelate complexes (ring complexes). These complexes are more stable than complexes formed from monodentate ligands. The enhanced stability is known as the chelate effect.

- **Macrocyclic ligands** are the chelating ligands that can form a large ring and surround the central atom or ion partially or fully and bond to it. The central atom or ion resides at the centre of the large ring. This complex formed is more rigid and inert as compared to the chelate compound and is known as macrocyclic complex. Heme is a macrocyclic complex in which the central iron atom is present at the centre of a porphyrin macrocyclic ring. Dimethylglyoximate complex of nickel is a synthetic macrocycle formed from the reaction of nickel ion with dimethylglyoxime (**Fgure 4.2**) in ammonical medium.

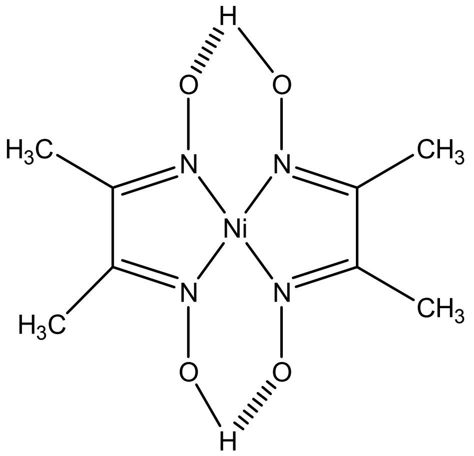


Figure 4.2: Nickel(II) bisdimethylglyoximate

The order of ligands to form stable compounds: Macrocyclic > Chelate > Monodentate

4.3.1.4 Type IV- Based on their use in reactions

- **Actor ligands** are those ligands which take part in chemical reaction.

- **Spectator ligands are tightly coordinating polydentate liangds** which do not take part in a chemical reaction. Phosphines, allyl groups in catalysis, trispyrazolylborates (Tp), cyclopentadienyl ligands (Cp) and many chelating diphosphines such as 1,2-bis(diphenylphosphino) ethane ligands (dppe) are spectator ligands.

4.2.2 Complex ion

A complex ion is an ion in which the metal ion is present at the center and a definite number of ligands surround it. The complex ion is enclosed in a large bracket. e.g.$[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$

4.2.3 Coordination number (CN)

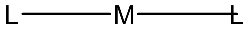
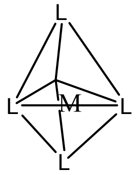
The coordination number of a metal atom/ion is the number of ligands attached to it in a complex compound. Coordination number may be two, three, four, five, six, seven, eight, nine or even higher in case of lanthanides and actinides (**Table 4.2**). Coordination number depends on size, charge and electronic configuration and nature of meal/ion and ligands. For example,

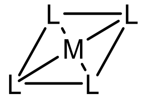
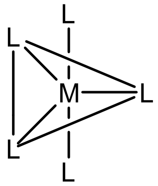
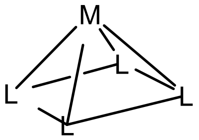
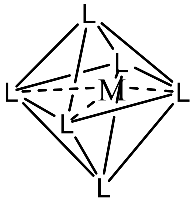
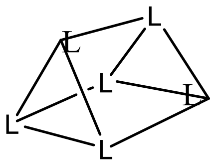
– large metal atoms show high CN

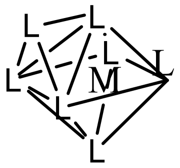
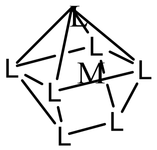
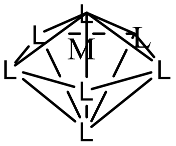
– bulky ligands reduce coordination number

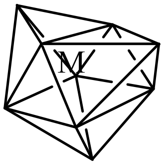
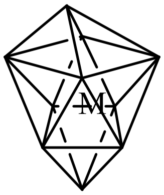
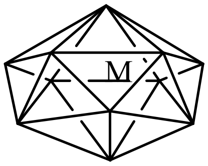
– Lewis bases easily donate electrons to metals and metals with lesser number of electrons can easily accept electrons.

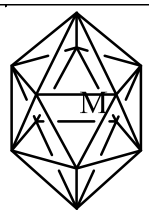
Table 4.2: Coordination numbers (CN) and geometry of coordination compounds

S.N.	CN	Metals	Ligands	Type of geometry	Geometry of complex
1.	2	d-electron rich metals like Cu^+, Ag^+ $[Ag(NH_3)_2]^+$ $[Cu(NH_3)_2]^+$ (uncommon)	Large ligands CH_3	Linear	
2.	4	Small, high oxidation state, lower d metals	Large	Tetrahedral	

		d^8 metal atoms or ions such as Ni^{2+}, Rh^+, Ir+, Pt^{2+}, Pd^{2+}, $Au^{3+, 6+}$ $[Cu(NH_3)_4]^{2+}$ $[Zn(CN)_4]^{2-}$	Pi bonding ligands	Square planar	
3.	5	Allows fluxionality and Berry pseudorotation $[Ni(CN)_5]^{3-}$ (Rare)		Trigonal bipyramidal Square pyramidal	 
4.	6	$[Fe(H_2O)_6]^{2+}$ $[Ni(NH_3)_6]^{2+}$ $[Fe(CN)_6]^{4-}$ (Very common) (Rare)	All types of ligands Three bidentate ligands such as dithiolates or oxalates	Octahedral Trigonal prismatic	 

5.	7	Generally shown by rare earths $K_3[NbOF_6]$ (Very rare) Uncommon		Capped octahedron Capped trigonal prism Pentagonal bipyramid	  
6.	8	Generally shown by rare earth metal ions (Very rare) Large metal ions (Rare) Uncommon	For eight equivalent ligands	Dodecahedron Cube Square antiprism	

		Common		Hexagonal bipyramidal	
7.	9	Very rare		Three-face centred trigonal prism (Tricapped trigonal prism)	
8.	10	Generally shown by rare earth elements		Bicapped square antiprism	
9.	11	Very rare		All-faced capped trigonal prism (Octadecahedron)	

10.	12	Generally shown by rare earths		Icosahedron	

4.2.4 Coordination sphere

The coordination sphere of a coordination compound comprises the central metal atom/ion and ligands attached to it. The coordination sphere is enclosed in brackets [ ].Coordination sphere $[Co(NH_3)_6]^{3+}$

4.2.5 Counter ions:

The ions excluding the coordination sphere are called as counter ions. In $K_4[Fe(CN)_6]$ compound, K^+ is the counter ion.

4.4 DEFINITIONS

Chelate: Chelate is a compound containing a ligand (typically organic) bonded to a central metal atom at two or more points.

Complex ion: A complex ion is an ion formed by the coordination of central metal ion with one or more ligands.

Coordination compound: A compound in which a central atom/ion is bonded to a definite number of ligands.

Coordination number: It is the number of ligands surrounding the central metal ion.

Effective Atomic Number: It is the sum of the electrons of metal atom/ion and electrons donated by ligand.

Ligand- Ligand is a charged or neutral molecule which can done electron pair to the metal atom to form a coordination compound.

Primary valency: Primary valency in a coordination compound is the number of negative ions that satisfy the positive charge on the central metal ion.

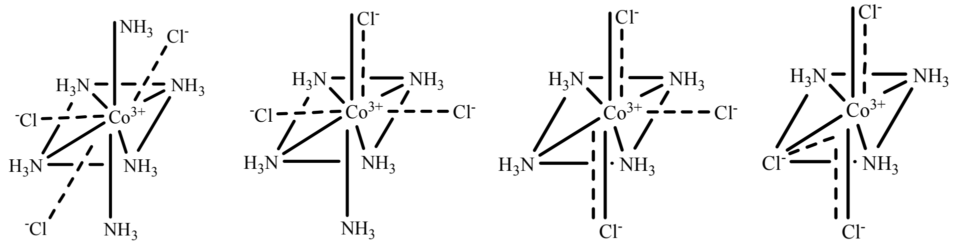
Secondary valency: Secondary valency in a coordination compound is defined as the number of ligands that are coordinated to the central metal ion. It is equal to the coordination number.

4.5 WERNER'S COORDINATION THEORY

Alfred Werner in 1893 suggested a new theory for explaining the nature of bonding in coordination compounds known as Werner's theory. According to this theory, there are two kinds of valences of metal atom/ion in coordination compounds: primary and secondary valences

- The attachment of species that satisfy both primary as well as secondary valences is shown by $\overline{\text{------}}$ solid-broken line

  Explanation of structure of Co(III) complexes on the basis of Werner's theory (**Figure 4.3**).



(a) (b) (c) (d)

Figure 4.3 Structure of Co(III) amine complexes on the basis of Werner's theory. In all the complexes the primary valency of Co is 3 and secondary valency is 6. (a) $CoCl_3.6NH_3$ $[Co(NH_3)_6]Cl_3$ (b) $CoCl_3.5NH_3$ $[Co(NH_3)_5Cl]Cl_2$ (c) $CoCl_3.4NH_3$ $[Co(NH_3)_4Cl_2]Cl$ (d) $CoCl_3.3NH_3$ $[Co(NH_3)_3Cl_3]$

Werner's theory can be explained on the basis of experimental evidences

- **Molar conductivity measurement method**

Compounds $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_3Cl_3]$ show decreasing order of conductivity due to the formation of 4 ions, 3 ions, 2 ions and no ions, respectively in solution.

$[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$ (1 complex ion + 3 chloride ions)

$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$ (1complex ion +2chloride ions)

$[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$ (1 complex ion+1chloride ion)

$[Co(NH_3)_3Cl_3] \longrightarrow [Co(NH_3)_3Cl_3]$ (No ions)

- **Precipitation method**

  When cobalt ammine chloride complexes react with $AgNO_3$, some of the Cl^- ions get precipitated with $AgNO_3$ to form AgCl. The number of Cl^- ions that are ionisable and present outside the coordination sphere can react with $AgNO_3$. Thus, coordination compounds $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$ react with 3, 2 and 1 mole of $AgNO_3$ to form 3, 2 and 1 mole of AgCl, respectively as there are 3, 2 and 1 ionisable Cl^- ions, respectively.

Defects of Werner's theory

- Although the theory describes the structure of many compounds, it can't explain the nature of bonding between metal atom/ion and ligands.
- Werner's theory was unable to explain why 4- and 6-coordination numbers are the preferred coordination numbers.

4.6 NOMENCLATURE OF COORDINATION COMPOUNDS

The coordination compounds are named according to the following steps suggested by IUPAC (International Union of Pure and Applied Chemistry) (**Figure 4.4**).

Step I: Naming of ions

- The positively charged metal ion is written first followed by the negative ions in **ionic compounds**.

- $FeCl_2$: Iron (II) chloride
- KCl: Potassium (I) chloride

- Name of **non-ionic or molecular complexes** are written as one word without any gap.
  - $K_4[Fe(CN)_6]$: Potassium (**positive ion**) hexacyano(ligand)ferrate (**central ion**)(III) (non ionic compound)

- $[Pt(NH_3)_4]^{4+}$: Tetraammineplatinum (IV)

The name in red is one word without any gap as it is a complex ion.

Step II: Naming coordination sphere

In case of the complex ion (coordination sphere), name of ligands written first than only central metal atom/ion along with its oxidation number in parenthesis should be written.

$[Ni(CO)_4]$ - Tetracarbonylnickel(0)

$[Pt(NH_3)_4]^{4+}$ - Tetraammineplatinum(IV)

Ending of name: If the complex is anionic, the suffix **ate** is added to the name of metal along with oxidation state in parenthesis.

$K_2[HgCl_4]$ Potassium tetrachloridomercur**ate**(II)

Step III: At the last, the name of anion which is present on the outside of the coordination sphere should be written, e.g.,

$[Pt(NH_3)_4]Cl_4$ - Tetraammineplatinum(IV) **chloride**

$[Co(NH_3)_6]Cl_3$ - Hexaamminecobalt(III) **chloride**

Names of some common ligands

Ligands are named alphabetically along with a prefix (di, tri, tetra, penta etc for simple ligands and bis, tris, tetrakis etc. for complicated ligands) of their number. Some of the common ligands are given in **Table 4.3.**

Table 4.3: Name and abbreviation of ligands

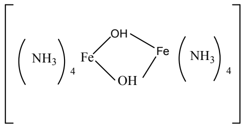
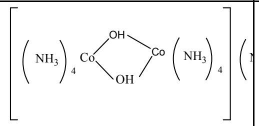
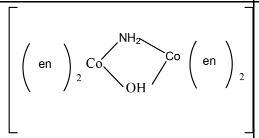
Type of ligands	Category of ligand	Formula	Name
Simple ligands	Neutral (written as a neutral molecule)	H_2O	Aqua
		NH_3	Ammine
		CO	Carbonyl
		NO	Nitrosyl
	Anionic (-o at the end of ligand's name) Cationic (-ium at the end of ligand's name)	F^-	fluorido
		Cl^-	chlorido
		Br^-	bromido
		I^-	iodido
		OH^-	hydroxido
		CN^-	cyanido
		$C_2O_4^{2-}$	oxalato
		NO_3^-	nitrato
		CO_3^{2-}	carbonato
		NH_2^-	amido
		H^-	hydrido
		NO_2^-	nitrito-N
		ONO^-	nitrito-O
		O^{2-}	oxido
		O_2^{2-}	peroxido
		N_3^-	azido
		S^{2-}	sulphido
		$C_6H_5^-$	phenyl
		NH_2^-	amido
		NH^{2-}	imido
		$C_5H_5^-$	cyclopentadienyl
		NO^+	Nitrosonium
		NO_2^+	nitronium
Complicated ligands with abbreviation	en	$C_2H_8N_2$	ethylendiamine
	py	C_5H_5N	pyridine
	ox	$C_2O_4^{2-}$	oxalato
	dmso	$(CH_3)_2SO$	dimethyl sulfoxide
	EDTA	$C_8H_{12}N_2O_8^{4-}$	ethylenediamine tetraacetato
	gly	$NH_2CH_2CO_2^-$	glycinato
	oxine	C_9H_7NO	8-hydroxyquinolinato
	phen	$C_{12}H_8N_2$	1,10-phenanthroline
	dmg	$C_4H_7N_2O_2$	dimethylglyoximato
	ur	NH_2CONH_2	urea
	tu	H_2NCSNH_2	Thiourea

Naming of bridging complexes

The bridging groups in the complexes are written first with a prefix μ by separating it from the complex by hyphen (-). This μ is used every time for each bridging ligand. Thereafter, the other liands with number prefix (di, tri or bis-, tris- etc.), metal with oxidation state in bracket and at last the negative species outside the cordination sphere.

Type of complex/ compound		Formula of compound	Name of compound
Simple (one ion is complex and other simple	Complexes with neutral coordination sphere	$[Ni(CO)_4]$	Tetracarbonylnickel(0)
		$[Fe(C_5H_5)_2]$	Bis(cyclopentadienyl)iron (II)
		$[Pt(en)_2Cl_2]$	Dichlorobis(ethylenediamine)platinum (II)
		$[Hg(CH_3)_2]$	Dimethylmercury(II)
		$[Mn_3(CO)_{12}]$	Dodecacarbonyltrimanganese (0)
		$[Ni(PF_3)_4]$	Tetrakis(trifluorophosphine)nickel(0)
	Complexes with anionic coordination sphere	$K_2[HgCl_4]$	Potassium tetrachloromercurate(II)
		$K_4[Cu(CN)_6]$	Potassium hexacyanocuperate(II)
		$Na_3[Co(NO_2)_6]$	Sodium hexanitrito-Ncobaltate(III)
		$K_2[Fe(CN)_5NO]$	Potassium pentacyanonitosylferrate(III)
		$Na[Au(CN)_2]$	Sodium dicyanoaurate(I)
		$K_3[Cr(CN)_6]$	Potassium hexacyanochromate(III)
		$K_4[Ni(CN)_4]$	Potassium tetracyanonickelate(0)
		$Na_3[Fe(C_2O_4)_3]$	Sodium trioxalatoferrate(III)
		$Fe[Fe(CN)_6]$	Iron hexacyanoferrate(III)
		$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
		$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate(III)
		$Na_2[ZnCl_4]$	Sodium tetrachlorozincate(II)

ion)	Complexes with cationic coordination sphere	$[Cr(C_2O_4)_3]^{3-}$	Trioxalatochromate(III)
		$[Co(N_3)(NH_3)_5)]SO_4$	Pentaammineazidocobalt(III) sulphate
		$[Cr(H_2O)_6]Cl_3$	Hexaaquachromium(III) chloride
		$[Cr(NH_3)_6]^{3+}$	Hexaammine chromium(III) ion
		$[Cr(H_2O)_4Cl_2]NO_3$	Tetraaquadichlorochromium(III) nitrate
		$[Cu(NH_3)_2(en)]Br_2$	Diammine(ethylenediamine)copper(II) bromide
		$[PtClBr(NH_3)py]$	Amminebromochloropyridinepalatinum(II)
		$[CuCl_2(CH_3NH_2)_2]$ Complex ligand	Dichloro**bis**(methylamine)copper(II) ion
		$[Co(NH_3)_5ONO]SO_4$	Pentaamminenitritocobalt(III) sulphate
		$[Co(NH_3)_2(H_2O)_2(CN)_2]Cl$	Diamminediaquadicyanocobalt(III) chloride
		$[Cr(NH_3)_2(H_2O)_3(OH)](NO_3)_2$	Diamminetriaquahydroxochromium(III) nitrate
Both cation and anion are complex		$[Pt(NH_3)_4][PtCl_4]$ (Firstly complex cation is named then only the	Tetraammineplatinum(II) tetrachloropalatinate(II)

	complex anion)	
	$[Cr(NH_3)_5(NCS)]$ $[ZnCl_4]$	Pentaammineisothiocyanatochromium (III) tetrachlorozincate(II)
Bridging complex ????	?????	Octaaqua-µ-dihydroxo-diiron(III) sulphae or Tetraammineiron(III)-µ-dihydroxo-tetraammineiron(III) or µ-dihydroxo-octaaquadiiron(III) sulphate or µ-Hydroxo-tetraaquairon(III)µ-hydroxo-tetraaquairon(III) sulphate
		µ-Dihydroxo-octaamminedicobalt(III) nitrate
		µ-Amido-µ-hydroxo-tetrakis(ethylenediammine)dicobalt(III) sulphate

Calculation of oxidation number of metal atom/ion

In coordination compound, $[M(L)_n]^{\pm}$ or $[M(L)_n]$, oxidation state of M can be calculated as Oxidation number of M + Oxidation number of L x n = ± or 0

For example,

1) Oxidation number (ON) of Co in $[Co(NH_3)_6]^{3+}$

ON of Co + 0 (ON of NH_3 is 0) = +3

Hence, ON of Co will be +3.

2) Oxidation number (ON) of Ni in $[Ni(CO)_4]$

ON of Ni + 0 (ON of CO is 0) = 0

4.7 VALENCE BOND THEORY (VBT) AND DISCUSSION OF INNER AND OUTER ORBIT COMPLEXES

Valence bond theory was given by Pauling and Slater in 1935. According to this theory:

- ✓ In coordination compounds, the ligands form covalent-coordinate bonds to the metal atom/ ion. The central metal atom/ ion provide vacant orbitals (s, p and /or d atomic orbitals) equal to its coordination number. These vacant orbitals hybridize and form the same number of new hybridized orbitals (atomic orbitals overlap) of equal energy.
- ✓ Ligands can donate at least one lone pair (in σ orbital) of electrons to the empty hybrid orbitals of the central metal atom/ ion.
- ✓ Each ligand with filled σ orbital then overlap with the empty hybrid orbital of central metal atom/ ion.

This theory helps in predicting the shape, stability and calculating magnetic moment (magnetic property: $\mu=\sqrt{n(n+2)}$ of the metal complexes.

Spectrochemical series of ligands

A spectrochemical series is the ordered arrangement on ligand strength from lower strength (small Δ_o) to higher strength (large Δ_o). The ligands on the left end are weaker ligands (σ-donor) which can donate a pair the electrons in (n-1)d orbitals of metal/ion. The right end ligands are stronger (π-acceptor) ligands and can accept pair of electrons from filled (n-1)d orbitals in the metal atom/ion. The spectrochemical series of ligands is given as:

$I^- < Br^- < S^{2-} < \underline{SCN^-} < Cl^- < NO_3^- < N_3^- < F^- < OH^- < \underline{C_2O_4^{2-}} \approx H_2O < \underline{NCS^-} < CH_3CN < py < NH_3 < en < phen < NO_2^- < PPh_3 < CN^- \approx CO$

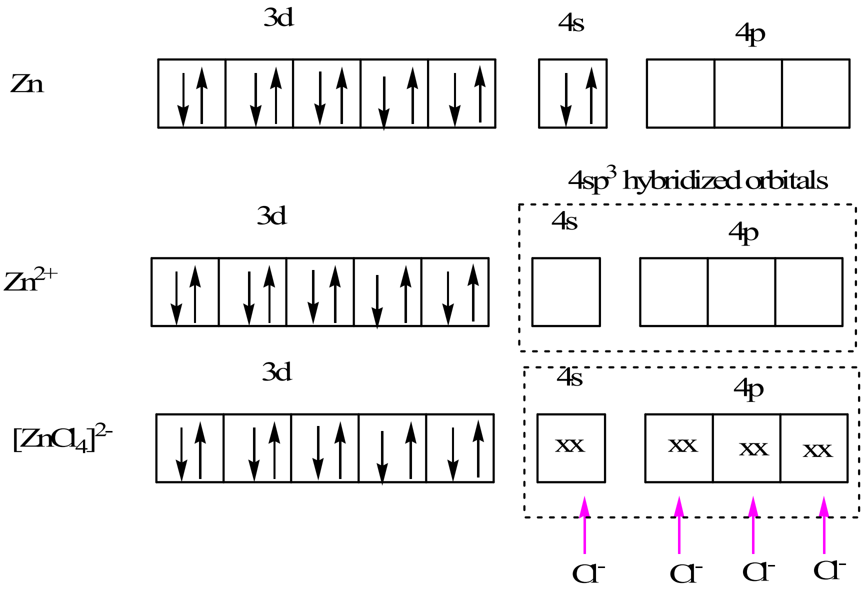
The position of ligand in the spectrochemical series and nature of central metal atom/ ion affects the hybridization, structure, stability and magnetic moment of complexes.

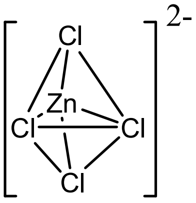
(A) Four coordinate compounds (Tetrahedral complexes)

In case of tetrahedral complexes, the central metal atom / ion provides four vacant orbitals (one s and three p). These four orbitals hybridize to form four sp^3 hybridized orbials. Each hybridized orbital then overlaps with the filled p orbitals of the each ligand. The geometry of such complexes will be tetrahedral. Hybridization and thus, geometry of a complex depends upon the type of ligand (σ-donor or π-acceptor) attached to the central metal atom / ion. Electrons of metal atom / ion are shown as ↑↓ , whereas those of the electron pair on ligand are depicted as xx. For example,

a. **[ZnCl$_4$]$^{-2}$:** Zn = $3d^{10}4s^2$ and $Zn^{+2} = 3d^{10}$

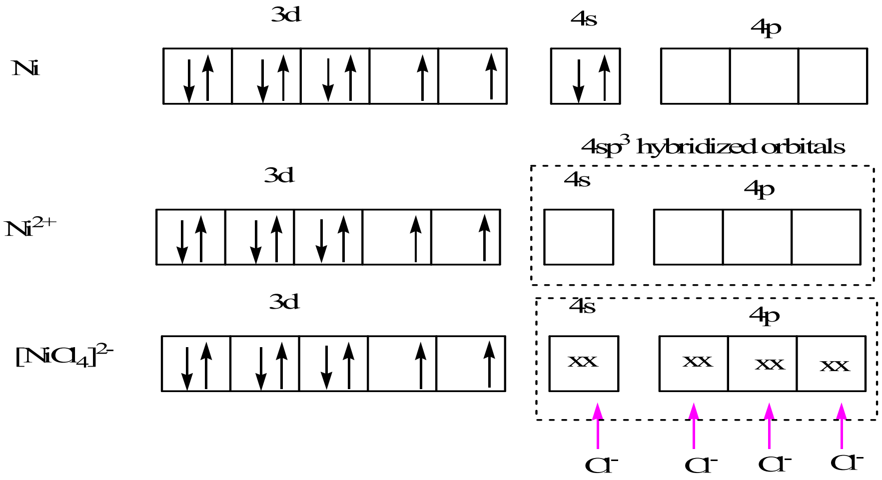
In this complex, the ligand is weak and the d orbitals of Zn^{2+} ion are filled. Hence, it is a diamagnetic substance (no unpaired electron) and the geometry is tetrahedral. The central metal ion; Zn^{2+} is sp^3 hybridized.

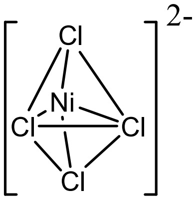




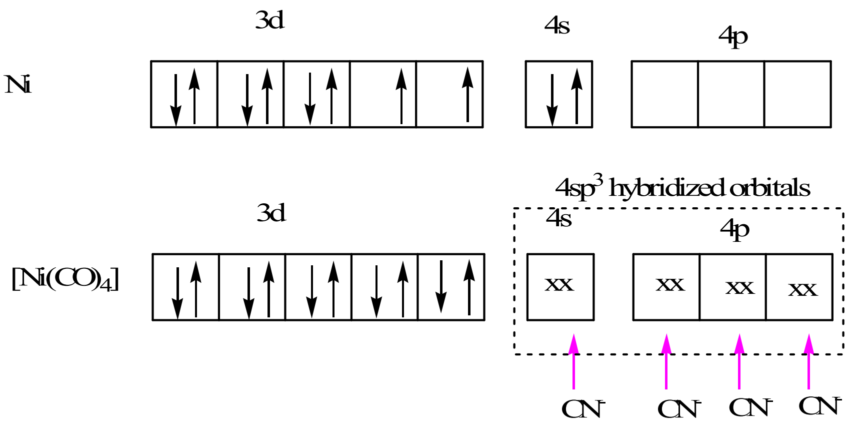
b. **$[NiCl_4]^{2-}$:** Electronic configuration of ^{Ni} is $3d^84s^2$ and hence, electronic configuration of Ni^{+2} is $3d^8$.

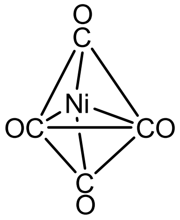
In this complex, the ligand is weak and no pairing of electrons will occur. There are two unpaired electrons in d orbitals of Ni^{2+}. Hence, it is a paramagnetic in nature. The central metal ion; Ni^{2+} is sp^3 hybridized and the geometry is tetrahedral.



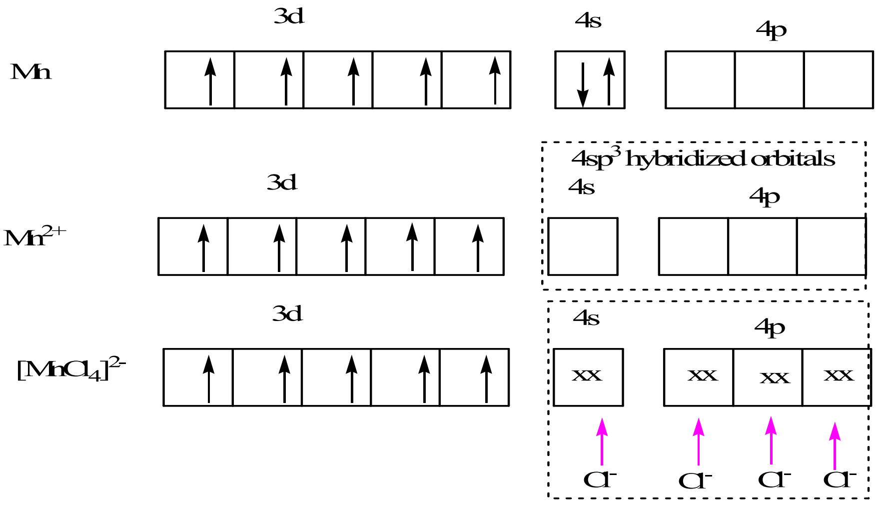


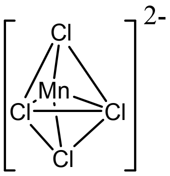
c. **$[Ni(CO)_4]$:** Ni = $3d^8\,4s^2$ .In this complex, Ni is in 0 oxidation state. The ligand is strong and hence, pairing of electrons will occur. There are no unpaired electrons in d orbitals of Ni^{2+}. Hence, it is a diamagnetic in nature. The central metal atom Ni is sp^3 hybridized and the geometry is tetrahedral.





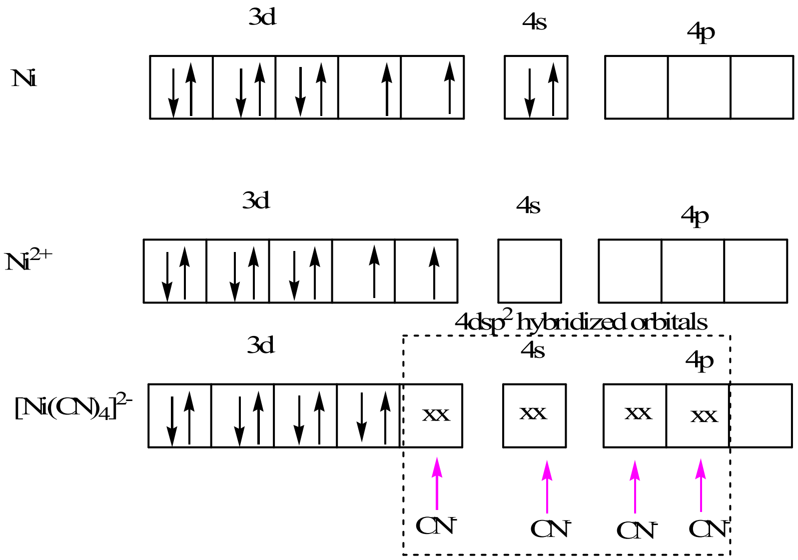
d. **$[MnCl_4]^{2-}$:** Electronic configuration of Mn (atomic number 25) is $3d^5\,4s^2$,and hence, the electronic configuration of Mn^{+2} is $3d^5$. In this complex, again the ligand is weak and no pairing of electrons will occur. There are five unpaired electrons in d orbitals of Mn^{2+}. Hence, it is a paramagnetic in nature. The central metal ion; Mn^{2+} is sp^3 hybridized and the geometry is tetrahedral.

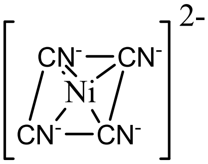




(B) Four coordinate compounds (Square planar complexes)

a. **$[Ni(CN)_4]^{2-}$:** As you know, the electronic configuration of Ni = $3d^8\ 4s^2$, nickel in this complex is in +2 oxidation state, hence $Ni^{+2} = 3d^8$. You also know that CN^- is a strong field ligand, hence pairing of electrons will occur. There will be no unpaired electrons in d orbitals of Ni^{2+}. Hence, it is diamagnetic in nature. The central metal ion; Ni^{2+} provides one inner d orbital and thus, is dsp^2 hybridized and square planar.

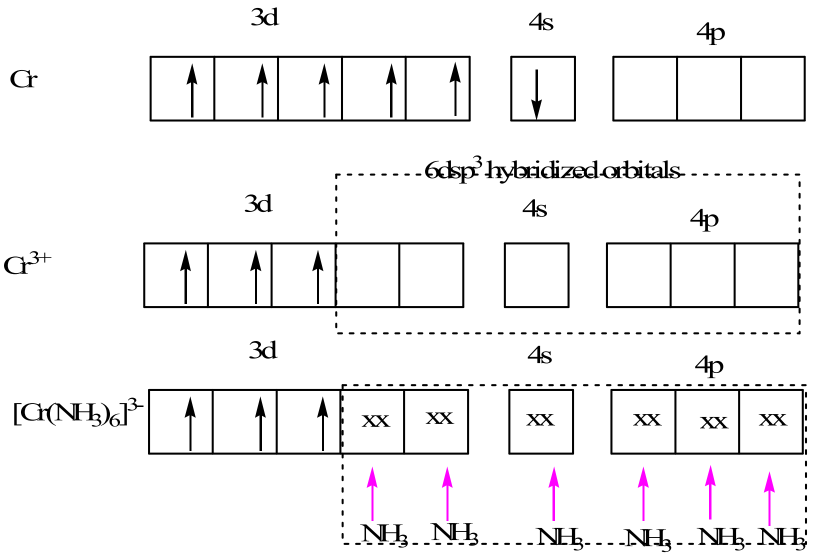


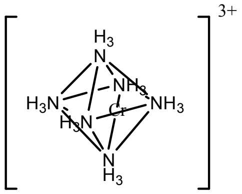


In 'dsp^2' hybridization,'d' preceeds 'sp^2' indicating that the lower (inner) shell d-orbital is used in hybridization that comes before the 's' and 'p' orbitals. This is called **inner shell hybridization** (form inner shell complexes). When outer shell d-orbitals are used in hybridization, it is called as **outer shell** (form outer shell complexes) hybridization.

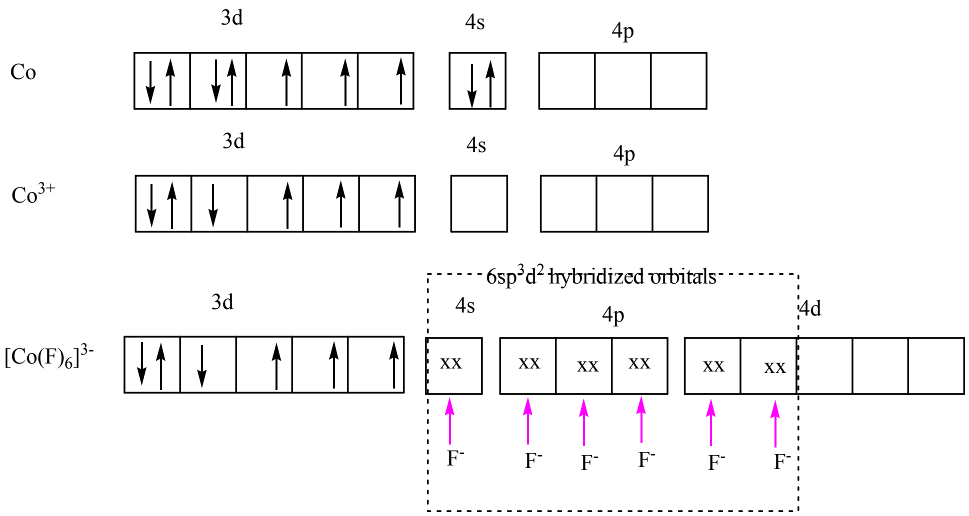
(C) Six coordinate compounds (Octahedral complexes)

a. **$[Cr\ (NH_3)_6]^{3+}$:** Chromium (atomic no. 24) has $3d^5 4s^1$ as valence shell configuration and is in +3 oxidation state in this complex. Cr^{+3} thus has $3d^3$ configuration. In this complex, although NH_3 is a strong field ligand, but no pairing of electrons is required. There are three unpaired electrons in d orbitals of Cr^{3+}. Hence, it is a paramagnetic in nature. The central metal ion; Cr^{3+} provides inner d orbitals and thus, is d^2sp^3 hybridized (inner shell orbital complex) and octahedral in shape.

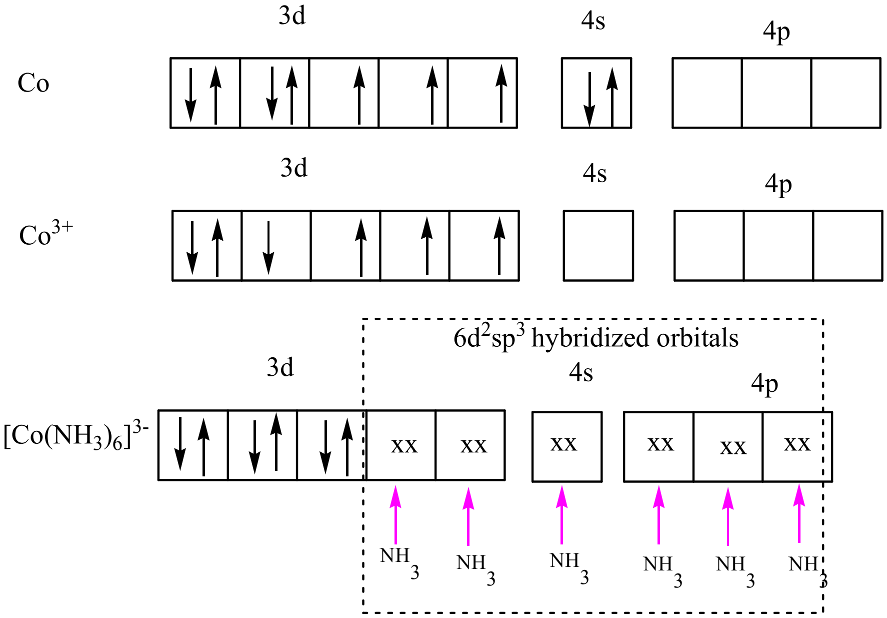




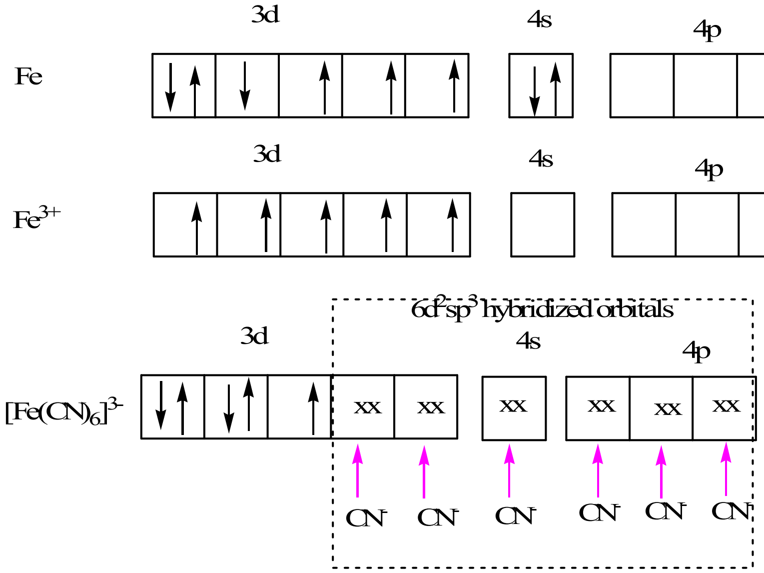
b. **$[CoF_6]^{3-}$** : Cobalt (atomic no. 27) has $3d^7\ 4s^2$ configuration. In this complex cobaly is in +3 oxidation state and thus the electronic configuration of Co^{+3} is $3d^6$. In this complex, the ligands are weak, so no pairing of electrons will occur. There are four unpaired electrons in d orbitals of Co^{3+}. Hence, it is paramagnetic in nature. The central metal ion Co^{3+} provides outer d orbitals and thus, is sp^3d^2 hybridized (outer shell orbital complex) and octahedral in shape.



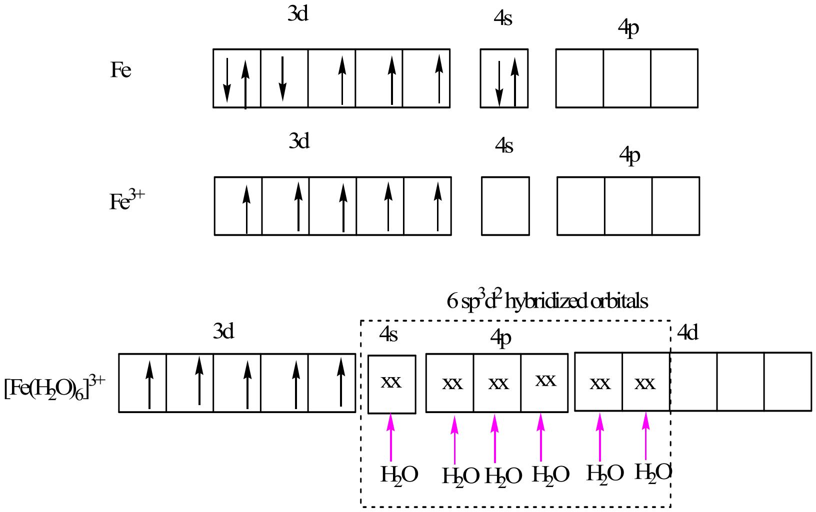
c. **$[Co(NH_3)_6]^{3+}$:** In this complex also, cobalt is in +3 oxidation state and has $3d^6$ configuration. As NH_3 is a strong field ligand, pairing of electrons will occur. There are no unpaired electrons in d orbitals of Co^{3+}. Hence, it is a diamagnetic in nature. The central metal ion Co^{3+} provides inner d orbitals for complex formation, is thus d^2sp^3 hybridized (inner shell orbital complex) and the complex is octahedral in shape:



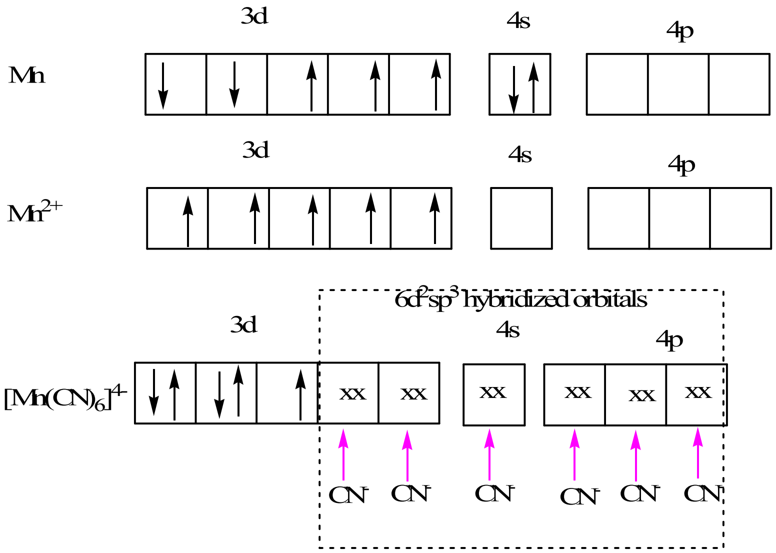
d. **$[Fe(CN)_6]^{3-}$:** Iron (atomic no. 26) has $3d^6\ 4s^2$ as valence shell configuration, with iron in +3 oxidation state; Fe^{+3} having $3d^5$ configuration. In this complex, the ligand CN^- is a strong field ligand, hence, pairing of electrons will takes place. There will be one unpaired electron in d orbital of Fe^{3+}. Hence, it will be paramagnetic in nature. The central metal ion, Fe^{3+}, provides inner d orbitals and thus, is d^2sp^3 hybridized (inner shell orbital complex) and octahedral in shape.



e. **$[Fe(H_2O)_6]^{3+}$:** Iron (atomic no. 26) has $3d^6 4s^2$ as valence shell configuration, with iron in +3 oxidation state; Fe^{+3} having $3d^5$ configuration. In this complex, the ligand water is a weak field ligand hence; pairing of electrons does not take place. There are five unpaired electrons in d orbitals of Fe^{3+}. Hence, it is paramagnetic in nature. The central metal ion Fe^{3+} provides outer d orbitals and is thus, sp^3d^2 hybridized (outer shell orbital complex) and octahedral in shape.



f. **$[Mn(CN)_6]^{4-}$**:Manganese (atomic no. 25) has $3d^5 4s^2$ as valence shell configuration, with manganese in +2 oxidation state; Mn^{2+} having $3d^5$ configuration. In this complex, the CN^- ligand is a strong field ligand. Hence, pairing of electrons takes place. However, there is one unpaired electron in d orbitals of Mn^{2+}, it is a paramagnetic in nature. The central metal ion Mn^{2+} provides inner d orbitals and is d^2sp^3 hybridized (inner shell orbital complex). Therefore, the complex, $[Mn(CN)_6]^{4-}$ has an octahedral structure:



Limitations of VBT:

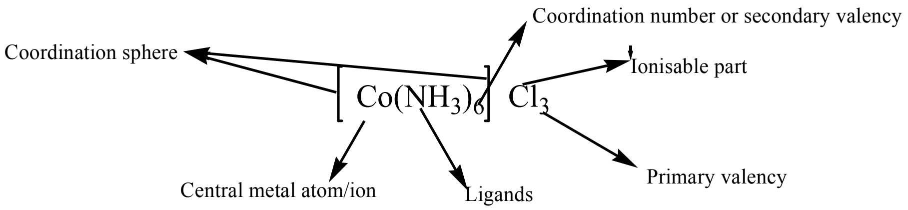
- ✓ Cannot explain colour of complexes.
- ✓ Cannot explain why magnetic moments of some metal complexes are temperature dependent.
- ✓ Cannot explain the structure of Cu^{2+} complexes.

Hence, ON of Ni will be 0.

4.8 SUMMARY

In this Unit, you have studied the following:

- Simple or double salts dissociate into their constituent ions while coordination compounds break up into complex ion and its counter charged ion.
- Coordination compounds comprise of two main parts; central metal atom/ion and ligands coordinated to the metal atom/ion.



- A wide variety of ligands including monodentae, polydentate, sigma donor, chelating, macrocyclic, actor and spectator ligands are involved in the formation of coordination compounds with metal atom/ion.
- Monodentate lingads can donate a pair of electrons to a central metal atom while a polydentate ligand can donate more than one pair of electrons to the metal atom/iom. Bidentate or polydentate ligands form cyclic compounds called chelats.
- Coordination compounds have various applications in different industries.
- Werner suggested that coordination number and oxidation number of metal depends on the nature of the metal.
- EAN rule decides the stability of a coordination compound.
- Nomenclature of coordination compounds is systematic.

4.9 TERMINAL QUESTIONS

A. Short answer questions

1. Which of the following ligands are weak or strong?

CN^-, CO, H_2O, NH_3

2. Classify the following ligands as pi acceptor or sigma donor ligands.

NO, Cl^-, NH_3, benzene

3. Give two examples of each neutral and positive monodentate ligands.

4. Select monodentate and polydentate ligands among the following:

NCS^-, NH_3, $C_2O_4^{2-}$, EDTA, en, Cl^-

5. Draw the structures of the following ligands:

EDTA, dmg, porphyrin, 8-quinoline, diethylenetriamine

6. Draw the geometry that describe five and six-coordinate compounds. Which structures are more common?

7. Give the geometry of the following compounds:

(i) $[Co(NH_3)_6]^{3+}$

(ii) $[Ag(NH_3)_2]^+$

(iii) $[Fe(CN)_6]^{4-}$

(iv) $[Fe(C_2O_4)_3]^{3-}$

8. Define coordination sphere.

9. On the basis of Werner's theory, draw the structure of $CoCl_3.6NH_3$ and $CoCl_3.5NH_3$.

10. Name the experimental methods to explain Werner's theory?

11. Calculate the oxidation number of the metal atom/ ion in the following coordination complexes:

a) $[CoCl_4]^{2-}$

b) $[Fe(CN)_6]^{3-}$

c) $[Ni(CO)_4]$

d) $[Cr(CO)_6]$

12. Name the following ligands:

Cl^-, H^-, NO^+, H_2O, NO_3^-, ONO^-, NH_2^-, $C_5H_5^-$

13. Name the following coordination compounds:

a. $Na_3[Co(NO_2)_6]$

b. $K_4[Ni(CN)_4]$

c. $[Mn_3(CO)_{12}]$

d. $K_3[Fe(CN)_6]$
e. $[Pt(NH_3)_4][PtCl_4$

14. Write down the formula of hexamminecobalt (III) chloride and tetracarbonyl nickel (0).
15. Draw the structure of the following complexes:
    a) Sodium hexafluoroslilicate (IV)
    b) Ammonium diamminetetra(isothiocyanato)chromate(III)
16. How does the conductivity of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ differ from each other?
17. Write the formula of the following compounds:
    a) Octaammine-μ-amido-μ-nitridocobalt(III) nitrate
    b) Dichlorobis(ethylenediamine)cobalt(III) chloride
    c) Hexaaquairon(II) sulphate
    d) Tetrachloroplatinate(II)
18. Explain the meaning of the terms monodentate, bidentate and tetradentate.

B. True (T) or False (F)

1. CO and NO are pi acceptor ligands.
2. Monodentate ligands are of three types: neutral, negative and positive
3. Ethylenediammine is a monodentate ligand.
4. Monodentate ligands form more stable compounds as compared to polydentatte ligands.
5. Spectator ligands are those ligands that take part in a chemical reaction.
6. Coordination number is also known as secondary valency.
7. Coordination number does not decide the geometry of coordination compound.
8. Octahedral and trigonal prismatic geometries are found in 6 coordinated compounds.
9. Complex $[Co\ (NH_3)_3Cl_3]$ will ionize to give two ions.
10. Complex $[Co\ (NH_3)_5Cl]Cl_2$ will react with three molecules of $AgNO_3$.
11. IUPAC name of $[Cr\ (NH_3)_6]^{3+}$ complex is hexaamminechromate (III).
12. Formula of the compound Tetrachloropalatinate (II) is $[PtCl_4]^{2-}$.

C. Long answer questions

1. What is the difference between chelating and macrocyclic ligands? Explain with the help of examples.
2. What are chelates? How are they important? Give examples.
3. Define ligand. Give detailed account on the classification of ligands.
4. How are the coordination compounds named? Describe with the help of examples?
5. What is EAN rule? Give details with examples.
6. Explain Werner's theory.
7. What do you mean by coordination number? How is it useful in deciding the geometry of coordination compounds? Explain with the help of examples.
8. What are primary and secondary valencies? Explain by giving suitable examples.
9. Discuss the basic postulates of Werner's theory of coordination compounds. Explain structure of $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$, $CoCl_3.3NH_3$ on the basis of Werner's theory.
10. Explain in detail about the stability of chelates.

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UNIT 5: ACIDS AND BASES

CONTENTS:

5.1 OBJECTIVES

The main goal of this Unit is to broaden your understanding about the following issues:

- Definitions of acids and bases,
- Different theories of acids and bases,
- Acid and base strength,
- Periodic variations of acidic and basic properties,

5.2 INTRODUCTION

We all know that acids and bases play an essential and important role in our everyday life. The knowledge of acid/base chemistry helps in classifying daily household substances and items. A substance can be classified as an acid or a base depending on certain properties. There are several theories to define and classify acids and bases that include Arrhenius theory, Bronsted-Lowry acid/base concept, Lux-flood acid/base theory and Lewis acid-base concept. The strength of acids and bases can be determined by measuring pH values of solutions. Every theory of acid and base shows some advantages and some limitations to overcome; the drawback of each theory. A new theory was proposed which was observed to be more advanced as compared to the previous one. This unit will throw light on different theories of acids/bases, their drawbacks and relative strengths of acids and bases.

5.3 GENERAL CONCEPT OF ACIDS AND BASES

In general, acids and bases can be classified on the basis of their properties. The basic concept of acids and bases can be summarized as follows:

Acids:

- They are sour in taste.
- They react with some metals and produce hydrogen:

  $2HCl_{(aq)} + Zn_{(s)} \rightarrow ZnCl_2 + H_2$

- They react with carbonate (Na_2CO_3) and bicarbonate ($NaHCO_3$) and produce CO_2:

  $NaHCO_3 + HCl_{(aq)} \rightarrow NaCl + H_2O + CO_2$

- Solution of acids in water conducts electricity.
- They change the colour of litmus from blue to red.

Base:

- They have bitter taste.
- They change colour of litmus from red to blue.
- They are slippery in nature.
- Aqueous base solution conducts electricity.

5.4 THEORY OF ACID AND BASES

The different theories to define acids and bases are discussed along with their advantages and drawbacks in this section.

5.4.1. Arrhenius theory (Water system concept, 1884):

In 1884, the Swedish chemist Arrhenius defined acid as the species which ionize in water to produce H^+ ion or (H_3O^+ ions) and bases as the substances that ionize in water to produce OH^- ions. For example,

$$\text{Acid} \rightarrow HCl_{(g)} \xrightleftharpoons{420} H^+_{(aq)} + Cl^-_{(aq)}$$

$$\text{Base} \rightarrow NaOH \xrightleftharpoons{420} Na^+_{(aq)} + OH^-_{(aq)}$$

The H^+ ion produced is always associated with a water molecule to form $H_3O^+(aq)$ (hydronium) ion. Hence, Arrhenius acids are called as proton donors / hydrogen ion donors / hydronium ion donors. The complete reaction will be –

$$HCl_{(s)} + H_2O_{(e)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(a)}$$

5.4.2. Bronsted–Lowry acids and bases (Protonic concept, 1923):

Arrhenius's definitions of acids and bases are limited to aqueous solutions. Hence, Bronsted in 1923 proposed that a substance capable of donating a proton to any substance is acid and a base can be defined as a species capable of accepting proton from any other substance.

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Bronsted acid

$NH_3 + H^+ \rightarrow NH_4^+$

Bronsted base

There are three types of acids and bases according to Bronsted-Lowry (Table 9.1).

Acids:

(i) Molecular acids

HCl, H_2SO_4, CH_3 COOH

$HCl \rightleftharpoons Cl^- + H^+$

$H_2SO_4 \rightleftharpoons HSO^- + H^+$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

(ii) Anion acids

$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$
(Bisulphate)

$HC_2O_4^- \rightleftharpoons C_2O_4^{2-} + H^+$
(bio-oxalate)

(iii) Cation acids

$H_3O^+ \rightleftharpoons H_2O + H^+$
Hydroxonium

$NH_4^+ \rightleftharpoons NH_3 + H^+$
Ammonium

Bases:

(i) Molecular bases

$$CH_3NH_2 + H^+ \rightleftharpoons CH_3NH_3^+ \text{ (Cations)}$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

(ii) Anion bases (OH^-, S^{2-}, CO_3^{2-}, Cl^-, Br^-, NO_3^-)

$$OH^- + H^+ \rightleftharpoons H_2O \text{ (Neutral molecule)}$$

$$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$$

(iii) Cationic bases

$$[Fe(H_2O)_5OH] \overset{2^+H^+}{\rightleftharpoons} (Fe(H_2O)_6)^{3+}$$

Acid-Base Neutralization reaction:

According to Arrhenius concept, acid-base neutralization reaction takes place in water, where a compound containing or making available H_3O^+ (or H^+) ions (acid) combines with a compound containing or making available OH^- ions (base) to form the salt and water:

$$\overset{\textbf{Acid}}{HCl} + \overset{\textbf{Base}}{NaOH} \xrightarrow{420} \overset{\textbf{Salt}}{NaCl} + \overset{\textbf{Water}}{H_2O}$$

Mechanism:

$$HCl \overset{420}{\rightleftharpoons} H^+ + Cl^-$$

$$NaOH \overset{420}{\rightleftharpoons} Na^+ + OH^-$$

$$HCl + NaOH \rightleftharpoons Na^+Cl^- + H^+[OH]^-$$

$$\text{Or } HCl + NaOH \overset{420}{\rightleftharpoons} NaCl + H_2O$$

This reaction is also known as salt formation reaction because salt formation takes place in this reaction.

Application (advantages) of Arrhenius concept:

(i) Aqueous solutions of non-metallic oxides (e.g. CO_2, SO_2, SO_3, N_2O_3, N_2O_5, P_4O_6, P_4O_{10} etc.) are acidic in nature, since they give H^+ ions in water:

$$SO_3 + H_2O \rightleftharpoons H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

$$N_2O_5 + H_2O \rightleftharpoons 2HNO_3 \rightleftharpoons 2H^+ + NO_3^-$$

(ii) Aqueous solutions of metallic oxides (e.g. CaO, Na_2O etc.) and the compounds like NH_3, N_2H_4, NH_4OH etc. are basic, since these substances give OH^- ions in aqueous solution:

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

(iii) The strength of an acid (HA) and a base (BOH) can be expressed quantitatively in terms of the ionization (or dissociation) constant of the acid and base in aqueous solution.

$$\underset{\text{acid}}{HA} \rightleftharpoons H^+ + A^-, \quad ka = \frac{CH^+ \times CA^-}{C_{HA}}$$

$$\underset{\text{Base}}{BOH} \rightleftharpoons B^+ + OH^-, \quad kb = \frac{CB^+ \times COH^-}{C_{BOH}}$$

(iv) The catalytic property of acids in many reactions can be explained because of H^+ ions that become available from the acid in aqueous medium.

Limitations of Arrhenius concept:

(i) According to this concept, the acid or base property of a substance is not supposed to inherit in the substance itself, but depends on its aqueous solution. For example, HCl is an acid, only when it is dissolved in water, but it is not considered as an acid in its gaseous state.

(ii) According to this concept, acid base neutralization reactions take place only in water and hence can't explain the reactions that occur in other solvents or in the gas phase. For example, the formation of $NH_4Cl_{(s)}$ by the combination of $NH_{3(g)}$ and $HCl_{(g)}$ cannot be explained by Arrhenius concept.

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$$

(iii) According to this concept, acids and bases undergo dissociation only in water (aqueous solvent). Thus, it is unable to explain the dissociation of acids and bases in non-aqueous solvents like liq. NH_3, liq. SO_2 etc.

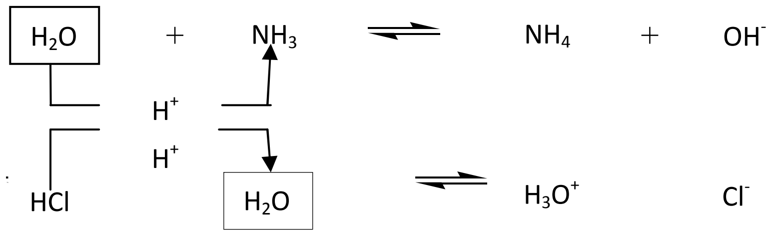
Table 5.1 Bronsted–Lowry acids and bases

Type	Acid	Base
Molecular	HCl, HBr, $HClO_4$, H_2SO_4, H_3PO_4, H_2O	NH_3, N_2H_4, amines, H_2O
Cationic	NH_4^+, $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$	$[Fe(H_2O)_5(OH)]^{2+}$ $[Al(H_2O)_5(OH)]^{2+}$
Anionic	HS^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$	Cl^-, Br^-, OH^-, HSO_4^-, CO_3^{2-}, SO_4^{2-}

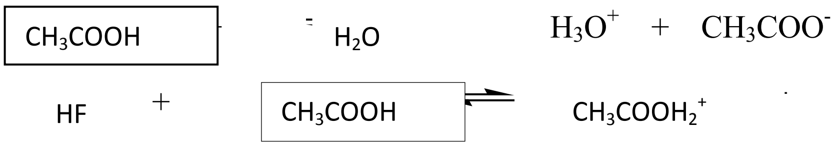
Amphoteric substances / Amphiprotonic substances:

A substance which acts both as an acid as well as a base in different reactions is called amphoteric. Molecules or ions that can lose as well as accept proton are called amphoteric substances i.e. the molecules or ions that can act as Bronsted acids (loss of proton) as well as Bronsted bases (gain of proton) are called amphoteric substances. For example, H_2O:

i) Acid_1 Base_1 Base_2 Acid_2



ii) Acid_1 Base_1 Base_2 Acid_2



Conjugate acids and bases:

Bronsted-Lowry also gave the concept of conjugate acid base pair. Conjugate base is a species that remains when one proton has been removed from the acid.

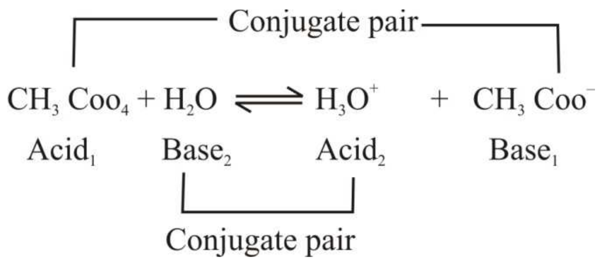
$$\text{Acid}_1 \rightleftharpoons H^+ + \underset{\text{Conjugate base}}{\text{base}}$$

Conjugate acid results from the addition of proton to a base

$$\text{Base}_2 \rightleftharpoons H^+ \rightleftharpoons \underset{\text{Conjugate acid}}{\text{acid}_2}$$

An acid base pair which is different by a proton is called conjugate acid base pair.

$$\text{Conjugate acid} \rightleftharpoons \text{Conjugate base} + H^+$$



The sum of these two reactions is

$$\text{Acid}_1 + \text{base}_2 \rightleftharpoons \text{Acid}_2 + \text{base}_1$$

Therefore, any acid-base reaction involves two acids and two bases. These acids and bases are called conjugate pairs.

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O} + \underset{\text{Base}_1}{Cl^-}$$

Relative strength of conjugate acid – base pairs

	Acid	Conjugate base
Strong acids	$HClO_4$	ClO_4^-
	HI	I^-
	HBr	Br^-
	HCl	Cl^-
	H_2SO_4	HSO_4^-
	HNO_3	NO_3^-

↓ Increasing base Strength

Weak acids	H_3O^+	H_2O
	HSO_4^-	SO_4^{2-}
	HF	F^-
	HNO_2	NO_2^-
	$HCOOH$	$HCOO^-$
	CH_3COOH	$HCOO$
	NH_4^+	NH_3
	HCN	CN^-
	H_2O	OH^-
	NH_3	NH_2^-

- Acids stronger than H_3O^+, react with water to produce H_3O^+ and their conjugate bases.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-_{(aq)}$$

- Acids weaker than H_3O^+, react with water to a much smaller extent. Bases like O^{2-} (oxide) stronger than OH^-, react with water to produce OH^-.

$$O^{2-}\ (aq) + H_2O \rightarrow 2OH^-\ (aq)$$

Therefore, oxide ion does not exist in solution.

$$NH_2^- + H_2O \longrightarrow NH_3 + OH^-$$

Advantages of Bronsted–Lowry Concept:

1. This concept can explain the acidic/basic nature of a substance in aqueous (H_2O) as well as in other protonic solvents like liq. NH_3, liq. HF.
2. This concept also explains acid base reaction taking place in gaseous phase.

$$\overset{\text{Acid}}{HCl\ (g)} + \overset{\text{Base}}{NH_3\ (g)} \rightleftharpoons \overset{\text{Acid}}{NH_4^+} + \overset{\text{Base}}{Cl^-} \text{ or } NH_4^+\ Cl^-$$

Limitations of Bronsted–Lowry concept:

This concept cannot explain the acid-base reactions taking place in non-protonic solvents, like liq. SO_2, liq. BF_3, BrF_3, $AlCl_3$, $POCl_3$ etc. in which no proton transfer takes place.

$$\underset{\text{Acid}}{SO_2} + \underset{\text{Base}}{SO_2} \rightleftharpoons \underset{\text{Acid}}{SO^{2+}} + \underset{\text{Base}}{SO_4^{2-}}$$

$$BrF_3 + BrF_3 \rightleftharpoons BrF_4^{+} + BrF_2^{-}$$

5.4.3 Lux-Flood concept

According to Lux-Flood concept, the base is an oxide donor and the acid is an oxide acceptor. Lux-Flood definition is useful for limited systems such as molten oxides.

$$\underset{\text{Acid}}{CO_2} + \underset{\text{Base}}{BaO} \rightleftharpoons BaCO_3 \qquad \underset{\text{Base}}{B} \rightleftharpoons \underset{\text{Oxide ion}}{O^{2-}} + \underset{\text{acid}}{A^{2+}}$$

$$\underset{\text{Acid}}{SiO_2} + \underset{\text{Base}}{CaO} \rightleftharpoons CaSiO_3$$

$$\underset{\text{Base}}{3Na_2O} + P_2O_5 \longrightarrow 2Na_3PO_4$$

$$\underset{\text{Base}}{ZnO} + S_2O_7^{2-} \longrightarrow Zn^{2+} + 2SO_4^{2-}$$

The Lux-Flood oxide transfer concept of acid-base reactions can be extended to any negative and positive ion species. Base is the species that can form negatively charged species and acid is the species that can produce positively charged species.

$$3NaF + AlF_3 \longrightarrow 3Na^{+} + (AlF_6)^{3-}$$

$$\underset{\text{Base}}{EtNa} + \underset{\text{acid}}{Et_2Zn} \longrightarrow Na^{+} + ZnEt_3^{-}$$

5.4.4 Solvent system (auto-ionization) concept (1928)

The concept was introduced by Franklin in 1905 and was extended by Cady-Esley in 1928. The definition of acids and bases given by this concept can be applied for protonic as well as for non-protonic solvents. According to this concept, the solvents usually undergo self ionization (auto-ionization) and give rise to cations and anions which are called solvent cations and solvent anions, respectively. The substances which form solvent cations when dissolved in that solvent are called acids while the substances which give solvent anions when dissolved in that solvent are called bases. We can now also conclude that solvent cations can also be called acid cations and solvent anions can also be called base anions.

Auto-ionization of water –

Water (H_2O) undergoes self-ionization in the following three ways:

(a) $H_2O \rightleftharpoons H^{+}$ (Hydrogen ions or protons) + OH^{-} (Hydroxyl ions)
(Solvent cations : acid ions) (solvent anions : base ions)

(b) $H_2O \rightleftharpoons H^{+} + OH^{-}$
$H^{+} + H_2O \rightleftharpoons H_3O^{+}$

$2H_2O \rightleftharpoons H^{+}O^{+}$ (Hydronium ions) + OH^{-} (Hydroxyl ions)
(Solvent cations : acid ions) (Solvent anions)
$K_w = [H_3O+] [OH^-] = 1.0 \times 10^{-14}$ at 25°C

(c) $3H_2O \rightleftharpoons 2H_3O^{+}$ (Hydronium ions) + O^{2-} (oxide ions)

These three different modes of ionization suggest that, according to the solvent system concept, the substance that gives H^+ or H_3O^+ ions in water, act as acid in aqueous solution, while the substances which furnish OH^- or O^{2-} ions in water, behave as bases.

HCl gives H^+ or H_3O^+ ions in water, hence; it behaves as an acid in aqueous solution.

$$HCl \overset{Water}{\rightleftharpoons} H^{+} + Cl^{-}$$

$$\text{Or Hcl} + H_2O \rightleftharpoons H_3O^{+} + Cl^{-}$$

Similarly, NaOH, which furnish OH^- ions in its aqueous solution, acts as a base.

$$NaOH \overset{Water}{\rightleftharpoons} Na^{+} + OH^{-}$$

Likewise, for a solvent system of BrF_3, the autoionization reaction is-

$$2BrF_3 \rightleftharpoons \underset{\text{acidic}}{BrF_2^{+}} + \underset{\text{base}}{BrF_4^{-}}$$

Hence, according to solvent system concept, the substance which can give BrF_2^+ in BrF_3 is acid and the substance which can form BrF_4^- is base.

$SbF_5 + BrF_3 \rightarrow BrF_2^{+} + SbF_6^{-}$
Acid

$KF + BrF_3 \rightarrow BrF_4^{-} + K^{+}$
Base

Advantages of solvent system concept:

1. The definition of acids and bases given by solvent system concept can be used for both protonic (e.g. H_2O, NH_3 etc.) as well as non-protonic (e.g. SO_2, $SOCl_2$ etc.) solvents.
2. The definition is applicable for aqueous (H_2O) as well as non-aqueous solvents (NH_3, HF, H_2SO_4 etc).

Disadvantages:

1. The definition of acids and bases is based on the nature of the solvent cation and solvent anion obtained by auto-ionization of the solvent.
2. Acid base reaction taking place in the absence of a solvent can't be explained, i.e., acid-base reaction takes place only in presence of solvent.
3. The concept can't account for the acid-base reaction occurring in non-ionizing solvents like C_6H_6, $CHCl_3$ etc.

5.4.5 Lewis concept: Electron pair acceptor-donor concept (1923)

According to G.N. Lewis, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor.

Lewis acid	Lewis base
Electrophile	Nucleophile
Contain vacant orbitals	Contain lone pair of electrons
Example – BeF_2, BH_3, BF_3 etc.	Example–NH_3, H_2O, H^- etc.

Neutralization reaction according to Lewis concept:

- Lewis acid reacts with Lewis base and forms a compound which is called adduct or complex compound.
- The compound contains (Lewis base – Lewis acid) co-ordinate bond.

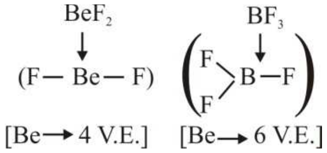
- Lewis acid + Lewis base → Adduct

  $BF_3 + : NH_3 \rightarrow [NH_3 \rightarrow BF_3]$

Examples of Lewis acids:

1. Molecules whose central atoms have vacant p-orbital or incomplete octet of electrons in its valence shell.

   Examples –



The Arrhenius, Bronsted-Lowry and solvent system neutralization reactions can be compared as follows:-

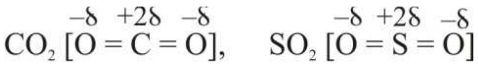
Arrhenius : acid + base → salt + water

Bronsted-Lowry: $acid_1 + base_2 \rightarrow base_1 + acid_2$

Solvent system: acid + base → solvent

Lewis system : acid + base → adduct / coordination compound.

2. Molecules whose central atoms have vacant d-orbitals in their valence shell.
   e.g. AlF_3, $AlCl_3$, GeX_4, $TeCl_4$, SF_4, SbF_3 etc.
3. Molecules whose central atom is linked with more electronegative atom by double bonds.
   e.g.



$$CO_2\ [\overset{-\delta}{O} = \overset{+2\delta}{C} = \overset{-\delta}{O}],\quad SO_2\ [\overset{-\delta}{O} = \overset{+2\delta}{S} = \overset{-\delta}{O}]$$

4. Simple cations, with low lying empty orbitals.

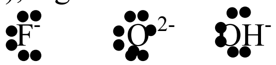
   e.g. Ag^+, Cu^{2+}, Cd^{2+} etc.

5. Elements which have a sextant of electrons in their valence shell.

   e.g.

Examples of Lewis base:

1. Molecules whose central atom has one or more unshared electron pairs (lone pair of electrons), e.g.

e.g. 

2. Molecules containing C = C double bond – ???

3. Halides, e.g. – XeF_2, XeF_4, CsF, $CoCl_2$ etc.

Pearson's classification of Lewis acids and Lewis bases into hard and soft acids and bases.

R. G. Pearson (1963) has classified the Lewis acids and Lewis bases as hard and soft acids and bases

Third categories whose characteristics are intermediate between those of hard and soft acids/bases are called borderline acids/bases.

Hard acids	Soft acids
d-orbitals are either vacant or non-existent	Nearly full d-orbitals
Smaller in size	Larger in size
Not so easily polarizable	Easily polarizable
These are mostly light metal ions generally associated with high positive oxidation state.	These are mostly heavy metal ions generally associated with low (or even zero) positive oxidation state.

Hard Acids	Borderline Acids	Soft Acids
H^+, Li^+, Na^+, K^+, Be^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Lu^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Si^{4+}, Ti^{4+}, U^{4+}, Ce^{3+}, Sn^{4+}, VO^{2+}, $UO_2{}^{2+}$, $MoO_3{}^{3+}$, BF_3	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+}, SO_2, NO^+, GaH_3	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Pb^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, Pt^{4+}, TI^{3+}, BH_3, $GaCl_3$, $InCl_3$, carbenes π - acceptor ligands I^+, Br^+, O, Cl, Br, I, N Zero valent metal atoms.

Hard bases	Soft bases
Donor atoms having low polarisabilities and high electronegativity	Donor atoms that can be easily polarized and have low electronegativity.

Hard Bases	Borderline Bases	Soft Bases
H_2O, OH^-, F^-, CH_3COO^-, PO_4^{3-}, SO_4^{2-}, Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-, ROH, RO^-, R_2O, NH_3, NH_2, N_2H_4	$C_6H_5NH_2$, C_6H_5N, N_3^-, NO_2, SO_3^{2-}, N_2, Br^-	R_2S, RSH, RS^-, I^-, SCN^-, $S_2O_3^{2-}$, R_3P, R_3As, CN^-, RCN, CO, C_2H_4, C_6H_6, H^-

According to HSAB principle, hard acids form stable complexes with hard bases and soft acids with soft bases.

Utility of Lewis Concept:

1. This concept includes those reactions also in which no protons are involved.
2. It is more significant than Bronsted – Lowry concept because according to this concept, acid-base behavior is independent of solvent's presence or absence.
3. It explains basic properties of metallic oxides and acidic properties of non-metallic oxides.
4. This concept also explains gas phase, high temperature and non-solvent reactions.

Limitations:

1. It is not possible to arrange Lewis acids and Lewis bases in order of their acid or base strength.
2. Protonic acids like H_2SO_4 and HCl are not covered under Lewis concept, as they do not establish a covalent bond by accepting a pair of electron (which a Lewis acid ought to).

3. According to this concept, acid-base reaction should be fast but it is not so in actual practice for many reactions due to kinetic factors.

4. The reactions catalyzed by Lewis acids are generally not catalyzed by the protonic acids.

Usanovich concept (1939):

Acid

- An acid is any chemical species which reacts with a base.
- It gives up cation or accepts anions or electrons.

Base

- A base is a species which reacts with acids.
- It gives up anion or electrons or combines with cations.

All the oxidizing agents are acids and the reducing agents as bases.

Example –

$$\underset{\text{(Base)}}{Fe^{2+}} \rightleftharpoons \underset{\text{(Acid)}}{Fe^{3+}} + e^{-}$$

Limitations:

This concept is very general and all chemical reactions are to be considered.

5.5. RELATIVE STRENGTHS OF ACIDS AND BASES

5.5.1. Acidity and basicity of binary hydrogen compounds

- Higher the values of K_a and K_b, stronger the acid or base
- Higher the pK_a or pK_b values, weaker the acid or base.
- The greater bond strength, less acidic is the hydride. On descending a group, the change in bond strength is greater than the change in the decreasing electronegativity.

- In a period from left to right, the change in electronegativity is greater than the changes in bond strength and the trend of electronegativity determines the trend in acidity.

Increasing order of acid strength as a result of increase in electronegativity →

Increasing order of acid strength as a result of decrease in bond energy ↓

CH_4 <NH_3< H_2O <HF
pK_a 58 35 16 3
Bond energy 414 389 464 565
(kJ/mole)

PH_3< H_2S < HCl
pK_a 27 7 -7
Bond energy 368 431
(kJ/mole)

H_2Se<HBr
pK_a 3 -9
Bond energy 305 364
(KJ/mole)

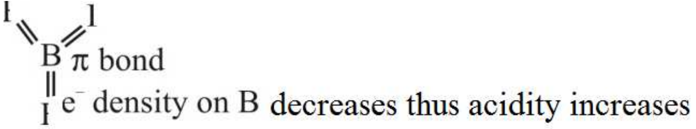
H_2Te< HI
pK_a 3 -10
Bond energy 238 299
(KJ/mole)

5.5.2. Inductive effect (I-effect)

The strength of acids and bases can be explained by inductive effect. In case of electronegative groups, due to –I effect, availability of electrons on the central metal atom decreased and thus, basicity of a base decreased. Electron donor groups (+I effect) like methyl (-CH_3) group, increase electron density on central atom, thus, increase its basicity. In case of aliphatic amines, steric factors are responsible for weak basicity of tertiary amine.

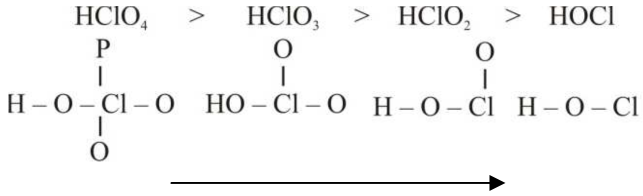
- PF_3 is weaker base than PH_3.
- Base strength order $NHMe_2 > NH_2Me > NMe_3 > NH_3$.
- Boron halides do not follow this argument, acid strength $BF_3 < BCl_3 < BBr_3$. In such cases, the atom with empty orbitals (like Cl and Br), receive electrons from filled valence orbitals (in boron, all the four orbitals are filled), thus, create a double bond between boron and halogen atom and boron atom become more electron deficient.

Bromine can more easily receive electrons from boron as compared to chlorine. Thus, BBr_3 is more acidic as compared to BCl_3.



5.5.3. Strength of oxoacids (Effect of electro negativity)

A) Presence of electronegative atoms tends to attract the shared pair of e⁻ towards themselves and thus, dissociation of O – H bond becomes easier and the acid will be stronger.

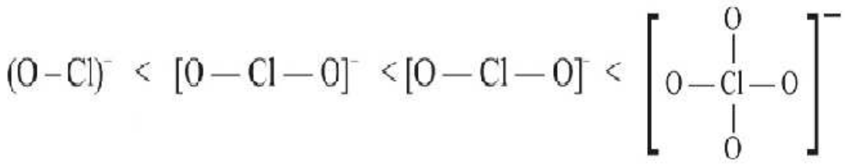


Order of acid strength

In $HClO_4$, the presence of maximum number of electronegative oxygen atoms increases its acidity.

$$Cl - OH - < OCl - OH < O_2Cl - OH < O_3Cl - OH$$

The other reason for the highest acidity of $HClO_4$ is that the negative charge after removing hydrogen can distribute over four oxygen atoms.



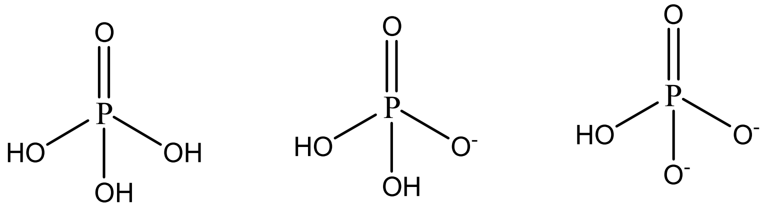
Maximum stability of ClO_4^- due to –ve charge distribution in four oxygen atoms, so minimum attraction of H^+ for distributed –ve charge and H^+ can be removed easily. While, in case of OCl^-, -ve charge delocalized on only one oxygen atom. Hence, shows minimum stability.

B) Among HClO, HBrO and HIO, HClO is the most acidic in nature.

$$HClO > HBrO > HIO$$

Electronegativity of I is lowest. Hence, the acidity of HIO will be the least.

C) For oxoacids of phosphorus, having more than one ionizable hydrogen, the pKa value increases with decrease in the number of ionizable hydrogen.



H_3PO_4 $H_2PO_4^-$ HPO_4^{2-}

pK 2 7 12

The negative charge of the conjugate base is spread over all the nonhydrogenated oxygens. The larger the number of these oxygen atoms, the more stable and weaker the conjugate base and stronger the hydrogened acid.

D) Acidity of cations in aqueous solution:

Metal ions with higher charges and smaller radii are stronger acids. The order of acidic strength is (Hydrated ions) alkali metals < alkaline earth metals < + 3 < +4 (transition metals). High positive charge promotes more hydrogen ion dissociation:

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$

more acidic less acidic

Solubility of metal hydroxide is also a measure of cation acidity. The stronger cationic acid, the less soluble the hydroxide. Transition metal +3 ions are acidic enough to form hydroxides.

- Higher charged ions are so strong acids in aqueous solutions that they exist only as oxygenated ions

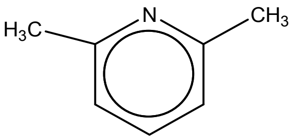
  CrO_4^{2-}, MnO_4^-, $Cr_2O_7^{2-}$, UO_2^+

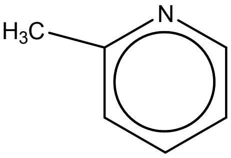
- $[Ni(OH)_4]^{2-}$ is a stronger base than $[Ni(OH)_4]^-$ ion

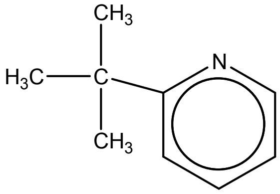
Acidity increases with increase of positive charge and basicity increases with increase in negative charge.

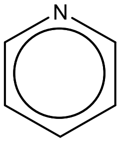
E) Steric effects:

Steric effects also influence acid-base behavior. Reactions of series of substituted pyridines with hydrogen ions show the following order of base strength:









2,6-dimethylpyridine > 2-methylpyridine > 2-t- butylpyridine > pyridine

5.6 SUMMARY

A compound may be acid or base on the basis of certain properties. There are different theories which classify and define the compounds into acids and bases. Some of the important theories are summaries below.

- According to the **Arrhenius concept**, acids are the compounds that give off H^+ ions in aqueous medium and **bases** are the compounds that release OH^- ions in aqueous medium.
- The **Bronsted-Lowry acids** are the compounds that give off H^+ ions to the other substances and **bases** are the compounds that accept H^+ from other substances. They also bring the concept of conjugate acids and bases.
- **Lewis acids** are the compounds that are electron deficient and can easily accept an electron pair while **bases** are the electron efficient compounds and can donate lone pair of electrons to other substances (Lewis acids).

- According to the **solvent concept, acids** are the positive species donor while **bases** are negative species donor in a solvent system.

- **Lux-Flood acids** are those compounds which can accept oxide ion and bases are oxide ion donor.

- In general acids have pH values in between 0 – 6.9 (<7), bases between 7.1 – 14 (>7) and neutral substances have a value of 7.

- The strength of acids and bases can be defined on the basis of pK_a and pK_b values. Higher the pK_a value, lower its acidity and similarly higher the pK_b values, weaker will be the base and *vice-versa.*

- The different factors that affect acidity or basicity are inductive effect, resonance, steric effect, electronegativity and charge on the species.

- The hydrides of 2nd period viz. CH_4, NH_3, H_2O and HF become more acidic as we move from CH_4 to HF. As the basicity of their conjugate base decreases from CH_3^- to F^-, the acidity of their conjugate acid increases from CH_4 to HF.

- Among the hydroacids of V or 15 Group elements viz. NH_3, PH_3, AsH_3, SbH_3, BiH_3, with the increase in size and decrease in electronegativity from N to Bi, there is decrease in electron density, thus basic character decreases.

  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

  Decreasing order of basic character

- The strength of hydrides as acids increases in the order

  $H_2O < H_2S < H_2Se < H_2Te$

  $HF < HCl < HBr < HI$

- For oxoacids containing the central atom, the acidity increases with increasing oxidation number.

$HClO < HClO_2 < HClO_3 < HClO_4$

Hence, basic strength of their conjugate base is –

$ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$

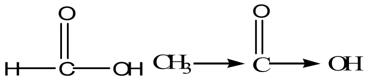
- The acidic character of oxoacids of different elements in same oxidation state decreases with the increase in atomic number of the central atom.

$HOCl > HOBr > HOI$

- $[Fe(H_2O)_6]^{3+}$ is stronger acid than $[Fe(H_2O)_6]^{2+}$ due to increase in positive charge.

A) **I Effect**	Electron withdrawing groups	Electron donating groups
	↓(-I)	↓ (+I)
	increases acidic strength & decreases basic strength	Decreases acidic Strength and Increases basic strength

1)

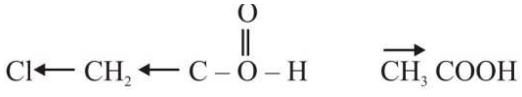


$H-\overset{\overset{O}{\parallel}}{C}-OH \quad CH_3\rightarrow\overset{\overset{O}{\parallel}}{C}\rightarrow OH$

Strong acid Weak acid

2) $CH_3COOH>CH_3CH_2COOH>(CH_3)_2CHCOOH$

4)



$Cl\leftarrow CH_2\leftarrow \overset{\overset{O}{\parallel}}{C}-O-H \qquad \overrightarrow{CH_3}\,COOH$

Strong acid Weak acid

$\overrightarrow{CH_3}\,COO^-$ (Less stable)

$Cl\overleftarrow{CH_2}\,COO^-$ (more stable)

5) $BMe_3 < BH_3 < BF_3$

6) $C_6H_5COOH > CH_3COOH$

(7) $NH_3 < CH_3NH_2 < R_3N < R_2NH$

(8) $C_6H_5NH_2 < NH_3$

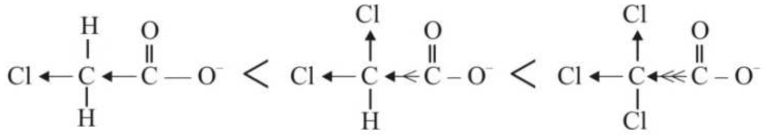
(B) Magnitude of –I effect (Order of acidic strength)

$FCH_2\,COOH > ClCH_2\,COOH > BrCH_2\,COON > CH_2COOH$

$CF_3CH_2OH > CCl_3CH_2OH > CH_3CH_2OH$

(C) Number of electron withdrawing groups

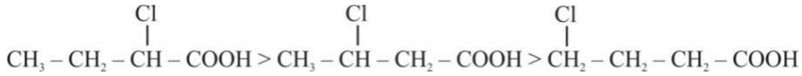
$CH_2ClCOOH < CHCl_2COOH < CCl_3COOH$



$$Cl \leftarrow \overset{H}{\underset{H}{C}} \leftarrow \overset{O}{\overset{\|}{C}} - O^- < Cl \leftarrow \overset{Cl}{\overset{\uparrow}{\underset{H}{C}}} \twoheadleftarrow \overset{O}{\overset{\|}{C}} - O^- < Cl \leftarrow \overset{Cl}{\overset{\uparrow}{\underset{Cl}{C}}} \lll \overset{O}{\overset{\|}{C}} - O^-$$

$NH_3 > NH_2(C_6H_5) > NH(C_6H_5)_2 > N(C_6H_5)3$

(D) Distance of electron withdrawing group from –COOH in aliphatic carboxylic acids



$$CH_3-CH_2-\overset{Cl}{\overset{|}{CH}}-COOH > CH_3-\overset{Cl}{\overset{|}{CH}}-CH_2-COOH > \overset{Cl}{\overset{|}{CH_2}}-CH_2-CH_2-COOH$$

(E) Steric effect

$(CH_3)_2\,NH > CH_3NH_2 > (CH_3)_3N$

(F) Charge on species

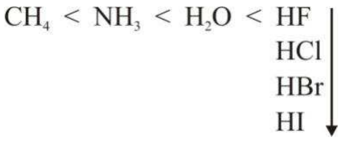
$$[M\,(H_2O)_6]^{3+} + H_2O \rightleftharpoons [M\,(H_2O)_5\,(OH)]^{(n-1)} + H_3O$$

Charge to size ratio → more polar the hydrated cation, weaker the O – H bond, more acidity.

$[Be(H_2O)_n]^{2+} > [Cu(H_2O)_n]^{2+} > [Mg(H_2O)_n]^{2+} > [Ca(H_2O)_n]^{2+}$

$[Fe(H_2O)_6]^{3+} > [V(H_2O)_6]^{3+} > [Cr(H_2O)_6]^{3+}$

(G) Effect of Electronegativity



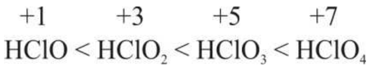
$$CH_4 < NH_3 < H_2O < \begin{array}{l} HF \\ HCl \\ HBr \\ HI \end{array}\Big\downarrow$$

$$HCl > HBrO > HIO$$

$$HClO_4 > HBrO_4 > HIO_4$$

$$H_3PO_4 > H_3A_sO_4 > H_3SbO_4$$

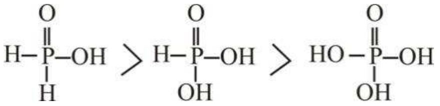
(H) Oxidation no of the central atom



$$\overset{+1}{HClO} < \overset{+3}{HClO_2} < \overset{+5}{HClO_3} < \overset{+7}{HClO_4}$$

$$HNO < HNO_2 < HNO_3$$

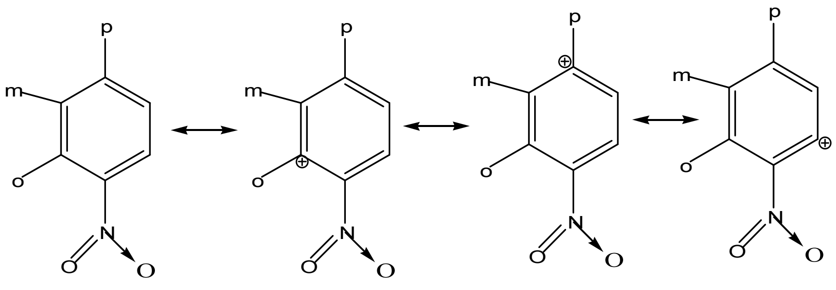
(I) Number of –OH groups per unhydroxyl O atom



$$H-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-OH > H-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH > HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH$$

(J) Resonance effects

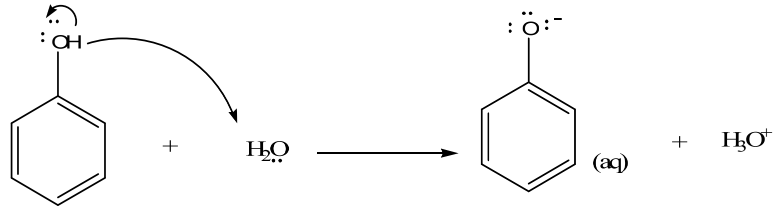
- C_6H_5COOH more acidic as compared to CH_3COOH.
- $C_6H_4NO_2COOH$ {ortho (o-) , meta (m-), para (p-)} are more acidic than C_6H_5COOH.

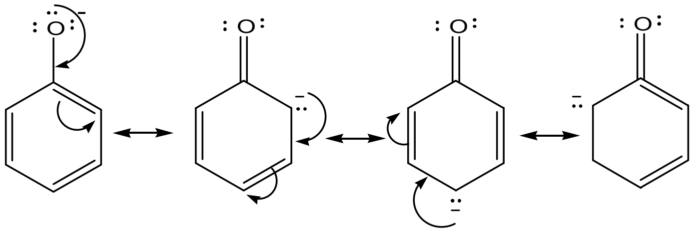


- The order of acidic strength of $C_6H_4NO_2COOH$ is

o-nitrobenzoic acid > p-nitrobenzoic acid > m-nitrobenzoic acid

- Phenol is more acidic as compared to C_2H_5OH.





Resonance structure of phenoxide ion

$$C_6H_5OH \longrightarrow C_6H_5O^- + H^+$$

Less stable species More stable

$$C_2H_5OH \longrightarrow C_2H_5O^- + H^+$$

More stable species Less stable

- Order of basicity of hydrides of fifth group is $NH_3 > PH_3 > A_5H_3 > SbH_3 > BiH_3$

As size of central metal increases, the lone pair occupies greater volume and hence, electron density around the central atom decreases. Therefore, the hydride with small sized central atom is more basic.

5.7. TERMINAL QUESTIONS

5.7.1. Fill in the blanks

i. In 1884, the Swedish chemist Arrhenius defined acid as the species which ionize in water to produce …….. or …….. ions.

ii. Arrhenius's definitions of acids and bases are limited to…………………...

iii. Hence, Bronsted in 1923 proposed that a substance capable of donating a proton to any substance is …………. and a ………… can be defined as a species capable of accepting proton from any other substance.

iv. Aqueous solution of ………………………….. oxides is acidic.

v. Aqueous solution of …………….. oxides and is basic.

vi. The strength of an acid (HA) and a base (BOH) can be expressed quantitatively in terms of the …………………………………………………. constant.

vii. A substance which acts both as an acid as well base in different reactions is called ……………………………..

viii. ……………………………. also gave the concept of conjugate acid base pair.

ix. Conjugate base is a species that remains when one ………….. has been removed from the acid.

x. An acid base pair which is different by a proton is called ……………. acid base pair.

xi. Acid stronger than H_3O^+, react with water to produce H_3O^+ and their …………………………….. bases.

xii. According to ……………… concept, the base is an oxide donor and the acid is an oxide acceptor.

xiii. Base is the species that can form …………… charged species and acid is the species that can produce …………………… charged species.

xiv. Solvent system concept was introduced by ……………….. in 1905 and was extended by ………………….. in 1928.

xv. According to solvent system concept, the substance which can give BrF_2^+ in BrF_3 is ……………..

xvi. According to G. N. Lewis, a ……………….. is an electron pair acceptor and a Lewis base is an electron pair donor.

xvii. According to HSAB principle, hard acids form stable complexes with …………………… and soft acids with……………………….

xviii. In Hard acids, d-orbitals are either ………….. or ....

xix. Higher the pK_a or pK_b values, ……………… the acid or base.

xx. PF_3 is ………………. base than PH_3.

xxi. Among HClO, HBrO and HIO, ……………… is the most acidic in nature.

xxii. Metal ions with higher charges and smaller radii are ………………….. acids.

xxiii. Higher charged ions are so strong acids in aqueous solutions that they exist only as ……………………… ions.

5.7.2. State True (T) or False (F)

i. Solution of acids in water conducts electricity.

ii. Arrhenius acids are called as proton donors / hydrogen ion donors / hydronium ion donors.

iii. H_3O^+ is a Bronsted acid.

iv. In the gas phase the formation of $NH_4Cl_{(s)}$ by the combination of $NH_{3(g)}$ and $HCl_{(g)}$ can be explained by Arrhenius concept.

v. The molecules or ions that can act as Bronsted acids as well as Bronsted bases are called amphoteric substances.

vi. Any acid-base reaction involves one acid and one base.

vii. The substances which form solvent cations when dissolved in that solvent are called bases while the substances which give solvent anions when dissolved in that solvent are called acids.

viii. Lewis acid reacts with Lewis base and forms a compound which is called adduct or complex compound.

ix. Molecules whose central atom is linked with more electronegative atom by double bonds are Lewis acids.

x. Pearson gave the classification of Lewis acids and Lewis bases into hard and soft acids and bases.

xi. Base strength order of amine and substituted amines is $NHMe_2 < NH_2Me < NMe_3 < NH_3$.

xii. $[Fe(H_2O)_6]^{3+}$ is more acidic as compared to $[Fe(H_2O)_5(OH)]^{2+}$.

xiii. $[Ni(OH)_4]^{-}$ is more basic as compared to $[Ni(OH)_4]^{2-}$.

xiv. Order of basic strength of substituted pyridine is 2,6-dimethylpyridine > 2-methylpyridine > 2-t- butylpyridine

5.7.3. Long answer questions

i. What are the general characteristics of acids and bases?

ii. Discuss Arrhenius theory of acids and bases.

iii. Write short notes on the following:

   a. Conjugate acid and base
   b. Neutralization reaction
   c. Lux-Flood concept
   d. Solvent system concept

iv. Discuss Lewis acid and base concept

v. Differentiate between hard and soft acids and bases.

vi. How electronegativity affect acid and base strength?

vii. Discuss strength of oxoacids.

5.8. ANSWERS

5.8.1. Fill in the blanks

i. H^+ or H_3O^+

ii. Aqueous solutions

iii. acid, base

iv. non-metallic

v. metallic

vi. ionization (or dissociation)

vii. amproteric

viii. Bronsted-Lowry

ix. proton
x. conjugate
xi. conjugate
xii. Lux-Flood
xiii. negatively, positively
xiv. Franklin, Cady-Esley
xv. acid
xvi. a Lewis acid
xvii. hard bases, soft bases
xviii. vacant, non-existent
xix. stronger
xx. weaker
xxi. HClO
xxii. Stronger
xxiii. Oxygenated

5.8.2. True (T) or False (F)

i. T
ii. T
iii. T
iv. F
v. T
vi. F
vii. F
viii. T
ix. T
x. T
xi. F
xii. T
xiii. F
xiv. T

UNIT 6: BASIC STEREOCHEMISTRY

CONTENTS:

6.1 OBJECTIVES

By the end of this unit you will be able to

- Describe isomers and explain the structural formulae for a variety of isomeric organic compounds
- Explain various kinds of structural and stereo isomerism along with their representation.
- Differentiate geometrical and optical isomers
- Represent three dimensional organic molecules in two dimensions
- Learn chirality, enantiomers, diastereomers and their relative/absolute configurations
- Learn the nomenclature (cis-trans, E/Z, D/L, d/l, erythro/threo and R/S) of different stereoisomers

6.2 INTRODUCTION

Stereochemistry deals with three dimensional representation of molecule in space. This has sweeping implications in biological systems. For example, most drugs are often composed of a single stereoisomer of a compound. Among stereoisomers one may have positive effects on the body and another stereoisomer may not or could even be toxic. An example of this is the drug thalidomide which was used during the 1950s to suppress the morning sickness. The drug unfortunately, was prescribed as a mixture of stereoisomers, and while one stereoisomer actively worked on controlling morning sickness, the other stereoisomer caused serious birth defects.

The study of stereochemistry focuses on stereoisomers and spans the entire spectrum of organic, inorganic, biological, physical and especially supramolecular chemistry. Stereochemistry includes method for determining and describing these relationships; the effect on the physical or biological properties.

6.3 TYPES OF ISOMERISM

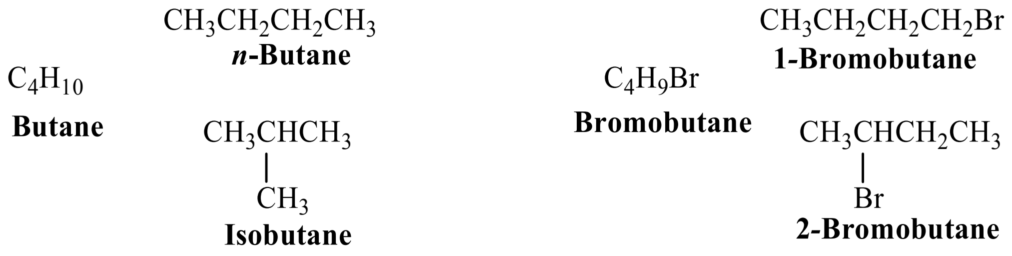
Generally isomerism can be divided in to two categories;

a. Structural (constitutional) Isomerism
b. Stereo (configurational) Isomerism

a. Structural (constitutional) Isomerism

Structural isomerism is also known as 'constitutional isomerism'. Structural isomerism arises when a molecule can be represented in to two or more than two different structures. The difference in structure is due to the difference in the arrangement of atoms within the molecules, irrespective of their position in space. In other words, structural isomers are compounds those have identical molecular formulae but different structural formulae; and the phenomenon is called structural isomerism.

Examples 1: Structural isomer of Butane (C_4H_{10}) and Bromobutane (C_4H_9Br)



C_4H_{10} **Butane**

$CH_3CH_2CH_2CH_3$ ***n*-Butane**

$$\underset{\displaystyle CH_3}{CH_3\overset{}{\underset{|}{C}}HCH_3}$$

Isobutane

C_4H_9Br **Bromobutane**

$CH_3CH_2CH_2CH_2Br$ **1-Bromobutane**

$$CH_3\underset{\underset{\displaystyle Br}{|}}{C}HCH_2CH_3$$

2-Bromobutane

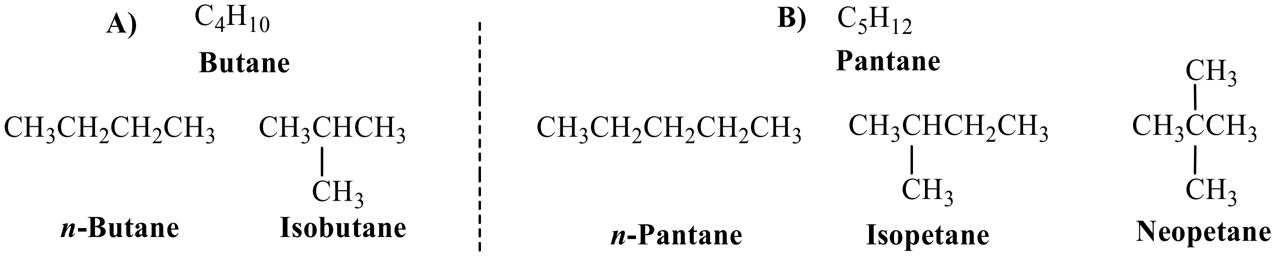
Structural isomerism can also be subdivided in to five types

1) Chain Isomerism
2) Functional Isomerism
3) Position Isomerism
4) Metamerism
5) Tautomerism

1) Chain Isomerism: Chain isomers are those isomers having difference in the order in which the carbon atoms are bonded to each other. In other words chain isomers have variable amounts of branching along the hydrocarbon chain.

☞ *If you observe two or more than two molecules having same molecular formulae, but difference in their hydrocarbon chain length, you should understand that these are chain isomers of each other.*

Example 2: Chain isomers of Butane (A) and Pentane (B)



A) C_4H_{10} **Butane**

$CH_3CH_2CH_2CH_3$ **n-Butane**

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$ **Isobutane**

B) C_5H_{12} **Pantane**

$CH_3CH_2CH_2CH_2CH_3$ ***n*-Pantane**

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$ **Isopetane**

$CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_3$ **Neopetane**

2)Functional Isomerism: Two or more than two molecules those having the same molecular formulae but have different functional groups are called functional isomers and the phenomenon is termed as functional isomerism.

☞ *If you observe two or more than two molecules having same molecular formulae, but difference in their functional groups, you should understand that these are functional isomers of each other.*

Example 3: Ethyl alcohol and Dimethyl ether

CH_3CH_2OH	CH_3OCH_3
Ethyl alcohol	**Dimethyl ether**

Example 4: *n*-Butyl alcohol and Diethyl ether

$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2OCH_2CH_3$
***n*-Butayl alcohol**	**Diethyl ether**

3) Position Isomerism: Two or more than two molecules those having same molecular formulae but having difference in the position of functional group on the carbon chain are called position isomers and the phenomenon is called as position isomerism.

☞ *If you observe two or more than two molecules having same molecular formulae, but difference in their functional groups, you should understand that these are functional isomers of each other.*

Example 5: 1-Butene and 2-Butene

$CH_3CH_2CH{=}CH_2$

1-Butene

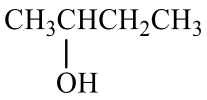
$CH_3CH{=}CHCH_3$

2-Butene

Example 6: 1-Butyl alcohol, 2-Butyl alcohol and *t*-Butyl alcohol

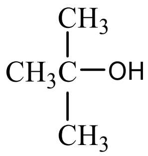
$CH_3CH_2CH_2CH_2OH$

1-Butyl alcohol



$CH_3\underset{\underset{OH}{|}}{C}HCH_2CH_3$

2-Butyl alcohol



$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

***t*-Butyl alcohol**

4) Metamerism: Two or more than two molecules those having same molecular formulae and functional group but having difference in the distribution of carbon atoms on either side of functional group are called metamers and the phenomenon is called the metamerism.

☞ *When you see two or more than two molecule with identical molecular formulae but while structural representation you observe there is a difference in the alkyl group attached to same functional group you should understand these molecules are metamers of each other.*

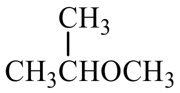
Example 7: Diethyl ether, Methyl propyl ether and isopropyl methyl ether

$CH_3CH_2OCH_2CH_3$

Diethyl ether

$CH_3CH_2CH_2OCH_3$

Methyl propyl ether



$CH_3\overset{\overset{CH_3}{|}}{C}HOCH_3$

Isopropyl methylether

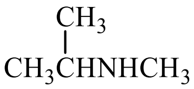
Example 8: Diethyl amine, Methyl propyl amine and isopropyl methyl amine

$CH_3CH_2NHCH_2CH_3$

Diethyl amine

$CH_3CH_2CH_2NHCH_3$

Methyl propyl amine



$CH_3\overset{\overset{CH_3}{|}}{C}HNHCH_3$

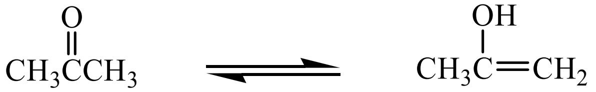
Isopropyl methylamine

5) **Tautomerism:** This is a special kind of isomerism where both the isomers are interconvertible and always exist in a dynamic equilibrium to each other. Due to their interconversion change in functional group takes place that gives two different isomers of an organic compound. This phenomenon is called Tautomerism.

> ☞*When you observe two different isomeric forms of an organic compound are rapidly interconvertible to each other you should recognize them as tautomer of each other.*

i. ***Remember:*** *Tautomers are not the resonance structure of same compound*

Example 9: Acetone exists in rapid equilibrium with Prop-1-en-2-ol

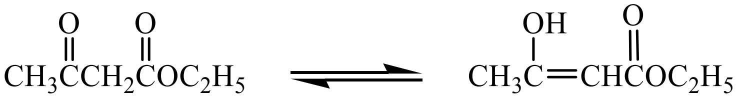


$$CH_3\overset{\overset{O}{\|}}{C}CH_3 \rightleftharpoons CH_3\overset{\overset{OH}{|}}{C}{=}CH_2$$

Acetone
(keto form)
<99%

Prop-1-ene-2-ol
(enol form)
>1%

Example 10: Tautomeric forms of Ethyl acetoacetate under rapid equilibrium



$$CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \rightleftharpoons CH_3\overset{\overset{OH}{|}}{C}{=}CH\overset{\overset{O}{\|}}{C}OC_2H_5$$

(keto form)
93%

(enol form)
7%

b. Stereo (configurational) Isomerism

Stereoisomerism is arises due to the difference in arrangement (configuration) of atoms or groups in space. When two or more than two isomers have the same structural formulae but having difference in the arrangement (configuration) of atoms in space are called stereo isomer and the phenomenon is called stereo isomerism.

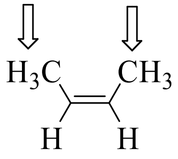
Stereo isomerism can be further classified as

i. Geometrical or cis-trans isomerism
ii. Optical isomerism

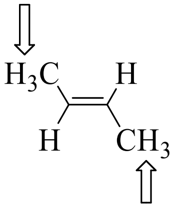
Geometrical isomerism is generally observed in alkenes and cyclic compounds due to their restricted rotation around carbon- carbon bond. For example *cis*- and *trans* 2-butene have same connection of bond and molecular formulae.

☞ *If you observe two similar groups are on the same side of C=C bond this is called cis- isomer; whereas, if two similar groups are on opposite side of C=C bond this is known as trans- isomer.*

Example 11: *cis*- and *trans*- isomerism in 2-butene



***cis*-2-butene**

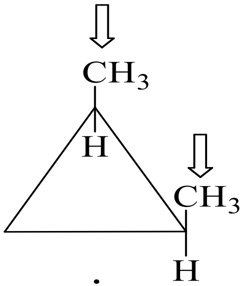


***trans*-2-butene**

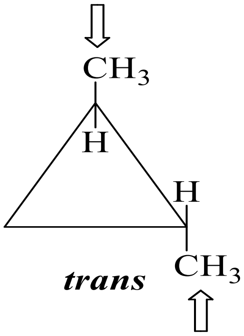
☞ *You can understand that due to the presence of one σ (sigma) and one π (pi) bond in carbon–carbon double bond, rotation around C=C bond is not possible. The restricted rotation around C=C bond is responsible for geometrical isomerism in alkenes.*

You can easily observe that rotation around C-C bond is also not possible in cyclic compounds as the rotation would break the bonds and break the ring. Thus geometrical isomerism is also possible in cyclic compounds.

Example 12: *cis*- and *trans*- isomers of 1,2-dimethylcyclopropane



cis



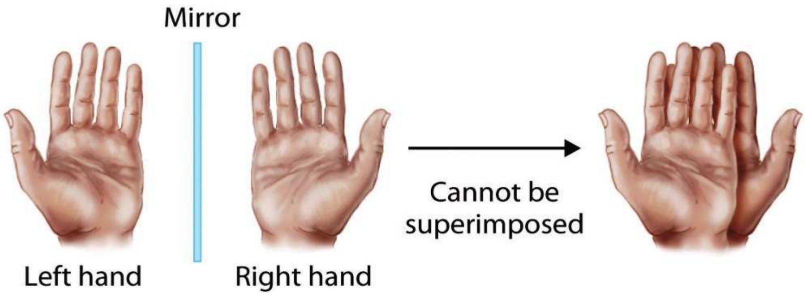
trans

6.4 CONCEPT OF ENANTIOMERS

The necessary condition for a molecule to have optical isomerism is that molecule should not have any kind of symmetry elements present in it, in other words the molecule should be dissymmetric. Such molecules are called '*Chiral'* and the property is called '*molecular chirality*'. Optically active chiral molecules which are non-superimposable on their mirror images are called '*enantiomers'* and the phenomenon is known as '*enantiomerism'*. To exhibit optical isomerism an organic compound must have at least one asymmetric carbon atom. An asymmetric carbon atom is that which is bonded to four different atoms or groups.

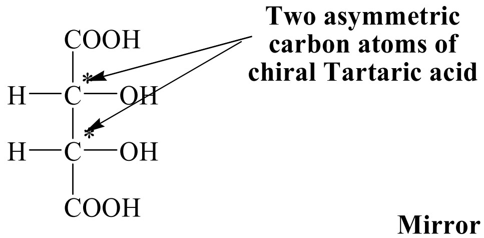
☞ *We can easily understand the chirality by comparing our hands (left hand and right hand). Our left hand and right hand are the best example of non-superimposable mirror image of each other. Each hand is therefore considered as chiral.*

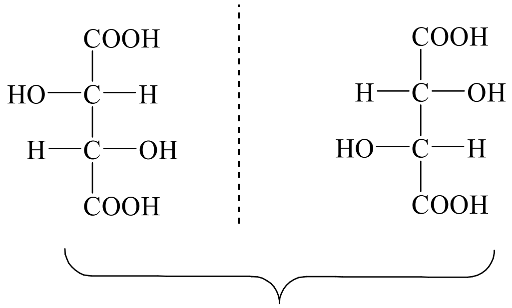
ii. **Remember:** *Our left hand and right hand are non-superimposable mirror image of each other each one of them is chiral.*



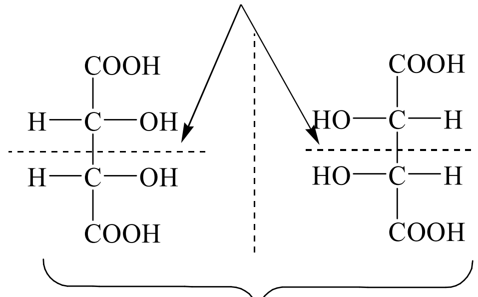
iii. **Remember:** *Chirality is the necessary and sufficient condition for the existence of enantiomers.*

Example 13. Tartaric acid has two asymmetric carbon and it exists in four forms, out of them two form are optically active and two are optically inactive.





Non-superimposable mirror images (Enantiomers)



Non-superimposable mirror images with each one having plane of symmetry optically inactive

Stereogenic Centre:

As we discussed in previous section that if a molecule contains one carbon atom which is directly bonded with four different groups or atoms, and the molecule do not have any kind of symmetry element present in it, such molecule is called asymmetric or chiral.

When the interchange of the position of two directly bonded groups or atoms of a centre carbon atom results a new stereoisomer, such chiral centre is called stereo centre or stereogenic centre.

If the new stereoisomer is a non-superimposable mirror image of the original molecule such carbon centre is called chiral carbon centre.

Remember: All the chiral centres are stereogenic centres but all stereogenic centres are not chiral centre.

Example 14: Bromochlorofluoroidomethane exhibits chiral carbon centre

Interchange of F and Cl results non-superimposable stereoisomers

6.5 OPTICAL ACTIVITY

It is already known to you (from section 4.5) that the optical activity is an ability of a chiral molecule to rotate the plane of plane-polarized light either towards left or right direction. The rotation is measured by an instrument called Polarimeter. When a beam of plane polarized light passes through a sample that can rotate the plane polarized light, the light appears to dim because it no longer passes straight through the polarizing filters. The amount of rotation is quantified as the number of degrees that the analyzing lens must be rotated to observe the no dimming of light appears. Optical rotation can be measured by using the following formulae

$$[\alpha]_{\lambda}^{t} = \frac{100\alpha}{lc}$$

Where α is observed angle of rotation; t is the temperature of during experiment; λ is the wavelength of light used; l is the length of the tube in decimeter; and c is the concentration of the compounds per 100 mL of solution.

Optically active chiral compounds that are non-superimposable mirror image of each other are called enantiomers.

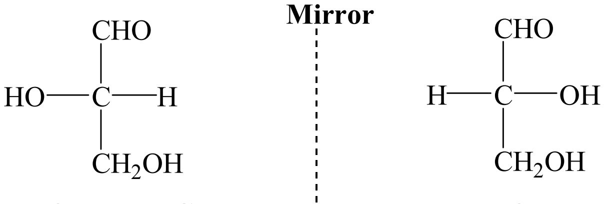
6.5.1 Properties of enantiomers:

The main properties of enantiomers are given as follow

- Enantiomers always exist in pair
- Enantiomers are non-superimposable mirror image to each other

- Enantiomers have same physical properties (like boiling point, melting point, solubility, density, viscosity, refractive index etc.) and chemical properties in achiral environment
- Each enantiomer have opposite behavior with respect to plane polarized light, if one of them will rotate the plane polarized light towards right hand direction then definitely the other will rotate the plane polarized light towards left hand direction.
- Each enantiomer shows the same chemical reactivity with achiral reagent; however they have different reactivity with chiral reagent.

Example 15: Glyceraldehyde molecule is a chiral molecule. It has a pair of enantiomer with same physical properties except their behavior towards plane polarized light



Molecular formula : $C_3H_6O_3$
Mol. Wt.: 90.08
Boiling point : 228°C
Melting point : 145 °C
Density : 1.455 g/cm^3

Molecular formula : $C_3H_6O_3$
Mol. Wt.: 90.08
Boiling point : 228°C
Melting point : 145 °C
Density : 1.455 g/cm^3

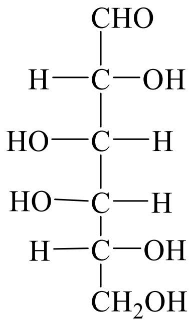
Enantiomeric pair of Glycerldehyde

☞ *You can see that the glyceraldehyde molecule can exists in two enantiomeric forms which differ only in the arrangement of bonded atoms around the centre chiral carbon. The physical properties (like molecular formula, molecular weight, melting point, boiling point and density etc.) of both the isomers are same. But if one isomer will rotate the plane polarized light towards right hand direction (dextrorotatory) then the other one will rotate the plane polarized light towards left hand direction (levorotatory).*

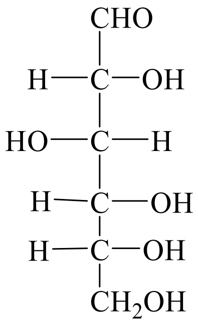
6.6 DIASTEREOMERS

Diastereomers are those stereoisomers that are not mirror image of each other, in other words you can understand the diastereomers are stereoisomers that are not enantiomers. Diastereomers are non-enantiomeric stereoisomers with two or more stereo centres. The pair of stereoisomer that differs in the arrangement of atoms/groups bonded with at least one stereocentres is called diastereomers.

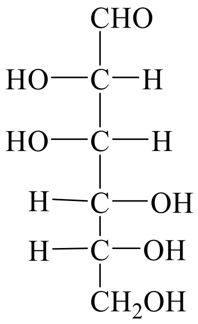
Example 16: D-Galactose, D-Glucose and D-Mannose are the non-mirror image stereoisomer of each other. Therefore are called diastereomers.



D-Galactose

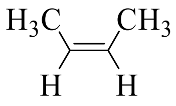


D-Glucose

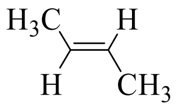


D-Mannose

Example 17: *cis*- and *trans*-2-butenes are non-mirror image stereoisomers of each other hence are called diastereomers.



***cis*-2-butene**



***trans*-2-butene**

6.6.1 Properties of Diastereomers

The main properties of diastereomers are given as follows:

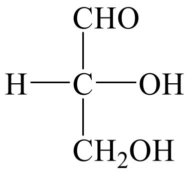
- All the stereoisomers except enantiomers are diastereomers.
- Diastereomers have different physical properties like boiling point, melting point, density, solubility, density, viscosity, refractive index etc.
- Diastereomers have different chemical properties like rates of reactions, reactivity even in achiral reaction medium.
- This difference in physical and chemical properties of diastereomers is very useful in the separation of enantiomers from their mixture.

6.7 RELATIVE AND ABSOLUTE CONFIGURATION

Relative and absolute configuration of a compound discusses about the spatial arrangement of atoms/groups around the centre chiral atom. Relative configuration is a comparison of the spatial arrangement of attached atoms/groups of two different chiral centres. Relative configuration is a geometrical property which do not changes on reflection; whereas, the absolute configuration is the precise arrangement of atoms in three dimensional space. The *D/L* system is usually known as relative configuration whereas, the *R/S* stereo descriptor or nomenclature system for chiral molecules is known as absolute configuration. The absolute configuration is a topographic property which changes on reflection.

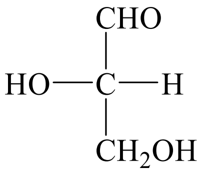
6.7.1 D*/L* nomenclature:

The *D/L* nomenclature is the oldest nomenclature system for enantiomers. In this nomenclature system the configuration of all the compounds were given with respect to glyceraldehyde molecule, where the configuration of glyceraldehyde molecule is taken as an arbitrary standard. According to this nomenclature if in glyceraldehyde molecule the –OH group on right and –H on left, the –CHO and $–CH_2OH$ groups being on top and bottom, respectively the molecule is designated as (+) Glyceraldehyde and it was arbitrary given the configuration symbol *D*. The mirror image of this compound (-) glyceraldehyde was given the configuration *L*.



$$\begin{array}{c} \text{CHO} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$$

***D*-(+)-glyceraldehyde**

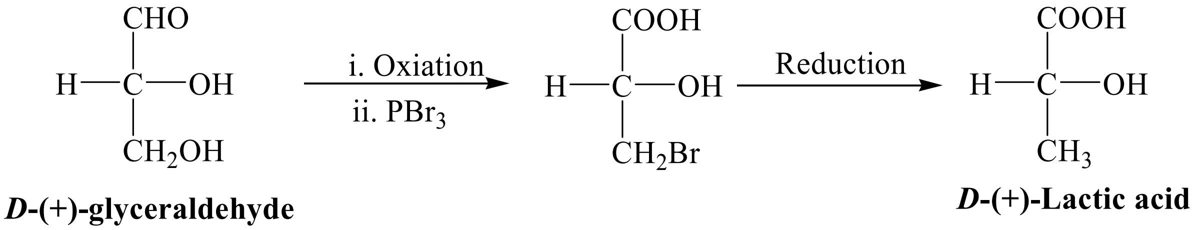


$$\begin{array}{c} \text{CHO} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{CH}_2\text{OH} \end{array}$$

***L*-(+)-glyceraldehyde**

Any compound that can be prepared, or converted in to *D*-(+)-glyceraldehyde will belong to *D* series (relative configuration), whereas, any compound that can be prepared, or converted in to *L*-(+)-glyceraldehyde will belong to *L* series.

Example 18: Lactic acid obtained from *D*-(+)-glyceraldehyde and hence assigned D configuration



Remember:

- *There is no correlation between the D and L designation and the sign of rotation. D form of isomer may be levorotatory, and L form of isomer may be dextrorotatory and vice versa.*
- *The D/L nomenclature is limited to the compound that can pe prepared or converted from the glyceraldehyde.*
- *It is limited to only one chiral atom.*

6.7.2 R/*S* nomenclature:

Since you have been noted from the above discussion on D/L configuration, there are several drawbacks associated with the D/L nomenclature system. Hence a definite and universally applicable nomenclature system was needed to specifying the absolute configuration of each chiral centre in a molecule. Cahn and coworkers (1956, 1966) have proposed a new and universally applicable nomenclature pattern for the determination of absolute configuration of any chiral molecule. This is known as the R/S system or Cahn-Ingold-Prelog (CIP) nomenclature. It involves following two steps.

- In first step we need to assign the priority to the four different atoms/groups attached to a chiral centre.
- Priorities to the groups/atoms can be assigned as per the **sequence rule**.
- After assigning the priority to the atoms/groups attached to the chiral centre, the molecule is oriented in such a way that the lowest priority group is directed away to the observer.
- Now the arrangement of the remaining atoms/groups is viewed by following deceasing order of priorities from highest priority to lowest priority.

- While viewing the atoms/groups in their decreasing order if your eyes follow the clockwise direction then the chiral centre will have *R* configuration; whereas if your eyes follow anticlockwise direction the chiral centre will have *S* configuration.
- When a molecule has two or more than two chiral centres then the same process should be followed to assign their configuration.

6.8 GEOMETRICAL ISOMERISM

Geometrical isomerism is generally observed in alkenes and cyclic compounds due to their restricted rotation around carbon- carbon bond. The rotation about a double bond in alkene or about a single bond in a cyclic/ring like compound is restricted. Double bonded system consists of a σ (sigma) and a π (pi) bond perpendicular to each other. It is not possible to rotate the molecule about carbon-carbon bond. The rotation will break the π bond as a result the molecule will lose its identity. In some cased the rotation about single bond is also restricted due to steric hindrance. Geometrical isomerism is shown by various groups of compounds the major class of compounds that exhibit geometrical isomerism are classified as:

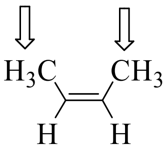
i. Compounds having double bond;

C=C, C=N, N=N

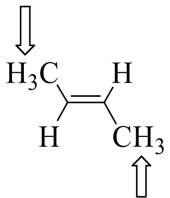
For example *cis*- and *trans*-2-butene have same connection of bond and molecular formulae.

☞ *If you observe two similar groups are on the same side of C=C bond this is called cis-isomer; whereas, if two similar groups are on opposite side of C=C bond this is known as trans- isomer.*

Example 19: *cis*- and *trans*- isomerism in 2-butene



***cis*-2-butene**



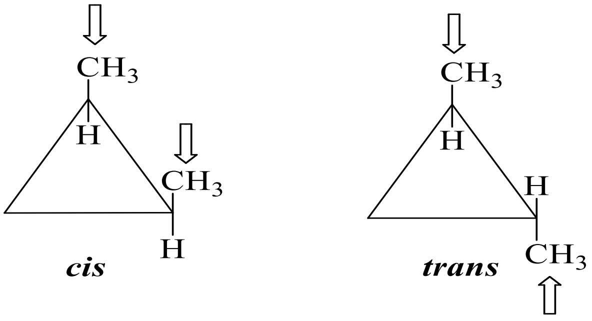
***trans*-2-butene**

- ☞ *You can understand that due to the presence of one σ (sigma) and one π (pi) bond in carbon–carbon double bond, rotation around C=C bond is not possible. The restricted rotation around C=C bond is responsible for geometrical isomerism in alkenes.*

ii. Cyclic compounds like homocyclic, heterocyclic and fused-ring systems

You can easily observe that rotation around C-C bond is also not possible in cyclic compounds as the rotation would break the bonds and break the ring. Thus Geometrical isomerism is also possible in cyclic compounds.

Example 20: *cis*- and *trans*- isomers of 1,2-dimethylcyclopropane



Conditions for geometrical isomerism:

Following two conditions are necessary for any compounds to show geometrical isomerism

a) There should be restricted (not allowed) rotation about a bond in a molecule.
b) Both substituents/atoms on each carbon about which rotation is not allowed should (restricted) be different.

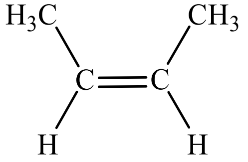
- ☞ ***Remember**: Geometrical isomers are non-mirror image of each other hence they are called diastereomers. Therefore their physical and chemical properties are different.*
- ☞ *Triple bonded molecules do not exhibit any kind of stereoisomerism because such molecule shows cylindrical symmetry.*

6.9 E & Z SYSTEM OF NOMENCLATURE

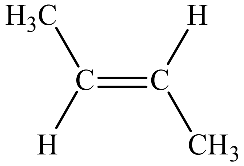
We have already discussed about the *cis*- and *trans*- nomenclature of geometrical isomerism. The *cis*- and *trans*- nomenclature is the oldest and most fundamental nomenclature system for geometrical isomerism. The *cis*- and *trans*- nomenclature system is applicable only for those geometrical isomers in which at least one identical atoms/groups is bonded with each double bonded carbon. If both the identical groups/atoms are on same side of double bond the isomer is called as *cis*- isomer; whereas, if both identical groups/atoms are on opposite side of the double bond the isomer is called as *trans*- isomer (see example 1 of this unit).

The *cis*- and *trans*- nomenclature method is limited to the molecule in which identical groups/atoms are attached to double bonded carbon. If all the atoms/groups on double bonded carbon are different then the configuration of such molecule could not be assigned as *cis*- and *trans*- nomenclature. A more general nomenclature (*i.e.* E/Z nomenclature) was introduced which was based on Cahn-Ingold-Prelog system. In E/Z system the configuration is specified by the relative positions of two highest priority groups/atoms on the two carbons of the double bond.

Let us understand the E/Z nomenclature system by considering an example which we have already discussed in the beginning of this Unit (example 1).



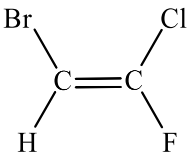
***cis*-2-butene**



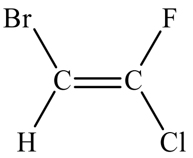
***trans*-2-butene**

You can easily identify which one is *cis*- isomer and which one is *trans*- just by looking the position of similar atoms/groups. It is a simple and visual way of telling the two isomers apart. *So why do we need another system?*

Now consider one another example in which we will change all the atoms/groups in above example by replacing one CH_3- by Br, other CH_3- by Cl, and one H- by F. Now try to predict the nomenclature of these two isomers of 2-bromo-1-chloro-1-fluoroethene (I and II). *Could you name these isomers using cis- and trans- nomenclature?* The simplest answer is ‘NO’.

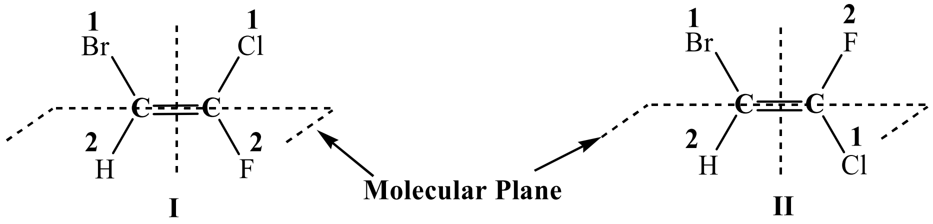


I

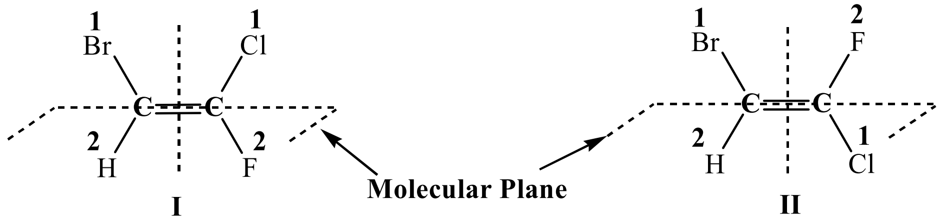


II

Because everything attached to the carbon-carbon double bond is different, there are not so simple so that you can predict them as *cis*- and *trans*- to each other. The E/Z system of nomenclature provides the most appropriate solution to above problem. This system is based on the priority of the attached atoms/groups on each double bonded carbon. The priority of the atoms/groups can be assigned as per the 'Sequence Rule' or 'CIP Rule' given by Cahn-Ingold-Prelog. We have already discussed the detail about 'Sequence Rule'. Now assign priority to atoms/groups attached to each double bonded carbon in above example.



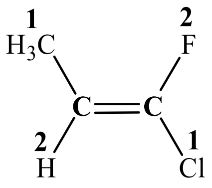
We can easily observe that the both higher priority atoms/groups on each double bonded carbon of isomer **I** are on same side; whereas, the higher priority atoms/groups on each double bonded carbon of isomer **II** are on opposite side. If the two groups with the higher priorities are on the same side of the double bond, such isomer is designated as the (*Z*)- isomer. So you would write it as (*Z*)-name of compound. The symbol *Z* comes from a German word *ZUSAMMEN*, which means together. If the two groups with the higher priorities are on opposite sides of the double bond, then such isomer is designated as (*E*)- isomer. *E* comes from the German *ENTGEGEN*, which means opposite. Thus in given example the isomer **I** is having both higher priority groups/atoms are on same side of double bond, hence it is *Z*- isomer; whereas, the isomer **II** is having both higher priority groups/atoms are on opposite side of the double bond, hence it is *E*- isomer.



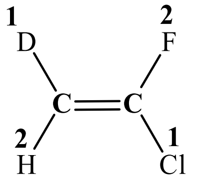
I
(*Z*)-2-bromo-1-chloro-1-fluoroethene

II
(*E*)-2-bromo-1-chloro-1-fluoroethene

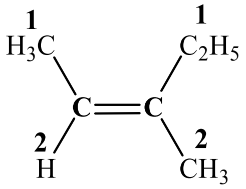
Example 21: Some other examples of geometrical isomers with *E* and *Z* configuration



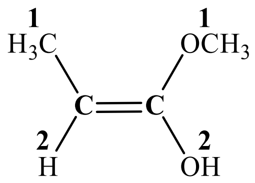
(*E*)-1-chloro-1-fluoroprop-1-ene



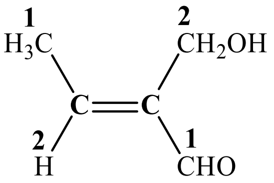
(*E*)-Deuterated1-chloro-1-fluoroprop-1-ene



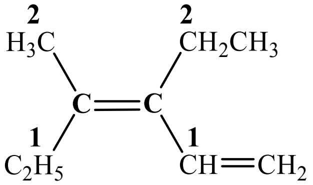
(*Z*)-3-methylpent-2-ene



(*Z*)-1-methoxyprop-1-en-1-ol



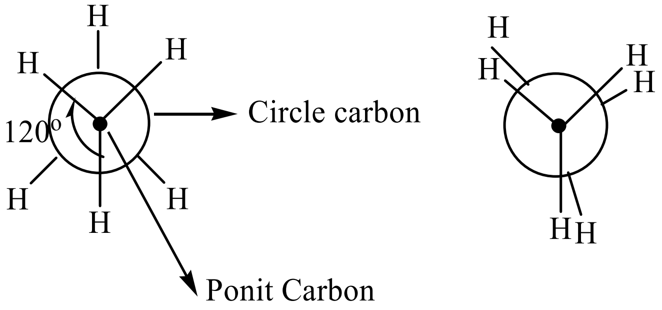
(*E*)-2-(hydroxymethyl)but-2-enal



(*Z*)-3-ethyl-4-methylhexa-1,3-diene

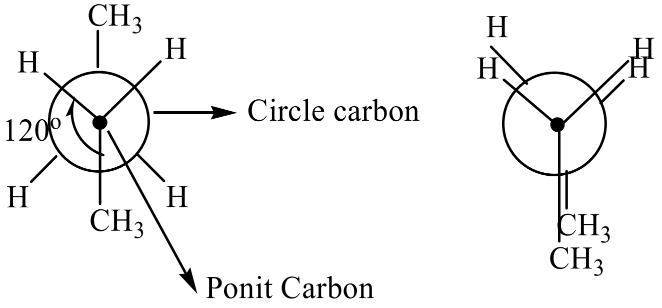
6.10 NEWMAN PROJECTION AND SAWHORSE FORMULA

The Newman representation formula: Newman Projections are used mainly for determining conformational relationships. Recall that, conformers are molecules that can be converted into one another by a rotation around a single bond. Newman Projections are also useful when studying a reaction involving prochiral molecules that have a double bond, in which the addition of a new group creates a new stereocenter. In this notation, you are actually viewing a molecule by looking down a particular carbon-carbon bond. The Newman representation formula is a planar representation of the sawhorse formula. The molecule is viewed along the axis of a carbon-carbon bond. The carbon atom in front of the viewer is represented by a dot (●), whereas the carbon atom away to the viewer is represented by circle. The rest of the atoms/groups are located on each carbon atoms at +120° or -120° angles to each other as shown below:



Newman representation formula of ethane

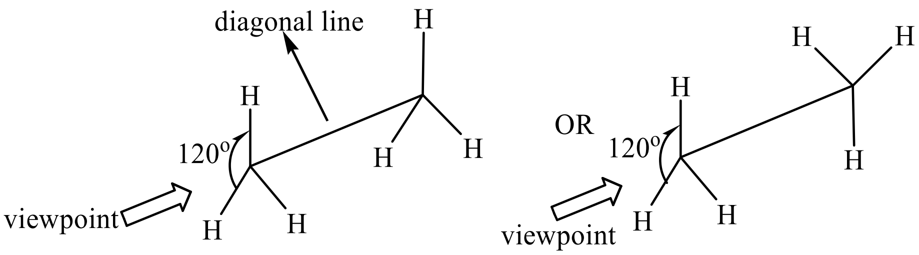
Addition of more carbons makes Newman Projections more complicated. For example, Newman Projections can be made for butane, such that it's eclipsed, gauche, and anti-conformations can be seen. (Recall that these three forms of butane are conformational isomers of one another.) In this case, the front dot represents the second carbon in the butane chain, and the back circle represents the third carbon in the butane chain. The Newman Projection condenses the bond between these two carbons.



Newman representation formula of butane

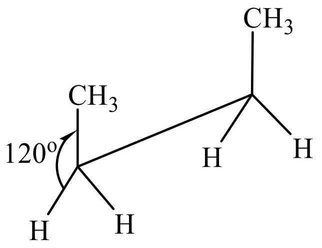
The Sawhorse representation formula: Sawhorse Projections are very similar to Newman Projections, but are used more often because the carbon-carbon bond that is compressed in a Newman Projection is fully drawn out in a Sawhorse Projection. When properly laid-out, Sawhorse Projections are useful for determining enantiomeric or diastereomeric relationships between two molecules, because the mirror image or superimposibility relationships are clearer.

Like with Newman Projections, a Sawhorse Projection is a view of a molecule down a particular carbon-carbon bond, and groups connected to both the front and back carbons are drawn using sticks at 120 degree angles. Sawhorse Projections can also be drawn so that the groups on the front carbon are staggered (60 degrees apart) or eclipsed (directly overlapping) with the groups on the back carbon. Below are two Sawhorse Projections of ethane. The structure on the left is staggered, and the structure on the right is eclipsed. These are the simplest Sawhorse Projections because they have only two carbons, and all of the groups on the front and back carbons are identical. The sawhorse representation formula is the spatial arrangement of all the atoms/groups on two adjacent carbon atoms. The bond between adjacent carbon atoms is represented by a diagonal line and rest of the atoms are located on each carbon at +120° or -120° angles to each other. The sawhorse representation is shown as:

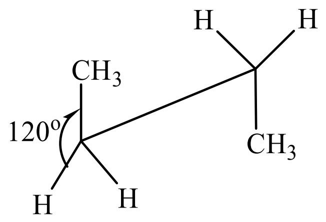


Sawhorse representation formula of ethane

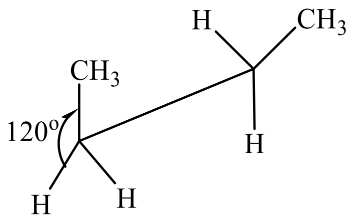
Addition of more carbons makes Sawhorse Projections slightly more complicated. Similar to Newman Projections, Sawhorse Projections can also be made for butane, such that it's eclipsed, gauche, and anti-conformations can be seen. (Recall that these three forms of butane are conformational isomers of one another).



Eclipsed



Anti



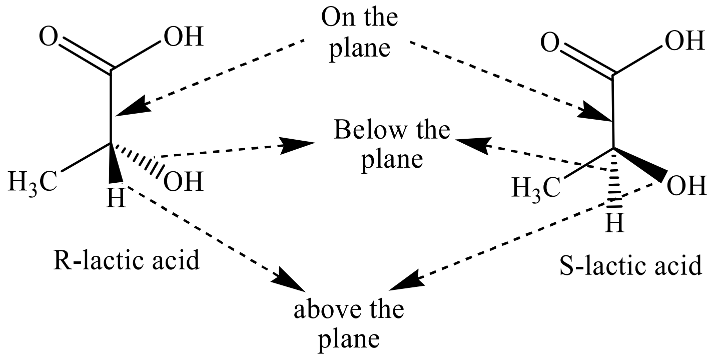
Gauche

Sawhorse representation formula of butane

6.11 FISCHER AND FLYING WEDGE FORMULA

The *sp*^{3} hybridized tetrahedral carbon is three dimensional in nature. Generally it is very difficult to represent a three dimensional structure in a two dimensional plane paper. There are many methods have been developed for two dimensional representation of a three dimensional structure. Out of them the flying-wedge and Fischer representation methods are most commonly used for two dimensional representation of a three dimensional structure.

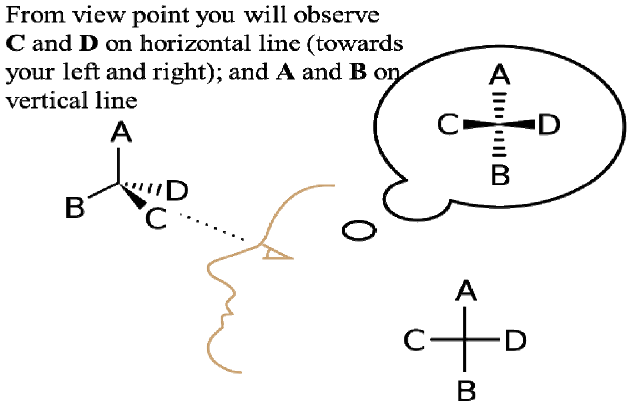
The flying-wedge: This is the most commonly used model for the two dimensional representation of a three dimensional molecule. In this model the bonds are presented in continuous, solid thick and dashed lines. A solid this line represents a bond projecting above the plane of the paper; it is considered that the bond with solid thick line is pointing towards observer. A dashed line represents a bond below the plane of the paper; it is considered that the bond with dashed line is pointing away to the observer. The bonds with continuous lines represent the bonds in the plane of paper. Let us consider an example of *R*-Lactic acid and *S*-Lactic acid.



Flying-wedge representation of *R*- and *S*-Lactic acid

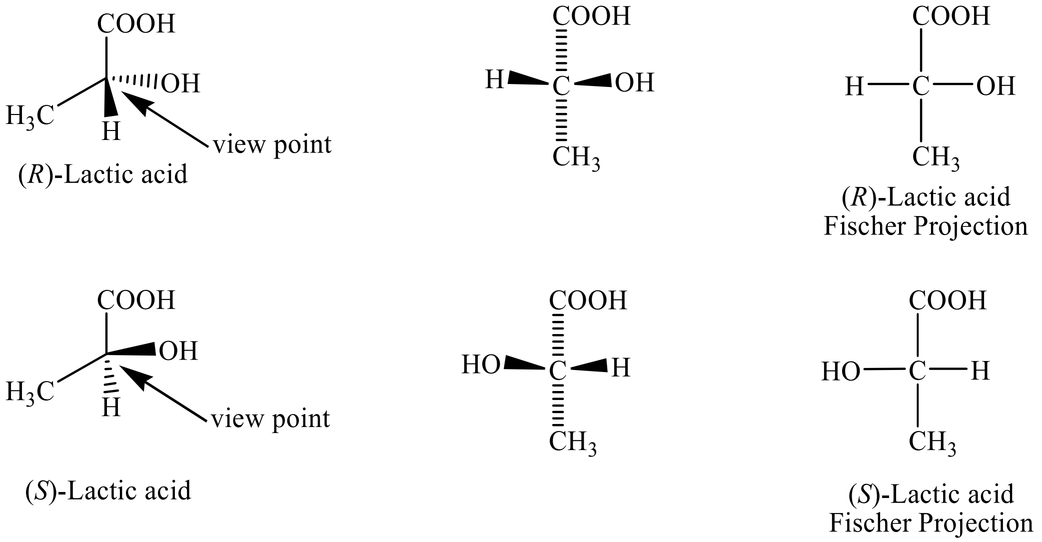
Fischer projection formula: It is a simplification of flying-wedge representation, in Fischer projection formula all bonds are drawn as solid lines in a plane paper. Fischer Projections are used often in drawing sugars and hydrocarbons, because the carbon backbone is drawn as a straight vertical line, making them very easy to draw. When properly laid-out, Fischer Projections are useful for determining enantiomeric or diastereomeric relationships between two molecules, because the mirror image relationship is very clear. In a Fischer Projection, each place where the horizontal and vertical lines cross represents a carbon. The vertical lines are actually oriented away from you (similar to dashes in the Wedge-Dash Notation) and the horizontal lines are oriented toward you (similar to wedges in the Wedge-Dash Notation).

Fischer projection is not as demonstrative as flying –wedge representation. It does not represent the actual shape of the molecule. Usually the Fischer projection formula is drawn so that the longest carbon chain in the molecule is vertical with the highly oxidized group on the top.



From view point you will observe **C** and **D** on horizontal line (towards your left and right); and **A** and **B** on vertical line

Let us consider an example for conversion of flying-wedge formula to Fischer projection formula for *R*- and *S*- Lactic acid.



(*R*)-Lactic acid

(*R*)-Lactic acid Fischer Projection

(*S*)-Lactic acid

(*S*)-Lactic acid Fischer Projection

Conversion of flying wedge to Fischer projection formula for Lactic acid

6.12 DIFFERENCE BETWEEN CONFIGURATION AND CONFORMATION

We have used the term conformer to explain isomers related to the rotation about C-C single bond of ethane and butane derivatives, and the term configuration to define some substituted methane and ethylene in the present unit and also in the previous unit (Unit 4). At first glance it seems straightforward to distinguish conformation and configuration. The stereoisomerism which is due to the rotation about a single bond is referred to as conformation. Conformers are easily interconvertible and it is difficult to isolate the isomer. On the other hand, when two compounds are different in their configuration, e.g., a pair of enantiomers of bromofluoromethane, or a pair of geometrical isomers, maleic acid and fumaric acid, these are distinguishable compounds, and their isolation is possible (see section 5.2.3 of this unit).

However, if maleic acid can be converted into fumaric acid by heat, there remains some ambiguity to classify conformational isomers and configurational isomers by their possibility of interconversion. It would be more practical to classify them by their facility of interconversion. A new nomenclature was proposed where stereoisomers with lower energy barrier of conversion are conformers (conformational isomers), while those with higher energy barrier are configurational isomers. If the barrier of interconversion is above 100 kJ mol^{-1}, these are configurational isomer while if it is lower than 100 kJ mol^{-1}, these are conformers. It was previously explained that the rotation about a C=C double bond is restricted by the overlap of p-orbitals, while the rotation about C-C single bond is relatively free. The rotation about a C=C double bond, however, can occur during the reaction; e.g., fumaric acid is converted into maleic acid by heating (see section 5.2.3 of this unit). Thus, the difference between the rotation about a C-C bond and that about a C=C bond might better be regarded as the difference of the required energy to achieve the transition state involved in the rotation.

6.13 SUMMARY

- Stereochemistry is all about the 3 Dimensional spatial aspects of chemistry.
- Molecules that differ only in the arrangement of bonds in 3Dimensional space are called "stereoisomers"

- Many objects (including molecules) are non-differentiable from their mirror images, but other objects, such as your left and right hands, are differentiable. An object that has a non-superimposable mirror image is said to be "chiral" (Greek = "handedness") and one that has a superimposable mirror image is called "achiral".
- Pairs of molecules that are non-superimposable mirror images of each other are called "enantiomers"
- The most common type of "chirality" is observed when a carbon atom has four different groups attached to it. This carbon atom is then described as a chiral or asymmetric or stereogenic center. This later term can also be contracted to a stereocenter.
- Enantiomers have the same chemical and physical properties (melting points, boiling points, heat of combustion etc.), except for their interaction with plane polarized light or with other chiral molecules (reagents, solvents, catalysts, etc). (Think about how your feet feel if you put them in the wrong shoes).
- Diastereomers are stereoisomers that are not enantiomers.
- If there is more of one enantiomer than the other, then the optical purity of a sample can be determined by measuring the rotation and comparing it to that of a pure enantiomer. This can be used to establish the enantiomeric excess (ee) of the mixture.

6.14 TERMINAL QUESTION

1. What do you understand by Isomerism? Give its types.
2. What is chirality? Explain the necessary condition for a molecule to be chiral.
3. What do you understand by optical activity? How is it measured?
4. What are enantiomers and diastereomers?
5. What are symmetry elements? How they affect optical isomerism?
6. Explain relative and absolute configuration.
7. What is racemization?

6.15 REFERENCES

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3. Stereochemistry of Organic Compounds by Ernest L. Eliel; Published by John Wiley; ISBN- 0-471-01670-5
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UNIT 7: REACTION MECHANISM

CONTENTS:

7.1 OBJECTIVES

Objective of this chapter is to provide readers with basics of organic reaction mechanisms. Like all chemical transformations, organic reactions also involve breaking and formation of chemical bonds. Thus, understanding of electron sharing between atoms and transfer of electrons is very important to understand the organic reaction mechanisms. This chapter sheds light on bond cleavage and curved arrow notations to denote the changes involving electron sharing. Concise detail on type of reagents affecting various organic reactions is also given. The chapter is developed such that the reader inculcates fundamental terminologies and notations pertaining to organic reaction mechanism. To offer students an easy and interesting learning experience, each of the topics covered is depicted with lucid diagrams and figures. Point to point discussion progresses as per the Organic Chemistry-I COURSE-II, BCH102 syllabus.

7.2 INTRODUCTION

Organic reactions involve breaking and formation of chemical bonds that is the changes in sharing of electrons between atoms in given molecules. Movement of electrons during organic reactions is denoted by curved arrow notations. For example, movement of odd electron is represented by half headed arrow whereas movement of electron pair is represented by full curved arrows. Understanding the correct arrow notation not only helps to describe how an organic reaction is taking place but also helps to quickly understand the peculiar mechanistic steps involved. Thus, content of this chapter is essential for beginning study of organic reaction mechanisms. Later, the chapter discusses important categories of organic reagents those are useful to carry out particular organic transformations. For example, nucleophilic reagents attack on electron deficient sites in a molecule while the electrophilic reagents react with electron rich species. Thus, this chapter is a suitable package to begin learning and understanding the organic chemistry transformations.

7.3 CURVED ARROW NOTATION

Chemical reactions involve breaking and formation of chemical bonds. It means sharing of electrons between atoms in given molecules changes during reactions. This change in sharing of electron or movement of electrons is denoted by different types of curved arrows depending on the reactions. For example, movement of odd electron (or single electron) is represented by half headed arrow whereas movement of an electron pair is represented by double headed curved arrows. How a double-headed or full-headed arrow and half-headed or fish-hook arrow is drawn in organic chemistry is depicted in Figure 7.1.

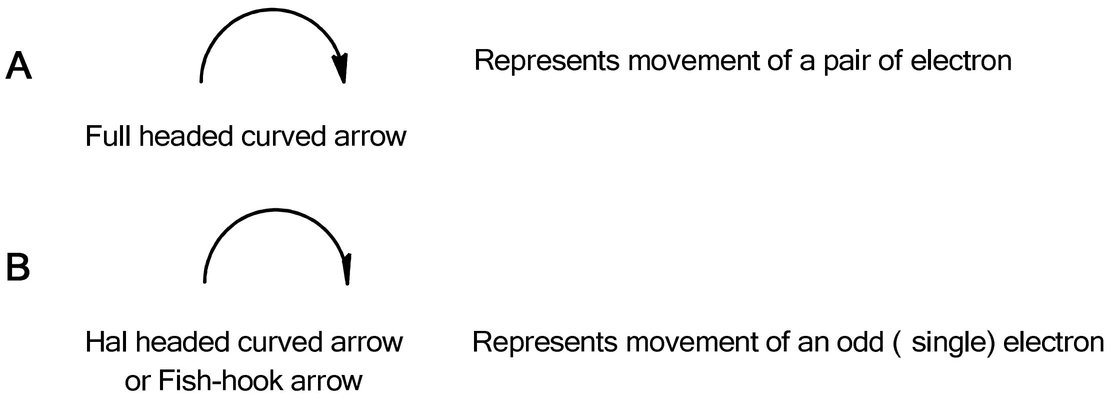
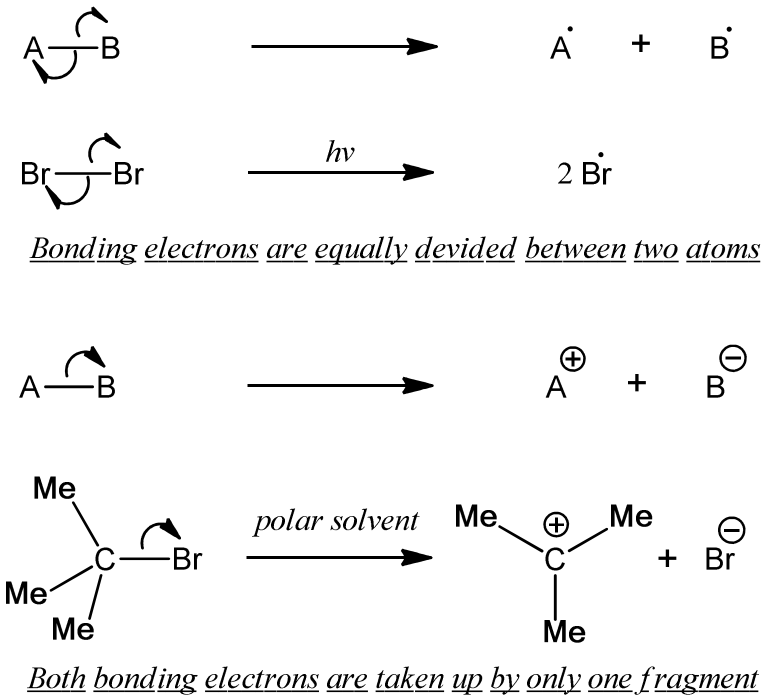


Figure 7.1 Depiction of full (A) and half (B) headed arrows

7.4 HOMOLYTIC AND HETEROLYTIC BOND CLEAVAGE/ FISSION

Chemical reactions involve breaking and formation of chemical bonds. How a chemical bond will break depends on factors such as temperature, reaction medium and solvent. Organic reactions usually involve breaking of covalent bonds followed by formation of new covalent bonds. The bond breaking, also termed as bond cleavage takes place in two possible ways, namely, homolytic and heterolytic bond fission.



Homolysis

Bonding electrons are equally devided between two atoms

Heterolysis

Both bonding electrons are taken up by only one fragment

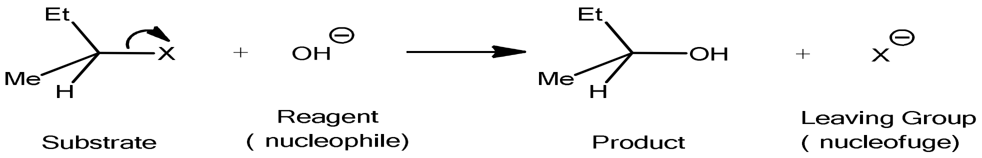
Figure 7.2 General and specific examples depicting homolysis and heterolysis of covalent bonds.

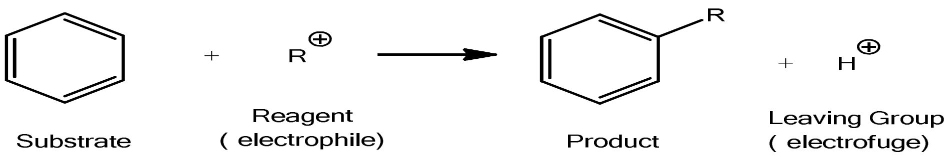
Homolytic bond cleavage is also called homolytic bond fission or homolysis. In homolysis, the two electrons in a cleaved covalent bond are divided equally between the products. On the other hand, heterolytic bond cleavage is also called heterolytic bond fission or heterolysis. In heterolysis, the two electrons in a cleaved covalent bond remain with one of the two fragments.

7.5 TYPE OF REAGENTS

Organic reactions are generally brought about by heterolysis of organic compounds. The breaking of bonds and formation of new bonds occur in presence of reagents. Thus reagents are substances or compounds that are added to bring about a reaction. In organic reactions it is convenient to call one reactant as substrate which will provide carbon to a new bond and the other is called as reagent. The attacking reagent can be (i) which provides an electron pair to the substrate, known as Nucleophile and the reaction is called a Nucleophilic reaction (ii) takes an electron pair from substrate is known as Electrophile and the reaction is called a Electrophilic reaction.

In reactions where the substrate bond is cleaved, the part that does not contain the carbon is called Leaving group. The leaving group that carries electron pair is known as Nucleofuge. If the leaving group moves out without the electron pair, it is called Electrofuge.

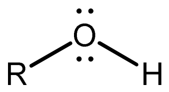




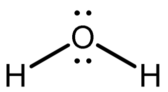
7.5.1 Nucleophilic Reagents or Nucleophiles

Nucleophile means nucleus loving. Reagents having unshared pair of electrons are known as Nucleophilic reagents or nucleophiles and they show tendency to share this lone pair of electrons with electron deficient species. They can be classified into three groups:

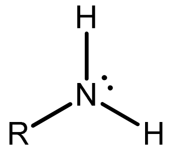
(i) Neutral Nucleophiles: These are electron rich species due to presence of non bonding pair of electrons. Central atom of such species should have a complete octet. Neutral nucleophiles are not charged and are electrically neutral.



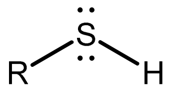
alcohol



water

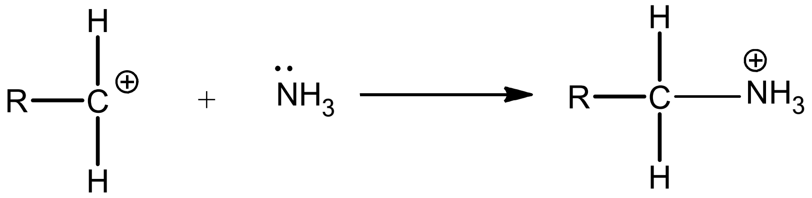


amine

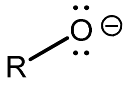


thiol

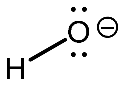
Organic compounds having C-C multiple bond/bonds also act as Neutral nucleophiles because these species have π electron cloud above and below the plane of the molecule. The addition reaction of a neutral nucleophile to a positively charged substrate gives a positively charged product.



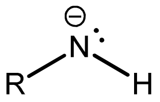
(ii) Negative Nucleophiles: These carry an electron pair and are negatively charged because of the presence of unpaired electrons.



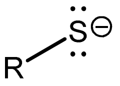
alkoxide



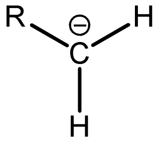
hydroxide



amide

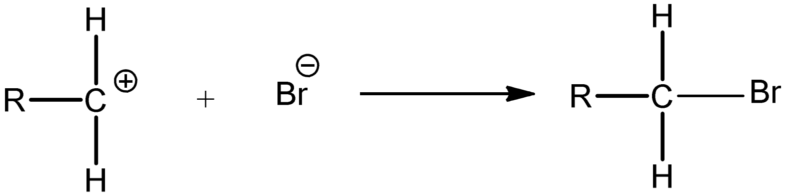


mercaptyl anion



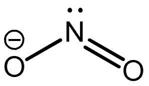
carbanion

Addition reaction of a negatively charged nucleophile to a positively charged substrate results in neutral molecule.

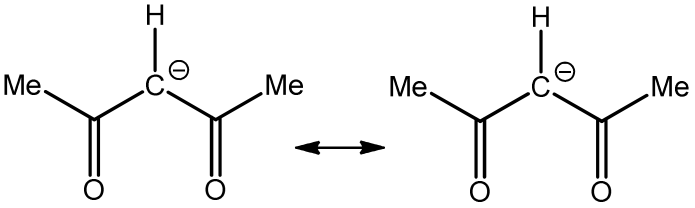


(iii) Ambident Nucleophiles: The nucleophiles which can attack through two or more atoms are called ambident nucleophiles. For Eg: CN^{-} can attack through N or C to give cyanide (RCN) or isocyanide (RNC) respectively.

cyanide/isocyanide



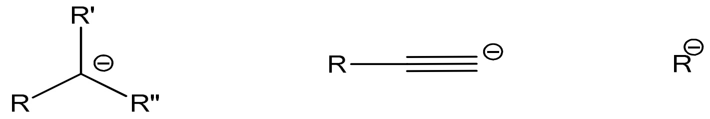
nitrite



resonance stabilized carbanion

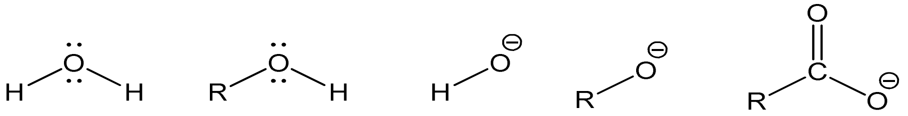
Nucleophiles can also be classified on the basis of the kind of atom that forms a new covalent bond. The most common nucleophiles on this basis are oxygen, nitrogen, sulfur, halogen and carbon nucleophiles.

carbon nucleophiles:

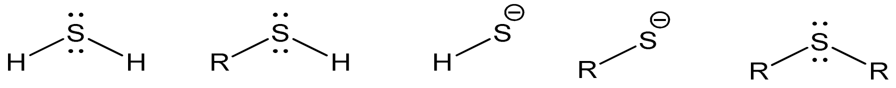


nitrogen nucleophiles: $:NH_3$ $R\ddot{N}H_2$ $R_2\ddot{N}H$ $R_3N:$ $\overset{\ominus}{N}H_2$

oxygen nucleophiles:



sulfur nucleophiles:



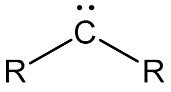
halogen nucleophiles: $Cl^{\ominus}$ $Br^{\ominus}$ $I^{\ominus}$

7.5.2 Electrophilic Reagents or Electrophiles

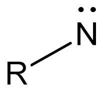
An electrophile (meaning electron loving) is a reagent that is electron deficient and due to this they show affinity for electrons. Electrophiles can also be of two types:

(i) Neutral Electrophiles: These electrophiles even though electron deficient does not carry positive charge. They have incomplete valence shells. Examples: $AlCl_3$, BF_3, carbene etc.

$AlCl_3$ $FeCl_3$ BF_3



carbene

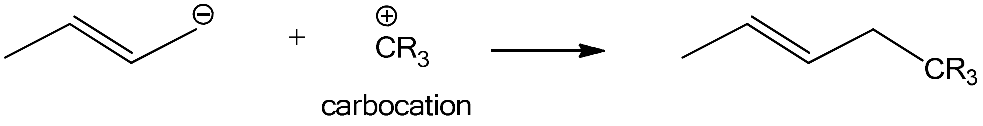


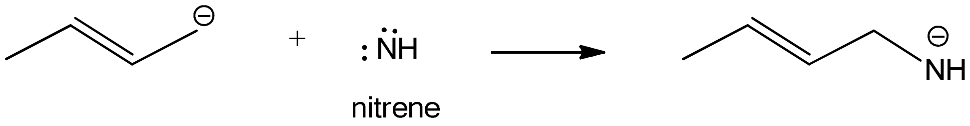
nitrene

(ii) Positive Electrophiles: These electrophiles carry positive charge on central atom and have incomplete octet.

$H^{\oplus}$ $\overset{\oplus}{S}O_3H$ $\overset{\oplus}{N}O_2$ $H_3O^{\oplus}$ $R_3C^{\oplus}$

The positive electrophile will attack the substrate (which is a negative nucleophile) and accepts an electron pair for sharing resulting in a neutral molecule. While, a neutral electrophile will attack a electron rich substrate (negative nucleophile) to form a negatively charged molecule.





7.6 TYPE OF ORGANIC REACTIONS

The chemical Reaction in which Organic compounds change chemicals is called Organic Reactions. In this Reaction, one type with unrelated or bound electrons "donates" an electron pair to a type that lacks an electron by forming a bond between the two types.

Different Types of Organic Reactions

1. Substitution Reaction
2. Addition Reaction
3. Elimination Reaction
4. Rearrangement Reaction
5. Condensation Reaction
6. Pericyclic Reaction
7. Polymerization Reaction

1. Substitution Reaction:

Substitution Reaction or displacement Reaction is a chemical Reaction in which one functional group in a chemical compound is substituted by another functional group. Substitution Reactions in Organic chemistry are categorized either as nucleophilic or electrophilic depending upon the reagent that are involved.

Nucleophilic Substitution:

InOrganic and inOrganic chemistry, nucleophilic Substitution is an important class of Reactions where a nucleophile selectively bonds and replaces a weaker nucleophile which then turns into a leaving group; The remaining positive or partly positive atom becomes an electrophile. The whole molecular unit of electrophile and the leaving group form the part known as the substrate. For example:

Nuc: + R-LG → R-Nuc + LG:

The electron pair (:) from the nucleophile attacks the substrate (R-LG) creating a new covalent bond (Nuc-R-LG). The previous state of charge is restored when the leaving group (LG) leaves with an electron pair. The main product, in this case, is R-Nuc.

Classification of Nucleophillic substitution reaction:

The Nucleophillic substitution Reaction is classified in to following two classes.

(1) SN1 (Unimolecular Nucleophilic Substitution reaction):

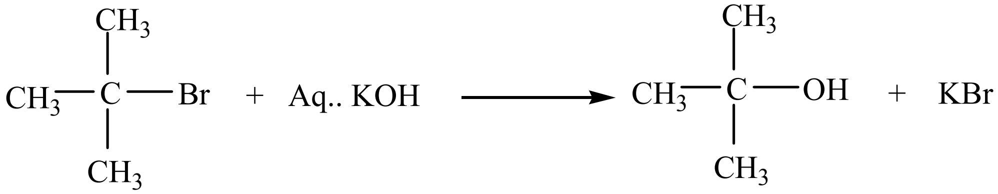
It is represents that Mononucleophillic substitution reaction. Generally such type of mechanism is carried by tert. alkyle halides and it is the two step mechanism.

Step-I

In this step the C-X bond undergoes heterolytic fission to give an intermediate carbonium ion and it is the slowest step. So it is the rate determining step.

Step-II

It is the faster one and in it the nucleophile is attack to the carbonium ion to form the required compound.



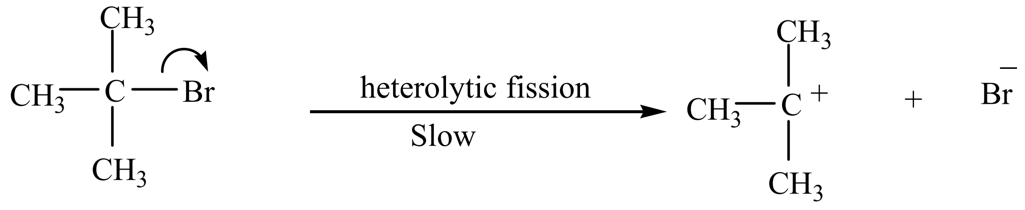
$$(CH_3)_3C{-}Br + \text{Aq.. KOH} \longrightarrow (CH_3)_3C{-}OH + KBr$$

Mechanism:

Formation of Nucleophile:

$$KOH \longrightarrow K^+ + OH^-$$

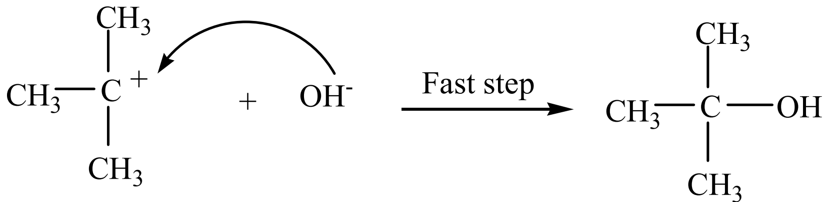
Step I- Slow step:



tert. butyl bromide

3^0 butyl carbonium ion

Step II Fast step:



3^0 butyl carbonium ion

tert. butyl alcohol

Formation of KBr:

$$K^+ + \overset{-}{Br} \longrightarrow KBr$$

It is clear from above mechanism that in the slowest step only one reactant (ter. butyl bromide) takes placed, hence the rate of reaction is depends upon the concentration of it, so it is first order reaction. So this reaction is known as uni-molecular nucleophilic substitution (SN^1) reaction.

Mathematically:

$$\frac{dx}{dt} = K\left[\text{Alkyl halide}\right]$$

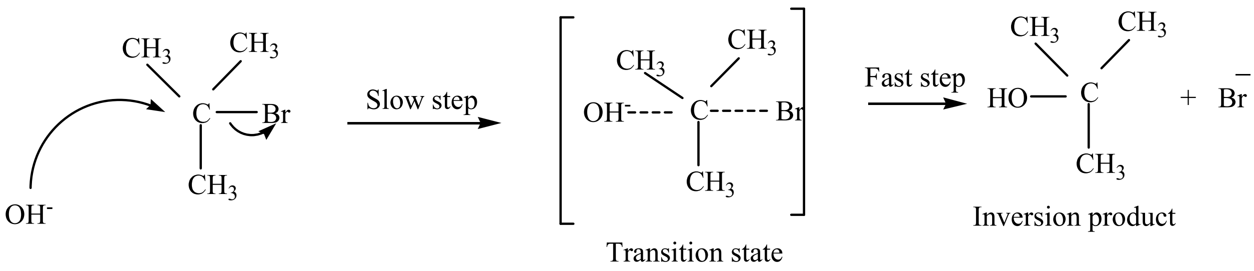
(2) SN^2 (Bi-molecular neicleophilic substitution reaction) Reaction:

This type of mechanism is generally followed by primary alkyl halides and it is the one step mechanism. In this type of mechanism Nu^- attacks to that carbon which is attached from the halogen atom, from the opposite side of the halogen carrying carbon atom because there is repulsion between nucleophilic and halogen. It is the slowest step.

Mechanism:

Formation of Nucleophile:

$$KOH \longrightarrow K^+ + OH^-$$



Formation of KBr:

$$K^+ \quad \overline{Br} \longrightarrow KBr$$

In the transition state or activated complex the C-Nu bond is partially formed and the C-Br bond is partially breaking. Hence in this stage the C-Nu bond start to form and the C-Br bond start to breaking and finally is formed. In this mechanism the C-H bond are like the spokes and are along the axel.

Since in the slowest step there are two reacting species one is alkali & other is R-X. So its rates depands upon the concentration of both. So its is Bi-molecular Nucleophilic Substitution reaction reaction SN^2.

Mathematically:

$$\frac{dx}{dt} = K\left[\text{Alkyl halide}\right]\left[\text{KOH}\right]$$

2. Addition Reaction

An Addition Reaction, inOrganic chemistry, can be explained in simple terms where two or more molecules combine together to produce a larger one.

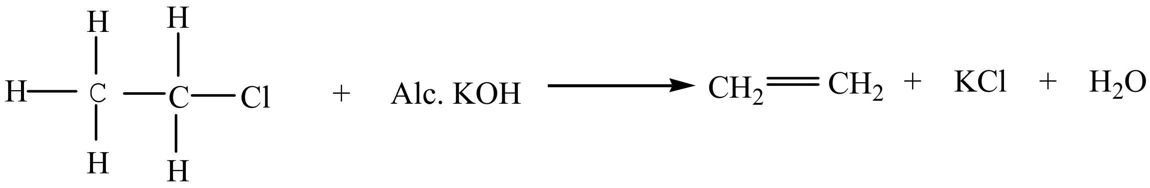
It's nothing but a complete Reaction when you're done. In a further Reaction, elements A and B are added to many carbon-carbon bonds and this is called a composite Reaction. In given Reaction below when hydrogen chloride is mixed to ethylene, it gives ethylene chloride.

$$HCl + CH_2{=}CH_2 \rightarrow CH_3CH_2Cl$$

3. Elimination Reaction:

In this type of reaction the atoms or group of atoms are eliminated from two adjacent C-atoms to give the product.

Example: R-X on react with KOH (alc.) gives alkene by undergoing dehydrohalogenation



$$H_3C{-}CH_2{-}Cl + \text{Alc. KOH} \longrightarrow CH_2{=}CH_2 + KCl + H_2O$$

Types of elimination reaction:

Elimination reactions are classified into two classes. One is E^1 and other is E^2 reaction**.**

1. E^1 Elimination (Uni-molecular Elimination Reaction): Generally such type of mechanism is observed in tert. alkyl halides and it is two step mechanism.

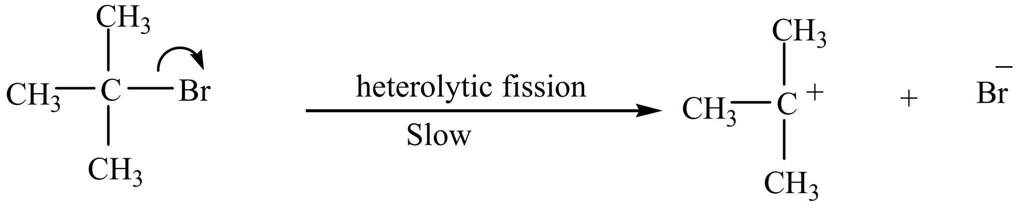
Step I: It is the slowest step. In this step the C-X bond undergoes hetrolytic fission to form an intermediate carbonium ion and this step is also known as rate determining step.

Step II: It is the faster one. In this step the Nu^- is eliminate a β- hydrogen from the carbonium ion and form alkene.

Mechanism:

$$KOH \longrightarrow K^+ + \underset{Nu^-}{OH^-}$$

Step I:

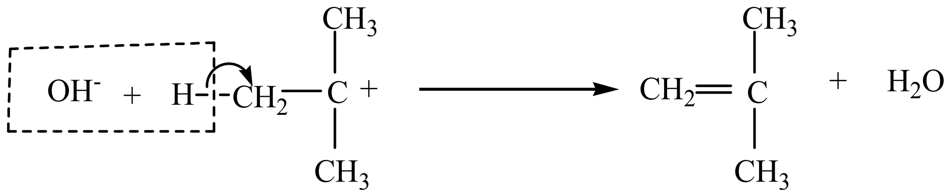


$$(CH_3)_3C{-}Br \xrightarrow[\text{Slow}]{\text{heterolytic fission}} (CH_3)_3C^+ + Br^-$$

tert. butyl bromide

3^0 butyl carbonium ion

Step II:



$$\boxed{OH^- + H}{-}CH_2{-}\overset{+}{C}(CH_3)_2 \longrightarrow CH_2{=}C(CH_3)_2 + H_2O$$

$$K^+ \quad + \quad \bar{Br} \longrightarrow KBr$$

2. E^2 Elimination (Bi-molecular Elimination Reaction): E2 mechanism is concerted process and a bimolecular reaction. Because the base removes a hydrogen at the same time the C— X bond is broken to form a halide ion the rate law for the rate determining step is dependent on both the alkyl halide and the base :

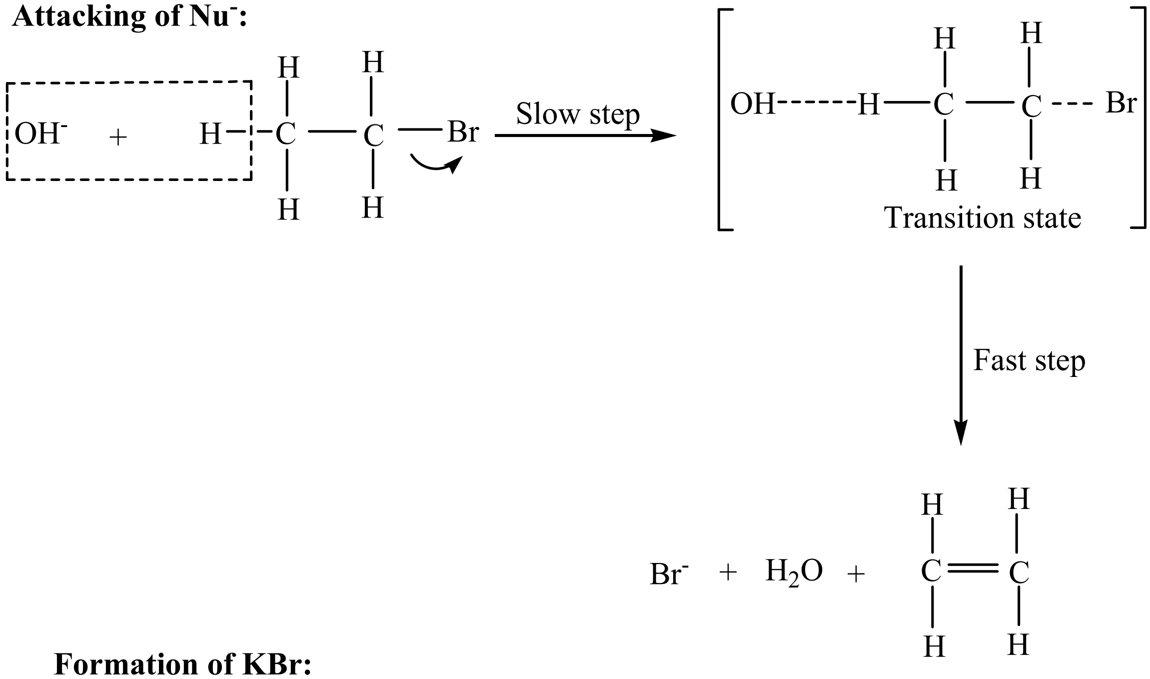
Rate = k [alkyl halide] [base]

The stronger the base the more likely it is that E2 mechanism will be in operation. E2 mechanism illustrate by reaction of 1-bromopropane with sodiumethoxide.

Formation of Nucleophile:

$$KOH \longrightarrow K^+ + OH^-$$

Attacking of Nu$^-$:



Formation of KBr:

$$K^+ \quad + \quad Br^- \longrightarrow KBr$$

Thus it is clear from above mechanism in the slowest step, which is rate determining step two reacting species takes palce. Hence the rate of reaction is depands upon both concentrations. So it is of two order reaction.

7.8 REACTION INTERMEDIATES

In the Organic Chemistry the reactions takes place in many steps. In these steps the reaction intermediates are also formed which are consumed during the reaction to give the product. So the reaction intermediates are defined as; "A neutral or charge species which is form during the reaction and by consumed gives the final product is known as reaction intermediates.

Reaction intermediates are highly reactive because they have strong tendency to convert in stable form and their life period is 10^{-12} sec.

A reactive intermediate is a short-lived, high-energy and highly reactive species. It generated in a chemical reaction and it will quickly convert into a more stable product. Only in exceptional cases can these compounds be isolated and stored, e.g. low temperatures, matrix isolation. When their existence is indicated, reactive intermediates can help explain how a chemical reaction takes place.

Most chemical reactions takes place more than one step to complete, and a reactive intermediate is a high-energy, yet stable, product that exists only in one of the intermediate steps. A reactive intermediate differs from a reactant or product or a simple reaction intermediate only in that it cannot usually be isolated but is sometimes observable only through fast spectroscopic methods. It is stable in the sense that an elementary reaction forms the reactive intermediate and the elementary reaction in the next step is needed to destroy it. Reactive intermediates based on carbon are Carbocations, Carbanions, Free radicals, Carbenes, Nirenes and Benzyne.

Types of reaction intermediate:

1. Carbocations
2. Carbanions
3. Free radicals
4. Carbenes
5. Nitrene

7.9 SUMMARY

This chapter covers description of basic concepts such as curved arrow notation (arrow pushing) and bond fission, which are vital to understand and write organic reaction mechanisms. The description on topics such as full headed & half headed curved arrow, nucleophiles and electrophiles, hemolytic and heterolytic bond fission is given in the chapter with sufficient details. Other significantly important terms such as nucleofuge, electrofuge, leaving group, substrate and attacking reagents are given with guiding figures. Understanding of these topics will help us to understand and gain interest in mechanisms of organic reactions.

7.10 TERMINAL QUESTIONS

Short Answer type questions

Q.1 Briefly describe the curved arrow notation for movement of odd electrons.

Q.2 Describe the full headed curved arrow notation used in reaction mechanisms.

Q.3 What is an electrofuge? Give two examples of electrofuge.

Q.4 Write short note on heterolysis of covalent bonds.

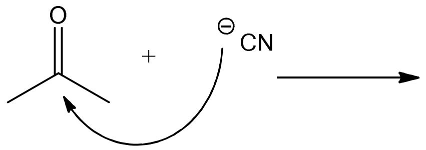
Q.5 Describe the terms substrate, reagent and leaving group.

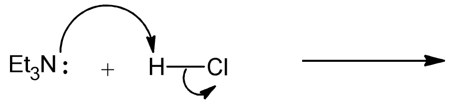
Q.6 Discuss neutral nitrogen containing neucleophiles.

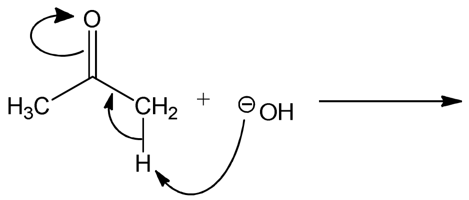
Q.7 What is the difference between neucleophile and electrophile?

Q.8 Give one example of a nucleophilic and an electrophilic substrate.

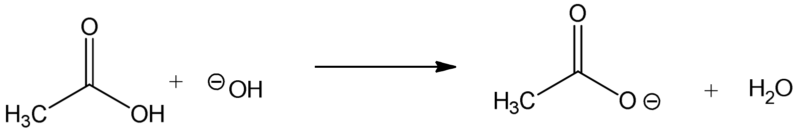
Q.9 Complete the following reactions:

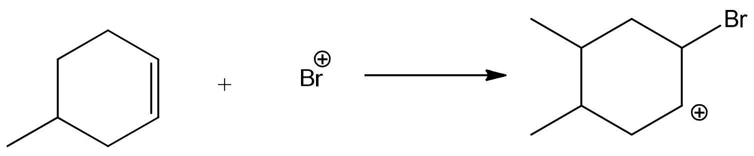






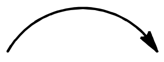
Q.10 Place the appropriate curved arrows to depict the electronic movement in following reactions.





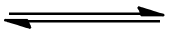
MCQ type questions

Q.1 Identify the correct arrow depicting movement of electron pair in organic reaction mechanisms:

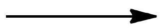


(i)

(ii)



(iii)



(iv)

(a) iii

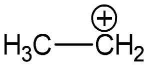
(b) i

(c)iv

(d)ii

Q.2 Select from the options given below the electrophilic species:

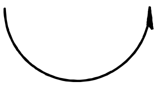
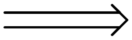
(a) SO_3

(b) 
$H_3C-\overset{\oplus}{C}H_2$

(c) BF_3

(d) both b and c

Q.3 Which one of the following represents movement of odd electron in organic reaction mechanisms:


(i) (ii) (iii) (iv)

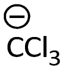
(a)iii

(b)i

(c)iv

(d)ii

Q.4 Select from the options given below the nucleophilic species:

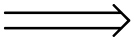
(a) 
$\overset{\ominus}{C}Cl_3$

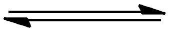
(b) $LiAlH_4$

(c) $H_3C-O-CH_3$

(d)all of the above

Q.5 Find the correct depiction for fish-hook arrow:






(i) (ii) (iii) (iv)

(a)ii & iii

(b)iii

(c)none

(d)i

Q.6 Identify the electrophile from the following options:

(a)CO_2

(b)SO_3

(c)$AlCl_3$

(d)Both a and b

Q.7 A leaving group is called so because:

(a)it detaches from the carbon in organic reaction

(b)it detaches from the attacking reagent

(c)it is part of incoming nucleophile

(d)it is part of incoming electrophile

Q.8 Which of the species given below behaves as ambident nucleophile:

(a) $CN^{\ominus}$

(b) $\overset{\ominus}{NO_2}$

(c) $\overset{\ominus}{NH_2}$

(d)Both a and b

Q.9 Which of the species given below is an ambident nucleophile:

(a) $Br^{\ominus}$

(b) $\overset{\ominus}{NO_2}$

(c) $\overset{\ominus}{NH_2}$

(d)All of the above

Q.10 Nucleofuge and Electrofuge are commonly called as:

(a)substrate

(b)leaving group

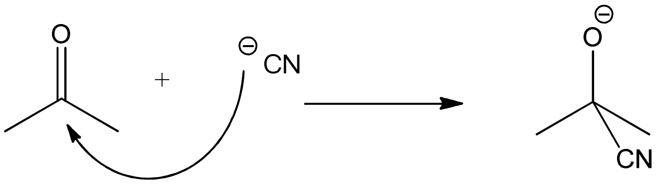
(c) incoming group

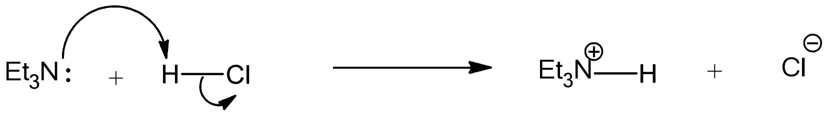
(d) attacking reagent

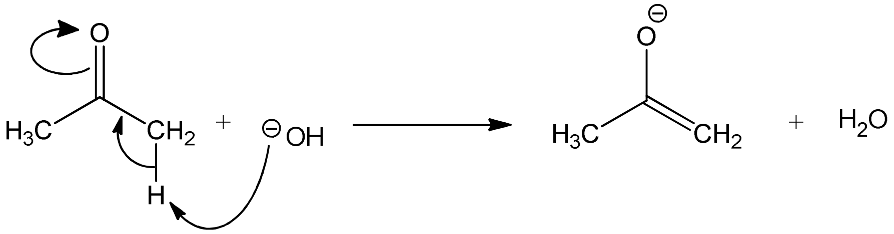
ANSWERS

Answers to the short answer type questions

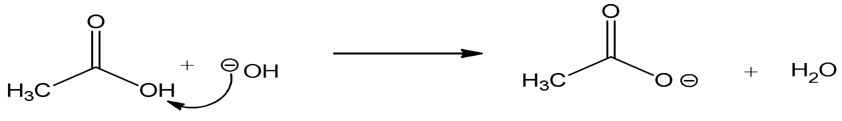
Q.9

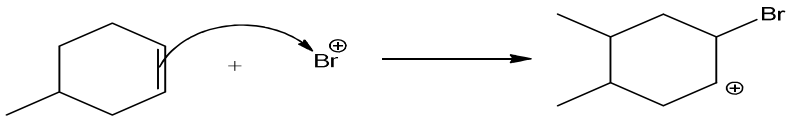






Q.10





Answers to the MCQ type questions

Q.1(a)

Q.2(d)

Q.3(b)

Q.4(d)

Q.5(c)

Q.6(c)

Q.7(a)

Q.8(d)

Q.9(b)

Q.10(b)

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1. Clayden, Jonathan; Greeves, Nick; Warren, Stuart; Wothers, Peter (2001). Organic Chemistry (1st ed.). Oxford University Press.
2. Daniel E. Levy, Arrow Pushing in Organic Chemistry: An Easy Approach to Understanding Reaction Mechanisms, (John Wiley & Sons, 2008).
3. Robert B. Grossman, The Art of Writing Reasonable Organic Reaction Mechanisms, (Springer, 2007).
4. William Ogilvy Kermack and Robert Robinson, J. Chem. Soc., Trans., 1922,121, 427-440.
5. Daniel P. Weeks, Pushing Electrons: A Guide for Students of Organic Chemistry, (Brooks Cole, 1998)
6. Morrison, Robert; Boyd, Robert (1989). Organic Chemistry (5th edition). Prentice Hall of India. ISBN 0-87692-560-3.
7. Lenoir, D.; Chiappe, C. Chem. Eur. J. 2003, 9, 1036.
8. Lapworth, A. Nature 1925, 115, 625.

UNIT 8: ALIPHATIC AND AROMATIC ORGANIC COMPOUNDS

CONTENTS:

8.1 OBJECTIVE

By the end of the course the student should be able to:

General discussion of aliphatic and aromatic organic compounds like alkanes, alkenes, alkynes, aromatic hydrocarbons, Preparation and properties of ethene and ethyne. Functional groups in organic compounds-alcohols, ethers, aldehydes, ketones and carboxylic acids.

8.2 ALKANES

The alkanes are hydrocarbons that only contain single covalent bonds between their carbon atoms. This means that they are saturated compounds, has no specific reactive functional groups and are quite unreactive. The simplest alkane has only one carbon atom and is called methane. These are saturated hydrocarbons because they have the maximum number of hydrogen atoms.

Name	**Condensed Structure**
Methane	CH_4
Ethane	CH_3CH_3
Propane	$CH_3CH_2CH_3$
Butane	$CH_3(CH_2)_2CH_3$
Pentane	$CH_3(CH_2)_3CH_3$
Hexane	$CH_3(CH_2)_4CH_3$
Heptanes	$CH_3(CH_2)_5CH_3$
Octane	$CH_3(CH_2)_6CH_3$
Nonane	$CH_3(CH_2)_7CH_3$
Decane	$CH_3(CH_2)_8CH_3$
Undecane	$CH_3(CH_2)_9CH_3$
Dodecane	$CH_3(CH_2)_{10}CH_3$

Alkanes are also called Paraffins because of little reactivity towards reagents. Members of a homologous series with general formula $\mathbf{C_nH_{2n+2}}$.

8.2.1 IUPAC Nomenclature

The root or parent name for an unbranched alkane is taken directly from the number of carbons in the chain according to a scheme of nomenclature established by the **International Union of Pure and Applied Chemistry (IUPAC)**, as shown below:

The IUPAC rules for naming linear and branched alkanes are given below:

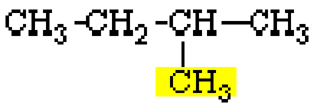
(i) The IUPAC name for an alkane is constructed of two parts:

(a) a prefix (meth... eth... prop..., etc.) which indicates the number of carbons in the main, or parent, chain of the molecule, and

(b) the suffix ...**ane** to indicate that the molecule is an alkane.

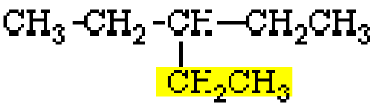
(ii) For branched-chain alkanes, the name of the parent hydrocarbon is taken from the **longest continuous chain** of carbon atoms.

(iii) Groups attached to the parent chain are called **substituents** and are named based on the number of carbons in the longest chain of that substituent, and are numbered using the number of the carbon atom on the parent chain to which they are attached. In simple alkanes, substituents are called **alkyl groups** and are named using the prefix for the number of carbons in their main chain and the suffix ...**yl**. For example, methyl, ethyl, propyl, dodecyl, etc.



$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

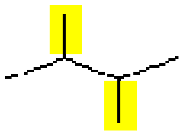
methyl



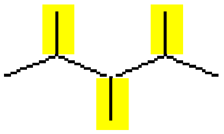
$CH_3-CH_2-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2CH_3$

ethyl

(iv) If the same substituent occurs more than once in a molecule, the number of each carbon of the parent chain where the substituent occurs is given and a multiplier is used to indicate the total number of identical substituents; i.e., **di**methyl... **tri**methyl... **tetra**ethyl..., etc.

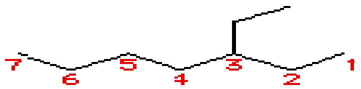


2,3-dimethylbutane

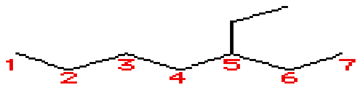


2,3,4-trimethylpentane

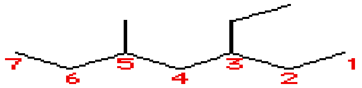
(v) Numbering of the carbons in the parent chain is always done in the direction that gives the lowest number to the substituent which is encountered first, or, the lowest number at the first point of difference. If there are different substituents at equivalent positions on the chain, the substituent of lower alphabetical order is given the lowest number.



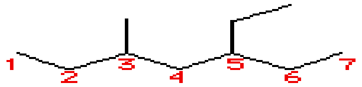
3-ethylheptane



not 5-ethylheptane

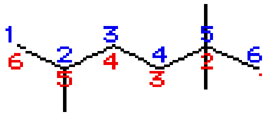


3-ethyl-5-methylheptane

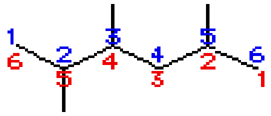


not 5-ethyl-3-methylheptane

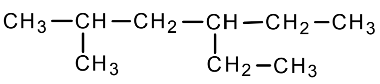
(vi) In constructing the name, substituents are arranged in alphabetical order, without regard for multipliers.



2,2,5-trimethylhexane
not 2,5,5-trimethylhexane

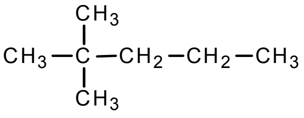


2,3,5-trimethylhexane
not 2,4,5-trimethylhexane



$$CH_3-\underset{CH_3}{CH}-CH_2-\underset{CH_2-CH_3}{CH}-CH_2-CH_3$$

4-ethyl-2-methylhexane

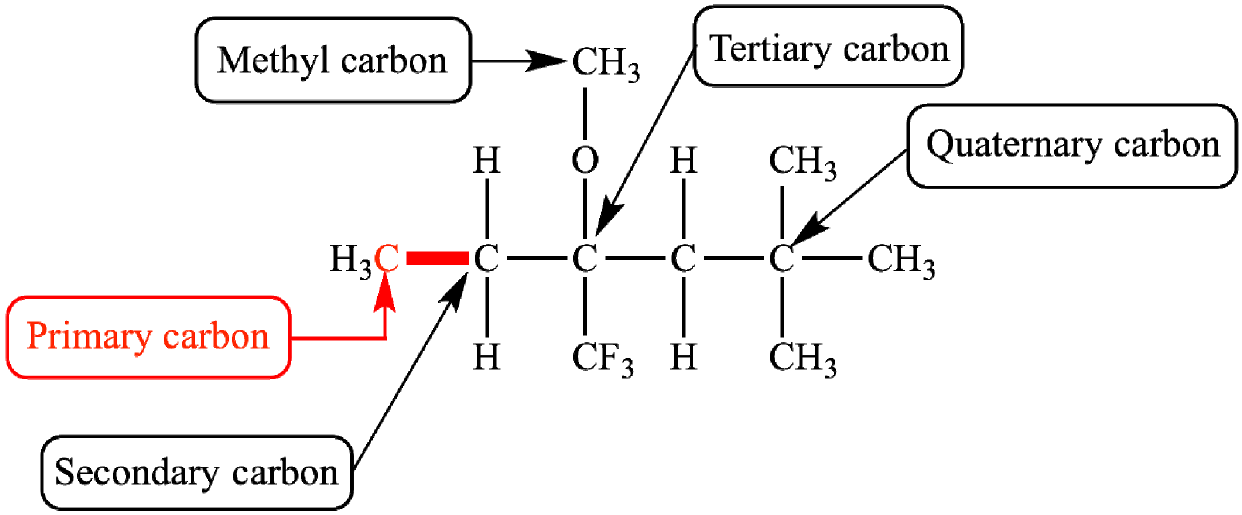


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3$$

2,2-dimethylpentane

8.2.2 Classification of carbon atoms in alkanes

By definition, a primary carbon is one which is attached to one other or no other carbon atom, a secondary carbon is one which is attached to two C- atoms, a tertiary carbon is attached to three other C-atoms, and a quaternary carbon is attached to four other carbon atoms; these are often abbreviated as 1°, 2°, 3° and 4° carbons.



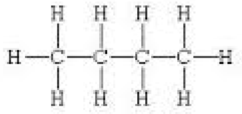
Hydrogens always take the same class as the carbons to which they are bonded. All hydrogens on a *primary* carbon are *primary*. All hydrogens on a *secondary* carbon are *secondary*.

e.g., $CH_3CH_2CH_3$: Propane contains **two** 1^{o} carbons and one 2^{0} carbon. There are six primary and two secondary hydrogens in propane.

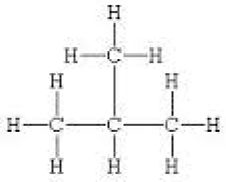
8.2.3 Isomerism of alkanes

Different compounds that share the same molecular formula are known as **isomers**. Alkanes exhibit structural isomerism.

e.g., the straight-chain structure and the branched chain structure represent the two isomers of butane, C_4H_{10}.



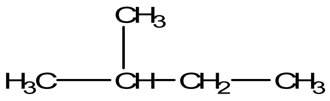
n-butane, $CH_3CH_2CH_2CH_3$



isobutane, $(CH_3)_3CH$

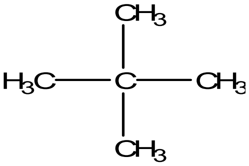
Isomers of pentane

$H_3C—CH_2—CH_2—CH_2—CH_3$



$H_3C—CH(CH_3)—CH_2—CH_3$ methylbutane

Pentane



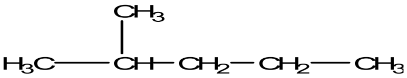
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

Dimethylpropane

Isomers of hexane

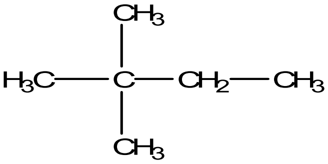
$H_3C-CH_2-CH_2-CH_2-CH_2-CH_3$

Hexane



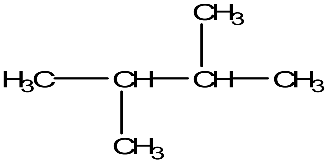
$H_3C-\overset{CH_3}{CH}-CH_2-CH_2-CH_3$

2-methylpentane



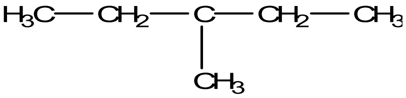
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$

2,2-dimethylpropane



$H_3C-\underset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$

2,3-dimethylpropane



$H_3C-CH_2-\underset{CH_3}{C}-CH_2-CH_3$

3-methylpentane

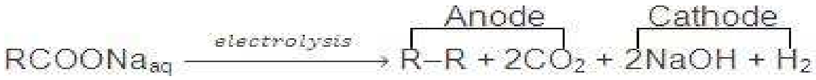
8.2.4 Natural sources

Petroleum and natural gas are the major sources of aliphatic hydrocarbon. The oil trapped inside the rocks is known as petroleum (PETRA – ROCK, OLEUM – OIL). The oil in the petroleum field is covered with a gaseous mixture known as natural gas. The main constituents of the natural gas are methane, ethane, propane and butane. Alkanes are primarily used as energy source through combustion and as raw materials for the chemical industry. The first operation in refining is fractional distillation, which yields different alkane fractions (still complex mixtures of many compounds) based on the volatility of its components. The high demand for valuable low-molecular-weight alkanes (gasoline) led to the discovery of other refining processes. Valuable industrial methods to prepare many hydrocarbons are the thermal and catalytic crackings (large hydrocarbons are broken into small fragments under the influence of heat and/or catalysts) and catalytic reforming.

8.2.5 Methods of formation

1. Kolbe's electrolysis method:

Alkanes are formed, on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated mono carboxylic acids. The electrochemical oxidative decarboxylation of carboxylic acid salts that leads to radicals, which dimerize. It is best applied to the synthesis of symmetrical dimmers.



$$RCOONa_{aq} \xrightarrow{electrolysis} \overbrace{R{-}R + 2CO_2}^{\text{Anode}} + \overbrace{2NaOH + H_2}^{\text{Cathode}}$$

Electrolysis of an acid salt gives symmetrical alkane. However, in case of mixture of carboxylic acid salts, all probable alkanes are formed.

$R^1COOK + R^2COOK \xrightarrow{electrolysis} R^1\text{-}R^2 + 2CO_2 + H_2 + 2NaOH$

($R^1\text{-}R^1$ and $R^2\text{-}R^2$ are also formed).

2. By Corey-House synthesis:

Alkyl chloride say chloroethane reacts with lithium in presence of ether to give lithium alkyl then reacts with CuI to give lithium dialkyl cuprate. This lithium dialkyl cuprate now again reacts with alkyl chloride to given alkane.

$CH_3CH_2CI + 2Li \xrightarrow{Ether} CH_3CH_2Li + LiCl$

$2CH_3CH_2Li + CuI \rightarrow Li(CH_3CH_2)_2\,Cu + LiL$

$Li(CH_3CH_2)_2Cu + CH_3CH_2CI \rightarrow CH_3CH_2CH_2CH_3 + CH_3CH_2Cu + LiCl$

3. Halogenation of alkane

Halogenation is a substitution reaction of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine or iodine). This reaction is a photochemical one. The products of this reaction are an alkyl halide or haloalkane and a hydrogen halide.

Alkanes are not very reactive molecules. However, alkyl halides are very useful reactants for the synthesis of other organic compounds. Thus, the halogenation reaction is of great value because it converts uncreative alkanes into versatile starting materials for the synthesis of desired compounds. This is important in the pharmaceutical industry for the synthesis of some drugs. In addition, alkyl halides having two or more halogen atoms are useful solvents, refrigerants, insecticides, and herbicides.

$$CH_4 + Cl_2 + \text{energy} \longrightarrow CH_3Cl + HCl$$

The reaction does not necessarily stop at one substitution, and the reaction between methane and chlorine produces dichloro-, trichloro- and tetrachloro- methane.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

The process of substitution is random, so all possible products result, though if there is excess methane the main one will be CH_3Cl, while a large excess of chlorine will give mainly CCl_4.

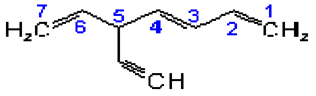
8.3 ALKENES

An alkene in organic chemistry is an unsaturated acyclic hydrocarbon containing at least one carbon to carbon double bond. The simplest alkenes, with only one double bond, form a homologous series, *the alkenes* with general formula **C_nH_{2n}**. A double bond is a σ bond and a π bond. A π bond is weaker than a σ bond and hence more reactive than σ bonds. Due to this, π bonds are considered to be a functional group. Alkenes are also called olefins (from Greek: 'oil-formers') and vinyl compounds. Terminal alkenes have the double bond at the end of the carbon chain (on a terminal carbon), whereas internal alkenes have the double bond on non-terminal carbon atoms.

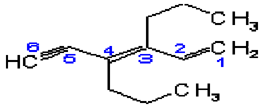
8.3.1 Nomenclature of alkene

According to IUPAC nomenclature, alkenes are identified by the suffix –ene. Number the chain beginning at the end closest to the double bond so that the double bond will have the lowest carbon number.

- Name branched or substituted alkenes in a manner similar to alkanes.
- Number the carbon atoms, locate and name substituent groups, locate the double bond, and name the main chain.
- *Cis* and *trans* isomers must be designated by the appropriate *cis*- or *trans*- prefix.



5-Ethynyl-1,3,6-heptatriene



3,4-Dipropyl-1,3-hexadien-5-yne

$CH_2=CH(CH_2)_5CH_3$

1- octene

$CH_2(CH_2)_2C=C-CH_3$

2- hexene

$CH_2=CH_2$

Ethene

$CH_3CH=CH_2$

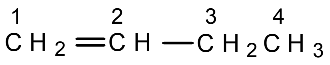
Propene

$CH_3C(CH_3)=CH_2$

2-Methylpropene

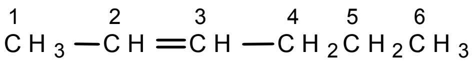
$CH_3CH_2CH_2CH_2CH{=}{=}CH_2$

1-Hexene



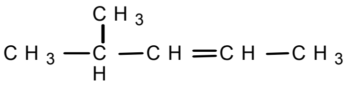
$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}\overset{4}{CH_3}$

but-1-ene



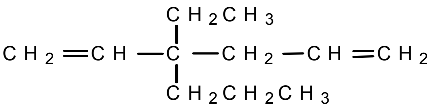
$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_3}$

hex-2-ene



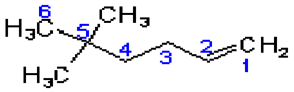
$CH_3-\underset{H}{\overset{CH_3}{C}}-CH=CH-CH_3$

4-methylpent-2-ene

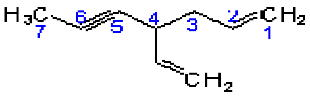


$CH_2=CH-\underset{CH_2CH_2CH_3}{\overset{CH_2CH_3}{C}}-CH_2-CH=CH_2$

3-ethyl-3-propylhexa-1,5-diene

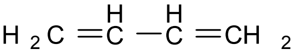


5,5-Dimethyl-1-hexene



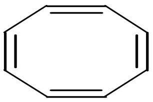
4-Vinyl-1-hepten-5-yne

Compounds with two double bonds are called dienes, three double bonds are trienes, etc. For branches, each alkyl group is given a number, but the double bond is still given preference when numbering the chain.



$H_2C=\overset{H}{C}-\overset{H}{C}=CH_2$

1,3-butadiene

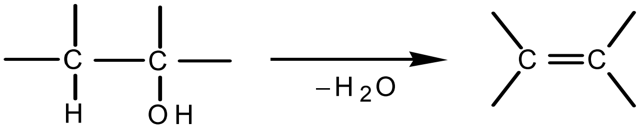


1,3,5,7-cyclooctatetraene

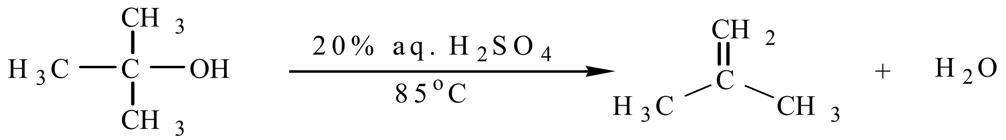
8.3.2 Methods of preperation

1. Dehydration of Alcohols:

Dehydration is a process of removal of the H_2O from a substrate molecule. When heated with strong acids catalysts (most commonly H_2SO_4, H_3PO_4), alcohols typically undergo a 1, 2-elimination reactions to generate an alkene and water. The more stable alkene is the major product; this product may arise from the rearrangement of the original carbon skeleton.



Tertiary alcohols are usually dehydrated under extremely mild conditions:



***tert*-Butyl alcohol** **2-Methylpropene (84%)**

The dehydration of alcohols can also be takes place by passing the vapors of an alcohol over heated alumina(Al_2O_3) at 623K (350°C).

$$\underset{\text{alcohol}}{RCH_2-CH_2OH} \xrightarrow[-H_2O]{Al_2O_3,\ 623\,K} \underset{\text{alkene}}{RCH{=}CH_2}$$

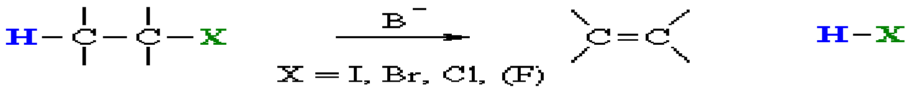
For example,

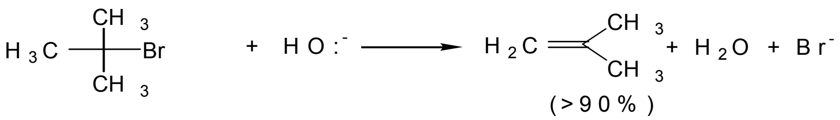
$$\underset{\text{ethanol}}{C_2H_5OH} \xrightarrow[-H_2O]{Al_2O_3,\ 623\,K} \underset{\text{ethene}}{CH_2{=}CH_2}$$

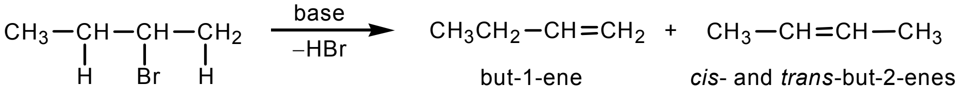
The order of the ease of dehydration of alcohols is, tertiary > secondary > primary.

2. Dehydrohalogenation of Alkyl Halides:

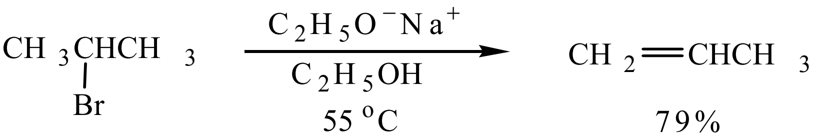
Dehydrohalogenation is the removal of a halogen atom and a hydrogen atom from adjacent carbons. When heated with strong bases (sodium or potassium hydroxides or alkoxides) in alcohol, alkyl halides typically undergo a 1,2-elimination reactions to generate alkenes. Regioselectivity is usually controlled by the relative stability of the product alkenes. The most stable alkene is usually the major product if more than one product is possible.



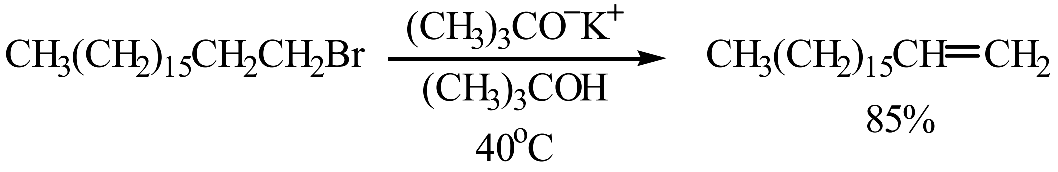




$$CH_3-\underset{H}{CH}-\underset{Br}{CH}-\underset{H}{CH_2} \xrightarrow[-HBr]{\text{base}} CH_3CH_2-CH{=}CH_2 + CH_3-CH{=}CH-CH_3$$



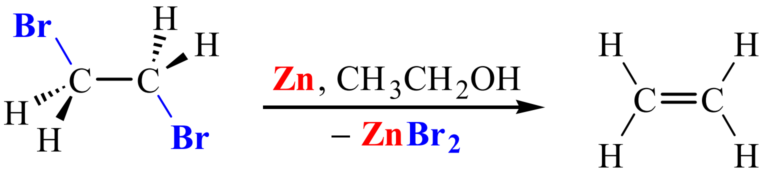
$$CH_3\underset{Br}{CH}CH_3 \xrightarrow[C_2H_5OH,\ 55\,^{\circ}C]{C_2H_5O^-Na^+} \underset{79\%}{CH_2{=}CHCH_3}$$



$$CH_3(CH_2)_{15}CH_2CH_2Br \xrightarrow[\substack{(CH_3)_3COH \\ 40^oC}]{(CH_3)_3CO^-K^+} \underset{85\%}{CH_3(CH_2)_{15}CH{=}CH_2}$$

3. Reduction of Vicinal Dibromides:

The action of zinc metal in acetic acid on vicinal dibromides to produce alkenes is elimination, a reduction and a dehalogenation reaction.



8.3.3 Physical properties of alkene

The physical properties of alkenes are comparable with alkanes. The physical state depends on molecular mass. The simplest alkenes, ethylene, propylene and butylene are gases. Like the alkanes, alkenes are nonpolar; insoluble in water; soluble in non polar organic solvents; less dense than water, flammable and nontoxic. Most alkenes, like alkanes exhibit only weak van der Waals interactions, so their physical properties are similar to alkanes of similar molecular weight. Alkenes have low melting points (m.p.) and boiling points (b.p.). M.p. and b.p. increase as the number of carbons increases because of increased surface area.

8.3.4 Chemical reaction of alkene

The alkenes are more reactive than the alkanes because of the C=C bond. . The carbon-carbon double bond consists of a strong sigma bond and a weak pi bond. The typical reactions of alkenes involve the breaking of this weaker pi bond and formation of two new sigma bonds. Because of the presence of the multiple bonds, characteristic reactions are the electrophilic additions. It is possible for the double bond to break, allowing each carbon to form a new bond, which is often energetically favourable.

$$\begin{array}{ccccc} CH_2{=}CH_2 & & CH_3{-}CH_3 & & \\ 152\ \text{kcal/mol} & - & 88\ \text{kcal/mol} & = & 64\ \text{kcal/mol} \\ & & & & \uparrow \\ \sigma + \pi & & \sigma & & \boxed{\pi\ \text{bond only}} \end{array}$$

1. Hydrogenation

In the presence of finely divided metals like Ni, Pt, Pd, Rh, and Ru, addition of a hydrogen molecule takes place on alkene at room temperature. When the catalyst is in a different physical state to the other reactants it is called heterogeneous catalysis (E.g. a solid catalyst with a liquid and a gas). In contrast a liquid catalyst in a reaction solution is an example of homogeneous catalysis (acid catalyzed alcohol dehydration). During catalytic hydrogenation, the hydrogen adsorbs onto the surface of the metal catalyst, and they add syn to the double bond. One face of the π system binds to the catalyst, then the bound hydrogen inserts into the π bond, and the product is liberated from the catalyst. This is a *syn* addition reaction, i.e., both hydrogen atoms attack from the same side of the molecule.

$$R{-}CH{=}CH{-}R' + H_2 \xrightarrow{\text{catalyst}} R{-}CH_2{-}CH_2{-}R'$$

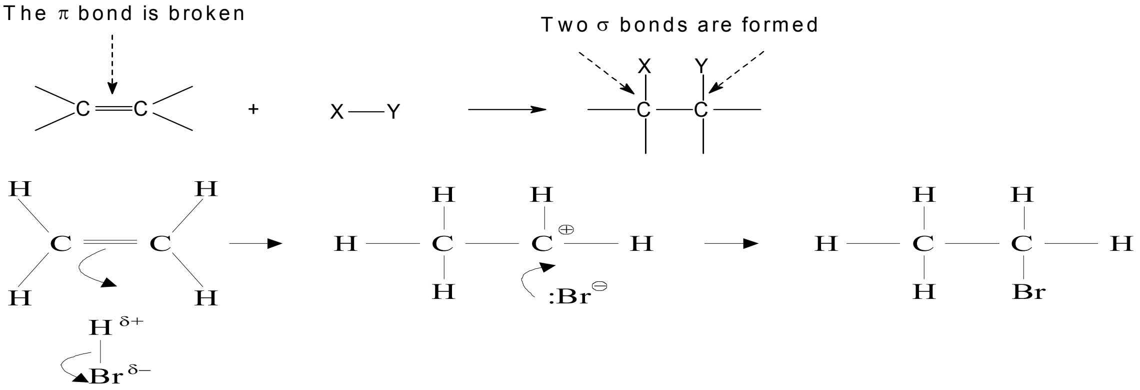
$$CH_2{=}CH_2 + H_2 \xrightarrow[25\ ^{o}C]{\text{Ni, Pd or Pt}} CH_3{-}CH_3$$

$$CH_3CH{=}CH_2 + H_2 \xrightarrow[25\ ^{o}C]{\text{Ni, Pd or Pt}} CH_3CH_2{-}CH_3$$

Finely divided metals activate molecular hydrogen and the hydrogen atoms add to the double bond. This is usually a *syn* addition, i.e., both hydrogen atoms attack from the same side of the molecule.

2. Electrophilic Addition.

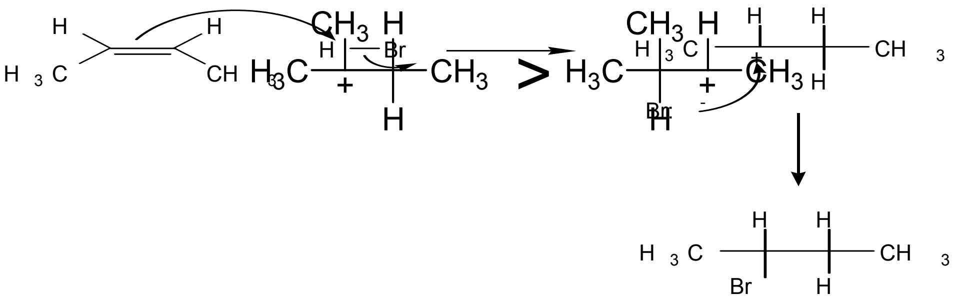
The most common chemical transformation of a carbon-carbon double bond is the addition reaction. The characteristic reaction of alkenes is electrophilic addition, because the π bond is both weak and electron rich (nucleophilic). An important feature of alkene reactivity is an ability to react with a variety of *electrophilic reagents*, those reagents attracted to the source of extra electron density. In an alkene, pi bond serves as a source of electron. An **electrophile** will attract pi electrons, and can pull them away to form a new bond. This leaves one carbon with only 3 bonds and a +ve charge (carbocation). The double bond acts as a **nucleophile** (attacks the electrophile). In most cases, the cation produced will react with another nucleophile to produce the final overall electrophilic addition product. Electrophilic addition is probably the most common reaction of alkenes.



The alkene abstracts a **proton** from the HBr, and a carbocation and bromide ions are generated.

The bromide ion quickly attacks the cationic center and yields the final product. In the final product, H-Br has been added across the double bond.

Consider the addition of H-Br to 2-methyl-2-butene:



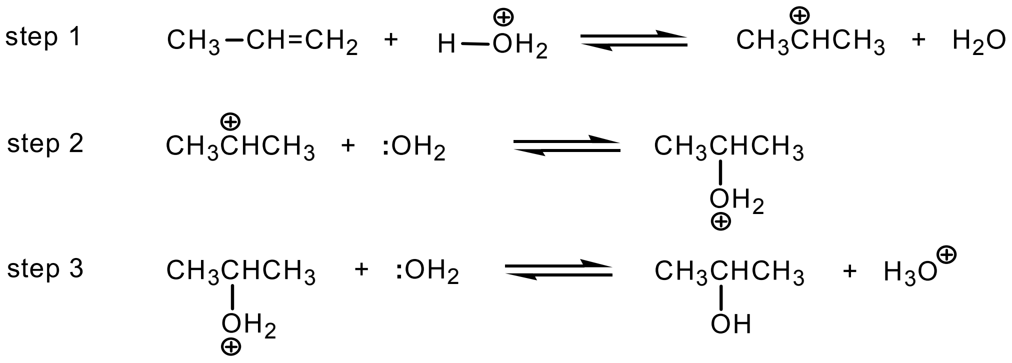
There are two possible products arising from the two different ways of adding H-Br across the double bond. But only one is observed. The observed product is the one resulting from the more stable carbocation intermediate.

Tertiary carbocations are more stable than secondary. The protonation occurs at the least highly substituted end so that the cation produced is at the most highly substituted end (and therefore more stable).

The acid-catalyzed process is a convenient method for the preparation of secondary and tertiary alcohols. The reaction is usually regioselective and follows *Markovnikov's rule.*

$$CH_3-CH=CH_2 \xrightarrow{H^+/H_2O} CH_3\underset{\underset{OH}{|}}{C}HCH_3 \qquad CH_2=CH_2 \xrightarrow{H^+/H_2O} CH_3CH_2OH$$

Mechanism:



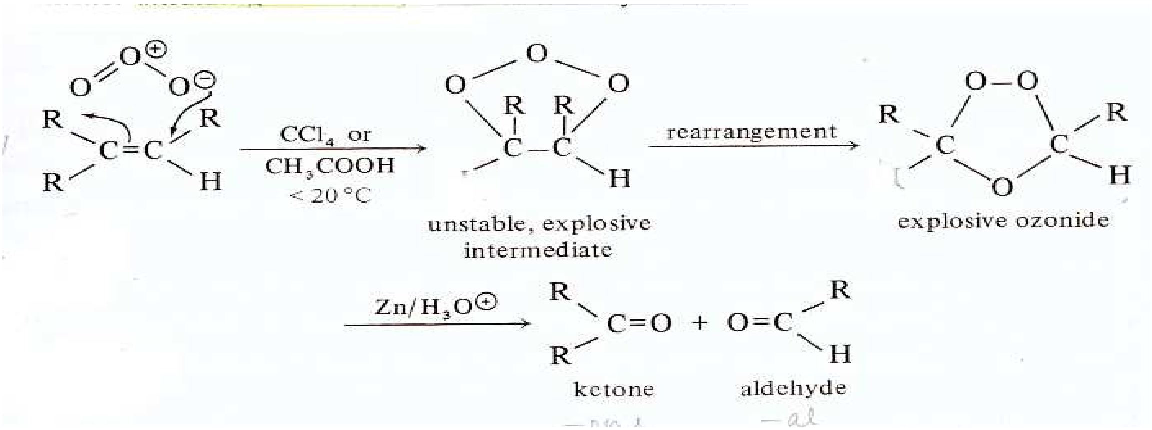
step 1 $$CH_3-CH=CH_2 + H-\overset{\oplus}{O}H_2 \rightleftharpoons CH_3\overset{\oplus}{C}HCH_3 + H_2O$$

step 2 $$CH_3\overset{\oplus}{C}HCH_3 + :OH_2 \rightleftharpoons CH_3\underset{\underset{\underset{\oplus}{OH_2}}{|}}{C}HCH_3$$

step 3 $$CH_3\underset{\underset{\underset{\oplus}{OH_2}}{|}}{C}HCH_3 + :OH_2 \rightleftharpoons CH_3\underset{\underset{OH}{|}}{C}HCH_3 + H_3O^{\oplus}$$

3. Ozonolysis:

Ozone, O_3, is highly reactive electrophile. Ozone adds to carbon-carbon double bonds forming a number of intermediates the most important of which is ozonide. Reactive ozonide is reduced by zinc in the presence of water to give aldehydes or ketones depending on the degree of substitution of the double bond. Each double bond yields two fragments if it is substituted asymmetrically. Both acyclic and cyclic alkenes are subject to degradative ozonolysis.



After reduction step of ozonolysis:

(i) an alkene with an unsubstituted carbon atom yields formaldehyde

(ii) an alkene with a monosubstituted carbon atom yields an aldehyde

(iii) an alkene with a disubstituted carbon atom yields a ketone

Hence these reactions can be useful for the characterisation of molecules of unknown structure which contain carbon-carbon double bonds. The position of the double bond is clearly determined by ozonolysis method.

8.4 ALKYNES

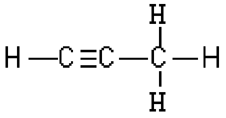
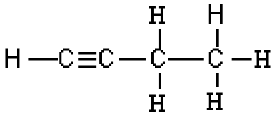
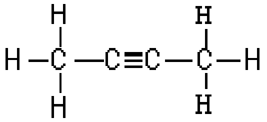
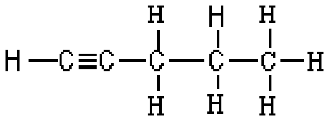
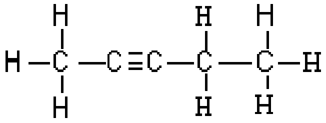
Alkynes are hydrocarbons which contain carbon-carbon triple bond. The triple bond is indicated by changing the ending of the name to -yne, in the same manner as the double bonds in alkenes are indicated by the ending -ene. Alkynes, like alkenes are unsaturated hydrocarbons with the general formula C_nH_{2n-2}. There suffix is –yne and the IUPAC name of them is written as Alkane-ane+ yne = Alkyne. For example, ethyne the simplest alkyne,

Structure of Ethyne, Acetylene

Which is more commonly known by its common name **acetylene**, is a gas often used as a fuel for cutting and welding torches because it burns with a very hot flame?

The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are starting materials for a large number of organic compounds. Hence, it is interesting to study this class of organic

The first few members of this series are represented by the following structures:

Name	Structure	Condensed structure
Ethyne	$H-C\equiv C-H$	$HC\vdots CH$
Propyne	 $H-C\equiv C-\overset{H}{\underset{H}{C}}-H$	$HC\vdots CCH_3$
But-1-yne	 $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	$HC\vdots CCH_2CH_3$
But-2-yne	 $H-\overset{H}{\underset{H}{C}}-C\equiv C-\overset{H}{\underset{H}{C}}-H$	$CH_3C\vdots CCH_3$
Pent-1-yne	 $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	$HC\vdots CCH_2CH_2CH_3$
Pent-2-yne	 $H-\overset{H}{\underset{H}{C}}-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	$CH_3C\vdots CCH_2CH_3$

8.4.1 Nomenclature and classification

The naming of the alkynes follows the exact rules as those used for naming alkenes except, of course, that the suffix – *yne* is used to indicate that a triple bond is now present.

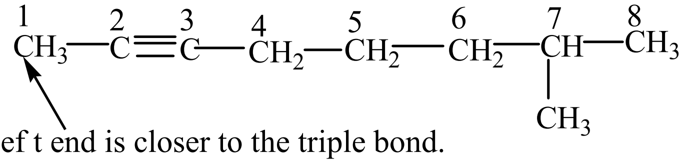
Naming Alkynes:

STEP 1: Name the main chain. Find the longest carbon chain of carbons containing the triple bond. The names of alkynes end with -yne. When there is more than one multiple bond, use numerical prefixes (diene, diyne, triene, triyne, etc.)

$CH_3-CH_2-CH_2-C\equiv C-CH_3$

Name as *hexyne* - a six C chain containing a triple bond.

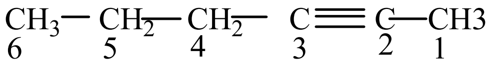
STEP 2: Number the carbon atoms in the main chain. Begin at the end nearer the multiple bond. If the multiple bond is at the same distance from both ends, begin numbering at the end nearer the first branch point.



$$\overset{1}{CH_3}-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{7}{CH}}-\overset{8}{CH_3}$$

The lef t end is closer to the triple bond.

STEP 3: Write the full name. Assign numbers to the branching substituents, and list the substituents alphabetically. Indicate the position of the multiple bond(s) in the chain by giving the number of the first multiple-bonded carbon. If more than one multiple bonds is present, identify the position of each multiple bond and use the appropriate ending diene, triene, tetraene, and so forth.



$$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{CH_2}-\underset{3}{C}\equiv\underset{2}{C}-\underset{1}{CH3}$$

2-hexyne or
hex-2-yne

Some common alkynes and their naming:

Structure	**Common Name**	**IUPAC**
$CH\equiv CH$	Acetylene	ethyne
$CH\equiv C-CH_3$	methyl acetylene	propyne
$CH_3-C\equiv C-CH_3$	dimethyl acetylene	2-butyne
$CH\equiv C-CH_2\text{-}CH_3$	ethyl acetylene	1-butyne

Classification of Alkynes: Generally alkynes can be categories in to following two categories.

a. **Terminal Alkyne**: A Terminal Alkyne is an alkyne in whose molecule there is at least one hydrogen atom bonded to a triply bonded carbon atom. Or simply, the alkynes in which the triple bonded carbon atoms are at the extreme positions.

$$R-C\equiv C-R$$

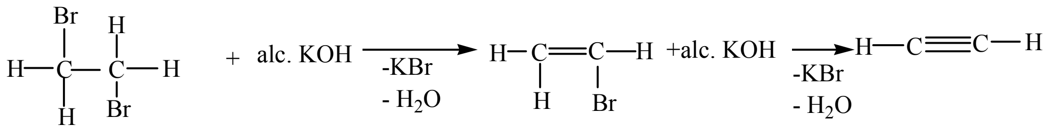
Where, both R will be H or same alkyl group

b. **Non-terminal alkynes:** Non-Terminal Alkynes,on the other hand have triple bond at any place other than the end positions.

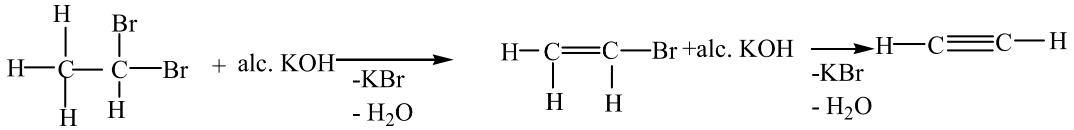
$$R-C\equiv C-H$$

8.4.2 Methods of formation

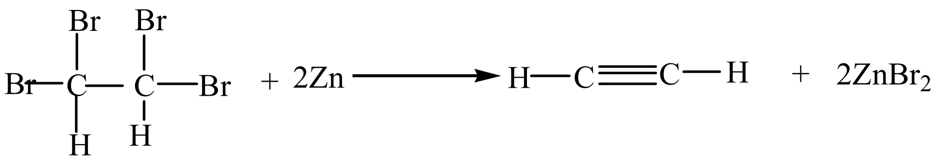
1. **From Vicinal di- halides:** Vic. di halides on react with alc. KOH gives alkynes.



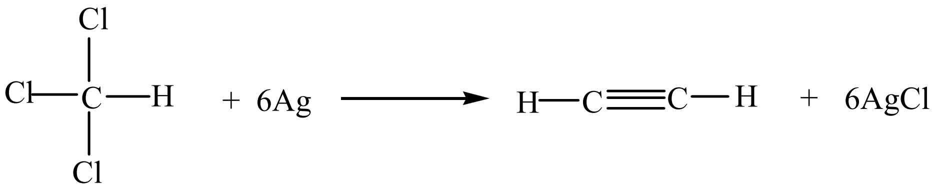
2. **From gem. dihalides:** 1,1- dihalides are known as gemdihalides, gem-dihalides on react with alc. KOH gives alkyne.



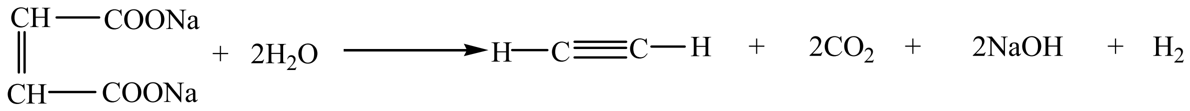
3. **From tetra halides:** Tetra halides on react with Zn form alkynes.



4. **From Chloroform:** The trihaligen derivatives of CH_4 are known as haloform. Such as CHX_3 (X= Cl, Br, I). Chloroform on react with Ag powder gives acetelene.



5. **From Kolbey's electrolysis method:** The Na or K salt of malic acid on react with H_2O and after electrolysis gives acetylene and CO_2 at anode and H_2 and NaOH at cathode.



Sodium malate

8.4.3 Physical properties

1. **Physical State:**

   The first three members of alkynes are gases while those containing five to thirteen carbon atoms are liquids and higher alkynes are solids.

2. **Melting and Boiling Points:**

   The melting and boiling points of alkynes are quite low and increase regularly with increase in molecular mass. Alkynes are less volatile than alkanes and alkenes.

3. **Solubility:**

   Alkynes are insoluble in water but are soluble in organic solvents such as benzene, hexane, ether, carbon tetrachloride, etc.

4. **Density:**

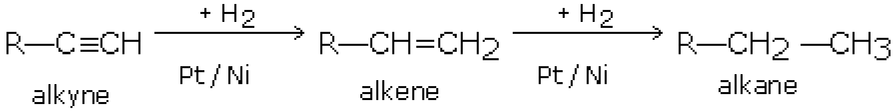
   All alkynes are lighter than water. Their densities increase regularly with increase in molecular mass.

8.4.4 Chemical reactions of alkynes

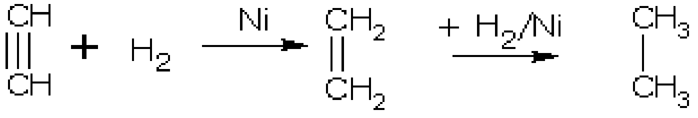
1. **Electrophilic Addition Reactions**

   Carbon-carbon triple bond, C=C, is a combination of one and two bonds. Alkynes give electrophilic addition reactions as they show reactivity due to the presence of bonds. This property is similar to alkenes but alkynes are less reactive than alkenes towards electrophilic addition reactions due to the compact CC electron cloud. Some typical electrophilic addition reactions given by alkynes are:

   a. **Addition of hydrogen:** An alkyne reacts with hydrogen in the presence of catalyst (Pt or Ni) at 250°C, first forming alkenes and finally alkane.

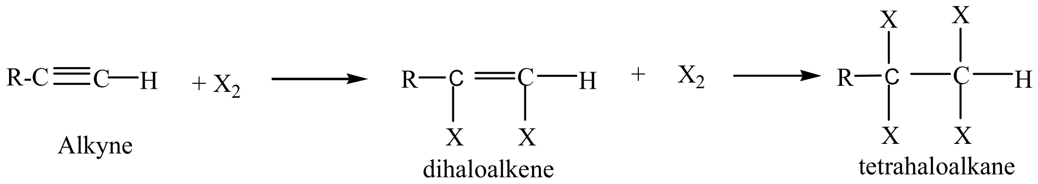


   For example, ethyne gives ethane in two steps.

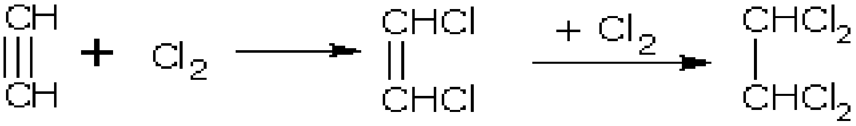


ethyne ethane ethane

b. **Addition of Halogens**: Alkynes when react with halogens (Cl_2 or Br_2) in the dark, initially it gives dihaloalkenes and then finally gives tetrahalo alkanes. The reaction gets accelerated in the presence of light or halogen carriers.

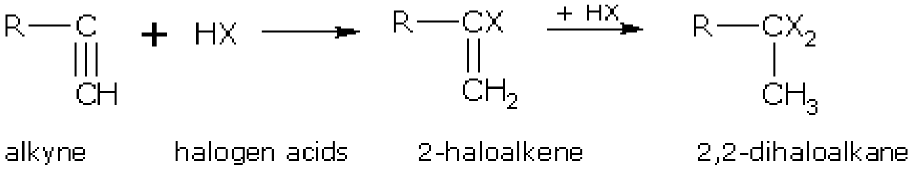


For example, ethyne (acetylene) with chlorine gives,

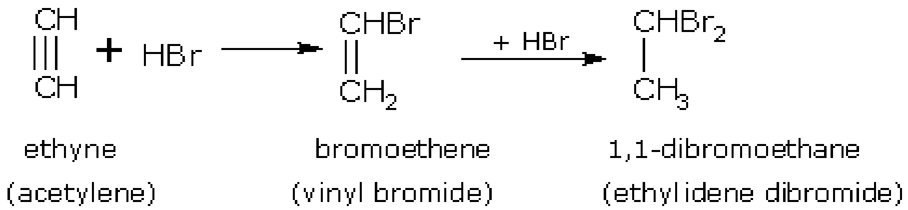


ethyne dichloroethene tetrachloroethane

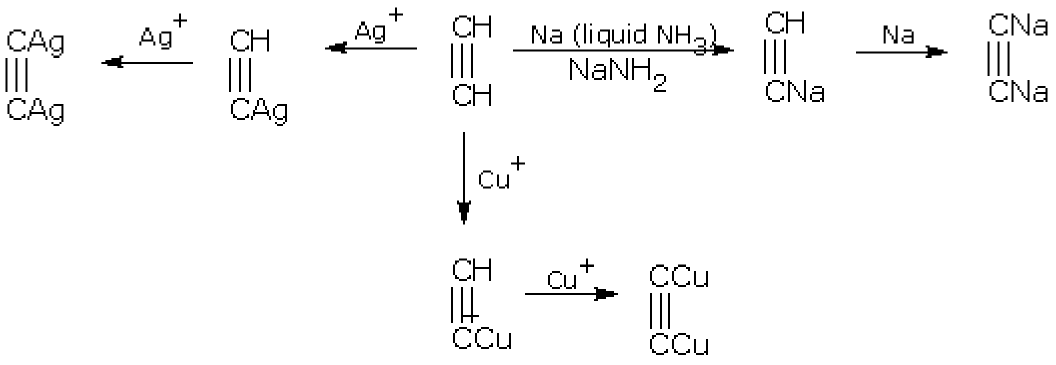
c. **Addition of Halogen Acids:** Alkynes reacts with halogen acids (HX, X= Cl, Br, I) according to the Markownikoff's rule to give initially mono-halo alkenes and then finally gives di-halo alkanes.



For example, ethyne (acetylene) with HBr gives,

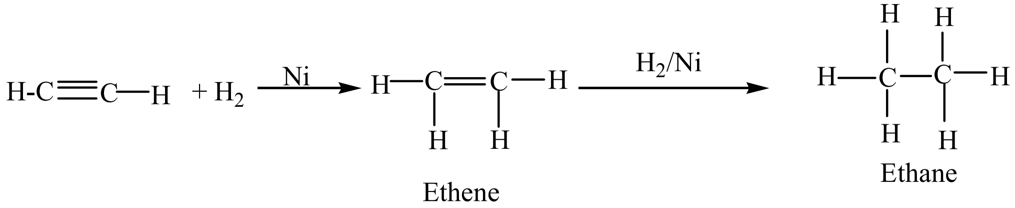


2. **Substitution Reactions:** Due to their acidic nature, alkynes form metallic salts called alkynides i.e. sodium, silver and copperous salts.



dicopper acetylide (red precipitate)

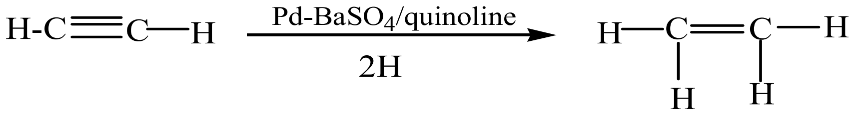
3. **Hydrogenation:**
   a. **Uncontrolled hydrogenation:** In the presence of Ni catalyst alkyne on react with H_2 gives alkane.



$$H\text{-}C\equiv C\text{—}H + H_2 \xrightarrow{Ni} H\text{—}\underset{H}{C}=\underset{H}{C}\text{—}H \xrightarrow{H_2/Ni} H\text{—}\overset{H}{\underset{H}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{—}H$$

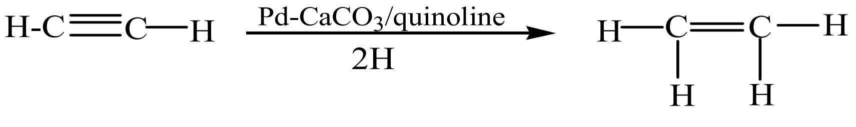
Ethene Ethane

   b. **Controlled hydrogenation:** Alkynes on react with H_2 in the presence of Pd-$CaCO_3$/Quinolin gives alkene. This reaction is known as controlled hydrogenation of alkenes.



$$H\text{-}C\equiv C\text{—}H \xrightarrow[2H]{Pd\text{-}BaSO_4/quinoline} H\text{—}\underset{H}{C}=\underset{H}{C}\text{—}H$$

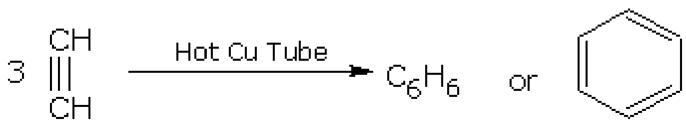
Ethene



$$H\text{-}C\equiv C\text{—}H \xrightarrow[2H]{Pd\text{-}CaCO_3/quinoline} H\text{—}\underset{H}{C}=\underset{H}{C}\text{—}H$$

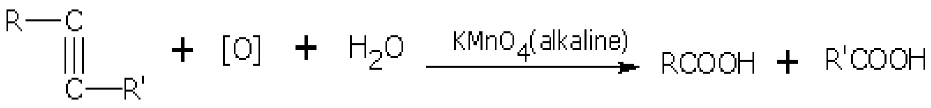
Ethene

4. **Polymerization:** In the presence of red hot Cu tube, three molecules of C_2H_2 are undergoes polymerization and give a polymer C_6H_6. This reaction is known as polymerization of C_2H_2.

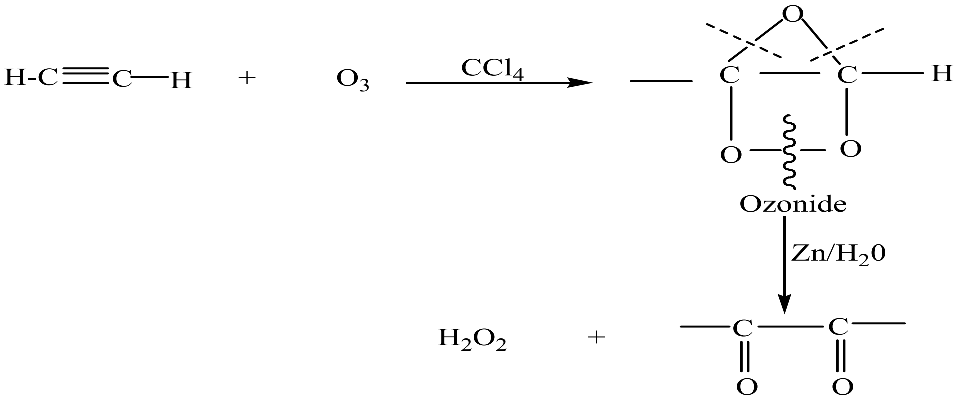


ethyne benzene

5. **Oxidation:** Oxidation of alkynes gives mono or dicarboxylic acids.



6. **Ozonolysis:** In the presence of CCl_4 alkyne on react with O_3 gives alkyne ozonimide which on react with Zn/H_2O gives di-carbonyl compound.

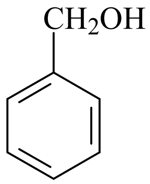


di- carbonyl compound

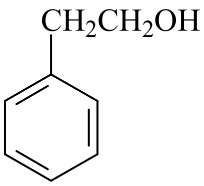
8.5 ALCOHOLS

Alcohols are organic compounds in which one or more hydrogen atoms from hydrocarbon have been replaced by hydroxyl (-OH) group. They are some of the most common and useful compounds in nature, in industry, and around the house. The general formula for a simple acyclic alcohol is $C_nH_{2n+1}OH$, where n=1, 2, 3, etc. The saturated carbon chain is often designated by the symbol R, so that ROH can represent any alcohol in the homologous series. Alcohols can be viewed as organic analogues of water in which one hydrogen atom is replaced by an alkyl group. The simplest and most commonly used alcohols are methanol and ethanol. They occur widely in nature and have many industrial and pharmaceutical applications.

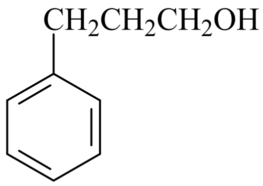
Aromatic compounds, which contain a hydroxy group on a side chain, behave like alcohols are called aromatic alcohol. In these alcohols, the —OH group is attached to a sp^3 hybridised carbon atom next to an aromatic ring.



benzyl alcohol



2- phenyl ethanol



3- phenyl propanol

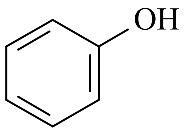
In some alcohols, the —OH group is attached to a sp^3 hybridised carbon next to the carbon-carbon double bond that is to an allylic carbon are known as allylic alcohols. In some alcohols —OH group bonded to a carbon-carbon double bond i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols. Allylic and benzylic alcohols may be primary, secondary or tertiary in nature.

$CH_2{=}CH{-}OH$

vinylic alcohol

$CH_2{=}CH{-}CH_2{-}OH$

allylic alcohol



phenol

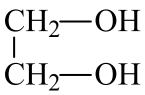
8.5.1 Classification of Alcohols

Alcohols are classified into following types on the basis of number of –OH groups present in the molecule and nature of carbon attached with –OH group as follow:

(a) Monohydric Alcohols: These compounds contain only one –OH group.

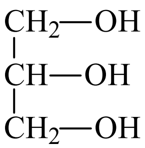
CH_3CH_2OH $CH_3CH_2CH_2OH$

(b) Dihydric Alcohols: These contain two –OH groups.



$$\begin{array}{l} CH_2—OH \\ | \\ CH_2—OH \end{array}$$

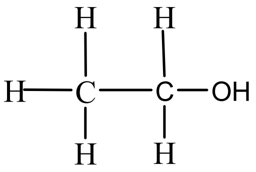
(c)Trihydric Alcohols: These contain three –OH groups.



$$\begin{array}{l} CH_2—OH \\ | \\ CH—OH \\ | \\ CH_2—OH \end{array}$$

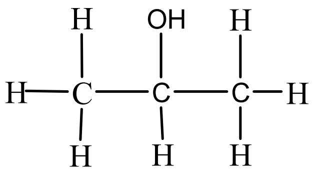
On the basis of nature of carbon atom attached with -OH group the mnohydric Alcohols can be further classified as primary (1°), secondary (2°), or tertiary (3°) depending on the number of carbon atoms bound to the hydroxyl-bearing carbon.

(a) Primary alcohol (1° alcohol): A primary alcohol has one alkyl group attached to the carbon bound to the –OH, *i.e.*, a compound in which the hydroxyl group is bounded to a primary carbon. Primary alcohols have the group –CH_2OH, where the carbon atom with the alcoholic hydroxyl group has at least two additional hydrogen attached to that carbon. Primary alcohol has –OH group bonded to a carbon which is bonded to one other carbon:

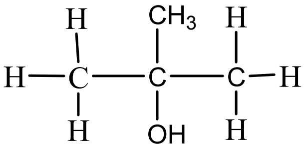


$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H— & C & — & C & —OH \\ & | & & | & \\ & H & & H & \end{array}$$

(b) Secondary alcohol (2° alcohol): A secondary alcohol has two alkyl group attached to the carbon bound to the –OH, i.e., the hydroxyl group is bounded to a secondary carbon. Secondary alcohols have the group –CHOH, where the carbon atom with the alcoholic hydroxyl group has only **one** additional H atom attached to it. There are two R groups (R stands for any other organic chain or group), and the alcoholic hydroxyl group is attached to a secondary carbon. Secondary alcohol has –OH group bonded to a carbon which is bonded to two other carbon:



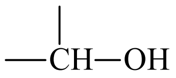
(c) **Tertiary alcohol (3° alcohol):** A tertiary alcohol has three alkyl group attached to the carbon bound to the –OH, i.e., the hydroxyl group is bounded to a tertiary carbon. Tertiary alcohols have the group –COH, where the carbon atom with the alcoholic hydroxyl group has no additional H atoms attached to it.



If we replace hydrogen with a –OH group we get the following groups for three alcohols:

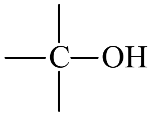
$—CH_2OH$

primary alcohol



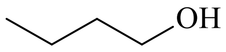
$—\overset{|}{C}H—OH$

secondary alcohol

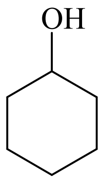


$—\overset{|}{\underset{|}{C}}—OH$

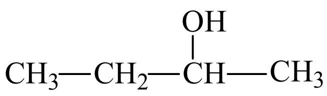
tertiary alcohol



primary alcohol

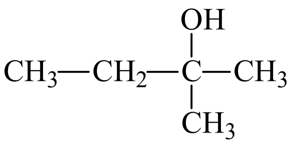


secondary alcohol



$CH_3—CH_2—\overset{OH}{CH}—CH_3$

secondary alcohol



$CH_3—CH_2—\underset{CH_3}{\overset{OH}{C}}—CH_3$

tertiary alcohol

8.5.2 Nomenclature of alcohols

According to the IUPAC system of nomenclature, alcohols are called alkanols. They are named as the derivatives of the corresponding alkane in which the *-e* of the alkane is replaced by ***-ol.*** The IUPAC have come up with a set of rules that are used to name any alcohol regardless of its complexity. These rules are summarized as follows:

Step 1. Name the longest continuous chain to which the hydroxyl (—OH) group is attached. Count the number of carbon atoms and identify the corresponding alkane. The name for this chain is obtained by dropping the final **-e** from the name of the hydrocarbon parent name and adding the ending **-ol.**

Step 2. Number the longest chain to give the lowest possible number to the carbon bearing the hydroxyl group.

Step 3. Locate the position of the hydroxyl group by the number of the carbon to which it is attached.

Step 4. Number the any other substituents according to their position on the chain.

Step 5. Combine the name and location for other groups, the hydroxyl group location, and the longest chain into the final name.

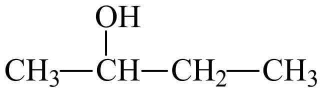
Step 6. If there are more than one –OH group do not remove the –e from the suffix, but add a di- or tri- prefix to the –ol suffix.

Step 7. Identify and locate the other branches on the chain so that they are named alphabetically and their carbon number is hyphenated onto the front of the name.

viz;

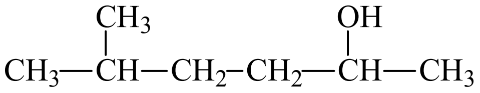
Alcohols	**Common name**	**IUPAC name**
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
CH_3CH_2 CH_2OH	n-Propyl alcohol	1-Propanol
$CH_3CHOHCH_3$	Isopropyl alcohol	2-Propanol
$CH_3(CH_2)_2CH_2OH$	n-Butyl alcohol	1-Butanol
$CH_3(CH_2)_3CH_2OH$	n-Pentyl alcohol	1-Pentanol

Other examples:



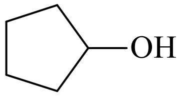
$$CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-CH_3$$

2 - butanol

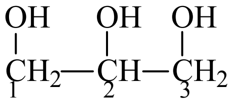


$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_2-\overset{OH}{\overset{|}{C}}H-CH_3$$

5 methyl 2 hexanol

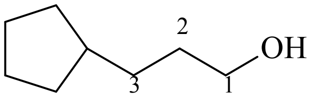


cyclopentanol

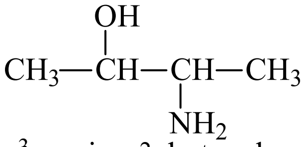


$$\overset{OH}{\overset{|}{\underset{1}{C}}}H_2-\overset{OH}{\overset{|}{\underset{2}{C}}}H-\overset{OH}{\overset{|}{\underset{3}{C}}}H_2$$

1, 2, 3- trihydroxy propane

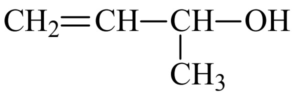


3-cyclopentyl-1- propanol



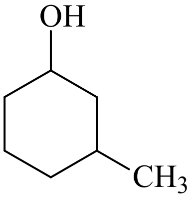
$$CH_3-\overset{OH}{\overset{|}{C}}H-\underset{NH_2}{\underset{|}{C}}H-CH_3$$

3--amino 2- butanol

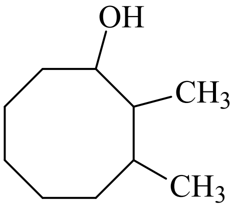


$$CH_2{=}CH-\underset{CH_3}{\underset{|}{C}}H-OH$$

3 - butene -2 - ol



3 - meyhylcyclohexanol



2,3 - dimethylcyclooctanol

8.5.3 Methods of preparation of alcohols

The following methods are used for the preparation of alcohols:

1. **Hydrolysis of haloalkanes:** Haloalkanes can be converted to corresponding alcohols using aqueous NaOH, KOH or Ca $(OH)_2$. With this method primary and secondary alcohols are formed from a primary and secondary halogenoalkanes. This is a type of nucleophilic substitution reaction (S_N). This reaction is useful only with reactants that do not undergo E_2 elimination readily.

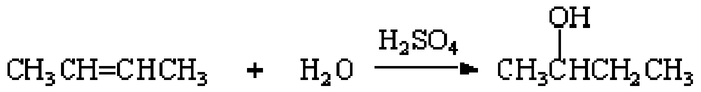
$$RX + \overset{\ominus}{O}H \xrightarrow{H_2O} ROH + X^{\ominus}$$

$$CH_3CH_2CH_2Br + NaOH(aq) \xrightarrow{H_2O} CH_3CH_2CH_2OH + NaCl$$

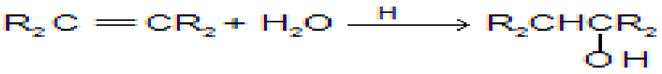
2. **From hydration of alkenes:** Hydration i.e.s addition of H^+ and OH^- across a C=C double bond to give alcohols. This is an electrophilic addition of H_2O to the alkene. Alcohols can be prepared by adding water to an alkene in the presence of a strong acid such as co. H_2SO_4. Because these reactions follow Markovnikov's rule, the product of the reaction is often a highly substituted 2° or 3° alcohol.

$$RCH=CH_2 + H_2SO_4 \rightarrow RCH\text{-}CH_3 \xrightarrow{H_2O} RCHOHCH_3$$

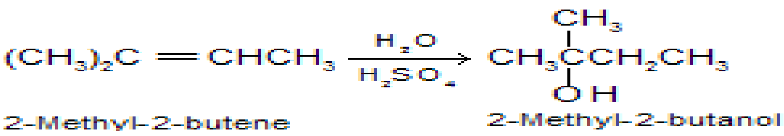
$$CH_2=CH_2 + H_2SO_4 \rightarrow CH_3\text{-}CH_2HSO_4 \xrightarrow{H_2O} CH_3CH_2OH$$



$$CH_3CH=CHCH_3 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{OH}{C}HCH_2CH_3$$



$$R_2C=CR_2 + H_2O \xrightarrow{H} R_2CH\underset{OH}{C}R_2$$



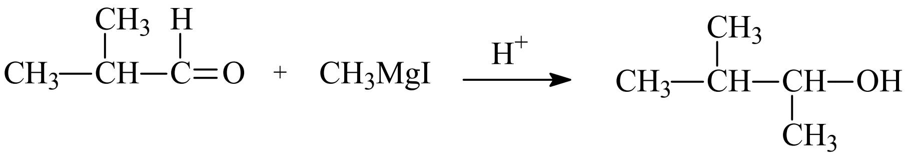
$$(CH_3)_2C=CHCH_3 \xrightarrow[H_2SO_4]{H_2O} CH_3\overset{CH_3}{\underset{OH}{C}}CH_2CH_3$$

2-Methyl-2-butene 2-Methyl-2-butanol

Ease of preparation is tert. > sec. > prim alcohol; ease of dehydration follows same sequence.

3. **From Grignard reagents** – Alcohol can easily be prepared by using Grignard (RMgX) reagent as follow:

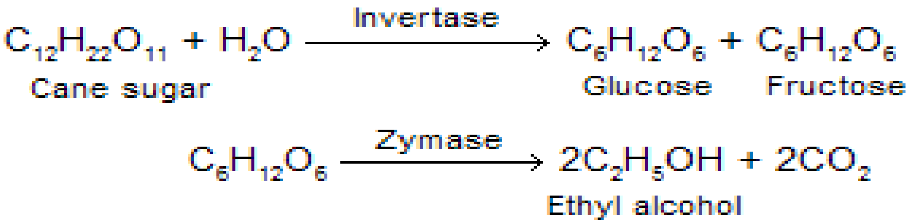
(a) By reaction with aldehydes & ketones: The reaction of Grignard reagents with formaldehyde produces a primary alcohol, with other aldehydes, secondary alcohols and with ketones, tertiary alcohols. In this method alcohol is prepared with the formation of new carbon-carbon bonds.



$$CH_3\text{—}\overset{CH_3}{C}H\text{—}\overset{H}{C}=O + CH_3MgI \xrightarrow{H^+} CH_3\text{—}\overset{CH_3}{C}H\text{—}\underset{CH_3}{C}H\text{—}OH$$

4. **Fermentation:** Ethanol is prepared on a large scale using fermentation process. It involves breaking down large molecules into simpler ones using enzymes. Usually, yeast is added as a

source of enzymes. Yeast converts the reactant glucose or fructose into ethanol and carbon dioxide in presence of zymase enzyme.



$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

8.5.4 Chemical reactions of alcohols

Alcohols acts both as nucleophiles as well as electrophiles. The bond between O-H is broken when alcohols react as nucleophiles and the bond between C-O is broken when they react as electrophiles. The chemical properties of any given aliphatic alcohol depend on the nature of the alkyl group and on the properties of the hydroxyl group. Based on the cleavage of O-H and C-OH bonds, the reactions of alcohols may be divided into two groups:

1. Acylation of alcohol:

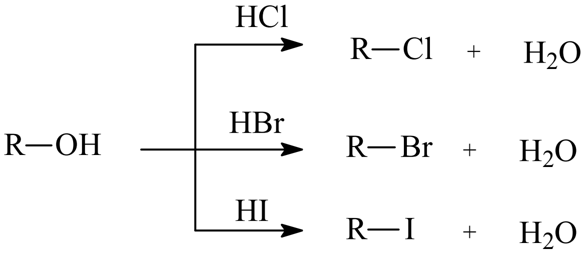
When alcohol reacts with acylhalide and anhydride substitution of hydrogen atom by acyl group is known as acylation of alcohols.

$$ROH + CH_3COCl \longrightarrow ROCOCH_3 + HCl$$

$$ROH + (CH_3CO)_2O \longrightarrow ROCOCH_3 + CH_3COOH$$

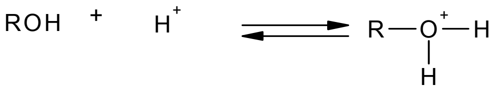
2. Halogenation: Alcohols can be converted to alkyl halides using one of three reactions:

(a) Reaction with hydrogen halides: Respective alkyl halides are formed by reacting with the appropriate hydrogen halide, HCl for chlorination, HBr for bromination, and HI for iodination. The reaction involves the initial protonation of the hydroxyl group of the alcohol. This improves the leaving group ability of the hydroxyl group.



Mechanism:

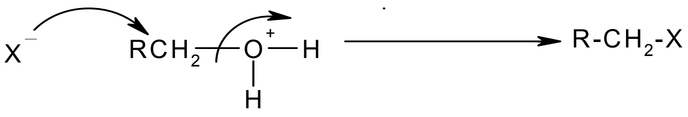
Step1: Protonation of the alcohols: The alcohol acts as a weak base and accepts the proton donated by the hydrogen halide.



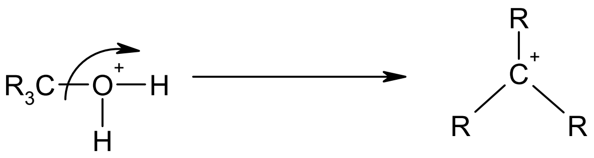
$$ROH + H^+ \rightleftharpoons R-\overset{+}{\underset{|\atop H}{O}}-H$$

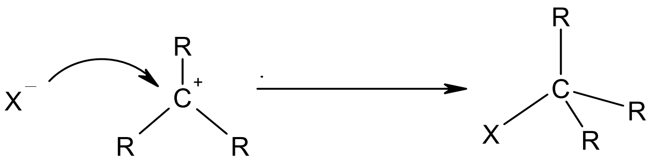
Step 2: Removal of a water molecule and formation of halide through S_N2 mechanism/ S_N1 mechanism as:

(i) For primary and secondary alcohols, it is a S_N2 reaction.



(ii) For tertiary alcohols, it is a S_N1 reaction.





(iii)Rate of the reaction for 1^0, 2^0 and 3^0 alcohols:

The order of rates of reaction:

3^0 alcohol > 2^0 alcohol> 1^0 alcohol

The rate can be shown by the turbidity in the aqueous layer since the chloroalkane formed is immiscible with water.

(b) Reaction with thionyl chloride, $SOCl_2$: Alcohols will react with thionyl chloride to produce alkyl halides. The reaction involves a nucleophilic attack of the alcohol on a $SOCl_2$ molecule displacing one of the chlorides. Then the chloride will act as the nucleophile in a second step and displace the oxygen from the carbinol carbon.

$$\text{R—OH} + SOCl_2 \longrightarrow \text{R—Cl} + SO_2 + HCl$$

(c) Reaction with phosphorus halides

Alcohols will react with phosphorus tribromide or phosphorus pentabromide to form alkyl bromides.

$$^{3}\,\text{ROH} + PBr_3 \longrightarrow {}^{3}\,\text{RBr} + H_3PO_3$$

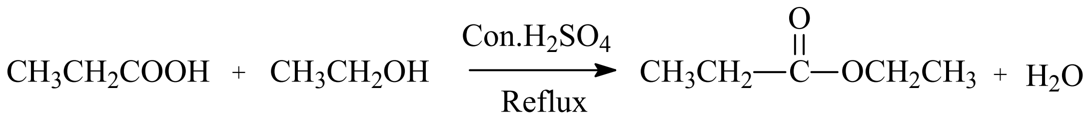
$$^{3}\,\text{ROH} + PI_3 \longrightarrow {}^{3}\,\text{RI} + H_3PO_3$$

The mechanism is very similar to the thionyl chloride reaction. The alcohol acts as the nucleophile and displaces a halide ion from the PX_3 or the PX_5.

$$\text{R-OH} + PCl_5 \longrightarrow \text{R-Cl} + HCl + POCl_3$$

3. Esterification: Alcohol reacts with carboxylic acids, acid chlorides and acid anhydrides to form esters. The reaction with carboxylic acid and acid anhydride is reversible, and therefore, water is removed as soon as it is formed. Esterification takes place much faster in the presence of a catalyst such as conc. H_2SO_4.

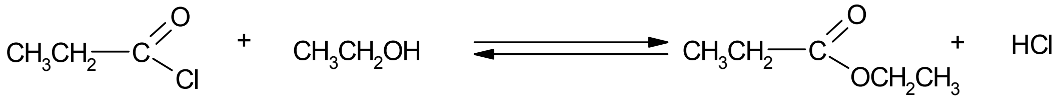
Example :

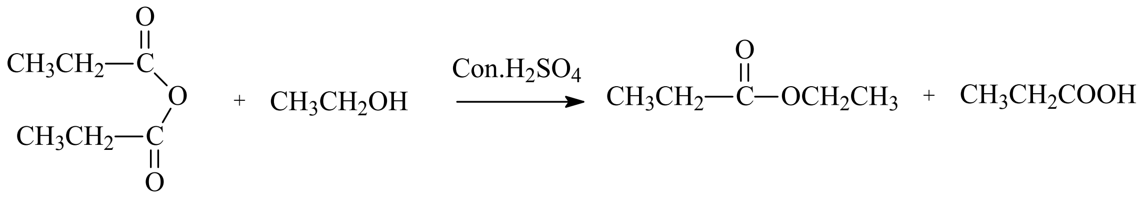


$$CH_3CH_2COOH + CH_3CH_2OH \xrightarrow[\text{Reflux}]{\text{Con.}H_2SO_4} CH_3CH_2-\overset{O}{\overset{||}{C}}-OCH_2CH_3 + H_2O$$

Alcohols can also react with acid chlorides and acid anhydrides to form esters. The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation.

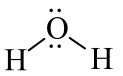
Example:

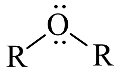




8.6 ETHERS

Ethers are compounds that containing single oxygen atom bonded to two alkyl groups, two aryl groups or one aryl and one alkyl group. The general formula, of ethers is $C_nH_{2n+2}O$. They are isomeric with the aliphatic monohydric alcohols with the general formula $C_nH_{2n+1}OH$. Thus, ethers can be represented as R -O –R', where R and R' may be alkyl or aryl groups. When the two substituent groups (R and R'are identical, then the ether is called a simple or symmetrical ether, otherwise if these two groups are different, then the ether is known as a mixed or unsymmetrical ether. Diethyl ether, $C_2H_5OC_2H_5$, is symmetrical ether whereas $C_2H_5OCH_3$and $C_2H_5OC_6H_5$ are unsymmetrical ethers. The symmetrical diethyl ether is commonly also referred simply as *ether* because of its wide use as a solvent for reactions and extraction of organic compounds. It was also used as an anaesthetic for over hundred years. Ethers are distinguished from other organic compounds because they lack a continuous chain of carbons.





Ethers are thought of as alkyl analogues of water.

Substitution of the hydroxyl hydrogens of alcohols by hydrocarbon groups gives compounds known as ethers. These compounds may be classified further as open-chain, cyclic, saturated, unsaturated, and aromatic, and so on.The oxygen atom of the ether can also be part of a ring, in which case the ether is known as cyclic ether or also called epoxide. Epoxides are formed when an oxygen atom is linked to carbon atoms of a carbon chain forming a three membered ring. Epoxides are heterocyclic compounds containing oxygen atom as a hetero atom. Epoxides have considerable ring strain. Epoxides are special kinds of ethers. These compounds are special because they have a three member ring that contains an oxygen atom. They are far more reactive than typical ethers. Tetrahydrofuran is one such cyclic ether which is used as a solvent. Ethers are commonly used as solvents for organic reactions.

$CH_3—O—CH_3$

symmetric ether

$CH_3—O—CH_3CH_3$

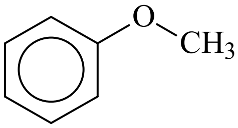
asymmetric ether

$CH_3CH_2—O—CH_3CH_3$

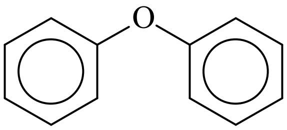
symmetric ether

$CH_3CH_2—O—CH_2—CH{=}CH_2$

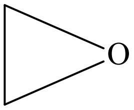
unsaturated ether



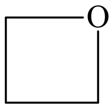
aryalkyl ether



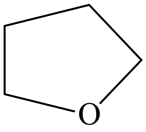
aryl ether



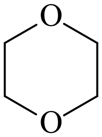
ethylene oxide



trihydrofuran



tetrahydrofuran



dioxane

Cyclic ethers

8.6.1 Nomenclature of ethers:

There are two methods of naming ethers. The first is the common method and is most useful with simple ethers. Common names “trivial names” of ethers add the suffix ether after naming the two groups on either side of the oxygen. The alkyl groups are listed in alphabetic order. There are spaces between the names of the alkyl groups and the word ether. If the two groups are the same, the prefix “di-” is used, although sometimes this is simply dropped (“ethyl ether”).

e.g. $H_3COCH_2CH_3$ Ethylmethyl ether

$C_2H_5 - O - C_2H_5$ Diethyl ether

$C_6H_5 - O - C_6H_5$ Diphenyl ether

$C_2H_5 - O - C_6H_5$ Ethyl phenyl ether.

In IUPAC nomenclature, the larger alkyl (or aryl) group is used as the root name as the *alkane.* Treat the oxygen and the remaining carbons as a side chain and the smaller alkyl group is named as an *alkoxy* (—OR = alkoxy group) substituent on this alkane. The *-yl* ending of alkyl substituents is replaced by *–oxy.*

—CH_3 methyl —OCH_3 methoxy

—CH_2CH_3 ethyl —OCH_2CH_3 ethoxy

For example, in ethyl methyl ether having ethyl and methyl groups, the ethyl group is larger than methyl group and hence this ether is treated as the ethane derivative.

$CH_3OCH_2CH_3$

Ethylmethyl ether

The remaining portion, *i.e.*, —OCH_3 part in this case, is called the methoxy substituent. Hence, the above ether is called methoxyethane. The numbering of the parent chain is done so that the carbon atom linked to the -O-atom gets the lowest number. Some more examples of IUPAC names of ethers are given below:

Examples:

$CH_3—O—CH_2CH_3$

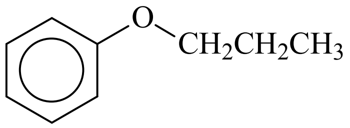
ethylmethyl ether

methoxy ethane

$CH_3CH_2—O—CH_2CH_2CH_2CH_3$

butylethyl ether

1 ethoxy butane



phenylpropyl ether

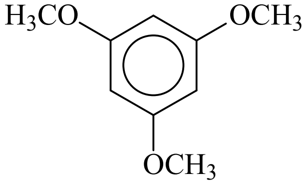
1 phenoxypropane

$CH_3—O—CH_2CH_2CH_3$

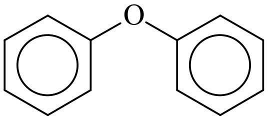
1 methoxypropane

$CH_2=CH—O—CH_2CH_3$

ethoxyethene



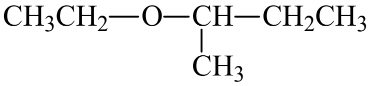
1, 3, 5 trimethoxybenzene



diphenyl ether

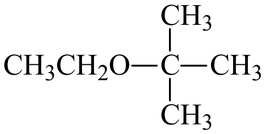
$ClCH_2—O—CH_2Cl$

bis(chloromethyl)ether



$CH_3CH_2—O—\underset{CH_3}{CH}—CH_2CH_3$

2 ethoxybutane

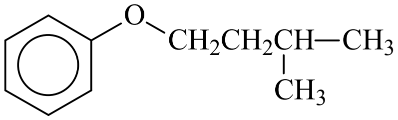


$CH_3CH_2O—\overset{CH_3}{\underset{CH_3}{C}}—CH_3$

2 ethoxy 2 methylpropane

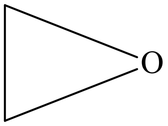
$CH_3O—CH_2CH_2—OCH_3$

1, 2 dimethoxyethane



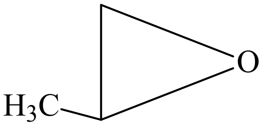
3 methylbutoxybenzene

Cyclic ethers generally termed as epoxides in IUPAC system. Epoxide contains a 3-membered ring between oxygen and two carbons ethers.



epxyethane

ethylene oxide



propylene oxide

1,2 epoxypropane

8.6.2 Methods of preparation:

There are different methods for the synthesis of ethers some of which are being described as follow:

1. By Dehydration of alcohols: (a) The formation of reaction product, alkene or ether depends on the reaction conditions. This method involves heating of excess of primary alcohol with concentrated sulphuric acid and the temperature has to be maintained around 413^0 K to get symmetrical ether. If alcohol is not used in excess or the temperature is higher, the alcohol will preferably undergo dehydration to yield alkene.

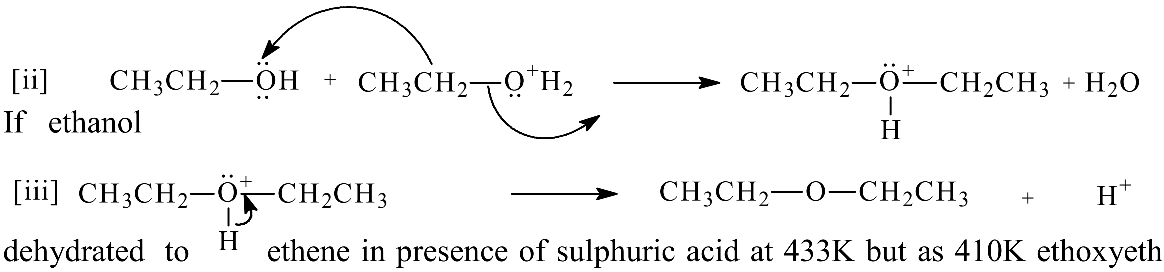
$$ROH \xrightarrow[heat]{H_2SO_4} R—O—R + H_2O$$

$$CH_3CH_2OH \xrightarrow[140^{o}C]{H_2SO_4} CH_3CH_2—O—CH_2CH_3$$

$$CH_3CH_2OH \xrightarrow[160^{o}\ C]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

Mechanism:

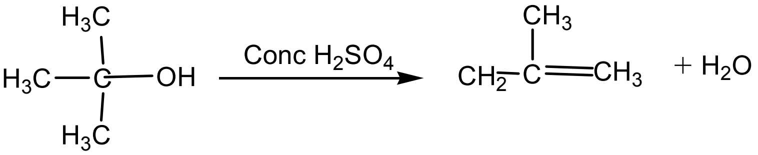
$$[i]\ CH_3CH_2—\ddot{\underset{..}{O}}H + H^+ \longrightarrow CH_3CH_2—\underset{..}{O}^+H_2$$



$$[ii]\ CH_3CH_2—\ddot{\underset{..}{O}}H + CH_3CH_2—\underset{..}{O}^+H_2 \longrightarrow CH_3CH_2—\underset{\displaystyle H}{\overset{..}{O}^+}—CH_2CH_3 + H_2O$$

$$[iii]\ CH_3CH_2—\underset{\displaystyle H}{\overset{..}{O}^+}—CH_2CH_3 \longrightarrow CH_3CH_2—O—CH_2CH_3 + H^+$$

If ethanol is dehydrated to ethene in presence of sulphuric acid at 433K but as 410K ethoxyethane is the main product. The dehydration of secondary and tertiary alcohols to get corresponding ethers is unsuccessful as alkenes are formed easily in these reactions.



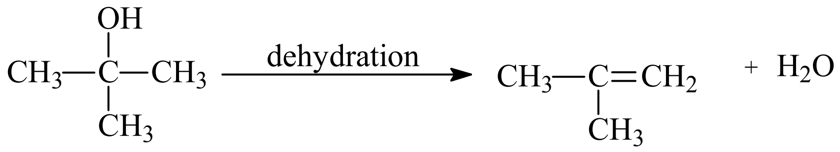
t -butyl alcohol Iso-butylene

(b)On passing alcohol vapours over heated alumina at 250°C, dehydration of alcohols leads to the formation of ethers.

$$\underset{vapour}{2\ ROH} \xrightarrow[250^{o}\ C]{Al_2O_3} R—O—R + H_2O$$

The secondary and tertiary alcohols on dehydration lead to the formation of alkene as main product.

$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow{\text{dehydration}} CH_3{=}CH-CH_3 + H_2O$$



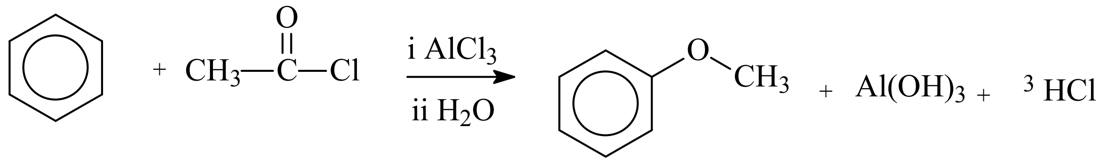
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow{\text{dehydration}} CH_3-\underset{\underset{CH_3}{|}}{C}{=}CH_2 + H_2O$$

2. By alkyl halides: Alkyl halides on heating with dry Ag_2O (in ether) give ethers.

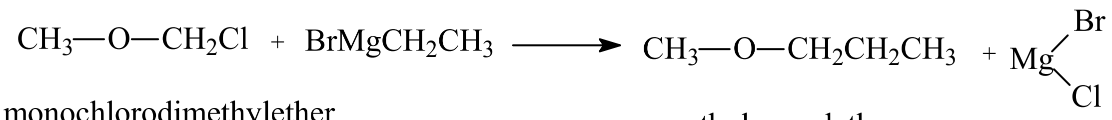
$$R-X + Ag_2O + R-X \xrightarrow{\text{heat}} R-O-R + 2\,AgBr$$

$$CH_3CH_2Br + Ag_2O + CH_3CH_2Br \xrightarrow{\text{heat}} CH_3CH_2-O-CH_2CH_3 + 2\,AgBr$$

4. From acyl chlorides: Aromatic ketones are formed from acyl chloride by Friedel Craft reaction. This reaction requires excess $AlCl_3$ due to tendency of complexation with carbonyl group and water to hydrolyze the Al salts



5. From Grignard reagent: This is a good method for the preparation of higher ethjer from lower members, in which a lower halogenated ethers when heated with Grignard reacent we get higher ethers.



$$CH_3-O-CH_2Cl + BrMgCH_2CH_3 \longrightarrow CH_3-O-CH_2CH_2CH_3 + Mg\genfrac{}{}{0pt}{}{Br}{Cl}$$

monochlorodimethylether

methylpropylether

8.6.3 Physical properties:

a) Physical state: Dimethylether and ethyl methyl ether are gases at ordinary temperature. The other lower homologes are colourless, pleasant smelling, volatile liquids with typical ether smell.

b) Boiling points: The C - O bonds in ether are polar and thus ethers have a net dipole moment. The weak polarity of ethers does not appreciably affect their boiling points which are comparable to those of the alkenes of comparable molecular mass. Ethers have much lower boiling points as compared to isomeric alcohols. This is because alcohols molecules are associated by hydrogen bonds while ether molecules are not.

Boiling point order: alcohols > ethers > alkanes

$CH_3CH_2—O—CH_2CH_3$

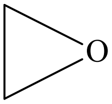
diethylether
ethoxyethane

b. p 35^{o}C

$CH_3—O—CH=CH_2$

methoxy ethene
methyl ethenyl ether

b. p 12^{o}C

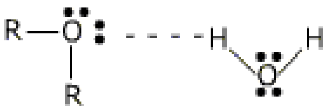


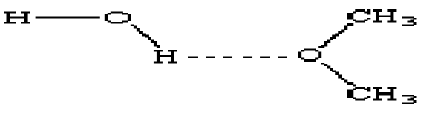
epoxide

b. p 11^{o}C

c) Solubility: Ethers are slightly polar, and can hydrogen-bond to water, although very weakly, through the oxygen atom. Because ethers have no O-H bonds, they cannot participate in hydrogen bonding to the same extent that alcohols do. Nevertheless, the oxygen in the ether can form a hydrogen bond to the hydrogen in water. The presence of only single site on the ether for a limited kind of hydrogen bonding interaction means that ethers generally have significantly smaller solubilities in water than do alcohols. Still they have higher solubilities than any hydrocarbon. These are extremely volatile and highly flammable (easily oxidized in air).

Ethers containing upto three carbon atoms are soluble in water, due to their hydrogen bond formation with water molecules.





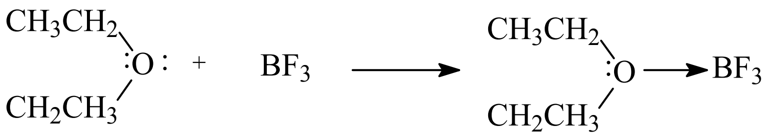
The solubility decreases with increase in the number of carbon atoms. The relative increase in the hydrocarbon portion of the molecule decreases the tendency of H-bond formation. Ethers are appreciably soluble in organic solvents like alcohol, benzene, acetone etc.

Water solubility order: alcohols > ethers > alkanes

8.6.4 Chemical properties:

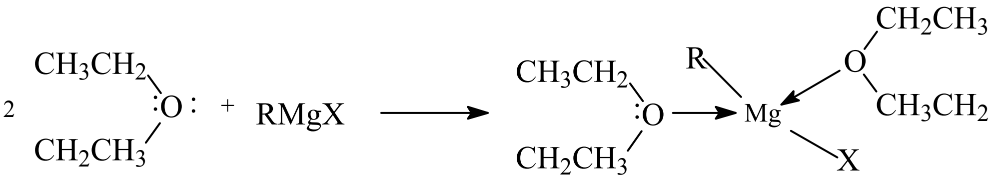
Ethers have geometry similar to water and alcohols. The oxygen atom is sp^3 hybridised. Since the carbon-oxygen bond is polar and the molecule has a bent structure, there is a net dipole moment and the ether molecule is polar is nature. Ethers, thus, act as polar solvents. Ethers are quite stable compounds. These are not easily attacked by alkalies; dilute mineral acids, active metals, reducing agents or oxidising agents under ordinary conditions.

1. Reaction with acids: Being Lewis bases, ethers form complexes with Lewis acids such as BF_3, $AlCl_3$, $FeCl_3$, etc. These complexes are called etherates.



boron trifluoride etherate (complex)

Similarly, diethyl ether reacts with Grignard reagent forming Grignard reagent etherate.



Grignard reagent eterate

Due to the formation of the etherate, Grignard reagents dissolve in ether. That is why Grignard reagents are usually prepared in ethers. However, they cannot be prepared in benzene, because benzene has no lone pair of electrons and therefore, cannot form complexes with them.

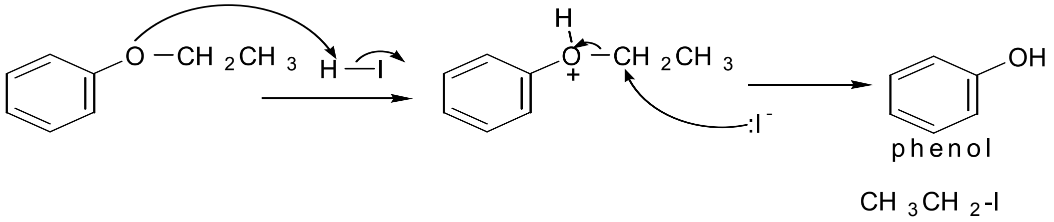
2. Action of hydroiodic acid: Following reactions takes place when ethers are treated with haloacids.

(a) With cold HI

$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + HI \longrightarrow \underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(b) With hot HI

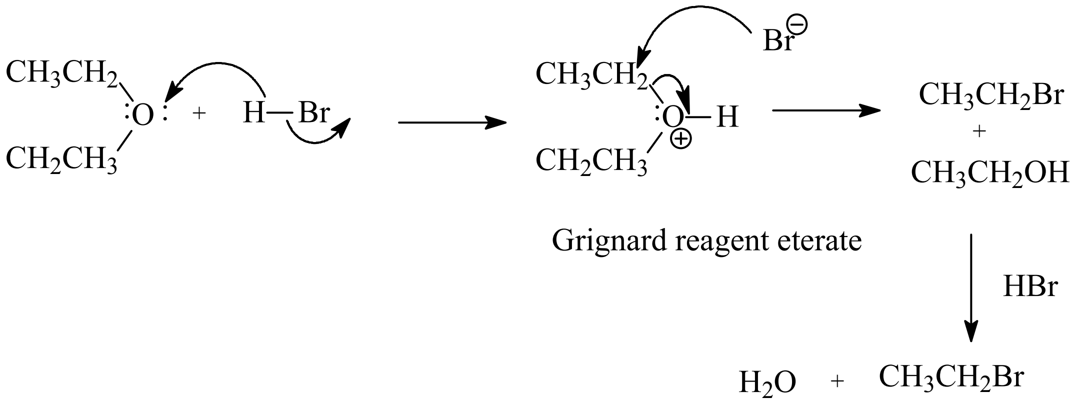
$$R – O – R' + 2HI \longrightarrow RI + R'I + H_2O$$



Phenyl ethers are slightly different, and cleave to give alkyl halides and phenols. The reaction stops at the phenol stage since the sp^2 carbon of the C-O bond does not allow the required S_N1 or S_N2 reactions to generate the second molecule of aryl halide.

3. Reaction wtih HBr:

Since the oxygen atom of ethers contains lone pairs of electrons, they can accept a proton from the acids. Thus, ethers are basic in nature. Ethers are stable to bases, but acidic conditions leads to the protonation of the ether oxygen, which then can undergo substitution reactions.



4. Dehydration: Upon dehydration at elevated temperature ethers provide alkenes

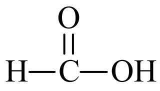
$$C_2H_5OC_2H_5 \xrightarrow[300^o]{Al_2O_3} 2CH = CH_2 + H_2O$$

8.7 ALDEHYDE

An aldehyde alkanals are an important class of an organic compounds containing a functional group with the structure −CHO, consisting of a carbonyl center (a carbon double-bonded to oxygen) with the carbon atom also bonded to hydrogen and to an alkyl/aryal group(s). The group—without alkyl/aryl moeity, also known as the formyl group. Aldehydes are common in organic chemistry. Industrially aldehydes are produced in lagre scale as starting material for synthesis of other important chemicals.viz HCHO is produced more than 1.4 ,million tons/uear for the preparation ofresin .Traces of many aldehydes are found in essential oils (terpenoids) and often contribute to their favorable odors, e.g. cinnamaldehyde, cilantro, and vanillin. Possibly because of the high reactivity of the formyl group, aldehydes are not common in several of the natural building blocks: amino acids, nucleic acids, lipids. Most sugars, however, are derivatives of aldehydes. These aldoses exist as hemiacetals, a sort of masked form of the parent aldehyde. For example, in aqueous solution only a tiny fraction of glucose exists as the aldehyde.

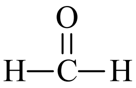
8.7.1 Nomenclature of aldehyde:

Common name for aldehydes are obtained from the names of the corresponding carboxyllic acids.



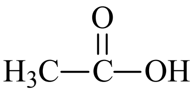
$H{-}\overset{O}{\overset{\|}{C}}{-}OH$

formic acid



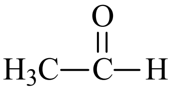
$H{-}\overset{O}{\overset{\|}{C}}{-}H$

acetaldehyde



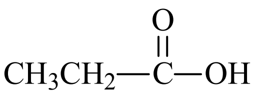
$H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH$

acetic acid



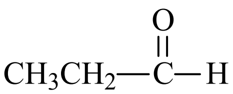
$H_3C{-}\overset{O}{\overset{\|}{C}}{-}H$

formaldehyde



$CH_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}OH$

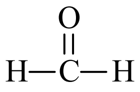
propionic acid



$CH_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}H$

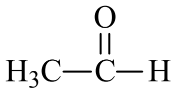
propionaldehyde

IUPAC names for aldehydes are obtained by replacing the ending –e of the corresponding alkane with –al-. Aldehyde functional group is always terminal in chain. When other substituents are present, the carbonyl carbon is assigned number 1.



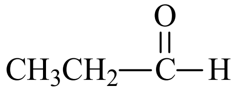
$H-\overset{\overset{O}{||}}{C}-H$

methanal



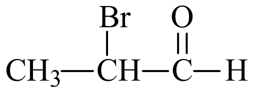
$H_3C-\overset{\overset{O}{||}}{C}-H$

ethanal



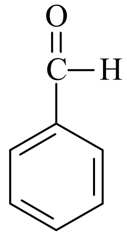
$CH_3CH_2-\overset{\overset{O}{||}}{C}-H$

propanal



$CH_3-\overset{\overset{Br}{|}}{C}H-\overset{\overset{O}{||}}{C}-H$

2–bromopropanal

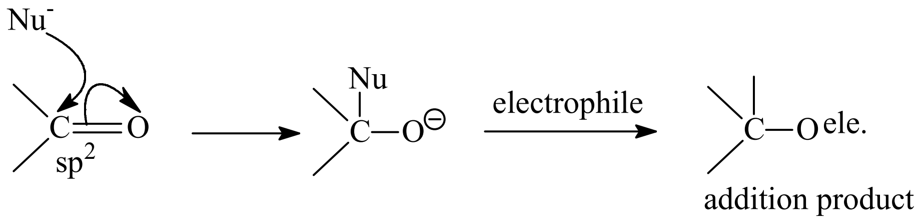


benzaldehyde

The electronegativity of carbon and oxygen is 2.5 and 3.5 respectively.

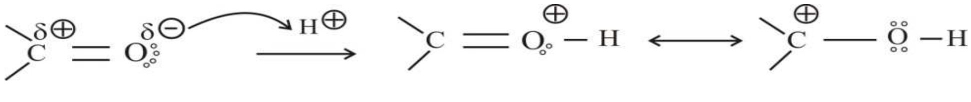
Bond energy of C = O bond is 720 kjmol^{-1}, Bond length of C = O bond is 1.21 A^{0}.

Carbonyl group C = O double bond is shorter then C – O single bond and stronger. C = O bond is polarized and carbon atom has some degree of positive charge and this charge attracts negatively charged nucleophiles and supports nucleophillic addition reaction.

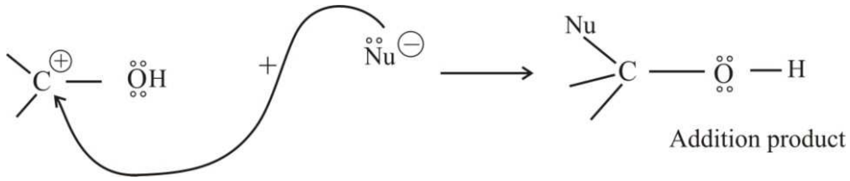


Nucleophillic addition reactions of Aldehydes may be catalysed by acids or bases.

Acid catalysis - Electrophillic protonation Addition :



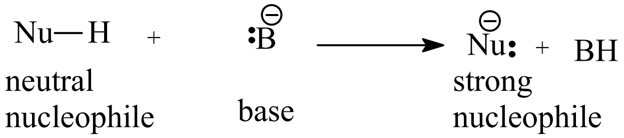
Hydrogen ion of acid attacks negatively charged carbonyl oxygen to give protonated carbonyl group. Protonated carbonyl which is resonance stabilized.

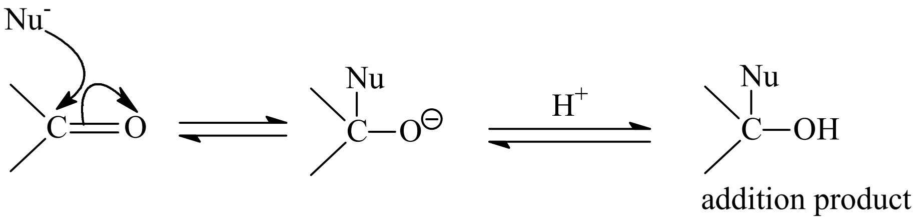


The nucleophile attacks the protonated carbonyl group to form the addition product.

Base catalysis – nucleophillic addition – protonation

Bases convert weak nucleophile to a strong one by deprotonation.





So, in carbonyl carbon two areas of reactivity, i.e. Lewis basic oxygen and electrophillic carbonyl carbon lead to addition of carbonyl π bond.

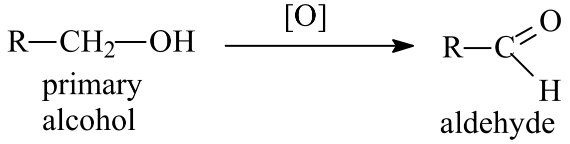
α-hydrogen :- A carbon next to the carbonyl group is called α- carbon and the hydrogen attached with it is referred to as an α-hydrogen. α-hydrogens of carbonyl carbon are acidic in nature with some pK_a values. Abstraction of α hydrogen by a nase (B^-) results in the formation of anion (enolate ion) which is reasonance stabilized by delocalisation of charge onto electronegative oxygen.

α- carbon of the enolate ion is an ambident ion. It can act as nucleophile and attack at electrophillic carbonyl carbon of other carbonyl group containing molecules and leads to condensation. Enolate ion can attach an alkyl group to the reactive carbon and it is called **C-alkylation.** Alkylation at oxygen is uncommon but protonation leads to **alkenol**.

8.7.2 Preparation of aldehydes

There are several reactions which can be used for the synthesis of aldehydes some of them are as follow:-

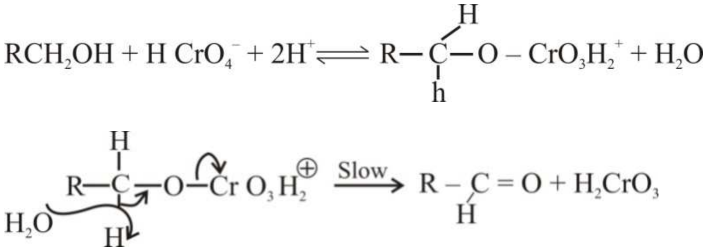
1. ***Oxidation of alcohols***: Oxidation of Primary Alcohols under controlled condition gives aldehyde.



Oxidising agents used are acidified K2Cr2O7 solution, alkaline $KMnO_4$, chromic acid $H_2 Cr_2O_7$, pyridine chlorochromate (PCC) $C_5H_6NCaO_3Cl$ in (DCM solvent) CH_2Cl_2.

Mechanism: Mechanism of oxidation of alcohol by dichromate is following:

$$Cr_2O_7^{2-} - H_2O \rightleftharpoons 2HCrO_4^-$$

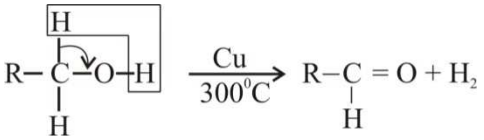


$$RCH_2OH + HCrO_4^- + 2H^+ \rightleftharpoons R-\overset{H}{\underset{h}{C}}-O-CrO_3H_2^+ + H_2O$$

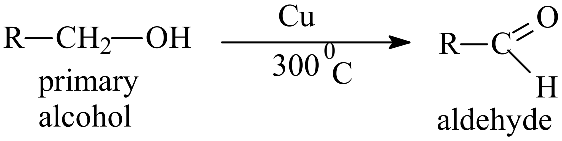
$$H_2O + R-\overset{H}{\underset{H}{C}}-O-CrO_3H_2^{\oplus} \xrightarrow{Slow} R-\underset{H}{C}=O + H_2CrO_3$$

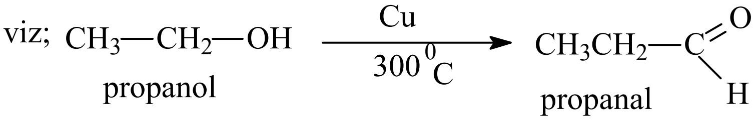
Similar ester intermediate is formed in oxidation with permanganate.

2. ***Catalytic dehydrogenation of alcohols***: - Aldehydes may be prepared by dehydrogenation of primary alcohol by passing vapours over copper catalyst at about 300^0C of alcohol.

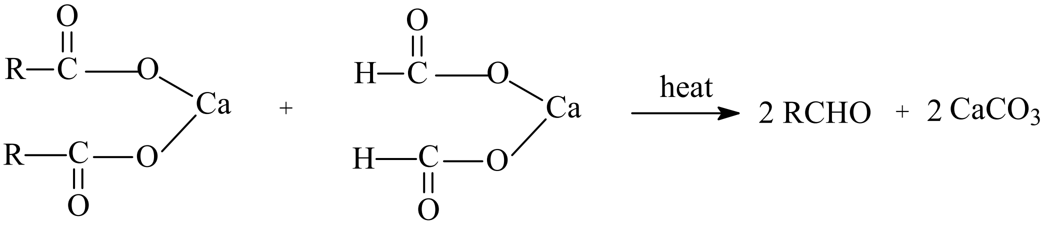


$$R-\overset{H}{\underset{H}{C}}-O-H \xrightarrow[300^0C]{Cu} R-\underset{H}{C}=O + H_2$$





3. By heating a mixture of the calcium salts of formic acid and any one of its homologue

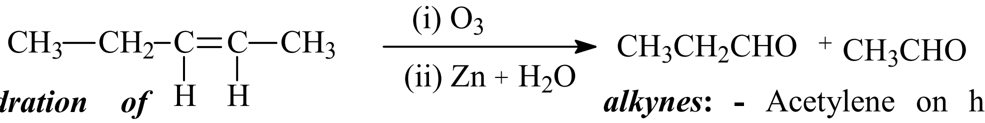


4. By passing a mixture of vapours of formic acid and any one of its homologues over manganous oxide a catalyst at 300^{0}C.

$$RCOOH + HCOOH \xrightarrow{MnO} RCHO + CO_2 + H_2O$$

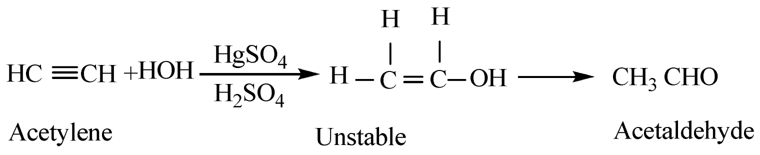
$$\text{viz; } CH_3COOH + HCOOH \xrightarrow{MnO} CH_3CH_2CHO + CO_2 + H_2O$$

5. Oxidation of alkenes (ozonolysis):- Oxidation of alkene viz;2-pentene with ozone gives ozonides which are often explosive in dry state and they are decomposed with Zn + H_2O to give carbonyl compounds.



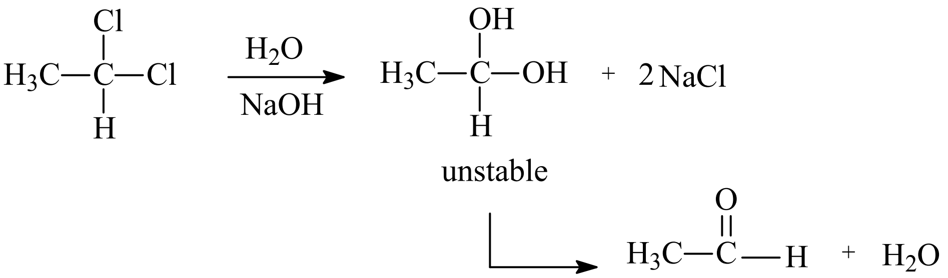
$$\underset{\text{2-pentene}}{CH_3—CH_2—\underset{H}{C}=\underset{H}{C}—CH_3} \xrightarrow[\text{(ii) Zn + } H_2O]{\text{(i) } O_3} CH_3CH_2CHO + CH_3CHO$$

***6. Hydration of alkynes*: -** Acetylene on hydration by passing into hot dilute H_2SO_4 in the presence of $HgSO_4$ as catalyst is converted into acetaldehyde.



$$HC\equiv CH + HOH \xrightarrow[H_2SO_4]{HgSO_4} H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-OH \longrightarrow CH_3CHO$$

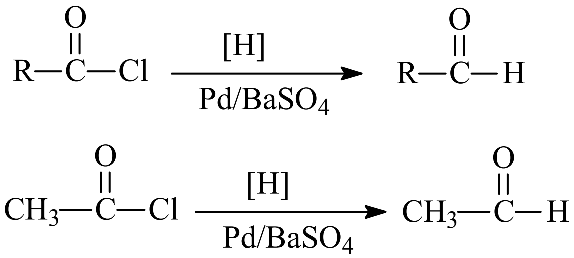
7. ***Alkaline hydrolysis of gem dihalides***: - The germinal dihalides (two halogens atoms are attached to the terminal carbon atom) gives Aldelyde



$$H_3C-\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}-Cl \xrightarrow[NaOH]{H_2O} H_3C-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-OH + 2NaCl$$

$$\longrightarrow H_3C-\overset{\overset{O}{||}}{C}-H + H_2O$$

8. ***Rosenmund's Reduction:* -** This is one of the most common method for the synthesis of aldehydes. In this method reduction of an acid chloride with hydrogen in boiling xylene using a poisoned palladium catalyst supported on $BaSO_4$ is used.



$$R-\overset{\overset{O}{||}}{C}-Cl \xrightarrow[Pd/BaSO_4]{[H]} R-\overset{\overset{O}{||}}{C}-H$$

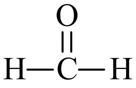
$$CH_3-\overset{\overset{O}{||}}{C}-Cl \xrightarrow[Pd/BaSO_4]{[H]} CH_3-\overset{\overset{O}{||}}{C}-H$$

Here $BaSO_4$ prevents further reduction of aldehyde to alcohol as it acts as a poison to Pd catalyst. So small amount of quinoline and sulphur is added to deactivate catalyst partially. Lithium tri-t.butoxy aluminum hydride (LTBA) can also be used as catalyst.

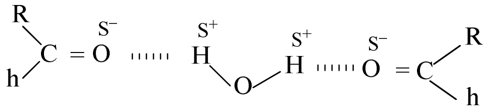
8.7.3 Physical properties of aldehydes

1. In aldehyde the first member HCHO is gaseous at room temperature. Acetaldehyde is liquid in nature with b.p. 20^0C. Lower aldehydes are colourless liquids.Benzaldehyde is liquid with characteristic smell of bitter almonds.

2. Lower members of aldehydes possess unpleasant smell.
3. Carbonyl group compounds are polar in nature due to dipole - dipole interactions of partial negative charge of carbonyl oxygen of one molecule and partial positive charge on the carbonyl carbon of another molecule. So boiling points of aldehydes and ketones are higher than those of alkanes which have comparable molecular weights. However these dipole - dipole interactions are weaker than hydrogen bonding interactions, hence aldehydes and ketones due to lack of intermolecular hydrogen bonding have low boiling points as compared to alcohols of comparable molecular weights.

	CH_3CH_3	 $H-\overset{\overset{O}{\|\|}}{C}-H$	CH_3OH
	ethane	methanal formaldehyde	methanol
Mol. wt.	30	30	32
b.p.	-89^0C	-21^0C	$64{\cdot}5^0C$

4. As aldehydes and ketones can form hydrogen bonds with water so lower aldehydes and ketones are soluble in water.



However solubility decreases as the hydrocarbon part of molecule increases. The lower aldehydes and ketones are soluble in organic solvents such as benzene, ether and CCl_4. Carbonyl compound also form hydrates with water i.e. corresponding germinal diols.

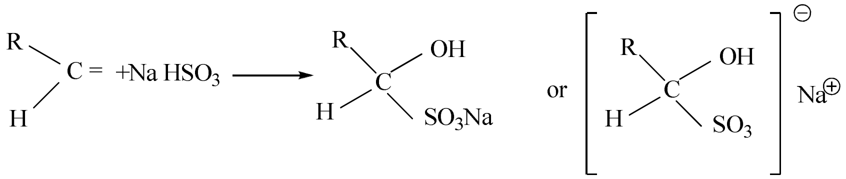
8.7.4 Chemical properties of aldehydes:

The slightly positive carbon atom in the carbonyl group can be attacked by nucleophiles. A nucleophile is a negatively charged ion (for example, a cyanide ion, CN^-), or a slightly negatively charged part of a molecule. Some of the important reactions of adlehydes are being given below

1. Addition reactions

During the reaction, the carbon-oxygen double bond gets broken. The net effect of all this is that the carbonyl group undergoes addition reactions.

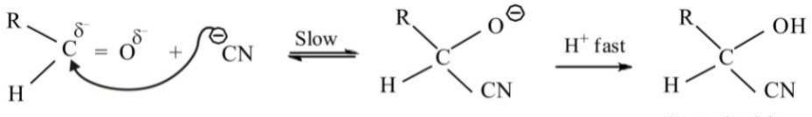
(1) Addition of Sodium Bisulphite – Aldehydes add on sodium hydrogen sulphite to form bisulphite compounds.



Thus the formed bisuphite compounds are hydroxysulphonic acid salts where sulphur atom is directly attached to the carbon atom. When bisulphate compounds are heated with dilute acid or Na_2CO_3 solution then carbonyl compound is regenerated.

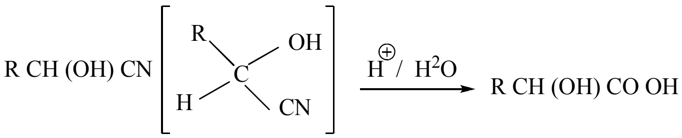
(2) Addition of hydrogen cyanide (HCN) - All Aldehydes add HCN in the presence of base catalyst to form cyanohydrins.

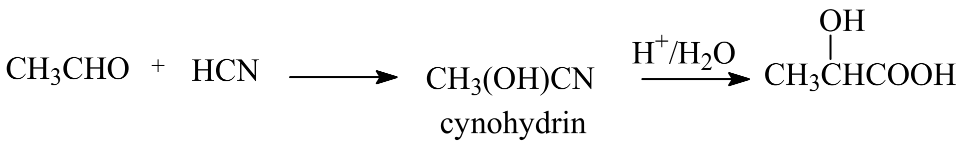
$$HCN + \overset{\ominus}{O}H \longrightarrow H_2O + \overset{\ominus}{C}N$$



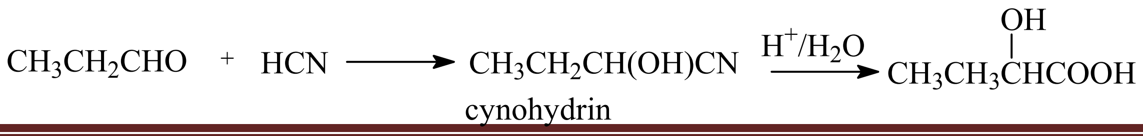
Cyanohydrin

Cyanohydrins can be hydrolysed readily to α hydroxy acids.



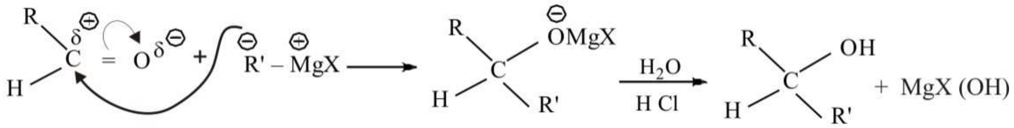


$$CH_3CHO + HCN \longrightarrow \underset{\text{cynohydrin}}{CH_3(OH)CN} \xrightarrow{H^+/H_2O} CH_3\overset{\overset{OH}{|}}{C}HCOOH$$

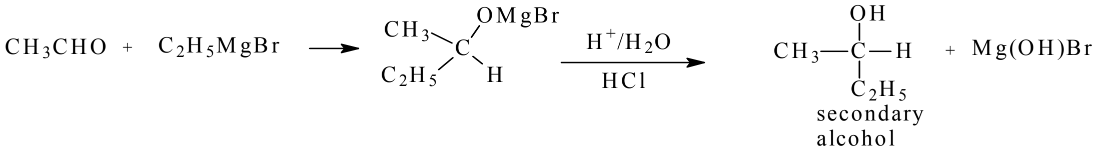


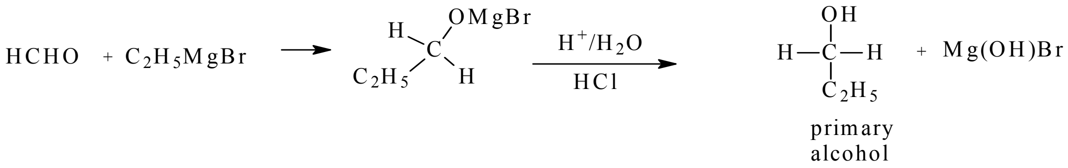
$$CH_3CH_2CHO + HCN \longrightarrow \underset{\text{cynohydrin}}{CH_3CH_2CH(OH)CN} \xrightarrow{H^+/H_2O} CH_3CH_3\overset{\overset{OH}{|}}{C}HCOOH$$

(3) Addition of Grignard Rreagents: Aldehydes react with Grignard reagents to form a complex dilute acids gives alcohol.



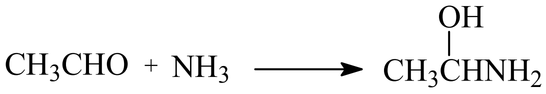
Formaldehyde gives primary alcohol. Other aldehyde gives secondary alcohols.





(4) Addition of ammonia

Aldehydes (except HCHO) react with ammonia in other to give aldehyde ammonia.



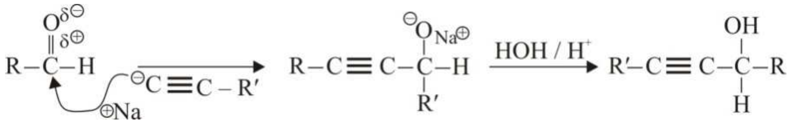
$$CH_3CHO + NH_3 \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HNH_2$$

Formaldehyde on treatment with ammonia gives hexamethylenetetratnine.

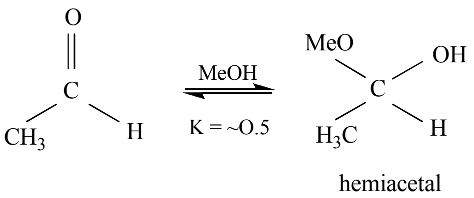
$$6HCHO + 4NH_3 \rightarrow (CH_2)_6\,N_4 + 6H_2O$$

Addition Reactions followed by loss of water

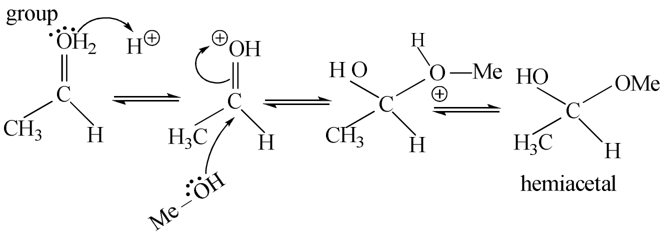
(5) Addition of terminal Alkynes – Sodium salt of terminal alkynes reacts with aldehydes to give alkynol. This reaction is known as Ethinylation.



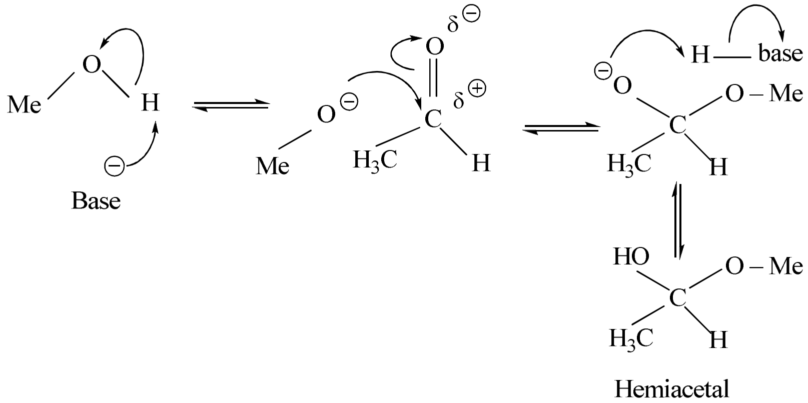
(6) Addition of alcohols – When acetaldehyde is dissolved in methanol it reacts to form hemiacetal which is unstable as compare to parent aldehyde.



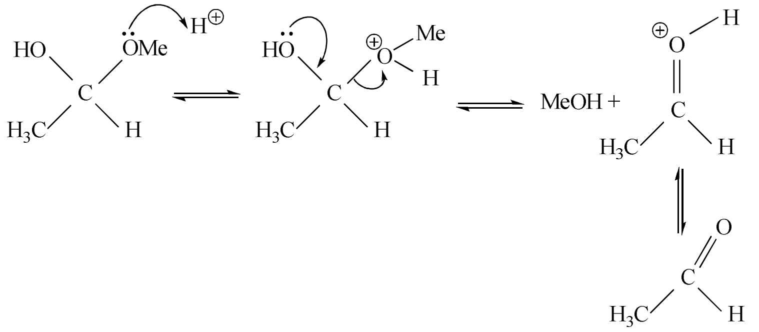
Rate of formation of hemiacetals is greatly increased either by acid or by base. Acid catalysts increase electrophilicity of carbonyl.

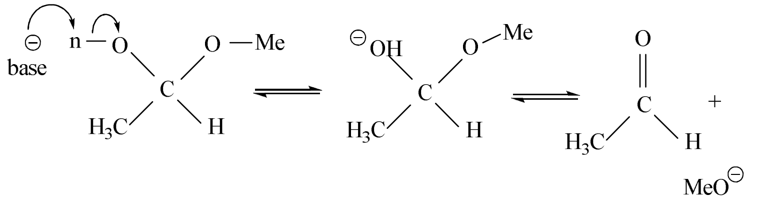


Base catalysts increase nucleophilicity of alcohol by removing the OH proton before it attacks the C = O group.

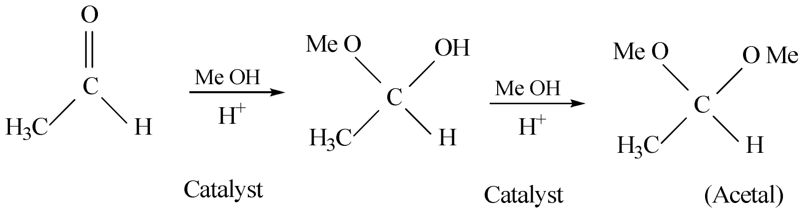


Hemiacetals are unstable. Here acid or base catalyse not only formation of hemiacetals but also decomposition them into aldehyde.

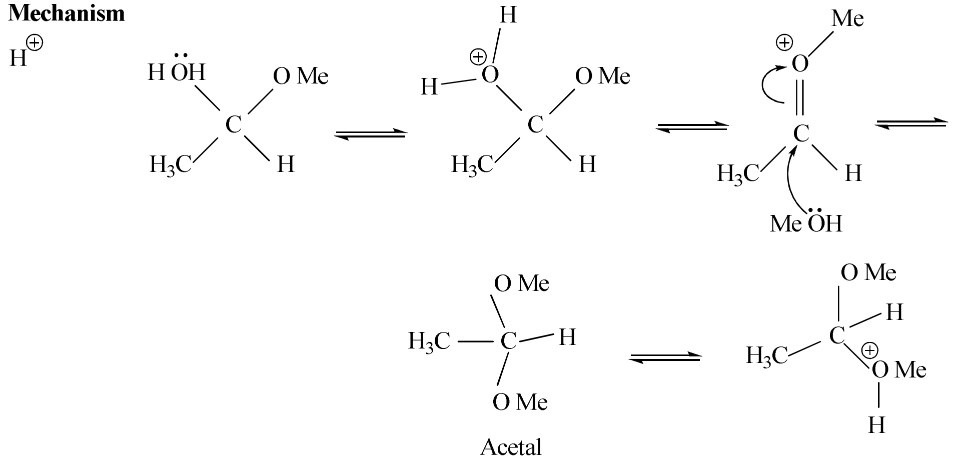




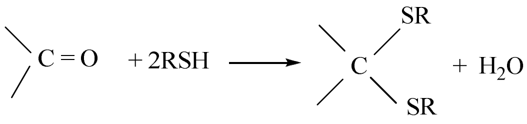
When catalytic acid is added to acetaldelyde-methanol mixture rate of reaction increases and two equivalents of alcohols are added to aldehyde to form new class of compound called acetal.



Mechanism



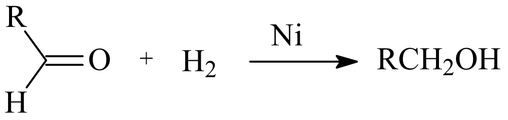
(7) **Addition of mercaptans:** Aldehydes condense with thioalcohols (mercaptans) in the presence of HCl to form mercaptals.



2. Reduction reactions of addehydes

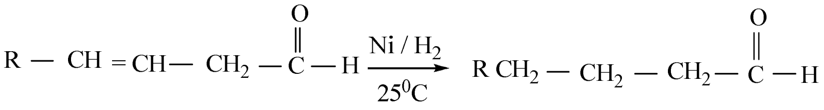
Adlehydes can be reduced to alcohols. In continuation to other reactions as discussed above the reduction reactions are being discyssed as follow.

(1) Aldehydes can be reduced to alcohols by treatment with Hydrogen and Ni or Pt catalyst.

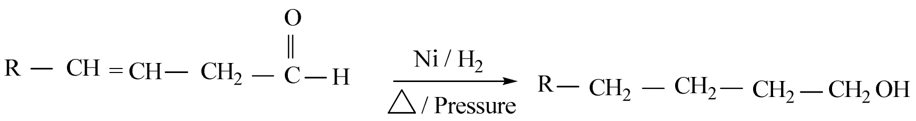


$CH_3CHO + H_2 \xrightarrow{Ni} CH_3CH_2OH$

If both double bond and carbonyl groups are present then either both are hydrogenated or preferentially double bond is hydrogenated leaving carbonyl group intact.

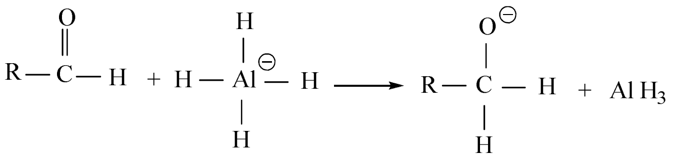


$$R-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[25^0C]{Ni/H_2} RCH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$$



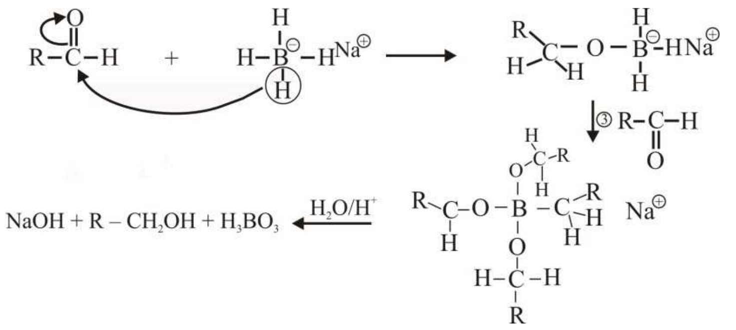
$$R-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\triangle/\text{Pressure}]{Ni/H_2} R-CH_2-CH_2-CH_2-CH_2OH$$

Some metal hydrides as LAH (lithium aluminium hydride) in anlydrous either or THF solvent and $NaBH_4$ (sodium borohydride) in water or alcohol as solvent can be used as reducing agent.

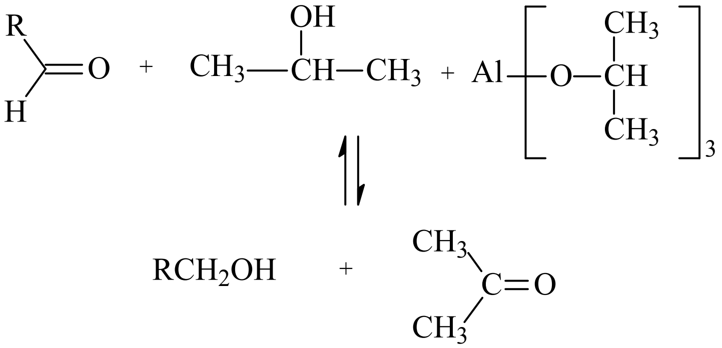


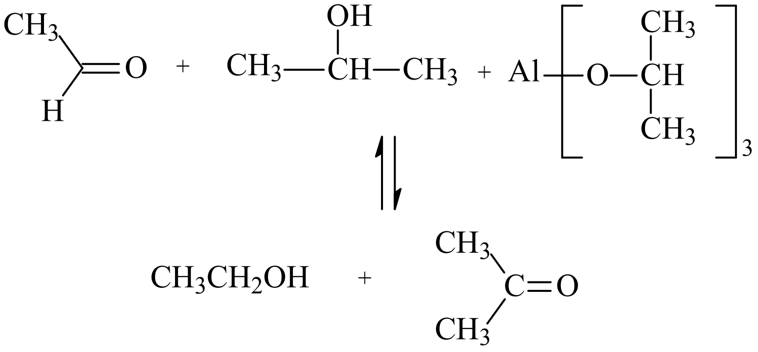
$$R-\overset{O}{\overset{\|}{C}}-H + H-\underset{H}{\overset{H}{Al^{\ominus}}}-H \longrightarrow R-\underset{H}{\overset{O^{\ominus}}{C}}-H + AlH_3$$

Each hydride ion can reduce one carbonyl group.

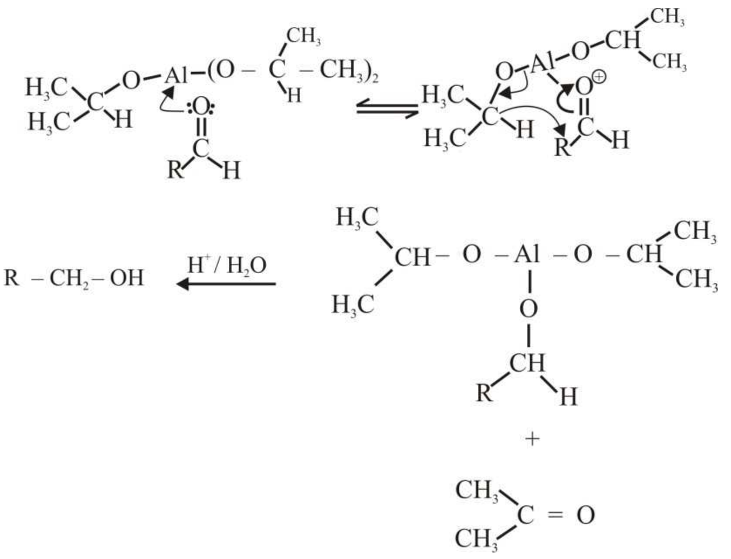


(2) Aldehydes can be reduced to corresponding alcohols by dissolving aldehydes in isopropyl alcohol containing aluminium isopropoxide. Here isopropyl alcohol is converted to acetone. This reaction is known as **Meerwein-Ponndorf-verely (MPV**) reduction.

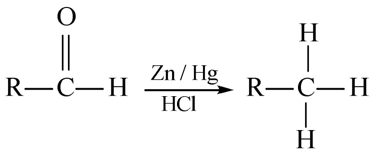




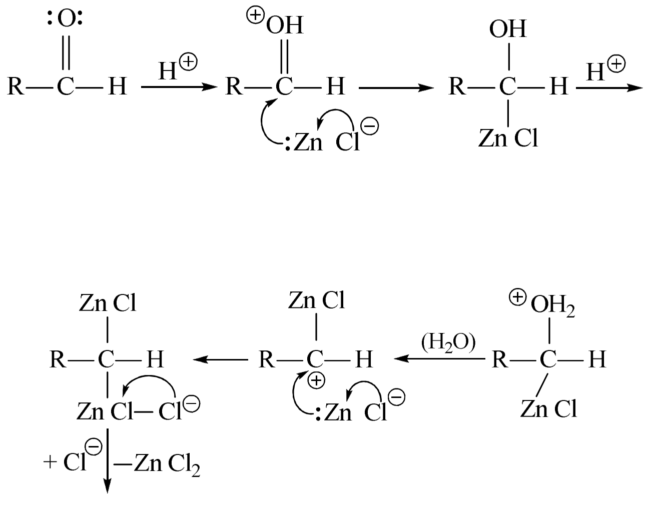
Mechanism:

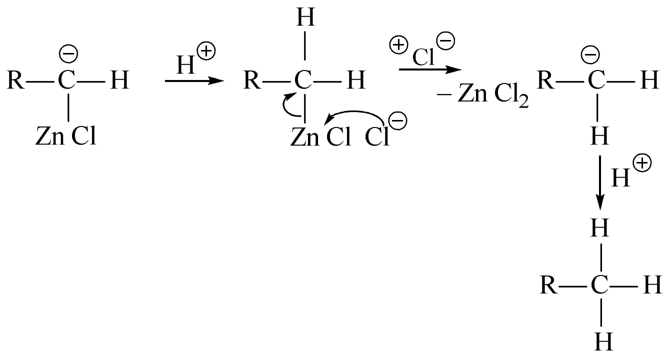


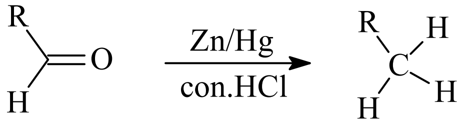
(3) Reduction to hydrocarbon: Carbonyl group of compound is reduced to methylene group by using zinc amalgam and hydrochloric acid.This reaction is called **Clemmensen reduction**.In this reaction carbonyl group is reduced to –CH_2- group. Ketones are more effective than aldehydes in this reduction. The mercury alloyed with the Zn does not participate in the reaction; it serves only to provide aclean active metal surface. Some times alcohols may be used as the solvent in **Clemmensen reduction**



$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow[HCl]{Zn/Hg} R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$





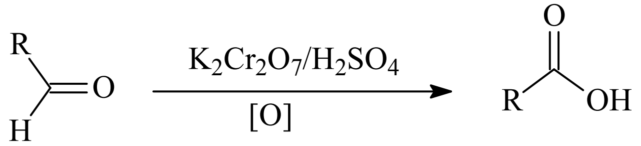


$$CH_3CHO \xrightarrow[\text{con.HCl}]{\text{Zn/Hg}} CH_3CH_2OH$$

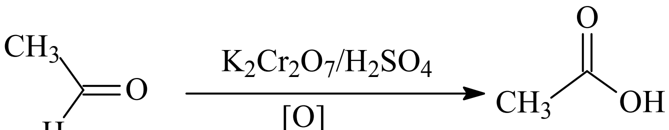
3. Oxidation reactions of addehydes

The aldehydes in presence of oxidizing agent can be oxidized to corresponding carboxylic acids in continuation the reactions are being described as follow.

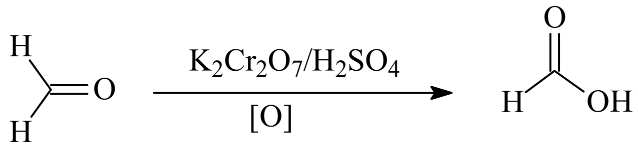
(1) (i) Aldehydes are easily oxidized with $K_2Cr_2O_7$ in Sulphuric acid, or $KMnO_4$.



aldehyde carboxylic acid



acetaldehyde acetic acid

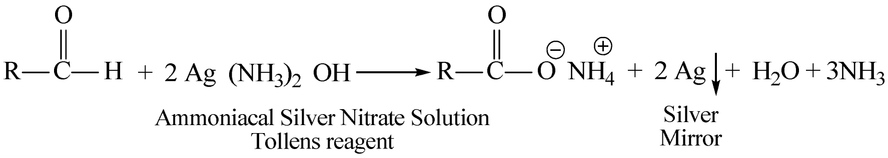


formaldehyde formic acid

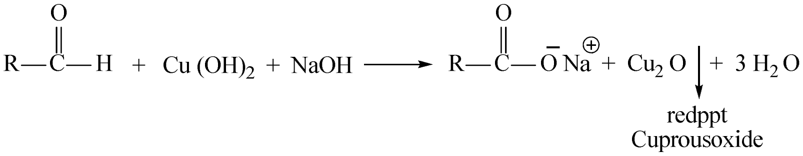
(ii) Aldehydes with methyl or methylene group adjacent to carbonyl group are oxidised to dicarbonyl compounds by Selenium oxide.

$$CH_3CHO + SeO_2 \longrightarrow OHC - CHO + Se + H_2O$$

(iii) Mild oxidizing agents like tollen's reagent [$Ag(NH_3)_2OH$], Fehling's solution i.e. alkaline solution of cupric ion or Benedict's solution i.e. alkaline solution of Cupric ion complexed with citrate ion; oxidize aldehydes.



$$R-\overset{\overset{O}{\|}}{C}-H + 2\,Ag\,(NH_3)_2\,OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}\,\overset{\oplus}{N}H_4 + 2\,Ag\downarrow + H_2O + 3NH_3$$

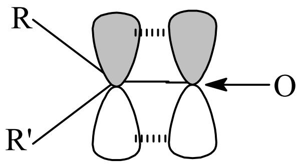


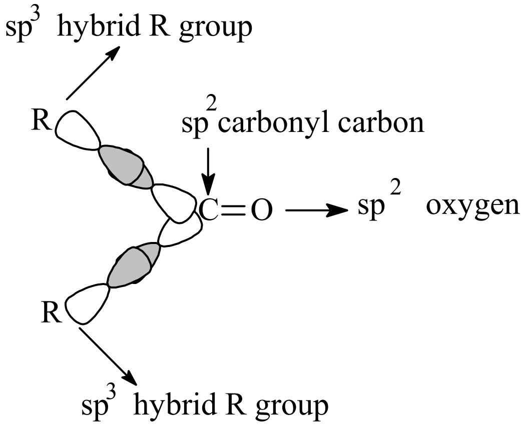
$$R-\overset{\overset{O}{\|}}{C}-H + Cu\,(OH)_2 + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-\bar{O}\,\overset{\oplus}{Na} + Cu_2O\downarrow + 3\,H_2O$$

Benzaldehyde gives positive test with Tollen's reagent but not with Fehling's and Benedict's solution because of + Resonance effect of Benzene ring which makes C-H bond stronger and weak oxidizing agents like Fehling and Benedict solutions could not oxidize aromatic aldehydes.

8.8 KETONES

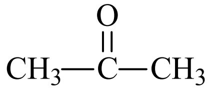
In chemistry, a ketones (alkanone**)** are an organic compound with the structure RC (=O) R', where R and R' can be a variety of carbon-containing substituents. Structurally the ketone carbon is often described as "sp^2 hybridized", a description that includes both their electronic and molecular structure. Ketones are trigonal planar around the ketonic carbon, with C−C−O and C−C−C bond angles of approximately 120° Basic skeletal structure of carbonyl group in ketone is same (Planer) as in aldehydes.





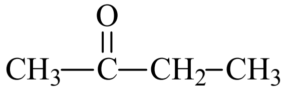
8.8.1 Nomenclature:

Common names of ketones are named on the basis of the alkyl group attached to the carbonyl group. In IUPAC nomenclature ketones are designated by suffix – one. Prefix is the name of hydrocarbon (Alkanones). Here longest hydrocarbon chain containing carbonyl carbon is selected and named it by substituting ‘e’ of Alkane with ‘one’. While numbering the chain lowest number is given to carbonyl carbon. Other substituents are numbered named and placed as prefixes in alphabetic order. If there are two carbonyl groups in a molecule, it is named as Alkanedione.



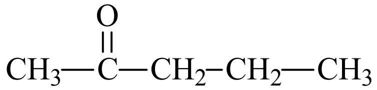
$CH_3-\overset{\overset{O}{||}}{C}-CH_3$

dimethyl ketone acetone



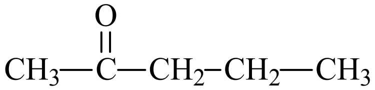
$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3$

ethyl methyl ketone



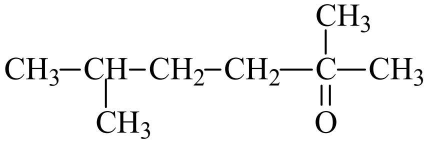
$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_3$

methyl propyl ketone



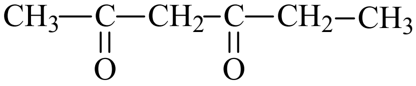
$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_3$

IUPAC 2 pentanone



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{O}{||}}{C}}-CH_3$

5 methy 2 hexanone



$CH_3-\underset{\underset{O}{||}}{C}-CH_2-\underset{\underset{O}{||}}{C}-CH_2-CH_3$

2, 4 hexadienone

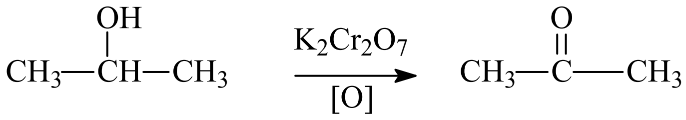
Polarised C = O bond (electronegativity C - 2.5, O - 3.5) makes carbon partially positively charged which attracts negatively charged nucleophiles (Here electrons from HOMO of nucleophile move to LUMO of electrophile i.e. C of C = O group).

Newly formed sigma bond converts trigonal sp^2 hybridized carbon atom of carbonyl group to tetrahedral SP^3 hybridized state attack of nucleophile is at approx. 107^0 to the C = O bond. And any part of molecule that causes steric hindrance to this will reduce rate of addition (nucleophillic addition).Acid and Base catalysis of carbonyl carbon in Nucleophilic addition reactions has been discussed in aldehyde unit.

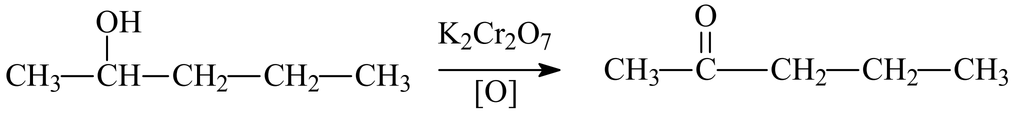
8.8.2 Synthesis of ketones:

Like aldehydes ketones are prepared/synthesized by number of methods some are being discussed as follow.

1. Oxidation of secondary alcohols: - Oxidation of secondary alcohols with $K_2\,Cr_2\,O_7$, MnO_2, or chromic anhydride in acidic medium yield ketones. Firstly sec. alcohol gives ketone with same number of carbon atoms as the original alcohol. However, prolonged treatment with oxidizing agents produce a mixture of acids, containing fewer number of carbon atoms than the original alcohol.



$$CH_3-\overset{OH}{\overset{|}{C}}H-CH_3 \xrightarrow[{[O]}]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

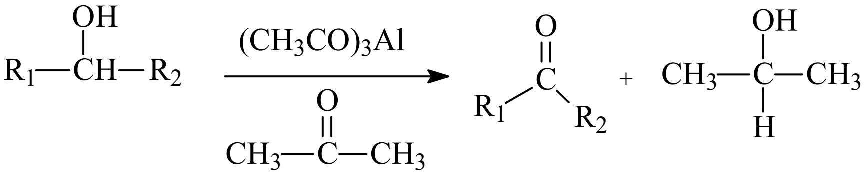


$$CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-CH_2-CH_3 \xrightarrow[{[O]}]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$$

Tertiary alcohols are resistant to oxidation in neutral or alkaline medium but they are oxidized in acidic medium resulting in formation of mixture of acid and ketone and each contains fewer number of carbon atoms than the original alcohol.

Alkaline $KMnO_4$ is also oxidizing agents.

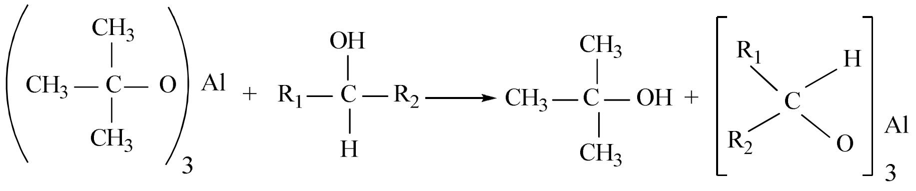
2. By Oppenauer oxidation: - It involves a special reagent alluminium-t-butoxide $[(CH_3)_3CO]_3$ Al, which is refluxed with secondary alcohol and acetone cyclohexanone is used as solvent. Here $[(CH_3)_3CO]_3Al$ acts as oxidizing agent and acetone accepts hydrogen as hydride ion from sec. alcohol.



$$R_1-\overset{OH}{\overset{|}{C}}H-R_2 \xrightarrow[CH_3-\overset{O}{\overset{\|}{C}}-CH_3]{(CH_3CO)_3Al} R_1-\overset{O}{\overset{\|}{C}}-R_2 + CH_3-\overset{OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}-CH_3$$

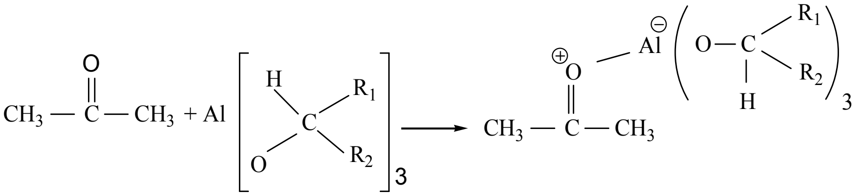
Mechanism: -

Step-I



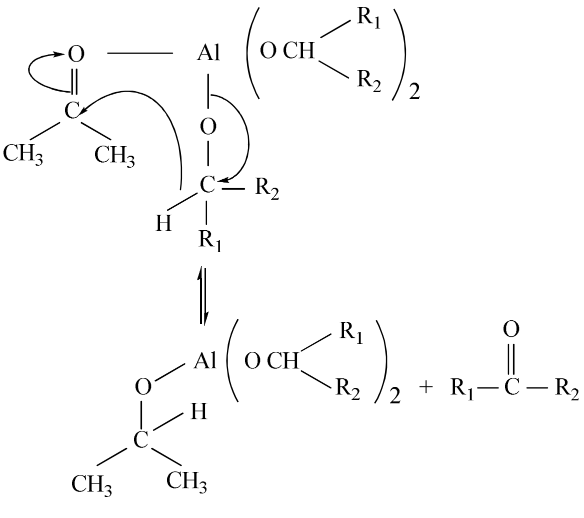
Here exchange reaction takes place

Step-II

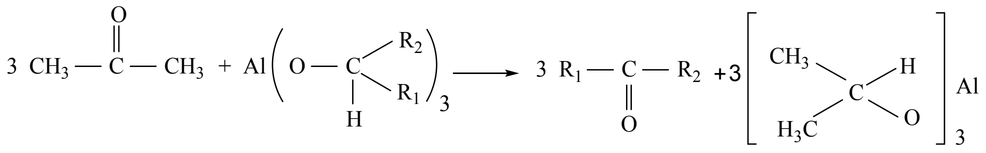


New complex is formed.

Step-III



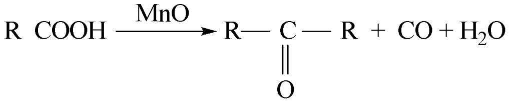
Similarly two more moles of acetone will react with above (one mole) formed complex and give two more moles of ketone product.



This reaction is useful as for oxidation of polyfunctional compounds as this reaction conditions are mild. For e.g. in unsaturated alcohols as it (reagent) does not affect double bond.

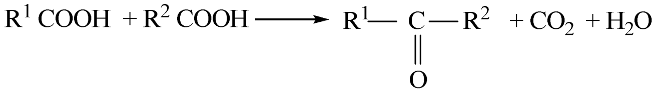
Primary alcohols can also be oxidized by [$(CH_3)_3CO]_3Al$ if in acetone is replaced by p benzoquinone as it is better hydrogen acceptor than acetone.

3. When vapours of any monocarboxylic acid except formic acid are passed over Manganous oxide at 300^0C then ketone is obtained.



$$R\ COOH \xrightarrow{MnO} R-\underset{\underset{O}{\|}}{C}-R + CO + H_2O$$

Mixture of monocarboxylic acids yield mixed ketones

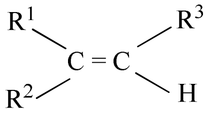


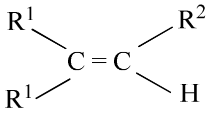
$$R^1\ COOH + R^2\ COOH \longrightarrow R^1-\underset{\underset{O}{\|}}{C}-R^2 + CO_2 + H_2O$$

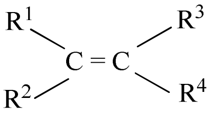
Besides this R′COR′ and R^2 COR^2 are also obtained.

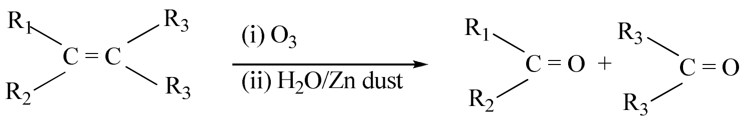
4. From Alkenes: Ketones can be prepared from alkenes as follow**.**

(a) Ozonolysis: - Alkenes of following types when treated with ozone, yield ozonides and this on subsequent treatment with H_2O and zinc dust yield ketones

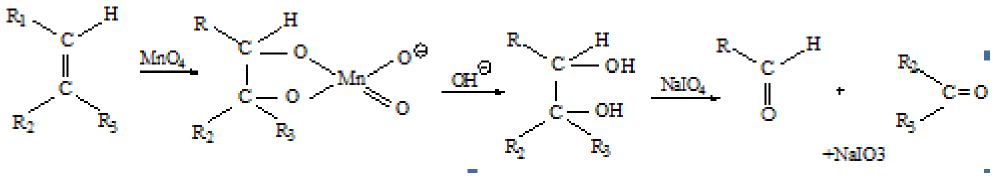






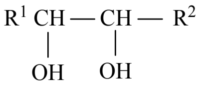


(b) Lemieux Reagent: - An aqueous solution of $NaIO_4$ and trace of $KMnO_4$, lemieux reagent cleaves alkene to is diol and then to aldehydes or ketones.

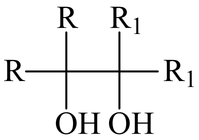


In place of $KMnO_4$, trace of OsO_4 can also be used and it prevents further oxidation to acids.

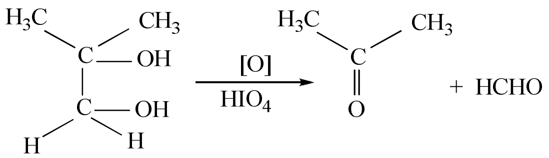
5. Oxidation of 1, 2 glycols: - The following types 1, 2 glycols are oxidised (by lead tetracetate $(CH_3\ COO)_4$ Pb or periodic acid HIO_4 or H_5IO_6) and form aldehydes and ketones respectively according to structure of glycols



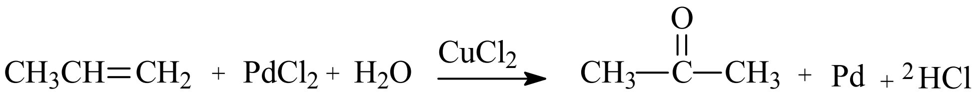
$$R^1\underset{\substack{|\\OH}}{CH}-\underset{\substack{|\\OH}}{CH}-R^2$$



$$R-\underset{\substack{|\\OH}}{\overset{\substack{R\\|}}{C}}-\underset{\substack{|\\OH}}{\overset{\substack{R_1\\|}}{C}}-R_1$$



6. Wacker's Process: - Alkenes on treatment with $PdCl_2$ and Cu Cl_2 give ketone



$$CH_3CH{=}CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3-\overset{\substack{O\\||}}{C}-CH_3 + Pd + 2HCl$$

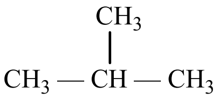
8.8.3 Physiical properties:

1. Lower ketones are colourless liquids.

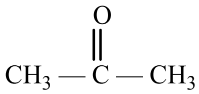
2. Lower ketones possess pleasant, sweet odours.

3.Density of ketones is less than water.

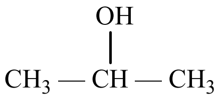
4. As discussed in aldehyde unit ketones have higher boiling points than corresponding alkanes but lower boiling points compared with those of alcohols of comparable molecular weights.



$CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_3$



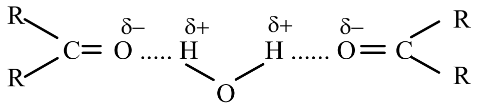
$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3$



$CH_3-\overset{\overset{\large OH}{|}}{C}H-CH_3$

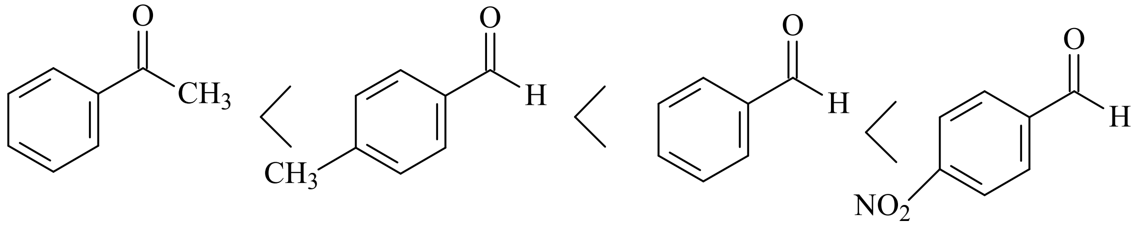
mol. wt.	58	58	60
boiling Point	–12^{0}C	56^{0}C	82.5^{0}C
	isobutane	acetone	isopropyl alcohol

5. Lower ketones are soluble in water as they form hydrogen bonding with water. As alkyl chain of molecule increases, solubility in water decreases..



In infrared spectrum strong C = O Stretching band is observed in 1700 – 1740 cm^{-1} region.

Relative Reactivity: As discussed in detail in aldehyde unit it is to be noted that relative reactivity of ketones is less than aldehydes towards nucleophillic addition reaction. Here electron releasing alkyl group reduce positive charge of carbonyl carbon and thereby decrease reactivity of carbonyl group. Moreover as compare to H atom alkyl group increases steric hindrance for attacking reagent (nucleophile) to reach at carbonyl carbon. Secondly after attack sp^2 hybridised carbonyl carbon becomes sp^3 hybridised in resultant adduct. Here bond angles are reduced from appr.120° to around 109°. This adducts also gets steric strain due to increase of bulky groups. This strain is higher in ketones as compared to aldehydes.



Acetophenone is ketone while other three are aldehyde. So, acetophenone is least reactive. *p*-toulaldehyde has electron donating methyl group at para position of benzene ring whereas *p*-nitrobenzaldehyde has an electron withdrawing nitro group at the para position and we know that reactivity of carbonyl group is inversely proportional to electron density at carbonyl carbon so *p*-toulaldehyde is less reactive than benzaldehyde while *p-n*itrobenzaldehyde is more reactive than benzaldehyde.α-hydrogen of ketones are acidic and removable by strong bases.

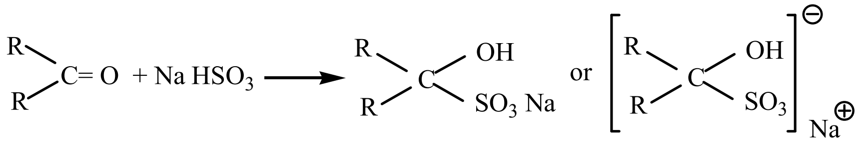
8.8.4 Chemical properties:

Ketones are reactive organic compounds and undergo many reactions like aldehydes.

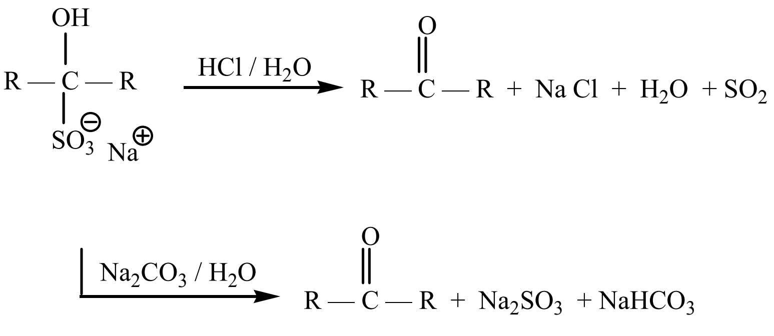
A. ADDITION REACTIONS:

Like aldehydes the reactive carbony group of ketones gives addition reactions.

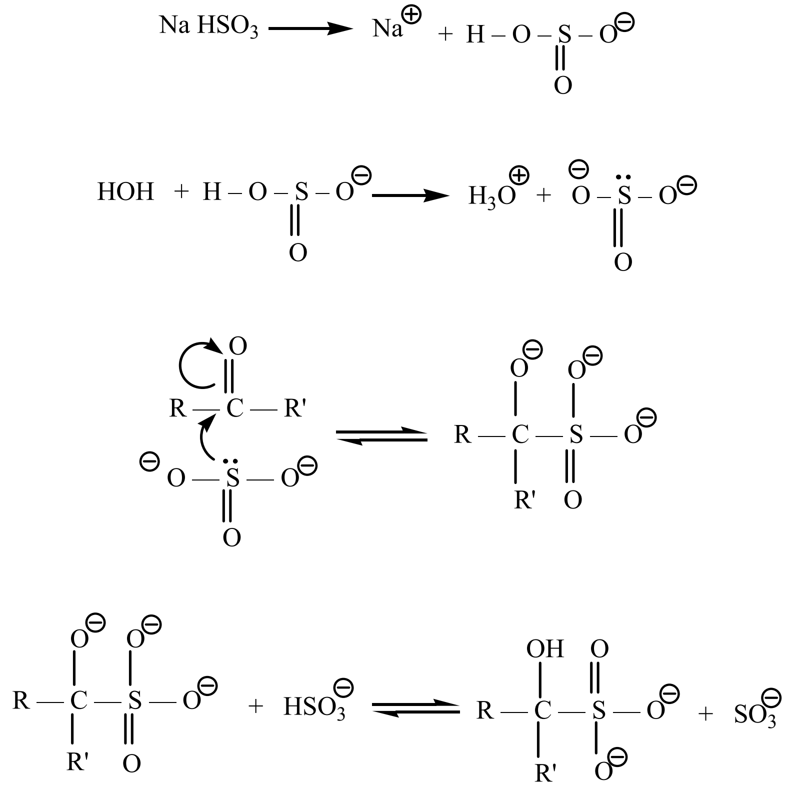
(1) Addition of sodium bisulphate ($NaHSO_3$) :- Ketones add on sodium hydrogen sulphite and form adducts called bisulphite addition compounds which are water soluble salts.



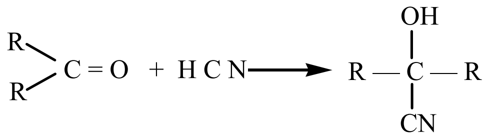
Thus formed adduct when treated with acid, base gives corresponding carbonyl compound.



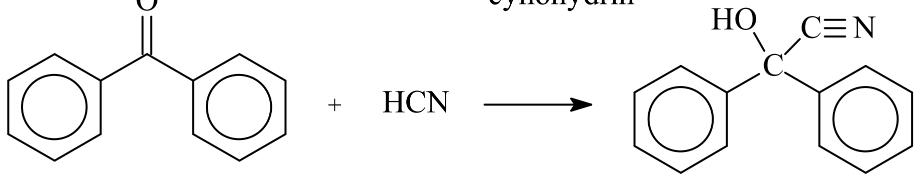
Mechanism: - In this reaction Na_2SO_3 acts as nucleophile through sulphur and attacks at carbonyl carbon which is followed by protonation of carbonyl anionic oxygen by bisulphite ion.



(2) Addition of hydrogen cyanide (HCN) :- Ketones add HCN in the presence of base catalyst to form cyanohydrins, which can further be hydrolysed to –COOH group



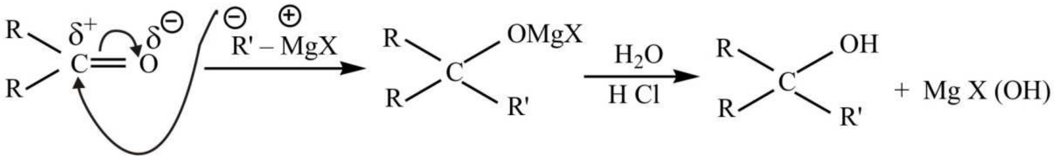
cynohydrin

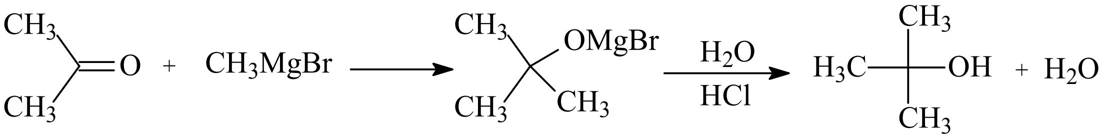


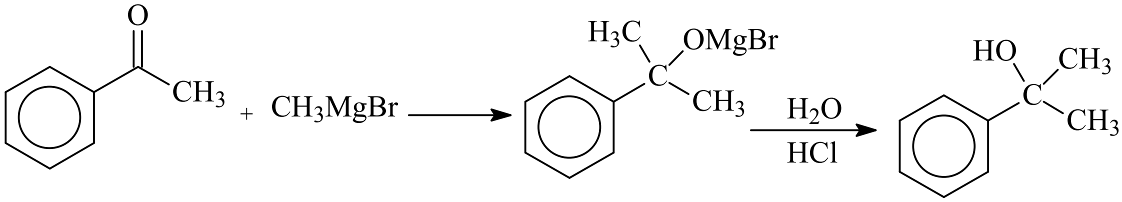
cynohydrin

The mechanism of formation of cynohydrin is similar as discussed in aldehyde unit, hence can be persuied from aldehyde unit.

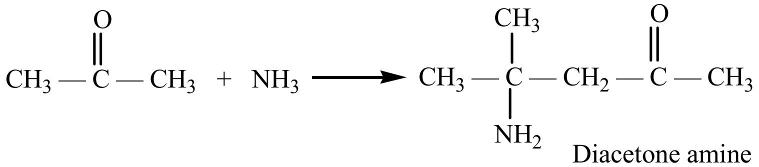
(3) Addition of Grignard reagents (RMgX): - ketones react with Grignard reagent to form complex which on hydrolysis with dilute acids gives tertiary alcohol.





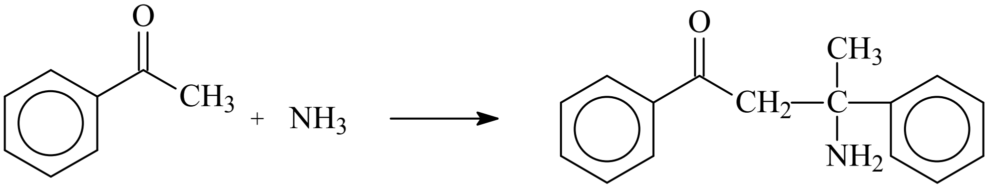


(4) Addition of ammonia (NH_3):- Ketones react with NH_3 and form complex condensation products.

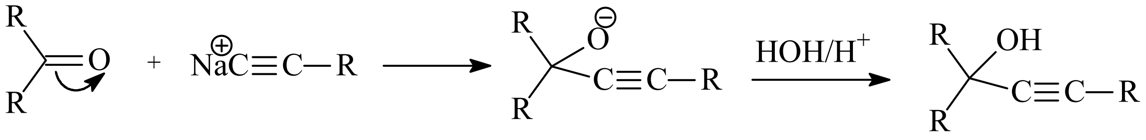


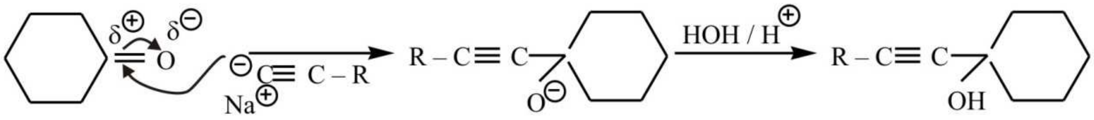
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + NH_3 \longrightarrow CH_3-\underset{NH_2}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

Diacetone amine



(5) Addition of terminal alkynes: - Ketones react with sodium salt of terminal alkynes to give alkynol.

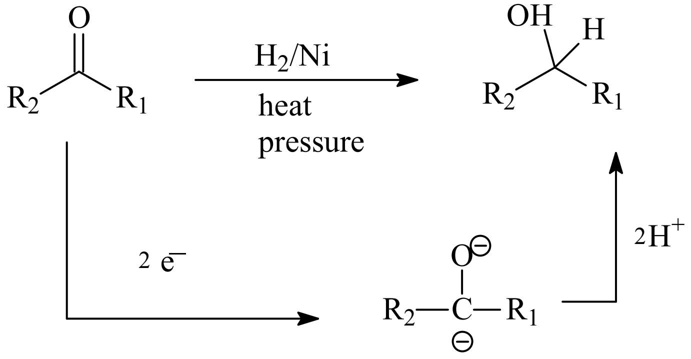




B. REDUCTION REACTIONS:

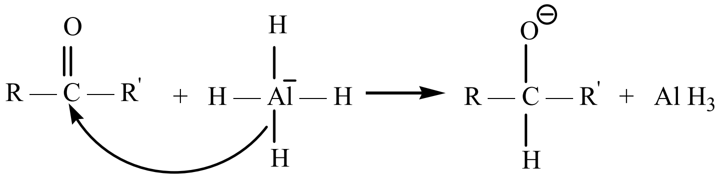
The carbonyl group of ketones can be reduced to $–CH_2$- or –CH by using reducing reagents. In continuation to other reactions the reductions are as follow.

(1) Ketones are reduced to secondary alcohol, when treated with H_2 and Ni, H_2 and Pt, $LiAlH_4$ (lithium aluminium hydride) in THF (tetrahydro furan), $NaBH_4$ (sodium borohydride) in water or alcohol.

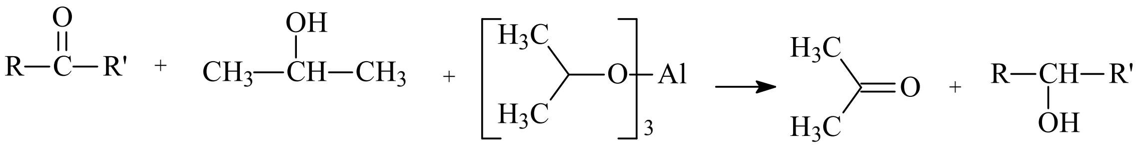


When reduction of unsaturated ketone with Ni and H_2 is carried out then preferentially double bond is hydrogenated or both double bond and carbonyl group are hydrogenated. But here only carbonyl group cannot be hydrogenated. $LiAlH_4$ and $NaBH_4$ type metal hydrides reduce carbonyl group but not isolated carbon-carbon double bond. C = C in conjugation with carbonyl group is sometimes reduced. $NaBH_4$ is milder reducing agent than $LiAlH_4$. So $NaBH_4$ is selective for carbonyl group if carbonyl and ester groups are present in same molecule.

Metal hydrides ($LiAlH_4$ and $NaBH_4$) transfer hydride ion to positive carbon of carbonyl group and then treatment with water or aqueous acid sets free alcohol from its salt.



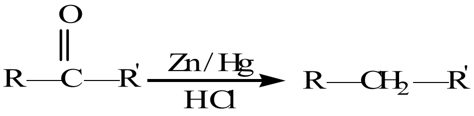
(2) Meerwein-Ponndorf-Verely reduction: - As discussed in aldehyde unit, ketones are also reduced to corresponding alcohol when ketones are dissolved in solution of isopropyl alcohol containing aluminium isopropoxide.



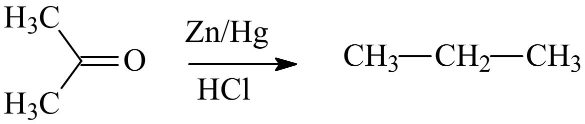
If aldehydes or ketones are unsaturated then it attacks only carbonyl group. Mechanism of MPV reduction of ketones is same as of aldehydes (discussed in aldehyde unit).

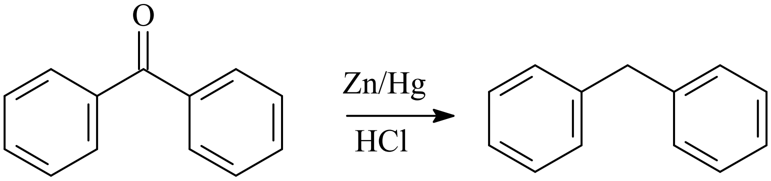
(3) Reduction to hydrocarbon: Ketones are reduced to $-CH_2-$ groups:

(a) Clemmensen reduction: - Carbonyl group of ketones is reduced to methylene group by using zinc amalgam and hydrochloric acid.



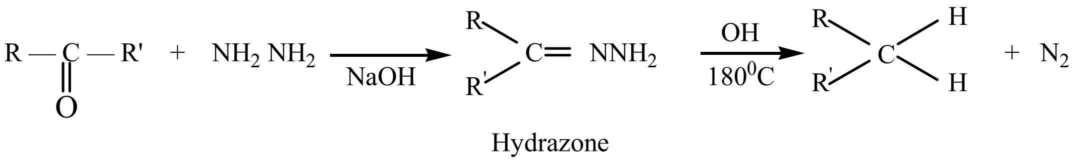
$$R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow[HCl]{Zn/Hg} R-CH_2-R'$$



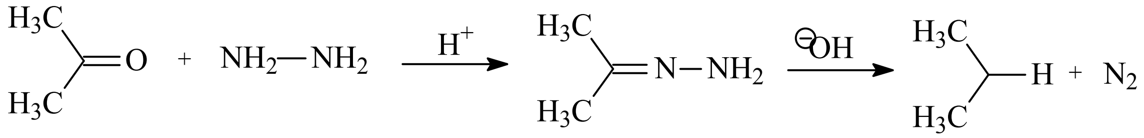


Mechanism of clemmensen reduction is already discussed in aldehyde unit.

(b) Wolf Kishner Reduction :- It involves conversion of carbonyl group to methylene group by heating ketones in the presence of excess hydrazine and a strong base (sodium ethoxide) at 180^0C.



Reaction can be carried out room temperature in the presence of polar solvents like DMSO. In α, β-unsaturated carbonyl compounds, the Wolf Kishner reduction lead to double bond migration.



C. OXIDATION REACTIONS:

Ketones like aldehydes are oxidized to carboxylic acids.The oxid. Reactions of ketones in continuation are as under.

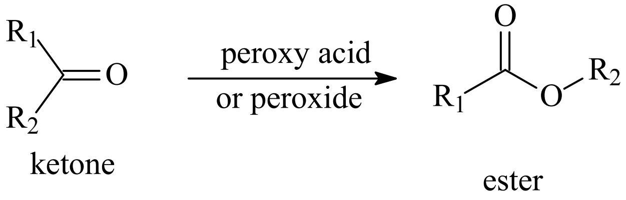
(1) Ketones can be oxidized by strong oxidizing agents such as alkaline $KMnO_4$ or hot concentrated HNO_3 etc. Here carbon atoms adjacent to carbonyl group are attacked and carbon atom joined to the smaller number of hydrogen atoms is oxidized preferably.

$$CH_3\,CO\,CH_2\,CH_3 \xrightarrow{[O]} 2CH_3\,COOH$$

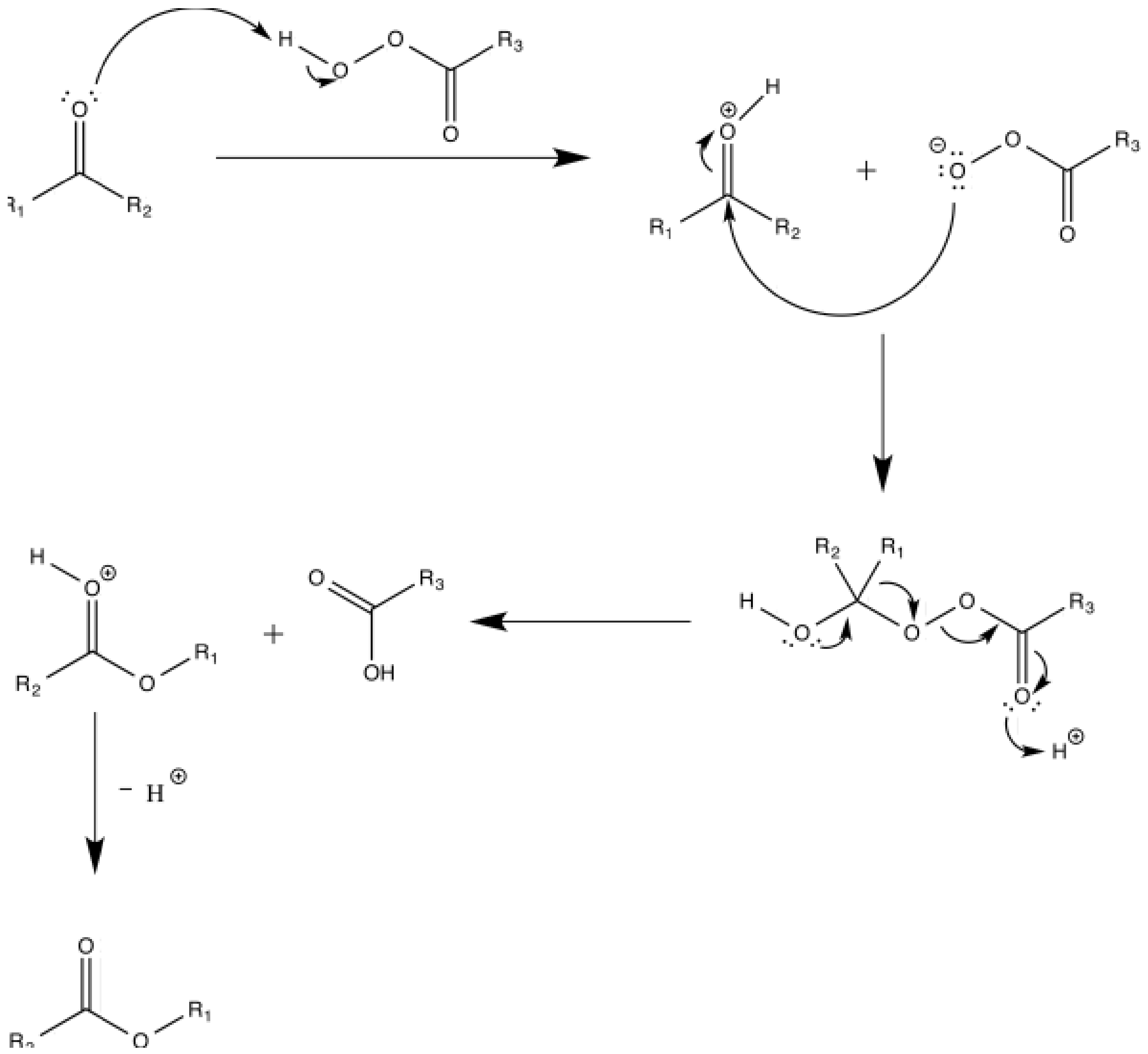
If adjacent carbon atoms have same number of hydrogen atoms, then smaller alkyl group retains carbonyl group.

Ketones donot reduce Fehling's solution, Benedict's solution or ammoniacal silver nitrate.

(a)Baeyer Villiger Oxidation: - Aliphatic ketones on treatment with perbenzoic, peracetic, and monoperphthalic acid or permonoculphuric acid H_2SO_5 forms esters called Baeyer Villiger Oxidation.

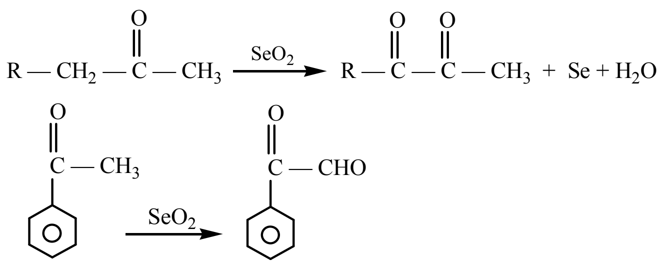


Mechanism: The sequential mechanism of Baeyer-Villiger reaction is as follow



This rearrangement is intramolecular and migratory aptitude of an alkyl group is $3^0 > 2^0 > 1^0$.

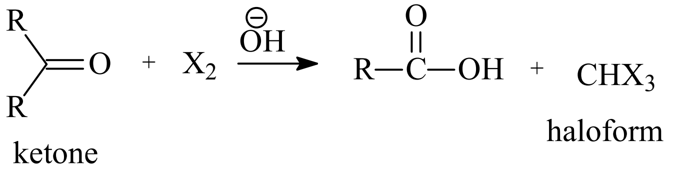
(b) Oxidation with SeO_2:- SeO_2 oxidises methylene group adjacent to the carbonyl group of aldehydes and ketones.

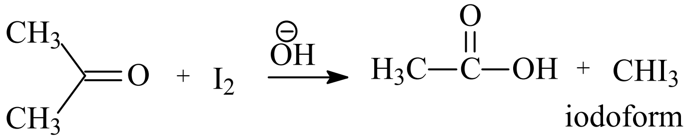


C. OTHER REACTIONS:

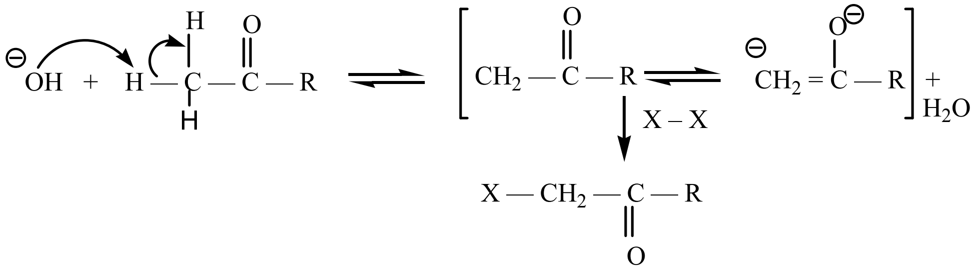
Earlier it has been discussed the acidity of α- hydrogens in carbonyl compounds which leads to different types of reactions in ketones eg. halogenation, condensation etc.In continuity some of the reactions of ketones are being discussed as follow

(1) Haloform Reaction: - Methyl ketones react rapidly with halogens (Cl_2, Br_2, I_2) in the presence of alkali to form mono, di and tri haloderivatives.

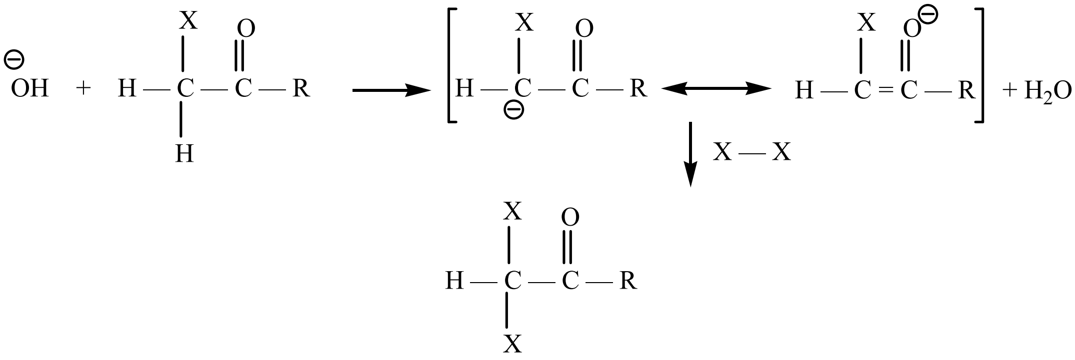


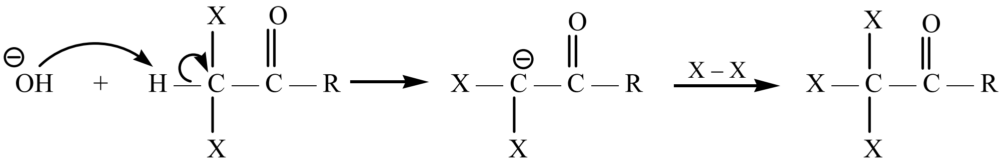


Mechanism

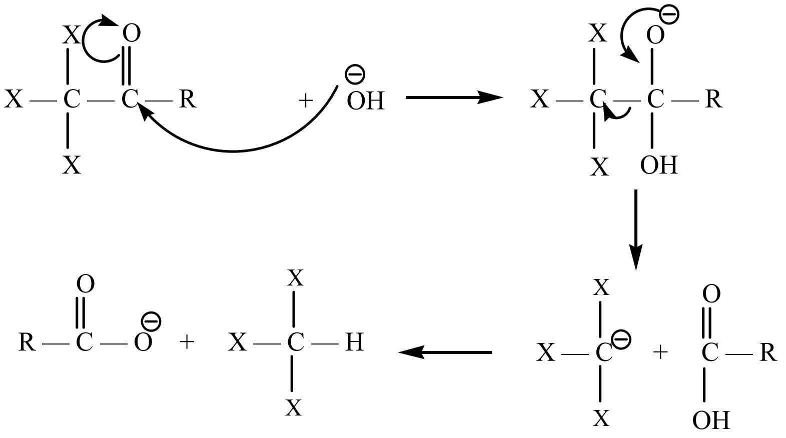


It involves abstraction of hydrogen by alkali and then resonance stabilization of conjugate base.Then carbanion displaces a halide from a halogen molecule.Introduction of halogen to methyl ketone enhances electronegativity of remaining α- hydrogens and they again undergo above process repeatedly forming trichalogenated ketones.

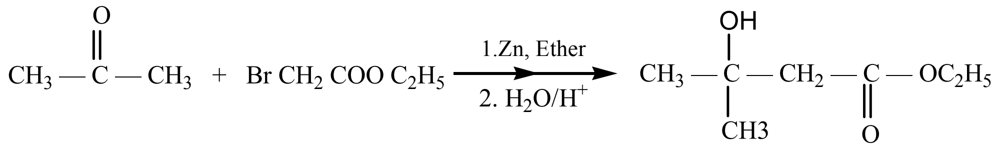




The trihalogenated ketones are unstable to base.



(2) Reformatsky Reaction: - Like aldehydes ketones also react with □ bromoester in the presence of Zinc which subsequently on acid hydrolysis result in □-hydroxy ester.

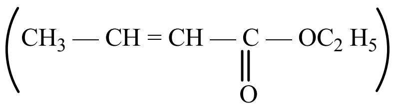


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + Br\,CH_2\,COO\,C_2H_5 \xrightarrow[2.\ H_2O/H^+]{1.Zn,\ Ether} CH_3-\underset{CH3}{\overset{OH}{C}}-CH_2-\underset{\overset{\|}{O}}{C}-OC_2H_5$$

Acetone

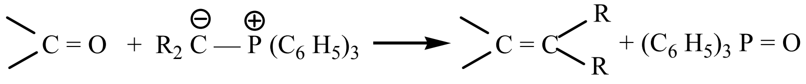
Ethyl 3-hydroxy-3-methyl butanoate

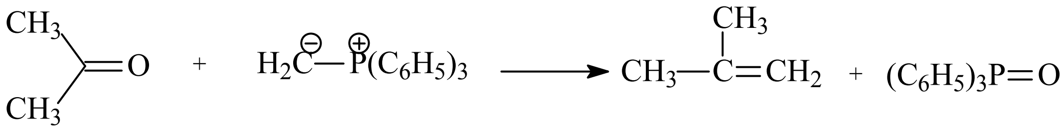
β- hydroxyl ester dehydrate to give unsaturated ester.



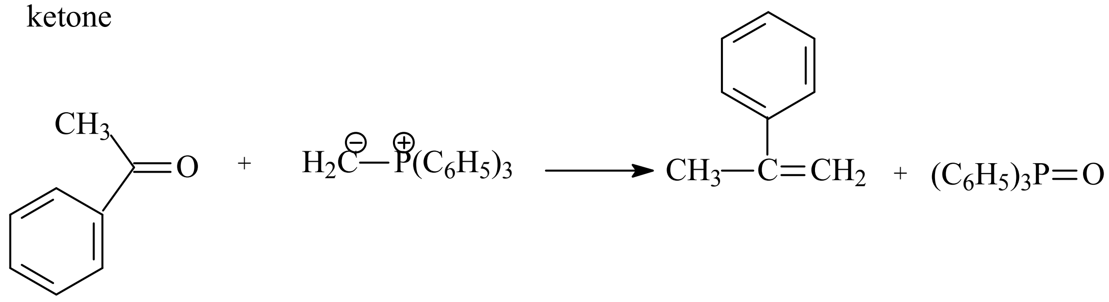
$$\left(CH_3-CH=CH-\underset{\overset{\|}{O}}{C}-OC_2\,H_5\right)$$

(3) Wittig reaction: - Ketones react with alkylidene-phosphoranes (phosphorus ylides) in an atmosphere of nitrogen leads to alkene synthesis.





ketone

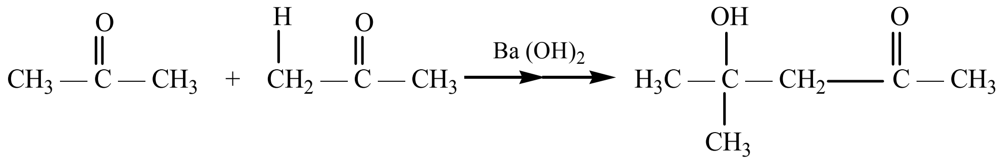


acetophenone

isopropenyl benzene

Mechanism of formation of phosphorus ylides and Witting reaction has been discussed in the previous unit pertaining to aldehydes. Reaction of ylides with ketones is slow as compared to aldehydes.

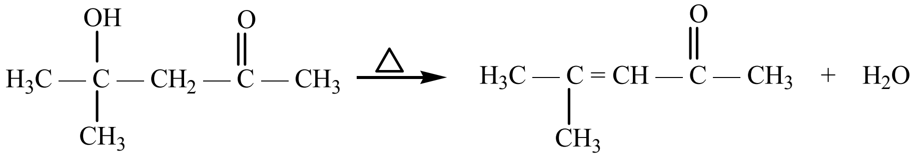
(4) Aldol condensation: - Analogues to aldehydes, ketones having a hydrogen undergo self condensation in the presence of $Ba(OH)_2$ to form ketols.



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + \overset{H}{\overset{|}{C}H_2}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Ba(OH)_2} H_3C-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

Acetone Diacetone alcohol

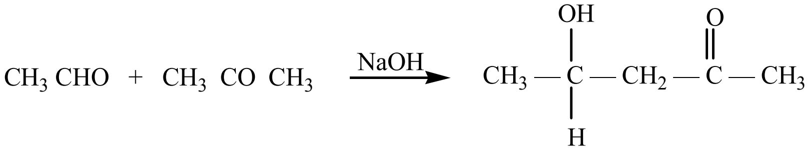
Ketols are easily dehydrated by heating or by dilute acids to form unsaturated ketones.



$$H_3C-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\triangle} H_3C-\underset{CH_3}{\underset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

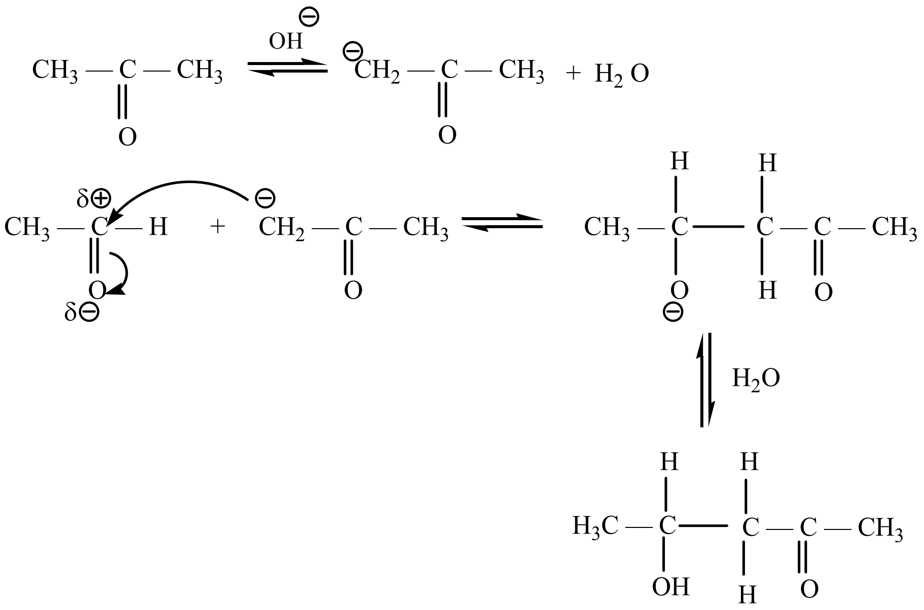
4-Methyl – 3 – penten – 2 – one

Mechanism of aldol condensation is similar to that of aldehyde which has already been discussed in aldehyde unit.However in mixed aldol condensation, when aldehydes condense with ketones in the presence of dil. alkali, it is the α- carbon (having hydrogen) atom of the ketone which is the attacking nucleophile.



$$CH_3CHO + CH_3COCH_3 \xrightarrow{NaOH} CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

Acetaldehyde Acetone 4 hydroxypentan – 2 one



8.9 CARBOXILIC ACIDS

Carboxylic acids are aliphatic or aromatic compounds which contain at least one carboxyl group (-COOH) in the molecule. The word "carboxyl" is derived from the names of two functional groups *i.e.* carbonyl and hydroxyl. Carboxylic acids are classified as mono, di, tri, or polycarboxylic acids according to the number of carboxyl groups present in the molecule. For example, the one –COOH group containing hydrocarbons such as formic acid, acetic acid, propionic acid, lactic acid, malic acid, benzoic acid etc. are called monocarboxylic acids whereas the two –COOH groups containing compounds such as oxalic acid, succinic acid, adipic acid, fumeric acid, malic acid, tartaric acid phthalic acid etc. are called dicarboxylic acids similarly like citric acid contains three -COOH group and termed as tri-carboxylic acid. The long chain monocarboxylic acids are also known as fatty acids such as stearic acid, palmitic acid, oleic acid etc. The general chemical formula of aliphatic carboxylic acids is $C_nH_{2n+1}COOH$.

8.9.1 Nomenclature of carboxylic acids:

In IUPAC system, carboxylic acids are named by replacing the suffix "***–e***" of the corresponding alkane with "***-oic acid"***. It is not necessary to indicate the position of the -COOH group because this group will be at the end of the parent chain and its carbon is assigned as C-1. The common names and IUPAC names for some straight chain saturated carboxylic acids are given in given below.

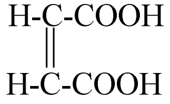
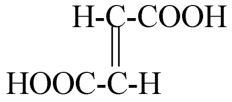
Table–Common names and IUPAC names of some straight chain saturated carboxylic acids

Carboxylic acids	**Common name**	**IUPAC name**
HCOOH	formic acid	methanoic acid
CH_3COOH	acetic acid	ethanoic acid
CH_3CH_2COOH	propionic acid	propanoic acid
$CH_3(CH_2)_2COOH$	butyric acid	butanoic acid
$CH_3(CH_2)_3COOH$	valeric acid	pentanoic acid
$CH_3(CH_2)_4COOH$	caproic acid	hexanoic acid
$CH_3(CH_2)_5COOH$	enanthic acid	heptanoic acid
$CH_3(CH_2)_6COOH$	caprylic acid	octanoic acid
$CH_3(CH_2)_7COOH$	pelargonic acid	nonanoic acid
$CH_3(CH_2)_8COOH$	capric acid	decanoic acid
$CH_3(CH_2)_9COOH$	-	undecanoic
$CH_3(CH_2)_{10}COOH$	lauric	dodecanoic

IUPAC nomenclature of di-carboxylic acids: If there are two -COOH groups are present in an acid; the acid is called dicarboxylic acid. To construct the IUPAC name of these compounds, add the suffix ***–dioic*** acid to the name of the parent alkane containing both carboxylic groups (*Table-)*.

Table 6. 2-Common names and IUPAC names of some di-carboxylic acids

Carboxylic acids	**Common name**	**IUPAC name**

HOOC-COOH	oxalic acid	ethanedioic acid
$HOOC.CH_2COOH$	malonic acid	propanedioic acid
$HOOC.CH_2CH_2COOH$	succinic acid	butanedioic acid
$HOOC(CH_2)_4COOH$	adipic acid	hexanedioic acid
 $\begin{array}{l}\text{H-C-COOH}\\ \quad \| \\ \text{H-C-COOH}\end{array}$	maleic acid	*cis*-2-butenedioic acid
 $\begin{array}{r}\text{H-C-COOH}\\ \| \quad\quad \\ \text{HOOC-C-H}\end{array}$	fumaric acid	*trans*-2-butenedioic acid

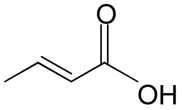
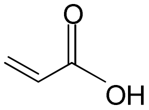
IUPAC nomenclature of hydroxyl derivatives of carboxylic acids: The hydroxyl derivatives of carboxylic acids are called hydroxyl carboxylic acids. In common system, the position of –OH group in a hydrocarbon chain is indicated by the *Greek alphabets* $\alpha, \beta, \gamma, \delta$ *etc.* whereas in IUPAC system the position of –OH group in a hydrocarbon chain is indicated by the *numbering, 1, 2, 3, 4 etc.*

Table -Common names and IUPAC names of some hydroxyl derivatives of carboxylic acids.

Carboxylic acids	**Common name**	**IUPAC Name**
$HOCH_2COOH$	glycollic acid	hydroxyethanoic acid
$CH_3CHOHCOOH$	lactic acid	2-hydroxypropanoic acid
$HOOCCH_2CHOHCOOH$	malic acid	2-hydroxybutanedioic acid
$HOOC(CHOH)_2COOH$	tarteric acid	2,3-dihydroxy butanedioic acid
$HOC(COH)((CH_2)COOH)_2$	citric acid	2-hydroxypropane-1,2,3 tri

carboxylic acid

Table: If a carboxylic compound contains double bond (alkene), then replace the infix from "–*an to –en*" and the placement of the infix is determined by the *numbering, 1, 2, 3, 4 etc***.** *(Table-6.4).*

Carboxylic acids	**Common name**	**IUPAC name**
	crotonic acid	*trans*-2-Butenoic acid
	acrylic acid	propenoic acid

IUPAC nomenclature of aromatic carboxylic acids: Aromatic carboxylic acids are named by adding the suffix ***"-carboxylic acid"*** to the name of a parent hydride.

Table –Common names and IUPAC names of some aromatic carboxylic acids:

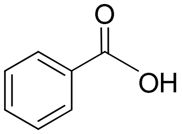
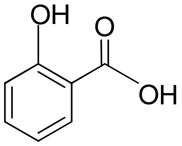
Carboxylic acids	**Common name**	**IUPAC name**
	benzoic acid	benzene carboxylic acid
	salicylic acid	2-hydroxybenzene carboxylic acid

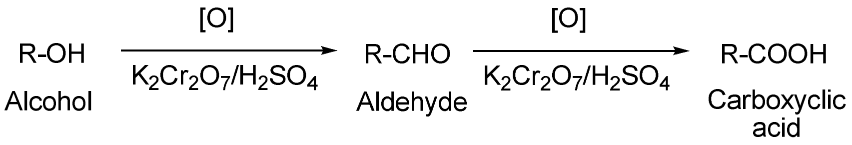
Table –If the two carboxylic acid groups are in the benzene ring it is named as *"di-carboxylic acid".*

8.9.2 Preparations of carboxylic acids:

The carboxylic acids can be synthesized by various methods as follow:-

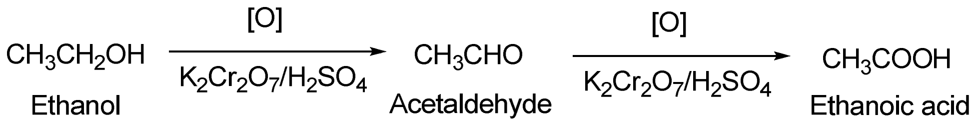
1. By the oxidation of primary alcohols and aldehydes

Carboxylic acids can be prepared by the oxidation of primary alcohols and aldehydes with acidic $KMnO_4$, or acidic $K_2Cr_2O_7$.

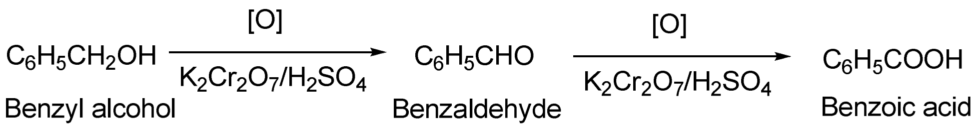


$$\text{R-OH} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \text{R-CHO} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \text{R-COOH}$$

For example:



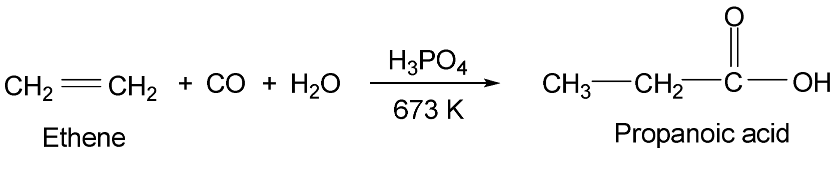
$$CH_3CH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} CH_3CHO \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} CH_3COOH$$



$$C_6H_5CH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} C_6H_5CHO \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} C_6H_5COOH$$

2. From Koch reaction

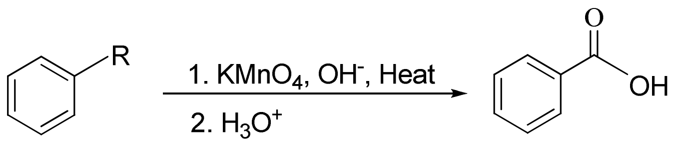
Koch reaction is an organic reaction used to convert olefins into tertiary carboxylic acids. In this reaction alkenes are treated with carbon monoxide and hydrogen in presence of strong mineral acids like phosphoric acid or hydrogen fluoride to form the tertiary carboxylic acids.



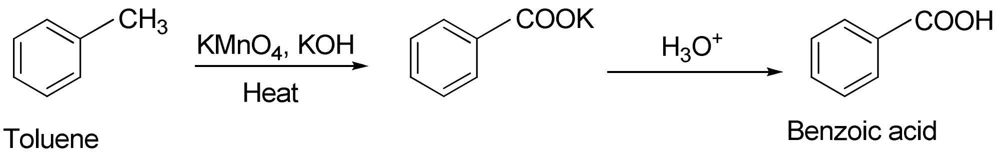
$$CH_2{=}CH_2 + CO + H_2O \xrightarrow[673\ K]{H_3PO_4} CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

3. By the oxidation of alkyl benzenes

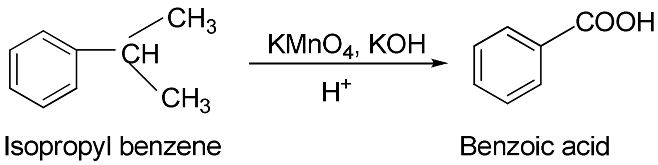
Aromatic carboxylic acids may be formed by the oxidation of alkyl benzene with $K_2Cr_2O_7$, or acidic or alkaline $KMnO_4$.

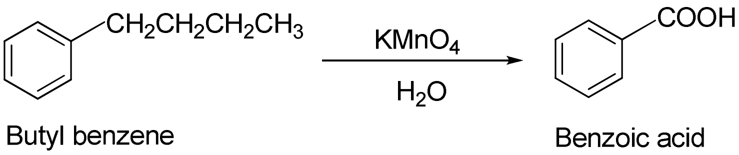


When toluene is heated with $KMnO_4$, it is oxidized to benzoic acid.

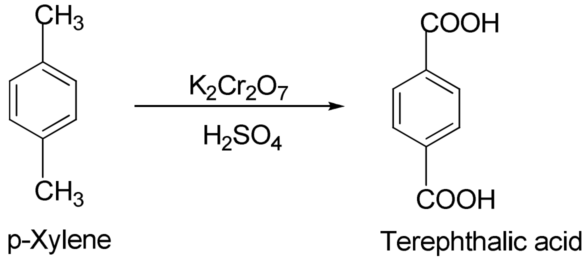


Similarly, the isopropyl benzene is oxidized into benzoic acid with alkaline $KMnO_4$.





Terephthalic acid can be obtained by the oxidation of *p*-xylene with acidic $K_2Cr_2O_7$.



4. By the hydrolysis of cyanides or nitriles

Alkyl halides react with sodium cyanide in S_N2 displacement to form a nitrile which on hydrolysis converted into carboxylic acid. The cyano group contains a hydrogen bond which under acid hydrolysis converted into carboxylic group.

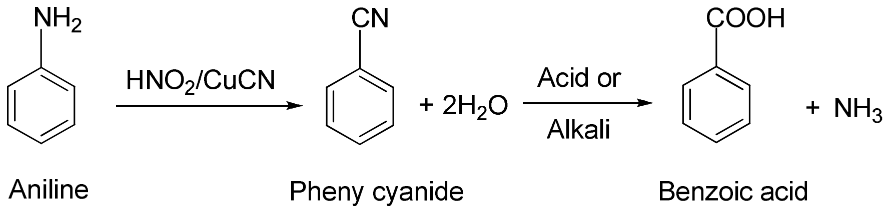
$$\underset{\text{Alkyl halide}}{R-X} \xrightarrow{NaCN} \underset{\text{Alkyl cynide}}{R-CN} \xrightarrow{HCl/H_2O} \underset{\text{Carboxylic acid}}{R-COOH}$$

(Where, R is an alkyl group and X is a halide)

$$\underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow[-NaCl]{NaCN} \underset{\text{Methyl cyanide}}{CH_3CN} + 2H_2O \xrightarrow[\text{Alkali}]{\text{Acid or}} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

Aromatic amine with nitrous acid produces aromatic nitrile which on acidic hydrolysis produces aromatic carboxylic acid.

$$Ar\text{-}NH_2 \xrightarrow{HNO_2/CuCN} Ar\text{-}NO_2 + 2H_2O \xrightarrow[\text{Alkali}]{\text{Acid or}} Ar\text{-}COOH + NH_3$$



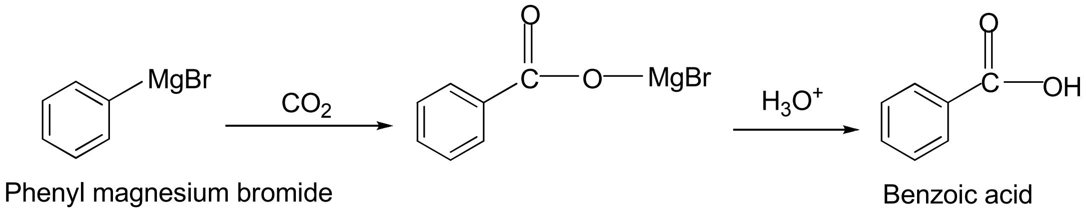
5. By Grignard's reagents

Grignard's reagents react with carbon dioxide to form salts of carboxylic acids which give carboxylic acids on reaction with mineral acids.

$$\underset{\text{Alkyl halide}}{R-X} \xrightarrow[\text{Ether}]{Mg} \underset{\text{Grignard reagent}}{R-MgX} \xrightarrow[2.\ H^+]{1.\ CO_2} \underset{\text{Carboxylic acid}}{R-COOH}$$

(Where, R is an alkyl or aryl group)

Benzoic acid is prepared by the action of carbon dioxide on phenyl magnesium bromide (Grignard's reagent).



6. By the hydrolysis of esters

Carboxylic acids can be prepared by the hydrolysis of esters either in acidic or alkaline medium. For example, the acetic acid is formed by the hydrolysis of ethyl acetate in acidic conditions.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \overset{H^+}{\rightleftharpoons} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

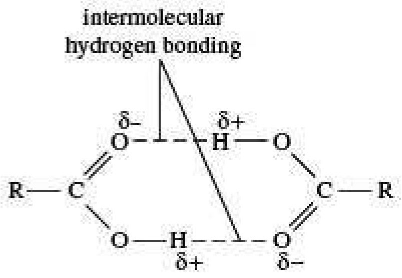
8.9.3 Physical properties

1. Physical state

Lower members (C_1-C_3) are colorless liquids having pungent smell. C_4-C_9 members are colorless oily liquids having an odor like goat butter. Higher members (C_{10} onwards) are colorless, odorless waxy solids.

2. Hydrogen bonding

The intermolecular hydrogen bonding occurs in carboxylic acids. The two molecules of carboxylic acids are associated by hydrogen bonding into dimers (pairs of molecules) in liquid state or gaseous state. The boiling points and solubility of carboxylic acids are associated with hydrogen bonding.



3. Boiling point

Carboxylic acids have higher boiling points than the organic compounds like, alcohols, ethers, aldehydes, or ketones of similar molecular weight. For example, acetic acid has higher boiling point (118°C) than the 1-propanol (97°C) although the two have similar molecular weights

(60.1). Similarly, the butanoic acid and 1-pentanol have similar molecular weights (MW 88.1), but the boiling point of butanoic acid (163 ºC) is more than that of 1-pentanol (137 ºC). Because the two molecules of a carboxylic acid form two hydrogen bonds with each other while two alcohol molecules can only form one hydrogen bond. The boiling points of carboxylic acids increase with increase in molecular weight.

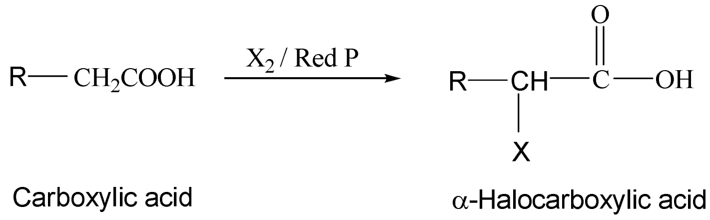
4. Solubility

The C_1-C_4 members are more soluble in water. This is due to the ability of the –COOH group to form hydrogen bonds with water molecules. Due to strong H……. bonding, carboxylic acids are more soluble in water than alcohols, ethers, aldehydes, or ketones of comparable molecular weight. The solubility of a carboxylic acid in water decreases as the molecular weight of carboxylic acids increases. This is due to, a carboxylic acid consists two different polarities: a polar hydrophilic carbonyl group and a non polar hydrophobic hydrocarbon chain. The hydrophilic carbonyl group increases water solubility whereas hydrophobic hydrocarbon chain decreases water solubility. Therefore, C_5 members are partly soluble and the higher carbon chain members are insoluble in water, but readily soluble in ethanol, ethers and benzene.

8.9.4 Chemical reactions of carboxylic acids

The carboxylic acids are reactive organiccompounds because of –OH and –CO group and undergo many reactions some of ther are as follow.

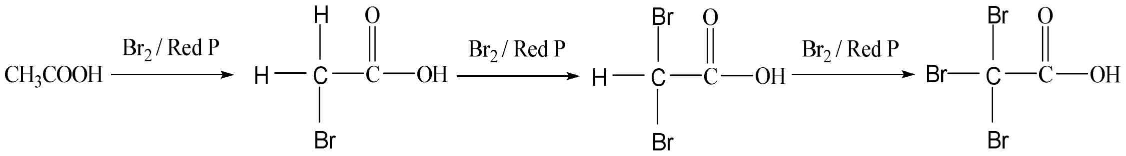
(1) α-Halogenation of aliphatic acids: Carboxylic acids undergo halogenation with chlorine or bromine in the presence of small amount of red phosphorus form α-halo or β-haloacids. The reaction is known as ***Hell Volhard Zelinsky reaction.*** In this reaction a carboxylic acids containing an α-hydrogen atom is replaced by a chlorine or bromine atom to form an α-halo carboxylic acid. The general reaction is as:



$$R\text{—}CH_2COOH \xrightarrow{X_2\,/\,\text{Red P}} R\text{—}\underset{\substack{|\\X}}{CH}\text{—}\overset{\substack{O\\ \|}}{C}\text{—}OH$$

(Where, X= Cl, Br)

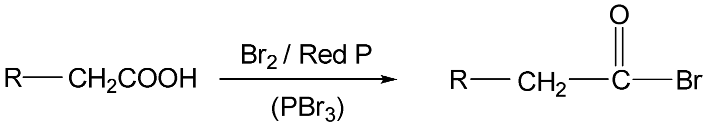
Bromination of acetic acid is a good example of this reaction.



$$CH_3COOH \xrightarrow{Br_2 / \text{Red P}} H-\overset{H}{\underset{Br}{C}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Br_2 / \text{Red P}} H-\overset{Br}{\underset{Br}{C}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Br_2 / \text{Red P}} Br-\overset{Br}{\underset{Br}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

Mechanism: The stepwise mechanism is as follow of HVZ reaction

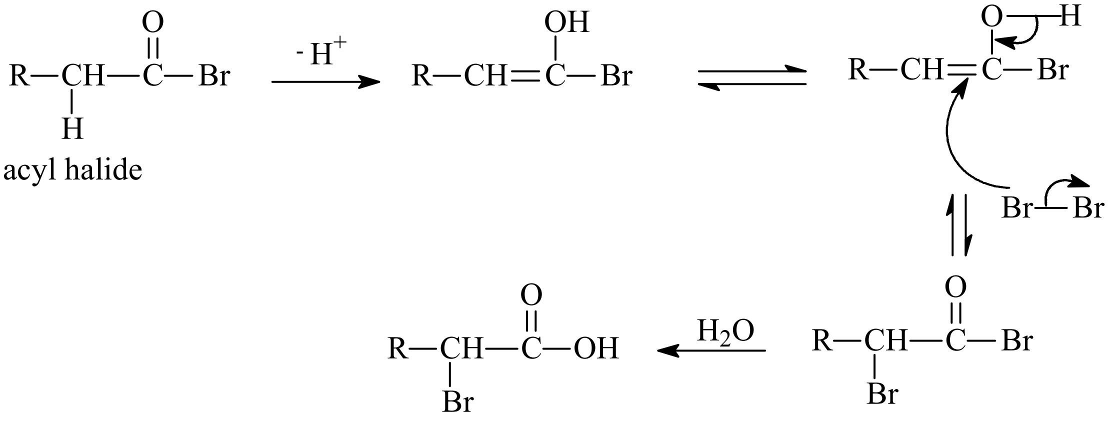
Step 1: Phosphorus reacts with bromine to form phosphorus tribromide, and in the first step this converts the carboxylic acid into an acyl bromide.



$$R-CH_2COOH \xrightarrow[(PBr_3)]{Br_2 / \text{Red P}} R-CH_2-\overset{O}{\overset{\|}{C}}-Br$$

Acyl halide

Step 2: The acyl bromide then tautomerizes to the enol form which subsequently attacks the halogen molecule to form a α-halo acyl halide. Water hydrolysis yields the final α-halo carboxylic acid product.



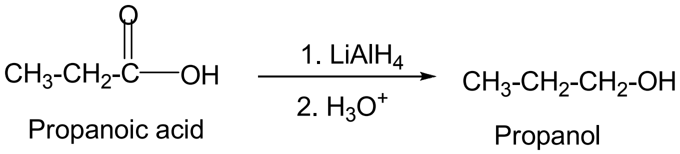
Although the α-bromination of some carbonyl compounds, such as aldehydes and ketones, can be accomplished with Br_2 under acidic conditions, this reaction will generally not occur with acids, esters, and amides because only aldehydes and ketones enolize to a sufficient extent to allow the reaction to occur.

(2) Reactions of -COOH group

(i) a. Reduction of carboxylic acid to alcohols by $LiAlH_4$: The carboxylic acids are reduced to primary alcohols with a strong reducing agent like lithium aluminium hydride ($LiAlH_4$). In this reaction the carbonyl group of a carboxyl group is reduced to $-CH_2$ group.

$$\text{R-COOH} \xrightarrow[\text{2. } H_3O^+]{\text{1. } LiAlH_4} \text{R-}CH_2OH$$

Propanoic acid is reduced to propanol in presence of lithium aluminium hydride ($LiAlH_4$).

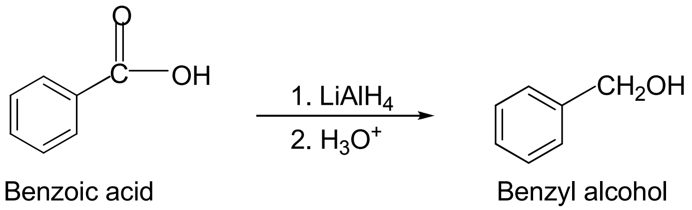


$$CH_3\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OH \xrightarrow[\text{2. } H_3O^+]{\text{1. } LiAlH_4} CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$$

Propanoic acid

Propanol

Similarly, benzoic acid is reduced to benzyl alcohol in presence of lithium aluminium hydride ($LiAlH_4$).



Benzoic acid

Benzyl alcohol

Higher carboxylic acids are also reduced to alcohols by hydrogen in presence of copper chromium oxide. This reaction is used to prepare detergents such as sodium lauryl sulphate from lauryl alcohol.

$$\underset{\text{Lauric acid}}{C_{11}H_{23}COOH} + 2H_2 \longrightarrow \underset{\text{Lauryl alcohol}}{C_{11}H_{23}CH_2OH} + 2H_2O$$

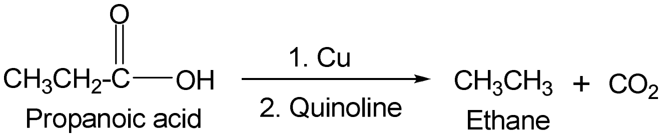
Carboxylic acids cannot be reduced by H_2/Ni, or Na/C_2H_5OH, or $NaBH_4$, or catalytic hydrogenation.

b. Reduction by HI: Carboxylic acids can be reduced to either primary alcohols or alkanes depend upon the reducing agent involve in reaction

(ii) Decarboxylation reaction: When an anhydrous sodium salt of a fatty acid is heated with sodalime (NaOH + CaO) or Cu/ quinoline, it loses carbon dioxide to form an alkane. This reaction is known as decarboxylation reaction. The general reaction is as:

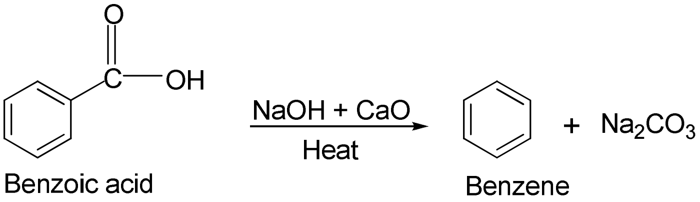
$$RCOONa \xrightarrow[\text{Heat}]{\text{NaOH + CaO}} R{-}H + CO_2$$

Simple copper salts such as copper chromate, copper hydroxide or copper carbonate can also be used in decarboxylation of aliphatic and aromatic acids.



$$\underset{\text{Propanoic acid}}{CH_3CH_2\text{-}\overset{\overset{\large O}{\|}}{C}{-}OH} \xrightarrow[\text{2. Quinoline}]{\text{1. Cu}} \underset{\text{Ethane}}{CH_3CH_3} + CO_2$$

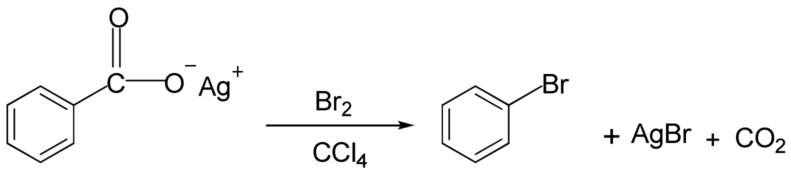
Aromatic carboxylic acids also react with sodalime to give benzene.



(iii) Hunsdiecker reaction: Silver salt of fatty acids on heating with a halogen (Cl or Br) undergo decarboxylate halogenations give alkyl or aryl halides. The general reaction is as:

$$RCOOAg + Br_2 \xrightarrow{\Delta} RBr + CO_2 + AgBr$$

For example,



(iv) Kolbe electrolysis: The electrochemical oxidation of sodium or potassium salts of fatty acids give alkanes having twice the number of carbon atoms present in the alkyl group of the acid. This process is known as *Kolbe's electrolysis*. For example; the electrolysis of potassium ethanoate forms ethane with carbon dioxide gas and hydrogen gas as side products.

$$2CH_3COOK \rightarrow 2CH_3COO^- + 2K^+$$

$$2H_2O \rightarrow 2H^+ + 2OH^-$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ (at cathode)}$$

$$2CH_3COO^- \rightarrow 2CH_3COO^{\cdot} \text{ (at anode)}$$

$$2CH_3COO^{\cdot} \rightarrow 2CH_3^{\cdot} + 2CO_2$$

$$2CH_3\cdot \rightarrow CH_3\text{-}CH_3$$

(3) Reactions with metals and alkalies: Some reactions which show the acidic character of carboxylic compounds are as follow:

(i) Reaction with metal: Carboxylic acids react with active metals like K, Ca, Mg to form salts by releasing hydrogen gas.

$$2RCOOH + 2Na \rightarrow 2RCOONa + H_2$$

$$2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2$$

(ii) Reaction with alkalies: Carboxylic acids react with alkalis like sodium hydroxide to form salts and water.

$$RCOOH + NaOH \rightarrow RCOONa + H_2O$$

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

(iii) Reaction with sodium bicarbonate: Carboxylic acids are weaker than mineral acids like sulphuric acid or nitric acid and able to react with weaker bases like carbonates and bicarbonates to evolve carbon dioxide with water.

$$RCOOH + NaHCO_3 \rightarrow RCOONa + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2\uparrow$$

The reaction with sodium bicarbonate is also used as functional group determination of carboxylic acid.

8.10 SUMMARY

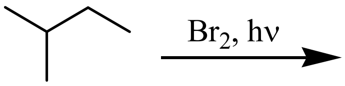
In this chapter we will able to understand the organic compounds of aliphatic and aromatic organic compound basically defined the physiochemical properties of various organic compounds like alkanes, alkenes, alkynes, alcohols, carbonyl compounds like aldehyde, ketones and carboxylic acids along with their preparations by various methods.

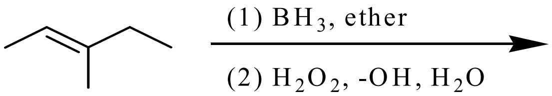
8.11 TERMINAL QUESTIONS

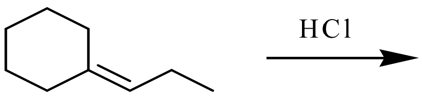
A. Long answer type questions

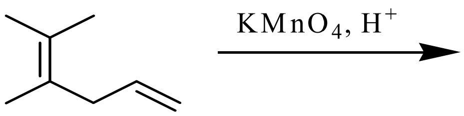
A. Alkenes:

1. Provide the major product for each of the following reactions, showing stereochemistry where appropriate.

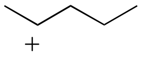




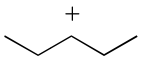




2. The intermediate of the following reaction



and



3. What are the possible products when 2-chloro-2-methylbutane is

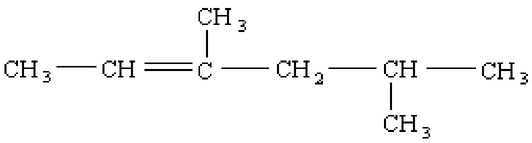
reacted with:

(i) aqueous potassium hydroxide

(ii) a solution of potassium hydroxide in ethanol

(iii) a solution of sodium ethoxide in ethanol?

4. Name the following compound.



$$CH_3-CH=\overset{\overset{\large CH_3}{|}}{C}-CH_2-\underset{\underset{\large CH_3}{|}}{CH}-CH_3$$

5. Name the straight-chain constitutional and stereoisomers of butene (C_4H_8).

B. Alkynes:

Discuss Kolbe's electrolytic method to prepare acetylene.

1. Convert Chloroform into acetylene.
2. Alkynes do not exhibit geometrical isomerism while alkenes do so why?
3. Alkynes are less reactive than alkenes towards electrophilic addition reaction why?
4. Convert acetylene into ethanol.
5. Why does acetylene behave like a weak acid?

6. Alkynes undergo both electrophilic and nuclephilic addition reactions. Why?

C. Alcohols:

1. Explain why Alcohols are acidic in nature.
2. Write the mechanism of dehydration of ethyl alcohol with conc. H_2SO_4.
3. Why boiling point of alcohols is higher than that of alkanes of corresponding molecular weight.

D. Ethers:

1. Discuss polarity of ethers and compare it with the polar characters of alcohols.
2. Why Grignard reagent is prepared in ether discuss with reaction and reason.
3. Write a note on: Williamson's synthesis.
4. How is diethyl ether prepared in laboratory? How does it react wit (i) PCl_5 (ii) O_2 (iii) cold concentrated H_2SO_4 (iv) Con. HI
5. Discuss different properties and uses of ether
6. Give general methods of preparation and properties of epoxides.

E. Aldehyde:

1. Writing the structures arrange the following compounds in increasing order of their reactivity in nucleophillic addition reaction.

(a) Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde

Ans :- p tolualdehyde < Benzaldehyde < p-Nitrobenzaldehyde

2. What is the structure of carbonyl group? How does it react with (i) HCN (ii) $NaHSO_3$
3. What happens when formaldehyde is treated with NaOH ?
4. Explain the reaction mechanism when acetaldehyde is treated with NaOH ?
5. Carbonyl compounds undergo nucleophillic addition reactions, why?
6. Write note on :-

(a) Witting reaction

(b) Reformatsky reaction

(d) MPV reaction

(e) Perkin reaction

7. What happens when Aldehydes combine with alcohols in the presence of dry HCl ?

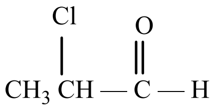
8. Aldehydes are powerful reducing agents. Explain.

9. α hydrogen of aldehydes is acidic. Discuss.

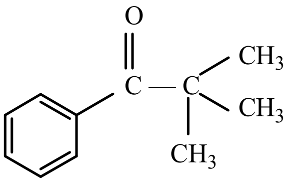
10. Different reagents give different products on reduction of carbonyl compounds. Elaborate it.

F. Ketones:

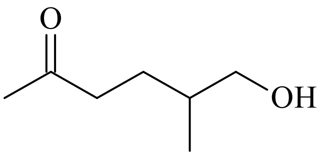
1. Write IU PAC names of following compounds :-

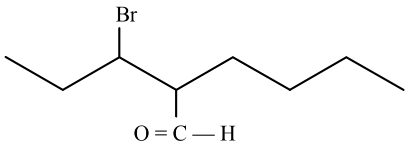


$\mathrm{CH_3\,\overset{Cl}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H}$,



,



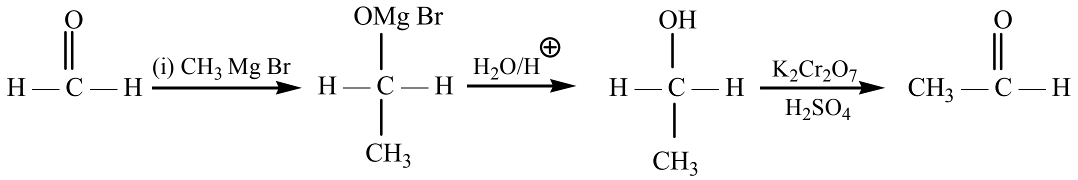


Ans: - 2-chloropropanal, 2, 2-dimethyl-1-phenyl propanone, 6-hydroxy -5 methyl -2-hexanone, 2-[1-bromoprophyl] hexanal.

2. Why boiling points of aldehydes and ketones are higher than those of corresponding alkanes?

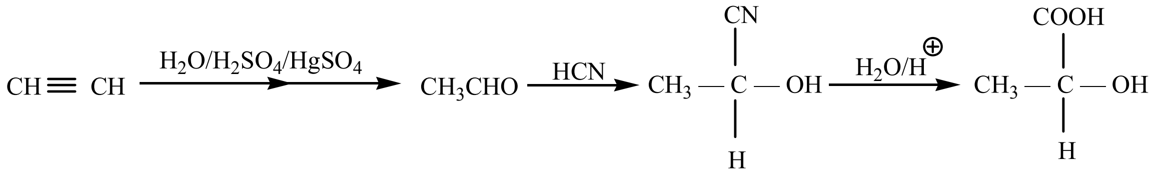
3. Why lower aldehydes are soluble in water?

4. How will you synthesize acetaldehyde from formaldehyde?



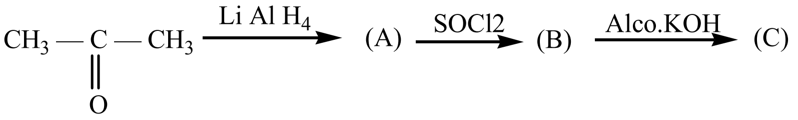
$$H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{\text{(i) } CH_3MgBr} H-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}}-H \xrightarrow{H_2O/H^{\oplus}} H-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-H \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{O}{\|}}{C}-H$$

5. How will you synthesize lactic acid from acetylene?



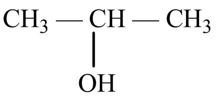
$$CH\equiv CH \xrightarrow{H_2O/H_2SO_4/HgSO_4} CH_3CHO \xrightarrow{HCN} CH_3-\underset{\underset{H}{|}}{\overset{\overset{CN}{|}}{C}}-OH \xrightarrow{H_2O/H^{\oplus}} CH_3-\underset{\underset{H}{|}}{\overset{\overset{COOH}{|}}{C}}-OH$$

6. Identify (A), (B) and (C)



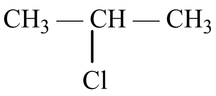
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{Li\,Al\,H_4} (A) \xrightarrow{SOCl2} (B) \xrightarrow{Alco.KOH} (C)$$

(A)



$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

(B)



$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$

(C) $CH_3-CH=CH_2$

7. How did you distinguish formaldehyde from acetaldehyde?

G. Carboxilic acids:

1. How can you synthesize carboxylic acids from cyanides?
2. Write a short note on the acid strength of carboxylic acids.
3. Write the physical properties of carboxylic acids.
4. Why the monochloroacetic acid is stronger than acetic acid?
5. Explain benzoic acid is more acidic than phenol.
6. Compare the acidic strength of acetic acid and halo acids.
7. What are carboxylic acids? Describe the structure and nomenclature of aliphatic and aromatic carboxylic compounds.
8. What are carboxylic acids? Give the general methods of preparation of carboxylic acids.
9. Describe the reduction and decarboxylation reactions of carboxylic acids.

10. What are halo acids? Give the general methods of preparation and chemical properties of halo acids.

11. How will you obtained?

    a. Carboxylic acids from acyl chlorides
    b. Carboxylic acids from aldehydes
    c. Carboxylic acids from alkyl benzene
    d. Carboxylic acids from nitriles

B. Multiple choice questions (MCQ)

1. Ethanol containing some methanol is called

A. Absolute sprit B. Rectified sprit

C. Power alcohol D. Methylated sprit

2. Glycerol is a:

A. Primary alcohol B. Monohydric alcohol

C. Secondary alcohol D. Trihydric alcohol

3. Which of the following can work as a dehydrating agent for alcohols?

A.H_2SO_4 B.Al_2O_3

C.H_3PO_4 D. All.

4. Primary and secondary alcohols on action of red hot copper give

A. Aldehydes and ketons respectivelyB.Ketones and aldehydes respectively

C. Only aldehydes D.Only ketones

5. Which one has highest boiling point?

A. Butan-2-ol B.Ethane

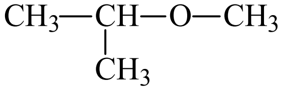
C.Butane D.Pentane

6. Which of the following has maximum hydrogen bonding?

A. Ethyl amine B.Ammonia

C. Ethyl alcohol D.Diethyl ether

7. IUPAC name of the following compound is



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-CH_3$$

A. 1-methoxy-1-methylethane B. 2-methoxy-2-methylethane

C. 2-methoxypropane D. isopropylmethyl ether

8. Ethers can exhibit isomerism

A. Metamesism B. Functional isomerism

C. Both A and B D.Geometrical

9. Ethers have:

A. Pungent odour B. Pleasant odour

C. Fishy odour D.Vinegar odour

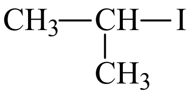
10. When diethyl ether is treated wit hot HI, it forms:

A. Ethyl iodide B. Acetyl iodide

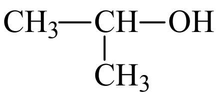
C. Propyl iodide D.Ethyl alcohol

10. Ethylisopropyl ether reacts with cold HI gives:

A. $CH_3CH_2CH_2I + CH_3CH_2OH$

B. 

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-I + CH_3CH_2OH$

C. 

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH + CH_3CH_2I$

D. $CH_3CH_2CH_2OH + CH_3CH_2I$

11. Because of following properties ether are used as inert (reaction) medium.

A. Neutral and good solvent B. Neutral and bad solvent

C. Acidic and good solvent D. Basic and good solvent

12. Ethoxy ethane is hydrolysed by using

A. KOH_{aq} B. H_2O

C. $NaHCO_3$ D. dil H_2SO_4 under pressure

13. Which of the following cannot be considered as use of ether?

A. Inert solvent B. Anaesthetic

C. Antipyretic D.Solvent of oil, fats and resins

14. When a mixture of ethyl alcohol and con. H_2SO_4 are heated at 413^0K gives diethyl ether. This reaction is:

A. Dehydration B.Desulphonation

C. Intermolecular dehydration D. Intramolecular dehydration

15. With boiling water or steam diethylether gives.

A. $(C_2H_5)_2SO_4$ B. C_2H_5OH

C. $CH_2{=}CH_2$ D.$C_2H_5OH + C_2H_5HSO_4$

16. The carbon of carbonyl carbon is ___________ hybridised.

(a) sp^3 (b) sp^2 (c) sp (d) sp^3d

Ans. :- (b)

17. Boiling points of primary alcohols are __________ than the boiling points of corresponding aldehydes.

(a) higher(b) lower

Ans :- (a)

18. Aldehydes are prepared by the oxidation of _____________

(a) Primary alcohol (b) Secondary alcohol (c) Tertiary alcohol

Ans :- (a)

19. Melting points of aldehydes tend to __________ with increasing molecular weight.

(a) decrease(b) increase(c) remain unchanged

Ans :- (b)

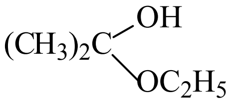
20. Aldehydes have ________ boiling points compared with those of alcohols.

(a) low(b) high

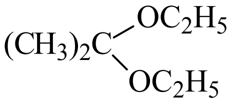
Ans. :- (a) low

21. Acetone is treated with excess of ethanol in the presence of HCl. The product obtained is

a.



b.



c. $CH_3CH_2CH_2COCH_3$

d. $CH_3CH_2CH_2COCH_2CH_2CH_3$

Ans. :- (b)

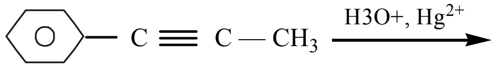
22. Clemmensen reduction of ketone is carried out in the presence of which of the following:-

(a) H_2 and Pt as catalyst(b) Glycol with KON(c) Zn – Hg with HCl

(d) Li Al H_4

Ans. :- (c)

23. Identify the product in reaction:-



(a) $C_6H_5CH_2CH_2CHO$(b) $C_6H_5COCH_2CH_3$(c) $C_6H_5CH_2COCH_3$

(d) C_6H_5 CO CO CH_3

Ans. :- (b)

24. Compound A react with HCN and forms cyanohydrin which on hydrolysis gives carboxylic acid acid. So compound A is –

(a) CH_3NH_2 (b) CH_3COCH_3(c) CH_3 CO_6 CH_5(d) C_6 H_5 OH

Ans :- (b)

25. The compound which forms acetaldehyde when heated with dilute NaOH.

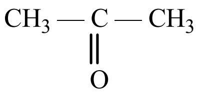
(a) 1, Chloroethane(b) 1, 1 dichloro ethane(c) 1, 2 dichloro ethane

(d) 1, 1, 1 trichloro ethane

Ans. :- (a)

26. An organic compound X is oxidized by using acidified $K_2 Cr_2 O_7$. Resultant product reacts with phenyl hydrazine but does not answer silver mirror test. So the possible compound X is

(a) $(CH_3)_2$ CHON (b) CH_3 CHO(c) CH_3 CH_2 OH(d)



$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

Ans. :- (a)

27. To distinct 2-pentanone from 3-pentanone ________ reagent should be employed.

(a) $K_2 Cr_2 O_7 / H_2 SO_4$(b) Zn – Hg / HCl(c) SeO_2

(d) Iodine / NaOH

Ans. :- (d)

28. In which of the following reactions new carbon – carbon bond is not formed-

(a) Cannizaro reaction(b) Wurtz reaction(c) Aldol condensation

(d) Benzoin condensation

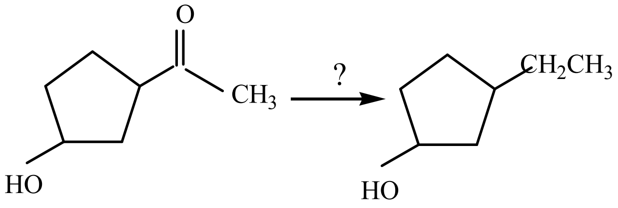
Ans. :- (a) (WB Jee 2009)

29. A strong base can abstract an a hydrogen from –

(a) Amine(b) Alkane(c) Alkene(d) Ketone

Ans. :- (d)

30.



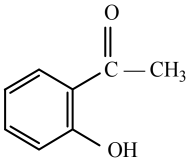
(a) Zn (Hg), HCl(b) NH_2 NH_2, OH(c) H_2, Ni

(d) $NaBH_4$

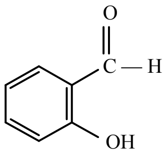
Ans.:- (b)

31. What is the correct structure for 2-hydroxy acetophenone?

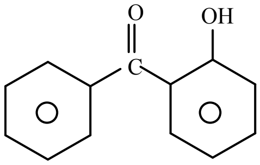
(a)



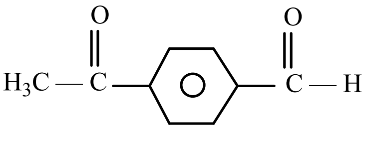
(b)



(c)

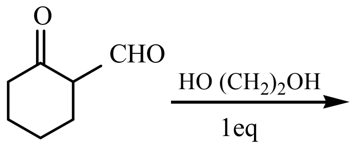


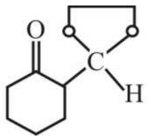
(d)

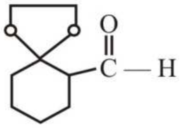


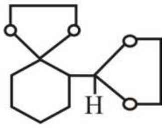
Ans. :- (a)

32. What is the major product of the following reaction ?



(a)


(b)


(c)


Ans. :- (a)

33. Cyclopentanol undergoes oxidation to give –

(a) Cyclopentene (b) Cyclophentanone (c) Cyclopentanal

Ans. :- (b)

34. Which of the following compounds gives positive iodoform test ?

(a) 3-Hexanone (b) 1-Pentanol (c) Acetone

(d) 3-Pentanone

Ans. :- (c)

35. Which functional group is present in a carboxylic acid?

(a) -COOH (b) –NH$_2$

(c) -RCOOR’ (d) –OR’

36. Which one of the followings is a monocarboxylic acid?

(a) Oxalic acid (b) Succinic acid

(c) Formic acid (d) Citric acid

37. What is the IUPAC name of HOOC (CHOH)$_2$ COOH ?

(a) 2-Hydroxypropionic acid (b) 2, 3-Dihydroxybutanedioic acid

(c) 2-Hydroxybutanedioic acid (d) Butanedioic acid

38. Carboxylic acids are more soluble in water than alcohols and ethers due to

(a) Their high molecular weight (b) Hydrogen bonding

(c) More reactive carboxyl carbon (d) Their acidic charecter

39. Carboxylic acid and alcohols both are formed hydrogen bonding with water but why carboxylic acids have higher boiling points than alcohols?

(a) Because acids are more reactive than alcohols.

(b) Because carboxylic acids are weak acids.

(c) Because alcohols are not ionized completely.

(d) Because the two molecules of a carboxylic acid form two hydrogen bonds.

40. Which of the following is the strongest acid?

(a) $CH_2ClCOOH$ (b) $CH_2BrCOOH$

(c) CH_2FCOOH (d) CH_2ICOOH

41. The weakest acid among the following is

(a) Cl_3CCOOH (b) $Cl_2CHCOOH$

(c) $ClCH_2COOH$ (d) CH_3COOH

42. Primary alcohols are oxidized with acidic $KMnO_4$ into

(a) Carboxylic acid (b) Amide

(c) Acid anhydride (d) Alcohols

43. Derivatives of carboxylic acids are hydrolyzed into

(a) Alcohols (b) Acyl chlorides

(c) Thioethers (d) Carboxylic acids

44. With $LiAlH_4$ the carboxylic acid reduced to

(a) Acids (b) Alcohols

(c) Amines (d) Ketones

UNIT 9: BIOMOLECULES

CONTENTS:

9.1 OBJECTIVES

After going through this unit you will be able to:

- Define carbohydrates,
- Differentiate and classify the three major groups of carbohydrates,
- Define anomers, mutarotatation, configuration and mechanism of osazone formation,
- Define Nucleic acids
- Define Structure of nuclocosides
- Define Ribonucleic acid (RNA)
- Differences between DNA and RNA

9.2 INTRODUCTION

Carbohydrates are a class of naturally occurring organic compounds of carbon, hydrogen and oxygen which are primarily produced by plants. They are extremely widespread in plants comprising upto 80% of dry weight. These are ultimate source of our food. In higher animals the simple sugar glucose is an essential constituent of blood and occurs in a polymeric form as glycogen in the liver and muscle.

In the green plants, carbohydrates are produced by a process called photosynthesis. This process involves the conversion of simple compounds CO_2 and H_2O into glucose ($C_6H_{12}O_6$) and is catalysed by green colouring pigment chlorophyll present in the leaves of plants. The energy required for this conversion is supplied by sun in the form of sunlight.

Carbohydrates are very useful for human beings. They provide us all the three basic necessities of life i.e., foog (starch containing grain), clothes (cellulose in the form of cotton , linen and rayon) and shelter (cellulose in the form of wood used for making our houses and furniture etc.). Carbohydrates are also important to the economy of many nations. For example, sugar is one of the most important commercial commotidies.

The term carbohydrates arose because the general formula for most of them could be written as $C_x\ (H_2O)_y$ and thus they may be regarded as hydrates of carbon. However, this definition was not found to be correct e.g., rhamnose, a carbohydrate, is having the formula $C_6H_{12}O_5$ while acetic acid having formula $C_2H_4O_2$ is not a carbohydrate. Simple carbohydrates are also known as sugars or saccharides (Latin: Saccharum; Greek : Sakcharon, Sugar) and the ending of the names of most sungars is –ose. Examples: glucose, fructose, sucrose, maltose, arabinose, etc.

Chemically, carbohydrates contain mainly two functional groups, carbonyl group (aldehyde or or ketone) and a number of hydroxyl groups. Accordingly carbohydrates are now defined optically active polyhydroxy aldehydes or polyhydroxy ketones or the compound that can be hydrolysed to either of them.

9.3 CLASSIFICATION AND NOMENCLATURE

9.3.1 Classification

Carbohydrates, in general, may be classified into two classes:

(i) **Sugars.** These are crystalline substances which are sweet and water soluble. For examples, glucose, fructose and cane sugar.

(ii) **Non-sugars**. These are tasteless, insoluble in water and amorphous. For example. Starch, cellulose, etc.

However, these days Carbohydrates are systematically classified into three major group:

(a) Monosaccharides. The simplest carbohydrates that cannot be hydrolysed into simpler carbohydrates, are called monosaccharides.depending upon whether they contain an aldehyde or keto groups, they may be called aldoses or ketoses. For example, a five carbon monosaccharide having aldehyde group is called aldopentose and six carbon monosaccharide containing a keto group is called keto-hexose. A few examples of monosaccharides are given below:

Aldotetroses. Erythrose and Threose; $CH_2OH(CHOH)_2\ CHO$.

Ketotetroses. Erythrulose, $CH_2OHCOCHOHCH_2OH$.

Aldopentoses. Ribose, arabinose, Xylose and Lyxose. $CH_2OH(CHOH)_3$ CHO.

All have a common molecular formula but different structures.

Ketopentoses. Ribulose and Xylulose; $CH_2OHCO(CHOH)_2$ CH_2OH.

Aldohexoses. Glucose, mannose, galactose; $CH_2OH(CHOH)_4$ CHO.

Ketohexoses. Fructose, Sorbose etc. $CH_2OHCO(CHOH)_3$ CH_2OH.

(b) Oligosaccharides. These are the carbohydrates which can be hydrolysed into a definite number of monosaccharide molecules. Depending upon the number of monosaccharides that are obtained from them on hydrolysis, they may be called di-, tri- or tetra-saccharides: For example:

Disaccharides: sucrose, lactose, maltose. All these have the same molecular formula $C_{12}H_{22}O_{11}$.

Trisaccharides: raffinmose ($C_{18}H_{32}O_{16}$).

Tetrasaccharides: stachyose ($C_{24}H_{42}O_{21}$).

(c) Polysaccharides. Carbohydrates that yield a large number of molecules (more than ten molecules) of monosaccharides on hydrolysis are called polysaccharides. The common examples are starch, cellulose, glycogen, etc.

9.3.2 Nomenclature

Carbohydrates contain hydroxy and aldehydic or ketonic groups. They are named according to IUPAC system of nomenclature

Compound	Common name	IUPAC name
$CH_2OHCHOHCHO$	Glyceraldehyde	2, 3-dihydroxy propanol
$CH_2OHCOCH_2OH$	Dihydroxyacetone	1,3-dihydroxy propanone
$CH_2OH(CHOH)_4$ CHO	Glucose	2,3,4,5,6-pentahydroxyhexanal
$CH_2OH(CHOH)_3COCH_2OH$	Fructose	1,3,4,5,6-pentahydroxyhexan-2-one

9.4 NUCLEIC ACIDS

Nucleic acids are colors, complex, amorphous compounds made up of three units : Nitrogenous bases (Purine or pyrimidine), sugar and phosphoric acid. These are obtained by the hydrolysis of nucleoproteins which is a class of conjugated proteins. Nucleic acids constitute the prosthetic group of nucleoproteins, whereas the protein protein part consists of protamines and histones. These are macromolecules of high molecular weight and are present in every living cell.

The nucleic acids are generally divided into two main groups, according to the nature of the sugar present:

The pentose nucleic acids or ribonucleic acids (RNA)

Deoxypentose nucleic acids or deoxyribonucleic acids (DNA).

RNA is found in all subdivisions of the cell, nucleus and cytoplasm, in particles and supernatant fluid. However, ribosomes are the richest in RNA followed by mitochondria. Because of their abundance in yeast, RNA is also called yeast nucleic acids or plasmonucleic acids; similarly DNA is called thymus nucleic acids or chromonucleic acids, because of their abundance in chromosomes (thymus).

The nucleic acids contain only six fundamental units. All the RNA contain ribose, a phosphoric acid group, and four nitrogen bases (adenine, guanine, cytosine, and uracil). All the DNAs contain-deoxyribose, a phosphoric acid group, and four nitrogen bases (adenine, guanine, cytosine, and thymine). The DNAs are macromolecules with molecular weight ranging from 6 million to 16 million, although in some cases very high molecular weight (120 million) has been reported. On the other hand, RNAs are generally much smaller with the molecular weight range of 20,000 to 40,000.

The following chart shows the nature of the products obtained by the stepwise hydrolysis of nucleic acids.

Nucleoproteins

↓

Nucleic acids + Proteins

↓

Nucleotides

↓

Nucleosides + Phosphoric acid

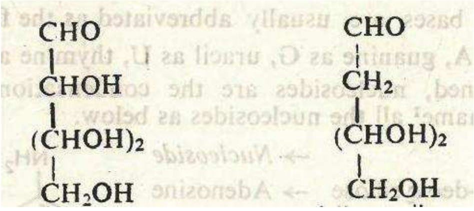
↓

Sugar-1-phosphate + Bases (Purines + Pyrimidines)

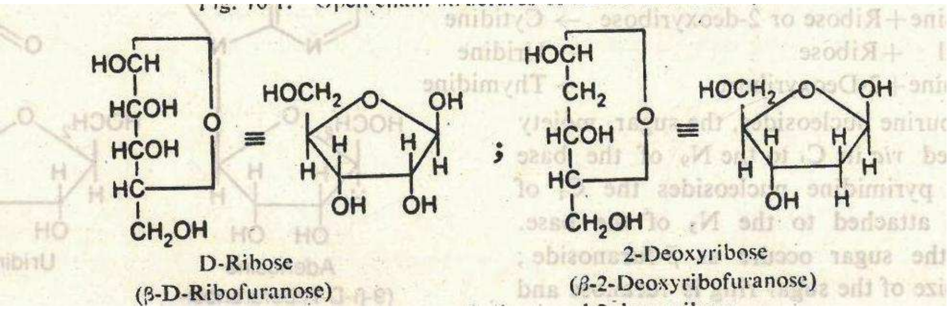
9.5 STRUCTURE OF NUCLOCOSIDES

These are the condensation products of a sugar and a base (nitrogenous) and are obtained by hydrolysis of nucleotides. Since we know that nucleosides on acidic hydrolysis give basis and sugar, therefore for knowing the structure of nucleosides we must have some knowledge about the structures of the various bases and sugars present in the nucleosides. It must be noted that pyrimidine nucleosides are much more stable to hydrolysis, unless the 4, 5-double bond is hydrogenated first by Raney nickel.

i) Sugars: Only two sugars have been isolated from the hydrolysates of nucleic acids ; both are pentoses : D-ribose and 2 - deoxy-D-ribose is present only in RNA whereas 2-deoxy-D-ribose is present only in DNA. The structure of these pentoses can be represented as below.



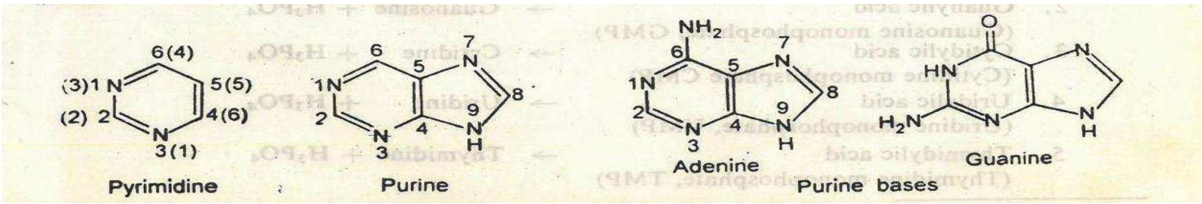
Open chain structures of ribose and 2-deoxyribose.



In the nucleic acids, both of the pentoses exits in the B-furanose form.

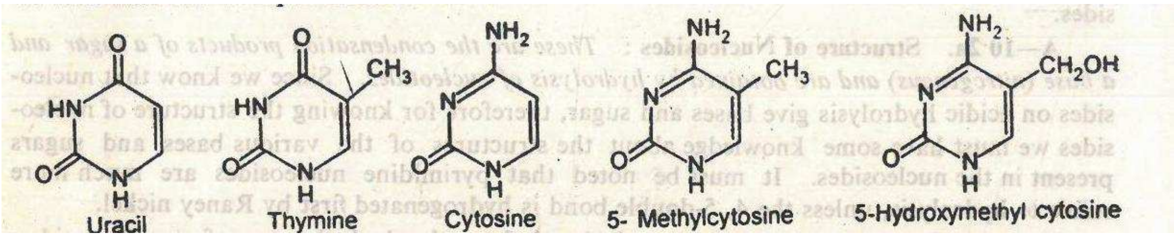
ii) Bases: Two types of bases have been isolated from the hydrolysis products of nucleosides; purines and pyrimidines.

The purine and pyrimidine bases are derivatives of the respective compounds purine and pyrimidine. The letter (pyrimidine) is a six-mimbered ring with two nitrogen and four carbon atoms, while the former (purine) consists of a pyrimidine ring fused with an imidazole ring. The structures and the numbering in the nuclei of the two present bases are given above.



The most common purine bases found in nucleic acids are adenine and guanine.

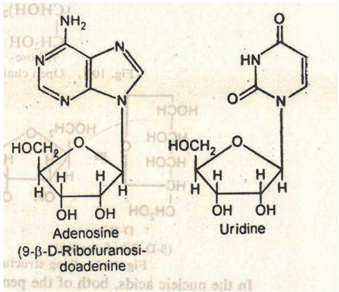
Similarly, the pyrimidine bases are uracil, thymine, cytosine, 5-methyicytosine and 5-hydroxymethyl cytosine. The last two pyrimidine bases are rarely found. The structure of each base can be represented as below.



Out of the five important bases (adenine, guanine, uracil, thymine and cytosine(, adenine, guanine and cytosine occur in both thy types of the acids, i.e. R.N.A. as well as in D.N.A. whereas uracil is present only in R.N.A. and thymine only in D.N.A. for convenience, the purine and pyrimidne bases are usually abbreviated as the first letter of the name. Thus adenine is designated as A, guanine as G, uracil as U, thymine as T, and cytosine as C.

As already mentioned, nucleosides are the condensation products of the bases with sugar; so we can now name all the nuclecosides as below.

Base		+Sugar		Nucleoside
1. Adenine	+	Ribose or 2-deoxyribose	→	Adenosine
2. Guanine	+	Ribose or 2-deoxyribose	→	Guanosine
3. Cytosine	+	Ribose or 2-deoxyribose	→	Cytidine
4. Uracil	+	Ribose	→	Uridine
5. Thymine	+	2-deoxyribose	→	Thymidine



Structure of Necleoside

In purine nucleosides, the sugar moiety is attached via its C1 to the N9 of the base while in pyrimidine nucleosides the C1 of sugar is attached to the N3 of the base. Further the sugar occurs as B-furanoside; i.e. the size of the sugar ring is furanose and its configuration is B.

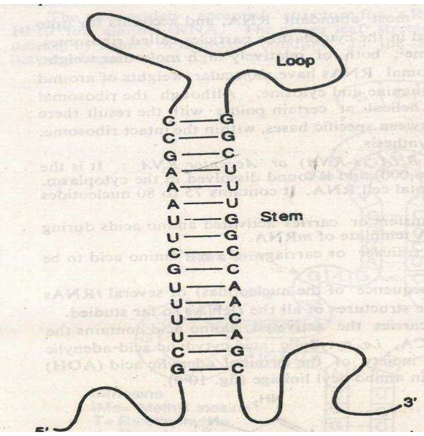
9.6 RIBONUCLEIC ACID (RNA)

Ribonucleic acid, like DNA, is a long unbranched macro-molecule consisting of nucleotides joined by 3' – 5' phosphodiester bonds. Although, RNA shares many features with DNA, it has several specific differences.

1. In RNA, the sugar moiety to which the phosphate and nitrogen bases are attached is ribose. (Recall that in DNA, the sugar moiety is 2-dioxy – ribose).
2. In RNA, one of the pyrimidine base is uracil (In place of thymine of DNA), although other three bases) *viz*, adenine, guanine and cytosine) are common in RNA as well as DNA. Uracil, like thymine of DNA, can form a base pair with adenine by two hydrogen bonds.
3. RNA exists as a single-strand, whereas DNA exists as a double-stranded molecule. However, given the proper complementary base sequence with opposite polarity (direction), the single strand of RNA may fold back on itself like a hairpin (Stem loop) and thus acquire the double-standard pattern. In the region of hairpin loops, A pairs* with U and G pairs* with C. However, the base pairing in RNA hairpins is frequently imperfect. Some of the opposing

bases may not be complementary and one or more base along a single strand may be lcoped out to facilitate the pairing of others.

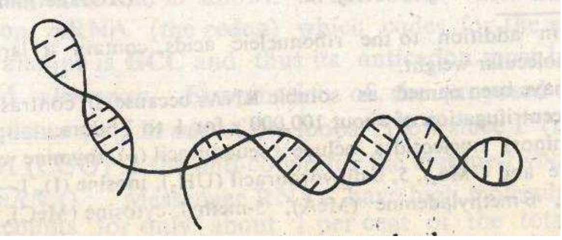
4. Since RAN is a single stranded molecule, its guanine content does not necessary equal its cytosine content and its adenine content does not necessarily equal its uracil content



Digarammatic representation of the secondary structure of single-stranded RNA molecule.

5. RNA can be hydrolyzed by alkali to 2',3'-cyclic diesters of the mononucleotides via an intermediate compound called 2',3',5'-triester. This intermediate can't be formed in alkali-treated DNA because of the absence of a 2'-hydroxyl group in its molecule. Thus RNA is alkali labile, while DNA is alkali stable. The alkali lability of RNA is useful dia-gnostically and analytically.

The structure of RNA is believed to be similar to that of DNA, except for the difference in its pentose (D-ribose) unit and the heterocylic base (uracil in place of thymine). Like DNA, these are also polynucleotides linked together by phosphate diester bonds between 3' and 5' position of ribose moieties. The purine bases adenine and guanine and the pyrimidine base cytosine and uracil are present. But they are not present in equimolar amounts. The molecule is less organized than the DNA molecule and with a few exceptions occurs as a single strand. There is internal hydrogen bounding within the chain to keep it in a coiled position. A helical pattern is formed not between two strands, but by the same coiled strand folding back on itself.



Single stranded RNA molecule.

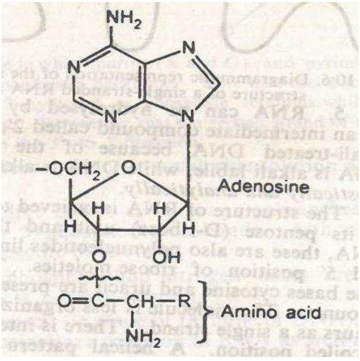
Although RNA exists mainly in the cytoplasm, about 10-20 per cent of cell RNA is found in the nucleus of the cell nucleus. There are three classes of ribonucleic acids which differ chiefly in molecular weight and base composition.

a) **Ribosomal RNA (r-RNA) :**

This the most abundant R.N.A. and accounts for upto 80 percent f the total cell RNA. It is located in the cytoplasmic particles called ribosome's. Two molecules of RNA occur in each ribosome, both of relatively high molecular weight, two molecules of RNA occurs in each ribosome, both of relatively high molecular weight, *viz* $0.7X10^6$ and 1.6×10^6. In general, ribosomal RNAs have molecular weights or around 0.5 to 1 million and contain relatively much guanine and cytosine. Although the ribosomal RNAs are also single-standard, the strands are helical at certain points with the result there is tight packing owing to hydrogen bonding between specific bases, within the intact ribosome. Ribosomal RNAs provide the site of protein synthesis.

b) **Transfer RNA (t-RNA) or Soluble2 RNA (s-RNA) or AcceptorRNA:**

It is the smallest molecular species of RNA (mol. Wt.-6,000) and is found dissolved in the cytoplasm. It accounts for about 15 to 20 per cent of the total cell RNA. It contains 75 to 80 nucleotides and relatively a lot of the more unusual bases[3].



Attachment of amino acid to adenosine (AOH) terminus of RNA

As the name indicates, transfer RNA transfers or carries activated amino acids during protein synthesis to the proper site on the RNA template of mRNA.

There is specific tRNA molecule for the transfer or carriage of each amino acid to be incorporated into proteins.

The entire primary structure (that is the sequence of the nucleotides) of several tRNAs are known. There are certain similarities in the structures of all the tRNAs so far studies.

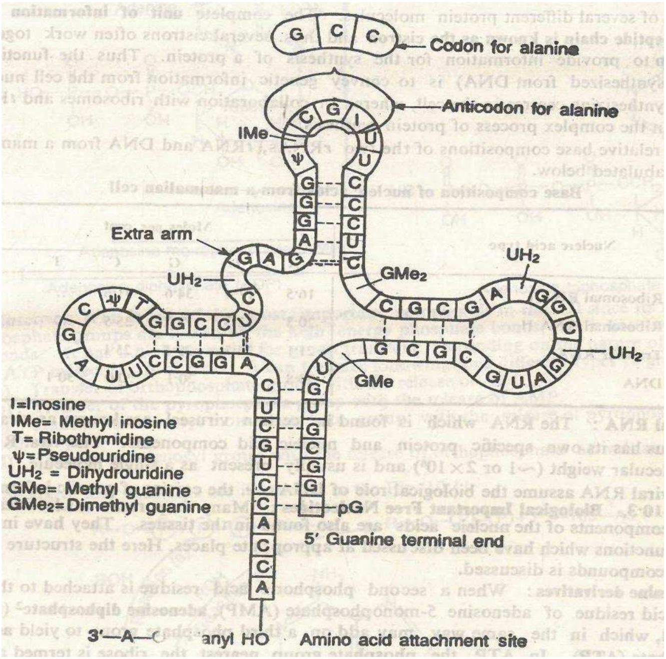
(i) The 3’ – end of the molecules which carries the activated amino acid contains the same trinucleotide with the base sequence CCA, i.e. cytydylic acid-cytydylic acid-adenylic acid. The C_3 hydroxyl group of the ribose moiety of the terminal adenylic acid (AOH) attaches the amino acid (to be transferred) via an amino acyl linkage as show in figure.

(ii) A guanine nucleotide (designated as pG) frequently occurs at the 5’_phosphate terminus of the tRNA molecule.

(iii) Although thymine is generally found only in DNA, a thymine containing nucleotide is found at the 23rd position in the tRNA molecule.

(iv) The nucleotide composition of tRNA is characterized by the presence of several minor base-containing nucleotides.

The most widely accepted structure for t-RNA is clover leaf which is shown in fig. for alanine tRNA. The clover leaf structure provides a maximum amount of base pairing by means of hydrogen bonding. In the loop regions, there is no hydrogen bonding between bases.



General clover leaf structure for alanine-tRNA from yeast.

Alanine-tRNA consists of 77 nucleotides (Holley and co-workers) and has 17 GC, 2 AU, and 1 GU base pairs. The trinucleotide which is specific for the amino acid to be carried is present in one of the three bases on mRNA (the codon) which codes for the amino acid carried. For example, the Condon for alanine is GCC and thus its anticodon must be CGG because G is complementary to C and vice versa. Examination of the proposed structure for the alanine-tRNA shows the sequence CGI (CGG) is the anti-codon for the alanine-tRNA.

(c) Messenger RNA (mRNA): Messenger RNA have high molecular weight (Perhaps upto several million) and accounts for only about 1 percent of the total RNA of the cell. These RNAs are unstable and short lived and their synthesis is directed by DNA, and thus in base composition they resemble a strand of DNA. These are synthesized in the nucleus and then get transferred to cytoplasm.

One of the strands of DNA acts as a template for synthesis of mRNA and thus a message may be derived only from certain discrete sections of the DNA strand. In other words. An active strand of DNA carries information for the synthesis of several different protein molecules. The complete unit of information for the protein peptide chain is known as the cistron and thus several of a protein. Thus the function of a mRNA (synthesized from DNA) is to convey genetic information from the cell nucleus to protein-synthesizing centers in the cell, where, in collaboration with ribosome and tRNA, it engages in the complex process of protein synthesis.

6. Viral RNA: The RNA which is found in certain viruses1 are known as viral RNA. Each virus has its own specific protein and nucleic acid components. The viral RNA has high molecular weight (-1 or 2 X 106) and is usually present as a single molecule. In these viruses viruses viral RNA assume the biological role of DNA, i.e. the carrier of genetic information.

9.7 FUNCTION OF NUCLEIC ACIDS

The main functions of nucleic acids are:

1.DNA replication.

2.Protein synthesis

1. Replication of DNA: One of the most important properties of DNA is that it can make exact copies of itself. This process is called replications.

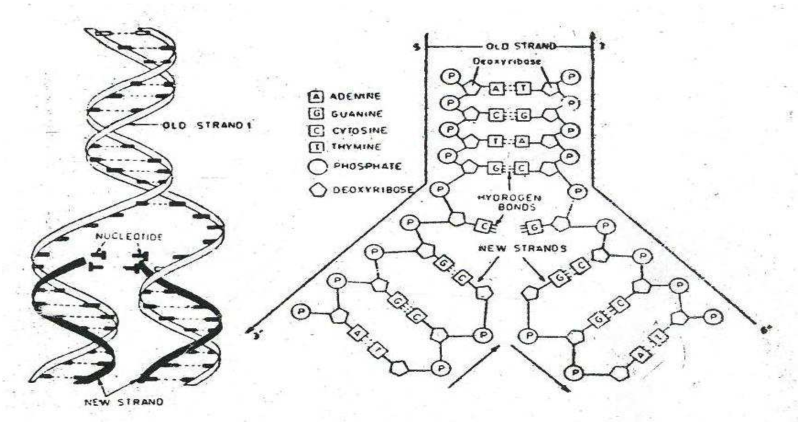
Replication is not quite the same as duplication. A duplicate is simply an exact copy of an original; a replica is a newly created structure made by using the original as a model or guide. The replication process is the very basis of life.

The replication of DNA can be explained most simply by assuming that the two strands separate by breaking the hydrogen bonds. Each single strand (also called primer) has now an exposed row of bases that serves as a template. The bases of free deoxyriboncleotides (monomers) form hydrogen bonds with these exposed bases. The template strand dictates the sequence in which the free nucleotides are assembled, i.e. the bonds can only be made between complementary base pairs (A-T, T-A, C-G, G-C) and thus a complementary chain to the template is formed. For example, if a segment of the template has the arrangement ATTGACAA from the free 5' to the free 3' end, the newly synthesized chain will be TAACTGGT from the free 3' to the free 5 end. As each strand produces its complementary strand, the two newly formed strands combine into a DNA molecule identical to the original.

The complex chemistry of replication is catalyzed by several DNA polymereses and DNA ligase.

Replication ensures that the genes, which are segments of the DNA molecule, are present in identical sets in all cells of the body or an individual. DNA fulfills the requirement of a genetical material, i.e., the ability to replicate.

Replication of DNA is shown diagrammatically as :



1. **Protein Synthesis:** Proteins are built up from about 20 amino acids. The sequence of amino acids has a bearing on the properties of a protein and is characteristic for a particular protein.

The basic mechanism of protein synthesis is that DNA makes RNA which in turn makes protein.

9.8 GENETIC CODE

It has been studied that the genetic information for protein synthesis is coded as a definite sequence of nucleotides in *m*-RNA, which in turn is derived from DNA, and thus indirectly in DNA. There is a specific sequence of three bases for a particular amino acid then as much as sixty four (4^3=64) such combinations are possible and thus the 20 different amino acids can be easily accommodated. These referred to as triplets. Now it was Nirenberg and Khorana who determined this specificity between a triplet base sequence and the amino acid and thus a definite triplet was named as the triplet code or codon of a particular amino acid. Each codon presumably forms base pairs with three complementary nucleotides of the t-RNA specific for the same amino acid. The portion of the t-RNA molecule that cobines with the m-RNA are known as anticodon.

The complete dictionary, codons to amino acids, is presented in the following table.

Table the Genetic Code

5'-OH terminal base	**Middle base**				**3'-OH terminal base**
	U	**C**	**A**	**G**	
U	Phe	Ser	Tyr	Cys	U
	Phe	Ser	Tyr	Cys	C
	Leu	Ser	Chain termination signal.	Chain term. signal	A
	Leu	Ser	Chain termination signal	Try	G
C	Leu	Pro	His	Arg	U
	Leu	Pro	His	Arg	C
	Leu	Pro	Gln	Arg	A
	Leu	Pro	Gln	Arg	G
A	Ile	Thr	Asn	Ser	U
	Ile	Thr	Asn	Ser	C
	Ile	Thr	Lys	Arg	A
	Met[1]	Thr	Lys	Arg	G
G	Val	Ala	Asp	Gly	U
	Val	Ala	Asp	Gly	C
	Val	Ala	Glu	Gly	A
	Val	Ala	Glu	Gly	G

It was found that the triplet code is degenerate, i.e. there may be more than one triplet code for a particular amino acid. For example, UUU and UUC both are the codons for phenylalanine, while there are six codons : UUA, UUG, CUU, CUC, CUA and CUG, for leucine.

9.9 DIFFERENCES BETWEEN DNA AND RNA

1.	DNA is the usual genetic material.	It is the genetic material of some viruses.
2.	Most DNA is found in the cytoplasm of the cell.	Most RNA, although synthesized in the nucleus by DNA, is found in the cytoplasm of the cell.
3.	DNA is usually double-stranded. In certain viruses, DNA is single strands, e.g., X174.	Most cellular RNA is single stranded. However, some viruses, e.g., Reovirus have double-stranded RNA.
4.	There is only one general structure for the DNA molecule.	There are three distinct RNA species.
5.	DNA is composed of a large number of nucleotides upto 4.3 million.	RNA is composed of fewer nucleotides, up to 12,000.
6.	In DNA, the pentose sugar is deoxyribose.	In RNA, the pentose sugar is robose.
7.	The common organic bases found in DNA are adenine, guanine, cytosine and thymine.	The common organic bases found in RNA are adenine, guanine cytosine and uracil.
8.	In DNA, adeninne pairs with thymine and guanine with cytosine.	In RNA, adenine pairs with uracil and guanine with cytosine.
9.	Pairing of bases is found throughout the length of the molecule.	Pairing of bases is found only in the helical region.
10.	DNA on replication forms DNA and on transcription forms RNA.	Generally, RNA does not replicate or transcribe. In certain cases, RNA can synthesize a RNA chain.
11.	Genetic messages are generally encoded in DNA.	The main function of RNA is to translate messages encoded in DNA into proteins.
12.	Most of the DNA has been found in the	Most of the RNA has been found on the

	chromosomes. Some DNA has also been found in the cytoplasm, e.g., in mitochondria and chloroplasts.	chromosomes and found in the nucleolus and cytoplasm. rRNA and rRNA are also found on the chromosomes and found in cytoplasm.

9.10 SUMMARY

Nucleic acids are high molecular weight polymers; there are constituents of practically all cells. In this unit we study the structure of nucleic acid. As nucleic acids are complex compound thus their structure studied with the structure of their component. In this unit we studied the structure of each component of nucleic Acid. We also discuss the different types of RNA present in the cells. In this unit we studied the DNA as a genetic material with structure also.

9.11 TERMINAL QUESTIONS

1. What is nucleic Acid? How do you say that nucleotides are energy carriers?
2. What do DNA and RNA stand for? What are points of different between the two?
3. What do you know about the structure of DNA? What is meant by replication of DNA?
4. What are various functions of DNA?
5. Define two following terms. (a) Nucleotide (b) Nucleoside.
6. Draw the structure of Nucleotide base.
7. Briefly outline the functional role of:

   (a) Messenger RNA (b) Transfer RNA (c) Ribosomal RNA?

8. What is the relationship between each of the following?

(a)Ribose and deoxyribose.

(b)A nucleoside and a nucleotide.

(c) A nucleotide and nucleic Acid.

9. Name the various bases present in DNA and RNA.

10. Write a note on the structure of RNA and DNA.

11. Define and classify carbohydrates with suitable examples.

UNIT 10: STATES OF MATTER

CONTENTS:

10.1 OBJECTIVES

After studying this chapter we are able to discuss the following:

- Postulates of kinetic theory of gases
- Derivation of kinetic gas equation
- Derivation of gas laws from kinetic gas equation
- Von Der Waal's equation of state
- Intermolecular forces
- Structure of liquids
- Characteristic properties of liquids
- Definition of space lattice and unit cell
- Structural differences between solid, liquid and gases

10.2 INTRODUCTION

Amongst the three common states of matter, the gaseous state is simplest. The laws of gaseous behaviour are more uniform and are better understood. The well known laws of gaseous behaviour are Boyle's law, Charle's law Graham's law, Dalton's law and Avogadro's law. There was no theoretical background to justify them. In the nineteenth century, however, Kronig, Clausius, Maxwell and Boltzmann developed a theory known as kinetic molecular theory of gases, which provided sound theoretical basis for the various gas laws.

In contrast with solids and liquids gases occupy the same volume as that of the closed vessel, they are characterised by low density and high compressibility.

The characteristic properties of gases are given below.

1. No definite shape and volume. Gases occupy all available space i.e. the shape and volume of the container in which they are filled.
2. Expansibility. Gases have limitless expansibility. They expand to fill the entire vessel they are placed in.
3. Compressibility. Gases are easily compressed by application of pressure.

4. Diffusibility. Gases can diffuse rapidly through each other to form a homogeneous mixture.
5. Pressure. Gases exert pressure on the walls of the container in all direction. You can site the example of a gas balloon.
6. Effect of heat. When a gas confined in a vessel is heated, its pressure increases. Upon heating in a vessel fitted with a piston, volume of the gas increases.

10.3 POSTULATES OF KINETIC THEORY OF GASES

It was earlier observed that the gas laws were based on experimental observations. The theoretical foundation or mathematical representation was missing. However several workers studied the properties of gases and found that the gases are essentially composed of freely moving molecules. The basic ideas of the workers were mentioned to explain the behaviour of the gases called the kinetic theory of gases. This theory succeeded to attain a rigid mathematical form due to the efforts of Joule, Kronig, Clausius, Maxwell, Boltzmann and many others. The main postulates of kinetic theory of gases may be given as follows.

1. Every gas consists of large number of tiny particles called point masses i.e. the actual volume of molecules is negligible when compared to the total volume of the gas. For the same gas, all molecules are of same size and mass.
2. The gas molecules are always in a state of rapid zig-zag motion in all directions. These molecules collide with each other and with the walls of the containing vessel.
3. A molecule moves in a straight line with uniform velocity between two collisions.
4. The molecular collisions are perfectly elastic so that there is no net loss of energy when the gas molecules collide with one another or against the walls of the vessel.

   Suppose two molecules collide having same mass m. Before collision the velocity of one molecule is v_1 and velocity of other molecule is v_2 and after collision the velocity of the molecules changes from $v_1$to $v_1^{/}$ and from v_2 to $v_2^{/}$ then if the collisions are elastic there is no loss of kinetic energy. This can be expressed as follows.

   Total kinetic energy of two molecules before collision is

   $\frac{1}{2} m_1 v_1^2 + 1/2\ m_2 v_2^2$

   And after collision total kinetic energy of both the molecules is

½ $m_1 v_1^{/2}$ + ½ m $v_2^{/2}$

If ½ $m_1 v_1^2$+1/2 $m_2 v_2^2$ = ½ $m_1 v_1^{/2}$ + ½ $m_2 v_2^{/2}$

i.e. total kinetic energy before collision is equal to total kinetic energy after collision then the collision is said to be an elastic collision.

5. There are no attractive forces operating between molecules or between molecules and the walls of the vessel in which the gas has been contained. The molecule move independently of one another.
6. The pressure of the gas is the hits recorded by the molecules on the walls of the container in which the gas is contained.
7. The average kinetic energy of gas molecules is directly proportional to absolute temperature. This means that the average kinetic energy of molecules is the same at a given temperature.

This must be clear to you that all the above postulates are applicable to ideal gases only i.e. the gas which obey Boyle's and Charle's law under all conditions of temperature and pressure. These are only approximately valid for real gases.

10.3.1Derivation of kinetic gas equation

Suppose a volume of gas enclosed in a cubical vessel (fig 2.2) at a fixed temperature.

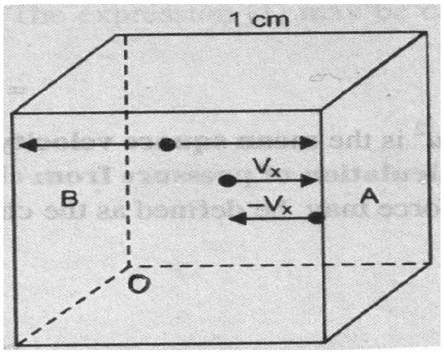


fig 10.1

Suppose that :

the length of each side of cube = l cm

the number of gas molecules = n

the mass of one molecule= m

the velocity of a molecule= v

Let us consider one single molecule of a gas can be evaluated by calculating the momentum during collisions.

According to kinetic model the molecules of the gas are moving in straight lines in all possible directions. They collide with one another frequently as also with the walls of the container. Since their mutual collisions are perfectly elastic and do not involve the loss of energy, these may be neglected. Here we will, therefore, assume that gas molecules move in all directions but rebound whenever they strike the wall of the container. Now you proceed to derive kinetic gas equation in the following steps

According to the kinetic theory, a molecule of a gas can move with velocity v in any direction velocity is a vector quantity can be resolved into components v_x, v_y, v_z along the X, Y and Z axes. These components are related to velocity v by the following expression.

$v^2 = v_x^2 + v_y^2 + v_z^2$ ....(1)

Let us consider a molecule moving in ox direction between opposite faces A and B. It will strike the face A with velocity v_x and rebound with velocity $-v_x$. To hit the same face again the molecule must travel l cm to

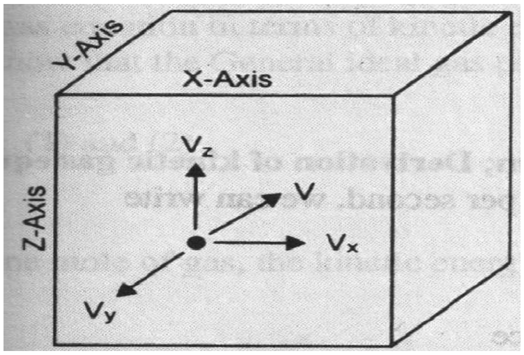


Fig 10.2

Collide with opposite face B and then again l cm to return to face A. Therefore time taken between two collisions can be calculated as follows

The molecule travels v_x cm in 1 sec

hence 1 cm in $1/v_x$ sec

And 2l cm in $2l/v_x$ sec ....(2)

In $2l/v_x$ sec molecule suffers 1 collision

In 1 sec no of collisions = $v_x/2l$ ....(3)

Each impact of the molecule on the face A causes a change of momentum which is mass x velocity.

Momentum of the molecule before impact = mv_x

Momentum of the molecule after impact = - mv_x

Hence change of momentum = $mv_x - (-mv_x) = 2mv_x$

But the number of collision per second on face A= $v_x/2l$

Therefore total change of momentum per second on face A caused by one

Molecule = $2mv_x \text{ x } v_x/2l$

$= mv_x^2/l$ ....(4)

As there are two faces along x- direction, total change of momentum per second considering both the faces along x-direction will be

$2mv_x^2/l$ ....(5)

This is change of momentum caused by one molecule along x-direction. The change of momentum caused by one molecule along y- direction per second will be $2mv_y^2/l$

and change of momentum caused by one molecule along z- direction per second will be $2mv_z^2/l$

Total change of momentum caused by one molecule considering along three direction will be

$2mv_x^2/l + 2mv_y^2/l + 2mv_z^2/l$

$= 2m/l\ (v_x^2+v_y^2+v_z^2)$

$= 2mv^2/l$ ....(6)

Since there are n molecules in the vessel then total change of momentum due to n molecules will be

$2mnv^2/l$ ....(7)

v^2 = mean square velocity

Since change of momentum per second is force

Hence force = $2mnv^2/l$

Since pressure = Total force/Total area

Since there are six faces in a cube, area of each cube is l^2. Hence total area is $6l^2$

Then pressure = $2mnv^2/l \text{ x } 1/6l^2$

$= mnv^2/3l^2$

As l^2= volume V

Hence pressure $P= 1/3\ mnv^2/V$ ....(8)

This is known as Kinetic gas equation. This equation has been derived for a cubical vessel. It is equally valid for vessel of any shape. The available volume in the vessel may be considered as made up of large number of infinitesimally small cubes, for each of them the equation is valid.

10.3.2 Derivation of gas laws from kinetic gas equation

10.3.2.1 Boyle's law

From his observations Boyle's in 1660 formulated a generalisation known as Boyle's law. Boyle's law states that at constant temperature, the volume of a given mass of gas is inversely proportional to its pressure.

According to kinetic theory, kinetic energy is directly proportional to temperature (in absolute scale).

Hence $\frac{1}{2} mnv^2 \;\alpha\; T$

Or $\frac{1}{2} mnv^2 = KT$ (K is constant)

$3/2 \times 1/3\, mnv^2 = KT$

$1/3\, mnv^2 = 2/3\, KT$

As $1/3\, mnv^2 = PV$

So $PV = 2/3\, KT$

At constant temperature PV= constant which is Boyle's law

10.3.2.2 Charle's law : for a definite quantity of gas at constant pressure, its volume is directly proportional to the absolute temperature. It was established in 1787.

From above discussion

$V = 2/3\, KT/P$

At constant pressure

$V = \text{constant} \times T$

Or $V \;\alpha\; T$ when P is constant.

This is Charle's law

10.3.2.3 Avogadro's law: It is states that equal volume of gases at same temperature and pressure contain equal number of molecules.

Suppose there are two gases for first gas mass of one molecule is m_1, velocity is v_1 and number of molecules are n_1. And for the second gas mass of one molecule is m_2, velocity is v_2 and number of molecules are n_2

Then for first gas PV= 1/3 $m_1n_1v_1^2$

For second gas PV= 1/3 $m_2n_2v_2^2$

As pressure and volume are same for both gases

Hence 1/3 $m_1n_1v_1^2$ = 1/3 $m_2n_2v_2^2$

Or $m_1n_1v_1^2 = m_2n_2v_2^2$ -------------(9)

If temperature is same average kinetic energy per molecule will be same for both gases that means

½ $m_1v_1^2$ = ½ $m_2v_2^2$----------------(10)

Comparing (9) and (10)

$n_1 = n_2$, this is **Avogadro's law**

10.3.2.4 Graham's law of diffusion (1829) – It states that rate of diffusion of a gas is inversely proportional to square root of density of the gas at constant pressure.

if m_1 and m_2 are masses and v_1 and v_2 the velocities of molecules of gas 1 and 2 respectively, then at same pressure and volume.

$PV_1 = 1/3\ m_1n_1v_1^2$

$v_1 = 3PV_1/m_1n_1$

$= 3p/d_1$

As m_1n_1/V_1 is total mass of gas and mass divided by volume equal to density of the gas equal to d

For second gas$v_2 = 3p/d_2$

$$v_1/v_2 = d_2/d_1$$

Since rate of diffusion is directly proportional to velocity. Hence

$$r\ \alpha\ v$$

$r_1/r_2\ \alpha\ d_2/d_1$

This is Graham's law of diffusion

10.3.2.5 Dalton's law of partial pressure: If two or more gases which do not react with each other are mixed, then total pressure will be sum of their individual pressures.

suppose n_1 molecule each of mass m_1 of gas A are contained in a vessel of volume V then from kinetic gas equation $P_a = m_1n_1\ v_1^2/3V$

Now suppose n_2 molecules of each of mass m_2 of gas B are contained in the same vessel at the same temperature when there is no gas present at that time

Then the pressure $P_b = m_2 n_2 v_2^2/3V$

If both the gases are present in the same vessel at the same time, the total pressure P is given by

$$P = m_1 n_1 v_1^2/3V + m_2 n_2 v_2^2/3V$$

$= P_a + P_b$

This is Dalton's law of partial pressure.

10.3.2.6 The combined gas law: Boyle's law and Charle's law can be combined into a single relationship called the combined gas law.

Boyle's law $V \alpha 1/P$

Charle's law $V \alpha T$

or $V \alpha T/P$

or $V = KT/P$ (K is constant)

or $PV = KT$

The value of constant K in this equation depends upon

(i) quantity of gas

(ii) the units in which P, V and T are expressed.

Avogadro's law states that one gram molecule of all gases under the same conditions of pressure and temperature occupies the same volume. So that the value of K will be the same for all gases if in every case one gram molecule of the gas is taken. When this is done, K is replaced by R which is known as universal gas constant.

Hence $PV = RT$ for n moles $PV = nRT$

10.4 VON DER WAAL'S EQUATION OF STATE

Von der Waal's 1873 studied the postulates of kinetic theory in detail and found that there are two faulty postulates.

(i) The molecules in a gas are point masses and possess no volume.

(ii) There are no intermolecular attractions in a gas.

Von der Waal's was the first to introduce systematically the correction terms due to the above two invalid assumptions in the ideal gas equation PV = nRT. His corrections are given below.

10.4.1 Volume correction

Volume of the gas in the available space for the movement of gas molecules. Volume V of an ideal gas is the same as the volume of the container. The dot molecule of ideal gas has zero-volume and the entire space in the container is available for their movement. But von der Waals assume that molecules of real gas are rigid spherical particles which posses a definite volume. The volume of real gas is, therefore ideal volume minus the volume occupied by gas molecules (Fig 2.6). If b is the effective volume of molecules per mole of the gas then corrected volume should be V-b = V_{ideal} For n moles V_{ideal} = V-nb b is also known as excluded volume.

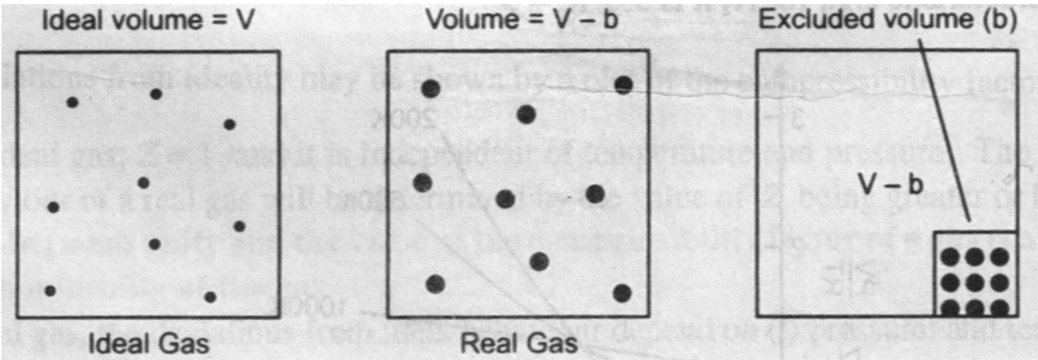
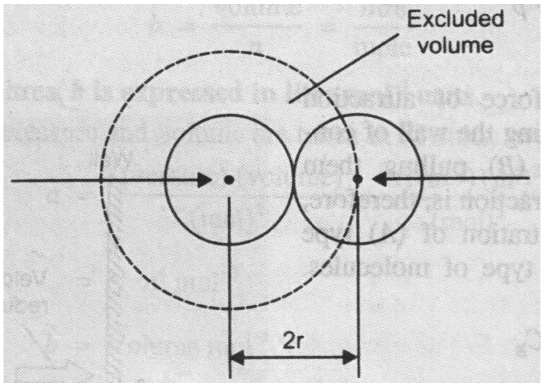


Fig 10.3

Now let us consider two molecules of radius r colliding with each other (Fig 2.7) Obviously they



cannot approach each other closer than a

Fig 10.4

Therefore, the space indicated by the dotted sphere having radius 2r will not be available to all other molecules of the gas. In other words the dotted space is excluded volume per pair of molecules. Thus,

Excluded volume for two molecules = $4/3\ \pi(2r)^3$

$= 8x4/3\pi r^3$

Excluded volume per molecule $= ½\ 8x4/3\pi r^3$

$= 4x\ 4/3\ \pi r^3$

$= b$

For n moles it is $nx4x\ 4/3\pi r^3$

$= nb$

10.4.2 Pressure correction

A molecule in the interior of a gas is attracted by other molecules on all sides. These attractive forces cancel out. But a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence it experiences an inward pull (fig 2.8) due to unbalanced forces.

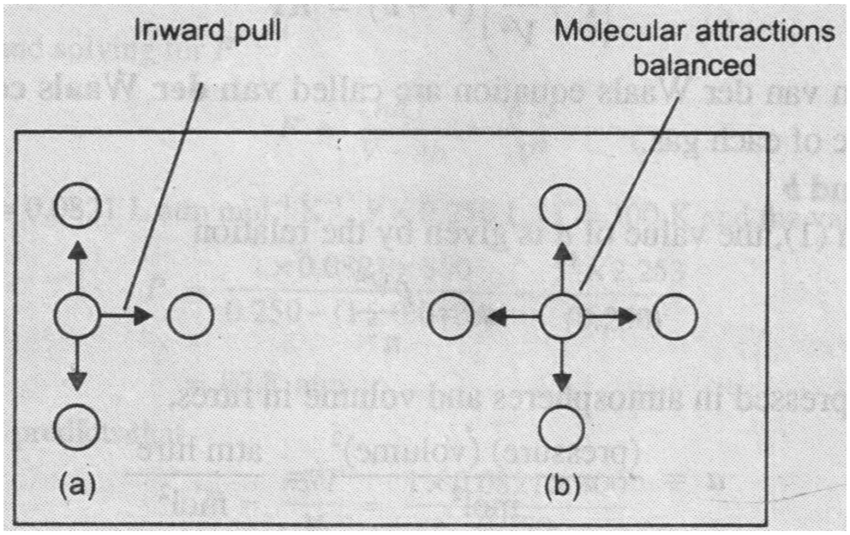


Fig 10.5

Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas P, will be less than ideal pressure if the pressure P, is less than P_{ideal} by a quantity p, we have

$P = P_{ideal} - p$

Or $P_{ideal} = P + p$

The value of p is determined by the force of attraction between molecules (A) stricking

the wall of the container and molecules (B) pulling them inward (Fig 2.9).

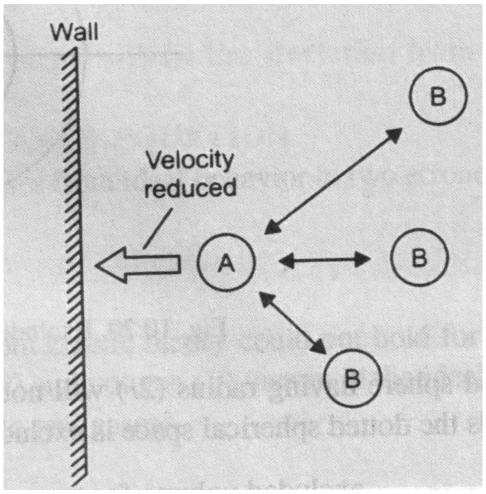


Fig 10.6

The net force of attraction is, therefore, is proportional to the concentration of (A) type molecules and also of (B) type of molecules:

That is $p \propto C_A . C_B$

$\propto A \frac{n}{V} \times \frac{n}{V}$

$p = an^2 / v^2$

n = total number of gas molecules in volume V.

Hence ideal pressure

$P_i = P + an^2/V^2$

Substituting the value of corrected volume and pressure in the ideal gas equation PV = nRT, we have

$(P + n^2a/V^2)$ $(V – nb) = nRT$

This is equation for n moles for one mole

We have

$(P + a/V^2)$ $(Vb) = RT$

von der Waal's equation can justify the deviations from ideal gas behaviour as given below

The equation can be written as

$PV – Pb + a/V – ab/V^2 = RT = P_iV_i$

As ab/V^2 is very small quantity it can be neglected

We get

$PV – Pb + a/V = P_iV_i$

(i) At low pressure Pb is small as compared to a/v

We have $PV +a/V = P_iV_i$

Or $PV = P_iV_i – a/V$

That means observed product PV is less then P_iV_i, the product of pressure and volume if the gas were ideal.

(ii) At high pressure, the term Pb over weighs the term a/v

Then the equation can be written as

$PV – Pb = P_iV_i$

$PV = P_iV_i + Pb$

That is observed product PV is greater than P_iV_i

(iii) At high temperature as V is large, Pb and a/V will be negligibly small.

We have $PV = P_iV_i$

(iv) Exceptional behaviour of hydrogen. This is due to the very small mass of the hydrogen molecule due to which the forces of attraction between molecules are almost negligible. Therefore neglecting the term a/V

We have

$PV = P_iV_i + P_b$

Therefore in the case of hydrogen even at low pressure PV is greater than P_iV_i.

10.5 INTERMOLECULAR FORCES

Since the molecules in a liquid are not far apart from each other, the intermolecular forces are fairly strong. The characteristic properties of liquid arise from the nature and the magnitude of these intermolecular forces.

Intermolecular forces in liquids are collectively called von der Waal's forces. These forces are essentially electrical in nature and result from the attraction of charges of opposite sign. The principle kinds of intermolecular forces are:

(i) Dipole-dipole interaction
(ii) London forces
(iii) Hydrogen bonding.

10.5.1 Dipole-dipole interaction

We have seen that HCl is an example of a polar molecule. Such molecule have a partial positive charge at one end and a partial negative charge at the other.

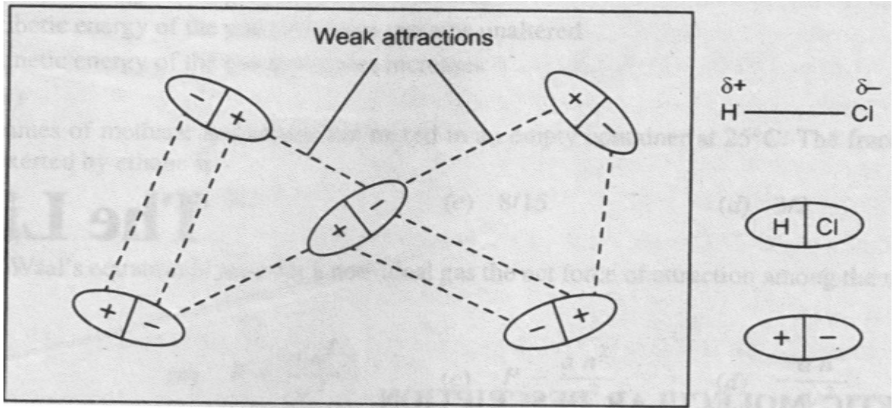


Fig 10.7 Weak attraction between polar HCl molecules

They are called dipoles. The positive end of one dipole attracts the negative end of the other. The thermal energy of molecules tends to disturb these attractions but still there exists a net attraction between the polar molecules. These forces are referred to as dipole-dipole attractions. Generally such attractions are about 1% as strong as covalent bond. It is to be noted that the attractions between the opposite poles are greater than repulsive forces between like poles. Thus these molecules have a net attraction to each other.

10.5.2 London forces

In 1930 Fritz London first offered a simple explanation of weak forces between nonpolar molecules or atoms. In a molecule (or atom) electrons are constantly moving. Most of the time electrons in the molecules could not be visualized as distributed symmetrically. However according to the principle of probability, for an instant the electrons may concentrate on one side of the molecule than the other. This causes the molecule (A) to become momentarily polar and we call it instant dipole.

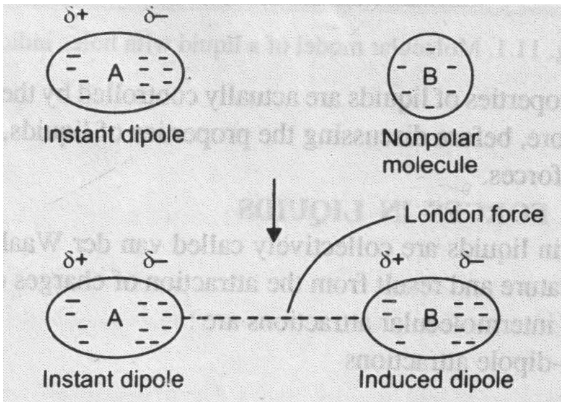


fig 10.8 Explanation of London forces

The negative side of the instantaneous dipole repels the electrons of an adjacent molecule (B). As a result the second molecule B also becomes a dipole by induced polarity. This is called induced dipole **.**

The instantaneous dipole A and the induced dipole B will now attract each other. Because the electrons keep moving an instant dipole may vanish the next moment and new are produced. This continual process produces a weak overall attraction between molecules of liquid.

The momentary attraction between the molecules of liquid caused by instantaneous-dipole and **induced- dipole attractions are called London forces.** These London forces are present in polar molecules also in addition to other von der Waal's forces.

The strength of the London forces depends as to how easily the electron cloud in a particular molecule is deformed. This is determined by the number of electrons and also on the size of the molecule. Thus Argon (-245.9^{0}C) with a greater number of electron and larger molecular weight has a higher boiling point than helium (-268.9^{0}C).

10.5.3 Hydrogen bonding

In compounds of hydrogen with strongly electronegative elements, such as fluorine, oxygen and nitrogen, the electron pair shared between the two atoms lies far away from the hydrogen atom as a result of which the hydrogen atom becomes highly electropositive with respect to other atom which become electronegative. This phenomenon of charge separation in water is represented as shown in the fig 4.3.

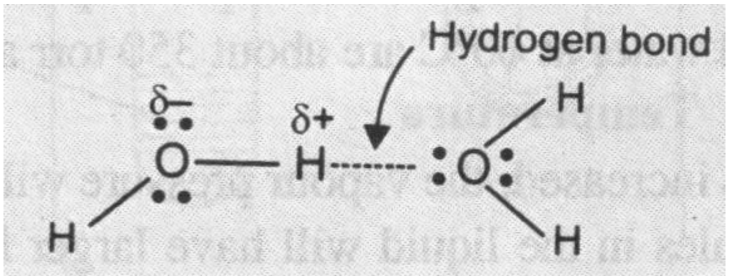


Fig 10.9 Hydrogen bond

The electronegativity difference in H and O is so large that the electron pair in the covalent bond, H-O is shifted toward O. It leaves a partial positive charge on the H atom. This leads to a strong electrostatic attraction between positively charged H atom and an unshared electron pair on the O atom of another molecule. Thus you can understand that two or more molecules may associate together to form large cluster of molecule. This is shown below for the association of several molecules of hydrogen fluoride.

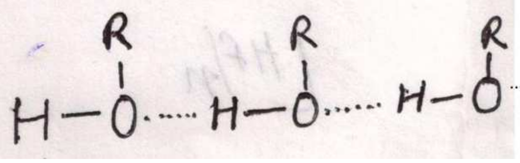
...$H^{+\delta}$ –$F^{-\delta}$ .....$H^{+\delta}$ –$F^{-\delta}$ ......$H^{+\delta}$ –$F^{-\delta}$ .....

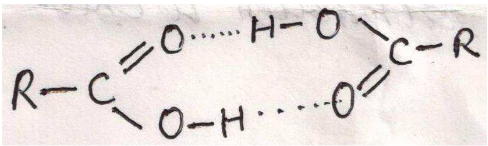
In this case, while the length of covalent bond between H and F atoms is found to be $1.00A^0$, the length of the hydrogen bond between H and F atoms of neighbouring molecules has been found to be $1.55A^0$. this cluster of HF molecules may be described as $(HF)_n$

The attractive force which binds hydrogen atom of one molecule with electronegative atom of another molecule, generally of the same substance is known as the hydrogen bond.

The hydrogen bonding is the strongest of all intermolecular forces including the dipole-dipole attractions and London forces.

In the above discussion you have seen that cluster of HF molecule is described as $(HF)_n$





and cluster of water molecule may be described as $(H_2O)_n$

Alcohols and carboxylic acids also form associated molecules for the same reason, as shown below

Alchohols **Carboxylic Acids**

10.6 STRUCTURE OF LIQUIDS

In a liquid, the molecules are not as rigidly fixed an in solid. They have some freedom of motion which, however, is much less than that in a gas. Liquids resemble solids in being compact, incompressible and in having a definite volume. These properties are indicative of a regular structure in liquids similar to that in solids.

From X-ray diffraction technique, it has been found that the resemblance of liquid state with solid state is valid with in a small range; i.e. within only small distance from a given molecule. In other words the regularly ordered structure which exists in crystalline solids is of short range in liquids. It means it exists in only within a short distance from any given molecule. A solid possesses short range as well as long range order since the ordered structure extends regularly throughout the whole crystal.

Now it should be clear to you that

(i) A gas consists of molecules separated wide apart in empty space. The molecules are free to move about throughout the container.

(ii) A liquid has molecule touching each other. However, the intermolecular space, permit the movement of molecule throughout the liquid.

(iii) A solid has molecules, atoms or ions arranged in a certain order in fixed position in the crystal lattice. The particles in a solid are not free to move about but vibrate in their fixed position.

10.7 CHARACTERISTIC PROPERTIES OF LIQUIDS

As you have studied earlier in this unit that the properties of liquids arise from

(i) The nature and

(ii) The magnitude of intermolecular forces of attraction existing between their molecules. The important properties of liquids are

1. Vapour pressure
2. Surface tension
3. Viscosity
4. Refraction

Now you will study these properties in detail

10.7.1 Vapour pressure

When a liquid is an open vessel, it evaporates. You have studied in the gases unit, that the gas molecules have a particular velocity. This is so in case of liquids also. Only a few liquid molecules have lower or higher velocity, i.e. lower or higher kinetic energies. The energy distribution of molecules in a liquid is shown in Fig 4.4.

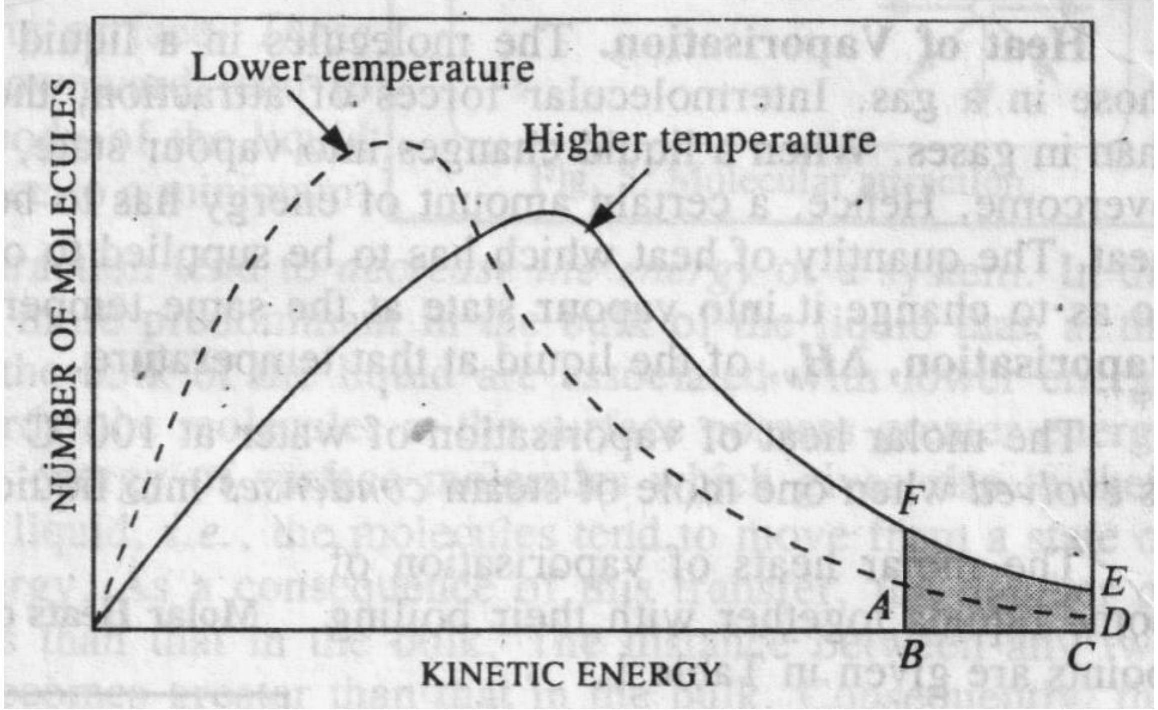


Fig 10.10 energy distribution of molecules of a liquid

It is clear from the **Fig 4.4** that the number of molecules with high kinetic energies, as shown by the shaded portion ABCD of the dotted curve is very small. This number, however, increases with rise in temperature, as shown by the shaded portion FBCE of the bold line curve.

When a liquid is placed in an open vessel it evaporates. The molecules in the liquid are moving with different kinetic energies. The molecules that possess above average kinetic energies can overcome the intermolecular forces that hold them in the liquid. These energies molecules escape from the surface as vapour. This process by which molecules of a liquid goes into gaseous state is called vaporisation or evaporation. The reverse process whereby gas molecules become liquid is called condensation.

When a liquid is place in a closed vessel, the molecules with high kinetic energies escape into space above the liquid as shown in fig 4.5. as the number of molecule in the gas phase increases, some of them strike the liquid surface and are recaptured (condensation).

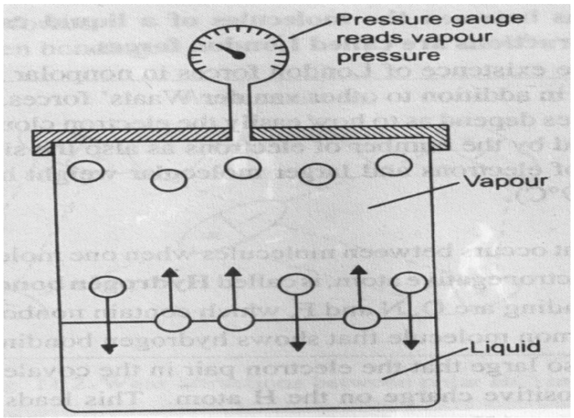


Fig 10.11 Illustration of vapour pressure

A stage comes when the number of molecules escaping from the liquid is equal to the number of molecules returning to the liquid. Thus a dynamic equilibrium is established between the liquid and the vapour at a given temperature.

Liquid $\rightleftarrows$ vapour

Now the concentration of the vapour in the space above the liquid will remain unchanged with lapse of time. Hence the vapour will exert a definite pressure at the equilibrium. Hence vapour pressure of a liquid defined as:

The pressure exerted by the vapour in equilibrium with the liquid at a fixed temperature is the vapour pressure of the liquid.

As the temperature rises, the number of molecules escaping from the liquid surface increases as there in increase in the number of vapour molecules in the space above the liquid when equilibrium is attained.

Hence vapour pressure of the liquid increases with increase of temperature.

4.5.1.1 Determination of vapour pressure

(a) Static method:

A simple apparatus used in this method is shown in fig 4.6. a sufficient amount of the liquid whose vapour pressure is to be determined in placed in the bulb connected to a mercury manometer and a vacuum pump.

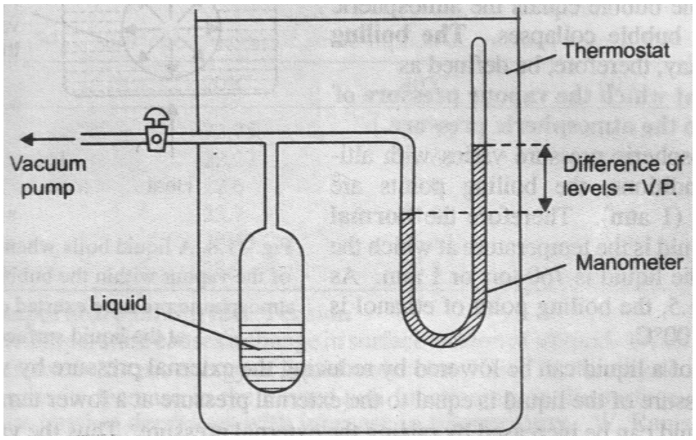


Fig 10.12 Determination of vapour pressure by static method

All the air from the bulb is removed by working the vacuum pump and the stopcock closed. A part of liquid evaporates. The system is then maintained at a fixed temperature for enough time so that equilibrium is attained. The difference in the levels of mercury in the manometer is equal to vapour pressure of the liquid. This method is used for liquids having vapour pressure up to one atmosphere.

(b) Dynamic method:

The apparatus used for the dynamic method is shown in fig 4.7.

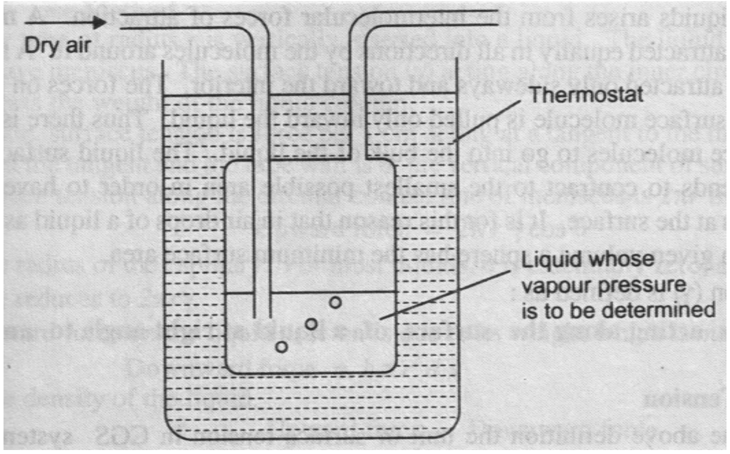


Fig 10.13 Dynamic method

An inert gas is passed through the given liquid at a constant temperature (T). The gas saturated with the vapour of the liquid leaves the flask at the exit tube. If V is the volume of the gas passed and m the loss in weight of the liquid the vapour pressure is given by the expression.

$$\text{Vapour pressure} = \frac{m}{MV}\ \text{RT}$$

Where M is the molecular weight of the liquid and R the gas constant. This method is particularly useful for liquids of very low vapour pressure

10.7.2 Surface tension

The existence of strong intermolecular forces of attraction in liquids gives rise to a property known as surface tension. The phenomenon of surface tension can be described as follows.

A molecule in the interior of a liquid is attracted equally in all directions by the molecules around it. A molecule in the surface of a liquid is attracted only sideways and towards the interior. The forces on the sides being counterbalanced, the surface is pulled only inward the liquid. These unbalanced attractive forces acting downward tend to draw the surface molecules into the body of the liquid and, therefore, tend to reduce the surface to minimum. The liquid then behaves as if it were under a strain or tension. It is this force which is called surface tension. It may be defined as **"the force in dynes acting on the surface of the liquid at right angles to one centimetre length of the surface".** It is represented by a symbol γ (gama).

In CGS system the unit of surface tension is dynes per centimetre (dyne cm^{-1}). In SI system, the unit is Newton per metre (Nm^{-1}). Both these units are related as follows

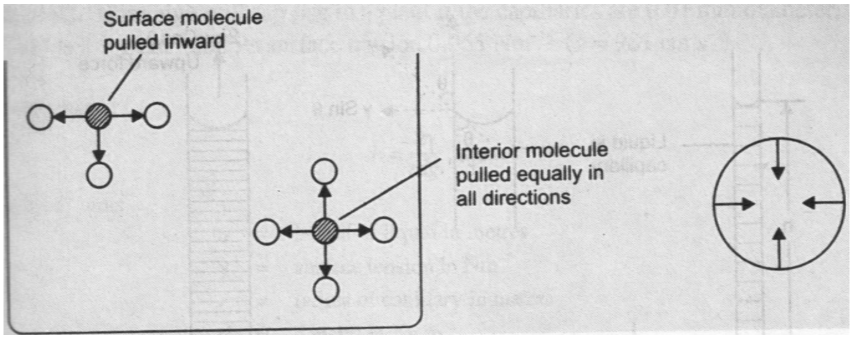


Fig 10.14 molecular attractions

$$\text{Surface energy} = \frac{\text{amount of work done}}{\text{amount of area extended}} = \frac{\text{forcexdistance}}{\text{area}}$$

Hence in CGS units we have

Surface energy= $\underline{\text{dyn x cm}}$= dyn x cm^{-1}= surface tension

cm^2

In SI units we have

$$\text{Surface energy} = \frac{N \times m}{m^2} = Nm^{-1}$$

obviously,

$1 \text{ dyne } cm^{-1} = (10^{-5}N)(10^{-2}m)^{-1}$

$= 10^{-3}Nm^{-1}$

Effect of temperature on surface tension

When temperature increases, there is increase in kinetic energy of liquid molecules (KE α T) thereby decreasing intermolecular forces. It results in decrease in inward pull functioning on the surface of the liquid. That means you can say surface tension decreases with increase in temperature. As surface tension arises of the attractional forces operating between the molecules, Ramsay and Shields gave the following relationship between the surface tension of a liquid and its temperature.

$$\gamma(M/d)^{2/3} = k(t_c - t - 6)$$

where k is constant

t_c is critical temperature and t any other temperature $\gamma\ (M/d)^{2/3}$ represents molar surface energy of liquid.

Determination of surface tension

(i) Capillary rise method:

In this method a capillary tube of radius r is vertically inserted into the liquid. The liquid rises to a height h and form a concave meniscus.

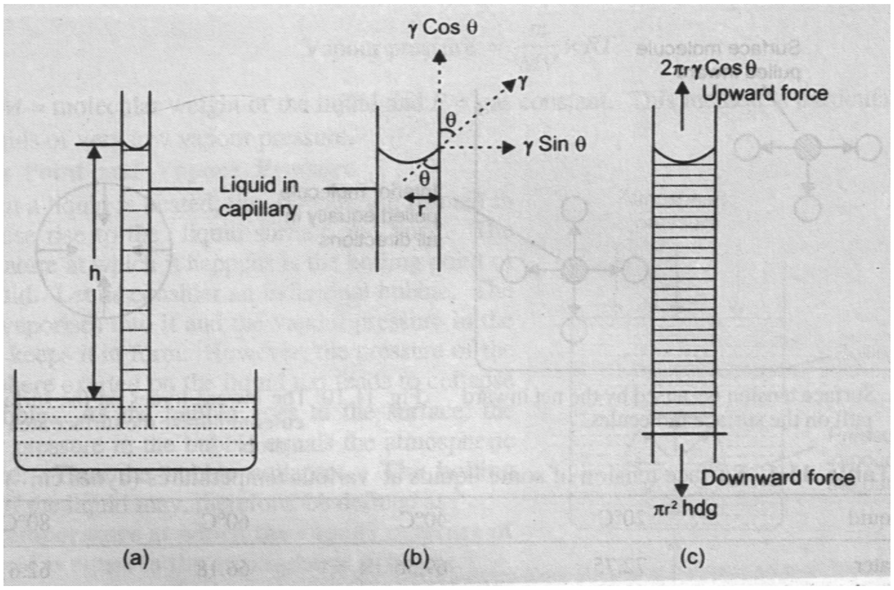


Fig 10.15 capillary rise method of surface tension

The surface tension γ acting in the inner circumference of the tube exactly supports the weight of the liquid column. By definition, surface tension is force per 1 cm acting at a tangent to the meniscus surface. If the angle between the tangent and the tube wall is θ, the vertical component of surface tension is γ cosθ. The total surface tension along the circular contact line of meniscus is 2πr times.

Therefore upward force = $2\pi r\gamma\cos\theta$

Where r is radius of capillary. For most liquids, θ is essentially zero, and cosθ=1 then the upward force reduces to $2\pi r\gamma$

The downward force on the liquid column is due to its weight which is mass x g, thus downward force is $h\pi r^2dg$, where d is density of the liquid

Now upward force = downward force

$2\pi r\gamma = h\pi r^2dg$

$\gamma = hrdg/2$ dynes/cm

once r, h and d are known γ can be calculated.

(ii) **Drop weight/ number method:**

When a liquid is allowed to flow very slowly through a capillary tube a drop will form which will increase upto a certain point and then fall. If the radius of the end of the tube be r, the total surface tension supporting the drop will be γ2πr. The drop falls down when its weight W is just equal to this force. Hence we have

$\gamma 2\pi r = W = mg$

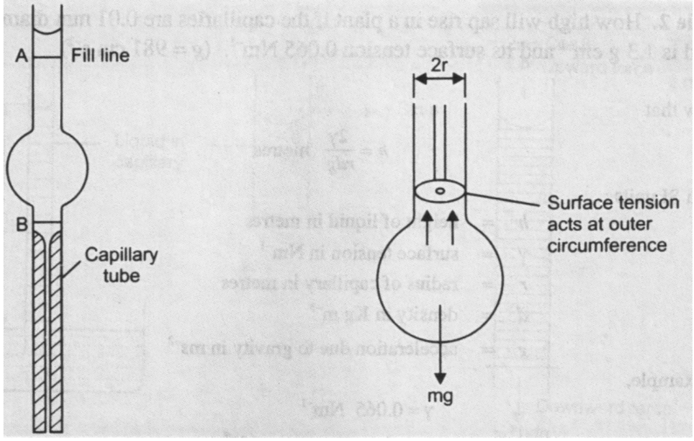


Fig 10.16 determination of surface tension by drop-pipette

The apparatus employed is a glass pipette with a capillary at the lower part. This is called a drop pipette or stalagmometer. It is cleaned, dried and filled with the experimental liquid, say upto the mark A. Then the surface tension is determined by any of the following two methods.

(a) Drop weight method:

About 20 drops of the given liquid are received from the drop-pipette in a weighing bottle and weighed. Thus weight of one drop is found. The drop-pipette is again cleaned and dried. It is filled with the second reference liquid (say water) and weight of one drop is determined as before.

Then we have

$m_1g = 2\pi r\, \gamma_1$ and $m_2g = 2\pi r\, \gamma_2$

$\gamma_1/\gamma_2 = \frac{m1}{m2}$

Thus knowing the surface tension of one liquid, the surface tension of other liquid can be found.

(b) Drop number method:

The drop pipette is filled up to the mark A with the liquid whose surface tension is be determined. The numbers of drops are counted as the meniscus passes from A to B. Similarly the pipette is filled with the reference liquid as the meniscus passes from A to B. Let n_1 and n_2 be the number of drops produced by the same volume V of the two liquids. Thus,

the volume of drop of the experimental liquids = V/n_1

mass of one drop of this liquid = $V/n_1 \, x d_1$

where d_1 is its density.

Similarly the mass of one drop of reference liquid = $V/n_2 \times d_2$

Then we have $$\gamma_1/\gamma_2 = \frac{(V/n_1)d_1}{(V/n_2)d_2} = \frac{n_2 d_1}{n_1 d_2}$$

The density d_1 can be determined by density bottle, once γ_2 and d_2 are known γ_1 can be calculated.

For most liquids surface tension at room temperature vary between 27 and 42 dynes cm^{-1}. For water however, γ is 72.8 dynes cm^{-1} at 20^0C.

This high value is obviously due to strong intermolecular forces which exists in water as a result of extensive hydrogen bonding.

Surface tension and chemical constitution

From the study of a large number of liquids, Maclead (1923) showed that

$$\frac{\gamma^{1/4}}{D-d} = C \text{ ....(1)}$$

Where γ is surface tension of the liquid, D its density and d density of vapour at the same temperature, C is a constant. Sugden (1924) modified this equation by multiplying both sides by M, the molecular weight of the liquid

$$M.\gamma^{1/4}/D-d = MC = [P] \text{ .....(2)}$$

The quantity P, which is a constant for a liquid, was given the name parachor. As d is negligible as compared to D equation (2) reduces to

$$M\gamma^{1/4}/D = [P]$$

or $$M/D\gamma^{1/4} = [P]$$

$$V\gamma^{1/4} = [P] \text{ ....(3)}$$

Where γ is molar volume of the liquid. If surface tension γ is unity then V= [P]

Thus parachor may be defined as the molar volume of a liquid at a temperature at which its surface tension is unity.

Use of parachor in elucidating molecular structure:

Sugden examined the experimental parachor values of several organic compounds of known molecular structure. He showed that parachor is both additive and constitutive property. That is parachor of an individual compound can be expressed as sum of

(i) Atomic parachors: which are the contributions of each of the atoms present in the molecule.

(ii) Structural parachors: which are the contributions of various bonds, rings and other structural factors present in the molecule. By correlating the experimental values of parachor with molecular structure, Sugden (1924) calculated the atomic and structural parameters. These values were further revised by Vogel (1948) on the basis of more accurate measurements of surface tension table.

Atom	**Parachor**	**Bonder ring**	**parachor**
C	8.6	single bond	0
H	15.7	double bond	19.9
O	20.0	coordinate bond	0
N	12.5	3-member ring	12.3
Cl	55.2	6- member ring	1.4
S	48.2	= CO	44.4

Table 10.1

You will see now that how these values are useful in elucidating molecular structure.

(i) Structure of benzene:

If the Kekule formula for benzene be accepted the parachor value can be calculated by using the data:

6xc6x8.6 = 51.6

6H6x15.7 = 94.2

3 =3x19.9 = 59.7

6 member ring = 1.4

Total parachor value= **206.9**

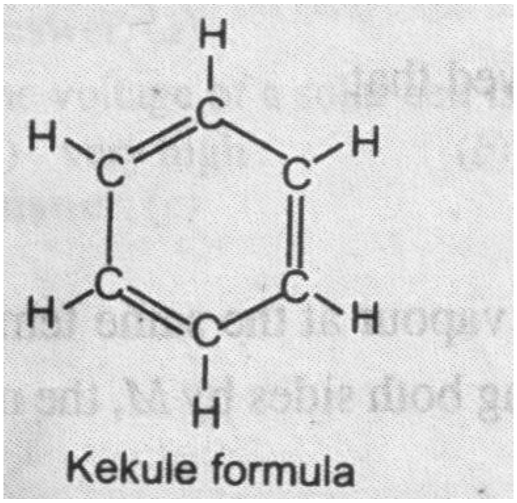


Fig 10.17

Experimental value of parachor of benzene is 206.2 since the calculated value tallys with that determined by experiment, the Kekule structure for benzene is supported.

(ii) Structure of quinone:

The two possible structural proposed for quinine are

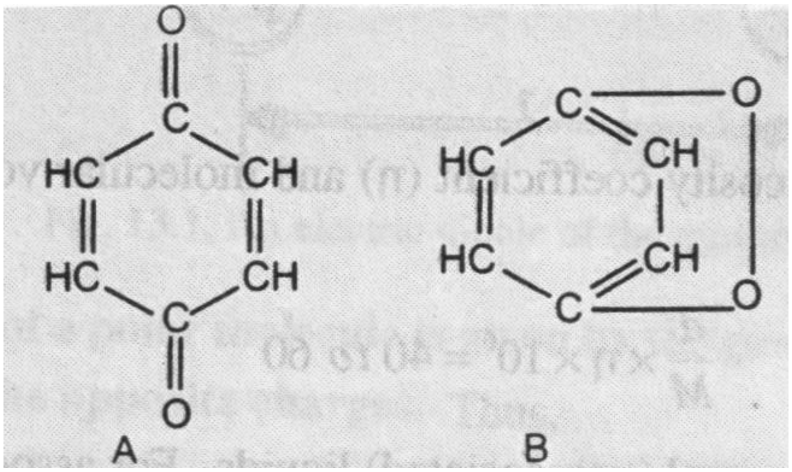


Fig 10.18

The parachor calculated for the two structure are:

	Structure A	Structure B
6C	6x8.6 = 51.6	6C6x8.6=51.6
4H	4x15.7 = 62.8	4H4x15.7= 62.8
2O	2x19.8 = 39.6	2O2x19.8 = 39.6
4(=)	4x19.9 = 79.6	3(=)3x19.9 = 59.7

1 six member ring = 1.4 2 six member ring 2.8

Total 235.0 Total 216.5

The observed value for quinine is 236.8 and hence the formula A represents correctly the structure of its molecule.

10.7.3 Viscosity

Some liquids flow more rapidly than others. In other words, liquid molecules pose resistance to the flow of one layer over the other. This property of liquids which determines their flow is termed viscosity. The property of the liquid which determines its flow is called viscosity of the liquid.

The resistance to flow of one layer of liquid molecules over another depends on the following factors.

1. The intermolecular attractive forces do not permit a free flow of molecules in a liquid. The strength of intermolecular forces gives a rough major of the viscosity of the liquids.
2. The molecular weight or mass of the molecules of a liquid also determines flow of the liquid. Thus heavier the molecule of a given liquid the greater will be its viscosity.
3. Structure and shape of the molecules of a liquid place an important role in influencing its viscosity. Liquids with the large irregularly shaped molecules are generally known to be more viscous than those with small and symmetrical molecule. Since only hard symmetrical molecules have perfectly elastic collision, the large and irregular molecules will have less elastic molecules amongst themselves. Thus collisions between large molecules involves the loss of kinetic energy and as a consequence the intermolecular forces dominating the molecules tends to stick together. This increases the viscosity of the liquid.
4. An increase in temperature decreases the viscosity of the liquid, the molecular motion increases at the expense of cohesive forces causing resistance to flow.
5. The increase of pressure goes to strengthen the cohesive forces between molecules. Hence with increase of pressure the viscosity of a given liquid increases somewhat.

The flow is a characteristic property of liquids. Let us consider flow of a liquid. A liquid may be considered to be consisting of molecular layers arranged one over the other. When shearing force is applied, it flows.

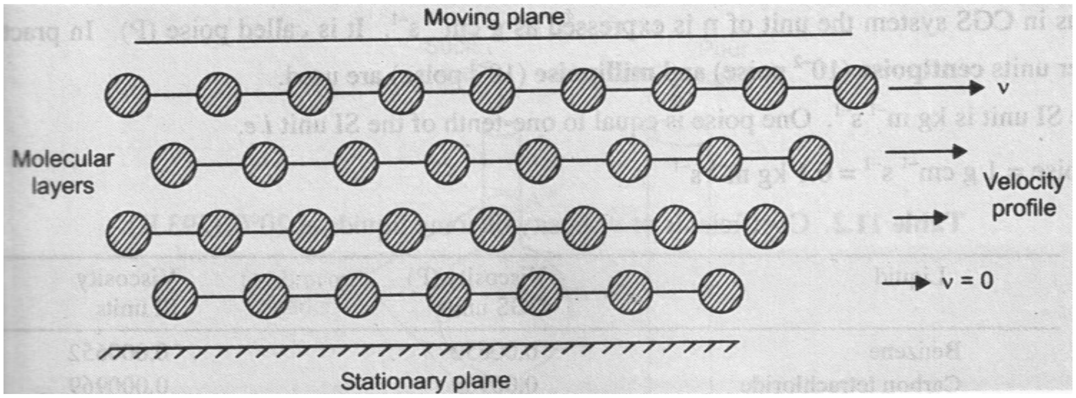


Fig 10.19 flow of liquid on a glass surface

However the force of friction between the layers offers resistance to this flow. Viscosity of a liquid is a measure of its frictional resistance.

Let us examine a liquid flowing on a glass surface. The molecular layer in contact with the stationary surface has zero velocity. The successive layers above it move with increasingly higher velocities in the direction of the flow.

Now consider two adjacent moving layers of a liquid (fig 4.11). Let these be separated by a distance dx having velocity difference dv. The force of friction (F) resisting the relative motion of the two layers is directly proportional to the area A and velocity difference dv, while it is inversely proportional to the distance between the layers dx.

Hence F α A d v/dx

=ή A d v/dx

or ή = F/A x dx/dv

where ή (eta) is the proportionality constant. It is known as coefficient of viscosity or simply viscosity of a liquid. It may be defined by the above equation as:

the force of resistance per unit area which will maintain unit different of velocity between two layers which are unit distance apart.

Unit of viscosity:

η = F/A x dv/dx

= force/area x distance/velocity

= mass x length x time^{-2}/length^{2} X length/length/time

= mass x length^{-1} x time^{-1}

In CGS system the unit of ή is expressed as g $cm^{-1}s^{-1}$, it is called poise. In practice smaller units centipoise (10^{-2} poise) and millipoise (10^{-3} poise) are used.

A liquid is said to have coefficient of viscosity as one poise when a force of one dyne maintains a velocity difference of one centimetre per second between two parallel layers of the liquid one cm apart and have an area of contact equal to on square cm. **The reciprocal of viscosity is known as fluidity.**

10.7.3.1 Effect of temperature on viscosity

As the temperature increases, the molecular motion increases at the expense of cohesive forces causing resistance to flow. Therefore, the viscosity of liquids is found to decrease by 1 to 2 per cent for each degree rise of temperature.

10.7.3.2 Determination of viscosity

The apparatus used for determination of viscosity in the laboratory is knwon as Ostwald's viscometer. A simple form of Ostwald viscometer is shown in fig 4.14, the left- hand limb is essentially a pipette with two celibration marks A and B. A length of capillary tube joins the pipette to the bulb D in the right-hand limb.

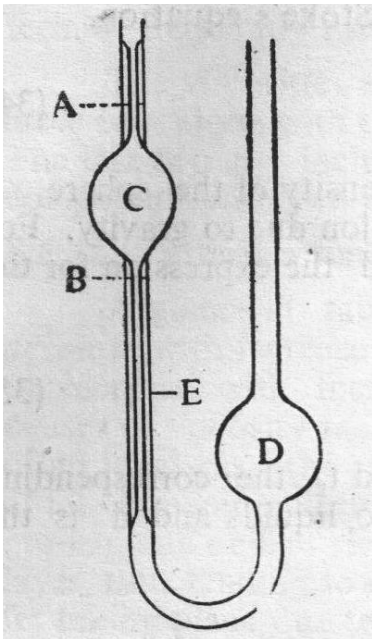


Fig 10.20 Ostwald viscometer

A definite volume of liquid (say about 25 ml) is poured into the bulb D with a pipette. The liquid is sucked up near to the top of the left-hand limb with the help of rubber tubing attached to it. The liquid is then released to flow back into the bulb D. the time t_1 to flow from A to B is noted with a stopwatch. Then the apparatus is cleaned and the experiment is repeated with water taking about the same volume. The time of flow of water t_2 from A to B is recorded. The density of the liquid d and that of water d_w are determined with the help of density bottle. The relative viscosity is calculated from the expression

$$\eta/\eta_w = dt_1/d_w t_2$$

where is η is coefficient of viscosity of the experimental liquid and η_w is the coefficient of viscosity of water. Knowing the value of coefficient of viscosity of water η_w at the temperature of experiment, the absolute viscosity coefficient η of the given liquid can be found.

10.7.3.3 Viscosity and chemical constitution

As you know viscosity is largly due to intermolecular attractions which resist the flow of liquid. Therefore some sort of relationship between viscosity and molecular structure should be there. Viscosity is also dependent on the shape, size and mass of the liquid molecules. The following general rules have been discovered.

(i) Dunstan Rule:

Dunstan in 1909 showed that coefficient of viscosity η and molecular volume (d/M) were related as $d/M \times \eta \times 10^6 = 40$ to 60

This expression holds only for normal (unassociated) liquids for associated liquids the value is much higher than 60. For example the value for benzene is 73 and for water it is 559 and for ethanol it is 189. This shows benzene is a normal liquid while water and ethanol are associated liquids.

(ii) Molar Viscosity:

The product of molar surface and viscosity is termed as molar viscosity. That is

molar viscosity = molar surface x viscosity

$= (M/d)^{2/3} \times \acute{\eta}$

Thorpe and Rodger (1894) found that molar viscosity is an additive property at the boiling point. They worked out the molar viscosity contributions of several atoms (C, H, O, S, etc) and groups. From these, they calculated the molar viscosity of liquid from its proposed structure. By tallying this value with the experimental one, they were able to ascertain the structure.

(iii) Rheochor:

Newton Friend (1943) showed that if molecular volume (M/d) be multiplied by the eighth root of the coefficient of viscosity it gives a constant value [R], it is termed as Rheochor

$$M/d \times \eta^{1/8} = R$$

Like parachor, rheochor is both additive and constitutive property.

10.8 DEFINITION OF SPACE LATTICE AND UNIT CELL

Crystals are bound by surface which is usually planner. These surfaces are called faces and where two faces intersect an edge is formed. The angle between the normals to the two intersecting faces is the interfacial angle or the angle between any two faces is called interfacial angle. Although the size of the faces or even shapes of crystals of one and the same substances may vary widely with the condition of formation or other factors, yet the interfacial angles between any two corresponding faces of the crystal remain invariably the same throughout. This is shown in fig 5.2. Now it is clear to you that although the external shape is different yet the interfacial angles are the same.

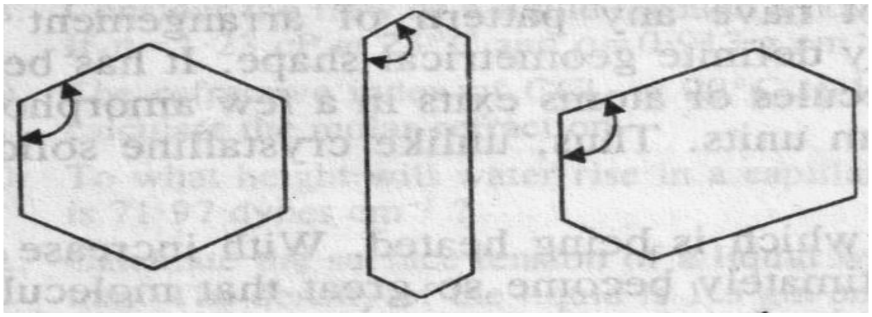


Fig 10.21 Constancy of interfacial angle

Space lattice

Rather than drawing the entire pattern, it is much more convenient to represent the unit of pattern by a point. Each point then represents the position of an atom, ion, molecule or group of ions and molecules. The regular three-dimensional arrangement of identical points in space gives rise to what is known as space lattice or crystal lattice (Fig 5.3) the positions occupied by the particles in the space lattice are called lattice sites or lattice points.

Unit cell:

It is defined as "the smallest geometrical portion of the crystal, which when repeated in three dimensional, would generate the complete crystal". Each unit cell, in turn, must be constituted of atoms, molecules or ions, as the case may be and arranged to give the particular geometrical configuration of the crystal.

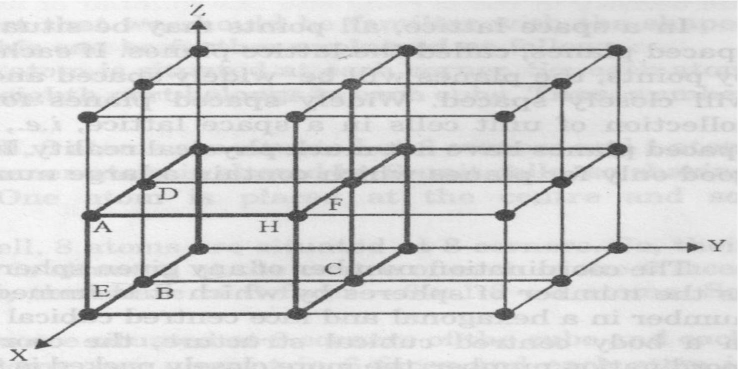


Fig 10.22 Space latice

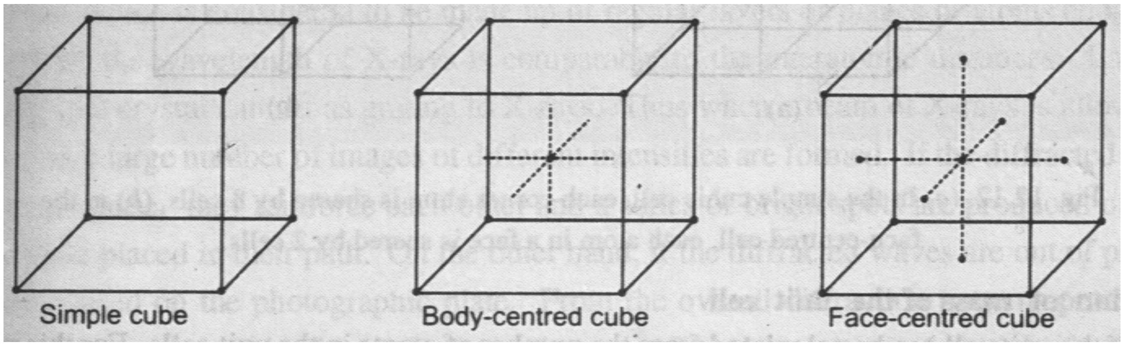
Unit cells are of following types;

(a) Simple or primitive unit cell (P): The simplest unit cell which has the lattice points at the corners is called a simple or primitive unit cell. It is denoted by P.

(b) Non primitive or multiple unit cell: When unit cell contains more than one lattice points, it is called non primitive or multiple unit cell. It is further divided into the following three categories:

(i) Face centred unit cell (F):

When a unit cell, besides the points present at the corners of the unit cell,



(a) (b) (c)

Fig 10.23 Three cubic unit cells

There is one point at the centre of each face, it is called face centred arrangement or face centred unit cell. It is denoted by F.

(ii) Body centred unit cell (I):

When in a unit cell, besides the points at the corners of the cell, there is one point at the centre with in its body, it is called body-centred arrangement or body-centred with cell. It is denoted by I.

(i) Side centre or end face unit cell:

When in a unit cell, besides the points at the corners of the cell, the points are located at the centre of any two parallel faces of the unit cell, it is called side-centred or end face unit cell. It is denoted by c.

10.9 STRUCTURAL DIFFERENCES BETWEEN SOLID, LIQUID AND GASES

Solids are characterised by definite volume and shape, liquids by their ability to adapt the shape of the container in which it is kept and gases by their ability to expand and adapt the shape as well as volume of the container. The table below points out the major differences between solid, liquids and gas phase for better comparison of the three phases:

Differences between solid, liquid and gases:

Basis	Solid	Liquid	Gas
Rigidity	Solids are rigid.	Liquids are not rigid.	Gases are not rigid.
Fluidity	Solids lack the ability to flow.	Liquids can flow from higher level (concentration) to lower level.	Gases can flow in all directions.
Volume and shape	Solids have definite shape and volume due to their rigid structure.	Liquids have definite volume but it lacks definite shape and can take the shape of the container in which it is stored.	Gases neither have a definite shape nor a definite volume.
Intermolecular interaction	Particles in a solid are packed closely	Intermolecular interaction is comparatively less than that	Here, the intermolecular interaction is least, so the

	together, so they are only able to vibrate but not move.	of solids, so the molecules or particles have enough energy to move around.	gas molecules or particles can move freely and quickly.
Compressibility	One cannot compress solid appreciably.	Can be compressed.	Can be compressed significantly.
Storage	It can easily be stored without a container or vessel.	Liquids cannot be stored without a vessel or container.	Gases can be stored in vessels only.
Examples	Cup, brick, chair, wood, etc.	Water, milk, honey, oil, etc.	Air, ozone, natural gas, etc.

10.10 SUMMARY

In this chapter you have different gas laws, namely: Boyle’s law, Charle’s law, Avogadros law, Graham’s law of diffusion and Dalton’s law of partial pressures. The postulates of kinetic theory are important as they are useful in deriving kinetic gas equation. Deviations from ideal behaviour and von der Waals equation has been discussed in detail. Though you have studied real gas equation i.e. von der Waals equation detail and their equation is useful to discuss the deviation from ideal behavior. Apart from these we will able to explain Intermolecular forces, Structure of liquids, Characteristic properties of liquids and Definition of space lattice and unit cell Structural differences between solid, liquid and gases.

10.11 TERMINAL QUESTIONS

(A) Multiple Choice Questions

1. Mathematically, Boyle’s law can be expressed as

(a) $V \alpha \frac{1}{P}$ (b) $V= \frac{K}{P}$ (c) VP=K(d) All of these

Ans (d)

2. Which of the following is the correct mathematical relation for Charle's law at constant pressure.

   (a) $V \alpha T$(b) $V \alpha t$(c) $V=Kt$(d) None of these.

   Ans (a)

3. The Average kinetic energy of gas molecule is

   (a) inversely proportional to its temperature.

   (b) directly proportional to its temperature.

   (c) equal to the square of its temperature.

   (d) directly proportional to the square root of its absolute temperature. Ans (b)

4. The compressibility factor Z is given by

   (a) $Z= PV/RT^2$ (b) $Z= PV/2RT$(c) $Z=PV/RT$(d) $Z=2PV/RT$

   Ans (c)

5. Which of the following gases will have the lowest rate of diffusion.

   (a) H_2(b) N_2(c) F_2(d) O_2

   Ans (c)

(B) Short answer questions

1. Define the following terms

(a) Critical temperature.

(b) Graham's law of diffusion

(c) Boyle's law

(d) Charle's law

2. Write two postulates of kinetic theory of gases.

3. Write a short note on critical constants.

4. Write a note on exceptional behaviour of hydrogen as given by von der Waals.

5. Write von der Waals equation for n moles of a gas.

(C) Long answer questions

1. Discuss the causes of deviation from ideal behaviour. How they are accounted for in the von der Waals equation?
2. What are the postulates of kinetic theory of gases and show how they are justified?
3. Derive the kinetic gas equation for an ideal gas.

UNIT 11: COLLOIDAL SYSTEM

CONTENTS:

11.1 OBJECTIVES

Matter exists in three states. These three states are solid, liquid and gaseous state. A gas consists of molecules separated wide apart in empty state. A liquid state molecule touching each other.

Solids are characterised by incompressibility, rigidity and mechanical strength. In solid state molecules, atoms or ions that make up the solid are closely packed. They are held together by strong cohesive forces and cannot move at random.

Some substance such as suger, salts, acids and bases when dissolved in water can pass through parchment membrane and form true solutions. Whereas substances such as gelatin, albumen, glue diffuse at a slow rate. These are called colloids.

The colloidal solutions are intermediate between true solutions and suspensions.

11.2 INTRODUCTION

During his research work Thomas Graham in 1861 found that while some substances diffused readily through parchment membrane, others diffuse at slow rate. The substance which diffuse at slow rate were given the name colloids (from Greek Kolla means glue like). These observations led to the development of a new branch of knowledge known as colloidal science.

Latter many investigators including Thomas Graham realised that distinction between crystalloids and colloids was not rigid, since many crystalline substances like sulphur, carbon and salt can be converted into colloidal form by suitable means. At the same time the so called colloidal like gum and gelatin, were shown to have a crystalline structure by X-ray examination. In fact, it is now well known that one and the same substance may show colloidal behaviour at one time and crystalloidal behaviour at another time depending upon the prevailing conditions for example, sodium salt of long chain fatty acids (the soaps) show colloidal character in water in which they are sparingly soluble but crystalloidal character in alcohol in which they are freely soluble. The term ‘colloidal substances’ has, therefore been discarded in favour of ‘colloidal state’ into which almost every substances can be brought by suitable means.

Hence colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions.

11.3 COLLOIDAL SYSTEMS

When the diameter of the particles of substance dispersed in a solvent ranges from about $10A^0$ to $2000A^0$, the system is said a colloidal solution, colloidal dispersion or simply a colloid, the material will particle size in the colloidal range is said to be in the colloidal state. A colloidal system is thus a two phase system consisting of a continuous phase or dispersion medium in which extremely minute particles, lying within the colloidal range of second substance termed as discontinuous phase or dispersed phase, are suspended.

Difference between suspensions, colloidal solutions and true solution

Property	Suspensions	Colloidal solutions	True solution
1. Nature	Hetrogeneous	Heterogeneous	Homogeneous
2. Size range	Greater than 2000A^0 or 200 mμ	Between 10A^0 to 2000 a^0 or 1 mμ to 200 mμ	Less than 10a^0 or 1 mμ
3. Visibility	Particles are visible under microscope even with a naked eye	Particles are visible under ultramicroscope	Particles are not visible even under ultramicroscope
4. Diffusibiltiy	Do not diffuse	Diffuse slowly	Diffuse rapidly
5. Tyndall effect and Brownian movement	Do not exhibit	Exhibit	Do not exhibit
6. Molecular weight	Low	High	Low

Table -1

11.3.1Types of Colloidal Systems

As we have seen in the above article, a colloidal system is made of two phases, the substance distributed as the colloidal particle is called the dispersed phase, the second continuous phase in which the colloidal particles are dispersed is called the dispersion medium. If we take colloidal solution of copper in water, copper particles constitute the dispersed phase and water dispersion medium (fig 8.1).

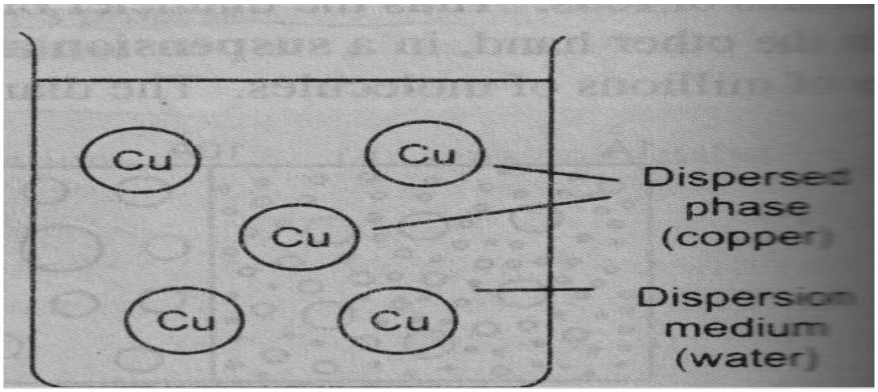


Fig 11.1

Now we see that either the dispersed phase or the dispersion medium can be gas liquid or solid, these are eight types of colloidal system possible.

A colloidal dispersion of one gas in another is not possible, since the two gases would give a homogeneous molecular mixture.

The various types of colloidal systems are given in table 2.

Dispersion medium	Name of the dispersion phase	Name of the colloidal system	Examples
1. Gas	Liquid	Liquid aerosol	Clouds, mist, fog
2. Gas	Solid	Aerosol	Smoke, dust
3. Liquid	Gas	Foam	Shaving cream, foam
4. Liquid	Liquid	Emulsions	Milk, hair cream, cod-lever oil
5. Liquid	Solid	Colloidal solutions	Colloidal gold
6. Solid	Gas	Solid foam	Foam rubber, occluded gases
7. Solid	Liquid	Gel or jelly	Butter, cheese, gels
8. Solid	Solid	Solid sol	Alloys, ruby glass (gold dispersed in glass)

Table-2

11.3.2Classification of Colloids

Substance like metal, metal sulphides cannot be brought into the colloidal state simply by bringing them in contact with solvent, these are known as lyophobic colloids (or hydrophobic colloid if water is solvent).

Substances like proteins, starch and rubber whose molecules are large enough to be close to the lower limit of colloidal range, pass readily into colloidal state when mixed with a suitable solvent are called lyophilic colloids (or hydrophilic colloids if water is solvent).

11.3.3 Distinction between Lyophilic and Lyophobic Colloids

Property	Lyophobic sols	Lyophilic sols
Preparation	Formed by special method	Formed easily
Nature	Particles are true molecules	Particle consists of aggregate molecules
Viscosity	Viscosity is almost the same as that of the medium	Viscosity is much higher than that of the medium
Visibility	Particle can be readily detected under ultra microscope	Particles cannot be readily detected even under ultramicroscope
Tyndall effect	More distinct	Less distinct
Reversibility	Lyophobic salts are irreversible	These are reversible
Surface tension	Surface tension is usually the same at that of the medium	Surface tension is generally lower than that of the medium
Migration in electric field	Particles migrate to anode or cathode	Medium particles migrate to anode or cathode, or not at all

Table -3

11.4 GENERAL PROPERTIES OF COLLOIDAL SYSTEMS

11.4.1 Heterogeneous character

As you have seen from the above discussion every colloidal system is a heterogeneous system. It consists of two phases, the dispersed phase and dispersion medium.

11.4.2 Visibility

Most of the sols appear to be true solutions with naked eye, but the colloidal particles can be seen through an ultramicroscope.

11.4.3 Colligative properties

The property which depends on the number of particles in solution and not in any way on the size or chemical nature of the particles, is known as a colligative property.

As you know that colloidal particles are aggregate of molecules, therefore all the colligative properties would be reduced. Hence colloidal systems have very low osmotic pressure, and freeze and boil at about the same temperature as the pure dispersion medium.

11.4.4 Diffusibility

The colloidal particles do not readily diffuse through a parchment paper or any other membrane.

11.5. OPTICAL PROPERTIES

11.5.1Tyndall effect

In 1867 Tyndall found that when a beam of light is passed through a true solution, it cannot be seen unless the eye is placed directly in the path. But when the same light beam is passed through a colloidal dispersion it is

visible as a bright beam. The phenomenon of the scattering of light by the sol particles is called Tyndall effect. The illumination of beam or cone formed by the scattering of light by the sol particles if often called as Tyndall beam or Tyndall cone.

This phenomenon is due to the scattering of light from the surface of colloidal particles. In true solutions the particle size is very small to scatter the light and hence the beam is invisible.

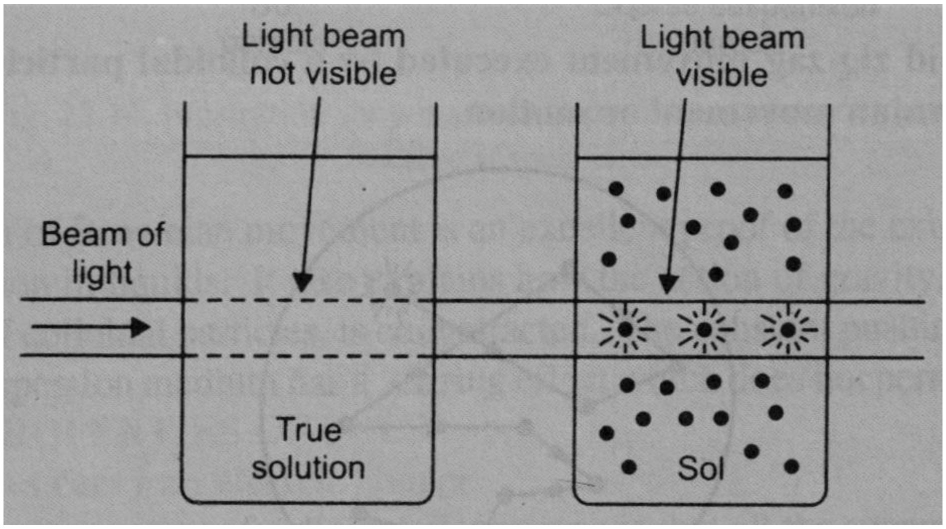


Fig-11.2

The intensity of the scattered light depends on the difference between the refractive indices of the dispersed phase and dispersion medium. In lyophobic sols, the difference is appreciable and hence the Tyndall effect is quite well-defined. In lyophilic sols the difference is small hence the Tyndall effect is much weaker.

Sol particles cannot be seen with microscope. Zsigmondy (1903) used the Tyndall phenomenon to set up an apparatus called ultramicroscope. The intense beam of light is focused on a sol contained in a glass vessel. The focus of light is then observed with a microscope at right angle to the beam individual sol particles appear as bright specks of light against a dark background. It may be noted that under the ultra microscope, the actual particles are not visible. It is the larger halos of scattered light around the particles that are visible. Thus the ultra microscope does not give any information regarding the shape and size of sol particles.

11.6 PROTECTION OF COLLOIDS

Lyophobic sols are easily precipitated by small amount of electrolyte. However these sols are often stabilized by the addition of lyophilic sols. When lyophobic and lyohilic sols are mixed and lyophilic sol is in excess then the resultant sols is avoided from being coagulated. The sol now is more stable to temperature changes and is not readily precipitated by electrolytes. The lyophilic colloids thus used for protecting the lyophobic colloids are known as protective colloids. Different protective colloids have different protective powers. Zsignondy investigated the protective action quantitatively and gave the concept of gold number.

11.6.1 Gold number

Gold number may be defined as 'the weight in milligrams of protective colloid which will just stop the coagulation of 10 ml of a gold sol on adding 1 ml of 10% solution of sodium chloride'. Gold sol is ruby red in color and becomes blue on coagulation.

Gold number of protective colloids

Sl No.	Colloid	Gold number
1.	Gelatin	0.005-0.01
2.	Casein	0.1
3.	Gum Arabic	0.15-0.25
4.	Dextrin	6-20
5.	Starch	25.0

Table-4

11.7 SUMMARY

In this chapter you have studied that colloidal system is a two phase heterogeneous system in which one phase is dispersed in a fine state of subdivision in another medium termed as dispersion medium. In actual instances the size limit is not rigid and may vary on either side but most systems conform to the above description.

The wide variety of proteins obtained from the living world form the most important group of naturally occuring macromolecules. These are produced from repetitive linking of various amino acids. As a result the proteins are amphoteric in nature.

The sub-topics studied in this chapter include definition, type of colloidal systems, properties of sols. Preparation of sols, purification of sols, zeta potential, electrophoresis, electro-osmosis, coagulation of colloids, origin of charge on colloidal particles.

Emulsions and gels and their properties have also been studied in this chapter. Most important above all is wide range of uses of colloids in different areas in our daily life and industry.

11.8 TERMINAL QUESTIONS

(A) Multiple choice questions:

(1)In a true solutions, the diameter of the dispersed particles is of the range from-

(a) $1A^0$ to $10A^0$ (b) $10A_0$ to $100\ A^0$

(c) $100\ A^0$ to $200\ A^0$ (d) $200\ A^0$ to $500\ A^0$

Ans (a)

(2) The precipitating power of Al^{3+}, Na^+ and Ca^{2+} is in the order

(a) $Na^+ > Ca^{2+} > Al^{3+}$ (b) $Na^+ > Al^{3+} > Ca^{2+}$

(c) $Ca^{2+} > Na^+ > Al^{3+}$ (d) $Al^{3+} > Ca^{2+} > Na^+$

Ans (d)

(3) Ice cream is a dispersion of ....in cream.

(a) Water (b) Water vapour

(c) Ice (d) Cooling agent Ans (c)

(B) Short answer questions:

(1)Define the following terms:

(a) Sol (b) Gel

(c) Lyophilic Colloids (d) emulsion

(2) How are colloidal solutions classified.What is meant by colloidal state of matter.

(3) Explain why-

(a) Deltas are formed at a place where the rivers pour their water into the sea.

(b) Define number average and weight average molecular weight.

(C) Long answer questions:

Q.1 What is a molecular colloid? How does a lyophilic colloid stabilise a lyophobic one? Give an account of gold number in this respect.

Q.2 Discuss the origin of charge on a colloidal particles. What is meant by electrical double layer?

Q.3 What are lyophilic and lyophobic sols? Discuss the main differences between lyophilic and lyophobic colloids.

Q.4 Explain the following:

(a) stability of colloids

(b) Difference between gels and emulsions.

(c) The Schulze-Hardy rule of coagulation.

Q.5 Equal number of molecules with M_1=10,000 M2=10,000. are mixed. Calculate number average molecular weight and mass average molecular weight.

Q.6 (a) What are various methods for determining size of the colloidal particles? Describe one method in detail.

(b) Write a note on Brownian movement.

UNIT 12: CHEMICAL KINETICS

COMMENTS:

12.1 OBJECTIVES

The chemical reactions can be classified into following categories on the basis of their speed:

(a) Fast reactions which proceed at very fast speed and it is practically very difficult to measure the speed of such reactions. Examples of fast reactions include

(i) Neutralisation of acids and bases
(ii) Organic substitution reactions
(iii) Explosive reactions of oxygen with hydrogen and hydrocarbons. The rates of such reactions can be measured by using special methods.

(b) Extremely slow reactions which proceed at a very slow speed and the speed is so slow that it not possible to measure the speed of such reactions. Rusting of iron is very slow reaction.

(c) Reaction which precede a measurable speed. These reactions are utilized in the study of chemical kinetics.

Examples are Inversion of cane sugar, saponification of ethyle acetate etc. The significance of study of kinetics of reactions is many fold. It provides very important information on how chemical reactions occur and what is their mechanism. The knowledge of rate of reaction is very valuable for the success of an industrial process where it is imperative to second optimum conditions of the reactions involved when these reactions proceed at a rate so as to give maximum yield.

12.2 INTRODUCTION

The branch of physical chemistry which deals with the speed or rate at which a reaction occurs is called chemical kinetics. **Chemical Kinetics is the study of rate of a reaction under different conditions like different concentrations, pressures, temperatures, catalyst, pH, dielectric constant of the medium, free radical scavengers, neutral salts etc and suggesting a suitable mechanism for the reaction**.

Chemical kinetics constitutes an important topic in physical chemistry. It concerns itself with measurement of rates of reactions proceding under given condition of temperature, pressure and concentration.

The study of chemical kinetics has been highly useful in determining the factors which influence rate of reaction as well as in understanding mechanism of a number of chemical reactions. The experimental data have led to the development of the modern theories of chemical reactivity of molecules.

12.3 CHEMICAL KINETICS AND ITS SCOPE

12.3.1 Scope of chemical kinetics

Thermodynamics predicts that at room temperature hydrogen and oxygen react to form water, all the reactants being essentially converted into products. When we carry out the experiment we find that the reaction proceeds so slowly that unless we are willing to wait indefinitely, practically no water results. On the other hand, experiment shows that N_2O_4 decomposes into NO_2 under atmospheric conditions almost instantaneously even though $-\triangle G^0$, which is a measure of spontaneity of a reaction, is far less for the decomposition of N_2O_4 than that for the reaction between hydrogen and oxygen to form water.

Above two examples suggest that there is essentially no correlation between thermodynamic instability and the rate of the chemical reaction. In fact, the rate of a reaction depends upon structural and energetic factors which are not uniquely specified by thermodynamic quantities such as the free energy change. Hence, chemical kinetics is a technique complementary to thermodynamics for studying a given reaction.

The first stage in studying the rate and the mechanism of a chemical reaction is the determination of overall stoichiometry of the reaction and to identify any side-reaction. The next step involves the determination of the change of the concentration of the reactant and product species with time. Since the reaction rate depends sharply on temperature, the temperature of the reacting mixture must be kept constant.

Several experimental techniques have been developed to monitor the concentration of the reactants and products and their variation with time. The selection of a typical method depends on the nature of the species involved and how rapidly their concentration change. For reactions that are relatively slow, conductometric, poteniometric, optical methods, polarimetry and spectrophotometry are used. The time taken for reactions to reach completion varies widely, from femtoseconds ($1fs = 10^{-15}$ s) to days.

For reactions in which one or more products are gases, the reaction rate involves monitoring pressure as in the reaction:

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

For optical method involves monitoring optical activitiy.

Reactions in solution involving ionic species may be studied by monitoring their conductivity. The change in EMF of an electrochemical reaction can be followed potentiometrically. Spectrophotometry, the measurement of intensity of absorbtion in a particular spectral region is widely used to monitor concentration. Reactions that involve a change in concentration of H^+ ions may be studied by monitoring pH of the solution with a glass electrode. Other methods of monitoring the composition include the detection of fluorescence and phosphorescence, mass spectrometry, gas chromatography and magnetic resonance.

In a real time analysis the composition of reaction mixture is analysed while the reaction is in progress by direct spectroscopic observation. In the quenching method, the reaction is stopped after being allowed to proceed for a certain time and the composition is analysed. The entire reaction mixture may be quenched either by sudden cooling or by adding to it a large volume of solvent. This method is applicable for reactions that are slow enough for there to be little reaction during the time it takes to quench the reaction mixture.

Femtochemistry has emersed as the most exciting field for investigating extremely fast reactions whose time-scale is of the order of femtoseconds. This method is due to A.H. Zewail, who was awarded Nobel Prize of chemistry in 1999.

Femtochemistry is extremely useful for studying biological processes such as the energy converting processes of photosynthesis and photostimulated processes of vision in which the primary energy and electron-transfer reactions occur on the femtosecond or picosecond time-scale.

12.3.2 Rate of a reaction

The rate of a reaction tells us to what speed the reaction occurs. Let us consider a simple reaction-

$A B \longrightarrow$

The concentration of A decreases and that that of B increases with time. The rate of a reaction is defined as the change in concentration of any

of reactant or product with time. As you know during the progress of a reaction the concentration of A keeps on falling with time. The rate of reaction at any given instant is given by the expression-

$r = -dC_A/dt = kC_A$……………………….(1)

where $-dC_A$ is very small decrease in concentration of A in a very small time interval dt, C_A gives the concentration of the reactant A at a given instant and k is constant called the rate constant or velocity of the reaction.

Now the concentration of product B increases with time. Hence rate of reaction can also be expressed in terms of increase in concentration of the product B as well. Thus

$r = dC_B/dt = kC_A$ ………………………….(2)

where dC_B is very small increase in the concentration of product B in a very small time interval of time dt.

Now it should be clear to you from (1) and (2)

$r = -dC_A/dt = dC_B/dt = kC_A$

and for a reaction $A+B \longrightarrow M+N$

the rate can be expressed

$r = -dC_A/dt = -dC_B/dt = dC_M/dt = dC_N/dt = kC_AC_B$………………(3)

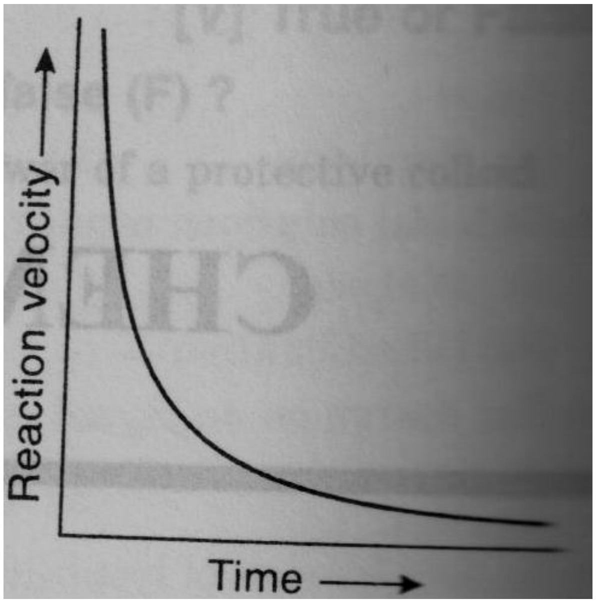


Fig-12.1

As the reaction proceeds the reactants are consumed where by their molecular concentration decreases. Hence the rate of a chemical reaction will also decrease with time. The graph between reaction velocity and time will be as shown in the fig. (6.1). Now it should be clear to you that reaction velocity is maximum to start with and then falls gradually with time. The reaction velocity become so slow in the latter states that it takes a

very long time for the reaction to be completed. It can be safely assumed that in the latter stages the reaction is nearly complete.

Now let us consider a reaction-

$$aA+bB \longrightarrow cC+dD$$

In this reaction a moles of A reacts with b moles of B to form c moles of C and d moles of D. the rates of such a reaction can be expressed either in terms of decrease in concentration of a reactant per mole or increase in concentration of a product per mole. Thus we can write as follows:

$$r= -1/a\ dC_A/dt = -1/b\ dC_B/dt =1/c\ dC_C/dt = 1/dC_D/dt = k\ C^a_A C^b_B$$

12.3.3 Units of rate

Reaction rate has the units of concentration divided by time. We express concentration in moles per litre (mole/litre) but time may be given in any convenient unit second(s), minutes (min), hours (h) days (d) or possibly years. Therefore, the units of reaction rates may be

mole/litre/secormole $l^{-1}s^{-1}$

mole/litre/ minutemol $l^{-1}m^{-1}$ and so on

12.3.4 Order of reaction and molecularity

The total number of reactant particles involved in the overall reaction, is called as molecularity of a reaction

Thus in the reaction -

$N_2O_5\,(g) \longrightarrow 2NO_2\,(g)+1/2O_2(g)$ it is unimolecular

$2HI\,(g) \longrightarrow H_2(g) + I_2(g)$ it is bimolecular

$2NO\,(g) + O_2(g) \longrightarrow 2NO_2$ it is trimolecular

Order of reaction depends only on the reactants upon which the rate of reaction depends. It means that order is in those reactants only, by changing whose concentration, the rate of reaction changes.

If reaction rate is independent of reactant concentration, the order is zero in that reactant.

We can say that “Order is the sum of powers of concentration of reactants as given in a rate law or rate equation or rate expression for the reaction under consideration”.

A reaction is said to be first order if its rate r (or dx/dt) is given by the following rate expression -

$R = dx/dt = kC_a$

The reaction is of second order and third order if its rate expressions are given by Eqn. (i) and (ii) respectively

$dx/dt = kCa^2$ or kC_aC_b ………………(i)

$dx/dt = kCa^3$ or $kC_a^2C_b$ or $kC_aC_b^2$ ……………….(ii)

The subscripts a, b and c stand for various reactants A, B and C respectively. When the rate expression is given by

$dx/dt = kC_a^{n_1} C_b^{n_2} C_c^{n_3}$

The order of reaction as a whole n is given by $n = n_1 + n_2 + n_3$…………

The molecularity of any process can only be small position integers, while order of reaction can have zero as well as fractional values.

Difference between order of reaction and molecularity:

	Molecularity	Order of reaction
1	It is equal to the number of molecules of reactants which take part in a chemical reaction.	1. It is equal to some of the power of the molar concentration of the reactants in the rate expression.
2	It is theoretical concept.	2. It is an experimentally determined quantity, which is obtained from the rate for the overall reaction. It depends on rate determining step in the reaction mechanism.
3	It is always a whole number.	3. It may be negative, zero or fractional value generally not more than 3.
4	It is obtained from a single balanced chemical equation.	4. It cannot be obtained from a balanced chemical equation
5	It does not reveal anything about reaction mechanism.	5. It reveals some basic facts about a reaction mechanism.

Table 12.1

12.4. ZERO, FIRST, SECOND AND THIRD ORDER REACTIONS

(1) Zero order reaction

Reactions, in which the reaction rate does not depend upon the initial concentration of the reactant, are said to be zero order reactions. The Law of mass action fails in these reactions

$AB \longrightarrow$

$$\frac{d[A]}{dt} = kA^0 = k$$

Examples of zero order reactions:

1. Thermal decomposition of hydrogen iodide at gold surface is found to be of zero order

$2HI \longrightarrow H_2 + I_2$

2. The decomposition of ammonia on platinum surface at 800^0C in kinetically of zero order.

$NH_3 \longrightarrow N_2 + 3H_2$

3. The phosphine decomposition on the surface of molybdenum or tungsten at high pressure is of zero order.

$2PH_3 \longrightarrow 2P + 3H_2$

(2) First order reaction

A first order reaction is that in which the sum of powers to which the concentrations of reactants must be raised while expressing the reaction rate, is one.

Expression for first order reaction is given by

$A \longrightarrow$ products

A P

a 0 initially

a-x x after time t

rate expression is given as

$r = -d[A]/dt$

$= d[P]/dt$

= dx/dt

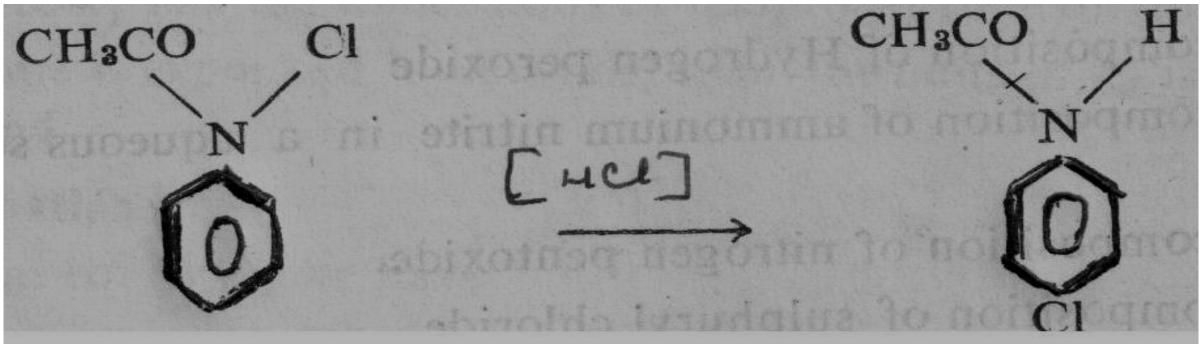
=k[A]

= kC_A

= k. A (at zero time)

=k (a-x) (at t time)

Example is conversion of N-chloroacetamide into parachloroacctanicide



(3) Second order reaction

A second order reaction is that in which the sum of powers to which the concentrations of reactants must be raised while expressing the reaction rate, is two.

dx/dt = kC^2_A for reaction 2A products ⟶

and dx/dt = $kC_AC_B$for reaction A+B products ⟶

Example of second order reactions are :

Hydrolysis of an ester by an alkali (Saponification of ester)

$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

(4) Third order reaction

Definition of third order reaction:

A third order reaction is that in which the sum of powers to which the concentrations of reactants must be raised while expressing the reaction rate, is three.

Reactions of third and higher order are rare, but there are infact reactions which are definitely of third or sometimes higher order. This is due to the effect that the probability of three molecules coming to a single point simultaneously is must less as compared to unimolecular and bimolecular reactions.

In a reaction of the third order the number of molecules where concentration alters as a result of chemical change is three, and the change may belong to any of the following types

$A + A + A \longrightarrow$ products

$A + A + B \longrightarrow$ products

$A + B + C \longrightarrow$ products

Note: Above given examples are of elementary reactions i.e. reactions in which order and molecularity are same and there is a single step mechanism. For complex reactions (involving more than one step in mechanism and difference in molecularity and order), order may be 3 even if the number of reactants is more than 3.

Examples of third order reaction is

(i)$2\ FeCl_3+SnCl_2 \longrightarrow 2\ FeCl_2+SnCl_4$
(ii)$O_2+2NO \longrightarrow 2NO_2$
(iii)$2NO + Cl_2 \longrightarrow 2NOCl$

12.5 CONCEPT OF ACTIVATION ENERGY

12.5.1 Effect of temperature on reaction rate

Temperature coefficient of a reaction:

Now let us consider effect of temperature on reaction rates

It has been found that generally an increase of temperature increases the rate of reaction. The ratio of rate constants of a reaction at two temperatures differing by 10^0C is known as temperature coefficient of the reaction. The temperatures usually selected for this purpose are 25^0C and 35^0C. Thus

$$\text{Temperature coefficient} = \frac{\text{Rate at } 35^0C}{\text{Rate at } 25^0C} = \frac{k_{35}}{k_{25}}$$

The value of temperature coefficient for most of the reactants is close to 2 and in some cases it approaches to 3.

$$\text{Hence temperature coefficient} = \frac{\text{Rate at } 35^0C}{\text{Rate at } 25^0C} = \frac{k_{35}}{k_{25}} = 2 \text{ to } 3$$

12.6 COLLISION THEORY OF REACTION RATE

Now let us study why such small rise of temperature speeds up a reaction to such a large extent. This can be explained on the basis of collision theory.

According to collision theory for chemical reaction to occur, there must be collisions between reacting molecules. But all collisions are not effective. Only a small fraction of collisions produce a reaction. Two main conditions for a collision between the reacting molecules to be productive are-

(i)The colliding molecules must possess sufficient kinetic energy to cause a reaction.

(ii)The reacting molecules must collide will proper orientation.

The molecules must collide with sufficient energy:

Let us consider a reaction

$$A\text{-}B + B\text{-}B \longrightarrow 2\ A\text{-}B$$

A chemical reaction occurs by breaking bonds between the atoms of reacting molecules and forming new bonds in the product molecules. For ***breaking the bonds energy is required and in forming the bonds energy is liberated.*** The energy for breaking the bonds comes from the kinetic energy possessed by the reacting molecules, before the collision.

The (figure 7.3) shows the energy of molecules A_2 and B_2 as the reaction

$A_2+B_2 \longrightarrow 2AB$ progresses.

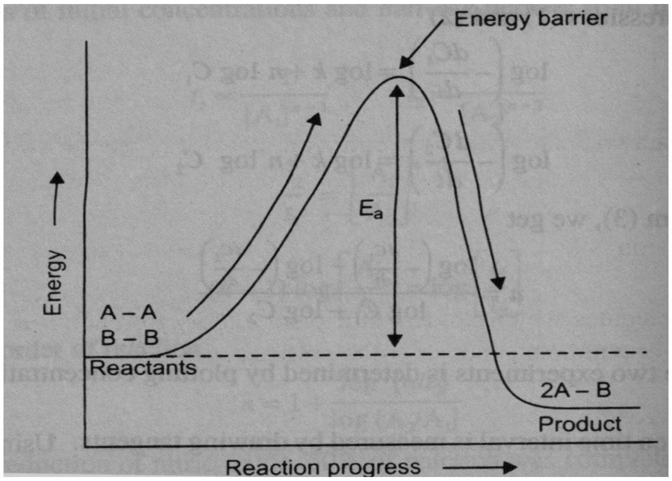
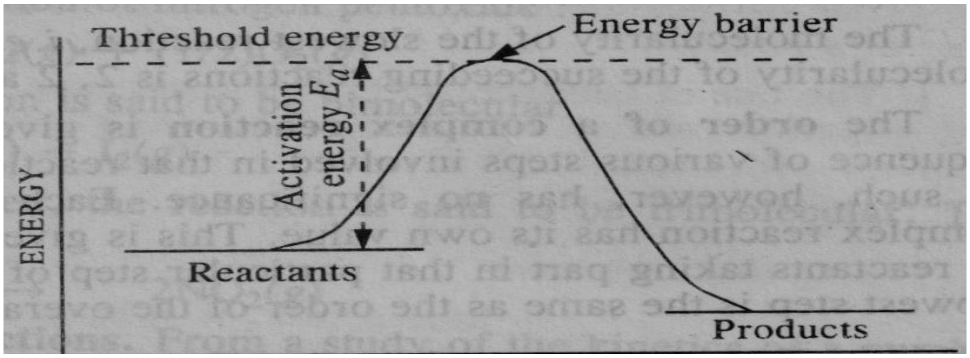


Fig 12.2

The figure 7.3 also shows the activation energy E_a, that is minimum energy required to cause a reaction between the colliding molecules. Only the molecules that collide will a kinetic energy greater than E_a are able to get over the barrier and react. The molecules colliding will kinetic energies less than E_a fail to cross the barrier.

As you have studied till now that for a reaction to occur there must be collision between molecules. And most of the collisions are ineffective. According to collision theory those collision results in chemical reaction in which the colliding molecules are associated with a certain minimum energy called threshold energy



Reaction progress ⟶

Fig- 12.3

Hence there is certain minimum energy called threshold energy which the colliding molecules must acquire before they are capable of reacting. Most of the molecules have much less kinetic energy than the threshold energy. The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to yield products is known as activation energy.

That means

Activation energy = threshold energy – energy possessed by the molecules.

Now you must have followed from the above discussion that there is energy barrier placed between reactants and products (fig 7.4) The barrier has to be crossed before reactants can yield product.

12.7 EFFECT OF CATALYST

As you have studied earlier a catalyst is a substance that can increase the rate of a reaction but which itself remains unchanged in amount and chemical composition at the end of the reaction. When a catalyst is added, a new reaction path with a lower energy barrier is provided (dotted curve in the fig 7.5). Since the energy barrier is reduced in magnitude, a larger number of molecules of the reactants can get over it. This increases the rate of the reaction.

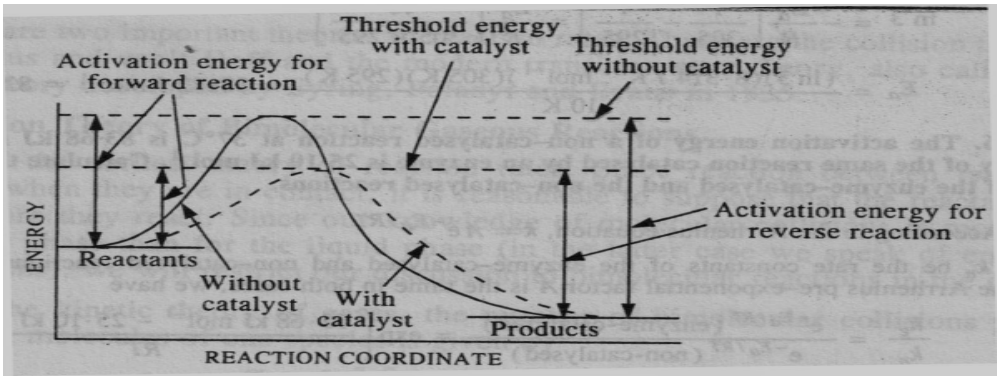


Fig- 12.4

12.8 SUMMARY

In this chapter you have studied different definitions associated with chemical kinetics, rate laws for zero, first, second and third order reaction and will examples also rate laws for zero order and first order reaction. The difference between order of reaction and molecularity has been discussed. The factors affecting rate of a reaction have also been studied namely the factors are temperature, pressure, concentration, catalyst and surface area.

The first stage in studying the rate and mechanism of a chemical reaction is the determination of the overall stoichiometry of the reaction and to identify any side reaction. The next step involves the determination of the change of the concentration of the reactant and product species with time. The reaction rate depends sharply on temperature; the temperature of the reaction mixture must be kept constant.

12.9 TERMINAL QUESTIONS

(A) Multiple Choice Questions

Q.1 The reaction $A+B+C \longrightarrow$ Products is found to obey the rate law.

$r = d[A]/dt = k[A]^2 [B]^{3/2} [C]^{-1/2}$ the overall order of reaction is

(a) 7/2 (b) 5/2 (c) 3 (d) 1

Ans (c)

Q.2 If the rate of reaction is given by $r = k[A]^2[B]^{1/2}$

The overall order of reaction is

(a) 5/2 (b) ½ (c) 2 (d) 1

Ans (a)

Q.3 Which reaction is pseudo-unimolecular reaction?

(a) $H_2+Cl_2 \longrightarrow 2HCl$ (b) Acid-catalyzed hydrolysis of an ester.

(c) Base-catalyzed hydrolysis of an ester.

(d) $N_2O_5 \longrightarrow N_2O_4 + 1/2O_2$

Ans (b)

Q.4 **Choose the correct statement:**

(a) The rate of a reaction decreases with T

(b) Order is always equal to molecularity

(c) Catalyst is always essential for a reaction

(d) For a zero order reaction the concentration of product increase linearly will time.

Ans (d)

Q.5 **Choose the correct statement:**

(a) The rate of reaction decreases with T

(b) Order of reaction is equal to molecularity of a reaction.

(c) The units of first order rate consistent are mole lit S^{-2}

(d) $t_{1/2}$ of the first order reaction is independent of initial concentration.

Ans (d)

Q.6 Reaction rates can change with

(a) Temperature

(b) The addition of a catalyst

(c) Reactant concentration

(d) all of these

Ans (d)

(B) Short Answer Questions:

Q.1 Derive mathematical expression for the rate constant of a reaction A. Products of the first order.

Q.2 Distinguish between reaction rate and rate constant.

Q.3 Explain why the rate of reaction cannot be measured by dividing the total amount of a substance reacted by the total time taken.

(C) Long answer/essay type questions questions:

Q.1. Explain the following terms.

(a) Rate of reaction (b) Molecularity of a reaction

(c) Order of reaction (d) Rate constant.

Q.2 What are different factors which affect the rate of a reaction, explain.

Q.3 What is meant by the terms rate constant and order of reaction?

Starting from the rate equations derive the units of the rate constant (k) for a zero order and first order reaction.

Q.4 Distinguish between molecularity and order of reaction. Why high molecularity reactions are rare explain?

UNIT 13: THERMODYNEMICS AND THERMOCHEMISTRY

CONTENTS:

13.1 OBJECTIVES

Literally speaking thermodynamics concerns itself with the flow of heat and it deals with relation between heat and work. Heat, as we all know, is a form of energy and the conversion of heat into useful work and vice versa come under the domain of thermodynamics. The science of thermodynamics governs not only the transformation of heat into work but also includes all types of inter-conversion of one kind of energy into another; e.g., electricity into work, chemical energy to electrical energy, etc.

13.2 INTRODUCTION

The study of flow of heat or any other form of energy into or out of a system as the system undergoes a physical or chemical transformation is called thermodynamics. The most distinguishing feature of thermodynamics, however, is its predominant concern with temperature and temperature-dependent variables.

Thermodynamics is essentially a practical science and it has its verification extending mainly to the fields of chemistry, physics and engineering. With the assistance of thermodynamics the chemist predicts the possibility of a chemical reaction or the maximum yield in a chemical process under a given set of circumstances. Using thermodynamic laws the physicist explains the phenomena where phase changes or inter-actions with radiations or electromagnetic field are involved. To the engineers it is the most powerful weapon to solve problems of power and consumptions, in the prediction of efficiencies of heat-engines and refrigerators, in the design of engines and so on.

The thermodynamic principles correlate different observable properties of a system but cannot always give us the exact magnitude of a property of the system. These relations help us in predicting the behaviour of a system or the ultimate result that a process would lead to. Thus, from thermodynamics we can predict under a set of defined conditions the maximum yield in a chemical process, but we cannot say anything about the rate of the reaction or the mechanism of the reaction.

Thermodynamics does not make any hypothesis as to the structure of matter. Thermodynamics derives from various laws, relations between properties experimentally observed but not offer any explanation as to why these properties arise in a system. The approach in thermodynamics is thus entirely different from that in the atomic constitution of matter. For example, in kinetic theory we consider the pressure of a gas is measure of the impact of the molecules on the wall per second, while in thermodynamics, pressure is a property of the state of a system. Similarly temperature is, according to kinetic theory, a measure of the average kinetic energy of the molecules while it is a simple property of state from the view-point of thermodynamics.

13.3 DEFINITION OF THERMODYNAMIC TERMS

13.3.1 Temperature

The hotness or the coldness of an object is understood fundamentally by our senses. The hotter body will have a higher temperature than the colder body. We also have another experience in nature. Suppose there are two bodies, A and B, A being hotter than B. If A is brought in contact with B, it is found that A gradually becomes colder and B becomes warmer. During this process, other changes in pressure or volume may also occur. Ultimately, we find that both A and B are equally warm, i.e. they have attained the same temperature. A and B are now said to be in thermal equilibrium. During this process, some energy (really the heat-energy) have moved from the hotter body A to the colder body B. Temperature then determines the direction in which in which heat would flow, namely, from the hotter body to colder body. In other words “temperature is the driving forces for the flow of heat.”

Zeroth law of thermodynamics:

Let us consider three systems A, B and C. Suppose A is in thermal contact with B through a diathermic wall. A diathermic wall is that which permits the systems in contact to influence each other. And again B is also in thermal contact with C (fig 10.1). Sufficient time being allowed A will be in thermal equilibrium.

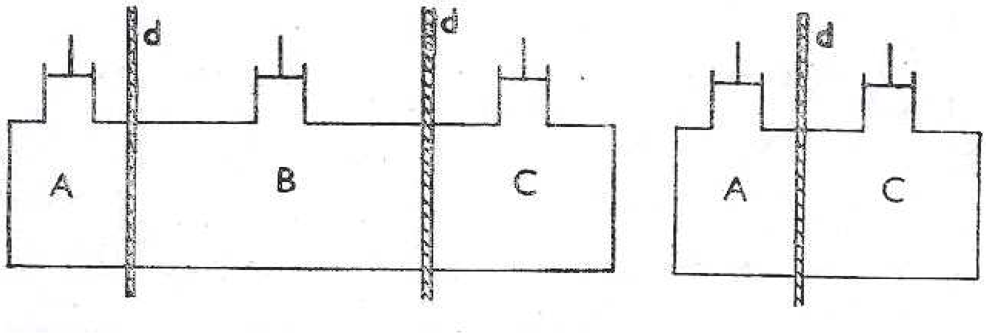


Fig 13.1 Zeroth law of thermodynamics

With B. Similarly, C will also in thermal equilibrium with B. If B is now removed and A is brought in thermal contact with C, it is found that there is no change in the coordinates of A and C. The systems A and C are in thermal equilibrium with each other. Hence

"Two systems in thermal equilibrium with a third are in thermal equilibrium with each other". This is Zeroth law of thermodynamics.

13.3.2 System and surroundings

A system may be defined as any specified portion of matter under study which is separated from rest of the universe with a bounding surface. A system may consist of one or more substances.

The rest of the universe which might be in a position to exchange matter and energy with the system with the system is called surroundings. The real or imaginary surface separating the system from the surroundings is called the boundary. The boundary may be real or imaginary.

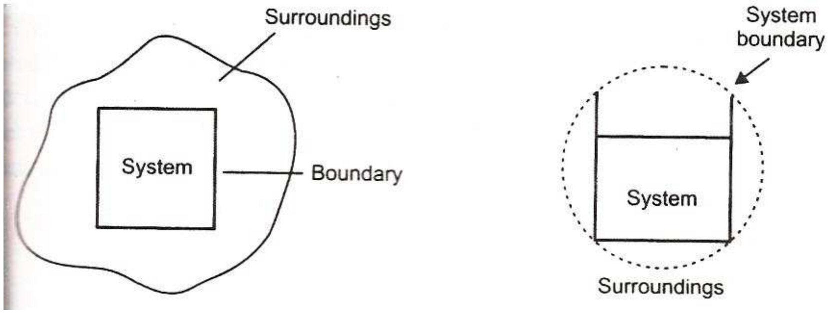


Fig 13.2 thermodynamic system and surroundings

A quantity of a gas in a closed cylinder has real and defined boundaries, but if the same gas flows through a zigzag pipe, its boundaries constantly change and have to be followed in imagination as it progresses. If say 250 ml of water contained in a beaker it will constitute a thermodynamic system. The beaker and the air in contact, are the surroundings.

If one mole of a gas confined in a cylinder fitted with a piston, is a thermodynamics system. The cylinder, the piston and all other objects outside the cylinder, form the surroundings. Here the boundary between the system (gas) and the surroundings (cylinder and piston) is clearly defined. A system and its surroundings constitute the universe.

System + surroundings = universe

13.3.3 Homogeneous and heterogeneous system

A system is said to be homogeneous if it is completely uniform throughout. In such a system there is only one phase. A phase is defined as a homogeneous, physically distinct and mechanically separable portion of a system. Examples of homogeneous system are pure single solid, liquid or gas, mixture of gases and true solution of solid in a liquid.

A system is said to be heterogeneous, when it is not uniform throughout. In such a system there are two or more phases. Examples of heterogeneous system are: ice in contact with water, ice in contact with vapour, etc. Here ice, water and vapour constitute separate phases.

13.3.4 Types of systems

There are three types of thermodynamics systems depending on the nature of boundary.

13.3.4.1Open system

A system which can exchange matter as well as energy with its surroundings is said to be an open system. Hot water contained in a beaker placed on laboratory table is an open system. Here the water vapour (matter) and also heat (energy) is transferred to the surroundings through the imaginary boundary.

13.3.4.2 Closed systemA system which can exchange energy not matter with its surroundings is called a closed system. A specific quantity of hot water contained in a sealed tube in an example of a closed system. While no water vapour can escape from this system, it can transfer heat through the walls of tube to the surroundings.

13.3.4.3 Isolated systemA system which can exchange neither matter nor energy with its surroundings is called an isolated system.

Let us consider a system 100 ml of water in contact with its vapour in a closed vessel which is insulated. Since the vessel is sealed, no water vapour (matter) can escape from it. Also as the vessel is insulated, no heat (energy) can be exchanged with its surroundings.

Isothermal and adiabatic systems:

If a system is maintained at a constant temperature it is termed as isothermal system. If a system is so insulated from its surroundings that no heat flows in or out of the system its termed as adiabatic system.

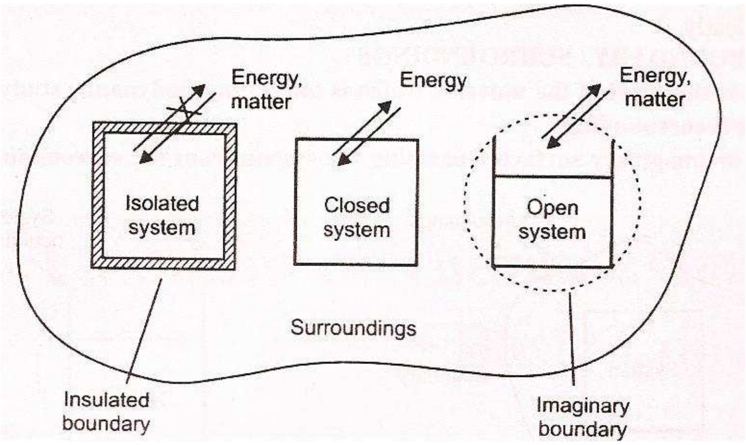


Fig 10.3 three types of thermodynamic systems

13.3.5 Intensive and extensive properties

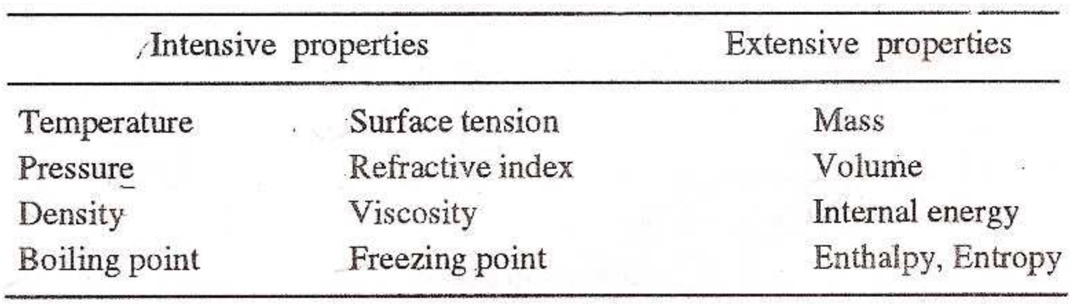
The macroscopic or bulk properties of a system (volume, pressure, mass etc.) can be devided into two classes

(a) Intensive properties

(b) Extensive properties

In intensive property of a system is that which is independent of the amount of the substance present in the system. The examples are temperature, pressure, density, concentration, viscosity. Refractive index, surface tension and specific heat.

A property that does depend on the quantity of matter present in the system is called an extensive property. Some examples of extensive properties are volume, no. of moles, enthalpy, entropy, mass and Gibbs free energy.



Intensive properties		Extensive properties
Temperature	Surface tension	Mass
Pressure	Refractive index	Volume
Density	Viscosity	Internal energy
Boiling point	Freezing point	Enthalpy, Entropy

Table 13.1 common properties of a system

13.3.6 Processes and their types

When a thermodynamic system changes from one state to another, the operation is called a process. When a system changes from one state to another it is accompanied by change in energy. In the case of open systems, there may be change of matter as well.

The following types of processes are known:

(1) Isothermal process:

A process is said to be isothermal if the temperature of the system remains constant during each state of process. For an isothermal process dT=0

(2) Adiabatic process:

A process is said be adiabatic if no heat enters or leaves the system during any step of the process. Adiabatic conditions can be approached by carrying the process in an insulated container such as 'thermos bottle.' High vacuum and highly polished surfaces help to achieve thermal insulation.

For an adiabatic process dq=0

(3) Isobaric process:

Those processes which take place at constant pressure are called isobaric processes. Heating of water to its boiling point and its vaporisation takes place at the same atmospheric pressure is an example of isobaric process.

For an isobaric process dP=0

(4) Isochoric process:

A process in which volume remains constant is known as isochoric process. The heating of a substance in a non-expanding chamber is an example of isochoric process.

For an isochoric process dV=0

(5) Cyclic process:

When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cyclic process.

For cyclic process dE=0, dH=0.

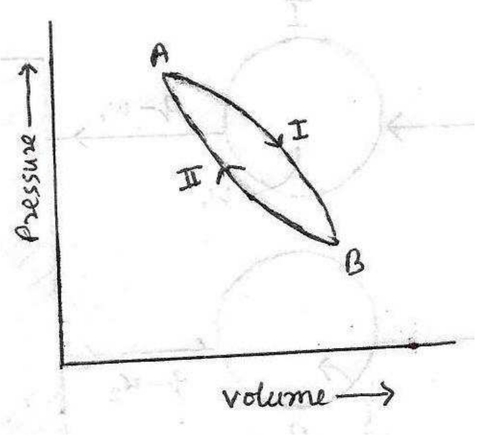


Fig 13.4 cyclic process

13.4 STATE OF A SYSTEM

A thermodynamic system is said to be in a certain state when all its properties are fixed. The fundamental properties which determine the states of a system are pressure (P), temperature (T), volume (V), mass and composition. Since the change in the magnitude of such properties alters the state of the system, these are referred to as **state variables or state functions or thermodynamic parameters.**

In actual practice, it is not necessary to specify all the variables because some of them are interdependent. In the case of a single gas composition is fixed, because it remains always 100 percent. Further, if the gas is ideal and one mole of gas is under examination, it obey's the equation PV=RT, where R is universal gas constant. Hence it is clear that if only two of the three variables (P,V and T) are known, the third can easily be calculated. The two variables, generally specified, are temperature and pressure. These are called **independent variables.** The third variable, **generally volume, is said to be dependent variable**, as its value depends on the value of P and T. Thus, the thermodynamic state of a system consisting of a single gaseous substance may be completely defined by specifying any two of the three variables, viz. temperature pressure and volume.

In a closed system, consisting of one or more components, mass is not a state variable.

13.5 STATE FUNCTION

State variables which are determined by the initial and final states of the system only and not by the path followed are called state functions. State variables which are determined or depend upon path followed are called path functions.

The state function is a property of a thermodynamic system which has a definite value for a particular state of the system. It is independent of the manner in which the state is reached. The change in the state function accompanying the change in the state of the system depends only on the initial and final states of the system and not on the path by which the change is brought about. Pressure, volume, temperature and energy are state functions. On the other hand work (ω) is not state function because the work done in a given change of state depends upon the manner in which the change is brought about. If the work is done reversibly its value is different than the value obtained irreversibly as you have seen above. And also work done would be zero if the gas expands in vacuum. First law equation ($\Delta E = q+w$), E is a definite quantity; hence if w is not a state function, q also is not a state function. Mathematically, this is expressed by saying that while the differential of energy, dE, is an exact differential, the differentials of heat and work, viz., dq and dw respectively, are inexact differentials. Exact differentials can be integrated between the appropriate limits. This cannot be done in the case of inexact differentials. Thus

$$\int_{E_1}^{E_2} dE = E_2 - E_1$$

But $\int_{q_1}^{q_2} dq \neq q_2 - q_1$ and $\int_{w_1}^{w_2} dw \neq w_2 - w_1$

13.6 FIRST LAW OF THERMODYNAMICS

Joule in his experiment, carried out the performance of work is diverse ways. The work was done by (a) agitating paddle wheels in a mass of water or mercury, (b) rubbing iron rings in mercury, (c) passing electricity through a wire of known resistance etc. The heat so produced was measured, latter on many workers namely Rowlands, Callender and Barnes, Laby and Hercus carried on the determination of the value of J with considerable accuracy. The accepted value of J is 4.1858×10^7 ergs per calorie.

This relation between heat and work is the origin of first law of thermodynamics. The first law can be enunciated as “If or whenever, heat is obtained from work the amount of heat produced is proportional to the work spent. There are many instances to show that not only heat can be converted into work but different form of energy are also interconvertible into one another. A given quantity of electrical energy which is comparatively easily measurable, was found to be equivalent to a definite amount of heat or mechanical work. You will study in this unit that such equivalent did not only exist between heat and work but between any two forms of energy.

Hence if

X units of energy A ≡ y units of energy B

Then mx units of energy A ≡ my units of energy B

The proportionality between quantities of two given forms of energy is universally constant and the constancy of this proportionality is essence of the first law.

The first law of thermodynamics is, in fact, an application of the broad principle known as the law of conservation of energy to the thermodynamics systems.

The first law of thermodynamics states that energy can neither be created nor destroyed, although in can be transferred from one form to another. Thus, whenever energy in one form disappears, an equal amount of energy in some other form must appear.

Since the disappearance of an amount of energy causes appearance of an equivalent amount of energy of another form, neither more nor less, we are compelled to accept that energy cannot be completely destroyed nor it can be created from nothing.

Clausius, therefore, enunciated that varied changes and transformation might occur but the total energy of the universe must remain constant, hence the first law of thermodynamics is really the law of conservation of energy.

13.7 INTERNAL ENERGY

Every substance is associated with a definite amount of energy which depends upon its chemical nature as well as upon its temperature, pressure and volume. Or by virtue of its pressure each substance is associated with certain amount of energy. This is known as internal energy of the system. This energy includes not only the translational kinetic energy of the molecules but also other molecular energies such as rotational, vibrational energies.

The total of all the possible kinds of energies of a system is called its internal energy.

The exact magnitude of this energy is not known because the chemical nature includes such factors as the translational, rotational and vibrational movements of the molecules, the manner in which the molecules are put together, the nature of the individual atoms, the arrangement and number of electrons, the energy possessed by the nucleus, etc. But, one thing is certain that the internal energy of a substance or a system is a definite quantity and it is a function only of the state (i.e., chemical nature, composition, temperature, pressure and volume) of the system at the given moment, irrespective of the manner in which that state has been brought about.

It is neither possible nor necessary to calculate the absolute value of internal energy of a system. In thermodynamics we concerned only with the energy changes when a system changes from one state to another. The amount of internal energy depends on the thermodynamics state and hence on thermodynamics parameters of the system. It is represented by E.

The internal energy is dependent on the internal structure and composition of the system. So, in a system of constant composition, the magnitude of E will depends upon other thermodynamics variables (P,V,T), any two of which may be regarded as independent variables. Thus,

$E = f(P,T)$; or $E=f(P,V)$, or $E=f(V,T)$

An explanation of the existence of the internal energy comes from the kinetic theory, the translator motion of the molecules, the vibrations and rotations of the atoms, the electronic revolutions etc. contribute to the internal energy.

13.8 INTERNAL ENERGY AND FIRST LAW OF THERMODYNAMICS

Suppose, a system is subjected to change of pressure and volume. Let the initial state is represented by A and the final state by B (fig. 11.1) and let E_A and E_B represent energies associated with the system in its state A and B

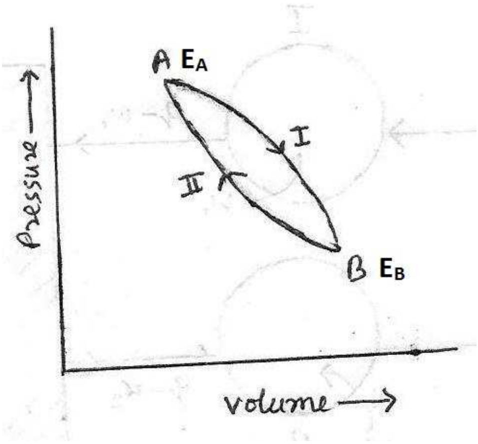


Fig 13.5 internal energy

respectively. These will be definite quantities as explained above. Then, the change in internal energy,

$$\Delta E = E_B - E_A$$

must be a definite quantity, irrespective of the path or the manner in which the change is brought about. If it were not so, it would again be possible to construct a perpetual motion machine, a machine which can produce energy without expenditure of energy. Suppose, that the system changes from state A to state B by following path I and is accompanied by change of energy equal to ΔE. Now suppose the same change of state is brought about by another path, say, path II and the change of energy is ΔE`. Suppose, ΔE >ΔE`, then coupling of these two processes:

$AB \longrightarrow$ (by path I) and

$AB \longrightarrow$ (by path II)

As shown in fig 13.5, the system would return to its initial state and at the same time a surplus of energy equal to ΔE-$\Delta E`$ would become available. By repeating the same cycle over and over again, energy would be generated continuously and a perpetual motion machine would be possible. This is contrary to the first law. Hence $\Delta E=\Delta E`$. Thus the energy change accompanying a process is a function only of the initial and the final states of the system and is independent of the path or the manner by which the change is brought about.

13.9 ENTHALPY OF A SYSTEM

In a process carried out at constant volume (say in a sealed tube), the heat content of a system is the same as internal energy E, as no PV work is done. But in a constant-pressure process, the system (a gas) also expends energy in doing PV work. Therefore, total heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy. This is called enthalpy of the system and is represented by the symbol H. Thus enthalpy is defined by the equation.

$H=E+PV$ 1

Suppose the change of state of a system is brought about at constant pressure. In that case, there will be change of volume, let the volume increases from V_A to V_B at constant pressure P. Then the work done (W) by the system will be given by

$W= -P(V_B-V_A)$ 2

Substituting the value of W in equation 11.5 we have

$\Delta E = q + [-P(V_B-V_A)]$

$= q - P(V_B-V_A)$

$= q- PV_B+PV_A$ 3

If E_A be internal energy in the initial state aw E_B the internal energy at final state, then

$\Delta E= E_B-E_A$

So equation 11.8 becomes

$E_B-E_A = q-PV_B+PV_A$

$E_B + PV_B = q+E_A + PV_A$ 4

As the quantity H=E+PV is known as enthalpy of the system. It represents the total energy stored in the system.

From equation 11.6 and 11.9

$H_B = q + H_A$

or $q = (H_B - H_A) = \Delta H$ 5

Since H_B and H_A are definite quantities, it is evident that ΔH, like ΔE, is a definite quantity depending only on the initial and final states of the system. Obviously, ΔH represents increase in the enthalpy of a system when it changes from state A to state B. Putting the value of q in equation 11.9 we get

$E_B - E_A = \Delta H - PV_B + PV_A$

$\Delta E = \Delta H - P\Delta V$

$\Delta H = \Delta E + P\Delta V$ 6

From equation 11.6 by definition of enthalpy

$H = E + PV$

Its differential form $dH = dE + PdV + VdP$

If a system undergoes a change at constant pressure then change in enthalpy,

$dH_P = dE_P + PdV_P$ 7

the suffix P used to indicate constancy of pressure.

The first law states

$\delta q = dE + \delta W$ 8

The work δW may be mechanical, electrical, chemical or any type. If we consider processes in which the entire work is mechanical, i.e., expansion or compression of the system, then δW would depend on the values P and V. Further, if the change of the system be carried out at constant pressure then,

$\delta W_P = PdV_P$

Hence from the first law, for change at constant pressure

$\delta q_p = dE_P + \delta W_P = dE_P + PdV_P$ 9

From equation 11.12 and equation 11.13

$\delta qp = dH_P$ 10

That is the increase in heat content of a system during a given transformation is the heat absorbed at constant pressure during the process.

13.10 BOND ENERGIES

Bond energy for any particular type of bond in a compound may be defined as the average amount of energy required to dissociate (i.e., break) one mole, Avogadro number of bonds of that type present in the compound. This is also called the enthalpy of formation of the bond.

Thus the bond energy of H-H bond is the energy required to break all the bonds in one mole of the gas. It is expressed in kcal per mole or kJ per mole. For example, bond energy of H-H bond is 433 kJ per mole or 103.58 kcal per mole.

Bond energies of some common bonds are given below.

(i) $H_2(g) \longrightarrow 2H_g(g)$; $\Delta H=433.1$ kJ

(ii) $O_2(g) \longrightarrow 2O(g)$; $\Delta H=489.5$ kJ

(iii) $N_2(g) \longrightarrow 2N(g)$; $\Delta H=937.4$ kJ

(iv) $C(s) \longrightarrow C(g)$; $\Delta H=719.6$ kJ

Suppose we have to determine the enthalpy of formation of C-H bond in methane. We should know the enthalpy of formation of methane. This had been calculated from the enthalpy of combustion of methane to be – 74.9 kJ. Thus

(v) $C(s) + 2H_2(g) \longrightarrow CH_4(g)$; $\Delta H= - 74.9$ kJ

Multiplying equation (i) by 2 we have

(vi) $2H_{2(g)} \longrightarrow 4H_{(g)}$; $\Delta H= 866.2$ kJ

Adding equation (iv) and (vi) and subtracting from equation (v) we have

$C(g) + 2H_2(g) \longrightarrow CH_4(g)$; $\Delta H= -1660.7$ kJ

It follows from above that -1660.7 kJ of energy is required to break four moles of C-H bonds in methane. Therefore the average bond energy per mole of C-H bond is -1660.7/4 = 415.2 kJ. This is also the enthalpy of formation of the C-H bond.

13.11 SUMMARY

You have studied in this unit that thermodynamics is an important branch of chemistry which deals with energy transformation in all types of physical chemical process. In studying and evaluating the flow of energy into or out of a system it is useful to consider changes in certain properties of the system. These properties include temperature, pressure, volume and concentration of a system. Measuring the changes in these properties from the initial state to the final state, can provide information concerning changes in energy and related quantities such as heat and work.

13.12 TERMINAL QUESTIONS AND ANSWER

(A)Objective type questions:

1.Thermodynamics is applicable to

(a) Microscopic systems only (b) macroscopic systems only

(c) Homogeneous systems only (d) heterogeneous systems only

Ans (b)

2.A gas contained in a cylinder fitted with a piston constitutes

(a) An open system (b) A closed system

(c) A heterogeneous system (d) An isolated system

Ans (b)

3. A system that can transfer neither matter nor energy to and from its surroundings is called

(a) an open system (b) a closed system

(c) an isolated system (d) a heterogeneous system

Ans (c)

4. The work differential dw is

(a) a state function (b) an exact differential

(c) an inexact differential (d) none of the above

Ans (c)

5. Two moles of an ideal gas expands spontaneously into a vacuum. The work done is

(a) 2 J (b) infinity (c) J (d) zero

Ans (d)

(B)Short answer type questions:

6.Define the terms

(a) Closed system

(b) Extensive properties

(c) Isothermal process

(d) Ideal gas

7.Define and explain the following terms

(a) Adiabatic process

(b) Open and closed systems

(c) Homogeneous and heterogeneous system

(d) Zeroth law of thermodynamics

(C)Long answer type questions:

8 (a) Differentiate clearly between reversible and irreversible processes.

(c) Calculate the work done in isothermal reversible explanation of an ideal gas.

9.Write notes on the following

(a) Euler reciprocal relation

(b) Sign convention of heat and work

(c) System and surroundings.

10.Differentiate between

(a) exact and inexact differentials

(b) homogeneous and heterogeneous systems

(c) intensive and extensive properties

(d) system and surroundings

Unit 14: Electrochemistry

CONTENTS:

14.1 OBJECTIVES

Most chemical reactions occur in solution. The study of such solutions constitutes one of the most important branches of physical chemistry. If we analyze the solubility of solutes in various solvents, we find that the polar solutes are more soluble in polar solvents whereas non polar solutes are soluble in non polar solvents. The general principle of solubility is like dissolves like. We see sodium chloride is soluble in water but it is insoluble in carbondisulphide or carbontetrachloride. The compounds which conduct electricity when dissolved in water or in the molten state are called electrolytes. Sodium chloride, copper sulphate etc are example of electrolytes. The substances which do not conduct electricity under these conditions are called non electrolytes.

14.2 INTRODUCTION

Substances like mica, wax, glass ebonite etc. strongly resist the flow of electricity and practically do not allow any current to flow through them. These substances are called non-conductors. On the other hand there are substances such as copper, silver, mercury, water solutions of salts acids etc. through which electric current can easily pass; these are called conductors. The conductors are broadly classified into two categories: (i) electric conductors or metallic conductors and (ii) electrolytic conductors or electrolytes.

Electronic conductors are included the metals, alloys, graphite etc. in which the electricity is carried exclusively by the transport of electrons. The electrons flow from a higher negative potential to a lower one; there is no transport of matter during the passage of electricity.

In electrolytes the flow of current is accompanied with actual transfer or migration of matter. Such transfer of matter leads to the decomposition of matter at the points where electricity enters or leaves the electrolyte and in the process helps in the transfer of electrons. The electrolytes are solutions of salts, acids, bases usually in water. The conducting capacity of different electrolytes is different.

Electrochemistry is the branch of physical chemistry that studies the relationship between electricity, as a measurable and quantitative phenomenon, and identifiable chemical change, with either electricity considered an outcome of a particular chemical change or vice-versa. These reactions involve electric charges moving between electrodes and an electrolyte (or ionic species in a solution). Thus electrochemistry deals with the interaction between electrical energy and chemical change.

14.3 ELECTRICAL TRANSPORT

14.3.1Conduction in metal and in electrolyte solution:

Metal in general allow an electric current to pass through and are called conductors of electricity. The phenomenon of an electrolyte by passing electric current through its solution is termed electrolysis. The process of electrolysis is carried in an apparatus called the electrolytic cell. The cell contains water-solution of an electrolyte in which dip two metallic rods, Electrodes. These rods are connected to the two terminals of a battery which is source of electricity. The electrode connected to the positive terminal of the battery attracts the negative ions (anions) and is called anode. The other electrode connected to the negative end of the battery attracts the positive ions (cations) and is called cathode.

14.3.1.1 Mechanism of electrolysis:

The process of electrolysis actually taking place is shown in fig 8.1. The cations migrate to the cathode and form a neutral atom by accepting electrons from.

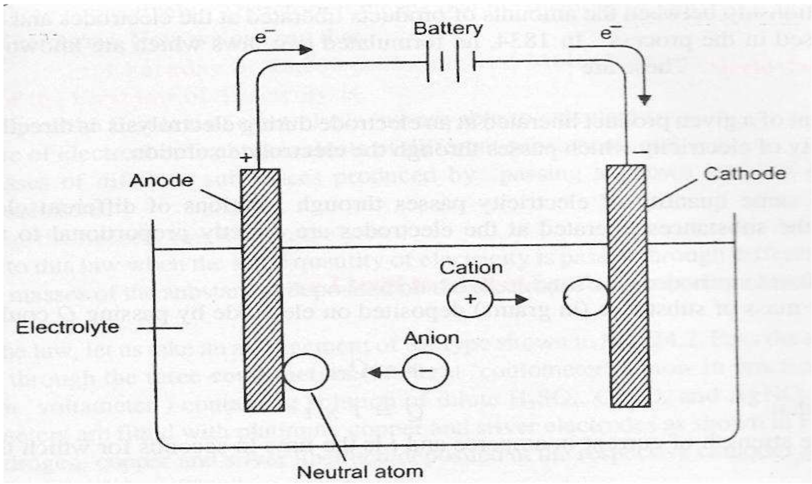


Fig 14.1 The mechanism of electrolysis

The anions migrate to the anode and yield a neutral particle by transfer of electrons to it. As a result of the loss of electrons by anions and gain of electrons by cations at their respective electrodes, chemical reaction takes place.

Let us consider the electrolysis of hydrochloric acid. In solution hydrochloric acid is ionised.

$$HCl \longrightarrow H^+ + Cl^-$$

In the electrolytic cell Cl^- ions will move towards the anode and the H^+ ions will move toward the cathode. At the electrode, the following reaction will take place.

At cathode:

$H^+ + e^- \longrightarrow H$ (reduction)

You see each hydrogen ion picks up an electron from the cathode to become a hydrogen atom. Paris of hydrogen then unite to form a molecule of hydrogen gas H_2.

At anode

$Cl^- \longrightarrow Cl + e^-$ (oxidation)

After the chloride ion loses its electron to the anode, pairs of chlorine atoms unite to form chlorine gas, Cl_2.

The net effect of the process is the decomposition of HCl into hydrogen and chlorine gases. The overall reaction is

$2\ HCl \longrightarrow H_2 + Cl_2$

	Cathode	Anode
Ions attracted	Cations	Anions
Direction of electron	Into cell	Out of cell
Movement		
Half reaction	Reduction	Oxidation
Sign	-ve; since it is attached	+ve; since it is attached
	to the –ve end of battery	to the +ve end of battery

Table 14.1 Description of the cell

Electrolytes obey Ohm's law, to the same extent as the metallic conductors. According to this law the current I flowing through a conductor is given by the relation I=E/R, where E is the electromotive force i.e., the difference of potential at the two ends of the conductor, and R is resistance

$I = E/R$

Electric units:

There are a few electrical units which you should understand before taking up the study of quantitative aspects of electrolysis. These are:

Amperes: Current strength is generally expressed in amperes. The ampere is defined as the current which deposits 0.00118 gram of silver per second from a 15 per cent solution of silver nitrate in a coulometer. Or we can say an ampere is a current of one coulomb per second.

Coulomb: The quantity of electricity passing through a conductor is the product of current strength and time and is generally expressed in coulombs. A coulomb is a unit quantity of electricity. It is the amount of electricity which will deposit 0.001118 gram of silver from 15 per cent solution of silver nitrate in a coulometer.

Ohm: The unit of electrical resistance is ohm. It is the resistance offered at 0^0C to a current by a column of mercury 106.3 centimeter long of about one square millimeter cross-sectional area and weighing 14.454521 grams.

Volt: A volt is a unit of electromotive force. It is the difference in electrical potential required to send a current of one ampere through a resistance of one ohm.

Faraday's law of electrolysis:

Faraday discovered that there exists a definite relationship between the amounts of products liberated at the electrodes and the quantity of electricity used in the process. He formulated two laws in 1834, which are known as Faraday's law of electrolysis. The laws are as follows

Faraday's first law of electrolysis:

The amount of a given product liberated at an electrode during electrolysis is directly proportioned to the quantity of electricity which passes through the electrolytic solution.

Faraday's second law of electrolysis:

When the same amount of electricity passes through solutions of different electrolytes, the amount of substance liberated at the electrodes are directly proportional to their chemical equivalents.

These two laws have been shown to hold very rigidly provided the passage of electricity takes place entirely by electrolytic conduction. It applies to molten electrolytes as well as to solution of electrolytes and is independent of temperature, pressure or nature of solvent.

If m is the mass of substance deposited on electrode by passing Q coulombs of electricity, then

$m \propto Q$

But $Q=I \times t$

Where I is the strength of current in amperes and t is time in seconds for which current has been passed.

Therefore, $m \propto I \times t$

or $m= z \times I \times t$

Here z is constant known as electrochemical equivalent of the electrolyte. If I=1 ampere and t=1 second then

$m=z$

from this it follows that, electrochemical equivalent is amount of substance deposited by one ampere current passing for one second (i.e., one coulomb)

It has been found that the quantity of electricity required to liberate one gram equivalent of substance is 96,500 coulombs. This quantity is known as Faraday and is denoted by the symbol F.

It is clear that the quantity of electricity to deposit one mole of substance is given by the expression,

Quantity of electricity= $n \times F$

Where n is the valence of the ion. Thus the quantity of electricity required to discharge.

one mole of $Ag^+ = 1 \times F = 1F$

one mole of $Cu^{2+} = 2 \times F = 2F$

one mole of $Al^{3+} = 3 \times F = 3F$

We can represent the reaction on the cathode as:

$Ag^+ + e^- = Ag$

$Cu^{2+} + 2e^- = Cu$

$Al^{3+} + 3e^- = Al$

It is clear that the moles of electrons required to discharge one mole of ions Ag^+, Cu^{2+} and Al^{3+} is one, two and three respectively. It means that the quantity of electricity in one Faraday is one mole of electrons. Now we can say

1 Faraday = 96500 coulombs= 1 mole electrons

Verification of the second law of electrolysis:

Faraday's second law states that when same quantity of electricity is passed through different electrolyte solutions, the masses of the substances deposited on the electrodes are proportional to their chemical equivalents.

To verify this law, let us take the arrangement of the type shown in fig. 8.2. Now pass the same amount of electricity through the three coulometers containing solutions of dilute sulphuric acid (H_2SO_4), copper sulphate ($CuSO_4$) and silver nitrate ($AgNO_3$) respectively. These coulometers are fitted with platinum, copper and silver electrodes as shown in fig. 8.2. The masses of hydrogen, copper and silver liberated/ deposited at the respective cathodes are in the ratio of their equivalent weights. That is

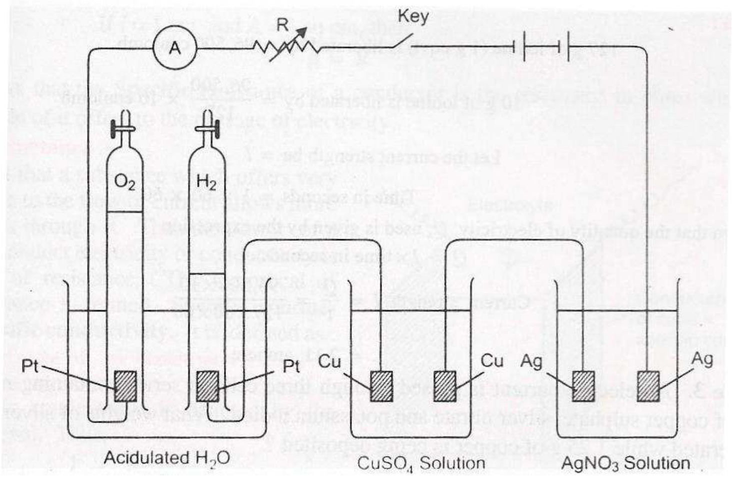


Fig. 14.2 Verification of Faraday's second law of electrolysis

$$\frac{\text{mass of hydrogen liberated}}{\text{mass of copper deposited}} = \frac{\text{equivalent weight of hydrogen}}{\text{equivalent weight of copper}}$$

and $$\frac{\text{mass of copper deposited}}{\text{mass of silver deposited}} = \frac{\text{equivalent weight of copper}}{\text{equivalent weight of silver}}$$

From this experiment, we can calculate the mass of hydrogen, copper and silver liberated at their respective cathodes by one coulomb of electricity. We find these are always

Hydrogen = 0.00001036 g

Copper = 31.78x0.00001036 = 0.0003292 g

Silver = 107.88x0.00001036 = 0.001118 g

Since the equivalent weights of hydrogen, copper and silver are 1. 31.78 and 107.88 g respectively, it follows that the electrochemical equivalents are proportional to chemical equivalents (or equivalent weights).

Faraday's second law of electrolysis helps to calculate equivalent weights of metals, the unit of electrical charge and the Avogadro number.

Examples:

(i) 0.1978 g of copper is deposited by a current of 0.2 ampere in 50 minutes. What is the electrochemical equivalent of copper?

Solution: Given t= 50x60 = 3000 seconds, I= 0.2 amperes, quantity of electricity used Q= Ixt = 3000x0.2 = 600 coulombs

Amount of copper deposited by 600 coulombs = 0.1978 g

Amount of copper deposited by one coulombs = 0.1978/600

= 0.0003296 g

This is chemical equivalent of copper

(ii) Calculate the current strength in amperes required to liberate 10 g iodine from potassium iodide solution in one hour. Equivalent weight of iodine in 127.

Solution:

127 g of iodine is liberated by 96500 coulombs

1 g of iodine will be liberated by $\frac{96500}{127}$ coulomb

10 g of iodine will be liberated by $\frac{96500}{127}$ x10 coulombs

Let the current strength be I

Time in seconds = 60x60 seconds

The quantity of electricity is given by Q=Ixt

$$I = Q/t = \frac{96500 \times 10}{127 \times 60 \times 60}$$

= 2.11 amperes

14.3.2 Electrolytic conduction:

From the above discussion it is clear that the flow of electricity through solutions of electrolytes is due to the migration of ions when potential difference is applied between the two electrodes. The power of electrolytes to conduct electrical currents is formed conductivity or conductance. It is defined as the reciprocal of resistance (R) of solution. Like metallic conductors, electrolytes obey Ohm's law. According to this law the current I flowing through a metallic conductor is given by the relation.

$$I = E/R$$

Where E is the potential difference at two ends (in volts); and R is the resistance measured in ohms (or Ω). The resitance R of a conductor is directly proportional to the length l and inversely proportional to the area of cross-section, A. That is

$$R \propto \frac{l}{A}$$

or $R = \rho \frac{l}{A}$ ……………………..(14.1)

where ρ "rho" is a constant of proportionality and is called resistivity or specific resistance. Its value depends upon the material of the conductor. From (8.1) we can write

$$\rho = Rx\frac{A}{\rho}$$

If $\rho = 1\ cm\ and\ A = 1\ sq.cm,\ then$

ρ=R

It means that the specific resistance of a conductor is the resistance in ohms which one centimeter cube of it offers to the passage of electricity. The reciprocal of specific resistance, i.e., 1/ ρ is called specific conductance.

Specific conductance:

It is evident that a substance which offers very little resistance to the flow of current allows more current to pass through it. Thus the power of a substance to conduct electricity is the converse of resistance. The reciprocal of specific resistance is termed specific conductance or specific conductivity. Hence,

The conductance of one centimeter cube (cc) of a solution of electrolyte is specific conductance (fig. 8.9). It is denoted by the symbol κ (kappa). Thus

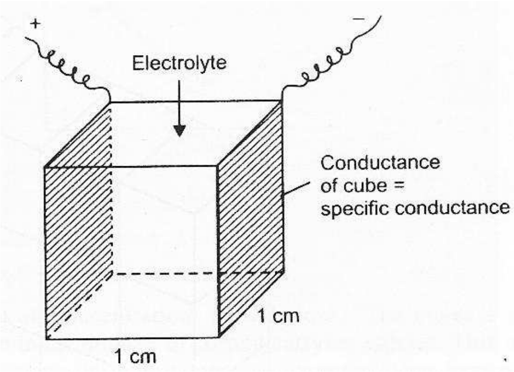


Fig. 14.3 specific conductance

$$\kappa = \frac{1}{\rho} = \frac{1}{R} x \frac{l}{A}$$

Unit of specific conductance:

Specific conductance is generally expressed in reciprocal ohms (r.o.) or mhos or ohm^{-1}. Its unit can be derived as follows:

$$= \frac{1}{A} . \frac{R}{R} = \frac{1}{cm^2} x \frac{cm}{ohm}$$

$$= \text{ohm}^{-1}\,\text{cm}^{-1}$$

The internationally recommended unit for ohm^{-1}(or mho) is Siemens. When s is used the conductance is expressed as s cm^{-1}. The Siemens unit is named after Sir Willian Siemens, who was a noted electrical engineer.

The specific conductance increases with: (i) ionic concentration, and (ii) speeds of the ions concerned.

In measuring the specific conductance of aqueous solution of an electrolyte, the volume of water in which certain amount of water electrolyte is dissolved is always measured in cubic centimeters and is known as dilution. If the volume of the solution is vcc, the specific conductance of the solution is written as κv.

Equivalent conductance:

Specific conductance, although a suitable property for characterizing metallic conductance, is not so for characterizing electrolytic conductance where the value, amongst other things, depends upon the concentration of the solution of the electrolyte as well. While measuring conductance of electrolytes in solutions, another quantity of much greater significance, known as equivalent conductance, is frequently used.

Equivalent conductivity is the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by Λ. It is equal to the product of the specific conductance, κ and the volume V in cc containing one gram-equivalent of the electrolyte at the dilution V.

Thus $\Lambda = \kappa.V$

This is shown in fig 8.4. A solution having one gram-equivalent water between electrode placed 1 cm apart has $\Lambda = \kappa$ x 9+

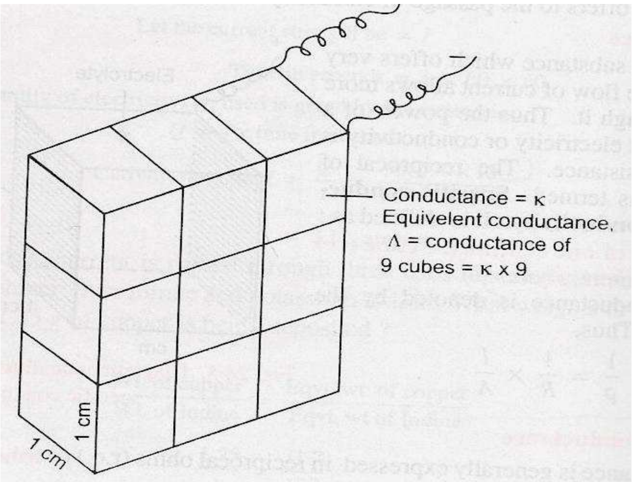


Fig14.4 solution of 1 g-equivalent dissolved in 9cc of the electrolyte dissolved in, say, 9cc water be placed between two electrodes. 1 cm. apart.

The solution could be considered as consisting of nine cubes, each of which has a conductance κ (specific conductance). Thus the total conductance of the solution will be 9 x κ. Similarly, Vcc of solution will form V cubes and the total conductance will be κ xV.

If an electrolyte solution contains N gram equivalents in 1000cc of the solution, the volume of the solution containing 1 gram-equivalent will be 1000/N. Hence

$$\Lambda = \frac{\kappa\, 1000}{N}$$

The unit of equivalent conductance may be deduced as follows

$$\Lambda = \kappa x V$$

$$= \frac{1}{R} . \frac{l}{A} x\ V$$

$$= \frac{1}{ohm} x \frac{cm}{cm_2} x \frac{cm_3}{eqvt}$$

$$= ohm^{-1}\ cm^2\ eqvt.$$

Molar conductance:

Some times molar conductance is helpful in comparing conductances of electrolytes. It is defined as:

The conductance of all ions produced by one mole (one gram-molecular weight) of an electrolyte when dissolved in a certain volume Vcc is known as molecular conductance. It is denoted by μ. the value of molecular conductance is obtained by multiplying the specific conductance, κ by the volume in κ containing one mole of electrolyte.

Molar conductance $\mu = \kappa x V$. Here V is the volume of the solution in cc which contains one mole of the electrolyte.

Since $\kappa = \frac{1}{R} x \frac{l}{A}$

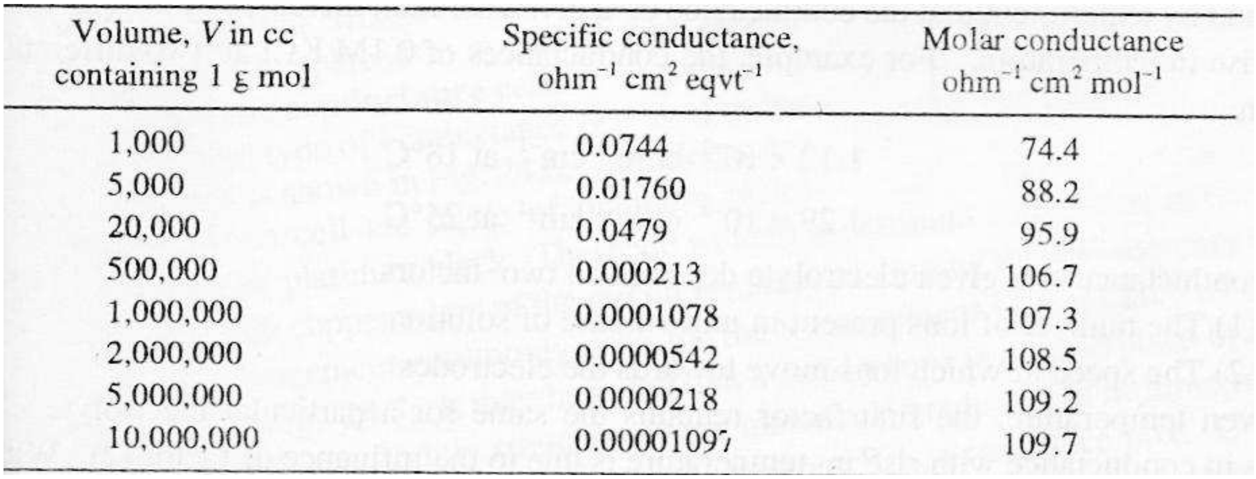
$$\mu = \frac{1}{\kappa} x \frac{l}{A} x\ V$$

$$= \frac{1}{ohm} x \frac{cm}{cm2} x \frac{cm3}{mol}$$

$$= ohm^{-1}\ cm^2\ mol^{-1}$$

Effect of dilution on specific conductance, equivalent conductance and molecular conductance:

Specific conductance is the conductance of one centimeter cube of a solution of an electrolyte. If we dilute the solution the specific conductance decreases. On diluting the solution the concentration of ions per cc decreases. Hence the specific conductance decreases. But the equivalent conductance and molar conductance increases with dilution. This is because equivalent conductance and molar conductance are the product of specific conductance and the volume of the solution containing one gram-equivalent or one mole of the electrolyte respectively. With dilution specific conductance decreases while volume increases. The increase in the second factor is much more than the decrease in the first factor. Also on dilution more and more electrolyte dissociates into ions and hence equivalent conductance and molecular conductance increases.



Volume, *V* in cc containing 1 g mol	Specific conductance, $ohm^{-1}\ cm^2\ eqvt^{-1}$	Molar conductance $ohm^{-1}\ cm^2\ mol^{-1}$
1,000	0.0744	74.4
5,000	0.01760	88.2
20,000	0.0479	95.9
500,000	0.000213	106.7
1,000,000	0.0001078	107.3
2,000,000	0.0000542	108.5
5,000,000	0.0000218	109.2
10,000,000	0.00001097	109.7

Table 14.2 specific and molar conductance of NaCl solution at 18^0C Strong and weak electrolytes:

Strong and weak electrolytes:

There are two classes of electrolytes, depending upon their ionisation

(i) Strong electrolytes

(ii) Weak electrolytes

Strong electrolytes:

A strong electrolyte is a substance that gives a solution in which almost all the molecules are ionized. Strong electrolytes have a high value of equivalent conductance even at low concentration. HCl, H_2SO_4, HNO_3, $HClO_4$, HI, HB_r, NaOH, KOH, Ca $(OH)_2$, Mg $(OH)_2$ and almost all salts are examples of some strong electrolytes.

Weak electrolytes:

A weak electrolyte is a substance that gives a solution in which only a small proportion of the solute molecules are ionized. Such solution is called a weak electrolytic solution. That has low value of equivalent conductance.

All organic acids such as acetic acid, oxalic acid; most organic bases and a few salts such as mercury chloride and lead acetate are some examples of weak electrolytes.

14.4 TYPES OF CELLS

In these unit different aspects of cells, their functioning, types of cells, electrode reactions, EMF of a cell and free energy change will be discussed.

14.4.1 Galvanic cell:

A galvanic cell is a device in which the free energy of a chemical process is converted into electrical energy. Usually such a cell consists of two electrodes immersed in one or more suitable electrolytes. When the electrodes are connected externally by a metallic conductor, current flows from one electrode to another and inside the cell chemical change occur at the surface of electrodes. On joining the electrodes externally oxidation occurs at one electrode and reduction at the other electrode. The electrode at which oxidation occurs is called a negative electrode or cathode while the electrode at which reduction occurs is called positive electrode or anode. The reason for this nomenclature is that oxidation is accompanied by liberation of electrons which are given up to the electrode at which oxidation occurs. The electrode, thus acquires a negative charge. Reduction, on the other hand, is accompanied by consumption or elimination of electrons from the electrode which thereby acquires a positive charge.

14.4.2Electrochemical cell:

Consider for example a copper rod dipping in a solution of copper sulphate and a zinc rod dipping in a solution of zinc sulphate. The two metal rods are connected by a metallic conductor.

When a bar of zinc is dipped in a solution of copper sulphate, copper metal is deposited on the bar fig 9.1. The net reaction is

$Zn + Cu^{2+}\ Zn^{++} + Cu \quad \longrightarrow$

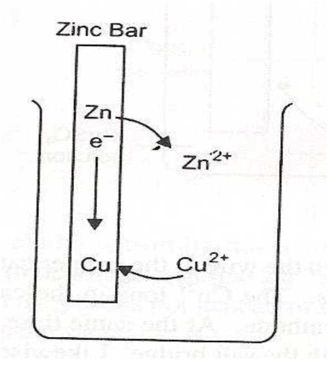
This is a redox reaction and the two half reactions are

$Zn\,Zn^{2+} + 2e^{-} \quad \longrightarrow$

$Cu^{2+} + 2e^{-}Cu \quad \longrightarrow$

In this change, Zn is oxidised to give Zn^{2+} and copper is reduced to Cu atoms. The electrons released in the first half-reaction are used up by the second half-reaction. Both the half-reaction occur on the zinc bar itself and there is not net charge.

Now let the two half reactions occur in separate compartments which are connected by a wire fig 9.2. The electrons produced in the left compartment flow through the wire to the other compartment. However, the current will flow for an instant and then stop. The current stops flowing because of the charge build on the two compartments. The electrons leave the left compartment and would become positively charged. The right compartment receives electrons and become negatively charged. Both these factors oppose the flow of electrons (electrical current) which eventually stops.



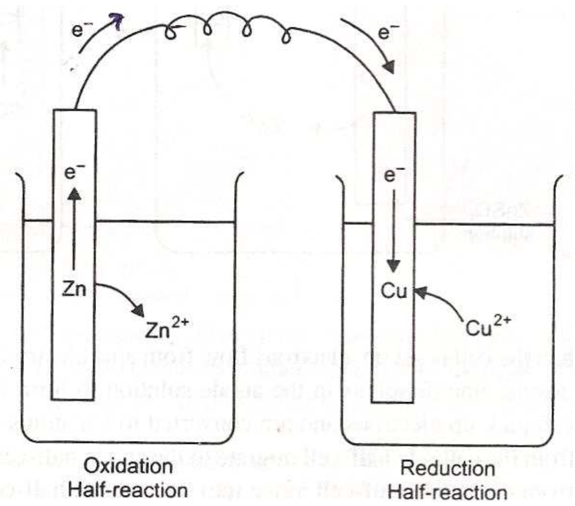


Fig 14.1 Redox reaction taking Place at zinc electrode Fig 9.2 Separate cell reactions cause flow of current

14.4.3Voltaic cell:

A voltaic cell also known as galvanic cell is one in which electrical current is generated by a spontaneous redox reaction, a simple voltaic cell is shown in fig 9.3.

A bar of zinc metal (anode) is placed in zinc sulphate solution in the left container. A bar of copper (cathode) is immersed in copper sulphate solution in the right container. The zinc and copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution in agar-agar jelly interconnects the solution in the anode compartment and the cathode compartment.

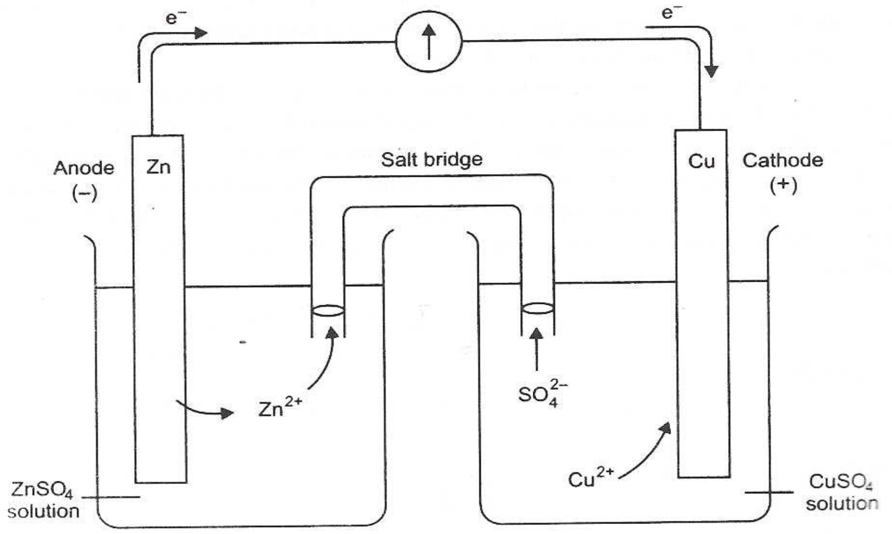


Fig 14.2 A simple voltic cell

The oxidation half-reaction occurs in the anode compartment.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

The reduction half-reaction takes place in the cathode compartment.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Net reaction in the cell is

$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$$

When the cell is set up, electrons flow from the zinc electrode through the wire to the copper electrode. As a result, zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the cathode half cell pick up electrons and are converted to Cu atoms on the cathode. At the same time SO_4^{2-} ions from the cathode half cell migrate to the anode half-cell through the salt bridge. Likewise Zn^{2+} ions from the anode half-cell move into the cathode half-cell. The flow of ions from one half-cell to the other completes the electrical circuit which ensures continuous supply of current. The cell will operate till either the zinc metal or copper ions are completely used up.

The cell is represented as

$Cu/Cu^{2+}/Zn/Zn^{2+}$

14.5 STANDARD HYDROGEN ELECTRODE

The potential of a reversible hydrogen electrode in which the gas at one atmospheric pressure is bubbled through a solution of hydrogen ions of unit activity (or, to be approximate, 1M concentration) has been fixed as zero. This electrode is known as standard hydrogen electrode (fig 9.6) and is represented

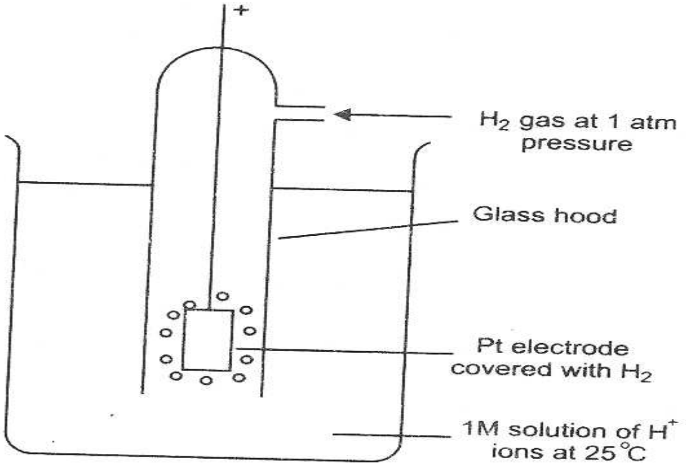


Fig 14.3 Standard hydrogen electrode

as: Pt; $H_2(g)$ (1atm), $H^+(aq)$ (c=1M)

All other single electrode potentials measured with respect to standard hydrogen electrode are referred to as potentials on the hydrogen scale.

If it is required to find the electrode potential of, say, zinc electrode dipping in a solution of zinc sulphate (i.e., Zn, Zn^{2+} electrode), all that is needed is to combine it with the hydrogen electrode so as to have a complete cell represented as:

Zn, Zn^{2+} (aq)/H_2 (g) (1 atm); H^+(aq) (C=1M) ; Pt

The e.m.f. of the cell determined potentiometrically is then equal to potential of the zinc electrode (on the hydrogen scale) since potential of the standard hydrogen electrode is taken as zero.

In this case, reduction occurs at the hydrogen electrode and oxidation takes place at the zinc electrode shown below:

Hydrogen electrode:

$$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (aq)$$

Zinc electrode:

$$Zn(s) \rightleftharpoons Zn^{2+} + 2e^-$$

∴ The net reaction is

$$Zn(s) + 2Hg^+ (aq) \rightleftharpoons Zn^{2+} + H_2 (g) (1atm)$$

If copper electrode is connected with the hydrogen electrode the oxidation takes place at the hydrogen electrode and reduction occurs at the copper electrode. The net reaction is then

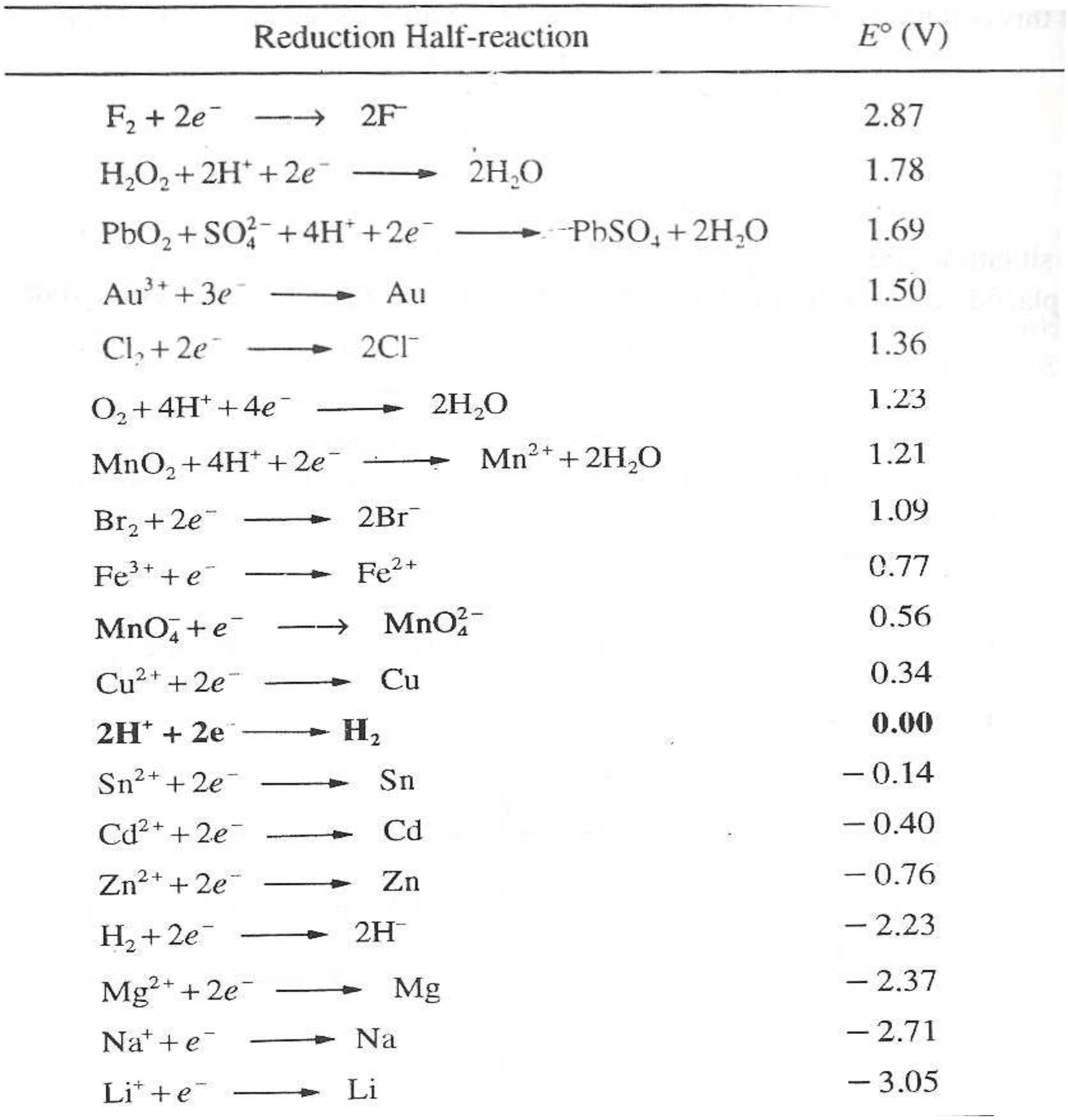
$$H_2 (g) + Cu^{2+} (aq) \rightleftharpoons Cu(s) + 2H^+(aq).$$

14.6 STANDARD ELECTRODE POTENTIAL

That the potential of an electrode at a given temperature we have discussed above, depends upon the concentration of the ion in the surrounding solution, if the concentration of the ions is unity and temperature 25^0C, the potential of the electrode is termed as the standard electrode potential.

The standard electrode potential of a number of electrodes is given in the table 9.1. These values are said to be on hydrogen scale since in these determinations the potential of a standard hydrogen electrode used as a reference electrode, has been taken as zero. The values of standard electrode potentials arranged in a decreasing order constitute what is called the electrochemical series

Table 14.1 electrochemical series, standard electrodes potential at 25^{0}C.



Reduction Half-reaction	$E°$ (V)
$F_2 + 2e^- \longrightarrow 2F^-$	2.87
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.78
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	1.69
$Au^{3+} + 3e^- \longrightarrow Au$	1.50
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.36
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	1.21
$Br_2 + 2e^- \longrightarrow 2Br^-$	1.09
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.77
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	0.56
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
$2H^+ + 2e^- \longrightarrow H_2$	**0.00**
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.40
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76
$H_2 + 2e^- \longrightarrow 2H^-$	−2.23
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.37
$Na^+ + e^- \longrightarrow Na$	−2.71
$Li^+ + e^- \longrightarrow Li$	−3.05

This table includes a large variety of electrodes (half-cell) along with their electrode reaction and standard electrode potential. The higher its positive value the greater is the tendency of the oxidized form to get reduced by accepting electrons. And, conversely, the greater the negative value, the greater is the tendency of the reduced form to get oxidized by donating electrons.

Now any two suitable half- cells can be combined to form a galvanic cell. The emf of the cell and the feasible cell reaction can be easily determined with the help of the information given in this table. For this the following rules have been suggested:

Representation of cell. The electrode on the right is written in the order : ion, electrode (e.g., Cu^{++},Cu) and the electrode on the left is written in the order :electrode, ion, (e.g., Zn, Zn^{2+}). In the galvanic cell formed by the combination of two electrodes, oxidation occurs at the left hand electrode and reduction at the right hand electrode so that the electric current (electrons) in the external circuit flow from the left hand electrode (L.H.E.)to the right hand electrode (R.H.E.).

Determination of cell the potential and the emf of the cell reaction:

According to the latest convention, both the half reactions are written as reduction reaction along with their standard electrode potentials in the form of chemical equations. After balancing the number of electrons if necessary, the half-cell reaction equation with a lower electrode potential is subtracted forms the one with a higher electrode potential. The result gives the cell potential as well as the feasible cell reaction.

The two half cell reaction in Daniell Cell are written as,

(i) $Cu^{2+}(as) + 2e^- \rightleftharpoons Cu(s)$: $E^0 = +0.34$ V

(ii) $Zn^{2+}(aq) + 2e^- \rightleftharpoons zn(s)$: $E^0 = -0.76$

Substracting eq. (ii) from eq. (i) we get

$Cu^{2+}(aq) + Zn(s) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$ as the feasible cell reaction and

0.34 – (-0.76) =1.10 Vas cell potential.

14.7 SUMMARY

In this unit you have studied various aspects of reversible cells and irreversible cells, determination of e.m.f. of cells, polarization over voltage, liquid junction potential and concentration cells with and without transport.

The applications of e.m.f. measurement has been described in detail, namely the valence of ions, determination of solubility of sparingly soluble salt, activity coefficients and some other uses.

14.8 TERMINAL QUESTIONS

B. Short answers type questions:

Q.1 Write a note on liquid junction potential.

Q.2 what are concentration cells?

Q.3 Write a note on over voltage.

Q.4 Define electrochemical cell.

Q.5 what do you mean by electrode potential.

Q.6 Write a short note on redox reactions.

C. Long answer type questions:

Q. 1 (a) what are reversible and irreversible cells? How e.m.f. of a cell is determined?

(b) Write a note on liquid junction potential? How it is eliminated.

Q. 2(a) Discuss the functioning of concentration cell with transport and concentration cell with transport.

(b) Describe applications of e.m.f. measurements.