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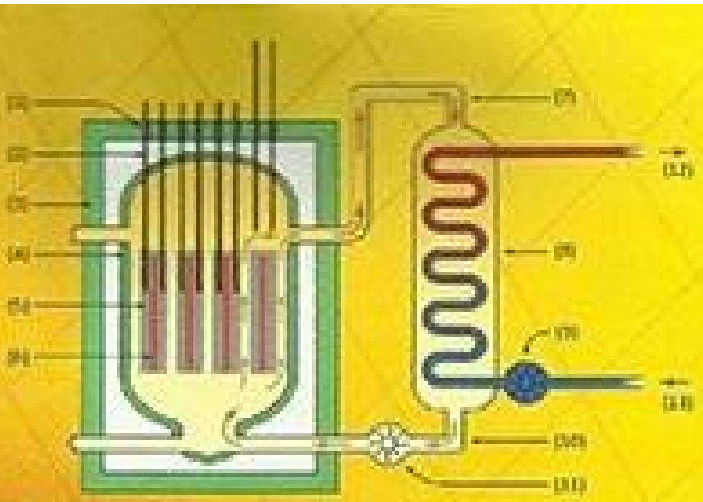
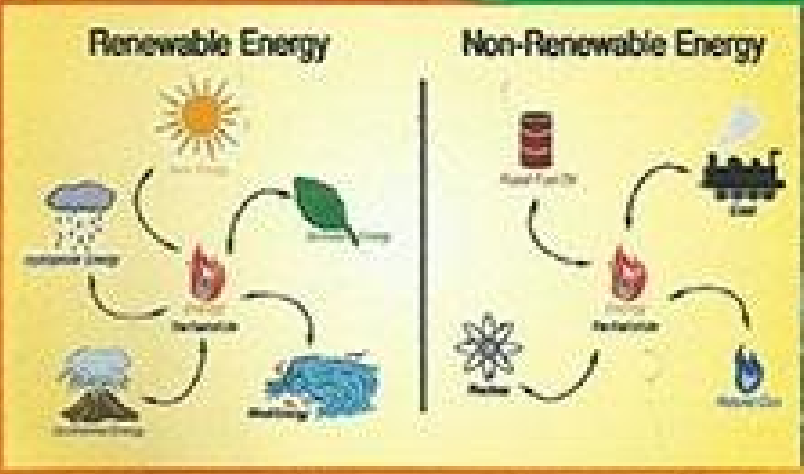


Engineering Chemistry

Jain • Jain



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ENGINEERING
CHEMISTRY

Preface

The object of the present book is to serve the students with a very elementary knowledge of chemistry. The syllabi of chemistry taught in the name of engineering chemistry in different engineering and technology degree colleges is of very diverse in nature. It is rather quite impossible to give a complete coverage of all the topics in a limited space, but the authors have dealt with modern views of the topics of the syllabi and attempted to give a major coverage of the recent syllabi taught in various institutions.

As teachers of some experience, the authors are well aware of the great value for attaching the short questions and answers as well as solutions of the numerical problems. They gave due weightage regarding the matter in writing the book.

In an effort to make the book as comprehensive as possible, a large number of topics have been dealt with and the authors hope that this will serve the purpose of making the book useful as a text book of chemistry for engineering degree colleges all over India.

The authors wish to express deep sense of gratitude to their beloved student Sri Rajib Das who assisted throughout in writing the book.

R Mukhopadhyay

Sriparna Datta

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Atoms and Molecules

WAVE MECHANICAL CONCEPT OF ATOM

Wave Nature of the Electron

We have seen upto Bohr's concept of atom that the electron is treated as a particle. The concept of wave nature of matter came from the dual character of radiation, which sometimes behaves as a wave and sometimes as a particle. de-Broglie pointed out in 1924 that radiation including visible light, infrared, ultraviolet and X-rays behave as waves in propagation experiments based on *interference* and *diffraction.* These experiments conclusively proved the wave nature of these radiations. However, radiation behaves as a particle in interaction experiments which include black body radiation, photoelectric effect and Compton effect. Here radiation interacts with matter in the form of *photons* or *quanta*. Of course radiation cannot exhibit its particle and wave properties simultaneously.

- A wave is specified by its (*i*) frequency, (*ii*) wavelength (λ), (*iii*) phase, (*iv*) amplitude, (*v*) intensity.
- A particle is specified by its (*i*) mass (*m*), (*ii*) velocity (*v*), (*iii*) momentum (*p*), (*iv*) energy (E). Moreover, a particle occupies a definite position in space.

In view of the above facts, it is rather difficult to accept two conflicting ideas, that radiation is a wave which is spread out over space and also a particle which is localised at a point in space.

de-Broglie's Equation (de-Broglie's matter waves)

His suggestion was based on: as radiation like light can act sometimes as a wave and sometimes like a particle, small particles like electron which are considered as minute particles should also act as waves for sometimes. According to his hypothesis, all matter particles like electrons, protons, neutrons, atoms or molecules have an associated wave with them which is called *matter wave* or *pilot wave* or *de-Broglie's wave*.

The wavelength of the matter wave is given by

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

where 'm' is the mass of the material particle, 'v' is the velocity and 'p' is the momentum.

The above equation is known as de-Broglie's wave equation.

According to the wave mechanical model of the atom, an electron behaves as a standing wave which goes round the nucleus in a circular orbit. The only necessary condition for the establishment of such a stationary wave is that the length of the orbit should be a whole number multiple of the wavelength of the electron as shown in the following Fig. (1.1).

If r is the radius of the circular orbit, then

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

Now, $$\lambda = h/mv.$$

$\therefore$ $$2\pi r = \frac{nh}{mv}$$

or $$mvr = nh/2\pi$$

where $n = 1, 2, 3$, etc.

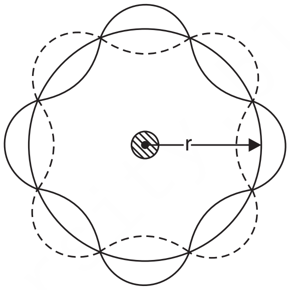


Fig. 1.1

Since 'mvr' is the angular momentum of the electron as a particle, we see that wave mechanical picture leads naturally to *Bohr's postulate that the angular momentum is an integral multiple of $h/2\pi$.* Other quantum conditions can also be derived similarly, *i.e.,* the *angular momentum is quantised.*

Moreover, the concept of an electron as a standing wave rather than a particle revolving in an orbit also removes the difficulty met in Bohr's theory regarding non-radiation of energy by the revolving electron.

The New Atomic Picture

In Bohr's atomic model, nucleus of an atom is surrounded by particles known as electrons, which revolve in defined shells or orbits. This model has been replaced by wave mechanical model, *i.e.*, replaced by de-Broglie's electron wave. These waves form stationary waves with their *nodes* and *antinodes.* Hence, instead of being localised at a point, the whole of electron mass and charge is spread out uniformly throughout the space immediately surrounding the nucleus of the atom (Fig. 1.2).

At nodes where the motion is practically zero, there is assumed to be a little or no charge while at the antinodes the amount of charge is maximum. However, it is still customary to talk of orbits and shells for the simple reason that even according to the new picture of the atom, electrons are found to distribute their charges in such a way that something analogous to shells is formed. New wave model accepts the electron distribution to be three dimensional.

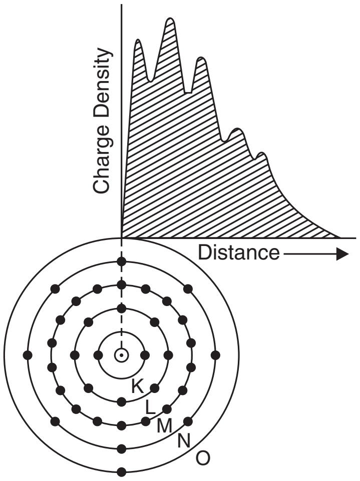


Fig. 1.2 Old and new models of an atom.

Old Bohr's model is represented by orbits of an atom (Z = 37) (Fig. 1.2) and the new wave model is represented by a graph of spherically symmetrical electronic charge with several maxima corresponding to the discrete K, L, M, N shells.

Heisenberg's Uncertainty Principle

The dual nature of the electron implies that any precise measurement of its position would create uncertainty in measurement of its momentum and position. The Heisenberg uncertainty principle states that

- **It is impossible to determine simultaneously both the position and the momentum of a particle with accuracy.**

$$\Delta x.\Delta p \geq h/2\pi.$$

The above expression is known as uncertainty relation where Δx = change in position, Δp = change in momentum and h = Planck's constant.

The relation implies that a simultaneous and precise measurement of both position and momentum (velocity) of a dynamic particle like electron is impossible and the extent of inherent uncertainty in any such measurement is of the order of h (Planck's constant).

Uncertainty Principle and Bohr's Theory—Concept of Probability

Bohr had postulated that electrons revolve in well defined orbits with fixed velocities (energy). But according to uncertainty principle since an electron possesses wave nature, it is impossible to determine its position and momentum simultaneously. On the basis of this principle therefore Bohr's model of atom no longer stands. The best way is to predict the probability of finding an electron with probable velocity with definite energy in a given region of space in given time. Thus the uncertainty principle which gives the wave nature of the electron only provides probability of finding an electron in a given space. It is for this reason the classical concept of Bohr's model of atom has been replaced by *probability approach.*

Schrödinger Wave Equation

It is a differential equation capable of describing the motion of an electron. In an ordinary material wave the displacement of whatever is vibrating about its mean position is given by

$$y = a \sin 2\pi \left(ft - \frac{x}{\lambda}\right) \quad ...(1)$$

where, y = displacement at time t and at distance x from origin.
a = maximum displacement from mean position.
λ = wavelength.
f = frequency of vibration.

When differentiated twice with respect to x, it becomes

$$\frac{d^2y}{dx^2} + \frac{4\pi^2}{\lambda^2} y = 0 \quad ...(2)$$

or

$$\frac{d^2y}{dx^2} + k^2 y = 0 \quad ...(3)$$

The above equation involves only distance as the independent variable. Its solution is $y = a \sin 2\pi\, x/\lambda$ which defines a standing wave. At each point along the wave in space, y varies periodically with frequency f.

Let us now see how this equation can be applied to specify an electron in motion. As we know, the total energy E of an electron is partly kinetic and partly potential.

$$\text{E} = \frac{1}{2} mv^2 + \text{V}$$

$$\therefore \quad mv = \sqrt{2m(\text{E} - \text{V})}\,.$$

Now, de-Broglie wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m(\text{E}-\text{V})}}.$$

Substituting this value in equation (1) and replacing y by ψ as is customary, we get

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(\text{E}-\text{V})\psi = 0 \quad \text{...(4)}$$

The equation (4) is known as the time-independent **Schrödinger equation** in one dimension. For three-dimensional motion of an electron, this equation becomes,

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

or

$$\boxed{\nabla^2\psi + \frac{8\pi^2 m}{h^2}(\text{E}-\text{V})\psi = 0} \quad \text{...(5)}$$

This Schrödinger equation is a basic equation of wave mechanics. As, $p = mf$ is a starting point of classical mechanics. It is seen from equations (3) and (4) that

$$k^2 = \frac{8\pi^2 m}{h^2} \times (\text{E}-\text{V}) \quad \text{...(6)}$$

So, Schrödinger equation can be employed for determining the total energy of an electron. The potential energy V of an electron is specified in terms of space co-ordinate not on time, *i.e.,* Schrödinger wave equation is time independent. Like other differential equation, the Schrödinger wave equation is also governed by boundary conditions. Generally its solutions are only attained for certain energy values called characteristic or *eigen values.* The corresponding wave function ψ which is generally complex is called characteristic or *eigen function.* So, we can write, $\psi = a + ib$ and its conjugate $\psi^* = a - ib$ and their product, $\psi.\psi^* = (a - ib)(a + ib) = a^2 + b^2$, which is real.

For a one dimension system, $|\psi^2|\,dx$ represents the probability of finding an electron within a range of x and $x + dx$. But in three dimension system $|\psi^2|\,d\text{V}$ represents the probability of an electron within the volume range of V to (V + dV).

Significance of ψ and ψ^2

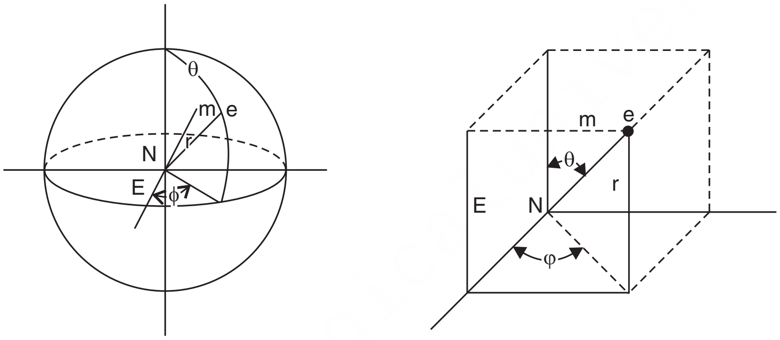
- ψ denotes the amplitude of a three dimensional stationary electron wave.
- According to the Heisenberg's uncertainty principle, it is impossible to locate an electron in an atom with precision but the nature of the wave function ψ is such that $|\psi|^2$ expresses the probability of finding an electron in a definite volume of space around the nucleus. This mathematical expression displays how the probability of finding an electron varies in space. The total probability of finding an electron in space extending to infinity is expressed as follows:

$$\int_{-\infty}^{+\infty} \psi^2 \, d\text{V} = 1$$

where $d\text{V} = dx.dy.dz$. This is known as the *condition of normalisation* and the corresponding wave function ψ is said to be normalised. Because of the spherical symmetry of an atom the wave functions are most satisfactorily expressed in terms of spherical polar co-ordinate system with nucleus at the origin, changing from the Cartesian co-ordinates to polar co-ordinates, the Schrödinger wave equation assumes the following form.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}+\frac{1}{r^2\sin\theta}.\frac{\partial}{\partial\theta}\left(\sin\theta.\frac{\partial\psi}{\partial\theta}\right)+8\pi^2\mu(\mathrm{E}-\mathrm{V})=0 \qquad \text{...(A)}$$

where r, θ and φ are the polar co-ordinates of the electron with respect to the nucleus (N) as origin [see Fig. 1.3 (*a*) and (*b*)].



(a) (b)

Fig. 1.3

It can be shown mathematically that each permitted solution of the wave equation (A) *i.e.,* wave function $\psi(r, \theta, \phi)$ can be expressed as

$$\psi\,(r, \theta, \varphi) = \mathrm{R}_{(r)}\,.\,\Theta_{(\theta)}\,.\,\Phi_{(\phi)}$$

where, $\mathrm{R}_{(r)}$ is a function that depends on the distance from nucleus, which depends on the quantum number n, l (the principal and azimuthal quantum numbers, respectively). The function $\Theta_{(\theta)}$ is function of θ depending on azimuthal quantum number (l) and magnetic quantum number (m_l). $\Phi_{(\phi)}$ is a function of φ which depends on magnetic quantum number (m_l). The total wave function $\psi(r, \theta, \phi)$, which gives the total probability of finding an electron is called the *atomic orbital*. The wave function $\psi(r, \theta, \phi)$ is denoted as a product of two functions, (*i*) radial wave function and (*ii*) angular wave function.

The *radial wave function* $\mathrm{R}_{(r)}$ shows the variation of wave function with r keeping θ and ψ constants *i.e.*, it represents the variation of ψ in the same direction. The *angular wave function* is a joint function θ and ϕ which determines the variation of ψ in different directions at a fixed radial distance r.

For any *s* orbital (1*s*, 2*s*, 3*s*, etc.), the angular part of the wave function is always the same whatever be the principal quantum number *n*. The angular dependence of *p*-orbital is also not influenced by the principal quantum number. This is also same for *d*-orbital.

Highlight: For a small particle like an electron moving in three dimension in the field of nucleus, the Schrödinger wave equation is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(\mathrm{E}-\mathrm{V})\psi=0$$

where m = mass of the electron,

(*contd...*)

V = potential energy of the electron,
E = total energy of the electron,
h = Planck's constant,
ψ = wave function or the eigen function of the electron representing the amplitude of the wave associated with the electron,
x, y, z = co-ordinates of the electron.

The solution of the above second order differential equation furnishes the values of E, the quantised or allowed or permitted energies of electrons and ψ is the wave function. Alternatively, the solution of the above equation produces the electron distribution in space as well as the allowed energy state of the electron. When this equation is applied to hydrogen atom, it is found that the equation can be solved when E assumes certain values which are related by integers. Hence, the concept of quantised energy levels and quantum numbers are the consequences of the wave theory.

Application of Schrödinger Equation

Particle in a box illustrating energy quantization (Like electrons in metals)

Let us consider a particle of mass m which is free to move in a *one dimensional box* of length l as shown in Fig. 1.4.

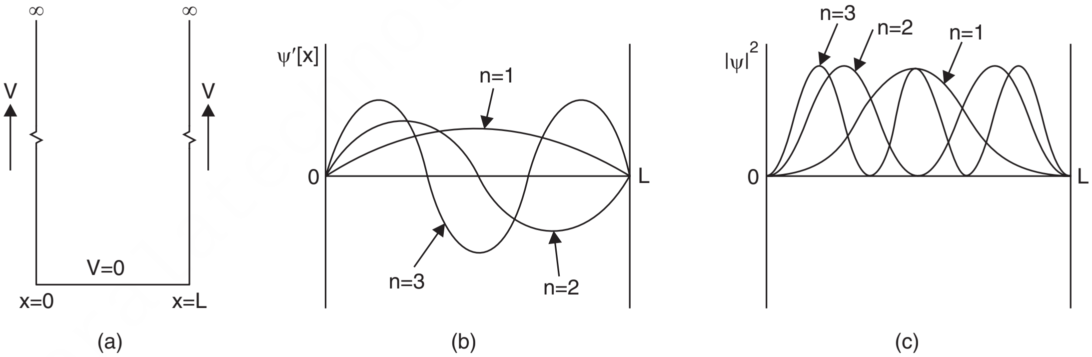


Fig. 1.4

The potential energy V of the electron at the bottom of the box is constant, may be taken as zero. Hence, inside the box V = 0.

Let the potential energy be infinite for $x < 0$ and $x > l$. So, ψ function has to be zero at $x = 0$ and for all negative values of x, since the particle is not allowed over the walls of the box. Similarly, ψ function must be zero for all values $x > l$. Alternatively, it can be stated that the particle is confined to the box and cannot exist outside.

A general solution of Schrödinger equation is:

$$\psi(x) = a \sin kx + b \cos kx$$

For boundary conditions, we have,

$$\psi(x) = 0 \quad \text{at} \quad x = 0 \quad \text{or} \quad \psi(0) = 0$$

$$0 = a \sin 0 + b \cos 0 \quad \text{or} \quad b = 0$$

Also $\psi(x) = 0 \quad \text{at} \quad x = l$

$$\therefore \quad a \sin kl + b \cos kl = 0$$

It can only be possible when,

$$kl = n\pi \qquad \text{or} \qquad k = \frac{n\pi}{l}$$

where x is called *quantum number* and is equal to 1, 2, 3 ... ∞.

Substituting this value in eqn. 4 and also putting V = 0; we get,

$$\frac{n^2\pi^2}{l^2} = \frac{8\pi^2 m}{h}\mathrm{E}$$

So, (E, the total energy of the electron) = K.E. of the electron.

$$\therefore \qquad \mathrm{E}_n = \frac{n^2h^2}{8ml^2} \qquad \text{where } n = 1, 2, 3 \ldots \infty.$$

The above equation means that the particle in a box does not possess any arbitrary amount of energy, rather it possesses discrete set of energy values *i.e.*, its energy is quantised. A few energy levels are given below:

$$\mathrm{E}_1 = \frac{h^2}{8ml^2}$$

$$\mathrm{E}_2 = \frac{4h^2}{8ml^2}$$

$$\mathrm{E}_3 = \frac{9h^2}{8ml^2}$$

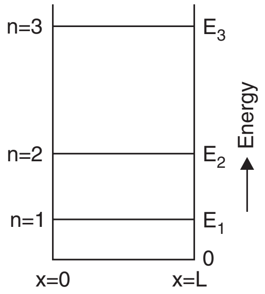


Fig. 1.5

The reason why a particle in a box *i.e.*, bound particle possesses a quantised energy whereas a free particle does not, can easily be deduced from the above equation.

Highlight: Calculation of minimum energy of a particle in a box from Heisenberg's uncertainty principle.

Here $\Delta x = l$, and the particle bounces back in the box. So, $\Delta p = 2p$ because the momentum changes from $+p$ to $-p$ continuously. So we can write,

$$\Delta x \times \Delta p = l \,.\, (2p) = h \qquad \text{or,} \qquad p = \frac{h}{2l}$$

$$\text{Now,} \qquad \mathrm{E} = \frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{p^2}{2m}$$

$$\therefore \qquad \mathrm{E} = \frac{h^2}{8ml^2}.$$

PROBABILITY DISTRIBUTION

The directional properties of an election in an orbital of the hydrogen atom cannot be represented in one diagram. Two separate diagrams are required to meet the demand.

These are namely (*i*) an *angular probability distribution i.e.,* how the angular position θ varies from nucleus with respect to a fixed axis and (*ii*) a *radial probability distribution i.e.,* how *r,* the distance from the nucleus does vary.

(*i*) *Angular probability distributions of orbitals i.e., shapes or boundary surfaces of orbitals* gives the probability of finding an electron in a particular direction.

An *s-electron* has no preferred direction in space *i.e.*, there is an equal chance of finding it in any direction around the nucleus. This is graphically shown in Fig. 1.6 below.

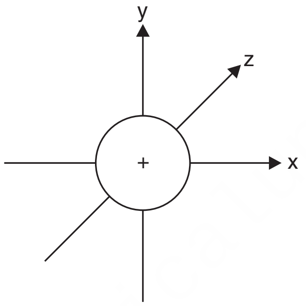


Fig. 1.6

In this diagram, the nucleus of the atom is at the origin and the surface of the sphere represents the probability of finding the *s*-electron which is therefore same in all directions.

A *p*-level has an accommodation for six electrons distributed over three *p*-orbitals to each value of the principal quantum number. These three orbitals are at right angles to each other and the three angular probability distributions are shaped like dumb-bells along the three co-ordinate axes and are named as p_x, p_y and p_z orbitals. In the absence of magnetic field these orbitals are equivalent in energy content and are said to be *triply degenerate.* In the presence of external magnetic field these vary in their energy content depending on the magnetic quantum number. The different shapes are shown in Fig. 1.7 below.

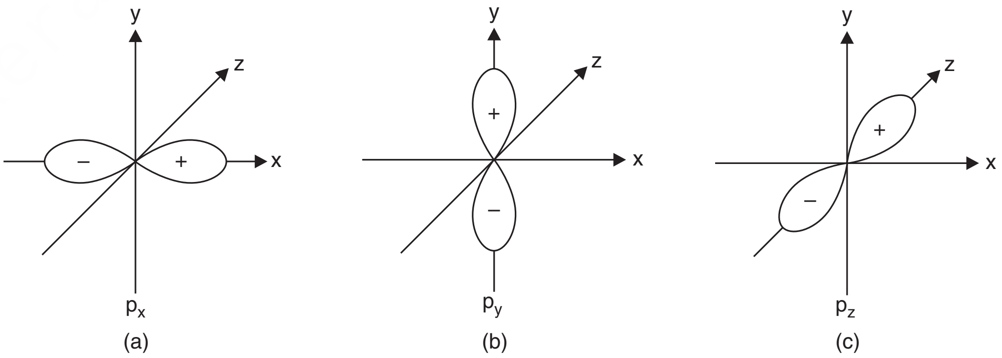


Fig. 1.7

It is most likely that in the p_x orbital the electron will be found in the direction of *x*-axis and there is no chance of it to be found in any of the directions perpendicular to *x*-axis *i.e., y-z* plane in this case is nodal plane with zero electron density. Similarly, in the case of p_y and p_z orbitals the electron will be found along *y* and *z* axes.

The angular probability distribution of five *d*-orbitals that can accommodate ten electrons is quite complicated. These five orbitals are named as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2}. These are shown in Fig. 1.8 below.

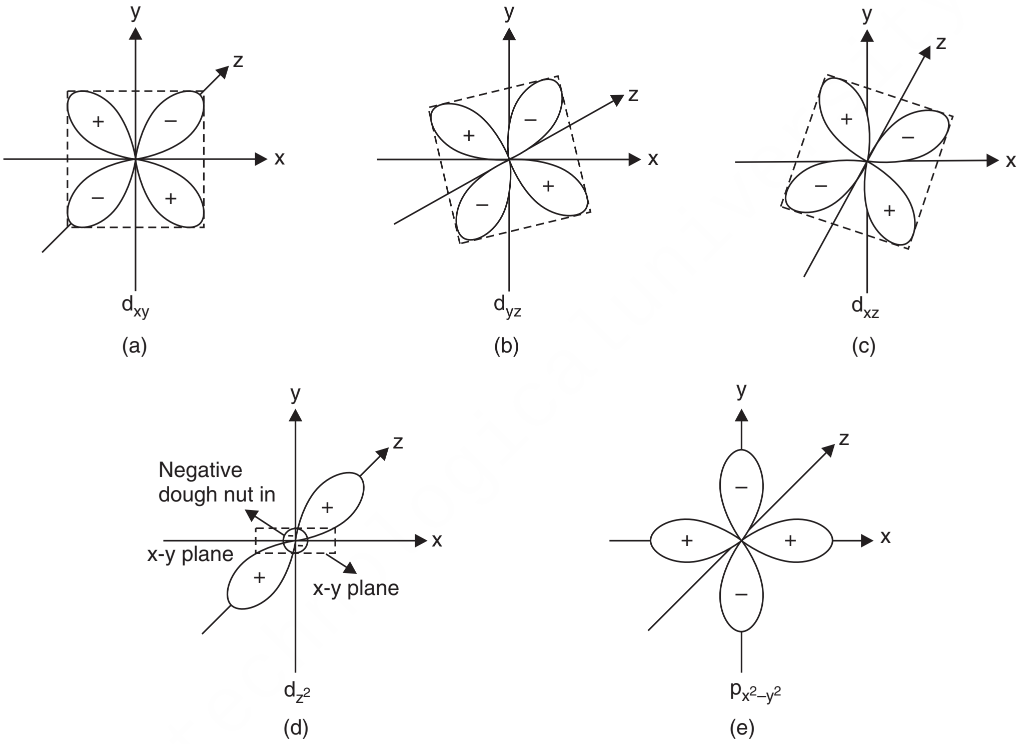


Fig. 1.8

All the *d*-orbitals are equivalent in energy in the absence of magnetic field and are said to be *five fold degenerate.*

The set of the three orbitals namely d_{xy}, d_{yz}, d_{zx} have their lobes lying symmetrically in between the co-ordinated axes indicated by the subscripts to *d*, *e.g.* the lobes of d_{xy} orbital are pointing or lying in between the *x* and *y* axes. This set is referred to as t_{2g} set.

The set of two orbitals *i.e.,* $d_{x^2-y^2}$ and d_{z^2} orbitals form e_g set having their lobes along the axes, *e.g.* The lobes of $d_{x^2-y^2}$ orbital lie along the *x* and *y* axes while those of dz^2 orbital lie along *z*-axis.

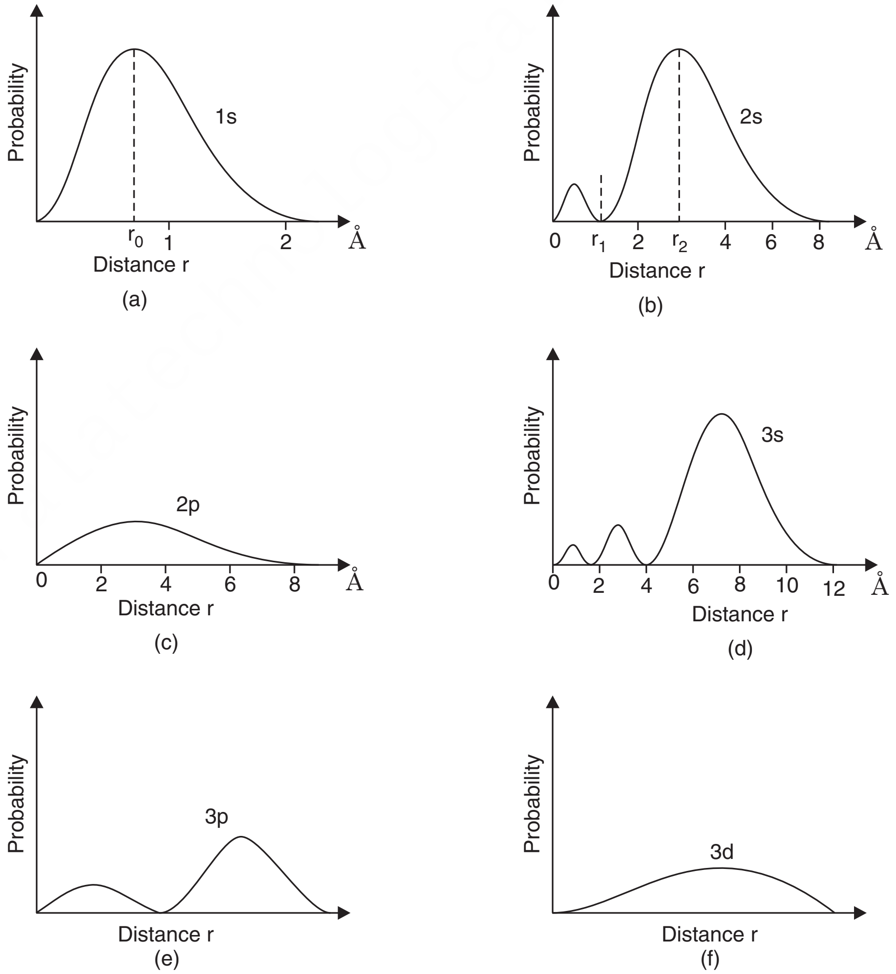
(*ii*) *The Radial Probability distribution*—The angular probability graphs indicate the most probable directions of the electrons but they do not give any indication of the probable distance of the electron from the nucleus. The probable distances of an electron are given by *radial probability distribution* diagram which are given in Fig. 1.9.

In these diagrams, the probability of finding an electron at a distance *r* from the nucleus is plotted against *r* (distance from the nucleus) to get 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals of hydrogen atom.

Highlights:

- The probability of finding an electron at the origin is zero which is the nucleus. This means the electron can never be at nucleus.
- The value of *r* which is the maximum probability in the graph of 1*s* distribution agrees with the value of *r* of Bohr's orbit of hydrogen atom (0.528Å).
- The distributions vary according to the principal quantum number. The larger the value of the principal quantum number the farther is the electron from the nucleus as the angular probability distribution remains uneffected by the value of principal quantum number.

All these facts are based on the proper interpretation of Schrödinger wave equation.



(a) (b) (c) (d) (e) (f)

Fig. 1.9 Radial probability distribution of 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals.

EXERCISES

1. What do you mean by wave nature of an electron?
2. Give the de-Broglie's wave equation?
3. Correlate Bohr's postulate of angular momentum with the wave mechanical model.
4. Give the new picture of an atom.
5. Write Heisenberg's uncertainty principle.
6. Write how the uncertainty principle leads to probability approach.
7. Write Schrödinger wave equation for one dimension.
8. Write Schrödinger wave equation for three dimension.
9. What are eigen values and eigen functions?
10. Give the probability expression for finding an electron in the volume range of V and V + dV.
11. Mention the significance of ψ and ψ^2.
12. Write the Schrödinger wave equation using polar co-ordinates.
13. Apply Schrödinger wave equation for particle in one dimensional box illustrating energy quantisation.
14. Draw angular and radial probability distributions of 2s, 3p, 3d orbitals.

2

Valency and Chemical Bonding

Atoms of elements combine to form molecules of compounds. During chemical combination, the electrons of the atoms rearrange to form the molecule of the compound. The electrons remain in the K, L, M and N shells in the atoms. The atoms containing eight electrons in the outermost shell cannot participate in the chemical combination and are known as inert elements. The electrons of the outermost shell of an atom take part in a chemical combination and are called *valence electrons*.

The inert elements, *viz*. He, Ne, Ar, Kr, Rn and Xe, have eight electrons in their outermost shells except He. The other elements have less than eight electrons in their outermost shells and they want to complete their outermost shells with eight electrons (octet theory) to gain the electronic structure of the inert gases. This is a very common nature of the atoms and for this sake, atoms either lose or gain electrons or share and this idea of electronic arrangement is the basis for *electronic theory of valency*. There are three types of valencies —

(*i*) *Electrovalency* or *Ionicvalency*
(*ii*) *Covalency*
(*iii*) *Co-ordinate covalency*.

Electrovalency: Na atom has got electronic structure ⇒ 2, 8, 1 and Cl atom has got electronic structure ⇒ 2, 8, 7. Na atom can attain inert gas structure by losing one electron and Cl atom can attain inert gas structure by gaining that electron. This sort of transfer of electron from one atom to the other results in the formation of Na^+ and Cl^- ions. These ions remain combined due to electrostatic force of attraction between the so-formed ions. The phenomenon can be represented pictorially as in Fig. 2.1.

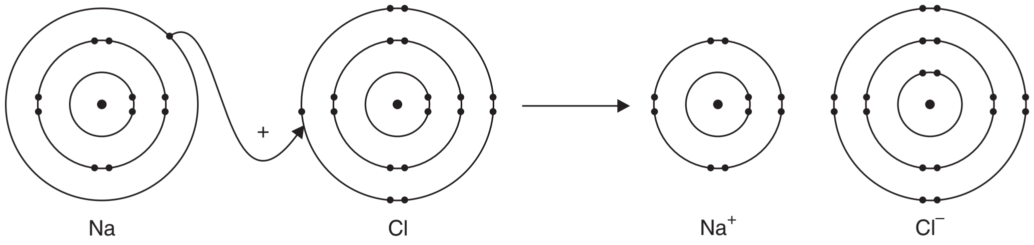
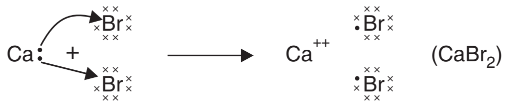


Fig. 2.1

This type of combination of two atoms by complete transfer of electrons from the outermost shell of one atom to the other is known as *electrovalency*. Other electrovalent compounds have been represented as follows by *dot-cross method.*

Some examples of electrovalent compounds :



$$\underset{(2,\,8,\,8,\,2)}{\text{Ca}} + \underset{2(2,\,8,\,18,\,7)}{2\text{Br}} = \underset{(2,\,8,\,8)}{\text{Ca}^{++}}\,.\;\underset{2(2,\,8,\,18,\,8)}{2\text{Br}^{-}}$$

Similarly

$$\underset{2(2,\,8,\,8,\,1)}{2\text{K}} + \underset{(2,\,8,\,6)}{\text{S}} = \underset{2(2,\,8,\,8)}{2\text{K}^{+}}\;\underset{(2,\,8,\,8)}{\text{S}^{--}}\;(\text{K}_2\text{S})$$

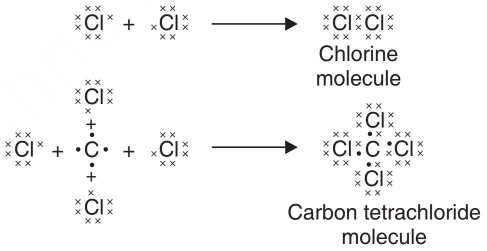
$$\underset{(2,\,8,\,2)}{\text{Mg}} + \underset{2(2,\,7)}{2\text{F}} = \underset{(2,\,8)}{\mu g^{++}}\;\underset{2(2,\,8)}{2\text{F}^{-}}\;(\text{MgF}_2)$$

Highlight: Electrovalency is seen in the case of atoms with a marked difference in electronegativity values when they combine.

Covalency

When atoms, of same or more or less same electronegativity values, combine to form molecules of a compound they share the electrons to fill up their octets in their outermost shells. This sort of combining of atoms is known as *covalency*.

Examples of covalent compounds :



Comparison of electrovalent and covalent compounds:

Electrovalent Compounds	*Covalent Compounds*
(*i*) They are Non-directional.	(*i*) They are directional in nature.
(*ii*) They cannot exhibit isomerism.	(*ii*) They can show isomerism.
(*iii*) m.p. and b.p. are high.	(*iii*) m.p. and b.p. are low.
(*iv*) They are conductors of electricity in solution or in their molten state.	(*iv*) They are nonconductors of electricity in solution or in molten state.
(*v*) They are soluble in polar solvents (H_2O) and insoluble in non-polar solvents (C_6H_6, CCl_4).	(*v*) They are soluble in organic solvents, generally insoluble in water.
(*vi*) They are polar in nature.	(*vi*) They are non-polar in nature.

Co-ordinate Covalency

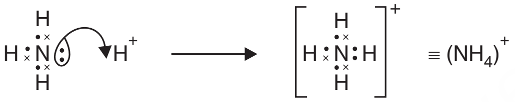
In covalency the bonding atoms contribute equal number of electrons to form a bond. In some cases during chemical combinations, a pair of electrons is being contributed by a single atom. The other atom contributes no electron towards the bond. After combination the bond acts as a purely covalent bond. This sort of bond formation is known as *co-ordiate covalency*. The atom which donates a pair of electrons is known as '*donor*' atom and the atom which accepts the pair of electrons is known as '*acceptor*' atom. The donor atom should have a lone pair of electrons. The phenomena can be represented as follows:

$$A\,\cdot + \cdot\,B \;\Rightarrow\; A:B \text{ or } A - B \text{ (Covalency)}$$

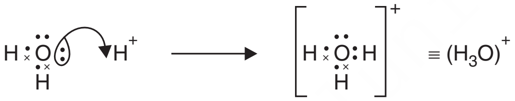
$$A: + B \;\Rightarrow\; A:B \text{ or } A \rightarrow B \text{ (Co-ordinate covalency)}$$

The co-ordinate covalency is indicated by the sign '→'.

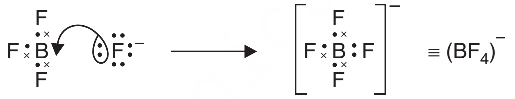
Some examples of coordinate bond formation:



Ammonium ion



Hydronium ion



Electronegativity

The attraction and repulsion powers of atoms of different elements are not same. As for example, F or O has got a greater tendency of attracting electron pairs of the bond towards them when they form a covalent bond with any other atom. In comparison, H atom has less tendency of this sort. The power of attracting electrons of one of the atoms in a covalent bond is known as its *electronegativity*. Comparative *values of electronegativities* of different elements taking the electronegativity value of H as 2.1 is given in Table 2.1 below.

Table 2.1: Electronegativity values (L. Pauling Scale)

Group → *Period↓*	*I (1)*	*II (2)*	*III (13)*	*IV (14)*	*V (15)*	*VI (16)*	*VII (17)*
1	H 2.1						
2	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
3	Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4	K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
5	Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
6	Cs 0.7	Ba 0.9	Ti 1.8	Pb 1.9	Bi 2.0	Po 2.0	At 2.2
7	Fr 0.7	Ra 0.9					

This sort of attractions give the covalent bond between two atoms a partial ionic character. Partial ionic character of a covalent bond is calculated as follows:

When electronegativity values (x) of the two atoms A and B are same, *i.e.*, $x_A = x_B$, the bond A – B is 100% covalent. When $x_A \neq x_B$, the bond gains partial ionic character and the molecule AB becomes polar, *viz*. HCl. Greater the difference $(x_A - x_B)$, greater is the ionic character of the bond. The relation is represented by the equation —

$$\% \text{ ionic character} = 100\left[1 - \exp\left\{1 - \frac{1}{4}(x_A - x_B)^2\right\}\right]$$

$$= 16(x_A - x_B) + 3.5\,(x_A - x_B)^2$$

Calculation of partial ionic character of HF molecule:

$$\% \text{ ionic character in HF molecule} = 16(4.0 - 2.1) + 3.5(4.0 - 2.1)^2$$

$$= 43\%.$$

Hydrogen Bond

Hydrogen atom has got only one electron. So, it can combine with one atom of a monovalent atom, *viz* F. If the second atom is electronegative, then electron pair of the bond is shifted towards the other atom, *i.e.,* F, due to its greater electron attraction power. As a result, the hydrogen will gain the positive charge partially but the electron will not be detached totally from the hydrogen atom. In this condition, if the charged hydrogen atom comes in contact with strongly electronegative element of the other molecules (hydrogen of HF), they are attracted by the hydrogen ($H^{+\delta}$) remaining in the previous molecule and a 'so-called' valency is formed as if hydrogen acts a bridge between two electronegative elements. This sort of bond is known as '*hydrogen bond*'. This type of bond is not very strong. The bond energy is less than that of covalent bonds.

Example of hydrogen bonding in HF molecules:

$$H^{+\delta} - F^{-\delta} \ldots H^{+\delta} - F^{-\delta} \ldots H^{+\delta} - F^{-\delta} \ldots H^{+\delta} - F^{-\delta}$$

hydrogen bond

Highlights:

- Conditions of hydrogen bond —
  - (*i*) Hydrogen should be attached to an electronegative element of a covalent bond.
  - (*ii*) The atomic radius of the electronegative elements should be small.
- Hydrogen bond is seen when hydrogen is attached to electronegative elements, like O, N and F (*i.e.*, when atomic radii are small).

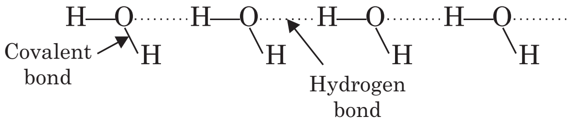
Hydrogen Bondings

There are two types of hydrogen bonding: (*a*) *Intermolecular* (*b*) *Intramolecular.*

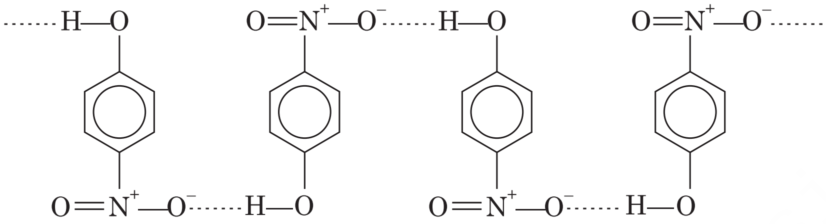
(*a*) **Examples of intermolecular hydrogen bonding :**

(*i*) ...... H–F ...... H–F ...... H–F ...... H–F......

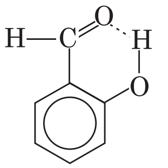
(*ii*)

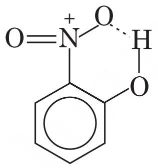


(*iii*)



(*b*) **Examples of Intramolecular hydrogen bonding:**

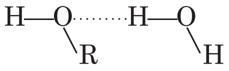

Salicylaldehyde


o-Nitrophenol

Properties gained by the molecules due to hydrogen bonding:

(*i*) Due to molecular association arising out of the intermolecular hydrogen bonding, the boiling points of the molecules become high, *i.e.*, volatility becomes less.

(*ii*) Solubility of the molecules in water arises out of hydrogen bonding with water molecule.



Dipole Moment

Every atom has got nucleus and requisite number of electrons. So within a molecule two or more positive nuclei are surrounded by electrons at different places. So within a molecule there is a centre of action of positive charges as well as centre of action of negative charges. These two points in a molecule may fall at the same point or at different places in the molecule. When they fall in different places *i.e.*, two charges (+ve and –ve) are separated by a distance, they develop a moment, known as *dipole moment*. The molecules containing the dipole moment are called polar molecules. If the magnitude of the charge at the centre of action is e and distance between them is d, then,

dipole moment, $\mu = e \times d$

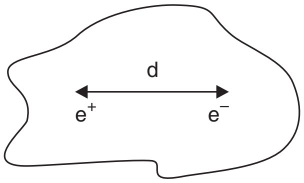


Fig. 2.2

Generally, the charge is expressed in 'e.s.u.' unit and the distance in 'cm' unit. So the unit of dipole moment is '*e.s.u-cm*'. 1×10^{-18} *esu-cm* is known as *1 Debye*. And this *Debye* unit is used to express the dipole moment.

Highlights:

- The dipole moment of H_2O molecule is 1.8 D. *i.e.*, its dipole moment is 1.8×10^{-18} *esu-cm*.
- HCl, H_2O, NH_3, CH_3OH are polar molecules *i.e.*, their centre of action of positive charges and centre of action of negative charges are not same and the molecule is not symmetrical.
- Cl_2, H_2, CH_4, C_6H_6, CO_2, etc. are non-polar molecules. The molecules are symmetrical, and in those molecules centre of positive charge action and centre of negative charge action are at the same place.

  i.e., $d \Rightarrow 0; \quad \therefore \quad \mu \Rightarrow 0.$
- The dipole moment of a molecule can be calculated from the formula:

$$R = \sqrt{\mu_1^{\,2} + \mu_2^{\,2} + 2\mu_1\mu_2 \cos\alpha}$$

where, μ_1 and μ_2 = dipole moments of the different bonds of the molecule.

R = Resultant moment of the molecule.

If R is zero, the molecule becomes non-polar and if R has got a positive value the molecule becomes polar.

α = Angle between the covalent bonds

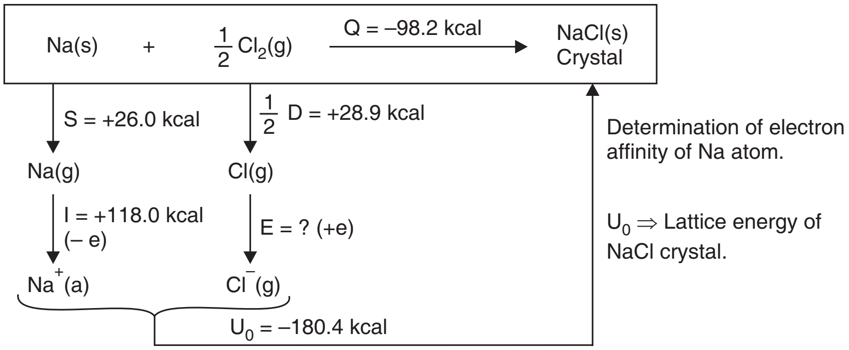
Born-Haber Cycle (Determination of Electron Affinity):

The electron affinity of an element is the quantity of energy released when an electron is gained or lost by an atom in the gaseous state to form an anion.

$$\underset{\text{Neutral gaseous atom}}{A(g)} + e^-(g) \longrightarrow \underset{\text{Anion}}{A^-(g)} + \underset{\text{(Electron affinity of atom A, } E_A)}{\text{Energy released}}$$

Electron affinity is represented by the '–ve' sign as energy is liberated in this case. When energy is supplied it is represented by '+ve' sign and called second electron affinity (E_2).

Born-Haber cycle is represented diagrammatically with the *formation of NaCl (s) from Na (s) and $\frac{1}{2}$ Cl_2 (g)* by direct combination to determine electron affinity of 'Cl' atom:



$$Q = S + \frac{1}{2}D + I + E + U_0$$

$$-98.2 = +26 + 28.9 + 118 + E - 180.4$$

$$\therefore \qquad E = -90.7 \text{ kcal/g atom of Cl}$$

Negative sign indicates that energy is released in the formation,

$$Cl(g) \longrightarrow Cl^-(g)$$

Highlights:

- Born-Haber cycle is a thermochemical cycle that can be used to calculate the lattice energy for a compound of a metal with a nonmetal.
- The cycle is an application of Hess's Law (see Chapter 4).
- A Born-Haber cycle can also help to determine whether the bonding in a compound is truly ionic.
- The lattice energy for NaCl is -780 kJ mol^{-1}, that for KCl is -711 kJ mol^{-1} and that for AgCl is -905 kJ mol^{-1} calculated as per Born-Haber cycle. The lattice energy for AgCl is greater than that of ionic bondings in NaCl and KCl indicating that there is a contribution of covalent bonding in AgCl.
- We have utilised Born-Haber cycle in determining the electron affinity of 'Cl' atom.

Chemical Bonding (Wave-Mechanical Concept)

The classical concept of covalency doesn't give any idea of the directional characteristic of a bond and also of the bond energy. The application of wave mechanics gives a satisfactory explanation of some of these problems. In this connection, two main approaches are —

1. Valence-bond theory
2. Molecular orbital theory.

Molecular orbital theory is gaining much importance. Both the theories admit that —

(*i*) A covalent bond is formed as a result of overlapping of the atomic orbitals,

(*ii*) When the overlapping takes place along the axes of the atomic orbitals maximum overlapping of atomic orbitals can occur,

(*iii*) Maximum overlapping gives a strong bond known as *sigma* (σ) *bond.*

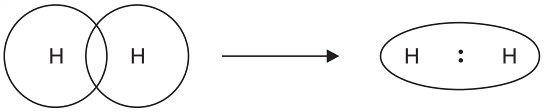


Fig. 2.3 Formation of H_2 molecule by the overlapping of two 1*s* atomic orbitals of two H atoms.

(*iv*) Each covalent bond requires overlapping of a pair of orbitals.

(*v*) The overlapping orbitals must be valence orbitals and must contain an odd electron.

Schematic representation of the formation of some simple molecules on the basis of valence bond theory:

(*i*) *s-s* overlapping ⇒ H_2 molecule

(*ii*) *s-p* overlapping ⇒ the formation of HF, NH_3, H_2O molecules

(*i*) **HF molecule**

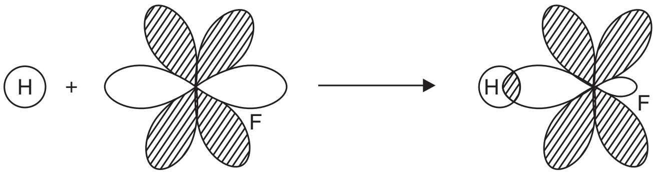


Fig. 2.4 (a) Formation of HFmolecule.

(*ii*) **NH_3 molecule**

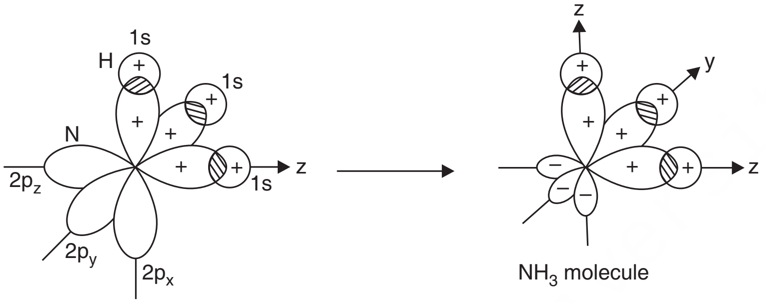


Fig. 2.4 (b) Formation of NH_3 molecule.

Here the overlapping takes place between the three (2*p*) orbitals of nitrogen atom with 1*s* orbital of each hydrogen atom. If it were the case, then bond angle in NH_3 should be 90°. But actually bond angle in NH_3 is 106° 45′. So some other concept becomes essential to explain the formation of NH_3 molecule. That concept is the concept of *hybridization*.

(*iii*) **Water molecule**

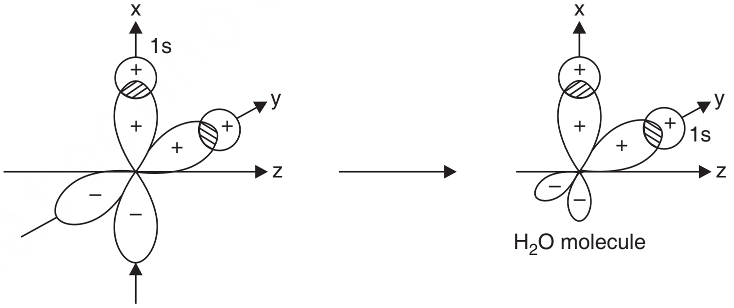


Fig. 2.5 Formation of H_2O molecule.

In this case also the bond angle appears to be 90°. But the actual bond angle in water molecule is 104° 27′. This fact also leads to the idea of hybridization of orbitals.

(*iv*) **Fluorine molecule :** *p-p* overlapping to form a σ-bond.

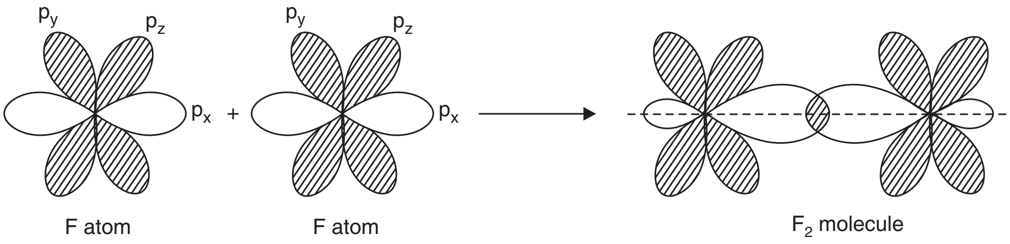


Fig. 2.6 p_x-p_x overlapping along the axis to form F_2 molecule.

(*v*) **N_2 molecule:** *p-p* overlapping to form σ and π bonds

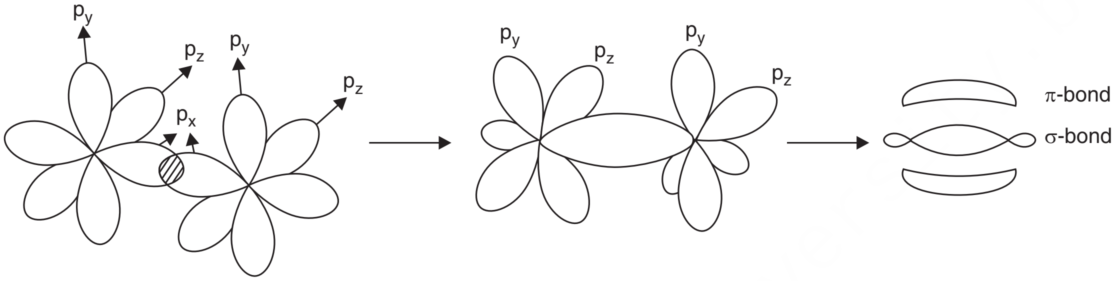
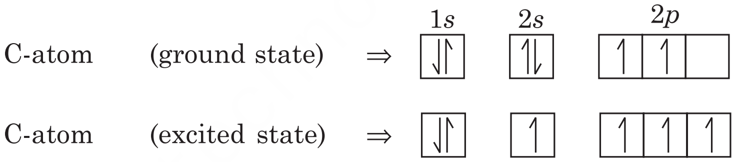


Fig. 2.7 σ and π bonds in N_2 molecule.

(*a*) *Overlapping of two p_x orbitals along the axes leads to the formation of a sigma bond.*

(*b*) *Lateral overlapping of two p_y and p_z orbitals leads to the formation of two π bonds.*

Hybridization: Carbon has electronic configuration: $1s^2\ 2s^2\ 2p^2$, but in CH_4, C atoms form four identical bonds with H-atom with equal energy. This can be explained only by the *Concept of hybridization.* If we consider that C forms four hybrid orbitals of equal energies out of 2*s* and 2*p* orbitals and then these hybrid orbitals overlap with *s*-orbitals of H-atoms along the axes, then bond angle and bond energies in CH_4 molecule can satisfactorily be explained as follows:



Now this one *s*-orbital and three *p*-orbitals of a carbon atom mix to give four hybrid orbitals of equal energies, the axes of hybrid orbitals are directed towards the vertices of a regular tetrahedron (Fig. 2.8).

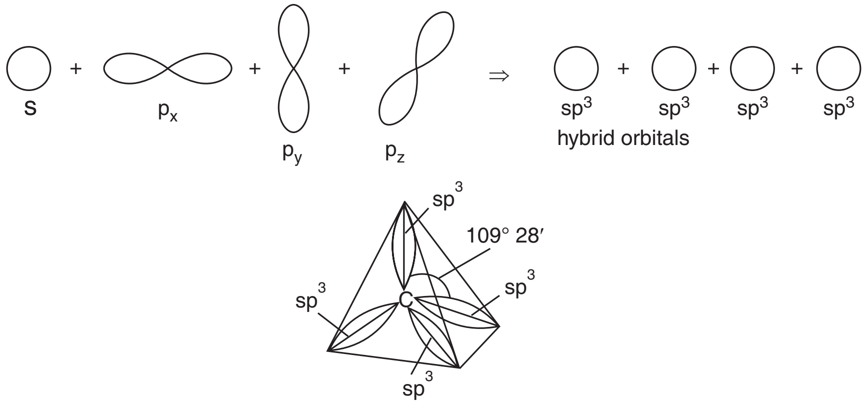


Fig. 2.8 *sp*³ hybridised C atom.

Now these four *sp*³ hybrid orbitals overlap along the axis with *s*-orbitals of four H-atoms to form a CH_4 molecule forming four covalent bonds of same energies.

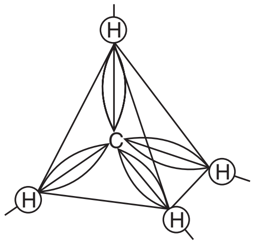
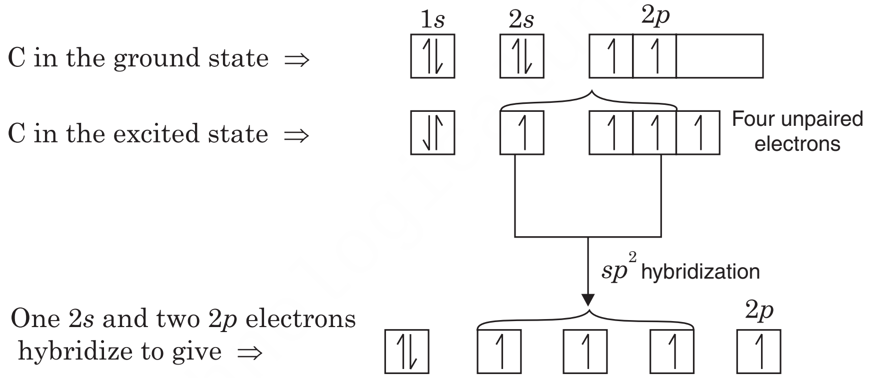


Fig. 2.9 CH_4 molecule.

sp^2-hybridization

Electronic configuration of :



2s and two of 2p orbitals hybridize instead of three 2p orbitals to form three sp^2 hybrid orbitals because the three hybrid orbitals are much more directed. The hybrid orbitals lie in a plane and the axes are directed towards vertices of an equilateral triangle and so, bond angle in this case is 120°. Three sp^2 hybrid orbitals of each C-atom form three sigma bonds in ethylene molecule.

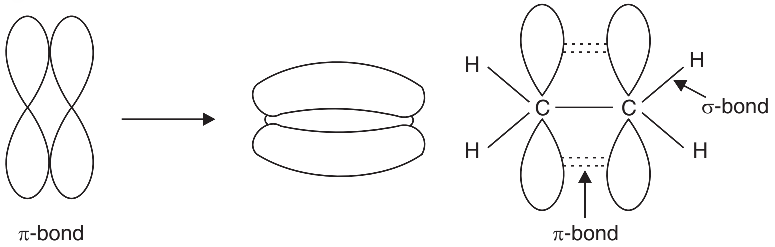


Fig. 2.10 Ethylene molecule.

Lateral overlapping of the two 2p orbitals of two C-atoms leads to the formation of a weak bond known as π-bond (See Fig. 2.10).

Highlights:

- Ethylene molecule contains five sigma bonds.
- Four sigma bonds are formed due to overlapping of sp^2-s orbitals and one out of sp^2-sp^2 overlapping. Residual 2p orbitals of each sp^2 hybridised C-atom overlap laterally to form a π-bond (Fig. 2.10).

In boron trifluoride the sp^2 hybrid orbitals of B atom overlap with p orbitals of three F atoms along the axes to form three sigma bonds (Fig. 2.11). Boron atom has electronic configuration, $1s^2\ 2s^2\ 2p^1$. $2s$ and $2p$ hybridise electrons to produce three sp^2 hybrid orbitals directed towards the vertices of an equilateral triangle.

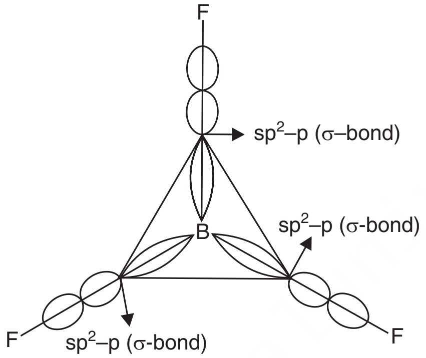
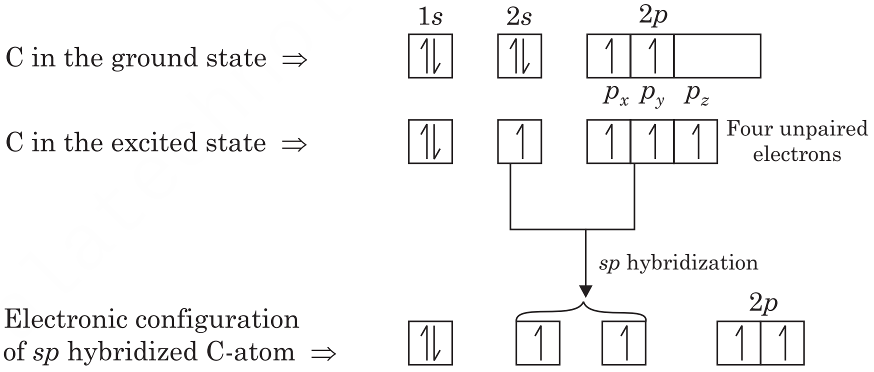


Fig. 2.11 Formation of triangular planar BF_3 molecule. (Another example of sp^2 hybridization).

sp-hybridization

Electronic configuration of:



In the structure of acetylene sp-hybridization takes place. In the excited state of C-atom there are two hybrid orbitals (sp) and two unchanged p-orbitals. During combination with H-atom, two sp-hybrid orbitals overlap along the axis to give a σ-bond. Then two C-atoms possess total four unchanged p-orbitals. They overlap laterally to give two π-bonds. So triple bond of acelylene molecule contains one σ-bond and two π-bonds.

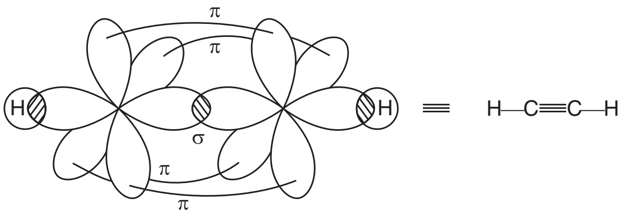
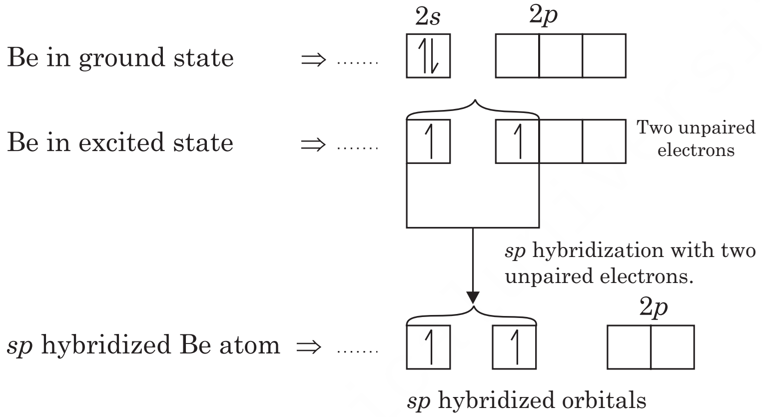


Fig. 2.12 Structure of acetylene.

In BeF_2 molecule the central atom Be has electronic configuration ⇒ $1s^2 . 2s^2$ in its ground state. Since, there is no unpaired electron, the Be atom cannot form any covalent bond.

In the excited state one of the $2s^2$ electrons jumps to $2p$-orbital before forming any bond. Now, the Be atom has the configuration ⇒ $1s^2\ 2s^1.\ 2p_x^{\ 1}\ 2p_y^{\ 0}\ 2p_z^{\ 0}$. Then these $2s$ and $2p_x$ orbitals mix to give two *sp*-hybridised orbitals. These two hybrid orbitals next overlap with *p* orbitals of two F-atoms along the axes making BeF_2 a linear molecule (Fig. 2.13).

Electronic configuration of:



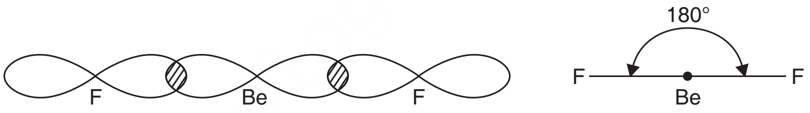


Fig. 2.13 Structure of BeF_2 (example of *sp* hybridisation).

Highlights:

- When orbitals overlap along the axes, there is σ-bonding. In this type of bonding, charge cloud exists symmetrically.
- In double bonds and triple bonds, there are lateral overlapping and due to this lateral overlapping the π-bonds are formed. In this type of bonding, the overlapped charged cloud is parallel to internuclear axis.
- π-bonds are comparatively weaker than σ-bonds, as they form by lateral overlapping. Hence, the π-bonds open easily and take part in the chemical reactions.
- When the number of bonds between the atoms increase the bond energy increases and bond length decreases.

Table 2.2: Displaying bond lengths and bond energies

Bond	C—C	C = C	C ≡ C	N—N	N ≡ N
Bond length (Å)	1.54	1.34	1.21	1.52	1.10
Bond energy (Kcal)	83	144	196	38	225

dsp^2-hybridization

In this type of hybridisation one *s*-orbital, two *p*-orbitals (p_x and p_y) and one *d*-orbital ($d_{x^2-y^2}$) mix to give four equivalent hybrid orbitals, axes of which are directed towards the corners of a square. So, the shape of the molecule becomes square planar and the bond angle is 90° (see Table 2.3).

dsp^3 or sp^3d hybridization

In this type of hybridization d_{z^2} orbital and one *s*-orbital and three *p*-orbitals mix to give five orbitals (Fig. 2.14). But in this case, the hybrid orbitals are not equivalent. The hybrid orbitals consist of one group of two equivalent oppositely directed orbitals and the second group of three equivalent orbitals. The shape of the molecule will be trigonal bipyramidal (Fig. 2.15).

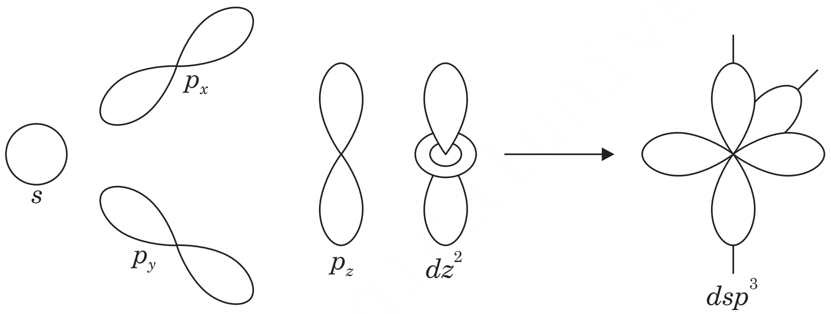
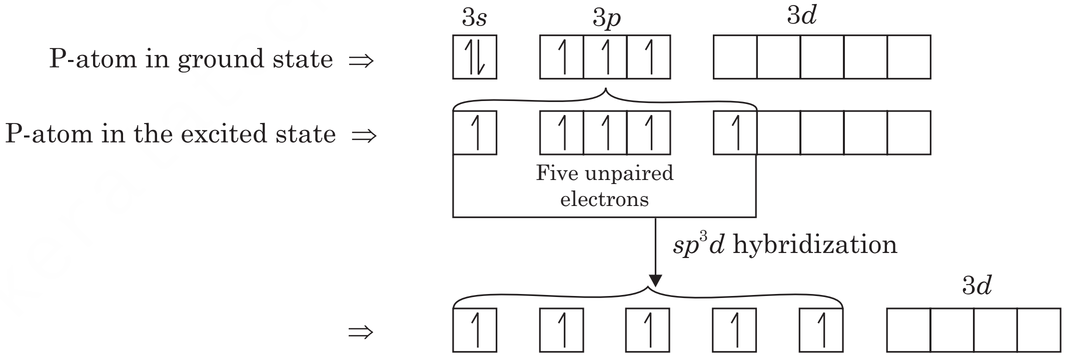


Fig. 2.14 sp^3d hybridization.

Example of sp^3d hybridization:

Electronic configuration of:



These sp^3d hybrid orbitals of one P-atom overlap with five *p* orbitals of five Cl atoms to form PCl_5. The shape of the molecule is trigonal bipyramidal (Fig. 2.15).

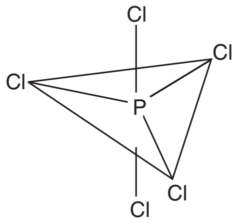
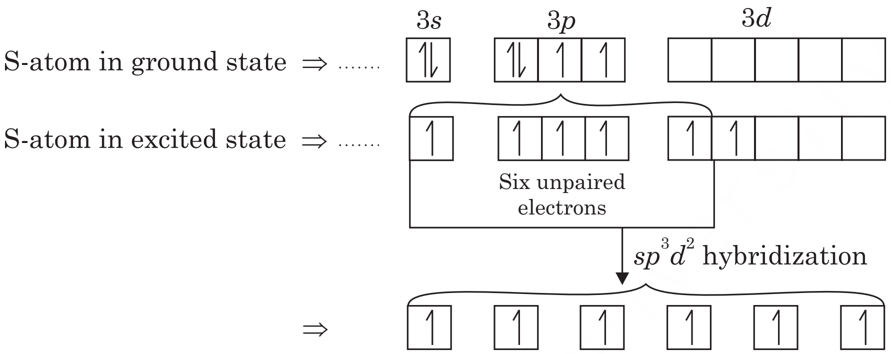


Fig. 2.15 Trigonal bipyramidal structure of PCl_5.

d^2sp^3 or sp^3d^2 hybridization

Electronic configuration of:



These sp^3d^2 hybrid orbitals of one S-atom overlap with *p*-orbitals of six F-atoms to form SF_6.

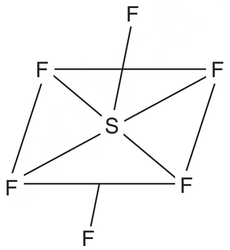
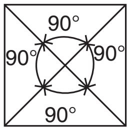


Fig. 2.16 Octahedral structure of SF_6 molecule.

Table 2.3

No. of electron pairs in outer shell of the atom	*Hybrid orbital*	*Shape of the molecule*	*Bond angles*	*Example*
2	*sp*	Linear	180°	BeF_2, C_2H_2
3	sp^2	Trigonal planar	120°	BF_3, C_2H_4
4	sp^3	Tetrahedral	109° 28′	CH_4, SiF_4
4	dsp^2	Square planar 	90°	$[Ni\ (CN)_4]^{2-}$, $(NH_3)_2\ Cl_2^{2-}$
5	dsp^3 or sp^3d	Trigonal bipyramidal	120° and 90°	PCl_5, $Fe(CO)_5$
6	d^2sp^3 or sp^3d^2	Octahedral	90°	SF_6, $Co(NH_3)_6$

VSEPR Theory and Molecular Model

It is interesting to note that if the central atom in a molecule is surrounded only by overlapped bonding orbital or orbitals containing shared pairs of electrons (Bond pairs, bp) in the valence shell, the molecule then acquires a regular geometry. When the central atom contains one or more lone pairs (lp) of electrons in the valence shell with bond pairs (bp) the shape of the molecule becomes distorted for minimum energy and for maximum stability, the orbitals containing lone pairs as well as the bond pairs are so arranged that there is maximum repulsion between them. The orbital containing lone pair of electrons in the valence shell occupies more space and the lone pair-lone pair repulsion is greater than the lone pair-bond pair repulsion. It is again greater than the bond pair-bond pair repulsion *i.e.,* we can write

lp-lp repulsion > lp-bp repulsion > bp-bp. repulsion.

Now, if the distribution of the orbitals about the central atom of the molecule can be predicted, *the shape of the molecule and bond angle may be predicted.*

This is the basis of *Valence Shell Electron Pair Repulsion (VSEPR) theory.*

Case I. *Central atom surrounded by two bonding pairs:*

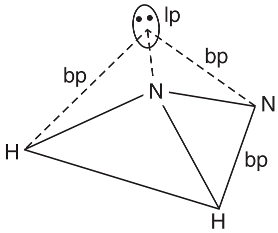
The two bonding pairs remain as apart as possible. The bond angle is 180°. Example: BeF_2.

Case II. *The central atom surrounded by three bond pairs:* They remain as apart as possible and the bond angle is 120°.

Case III. *Central atom surrounded by four bond pairs:* Example methane. Here there are four bond pairs and the shape of the molecule is tetrahedral.

In all the above cases there were only bond pairs in the molecules and the molecules have a regular geometry.

Case IV. *Molecule containing lone pair and bond pair:* Example ammonia molecule:



The geometry of the molecule is distorted tetrahedron. In NH_3, there is sp^3 hybridization and one hybrid orbital contains lone pair of electrons.

But the bond angle here is 107°. Here lp-bp repulsion is greater than the bp-bp repulsion. So the bond angle is reduced (107°) and if we overlook the fourth corner of tetrahedron occupying an orbital containing an unshared pair of electrons, the shape of the molecule becomes pyramidal (Fig. 2.17).

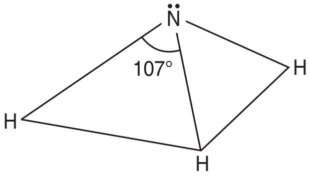


Fig. 2.17

H_2O molecule:

Here O-atom is sp^3 hybridized and only two H-atoms occupy the two corners of a tetrahedron. The other two corners of the tetrahedron is occupied by the two sp^3 hybrid orbitals containing unshared pairs of electrons. Overlooking those two corners of the tetrahedron the H_2O molecule becomes 'V' shaped (Fig. 2.19).

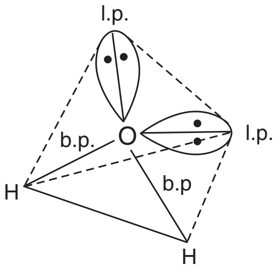


Fig. 2.18 sp^3 hybridized 'O' atom.

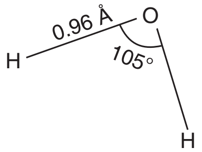


Fig. 2.19 V-shaped water molecule.

Here the bond angle is 105°, the existence of the two pairs of unshared electrons repel each other strongly and the bond pairs come close to each other than that in the NH_3 molecule. The bond angle becomes more reduced (Fig. 2.20).

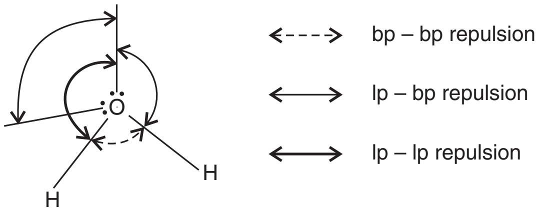


Fig. 2.20 Showing repulsions.

Highlight:

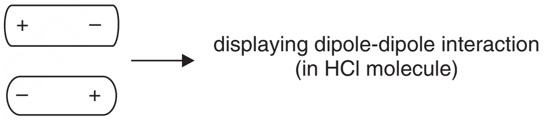
NH_3 and H_2O molecules are examples of distorted molecules due to the presence of lone pairs in the hybrid orbitals and lp-bp, lp-lp repulsions.

Intermolecular forces:

In a crystalline solid, the particles act as structural units, ions of molecules are arranged in a symmetrical way. So melting of such solids occurs when the highly ordered arrangement of particle in the crystalline lattice changes to the more random arrangements (characteristic of a liquid). In non-ionic compound (covalent compound) where the atoms are held by covalent bonds, the intermolecular forces are very weak. So energy requirement for melting is less compared to ionic compounds. There are two kinds of intermolecular forces:

(*a*) dipole-dipole interaction,

(*b*) van der Waals forces.



As a result of dipole-dipole interaction, polar molecules are held to each other more strongly than non-polar molecules (purely covalent molecules). This difference in strength of intermolecular forces is reflected in their physical properties.

There must be some forces between the molecules of a non-polar compound. Since, they can solidify. Such attraction is known as *van der Waals force of attraction*. These van der Waals forces have very short range. They act only between the portions of different molecules that are in close contact, *i.e.,* van der Waals forces are weak intermolecular forces which are responsible for weakest attractions between nonpolar molecules.

Every atom has an effective ‘size’. This is called van der Waals radius. When two non-bonded atoms come closer, the attraction between them steadily increases and reaches a maximum when they are just “touching”, when the distance between the nuclei is equal to the sum of the van der Waals radii, if the atoms are forced to come still closer then *van der Waals attraction* will be replaced by *van der Waals repulsion*. Thus, we can say, non-bonded atoms strongly resist crowding. Thus, both attractive and repulsive van der Waals forces are important for our understanding of molecular structure.

Molecular orbital theory [linear combination of atomic orbitals, LCAO]

Homonuclear diatomic molecule:

Let, two H-atoms designated by H_A and H_B containing two 1*s*-atomic orbitals overlap to form M.O. Then expression for two molecular orbitals (M.O.) will be one bonding (ϕ_B) and the other antibonding (ϕ_A):

$$\phi_B = \psi_A(1s) + \psi_B(1s)$$
$$\phi_A = \psi_A(1s) - \psi_B(1s)$$

(*i*) The two conditions can be represented pictorially (Fig. 2.21)

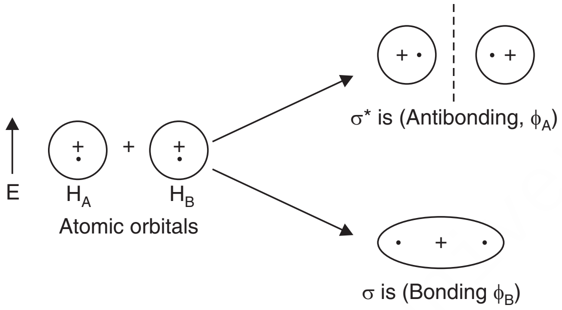


Fig. 2.21 Bonding and antibonding orbitals.

Linear combination of 1*s*-atomic orbitals (σ-symmetry) of two H-atoms to give bonding and antibonding molecular orbitals (σ-symmetry).

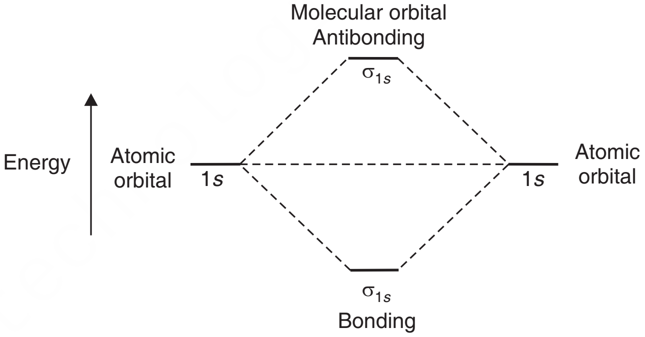


Fig. 2.22 Representation of M.O. diagram.

Energy level diagram (Fig. 2.22) illustrating the formation and relative energies of σ_{1s} (bonding) and σ^*_{1s} (antibonding) molecular orbitals resulting from the combination of two 1*s*-atomic orbitals on two H-atoms in H_2 *molecule.*

(*ii*) Molecular orbitals from *p* atomic orbitals:

(*a*) End-end overlap

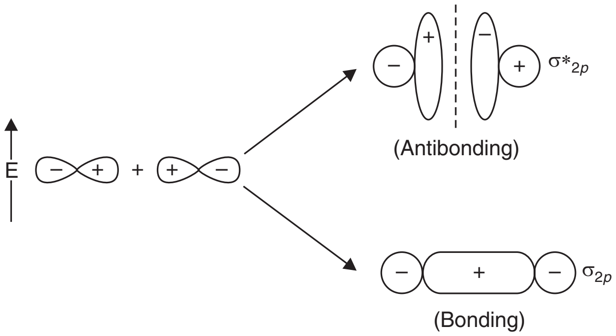


Fig. 2.23 Linear combination of two $2p_x$ orbitals to form σ2p (bonding) and σ*2p (antibonding) molecular orbitals (σ-symmetry).

(*b*) Side-by-side overlap (Fig. 2.24):

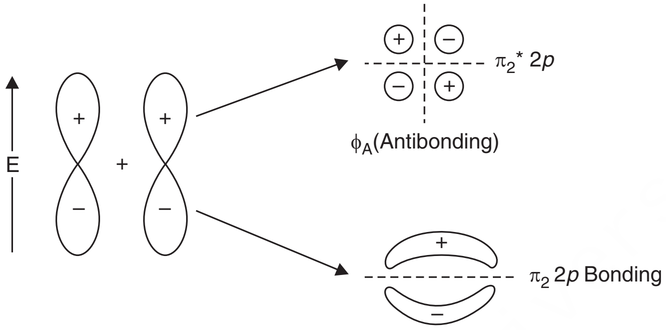


Fig. 2.24 π-Bonding.

Linear combination of two $2p_z$ orbitals to form $\pi_z 2p$ (bonding) and $\pi_z 2p^*$ (antibonding) molecular orbitals (π-symmetry).

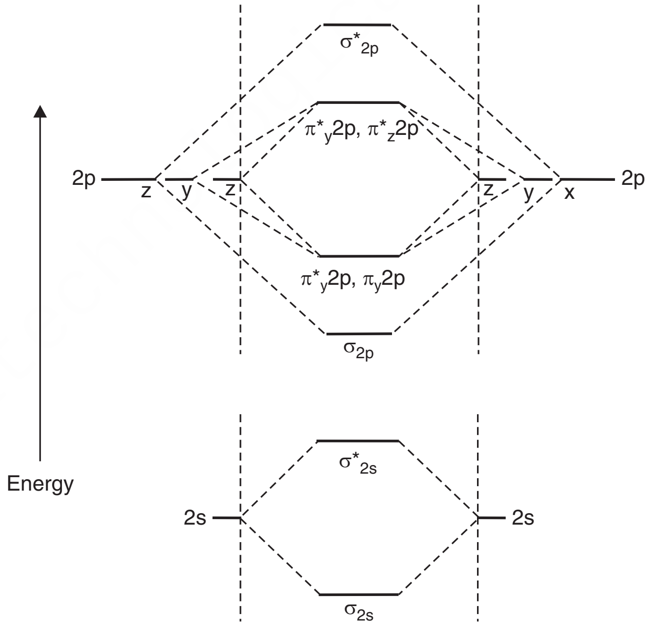


Fig. 2.25 Order of energy of molecular orbitals (M.O.).

(Energy level diagram of molecular orbitals for a homonuclear diatomic molecule)

So, the order of energy for molecular orbital is:

$$\sigma_{1s} < \sigma_{1s}{}^* < \sigma_{2s} < \sigma_{2s}{}^* < \sigma_{2p} < \begin{matrix} \pi_y 2p \\ \pi_z 2p \end{matrix} < \begin{matrix} \pi_y{}^* 2p \\ \pi_z{}^* 2p \end{matrix} < \sigma^* 2p$$

Bond-Order (B.O.):

Bond-order (B.O.) of a molecule is calculated as follows:

B.O. ⇒ $\dfrac{\text{N.B.} - \text{N.A.}}{2}$

N.B. ⇒ no. of electrons in bonding molecular orbitals.

N.A. ⇒ no. of electrons in antibonding molecular orbitals.

Table 2.4

B.O.	*Significance*
0	molecule is unstable and does not exist.
–ve	unstable and does not exist.
+ve	*stable and exists.

*Greater the value of B.O. greater is the stability of the molecule.

- *Rules for filling up of molecular orbitals with electrons:*

(*i*) The molecular orbitals are filled in the increasing order of their energies. Thus molecular orbital posses3ing the lowest energy will be filled first and that possessing the highest energy will be filled up in the last.

(*ii*) The maximum number of electrons that can fill a molecular orbital is two.

(*iii*) According to Hund's rule of maximum multiplicity, if there are two molecular orbitals having the same energy (*i.e.,* degenerate molecular orbitals), the electrons will first fill them singly and when both of them have been filled singly, pairing of electrons will occur. Thus $\pi_y 2p$ and $\pi_z 2p$ bonding molecular orbitals which are degenerate are first singly filled and pairing takes place only when more electrons are to be accommodated. In a similar fashion $\pi_y{}^*2p$ and $\pi_z{}^*2p$ antibonding degenerate molecular orbitals are filled just like degenerate bonding orbitals.

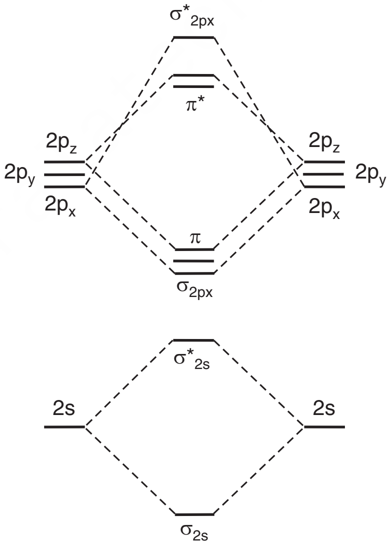


Fig. 2.26 Molecular orbital diagram from 2*s* and 2*p* atomic orbitals.

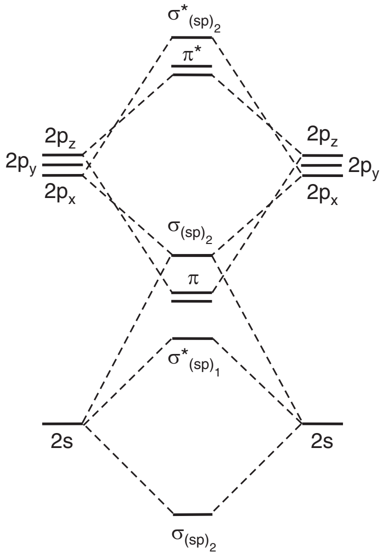


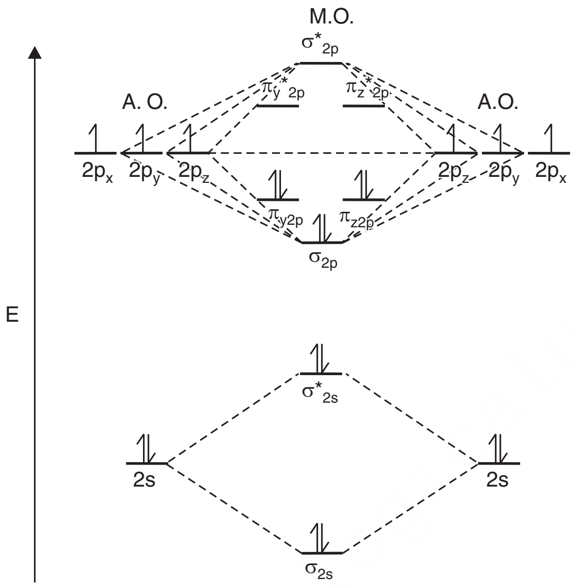
Fig. 2.27 Molecular orbital diagram allowing *s-p* interaction.

- *Energy level diagram for N_2 molecule:*

The electronic configuration of N-atom is $1s^2\ 2s^2\ 2p^3$. In N_2 molecule there will be all total 14 electrons of which 4 will be in the K shells which is denoted by KK.

So, the electronic configuration of N_2 molecule will be

$$KK(\sigma 2s^2)\ (\sigma^* 2s^2)\ (\sigma 2p^2)\ (\pi_y 2p^2)\ (\pi_z 2p^2)\ [KK \text{ denotes } (\sigma 1s^2)\ (\sigma^* 1s^2)]$$



$B.O. = \frac{8-2}{2} = 3$

N_2 molecule has triple bond (N ≡ N)

Fig. 2.28 M.O. diagram for N_2.

- Energy level diagrams of other molecules:

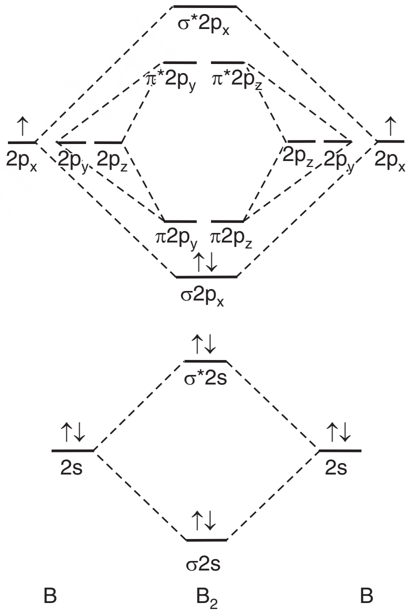


Fig. 2.29 Molecular orbital diagram of B_2 (without s-p interaction).

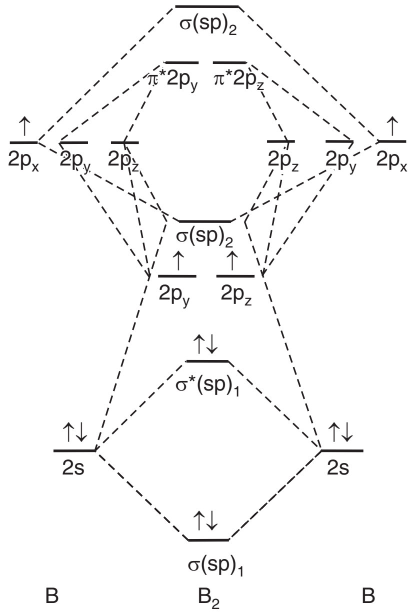


Fig. 2.30 Molecular orbital diagram of B_2 (with s-p interaction).

- Electronic configuration of B_2 molecule:

$$KK(\sigma 2s^2)\ (\sigma^* 2s^2)\ (\sigma 2p^2)$$

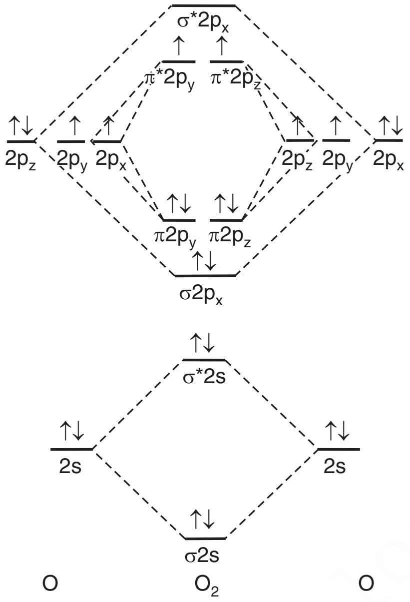


Fig. 2.31 Molecular orbital diagram of O_2 (without s-p interaction).

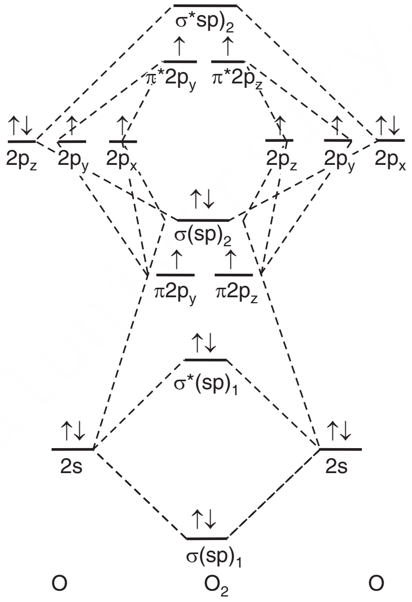


Fig. 2.32 Molecular orbital diagram of O_2 (with s-p interaction).

- Electronic configuration of O_2 molecule:

$$KK(\sigma 2s^2)\ (\sigma^* 2s^2)\ (\sigma 2p^2)\ (\pi_y 2p^2)\ (\pi_z 2p^2)\ (\pi_y^* 2p^1)\ (\pi_z{}^* 2p^1)$$

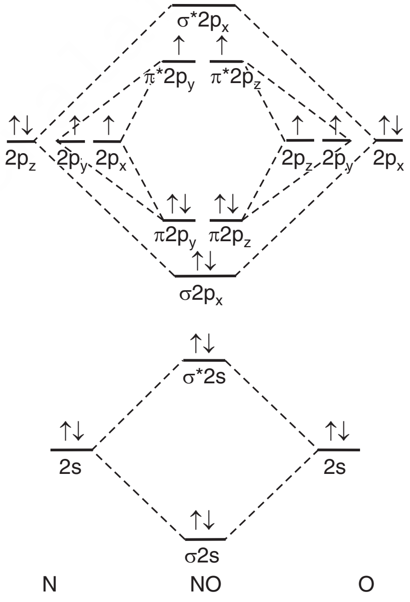


Fig. 2.33 Molecular orbital diagram of NO (without s-p interaction).

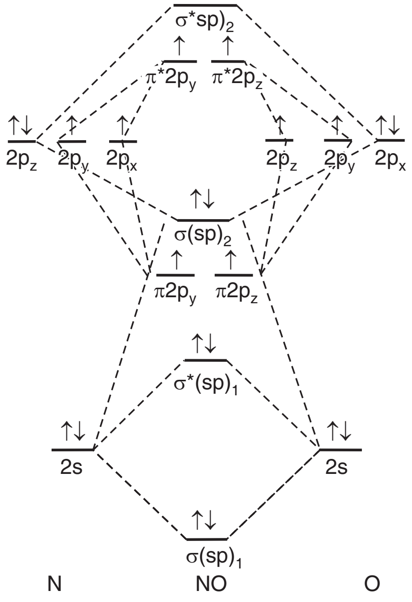


Fig. 2.34 Molecular orbital diagram of NO (with s-p interaction).

[Energy level diagram for heteronuclear diatomic molecule]

Table 2.5: Electron Distribution in Molecular Orbitals of some Simple Molecules shown in above M.O. diagrams

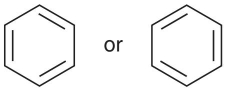
Molecule	$\sigma(sp)_1$	$\sigma^*(sp)_1$	$\pi(2p)$	$\sigma(sp)_2$	$\pi^*(2p)$	$\sigma^*(sp)_2$	*unpaired electrons*
B_2	↑↓	↑↓	↑ ↓				2
C_2	↑↓	↑↓	↑↓ ↑↓				0
N_2	↑↓	↑↓	↑↓ ↑↓	↑↓			0
O_2	↑↓	↑↓	↑↓ ↑↓	↑↓	↑ ↑		2
CO	↑↓	↑↓	↑↓ ↑↓	↑↓			0
NO	↑↓	↑↓	↑↓ ↑↓	↑↓	↑		1

Aromatic Character

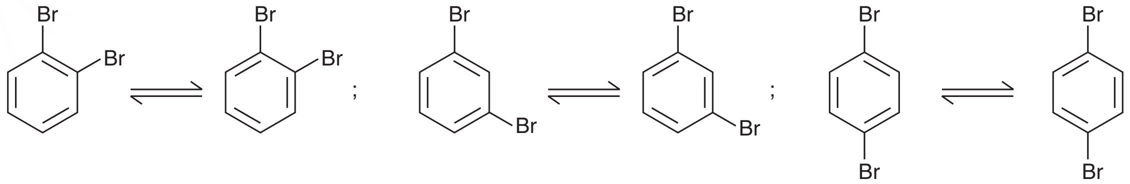
Organic compounds have been classified into two broad subdivisions: (*i*) *aliphatic* and (*ii*) *aromatic.*

The word aliphatic came from ‘fatty’ and the word aromatic came from ‘fragrant’, have no longer their significance. Aliphatic compounds are mainly open chain compounds. They may be cyclic also but they resemble the open chain compounds in their properties. Aromatic compounds a2e benzene or the compounds that resemble benzene in chemical behaviour.

Kekule established the structure of benzene as follows:



According to the Kekule’s structure there should be four isomeric di-substituted benzenes, too:



Kekule’s structure fails to explain certain characteristics of benzene *viz*:

(*i*) Benzene undergoes substitution reaction rather than addition.

(*ii*) Heat of hydrogenation of benzene is lower than that expected.

(*iii*) The C—C bond lengths in benzene are equal and intermediate between a single and a double bond.

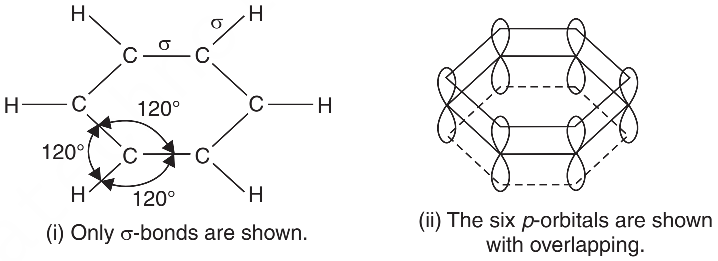
The idea of resonance could explain all the three above anomalies and established the structure of benzene as put forward by Kekule.

Highlights:

- The idea of resonance explains six identical bonds in benzene, which is a new type of bond, a hybrid bond or *benzene bond*, *i.e.,* it is an intermediate in length, (1.39Å) between a single and a double bond.
- Benzene is more stable than expected. Because the resonating Kekule's structures have a resonance hybrid structure, which has 36 Kcal mole^{-1} extra stability.
- As a result of this resonance stabilisation, benzene possesses chemical properties that are not intermediate between compounds containing single or double bond. The 36 Kcal of resonance energy is responsible for a new set of properties, known as *aromatic properties.*
- We see that addition will lead to a less stable product by destroying the resonance stabilized benzene ring system. As for example, hydrogenation of benzene requires 5.6 Kcal mole^{-1} to be converted into cyclohexadiene. So, benzene follow an entirely different path, which is substitution in which the benzene ring system is retained.

Orbital Picture of Benzene

Benzene is a flat molecule, as its six carbon atoms are sp^2 hybridised. If we fit the six sp^2-hybridized carbon atoms, we get a regular hexagon with a bond angle 120°. And there still remains six electrons in the six *p*-orbitals with two equal lobes, one lying above the plane and the other lying below the plane of paper.



(i) Only σ-bonds are shown.

(ii) The six *p*-orbitals are shown with overlapping.

Fig. 2.35

Each *p*-orbital of one C-atom can overlap equally well with the *p*-orbitals of the other two carbon atoms on both the sides. When overlapping is not restricted between two nuclei and it occurs between more than two nuclei, the phenomenon is known as *delocalisation.* And this delocalisation gives extra stability to the molecule resulting in formation of stronger bonds and this stability is accounted by the term *delocalisation energy*. This *delocalisation energy* is frequently used instead of *resonance energy*.

The delocalisation in benzene molecule gives π-clouds above and below of the plane of the ring as shown in the Fig. (2.36).

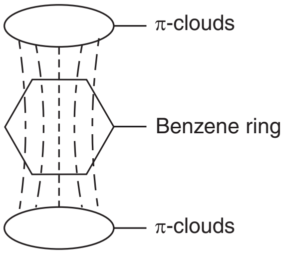


Fig. 2.36 Delocalised π clouds in benzene.

So, necessary and sufficient conditions for aromaticity are:

(*i*) The molecule should be cyclic and flat.

(*ii*) The molecule should contain delocalised π-cloud.

(*iii*) The π-cloud must contain a total of $(4n + 2)$ π electrons where $n = 0, 1, 2, 3$, etc.

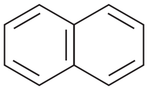
This requirement is called $(4n + 2)$ π rule or Hückle rule.

Benzene has six π-electrons (known as aromatic sextet). Here Hückle number corresponds to $n = 1$. Benzene molecule is flat. In that sense benzene is an ideal aromatic compound and forms the foundation stone of aromatic chemistry.

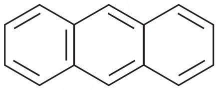
Highlights:

- Benzenoid aromatic compounds: naphthalene ($n = 2$), anthracene ($n = 3$), phenanthrene ($n = 3$)
- Heterocyclic compounds: pyrrole ($n = 2$), pyridine ($n = 2$) etc.
- Non-benzenoid aromatic compounds: cyclopentadienyl anion, tropylium ion.

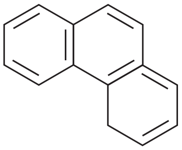
Benzenoid aromatic compounds:



naphthalene
10 π electrons

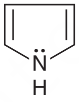


antenacene (Anthracene)
14 π electrons

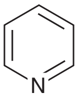


phenanthrene
14 π electrons

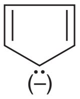
Non-benzenoid aromatic compounds:



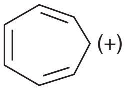
pyrrole
6 π electrons



pyridine
6 π electrons



cyclopentadienyl anion
6 π electrons



tropylium ion
6 π electrons

SHORT QUESTIONS AND ANSWERS

Q. 1. *What is a molecule?*

Ans. When a group of atoms of same and different elements stay together with a definite combination (of atoms), possessing properties entirely different from constituent atoms is known as a molecule.

Q. 2. *What is a chemical bond?*

Ans. It refers to the bonding force that holds together the constituent atoms in a molecule.

Q. 3. *Mention the types of bonds.*

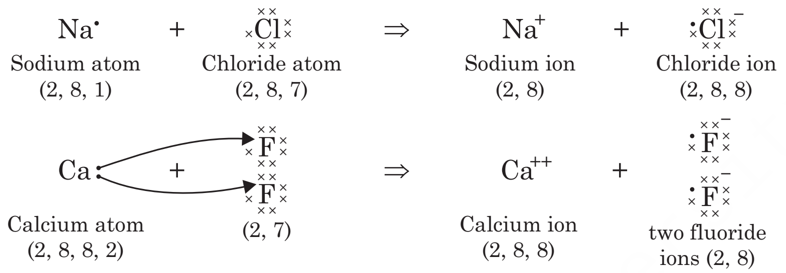
Ans. Most important types are: (*i*) Electrovalent, (*ii*) Covalent and (*iii*) Co-ordinate bonds.

Q. 4. *What is the special feature of an electrovalent bond or ionic bond?*

Ans. Such a bond is formed by complete transfer of electrons from one atom to the other. Such electron transfer occurs from metals to nonmetals. Thus ions are formed. Ionic bonding is the result of *electrostatic forces of attraction* between the positive metal ions and negative non-metal ions.

Q. 5. *Give dot and cross diagrams for NaCl and CaF_2 molecule formation.*

Ans.



$$Na^{\bullet} + \overset{\times\times}{\underset{\times\times}{{}_{\times}Cl^{\times}_{\times}}} \Rightarrow Na^{+} + \overset{\times\times}{\underset{\times\times}{:Cl^{\times}_{\times}}}{}^{-}$$

$$Ca: + 2F \Rightarrow Ca^{++} + 2\,{:F}^{-}$$

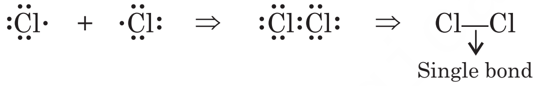
Q. 6. *What is a covalent bond?*

Ans. Covalent bond is formed when two atoms participating in bond formation share equally their electrons to produce a molecule of an element or a compound.

Q. 7. *Give examples of single, double and triple covalent bonds by dot and cross diagrams.*

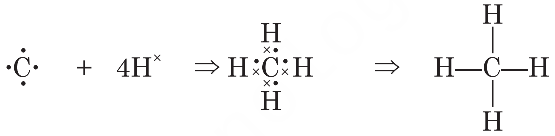
Ans. (*i*) *Single covalent bond.*

(*a*)



$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \Rightarrow :\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}: \Rightarrow Cl\underset{\downarrow}{—}Cl$$

(*b*)



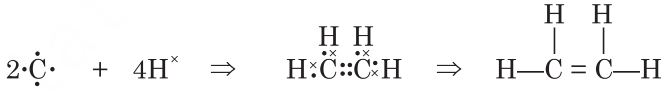
$$\cdot\dot{\underset{\cdot}{C}}\cdot + 4H^{\times} \Rightarrow H\overset{H}{\underset{H}{\dot{\times}C\dot{\times}}}H \Rightarrow H—\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}—H$$

(*ii*) *Double covalent bond.*

(*a*)

$$\ddot{\underset{\cdot\cdot}{O}}: + :\ddot{\underset{\cdot\cdot}{O}} \Rightarrow \ddot{\underset{\cdot\cdot}{O}}::\ddot{\underset{\cdot\cdot}{O}} \Rightarrow O\underset{\downarrow}{=}O$$

(*b*)



$$2\cdot\dot{\underset{\cdot}{C}}\cdot + 4H^{\times} \Rightarrow H\dot{\times}\overset{H}{C}::\overset{H}{C}\dot{\times}H \Rightarrow H—\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}—H$$

(*iii*) *Triple covalent bond.*

(*a*)

$$\ddot{\underset{\cdot\cdot}{N}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{N}} \Rightarrow \ddot{N}\vdots\vdots\ddot{N} \Rightarrow N\underset{\downarrow}{\equiv}N$$

(*b*)

$$2\cdot\dot{\underset{\cdot}{C}}\cdot + 2H^{\times} \Rightarrow H\dot{\times}C\vdots\vdots C\dot{\times}H \Rightarrow H—C\equiv C—H$$

Q. 8. *How are the atoms held together in a covalent bond?*

Ans. The atoms held together by the attraction between the positive charges of the nuclei of the atoms participating in the bond formation and the negative charges of the shared electrons by the atoms.

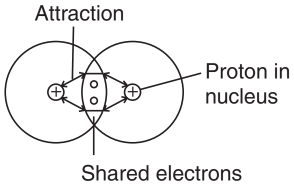


Fig. 2.37 (*a*) Forces of attraction during H_2 molecule formation.

Q. 9. *What are polar and non-polar covalent bonds?*

Ans. A *nonpolar bond* is formed when sharing takes place between the atoms of same electronegativity *i.e.,* between similar atoms during bond formation. *e.g.,*

$$H—H, O = O, Cl—Cl, Br—Br, \text{etc.}$$

A *polar bond* is formed when sharing takes place between the atoms of different electronegativities *i.e.,* between dissimilar atoms during bond formation *viz.,*

$$H^{+\delta} \longrightarrow Cl^{-\delta}$$

Q. 10. *What is the special feature of a covalent bond?*

Ans. (*a*) Covalent bond holds together the atoms of nonmetals in a molecule and giant structures. (*b*) Molecules have a definite shape because covalent bonds have a definite length and direction.

Q. 11. *What is covalent radius?*

Ans. The covalent radius of an element is half the bond length. When two atoms of the element (same or different) are joined by a single covalent bond, the length of single covalent bonds between atoms of different elements can be determined fairly accurately by adding the covalent radii of the two atoms. Covalent radius of an atom is half of the distance between the nuclei of two like atoms bonded together by a single covalent bond.

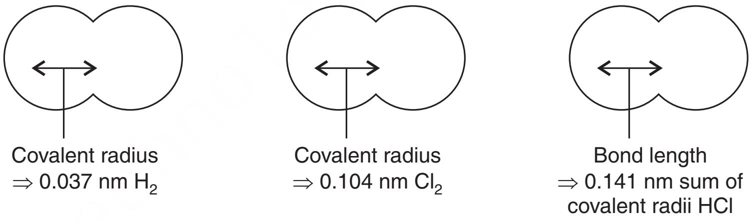


Fig. 2.37 (*b*) Forces of attraction during H_2 molecule formation.

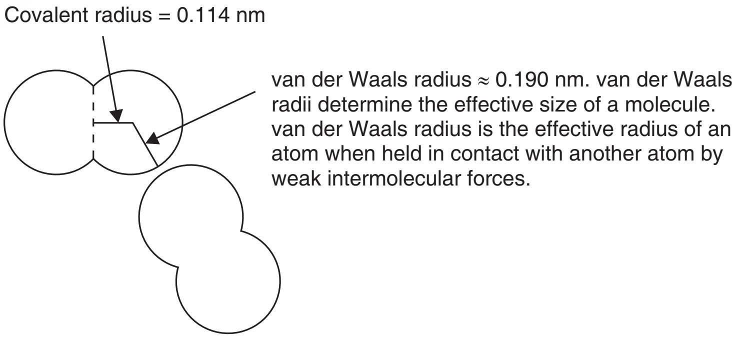


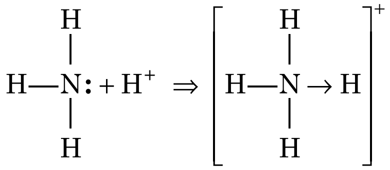
Fig. 2.37 (*c*) Covalent and van der Waals radii for bromine.

Q. 12. *Mention special types of bonds.*

Ans. (*i*) Metallic bond, (*ii*) van der Waals bond, (*iii*) Hydrogen bond.

Q. 13. *What is the special feature of a coordinate bond?*

Ans. This type of bond is formed by unequal sharing of electron pair, one of the participating atoms in the bond formation donates both the electrons for bond formation. The coordinate bond is indicated by an arrow to express this unequal sharing.



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{N}}{:}} + \mathrm{H^+} \Rightarrow \left[\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{N}} \rightarrow H}\right]^+$$

Q. 14. *What is a sigma bond?*

Ans. This type of bond is formed by axial overlapping of *s-s*, *p-p* or *sp* orbitals and also sp^3-*s*, sp^2-*s*, *sp-s*, sp^3-*p*, sp^2-*p* etc. of different atoms whereby maximum overlapping of orbitals is possible.

Q. 15. *What is a π-bond?*

Ans. π-bond is formed by sideway overlapping of mainly *p*-orbitals of different atoms.

Q. 16. *What are special features of single, double and triple bonds?*

Ans. A single bond is always a σ-bond. A double bond contains one σ and one π bond and a triple bond contains one σ and two π bonds.

Q. 17. *What do you mean by dipole moment?*

Ans. The dipole moment in a molecule develops due to the separation of positive and negative charges by a distance; as the centre of action of positive charge due to nuclei and centre of action of negative charge due to electrons do not coincide. Mathematically dipole moment is expressed as:

$$\mu = e \times d$$

where, μ = dipole moment,

e = magnitude of charge separated in esu,

d = distance in cm.

Q. 18. *What do you mean by bond energy?*

Ans. Bond energy (or enthalpy) is the mean value of bond dissociation energies (or enthalpies) (D) used for approximate calculation estimating the enthalpy changes for the reaction. Bond dissociation energy is the energy (or enthalpy) for breaking one mole of a covalent bond in a gaseous molecule. Energy is needed to break covalent bonds.

Bond breaking is endothermic, so enthalpy change is always positive.

$$\mathrm{HCl}\,(g) \quad \Rightarrow \quad \mathrm{H}(g) + \mathrm{Cl}(g) \quad \Delta\mathrm{H} \quad \Rightarrow \quad +\,432 \text{ kJ mol}^{-1}.$$

Q. 19. *In water molecule, are the two bond dissociation energies same?*

Ans. In H—O—H (*g*) molecule, the energy needed to break the first O—H bond is 498 kJ mol^{-1}, the energy needed to break the second O—H bond is 428 kJ mol^{-1}. So the bond dissociation energies of two or more bonds between similar atoms are not the same.

Q. 20. *Calculate the C–H bond energy in CH_4 molecule.*

Ans.

$$\begin{array}{lclcl}
\mathrm{CH_4} & \rightarrow & \mathrm{CH_3 + H^\circ} & \mathrm{D} \Rightarrow & 102 \text{ Kcal mol}^{-1} \\
\mathrm{CH_3} & \rightarrow & \mathrm{CH_2 + H^\circ} & \mathrm{D} \Rightarrow & 105 \text{ Kcal mol}^{-1} \\
\mathrm{CH_2} & \rightarrow & \mathrm{CH + H^\circ} & \mathrm{D} \Rightarrow & 108 \text{ Kcal mol}^{-1} \\
\mathrm{CH} & \rightarrow & \mathrm{C + H^\circ} & \mathrm{D} \Rightarrow & 83 \text{ Kcal mol}^{-1} \\
\hline
 & & & \text{Total D} \Rightarrow & 398 \text{ Kcal mol}^{-1}
\end{array}$$

C—H bond energy in CH_4 is mean value of D values *i.e.,*

$$E(C—H) \;\Rightarrow\; \frac{398}{4} = 99.5 \text{ Kcal mole}^{-1}.$$

Q. 21. *What do you mean by bond length?*

Ans. Bond length is the distance between the nuclei of atoms bonded by one or more covalent bonds. For the same two atoms triple bonds are shorter than double bonds which, in turn, are shorter than single bonds.

$$\underset{\substack{\downarrow \\ 0.157\text{nm}}}{C-C} \qquad \underset{\substack{\downarrow \\ 0.134\text{nm}}}{C=C} \qquad \underset{\substack{\downarrow \\ 0.120\text{nm}}}{C\equiv C}\,.$$

Q. 22. *What do you mean by electronegativity?*

Ans. The pulling power of an atom of the bonding electrons towards itself when linked by a covalent bond with another atom is known as electronegativity. The stronger the pulling power of an atom, the higher its electronegativity. The bigger the difference in the electronegativity of the elements forming a bond, the more polar the bond.

$$H^{+\delta}\underset{\substack{\downarrow \\ \text{polar bond.}}}{—}Cl^{-\delta}$$

Q. 23. *When does a bonding in a covalent compound become fully ionic?*

Ans. The bonding in a compound becomes ionic if the difference in electronegativity of the two bonded atoms becomes so large that the more electronegative atom can remove completely the electron from the other atom. This happens in compounds like NaCl, MgO, CaF_2 etc.

Q. 24. *Give the conception of a bonding molecular orbital.*

Ans. The bonding molecular orbital is a region in space where the probability of finding the bonding electrons is maximum. Molecular orbitals are the solutions to the Schrödinger wave equation like atomic orbitals. In a simplified form, it may be stated that molecular orbitals (M.O.) are obtained by the overlapping of atomic orbitals of the atoms linked by a covalent bond.

Bonding M.O. (ϕ_B) is obtained when ++ regions of both the atomic orbitals (A.O.) overlap along the internuclear axis (see Figs. 2.21 and 2.23) *i.e.,* M.O. is produced by addition of two atomic orbitals ($\phi_B = \psi_A + \psi_B$).

Q. 25. *Give the concept for antibonding molecular orbitals.*

Ans. Antibonding orbitals (ϕ_A) are also solutions to the Schrödinger wave equation like the bonding molecular orbitals. But in this case, ϕ_A results from subtraction of the two atomic orbitals ($\phi_A = \psi_A - \psi_B$) *i.e.,* by the overlapping of + – regions of the atomic orbitals (see Figs. 2.21 and 2.23).

Q. 26. *Interpret the idea of bond order.*

Ans. Bond order (B.O.) is given by the expression,

$$\text{B.O.} = \frac{N_b - N_a}{2}$$

where, $N_b \Rightarrow$ number of bonding electrons.

$N_a \Rightarrow$ number of antibonding electrons.

Higher the bond order, stabler is the molecule. Bond order zero and negative indicates that molecule does not form or exist.

Q. 27. *What is hybridisation of atomic orbitals?*

Ans. The intermixing the atomic orbitals of slightly different energies so as to redistribute their energies and to give a new set of orbitals (known as hybrid orbitals) of equivalent energies and shape is known as hybridisation.

Q. 28. *Mention the types of hybridisation.*

Ans. (*i*) sp^3, (*ii*) sp^2, (*iii*) sp, (*iv*) dsp^2, (*v*) sp^3d, (*vi*) d^2sp^3.

Q. 29. *What do you mean by hybrid orbitals?*

Ans. Hybrid orbitals are formed from the mixing of atomic orbitals of different types and are oriented in space in a characteristic manner determined by the type of hybridisation.

Q. 30. *Calculate the bond orders of: (i) H_2O, (ii) H_2^+, (iii) He_2^+, (iv) He_2 and interpret the result.*

Ans. (*i*) $$\text{B.O.} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

H-atoms are held together by one covalent bond.

(*ii*) $$\text{B.O.} = \frac{1-0}{2} = \frac{1}{2}$$

H_2^+ has a transient existence. Here the number of bonding electrons exceeds the number of electrons in antibonding orbital.

(*iii*) $$\text{B.O.} = \frac{2-1}{2} = \frac{1}{2}$$

He_2^+ also has transient existence. Here, the number of electrons in s-orbital is greater than the number of electrons in s*-orbital.

(*iv*) $$\text{B.O.} = \frac{2-2}{2} = 0$$

Here the number of electrons in σ-orbital = the number of electrons in σ*-orbital. The molecule does not exist. So He is monoatomic.

Q. 31. *O_2 molecule is paramagnetic. Explain.*

Ans. The electronic configuration of:

$$\text{O-atom} \Rightarrow 1s^2\ 2s^2\ 2p^4$$

The electronic configuration of:

$$O_2\text{-molecule} \Rightarrow KK(\sigma 2s^2)(\sigma^* 2s^2)(\sigma 2p^2)(\pi_y 2p^2)(\pi_z 2p^2)(\pi_y{}^* 2p^1)(\pi_z{}^* 2p^1)$$

$$\text{B.O.} \Rightarrow \frac{N_b - N_a}{2} \Rightarrow \frac{8-4}{2} = 2$$

So, O_2 molecule contains double bond (O = O), one is σ and the other is π-bond. According to Hund's rule two unpaired electrons fill the degenerate (orbitals of same energy) $\pi_y{}^*2p$ and $\pi_z{}^*2p$ orbitals (see Figs. 2.31 and 2.32). That is why, O_2 molecule is paramagnetic.

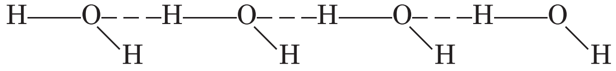
Q. 32. *Explain why HF is liquid, HCl is gas and HF is less acidic than HCl.*

Ans. $\overset{+\delta}{H}-F^{-\delta} \ldots \overset{+\delta}{H}-F^{-\delta} \ldots \overset{+\delta}{H}-F^{-\delta} \ldots \overset{+\delta}{H}-F^{-\delta}$

Due to hydrogen bonding, there is molecular association in HF and effective molecular weight of HF is high and that is why its volatility is less and it is liquid whereas in HCl molecule there is no hydrogen bonding because Cl is less electronegative than F and atomic radius of Cl is greater than that of F. Hydrogen bond in HF inhibits release of H^+ partially in aqueous solution, so it is less acidic.

Q. 33. *Explain H_2O is a liquid and H_2S is a gas.*

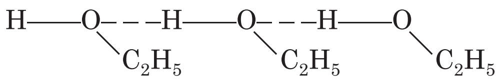
Ans.



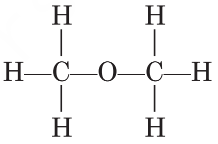
The reason is same as in Q no. 31 above.

Q. 34. *Explain, ethyl alcohol is less volatile than dimethyl ether though both have the same mol. formula, C_2H_6O.*

Ans.



H-bonding in ethyl alcohol.



Dimethyl ether

There is H-bonding in ethyl alcohol and due to molecular association H is attached to O-atom in every molecule of ethyl alcohol. But there is no H-bonding in dimethyl ether molecule as H here is not attached to O-atom. So, there is no molecular association due to H-bonding in dimethyl ether, so it is more volatile than ethyl alcohol.

Q. 35. *The density of water is greater than that of ice. Explain.*

Ans. In H_2O molecule, every oxygen atom is connected to two hydrogen atoms as covalent bonds. And each oxygen atom contains two lone pairs. These electrons can form hydrogen bonds. By X-ray crystallography, it has been established that in a crystal of ice, a molecule of water is surrounded by four water molecules and every molecule of water form hydrogen bonds giving a tetrahedral structure. So a crystal of ice is not a single molecule but an associated molecule. Due to tetrahedral structure, there is some void space in ice. When ice melts, this tetrahedral structure is destroyed. And the water molecules are hydrogen bonded in a chain. Due to loss of this void space, when ice melts its volume reduces and density increases.

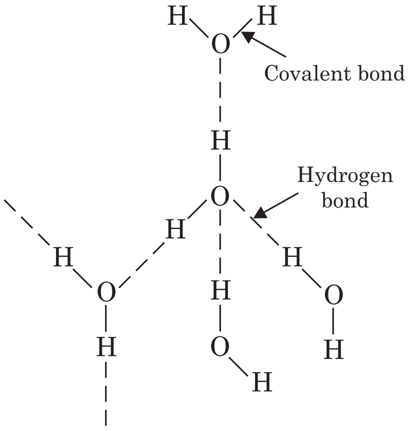


Fig. 2.38 H-bonding in ice.

EXERCISES

1. What is hybridisation? Give different types of hybridisations with examples.
2. Explain *sp*, sp^2 and sp^3 hybridisations with examples.
3. Write a note on co-ordinate bond.
4. Give the state of hybridisation, bond angle and shape of the following molecules:
   (*i*) BeF_2, (*ii*) BF_3, (*iii*) $CH_2 = CH_2$, (*iv*) $CH \equiv CH$, (*v*) NH_3, (*vi*) H_2O.
5. (*a*) Explain the structure of benzene. (*b*) Give a concise account of delocalisation of benzene.
6. Discuss hydrogen bonding and explain why density of ice is less than that of water.
7. Write a short note on ionic bonding.
8. Explain the bond order of N_2 molecule.

9. Explain inter and intramolecular hydrogen bonding with examples.

10. (*a*) Explain hydrogen bonding. (*b*) Give the characteristics of covalent bond. (*c*) Explain sp^3-hybridisation.

11. What is VSEPR theory of molecular model? Explain with suitable examples.

12. What is dipole moment? How is dipole moment of a molecule calculated?

13. Discuss Born Haber cycle with an example.

14. Write short notes on: (*a*) Intermolecular forces, (*b*) Molecular orbital theory, (*c*) Resonance, (*d*) Hund's rule, (*e*) Delocalization, (*f*) Aromaticity.

15. Two elements having the atomic numbers 11 and 17, respectively, combine to form a compound. State the nature and formula of the compound so formed. Give its name also.

16. Give the molecular orbital diagrams of H_2 and O_2 molecules.

3

Nuclear Chemistry

Nuclear Chemistry is the branch of chemistry that deals with the changes in the nuclei. It is quite obvious that the conventional energy sources, such as coal, petroleum will be exhausted in near future. So scientists are searching for non-conventional energy sources such as–solar energy, nuclear energy etc. The idea of exploiting nuclear energy came after the discovery of radioactivity. So we are to discuss, in brief, the idea of radioactivity before going to discuss the source of nuclear energy which is the main feature of nuclear chemistry.

RADIOACTIVITY

Becquerel in 1896 observed that uranium or its compounds emit a kind of rays spontaneously. These rays can affect photographic plate. He named this phenomenon of emission of spontaneous radiation by uranium as *radioactivity*. The atoms of some of the elements were found to exhibit radioactivity, such as—radium, thorium, polonium etc. As compounds of those elements exhibit radioactivity, so it can be said that radioactivity is a nuclear phenomenon. Radioactive elements emit the radiation and create new elements. Radioactivity is an *irreversible process* and emits more heat than that of any of the chemical processes (10^9 cal mol^{-1}). The rays emitted are classified as alpha [$^4_2He^{++}$], beta (uninegative charge), and gamma (neutral). A comparative study of the rays emitted during radioactive disintegration is displayed in the following table.

Table 3.1: Comparison among α, β, and γ Rays

Property	*α-Rays*	*β-Rays*	*γ-Rays*
(*i*) **Nature**	(*i*) Streams of positively charged particles which are merely nuclei of He atoms, each consisting of 2 protons and 2 neutrons.	(*i*) Streams of fast moving negatively charged particles which have the same *e*/*m* value as the cathode rays.	(*i*) It is similar to X-rays and neutral in nature. They have very small wavelengths of the order of 10^{-10} to 10^{-13} m.
(*ii*) **Representation**	(*ii*) $[_2He^4]^{+2}$ or α	(*ii*) $_{-1}e^\circ$ or $_{-1}\beta^\circ$ or β.	(*ii*) γ

(*Contd.*)

(*iii*) **Mass**	(*iii*) 4 a.m.u.	(*iii*) $\frac{1}{1836}$ of hydrogen atoms or 0.000548 a.m.u.	(*iii*) No mass (0)
(*iv*) **Charge**	(*iv*) Possess positive charge of 2 units $= 9.6 \times 10^{-10}$ e.s.u. or 3.2×10^{-19} coulomb.	(*iv*) Possess negative charge of 1 unit $= 4.8 \times 10^{-10}$ e.s.u. or 1.6×10^{-19} coulomb.	(*iv*) No charge (0)
(*v*) **Velocity**	(*v*) Nearly 1/10 the speed of light or 20,000 to 30,000 km per sec.	(*v*) 2.36×10^8 to 2.83×10^8 m/sec.	(*v*) Nearly same as light 3×10^8 m/sec.
(*vi*) **Penetrating power**	(*vi*) Low	(*vi*) Medium	(*vi*) Maximum

It has been observed that heavier elements in which neutron-proton ratio (N/p) exceed 1.5 show radioactivity. These nuclei are unstable and emit spontaneously α, β, or γ-rays to give *daughter elements.*

Nuclear Stability

1. Nuclei with 84 or more protons are radioactive.
2. Nuclei containing 2, 8, 20, 50, 82 and 126 protons or neutrons are more stable than other nuclei containing different number of protons and neutrons. These numbers are magic numbers.
3. Nuclei with even numbers of protons and neutrons are more stable than that with odd numbers.

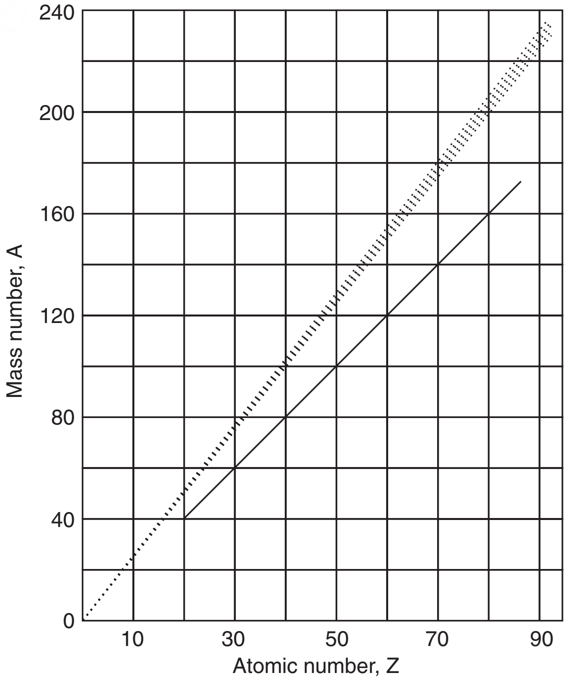


Fig. 3.1

The graph (Fig. 3.1) is a plot of proton number (Z) vs mass number (A). The graph is more or less linear. When the value of Z is less, then the ratio A/Z for a nucleus is 2 *i.e.,* light elements possess equal number of protons and neutrons and the nucleus is stable; when the proton number of the nucleus exceeds 20 the nucleus shows the tendency to be unstable and when the proton number (Z) exceeds 83 the nucleus becomes more or less unstable. As the difference of Z and A increases the nucleus becomes totally unstable. So it can be said that radioactivity is a phenomenon to stabilize the nucleus by decreasing the ratio A/Z of the nucleus.

Radioactive Decay

The radioactive decay follows an exponential law. At any instant of time, the rate of disintegration is proportional to the number of atoms (N) present, *i.e.,*

$$-\frac{dN}{dt} \propto N \quad \text{or} \quad -\frac{dN}{dt} = \lambda N \quad \text{or} \quad \lambda = -\frac{dN/dt}{N}$$

where λ = disintegration constant may be defined as the ratio of the amount of the substance which disintegrates in a unit time to the amount of substance present.

The 'negative sign' indicates that with passage of time '*t*' the number of atoms decreases.

So, $$\frac{dN}{N} = -\lambda dt$$

Integrating we have, $\log_e N = -\lambda t + C$ [C = integration constant]

If 'N_0' be the number of atoms present initially, *i.e.,* when $t = 0$

then $$\log_e N_0 = C$$

$\therefore$ $$\log_e N = -\lambda t + \log_e N_0$$

or $$\log_e \frac{N}{N_0} = -\lambda t$$

$\therefore$ $$\boxed{N = N_0 . e^{-\lambda t}}$$

When M_0 = original mass and M = mass at time *t*, the equation is

$$\boxed{M = M_0 . e^{-\lambda t}}$$

Hence, the decay curve is exponential in nature (Fig. 3.2).

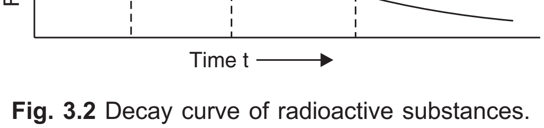


Fig. 3.2 Decay curve of radioactive substances.

If T is the half-life of the radioactive element, then we can write,

$$\frac{N}{N_0} = \frac{1}{2} = e^{-\lambda T}$$

$$\therefore \qquad T = \frac{\log e^2}{\lambda} = \frac{0.693}{\lambda}.$$

The above equation is a relation between half life (T) of a radioactive element and its disintegration constant (λ).

Half-Life

Half-life of a radioactive element is the time required for half of the atoms to decay away. Half-lives for radioactive isotopes can be as short as a fraction of a second or as long as millions of years.

Units of Radioactivity

The unit of radioactivity is '*curie*'. The curie is defined as that quantity of any radioactive substance which gives 3.7×10^{10} disintegrations per second. The curie is a very large unit. Hence for all practical purposes millicurie [$1 \text{ mCi} = 10^{-3} \text{ Ci}$] and the microcurie [$1 \mu\text{Ci} = 10^{-6} \text{ Ci}$] are used.

Radioactive Disintegration Series

Number of naturally occurring radio isotopes is about forty. Naturally occurring radioactive disintegration series are shown below. The series are $4n$ or Thorium series; $4n + 2$ or Uranium series and $4n + 3$ or Actinium series. The term $4n$ means mass number is divisible by 4; whereas $4n + 2$ and $4n + 3$ means mass number when divided by 4 gives a remainder of 2 and 3, respectively.

In the $4n$ series **starting element is $^{232}_{90}\text{Th}$** and through a chain of successive disintegration it produces **ultimately $^{208}_{82}\text{Pb}$.**

Starting element of ($4n + 2$) series is $^{238}_{92}\text{U}$ and end product is $^{206}_{82}\text{Pb}$.

For ($4n + 3$) series starting element is $^{235}_{92}\text{U}$ and end product is $^{207}_{82}\text{Pb}$.

An artificially made disintegration series is Neptunium series ($4n + 1$). It starts with $^{237}_{93}\text{Np}$ and ends at $^{200}_{82}\text{Bi}$.

Details of disintegration chart of ($4n + 2$) series is given below:

$$^{238}_{92}\text{U} \xrightarrow{\alpha} {}^{234}_{90}\text{Th} \xrightarrow{\beta} {}^{234}_{91}\text{Pa} \xrightarrow{\beta} {}^{234}_{92}\text{U} \xrightarrow{\alpha} {}^{230}_{90}\text{Th} \xrightarrow{\alpha}$$

$$^{226}_{88}\text{Ra} \xrightarrow{\alpha} {}^{222}_{86}\text{Rn} \xrightarrow{\alpha} {}^{218}_{84}\text{Po} \xrightarrow{\alpha} {}^{214}_{82}\text{Pb} \xrightarrow{\beta} {}^{214}_{83}\text{Bi} \xrightarrow{\beta}$$

$$^{214}_{84}\text{Po} \xrightarrow{\alpha} {}^{210}_{82}\text{Pb} \xrightarrow{\beta} {}^{210}_{83}\text{Bi} \xrightarrow{\beta} {}^{210}_{84}\text{Po} \xrightarrow{\alpha} {}^{206}_{82}\text{Pb} \text{ (Stable Lead)}$$

Group displacement (Radioactive displacement) law:

When an α-particle is emitted the new element formed is shifted two columns back (left side) of the original element, in the periodic table *i.e.,* atomic number of the daughter element decreases by two units. When a β-particle is emitted the daughter element formed shifts to one column forward (right side) in the periodic table *i.e.,* atomic number of daughter element is increased by one unit.

Artificial Radioactivity

If an atom of a non-radioactive element is bombarded by a powerful particle, it is converted to a radioactive atom, *e.g.* if we bombard $^{27}_{13}\text{Al}$ with an alpha (α) particle, we get radioactive phosphorus which is ultimately converted to silicon.

$$^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}n$$

$$^{30}_{15}\text{P} \longrightarrow {}^{30}_{19}\text{Si} + {}^{0}_{1}e.$$

This phenomenon is known as *Artificial Radioactivity*.

Atomic Mass Unit

Masses of atoms are usually expressed in atomic mass units (a.m.u.).

$$1 \text{ a.m.u.} = \frac{1}{12} \times {}^{12}_{6}\text{C}$$

So, $$1 \text{ a.m.u.} = \frac{1}{12} \times \frac{12}{\text{N}} \text{ g} = \frac{1}{\text{N}} \text{ g}$$

where N (Avogadro number) = 6.023×10^{23}

$$1 \text{ a.m.u.} = \frac{1}{6.023 \times 10^{23}} = 1.66 \times 10^{-24} \text{ g}.$$

Mass–Energy Equivalence

In 1905, Einstein established from theoretical standpoint that mass and energy are mutually convertible. The famous equation in this regard is

$$\text{E} = mc^2$$

where E = energy ; c = velocity of light.

The year 2005 has been declared as *year of physics* to observe the centenary of this famous equation.

Highlight:

$$\begin{aligned} \text{E} &= mc^2 \\ &= 1 \times (3 \times 10^{10})^2 \text{ g cm}^2 \text{ sec}^{-2} \\ &= 9 \times 10^{20} \text{ g cm}^2 \text{ sec}^{-2} \\ &= 9 \times 10^{20} \text{ ergs} \\ &= 9 \times 10^{13} \text{ joules.} \end{aligned}$$

So, 1 g of matter is equivalent to 9×10^{13} J of energy.

Mass-Energy conversion factor

We know that, $1 \text{ eV} = 1.6 \times 10^{-12}$ ergs.

So, $1 \text{ MeV} = 1.6 \times 10^{-6}$ ergs

and $1 \text{ a.m.u.} = 1.66 \times 10^{-24}$ g.

$$\therefore \quad 1 \text{ a.m.u.} = \frac{1.6 \times 9 \times 10^{20}}{1.6 \times 10^{-6}} \approx 931 \text{ MeV}.$$

Nuclear Fission

In 1939, German scientists Hahn and Strasman bombarded uranium atom with neutrons and obtained two elements with atomic numbers 56 and 36.

$$^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{266}_{92}\text{U} \longrightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3{}^{1}_{0}n.$$

This phenomenon of splitting a nucleus into two approximately equal fragments is called *nuclear fission* or *simply fission*. The generated neutrons again can bombard another ^{335}U atoms and another fissions can occur and this phenomenon will occur in chain within 10^{-8} sec. This process of repeated fission is known as *chain reaction* (Fig. 3.3) and as a result it can generate a huge amount of energy, 1 g of U-235 will generate 2×10^7 kcal, and this amount of energy will be generated within 10^{-6} second. So, the generation of huge amount of energy leads to an explosion with a temperature of one crore degree. This nuclear fission reaction is the principle of an atom bomb.

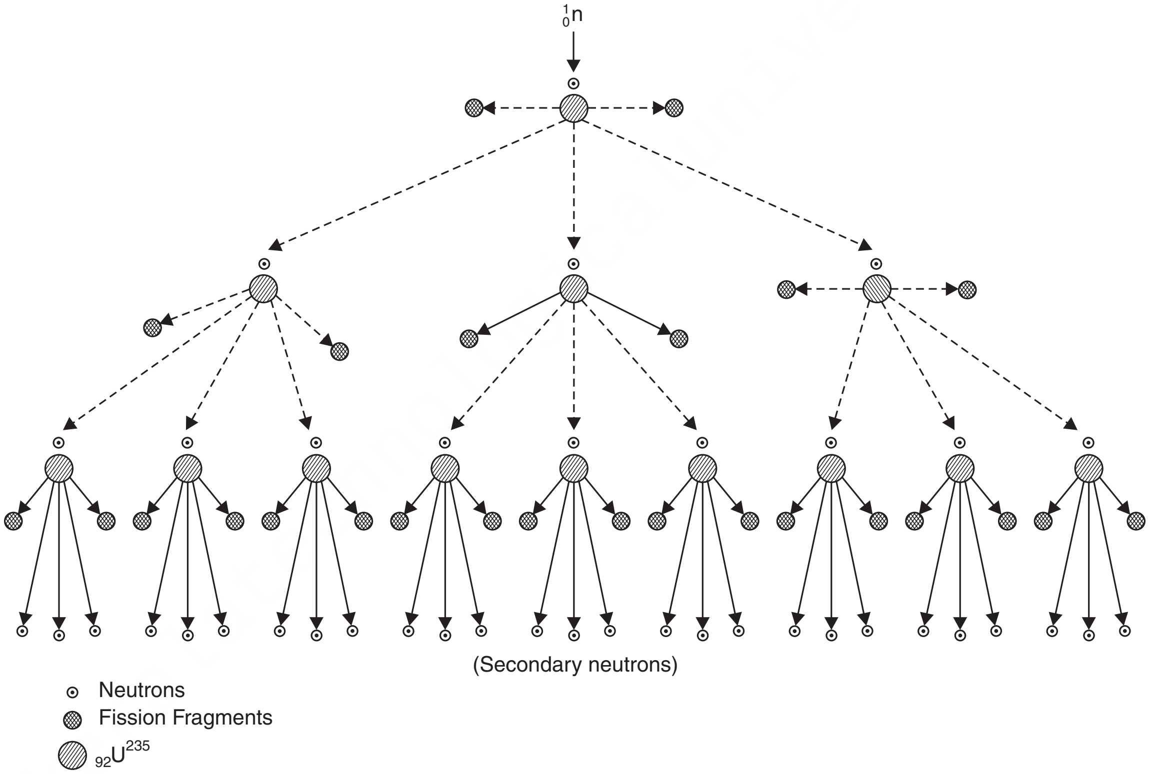


Fig. 3.3 Chain reaction as a result of bombardment of $_{92}$U^{235} with one neutron and perfission three secondary neutrons are released.

Energy Released in a Fission Reaction

It has been estimated that the mass generated after fission is not equal to the total weight of uranium fissioned and bombarding neutrons. A small fraction of mass is lost and is converted to energy according to the equation: E = mc^2.

For the reaction,

$$^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3{}^{1}_{0}n.$$

Initial masses			*Final masses*		
$^{235}_{92}$U	⇒	235.0439 a.m.u.	$^{141}_{56}$Ba	⇒	140.9139 a.m.u.
$^{1}_{0}n$	⇒	1.0087 a.m.u.	$^{92}_{36}$Kr	⇒	91.8973 a.m.u.
		236.0526 a.m.u.	$3{}^{1}_{0}n$	⇒	3.0261 a.m.u.
					235.8373 a.m.u.

So, the mass lost is 0.2153 a.m.u., which is equivalent to an energy of 0.2153 × 931 ≈ 200 MeV.

Highlight:

It can be shown that when 1 kg of uranium is completely fissioned, the energy released would be 8.2×10^{13} J, which is sufficient to supply energy at the rate of 2.2 megawatt continuously for one year.

To utilise the energy released during the fission, we are to control the chain reaction to get the heat energy according to necessity. Now-a-days, in an atomic reactor, the motion of neutrons are retarded by graphite or heavy water to control the chain reaction. So, fission reaction is retarded and thereby controlled and the heat generated is being absorbed by molten Na–K alloy and this heat is utilised in generating steam for thermal power.

Atomic Fusion

At a very high temperature, two nuclei combine to give a comparatively heavy nucleus, *i.e.*, two nuclei combine to give a new atom. This phenomenon is known as *atomic fusion.* And during this fusion reaction some mass is destroyed, that means such a fusion process would also lead to liberation of huge amount of energy which causes explosion.

$$^{2}_{1}\text{H} + ^{2}_{1}\text{H} \longrightarrow ^{4}_{2}\text{He} + \text{Energy}$$

$$2 \times 2.0162 \longrightarrow 4.00389$$

$$\therefore \qquad \Delta m = 0.02863 \text{ a.m.u.}$$

which is equivalent to 0.02863 × 931 MeV

$$= 26.6545 \text{ MeV. (Energy released due to above fusion)}$$

The difficulty is to attain the high temperature for such fusion process. But it is believed that such condition is attained for preparing thermonuclear bombs such as *hydrogen bomb.*

The transformations for fusion reactions are:

(*i*) $^{3}_{1}\text{H} + ^{2}_{1}\text{H} \longrightarrow ^{4}_{2}\text{He} + ^{1}_{0}n + 17 \text{ MeV}$

(*ii*) $^{3}_{1}\text{H} + ^{1}_{1}\text{H} \longrightarrow ^{4}_{2}\text{He} + 20 \text{ MeV}$ etc.

Mass Defect and Binding Energy

After the discovery of isotopes, Aston examined the atomic weights of various elements and concluded that the atomic weights of all the elements would be a whole number. But due to the presence of isotopes in unequal amounts, the atomic weights become fractions. Besides that, the atomic weights of the different elements depend upon another factor: in a.m.u. the atomic weights are calculated from number of protons, electrons and neutrons. The calculated mass (M) and actual weight (A) is determined considering the contribution for the presence of isotopes. The difference of these two quantities is called mass defect (Δ) or Δm

$$\therefore \qquad \Delta = \text{M} - \text{A}.$$

For a $^{7}_{3}\text{Li}$ atom, the atomic weight will be

$$3 \times 0.0005486 + 3 \times 1.00758 + 4 \times 1.00893$$

$$= 7.0601058 \text{ a.m.u.}$$

But actual atomic weight of $^{7}_{3}\text{Li}$ is 7.01818 a.m.u. (in ^{16}O scale)

So, mass defect (Δ) = 7.0601058 – 7.01818

$$= 0.0419258 \text{ a.m.u.}$$

When protons and neutrons unite a small fraction of mass is converted to nuclear binding energy, and this is the reason for *mass defect*.

So, the nuclear binding energy will be

$$0.0419258 \times 931 = 39.03 \text{ MeV}.$$

When mass defect is divided by mass number, a fraction is obtained which is known as *packing fraction* (*f*)

$$f = \frac{m - \text{A}}{\text{A}} \times 10^4 = \frac{0.0419258}{4} \times 10^4$$
$$= 104.81$$

Therefore, packing fraction is average mass defect for any particle. The value of packing fraction is very small, so it has been expressed by multiplying 10^4. A small value of packing fraction indicates greater stability of the nucleus, a higher value indicates looseness of packing of protons and neutrons in the nucleus and as such lower stability of the atom (Fig. 3.4).

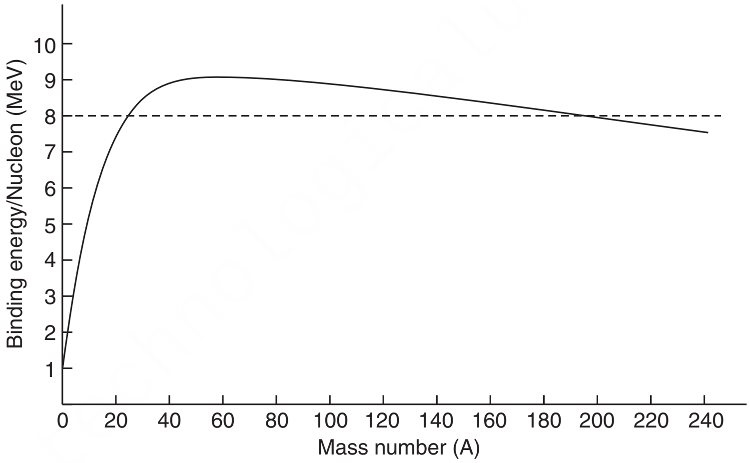


Fig. 3.4 The graph is a plot of binding energy/nucleon vs. mass number (A).

NUCLEAR REACTORS

"A nuclear reactor is an apparatus in which nuclear fission is produced in the form of a controlled self sustaining chain reaction." In other words it is a device where controlled nuclear fission of ^{235}U, ^{233}U or ^{239}Pu and also chain reaction takes place and produces, heat, neutrons and radio-isotopes. Nuclear reactors may be looked upon as a nuclear furnace where fuel is ^{235}U, ^{233}U etc.

The mechanism for heat generation: In the nuclear reactors due to the fission fragments which move at high speed because they take bath in a dense mass of metal, they are rapidly slowed down and brought to rest due to collison with other atom of the metal. In doing so energy is converted to heat.

Nuclear reactors are of various types depending on their neutron spectrum, construction, composition and the purpose for which they are used. The reactors are differentiated by the following features.

- **Neutron energies:**
  (*a*) High energy—as in fast reactors
  (*b*) Intermediate energy
  (*c*) Low energy—as in thermal reactors.

- **Types of fuel:**
  (*a*) Natural uranium (${}^{238}U = 99.28\%$; ${}^{235}U = 0.714\%$)
  (*b*) Enriched uranium (Higher % of ${}^{235}U$)
  (*c*) Uranium 233 (obtained from ${}^{232}Th$)
  (*d*) ${}^{234}Pu$ (obtained from ${}^{238}U$)
- **Types of fuel moderator assembly:**
  (*a*) Homogeneous–in which fuel is dissolved in the moderator.
  (*b*) Heterogeneous–where moderator remains separated from the fuel.
- **Moderators:**
  (*a*) Heavy water (D_2O) (*b*) Ordinary water (H_2O)
  (*c*) Graphite (*d*) Beryllium
  (*e*) Beryllium oxide.
- **Types of Coolants:**
  (*a*) Gaseous (air, CO_2) (*b*) Water or organic liquids
  (*c*) Liquid metals.
- **Purposes:**
  (*a*) For research (*b*) For production of ${}^{239}Pu$
  (*c*) For power generation.

Depending on the above factors, the nuclear reactors are:

(*i*) Thermal, natural uranium, graphite moderated, Heterogeneous, air cooled, research reactor.

(*ii*) Fast, enriched uranium, heterogeneous, liquid metal cooled, power breeder reactor.

A nuclear reactor is constructed of the following components:

1. Reactor Core: Reactor cores are generally a right circular cylinder with dia. 0.5 m to 15 m. The cylinder is enclosed in a pressure vessel. The cylinder with the pressure vessel is considered as reactor core. The reactor core consists of an assembly of fuel elements, controlled rods, coolant and moderator. In the reactor core, the fission chain reaction takes place and the energy is liberated in the form of heat.

The fuel elements are either in the form of plates or rods of uranium metals. They are usually clad in a thin sheath of Zr or Al stainless steel. This provides retention of radioactivity and corrosion resistance. For the passage of the coolants, enough space is provided between the individual rods (Fig. 3.5).

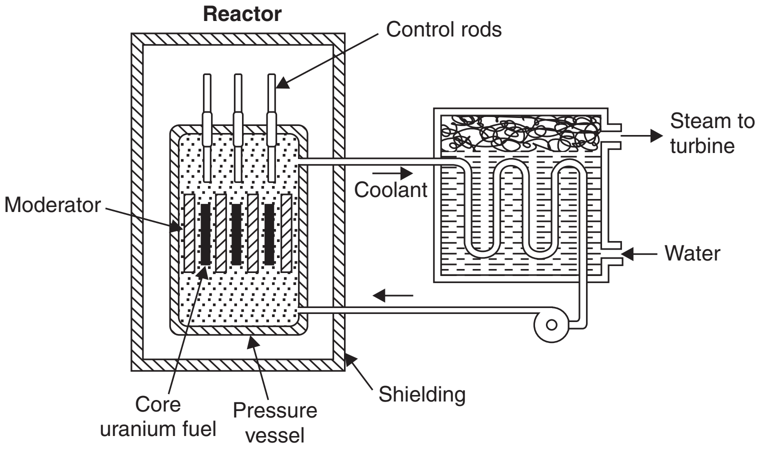


Fig. 3.5 Nuclear reactor.

2. Reflector: A reflector is usually made of the same material as the moderator (not shown in the figure). It is used to reflect back some of the leaking neutrons from the reactor core.

3. Control mechanism: This part is an essential part of the reactor and serves the following purposes:

(*i*) To bring the reactor to its normal operating level.

(*ii*) To keep power production steady.

(*iii*) To shut down the reactor normally or under emergency condition.

The control system also plays an important role to control the chain reaction, so that violent and damaging consequences may be avoided. The control system works on the simple principle of absorbing excess neutrons generated due to fission with the help of control rods made of either boron strips or cadmium strips. The advantage is, they do not become radioactive due to neutron capture. Three rods are sufficient for any amount of excess neutrons. To shut down a reactor the control rods are inserted to a considerable depth so that the chain reaction ceases. To start up the reactor it is necessary to carefully withdraw the control rods and adjust them. Movement of control rods can be made mannual or automatic.

4. Moderator: Function of moderator is to slow down the fast moving fission neutrons. A moderator should have the following characteristics:

(*a*) low mass number elements to have a high flowing capacity.

(*b*) a low cross-section is used for better neutron absorption.

The excellent moderator is D_2O because it slows down the neutrons efficiently and it can be used as coolants as well. The following are the drawbacks of D_2O:

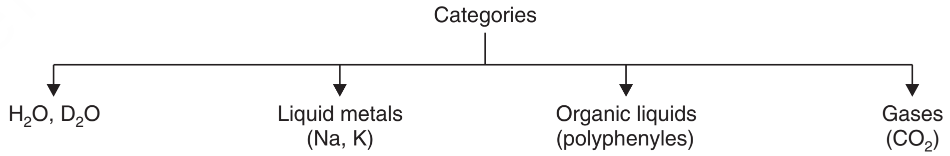
(*i*) Low boiling point,

(*ii*) necessitating the use of pressure

(*iii*) It is very expensive but its advantage outweighs its high cost.

Beryllium (Be) can withstand high temperature, being very expensive it is used in special cases. Reactor grade graphite is not good as a moderator but it is cheaper than Be.

5. Coolants: Function of the coolants is to remove the heat produced in the reactors.



Highlights:

- D_2O, H_2O are good coolants. They can act also as the moderator. Their boiling points are low. They need pressurisation. Water is corrosive at high temperature.
- Molten metallic Na or K are excellent coolants. However, Na is highly reactive to O_2 and H_2 and becomes radioactive by capturing the neutron. So it needs shielding.
- Use of polyphenyls are advantageous for—(*i*) they do not require pressurisation, (*ii*) they do not become radioactive by neutron capturing, (*iii*) they are not corrosive and (*iv*) stable at high temperature. The only disadvantage is they are inferior to H_2O or liquid metals as coolants.
- Air cooling is suitable for low power reactors.

6. Shielding: It is an important consideration for a reactor installation. Its purpose is to weaken the γ-rays and neutrons coming out of the reactors so that they cannot do any harm to the persons in immediate vicinity. In high power reactors, two shields are used.

(*a*) *Thermal Shield:* It is kept very close to the reactor core, it is a thick steel or iron covering.

(*b*) *Biological Shield:* It is a layer of concrete of few decimeter thick surrounding the thermal shield. It is used to absorb γ-rays and the neutrons leaking through the inner thermal shield.

Breeder Reactor

The conversion factor is defined as **"The ratio of the number of secondary fuel atoms produced to the number of primary fuel atoms consumed".** In general type of reactors the conversion factor is 0.9. A reactor with the conversion factor above unity is known as *breeder reactor*. In the breeder reactor, ^{235}U is fissioned by the slow moving neutrons. In this case, per nuclear fission, 2.5 neutrons remain in the reactor and 0.5 neutrons escape out of the reactor. Among which one neutron is used to maintain the steady chain reaction. The residual 1.5 neutrons is used up as follows:

(*i*) ^{238}U captures 0.9 neutrons

(*ii*) Moderator, coolant absorbs 0.6 neutrons.

^{235}U produces ^{239}Pu by capturing those 0.9 neutrons and it is noteworthy to mention that ^{239}Pu is a manmade nuclear fuel.

Uses of Radioisotopes

Radioisotopes provide a powerful tool for the solutions of enormous problem in chemistry, industry, physics, biology and physiology. The application of isotopes depends on the fact that the chemical properties of the isotope of a given element are essentially identical. The detection of a radioisotope is made on the basis of its radioactivity and a stable isotope by means of a mass spectrometer. The radioactivity or mass of an isotope can act as a 'tag' or 'label' which permits the fate of the element or of a compound containing this element to be traced through a series of chemical and physical changes. The element which is 'labelled' or 'tagged' is called a 'tracer element'. A few example of the use of radioactive tracers are given below:

(*a*) **Photosynthesis in plants:** When plants come in contact with sunlight, they can take up CO_2 and water, which are then converted into sugar and starches. At the same time, O_2 is liberated. The O_2 produced may come from CO_2 or H_2O molecules or from both. By performing experiments with labelled oxygen in CO_2 or H_2O, it was found that O_2 came only from water.

$$6CO_2^* + 10H_2O \longrightarrow C_6H_{12}O_6^* + 6H_2O^* + 6O_2$$

$$6CO_2 + 12H_2O^* \longrightarrow C_6H_{12}O_6 + 6H_2O + 6O_2^*$$

(*b*) **Agriculture:** During growth, plant absorbs elemental P both from the soil and from the added fertilizer. How much of the P is consumed from the fertilizer by the plant can only be determined by tracer technique.

(*c*) **Medicine and diagnosis:** (*i*) Radioisotopes are used to locate the presence of tumours, particularly brain tumours.

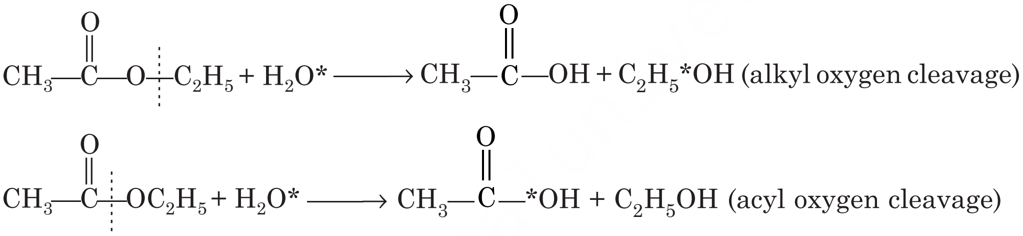
(*ii*) ^{59}Fe is used to diagnose the blood disorder.

(*iii*) ^{131}I is used to diagnose malfunctioning of liver, kidney, etc.

(*iv*) ^{60}Co (γ-radiations) is used in cancer therapy.

(*d*) **Industry:** (*i*) In steel industry to test whether P is removed completely from cast iron radiophosphorus is used. The disappearance of radioactivity indicates that all the P have been removed. (*ii*) The wear and tear of engines can be determined by making the metal of the piston rings radioactive. The appearance of radioactivity in engine oil or in lubricants shows that the process of wear and tear of the pistons has started.

(*e*) **Research:** Reaction mechanism can be ascertained with radioactive tracer technique. In ester hydrolysis, the acyl oxygen cleavage or alkyl oxygen cleavage can be determined as follows:



$$CH_3-\overset{\overset{O}{\|}}{C}-O\,\vdots\,C_2H_5 + H_2O^* \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH + C_2H_5{}^*OH \text{ (alkyl oxygen cleavage)}$$

$$CH_3-\overset{\overset{O}{\|}}{C}\,\vdots\,OC_2H_5 + H_2O^* \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-{}^*OH + C_2H_5OH \text{ (acyl oxygen cleavage)}$$

(*f*) **Biological research:** Isotopic tracers have been widely used in cellular biology. In mitosis, behaviour of cells has been studied with the help of labelled DNA molecules.

(*g*) **Isotopic dating in Geology:** The age of a rock or mineral containing uranium can be determined by its radioactive decay.

The radioactive decay equation is,

$$N = N_0 e^{-\lambda t}$$

where, N_0 = amount of U^{238} in the rock when it was formed.

N = amount of U^{238} still left.

t = lapse of time (age of rock).

Since all U^{238} has been decayed to Pb^{206}.

amount of Pb^{206} present in the mineral = $N_0 - N$

So, we can write,

$$U^{238} = (U^{238} + Pb^{206})e^{-\lambda t}$$

where, U^{238} = amount of U^{238} in the rock

Pb^{206} = amount of Pb^{206} in the rock

λ = decay constant

t = age of the rock.

A similar relation holds good for U^{235}, so we have

$$U^{235} = (U^{235} + Pb^{207})\ e^{-\lambda' t}$$

where λ' = decay constant for U^{235}.

From the above two equations, we have,

$$\frac{Pb^{206}}{Pb^{207}} = \frac{U^{238}\ (e^{\lambda t} - 1)}{U^{235}\ (e^{\lambda' t} - 1)}$$

The present ratio of U^{238} to U^{235} is 139. λ and λ' can be determined from the half-lives of two isotopes of U.

Hence, the age of the rock can be calculated, provided the ratio Pb^{206} to Pb^{207} is determined with the help of a mass spectrometer.

Alternatively, the age of a rock can be determined as follows. The radioactive decay follows the first order rate law,

$$\lambda = \frac{2.303}{t} \log \frac{a}{a - x}$$

a = amount of U^{238} originally present in the rock at the time it was formed.

$(a - x)$ = amount of U^{238} still left after the lapse of time (t).

λ = decay constant of U^{238}.

U^{238} present in the rock at time t is:

$$a = U^{238} + Pb^{206} \quad \text{and} \quad (a - x) = U^{238}$$

where, U^{238}, Pb^{206} represent their respective masses.

So,
$$\lambda = \frac{2.303}{t} \log \frac{U^{238} + Pb^{206}}{U^{238}}$$

$$\lambda = \frac{2.303}{t} \log \left(1 + \frac{Pb^{206}}{U^{238}}\right).$$

Since, values of Pb^{206} and U^{238} can be determined experimentally, the decay constant of U^{238} is known from the relation

$$\lambda = \frac{0.693}{t_{1/2}}$$

Thus, age of the rock (t) can be calculated,

$$t = \frac{2.303\, t_{1/2}}{0.693} \log \left(1 + \frac{Pb^{206}}{U^{238}}\right).$$

(h) **Radio-carbon dating technique:** The age of a piece of wood or animal fossil can be determined by radio-carbon dating technique. C^{14} is formed in the atmosphere as follows :

$${}_7N^{14} + {}_0n^1 \text{ (from cosmic rays)} \longrightarrow {}_6C^{14} + {}_1H^1$$

This is present in atmosphere as $C^{14}O_2$ with $C^{12}O_2$.

In radio-carbon dating ratio C^{14} to C^{12} is assumed constant in the plant; as the plant assimilates CO_2 with $C^{14}O_2$ during photosynthesis. After the death of the plant, no more CO_2 is assimilated so ratio C^{14} to C^{12} in the plant changes, by measuring C^{14} to C^{12} ratio and $t_{1/2}$ of C_{14} (5,730 yrs) age of the wood (t) can be calculated.

$$t = \frac{2.303\, t_{1/2}}{0.693} \log \frac{a}{a - x}.$$

Here, $a = \frac{C^{14}}{C^{12}}$ ratio in the fresh plant

$(a - x) = \frac{C^{14}}{C^{12}}$ ratio in dead plant.

So, by measuring the ratio C^{14} to C^{12} in the fresh and dead plants, age of the wood (t) can be calculated.

Example 1. *Assuming that it were to remain undisturbed since 1898 A.D., calculate how much of Madam Curie's 200 mg of radium would be left in the year 8378 A.D. ($t_{1/2}$ of radium is 1620 years).*

Sol. Total time = (8378 – 1898) = 6480 yrs.

$$\text{No. of half-lives } (t_{1/2}) = \frac{6480}{1620} = 4$$

$$\text{Mass of radium left} = M_0 \left(\frac{1}{2}\right)^n$$

$$= 200 \left(\frac{1}{2}\right)^4 = 12.5 \text{ mg.}$$

Example 2. *A radioactive source contains one microgram (μg) of Pu^{239}. This source is estimated to emit 2300 α-particles/sec. in all directions. Estimate half-life of Pu^{239} from this data.*

Sol. Mass of one α-particle $= 4.00387$ a.m.u.

$$= 4.00387 \times 1.66 \times 10^{-24} \text{ g}$$

$$= 6.646 \times 10^{-24} \text{ g}$$

Mass of 2300 α-particles $= 2300 \times 6.464 \times 10^{-24}$ g

$$= 14.8672 \times 10^{-21} \text{ g}$$

As
$$-\frac{dM}{dt} = \lambda M$$

So
$$\lambda = \frac{-dM/dt}{M} = \frac{-14.867 \times 10^{-21}/1}{1 \times 10^{-6}} = 14.8672 \times 10^{-15} \text{ sec}^{-1}.$$

Half-life ($t_{1/2}$) of Pu^{239}
$$= \frac{0.693}{\lambda} = \frac{0.693}{14.8672 \times 10^{-15}} \text{ sec.}$$

$$= 1.478 \times 10^6 \text{ years.}$$

Example 3. *Prove that $N \approx 0.37\ N_0$.*

Sol. We have,
$$N = N_0 e^{-\lambda t}$$

when $t = \frac{1}{\lambda}$, then the above equation will take the form,

$$N = N_0 e^{-\lambda \cdot \frac{1}{\lambda}} = N_0 e^{-1} = \frac{N_0}{e}$$

$$\frac{N_0}{2.718} = 0.368\ N_0 \approx 0.37\ N_0.$$

Highlight:

- The radioactive constant (λ) may also be defined as the reciprocal of time during which the number of a radioactive element falls to 37% of its original mass.

Example 4. *A radioactive sample initially contains 4.0 mg of* $_{92}U^{234}$. *(a) How much of it will remain unchanged after 62,000 years ? (b) What will be its activity at the end of that time?* ($t_{1/2} = 2.48 \times 10^5$ *yrs.,* $\lambda = 8.88 \times 10^{-14}\ s^{-1}$).

Sol. (*a*) Let, M_0 = Initial mass of $_{92}U^{234}$

M = Mass at the end of 62,000 yrs.

We have, $M = M_0 e^{-\lambda t}$

and
$$\lambda t = \frac{0.693}{t_{1/2}} \times t = \frac{0.693 \times 62000}{2.48 \times 10^5} = 0.173$$

λt may also be calculated, as follows:

$$\lambda t = 8.88 \times 10^{-14} \times 62000 \times 365 \times 24 \times 3600$$
$$= 0.173$$

$\therefore$ $M = M_0 e^{0.173}$

or, $M_0 = M \,.\, e^{0.173} = 1.189\ M$

or,
$$M = \frac{M_0}{1.189}$$

$\therefore$ Mass of $_{92}U^{234}$ left unchanged $= \dfrac{4}{1.189} = 3.364$ mg.

(*b*) Activity of $_{92}U^{234}$ is:

$$A = \lambda N = 8.88 \times 10^{-14} \times \frac{3.364 \times 10^{-3} \times 6.023 \times 10^{23}}{234}$$
$$= 7.69 \times 10^5 \text{ disintegrations/sec.}$$

Example 5. *The half-life period of radium is 1620 years. In how many years will one gram of pure element (a) lose one centigram (b) be reduced to one centigram?*

Sol. (*a*) We know,

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{1620} = 4.28 \times 10^{-4} \text{ year}^{-1}.$$

Let, time during which one centigram of radium is lost due to disintegration be = t.

The mass of radium would be left behind at the end of time $t = 1 - 0.01 = 0.99$ g.

Now, $N = N_0 e^{-\lambda t}$

or,
$$\frac{N_0}{N} = e^{\lambda t}$$

or,
$$\log_{10} \frac{N_0}{N} = \lambda t \times 0.4343$$

or,
$$\log_{10} \frac{100}{99} = 4.28 \times 10^{-4} \times t \times 0.4343$$

$\therefore$ $t = 23.68$ years.

(*b*) Here
$$\frac{N_0}{N} = \frac{1}{0.01} = 100$$

$$\therefore \qquad \log_{10} 100 = 4.28 \times 10^{-4} t \times 0.4343$$

$$\therefore \qquad t = 10{,}760 \text{ years.}$$

Example 6. *The unit for measuring radioactivity is curie (Ci). One Ci is defined as that quantity of a radioactive material which gives 3.7×10^{10} disintegrations/sec. Calculate the mass of RaB in gram which gives 3.7×10^{10} dis/s.*

Sol. The number of atoms of RaB contained in mass (m)

$$= \frac{m \times 6.02 \times 10^{23}}{214}$$

Now,

$$-\frac{dN}{dt} = \lambda N$$

$$\therefore \qquad 3.7 \times 10^{10} = 4.31 \times 10^{-4} \times \frac{m \times 6.02 \times 10^{23}}{214}$$

$$\therefore \qquad m = 3.1 \times 10^{-8} \text{ g.}$$

Highlights:

- A new absolute unit of radioactivity is rutherford (rd). One rutherford is defined as that quantity of a radioactive substance which gives 10^6 dis.s^{-1}.
- Smaller units like millirad (mrd) and microrad (μrd) are also used.

Example 7. *Calculate the mass for RaB for 1 rd activity.*

Sol. For 1 rd activity,

$$\frac{dN}{dt} = 10^6 \text{ dis.s}^{-1}$$

$$\therefore \qquad 10^6 = 4.31 \times 10^{-4} \times \frac{m \times 6.023 \times 10^{23}}{214}$$

$$\therefore \qquad m = 8.3 \times 10^{-13} \text{ g.}$$

Highlights:

- For one curie, the mass of ${}_{92}U^{238}$ ($\lambda = 0.693/4.5 \times 10^9 \times 365 \times 24 \times 3600$ and $t_{1/2} = 4.5 \times 10^9$ years) is:

$$3.7 \times 10^{10} = 4.9 \times 10^{-18} \times \frac{m \times 6.023 \times 10^{23}}{238}$$

$$\therefore \qquad m = 3.2 \times 10^6 \text{ g.}$$

- For one rutherford, the mass of ${}_{92}U^{238}$ is

$$10^6 = 4.9 \times 10^{-18} \times \frac{m \times 6.023 \times 10^{23}}{238}$$

$$\therefore \qquad m = 80.98.$$

Example 8. *The ratio of mass of Pb^{206} to the mass of U^{238} in a certain rock specimen is found to be 0.5. Assuming that the rock originally contained no lead, estimate its age. ($t_{1/2}$ for U is 4.5×10^9 years)*

Sol. We know that,

$$U^{238} = (U^{238} + Pb^{206})\, e^{-\lambda t}$$

or, $$1 = \left(1 + \frac{\text{Pb}^{206}}{\text{U}^{238}}\right) e^{-\lambda t}$$

or, $$1 = (1 + 0.5)\, e^{-\lambda t} = 1.5\, e^{-\lambda t}$$

$$\therefore \quad e^{\lambda t} = 1.5$$

or, $$\lambda t = 2.303 \times \log_{10} 1.5 = 2.3 \times 0.1761$$

$$\therefore \quad \frac{0.693}{4.5 \times 10^9}\, t = 0.23 \times 0.1761$$

$$\therefore \quad t = 2.63 \times 10^9 \text{ years.}$$

Example 9. *A sample of U^{238} is found to contain 11.9 g of U^{238} and 10.3 g of Pb^{206}. Calculate the age of the ore.* ($t_{1/2}$ *= 4.5 × 10^9 years*)

Sol. $$\text{Mole of U}^{238} = \frac{11.9}{238} = 0.05$$

$$\text{Mole of Pb}^{206} = \frac{10.3}{206} = 0.05$$

We have, $$t = \frac{2.303\, t_{1/2}}{0.693} \log\left(1 + \frac{\text{Pb}^{206}}{\text{U}^{238}}\right)$$

$$= \frac{2.303 \times 4.5 \times 10^9}{0.693} \log\left(1 + \frac{0.05}{0.05}\right)$$

$$= \frac{2.303 \times 4.5 \times 10^9}{0.693} \log 2 = 4.5 \times 10^9 \text{ years.}$$

Example 10. *The amount of ${}_6C^{14}$ isotope in a piece of fresh wood is found to be 1/6th of the total carbon. Calculate the age of wood.* ($t_{1/2}$ *of C = 5577 yrs*).

Sol. We have,

$$t = \frac{2.303\, t_{1/2}}{0.693} \log \frac{1}{1/6}$$

$$= \frac{2.303 \times 5577}{0.693} \log 6$$

$$= \frac{2.303 \times 5577 \times 0.7782}{0.693} = 20{,}170 \text{ yrs.}$$

Example 11. *Half-life period of C^{14} is 5760 years. An old piece of wood in a museum has a disintegration rate which is 25% of the disintegration rate of an equal weight of a new piece of wood. What is the age of the old piece of wood?*

Sol. We have,

$$t = \frac{2.303 \times 5760}{0.693} \log \frac{1}{1/4}$$

$$= \frac{2.303 \times 5760 \times 0.6021}{0.693} = 11{,}525 \text{ yrs.}$$

Example 12. *The half-life of* Ac^{222} *is 6.13 hrs. Calculate the fraction of the sample of this substance present at the end of 10 hrs.*

Sol.

$$t = \frac{2.303\, t_{1/2}}{0.693} \log \frac{1}{1/x}$$

or
$$10 = \frac{2.303 \times 6.13}{0.693} \log x$$

or
$$\log x = \frac{10 \times 0.693}{2.303 \times 6.13} = 0.4696$$

$\therefore$
$$x = \text{Antilog } 0.4696 = 2.948$$
$$x \approx 3$$

$\therefore$ the fraction of the Sample = $\frac{1}{3}$.

Example 13. *(a) What is Q-value for a nuclear reaction?*

(b) Calculate the Q-value for the following nuclear reaction:

$$_7N^{14} + {}_2He^4 \longrightarrow {}_8O^{17} + {}_1H^1.$$

Sol. (*a*) The overall energy liberated or absorbed in a nuclear reaction is called *nuclear reaction energy*. This energy which is generally abbreviated by Q is also known as *energy balance* of the reaction as per Einstein's theory or more commonly as *Q-value*. If Q-value is positive, the reaction is accompanied by liberation of energy, there is *decrease in mass* in the reaction, such a reaction is *exothermic* or *exoergic*. On the other hand, if Q-value is negative, there is absorption of energy, there is *gain of mass* in the reaction, and such reaction are called *endothermic* or *endoergic*.

(*b*)

Interacting particles	Mass (a.m.u.)	Product particles	Mass (a.m.u.)
$_2He^4$ $_7N^{14}$	4.00387 14.00753	$_8O^{17}$ $_1H^1$	17.0045 1.00814
	Total = 18.01140		Total = 18.01264

Increase in mass = 18.01264 – 18.01140 = 0.00124 a.m.u.

$\therefore$ Q-value = 0.00124 × 931 MeV [$\because$ 1 a.m.u. = 931MeV]

= 1.15 MeV

So, the reaction is $_2He^4 + {}_7N^{14} = {}_8O^{17} + {}_1H^1 + Q$

$\therefore$ Q-value of the reaction is = – 0.00124 a.m.u. = – 1.15 MeV

The Q-value for the reaction is negative, there is increase in mass and absorption of energy, so the reaction is endoergic.

Example 14. *Show the following reaction is exoergic*

$${}_3Li^7 + {}_1H^1 = {}_2He^4 + {}_2He^4.$$

Sol.

Interacting particles	Mass (a.m.u.)	Product particles	Mass (a.m.u.)
${}_3\mathrm{Li}^7$ ${}_1\mathrm{H}^1$	7.01822 1.00814	${}_2\mathrm{He}^4$ ${}_2\mathrm{He}^4$	4.00387 4.00387
	Total = 8.02636		Total = 8.00774

$\therefore$ ${}_3\mathrm{Li}^7 + {}_1\mathrm{H}^1 = {}_2\mathrm{He}^4 + {}_2\mathrm{He}^4 + \mathrm{Q}$

$\therefore$ Q = Decrease in mass

= (8.02636 – 8.00774) = 0.01862 a.m.u.

= 0.01862 × 931 = + 17.3 MeV.

Here, Q value is positive, the reaction is accompanied by liberation of energy (decrease in mass).

So the reaction is exothermic of exoergic.

Example 15. *Calculate the energy released from the fusion of* ${}_3Li^6$ *and* ${}_1D^2$ *by the reaction,*

$${}_3Li^6 + {}_1D^2 = {}_2He^4 + {}_2He^4 + Q$$

where isotopic masses are, ${}_3Li^6 = 6.01702$ *a.m.u.*

${}_1D^2 = 2.01474$ ${}_2He^4 = 4.00387$ a.m.u.

Sol. From the above equation,

Q = (2.01474 + 6.01702) – (2 × 4.03387)

= 0.03402 a.m.u.

= 0.03402 × 931 = 31.67 MeV.

Example 16. *Calculate the energy released in the following fission reaction:*

$${}_{92}U^{235} + {}_0n^1 \longrightarrow {}_{36}Kr^{95} + {}_{57}Ba^{139} + 2\ {}_0n^1.$$

Sol. The reaction is ${}_{92}\mathrm{U}^{235} + {}_0n^1 = {}_{36}\mathrm{Kr}^{95} + {}_{57}\mathrm{Ba}^{139} + 2\ {}_0n^1 + \mathrm{Q}$

or Q = (235.124 + 1.0099) – (94.945 + 138.954 + 2 × 1.0099)

= 0.2151 a.m.u.

$\therefore$ Energy released = 0.2151 × 931 MeV = 200.258 MeV.

Example 17. *Calculate the limiting energy per nucleon* ${}_{20}Ca^{40}$*, which has atomic mass of 39.975 a.m.u. The mass of proton is 1.0078 a.m.u. and the mass of neutron is 1.0086 a.m.u.*

Sol. Mass defect Δm for Ca-atom

= (20 × 1.0078 + 20 × 1.0086) – 39.975 a.m.u.

= 0.353 a.m.u.

$$\therefore \text{ Binding energy per nucleon} = \frac{0.353 \times 931}{40} \text{ MeV.}$$

= 8.216 MeV.

Example 18. *Calculate (i) the fission rate of* U^{235} *for producing power of 1 watt and (ii) the energy released in the complete fission of 1 kg of* U^{235}*. (energy released/fission of* U^{235} *MeV = 200 MeV).*

Sol. (*i*) Energy released per fission of U^{235} nuclide

$$= 200 \text{ MeV}$$

$$= 200 \times 1.6 \times 10^{-13} \text{ J} = 3.2 \times 10^{-11} \text{ J or W.s.}$$

Hence, fission rate for generation of 1 watt

$$= \frac{1}{3.2 \times 10^{-11}} = 3.1 \times 10^{10} \text{ fissions sec}^{-1}.$$

(*ii*) 1 kg atom of U^{235} = 235 kg = 6.023×10^{26} atoms or nuclides.

So, energy released per 1 kg of U^{235}

$$= \frac{200 \times 6.023 \times 10^{26}}{235} \text{ MeV.}$$

$$= 8.2 \times 10^{13} \text{ J.} \qquad (\because \quad 1 \text{ MeV} = 1.6 \times 10^{-13} \text{ J})$$

Example 19. *A city requires 100 MW of electrical power on an average. If this is to be supplied by a nuclear reactor of efficiency 20%, using* U^{235} *as the nuclear fuel, calculate the amount of fuel required for one day's operation. Given that energy released per fission of* U^{235} *is 200 MeV.*

Sol. Energy consumed in the city in a day

$$= 100 \times 10^{6} \times 24 \times 3600 = 864 \times 10^{10} \text{ J}$$

Since efficiency of the reactor is 20%,

Energy required to be produced in a day

$$= \frac{864 \times 10^{10}}{0.2} = 432 \times 10^{11} \text{ J}$$

Energy released/nuclide = $200 \times 1.6 \times 10^{-13}$ J

$$= 32 \times 10^{-12} \text{ J.}$$

$\therefore$ No. of U^{235} atoms to be fissioned

$$= \frac{432 \times 10^{11}}{32 \times 10^{-12}} = 13.5 \times 10^{23}$$

6.023×10^{26} atoms of U^{235} are present in 235 kg

$\therefore$ 13.5×10^{23} atoms of U^{235} are present in

$$= \frac{235 \times 13.5 \times 10^{23}}{6.025 \times 10^{26}} \text{ kg}$$

$$= 530 \times 10^{-3} \text{ kg} = 0.53 \text{ kg.}$$

SHORT QUESTIONS AND ANSWERS

Q. 1. What do you mean by nuclear chemistry?

Ans. Nuclear chemistry is concerned with changes of the nuclei *i.e.,* its stability, disintegration, etc.

Q. 2. How does a nuclear reaction differ from a chemical reaction?

Ans. Nuclear reaction involves the changes of the nucleus whereas ordinary chemical reaction involves the changes in extranuclear electrons of the atoms, nuclei of the atoms remain unaffected in a chemical reaction.

Q. 3. What is radioactivity?

Ans. The phenomenon of spontaneous emission of radiations from the nuclei of heavy elements is called radioactivity.

Q. 4. What is the theory behind radioactivity emission?

Ans. Rutherford and Soddaz postulated that,

(*i*) The nuclei of radioactive elements are unstable.

(*ii*) The nuclei of radioactive elements disintegrate forming atoms of new elements called 'daughter elements'.

(*iii*) α- and β-particles are emitted from the nucleus.

(*iv*) γ-rays are the secondary effects of the nuclear disintegration.

Q. 5. What is α-emmision?

Ans. The emission of an α-particle from a radioactive nucleus is designated as α-emission. The transformation of UI to UXI by α-emission may be represented as follows:

$${}_{92}\text{UI}^{238} \xrightarrow{-\alpha} {}_{2}\text{He}^{4} + {}_{90}\text{UXI}^{234}.$$

Q. 6. What is β-emission?

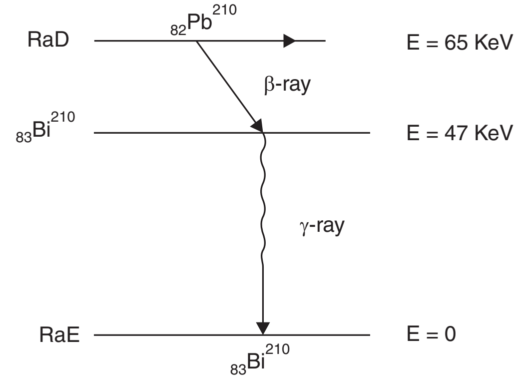
Ans. The emission of a β-particle from a radioactive element is known as β-emission. A β-particle is a single negatively charged particle and positive nucleus does not contain any electron. So it appears strange. β-particle is generated in the nucleus as follows:

$${}_{0}n^{1} \longrightarrow {}_{-1}e^{0} + {}_{1}\text{H}^{1}$$

So, on emission of a β-particle, nucleus gains a proton at the cost of a neutron. Thus, the atomic number of the daughter element increases by one unit.

Q. 7. What is γ-decay?

Ans. γ-rays have been proved to arise from the transition of a nucleon from one energy state to the other. A γ-decay has been depicted in the following figure.



Q. 8. What do you mean by natural radioactivity and artificial radioactivity?

Ans. Natural radioactivity is exhibited by heavier elements found in nature. Whereas modern techniques of artificial transmutation of elements have made it possible to produce radioactivity in many other lighter elements. Such type of radioactivity is known as "artificial or induced radioactivity".

Q. 9. What do you mean by radioactive series?

Ans. If, during radioactive disintegration, the daughter element is also radioactive then it decays further and the process continues till a stable isotope is reached. This chain of successive disintegrations is termed 'radioactive series'.

Q. 10. What do you mean by radioactive decay constant?

Ans. The radioactive decay equation is,

$$-\frac{dN}{dt} = \lambda N$$

or

$$\lambda = \frac{-dN/dt}{N}$$

So, the radioactive decay constant (λ) may be defined as the ratio of the amount of the substance, which disintegrates in a unit time to the amount of the substance present.

Alternatively, it may be defined as the rate of disintegration when the number of radioactive nucleus present is one.

Q. 11. Compare radioactive change and chemical change.

Ans.

Radioactive change	Chemical change
(*i*) Radioactive change does not depend upon external conditions like temperature, pressure, etc.	(*i*) Chemical change depends upon external conditions like pressure, temperature, etc.
(*ii*) Radioactive change is irreversible.	(*ii*) Chemical change is mostly reversible.
(*iii*) Radioactive change is always exothermic.	(*iii*) Chemical change may be exothermic or endothermic.
(*iv*) Radioactive change is a nuclear phenomenon.	(*iv*) Chemical change involves only outermost electrons of the atoms. No change takes place of the nucleus of the atom.

Q. 12. What do you mean by nuclear fission?

Ans. The division of a nucleus into two approximately equal parts is termed 'nuclear fission'. As for example:

$$ {}_{92}U^{235} + {}_{0}n^{1} \longrightarrow {}_{92}U^{236} \left. \begin{array}{l} \rightarrow {}_{56}Ba^{140} + {}_{36}Kr^{93} + 3\,{}_{0}n^{1} \\ \rightarrow {}_{54}Xe^{144} + {}_{38}Sr^{90} + 2\,{}_{0}n^{1} \\ \rightarrow {}_{55}Cs^{144} + {}_{37}Rb^{90} + 2\,{}_{0}n^{1} \end{array} \right. $$

A huge amount of energy is released during nuclear fission according to famous Einstein's equation E = mc^2, and this reaction is the principle for atom bomb.

Q.13. What do you mean by nuclear fusion?

Ans. When two light nuclei combine with release of a huge amount of energy, the phenomenon is known as 'nuclear fusion'.

$${}_1H^2 + {}_1H^2 \longrightarrow {}_2He^4 + \text{energy}$$

$${}_1H^1 + {}_1H^3 \longrightarrow {}_2He^4 + \text{energy.}$$

Nuclear fusion is the source of energy of the sun and the other stars. It is also the process that accounts for the origin of all the elements. In the sun, at a temperature of ten million degrees; the following fusion takes place.

$$4\ {}_1H^1 \longrightarrow {}_2He^4 + 2 \text{ positrons} + 10^9 \text{ kJ.}$$

Q. 14. Why the elements with even proton numbers are more abundant than other elements?

Ans. The pressure and temperature at the centre of very large stars is high enough for ${}_2He^4$ nuclei to fuse to form heavier elements such as C, Si, Fe, since ${}_2He^4$ has even number of nucleons, they fuse to produce elements with even proton numbers.

Q. 15. How are nuclear reactions carried out? Mention the uses of nuclear reactions.

Ans. Nuclear reactions are the changes affecting the nuclei of atoms. Nuclear reactions are brought about by bombarding nuclei with high energy particles in particle accelerators or with beams of neutrons from nuclear reactors.

Apart from atom bombs and alternative energy sources, nuclear reactions can be used to make elements that do not occur in nature; with higher proton numbers than uranium.

$${}_{92}U^{238} + {}_0n^1 \longrightarrow {}_{92}U^{239} \xrightarrow{\beta} {}_{93}Np^{239} \xrightarrow{\beta} {}_{94}Pu^{239}$$

Nuclear reactions are used to give birth to radioactive isotopes to be used as tracers.

Q. 16. Compare fission and fusion reactions.

Ans.

Fission	Fusion
(*i*) Fission involves breaking up of a heavy nucleus into lighter ones with release of large amount of energy.	(*i*) Fusion involves, combining of two lighter nuclei into a heavy nucleus with release of large amount of energy.
(*ii*) Fission takes place at ordinary temperature.	(*ii*) Fusion takes place at very high temperature (10^6 K).
(*iii*) During fission, neutrons are emitted.	(*iii*) During fusion, positrons are emitted.
(*iv*) Fission gives rise to chain reaction.	(*v*) Fusion does not give rise to chain reaction.

EXERCISES

1. What is radioactivity? Give an account of the discovery of radioactivity?
2. How will you show that radioactivity is nothing but a nuclear property?
3. If you are given a piece of mineral, how can you determine by simple experiments if the mineral is radioactive?

4. What are α-, β- and γ-rays? Compare their ionising power, range and velocity.

5. Explain the terms:

(*i*) Disintegration constant

(*ii*) Half-life period

6. What are the units of radioactivity?

7. Give a relation between half-life and the decay constant of a radioactive substance.

8. What are the causes of nuclear instability? Explain with suitable examples.

9. State and explain the law of radioactive disintegration. What do you mean by the half-life period of a radioactive element? Show that the half-life is independent of the amount of the substance.

10. Explain artificial radioactivity with suitable examples.

11. What is radioactive displacement law?

12. Write notes on:

(*i*) Radioactive equilibrium

(*ii*) Atomic weight of lead in radioactive minerals

(*iii*) Tracer technique.

13. Why is natural radioactivity mostly limited among heavier elements?

14. What is a nuclear reaction? Discuss some uses of nuclear reactions.

15. What is nuclear binding energy?

16. What are radio-isotopes? How are they prepared? Mention their uses.

17. Give a comparative account of the nuclear binding energy curve and packing fraction curve. What informations are available from these curves?

18. Write a short note on nuclear transmutation.

19. What is nuclear fission? Show how nuclear fission is a chain reaction.

20. Write a short note on nuclear fusion.

21. Give a brief account of the nuclear reactors. Derive a relation between mass defect and nuclear binding energy.

22. Where is the radioactive displacement law invalid?

23. Calculate the amount of energy released during the bombardment of ${}^{1}_{0}n$ on ${}^{235}_{92}\text{U}$.

24. Write a short note on radio-carbon dating.

25. Complete the following nuclear reactions:

$$
\begin{gathered}
{}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + \ldots \\
{}^{24}_{11}\text{Na} \longrightarrow {}^{24}_{12}\text{Mg} + \ldots \\
{}^{238}_{92}\text{U} \longrightarrow {}^{239}_{90}\text{Th} + \ldots \\
{}^{10}_{5}\text{B} + {}^{4}_{2}\text{He} \longrightarrow \ldots + {}^{1}_{1}\text{H} \\
{}^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \longrightarrow \ldots + {}^{7}_{4}\text{Be}.
\end{gathered}
$$

26. Calculate the time required for 10% disintegration of a sample of thorium. Given the $t_{1/2}$ of thorium = 1.4×10^{10} yrs. [**Ans.** 6.93×10^{-5} yrs.]

27. Calculate the binding energy in MeV per nucleon of ${}^{12}_{6}\text{C}$.

Given: Mass of H-atom = 1.00782 a.m.u.
Mass of neutron = 1.00866 a.m.u.
Actual mass of C-atom = 12.04
1 amu = 931.4 MeV. [**Ans.** 54.76 MeV]

28. The half-life of radium is 1590 years. How long will it take for 1 g of the element to lose 0.1 g? [**Ans.** 2385 yrs.]

29. A piece of wood was found to have $^{14}C/^{12}C$ ratio 0.7 times that in a living plant. Calculate the approximate life period when the plant died. Given $t_{1/2}$ = 5760 years. [**Ans.** 2970 years]

30. A sample of uranium ore is found to contain 11.9 g of ^{238}U and 10.33. of ^{206}Pb. Calculate the age of the rock. Given $t_{1/2}$ of uranium = 4.5×10^9 yrs. [**Ans.** 4.5×10^9 years]

31. Half life of ^{222}Rn in 3.82 days. Calculate the weight of 1 curie of ^{222}Rn. [**Ans.** 6.5×10^{-6}]

32. A radioactive element disintegrates to 1/16th of its original mass in 160 days. What is its half-life period? [**Ans.** 40 days]

33. Calculate the energy released in MeV from the reaction:

$$^{10}_{5}B + ^{2}_{1}H \longrightarrow ^{11}_{5}B + ^{1}_{1}H$$

Given: Mass of ^{10}B = 10.01605 a.m.u.
Mass of ^{11}B = 11.01286 a.m.u.
Mass of 2H = 2.01472 a.m.u.
Mass of ^{1}H = 1.00812 a.m.u. [**Ans.** 9.114 MeV]

34. A neutron breaks into a proton and an electron. Calculate the energy produced in MeV.

Given: Mass of neutron = 1.6747×10^{-24} g.
Mass of proton = 1.6725×10^{-24} g.
Mass of electron = 9×10^{-28} g.
1 a.m.u. = 931 MeV. [**Ans.** 0.73 MeV]

35. Calculate the decay constant of ^{60}Co. Given the $t_{1/2}$ of cobalt = 5.3 years. [**Ans.** 0.13 yr^{-1}]

36. Calculate the energy released in the nuclear fusion reaction:

$$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$$

Given: Mass of $^{2}_{1}H$ = 2.014 a.m.u.

Mass of $^{3}_{1}H$ = 3.016 a.m.u.

Mass of $^{4}_{2}He$ = 4.003 a.m.u.

Mass of $^{1}_{0}n$ = 1.009 a.m.u. [**Ans.** 16.76 MeV]

37. An old wooden article shows 2.0 counts min^{-1} g^{-1}. A fresh sample of wood shows 15.2 counts min^{-1} g^{-1}. Calculate the age of the wooden article.

Given: $t_{1/2}$ for $^{14}_{6}C$ = 5,760 yrs. [**Ans.** 16,862 years]

38. Distinguish between nuclear fuel and a chemical fuel.

39. Write short note on components of a nuclear power reactor and their functions.

4

Thermodynamics

Thermodynamics is concerned with the flow of heat and therefore deals with the quantitative relationship between heat and work. The science of thermodynamics actually covers a much wider field covering energy-changes in all physical and chemical processes as well as mutual transformations of all the different forms of energy. Thermodynamic deductions are not made on the basis of any hypothesis about the molecular structure of matter but the three simple laws of thermodynamics are based on human experience and these relations were tested experimentally for centuries starting from heat engines to cellular enzymatic processes and are considered inviolable. Thus, Einstein comments: "It (thermodynamics) is the only physical theory of universal content concerning which I am convinced that, within the framework of applicability of its basic concepts, it will never be overthrown".

- *Before beginning with the laws of thermodynamics following terms are needed to be defined.*

1. Thermodynamic systems. A *system* is defined as any matter or its part, chosen for study and separated from the rest of the universe by a real or imaginary boundary. The rest of the universe is called the *surroundings*.

A system is said to be an *isolated system* when it is capable of exchanging either energy or matter with the rest of the universe. Hence, the energy and matter remain constant for the system. There is no such perfectly isolated system other than our universe itself.

A *closed system* is one, which is capable of exchanging only energy with the surroundings but no mass transfer across the boundary is permitted; example is a sealed flask containing matter in a closed system.

An *open system* is a system, which can exchange both mass and energy across the boundary; example is a plant or any living being.

2. Properties of a system. The physical characteristics which are experimentally measurable and which enable us to define a system are called thermodynamic parameters or properties of the system. Composition, volume, pressure and temperature are the fundamentally important properties. Refractive index, viscosity, dielectric constant are also other properties.

Extensive property. Properties like volume, surface area, energy, etc., are dependent upon the mass of the system and are called extensive property.

Intensive property. Properties like temperature, pressure, surface tension, viscosity, specific heat, density, refractive index, etc., are independent of the mass of the system and are called intensive properties.

3. State of a system. The set of thermodynamic variables such as pressure, volume, temperature, composition, etc., which describe a system is called the "state of the system".

When one or more of these variables undergo change, the system is said to have undergone a change of state.

If, as a result of a series of changes, the system returns to its initial state, its thermodynamic parameters also return to their original values, such a process is called a *cyclic process.*

If a change takes place at a constant temperature maintained throughout, it is called an *isothermal process.*

If a change takes place in a thermally insulated system which does not permit heat exchange with the surrounding, the process is called an *adiabatic process* and the temperature of the system may increase or decrease.

If a process is carried out at constant pressure, the process is called an *isobaric process,* which is accompanied by volume changes.

If a change takes place in which the volume of the system remains constant the process is called an *isochoric process.* A process is said to be *reversible* if the energy change in each step of the process can be reversed in direction by an infinitesimal change in any of the variables acting on the system. A process can be made reversible by performing the change very slowly with no friction and no finite temperature differences.

An irreversible process is such that the system and the surrounding after undergoing changes cannot get back to their initial state and tend to proceed to a definite direction but cannot proceed to the reverse direction. All the natural processes are irreversible, example, expansion of gases from high pressure to low pressure, heat flowing from a hotter to a colder body, etc. *Irreversible processes are all spontaneous processes.*

Equilibrium state. A system is said to be in equilibrium when its composition is fixed, temperature is uniform and also same with the surroundings and there is no unbalanced force the system and also between the system and the surroundings. Hence, a system in equilibrium state has definite temperature, pressure and composition.

State function is a thermodynamic property, which depends only on the state of the system but not on the paths followed for the change. Internal energy change (ΔE), enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) are such functions.

Internal energy. Every system within itself has a quantity of energy which is called the internal or intrinsic energy. This energy is a function of the temperature, chemical composition, pressure and volume of the system. The magnitude of internal energy of a system is determined by the kinetic, rotational, vibrational movements of the molecules of the system. It is an extensive property. Five moles of a substance in a specified state has five times the internal energy possessed by a single molecule in a similar state. The absolute value of the internal energy of a system cannot be ascertained. When a system changes from a *thermodynamic state 1 to a thermodynamic state 2, the change in the internal energy* $\Delta E = E_2 - E_1$ *is independent of the path of transformation but depends on the initial and final conditions of the system.*

If a system undergoes a series of changes and returns to its initial state *i.e.*, if a cyclic process is completed, internal energy is found to return to its original value, hence the sum of the changes of internal energy for a cyclic process *i.e.,* $\sum \Delta E = 0$. So internal energy (E) is a state function. Otherwise, it can be stated that when a system changes from initial state (1) to a final state (2) and comes back to (1) (Fig. 4.1), net change in internal energy is zero *i.e.,* $\oint dE = 0$ (cyclic integration of E is 0), so dE is path independent and E is a state function.

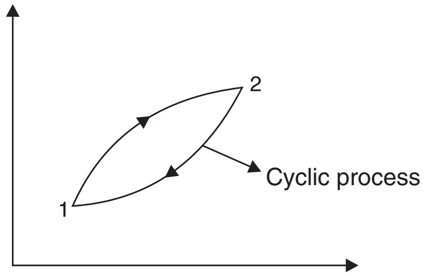


Fig. 4.1

THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is simply the law of conservation of energy, and it may be stated as "the energy of an isolated system remains constant and whenever a quantity of some form of energy disappears, an exactly equivalent quantity of some other form of energy must make its appearance".

The law was first stated by Mayer in 1842 and Fouli's classical research on equivalence between heat and work established the fact in 1845 and finally generalised by Helmholtz in 1847.

Mathematical formulation of the first law

Let us suppose, heat supplied to a system is q. Since heat energy cannot be lost, it may be used up by the system as partly increasing the internal energy of the system and partly in doing mechanical work. Thus, according to the first law

Heat absorbed = Increase of internal energy + Work done by the system

i.e., $q = \Delta E + W$

or $\Delta E = q - W$

If the above change is infinitesimally small, we can write

$$dE = dq - dw$$

where dE is the increase in internal energy, dq and dw represent small quantities of heat absorbed and external work done by the system, respectively. *For an adiabatic change,* $q = 0$, $\therefore W = -\Delta E$. So in an adiabatic process, work done by the system = decrease in internal energy of the system. If the system is under a pressure P and volume increases by dV, the work done becomes $P\,dV$ and hence the mathematical expression of first law becomes, $dE = dq - P.\,dV$ for very very small changes.

Here the work, exclusively, is of pressure × volume type. When the volume (V) is constant,

$dV = 0$, hence $dE = dq - P \times 0$ $[\because\ dv = 0]$

$\therefore$ $dE = dq$ or $\Delta E = qV$

Cyclic process: We have already found that if a system undergoes change through path (1) and returns to its original state via path (2), it completes a cyclic path and the overall change of energy (E) *i.e.,* $\Delta E = 0$.

Hence, from first law, $\Delta E = q - W = 0$

$\therefore$ $q = W$.

Hence, we arrive at a very important relation that for a cyclic process, the algebraic sum of all the heat terms is equal to the algebraic sum of all the work terms.

Joule-Thomson effect

Joule-Thomson effect states: "When a gas under high pressure is permitted to expand into a region of low pressure, it suffers a fall in temperature".

Joule and Thomson performed an experiment where a gas was allowed to expand adiabatically through a porous plug against a constant pressure. Thus, the gas was allowed to do no work and there was no interchange of heat with the surroundings.

Suppose V_1 volume of gas at pressure P_1 is forced through the porous plug and expands to a volume V_2 at a lower pressure P_2.

Hence, work done by the gas is, $P_2V_2 - P_1V_1 = W$.

For an ideal gas, $P_1V_1 = P_2V_2 \quad \therefore \quad W = 0$.

Hence, from first law of thermodynamics,

$$\Delta E = q - W = q - 0 = q.$$

Hence, for an ideal gas, there should be no change in temperature. But Joule-Thomson observed that most gases cooled down by such a pressure drop. Since the expansion is carried out adiabatically *i.e.,* when $q = 0$, the energy of the gas falls *i.e.,* $\Delta E = -\text{ve}$; thus the gas while expanding does some work and hence the temperature falls. The work done is at the expense of the kinetic energy of the molecule while they are separated from each other.

Heat content or Enthalpy of a system

The pressure (P) and volume (V) of a system are thermodynamic variables and their product PV is expressed as energy. Suppose, a system at constant pressure is undergoing a change from states 1 to 2. The volume increase is from V_1 to V_2. Heat absorbed by the system is q. Hence, from the first law of thermodynamics

$$\begin{aligned} q &= (E_2 - E_1) + W \\ &= (E_2 - E_1) + (P_2V_2 - P_1V_1) \\ &= (E_2 + P_2V_2) - (E_1 + P_1V_1) \\ &= H_2 - H_1 = \Delta H. \end{aligned}$$

The quantity (E + PV) is universally represented as H and called the heat content or enthalpy of a system. Since E is a characteristic of the system (state function), according to the first law, H is a similar state function. Hence, ΔH will depend only on the initial and final states of the system, not on the path followed during the change.

$$\begin{aligned} \Delta H &= (E_2 + P_2V_2) - (E_1 + P_1V_1) \\ &= (E_2 - E_1) + (P_2V_2 - P_1V_1) \end{aligned}$$

∴ At constant pressure,

$$\Delta H = \Delta E + PV = \Delta E + W = q \text{ (heat absorbed)}$$

and at constant volume, $\Delta V = 0$.

$$\therefore \qquad \Delta H = \Delta E + 0 = \Delta E.$$

i.e., Change in enthalpy = change in internal energy.

So, if the process is carried out at constant volume change in enthalpy and change in internal energy are equal.

Constancy of Enthalpy (isoenthalpic) in Joule-Thomson expansion

Joule-Thomson experiment is carried out adiabatically, when heat does not flow out of the system nor does it come into system from the surrounding, *i.e.,* $q = 0$. The gas expands is passing through porous plug (Fig. 4.2) and the work done is $P_2V_2 - P_1V_1$.

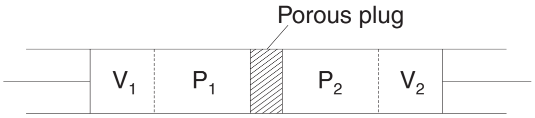


Fig. 4.2 Joule-Thomson expansion.

Hence, from first law, $\Delta E = q - W$

$$= 0 - (P_2V_2 - P_1V_1)$$

i.e., $$E_2 - E_1 = - P_2V_2 + P_1V_1$$

$\therefore$ $$E_2 + P_2V_2 = E_1 + P_1V_1$$

or $$H_2 = H_1.$$

$$\Delta H = \Delta E + P\Delta V = \Delta E + P(V_2 - V_1)$$

$$= \Delta E + w = q_P \text{ (heat absorbed at constant pressure)}$$

i.e., change in enthalpy is equal to heat absorbed at constant pressure.

Inversion temperature

If the gas in above expansion suffers a fall in temperature by dT, for a lowering of pressure dP, we can define Joule-Thomson coefficient (μ) by the relation,

$$\mu = \left(\frac{\delta T}{\delta P}\right)_H$$

μ is zero for an ideal gas ($PV = nRT$). For van der Waals gas,

$$\mu = \frac{2a}{RT} - b$$

The significance of μ is fall in temperature in degrees by a gas in free expansion for a pressure drop of 1 atm. under adiabatic conditions.

For gases having positive μ value cools on expansion but for H_2 gas μ is negative *i.e.,* H_2 warms up on expansion.

The cooling effect is seen when the temperature is low. But, if the temperature is high, then instead of cooling the gases are heated, *i.e.,* μ becomes negative. For every gas there is a temperature where $\mu = 0$, when neither heating nor cooling of the gases occurs on expansion after pasing through orifices. This temperature is called the "*inversion temperature*, T_i" of the gas.

Work done in a reversible isothermal expansion: Suppose n moles of a gas is enclosed in a cylinder by a frictionless piston (Fig. 4.3).

The cylinder is kept in a constant temperature bath *i.e.,* thermostat at T K. *i.e.,* isothermal condition is maintained. The gas has a volume V_1 and the piston is at point A. The gas is to be expanded from volume V_1 to volume V_2. The work of expansion (W) will be given by the product of opposing force and the displacement.

$$W = \text{force} \times \text{displacement}$$
$$= \text{force} \times \text{area} \times \text{distance}$$
$$= P \times a \times l.$$

At every step a minute distance (Δl) of the piston may be made so that work done (W) is,

$$W = P \times a \times \Delta l.$$

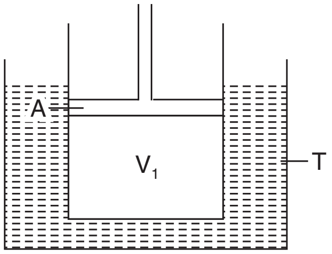


Fig. 4.3

$a \times \Delta l$ is the volume swept by the piston, it is dV

Then, $$W = \int_{V_1}^{V_2} P\,dV = \int_{V_1}^{V_2} \frac{nRT}{V}\,dV \qquad [\because \quad PV = nRT]$$

$\therefore$ $$W = nRT \ln \frac{V_2}{V_1}$$

Since, $\frac{V_2}{V_1} = \frac{P_2}{P_1}$ in an isothermal expansion of a perfect gas.

Then, $$W = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

So, for 1 mole of an ideal gas, work done (W) during reversible isothermal expansion is,

$$W = RT \ln \frac{V_2}{V_1}.$$

Enthalpy of a gaseous reaction

n_1 moles of reactant gases react to produce n_2 moles of gaseous products, thereby volume changes from V_1 to V_2 at constant temperature T and pressure P.

For n moles of an ideal gas, $PV = nRT$.

$$\therefore \quad P(V_2 - V_1) = (n_2 - n_1)\,RT.$$

or $$P\Delta V = \Delta n \,.\, RT.$$

From first law of thermodynamics, $\Delta H = \Delta E + P\Delta V$.

$$\therefore \quad \Delta H = \Delta E + \Delta n.RT.$$

When the reaction involves gaseous expansion,

Δn is positive, $\therefore \quad \Delta H > \Delta E$.

When the reaction involves gaseous contraction,

Δn is negative $\therefore \quad \Delta H < \Delta E$.

When there is no volume change, $\Delta H = \Delta E$.

Heat capacity

Heat capacity (C) of a substance is the amount of heat needed to raise the temperature of 1 gm of the substance by 1°C. Similarly, molar heat capacity of the substance is the amount of heat required to raise the temperature of 1 mole of the substance by 1°C.

Molar heat capacity at constant volume is C_v, which is molar heat capacity measured at constant volume condition.

If dq heat is required for dT increase in temperature then for 1 mole of substance,

$$C = \frac{dq}{dT}$$

At constant volume condition, $C_v = \left(\frac{\partial E}{\partial T}\right)_V$.

Molar heat capacity at constant pressure is measured by keeping the pressure constant

$$\therefore \quad C_p = \frac{dq}{dT} = \left(\frac{\partial H}{\partial T}\right)_P.$$

Relation between C_p and C_v:

We know, $$\Delta H = \Delta E + \Delta(PV)$$

or $$\frac{\Delta H}{\Delta T} = \frac{\Delta E}{\Delta T} + \frac{\Delta(PV)}{\Delta T}$$

or $$C_p = C_v + \frac{\Delta(PV)}{\Delta T}$$

For an ideal gas, $PV = RT$ (for 1 mole)

$$\Delta PV = R\Delta T$$

$$\therefore \quad C_p = C_v + \frac{R\Delta T}{\Delta T}$$

$$\therefore \quad C_p = C_v + R \quad \text{...for gas or} \quad \boxed{C_p - C_v = R}$$

for liquids and solids, $\Delta H = \Delta E$

$$\therefore \quad C_p = C_v.$$

Kirchoff's equation. (Influence of temperature on ΔH and ΔE). If a system undergoes a change from a given state (1) to another state (2) both the heat content and the internal energy will change. We can denote,

$$E_2 - E_1 = \Delta E \text{ and } H_2 - H_1 = \Delta H$$

Differentiating these two relations with respect to temperature at constant volume for E and at constant pressure for H, we get,

$$\left[\frac{\delta(\Delta E)}{\delta T}\right]_v = \left[\frac{\delta E_2}{\delta T}\right]_v - \left[\frac{\delta E_1}{\delta T}\right]_v = C_{v_2} - C_{v_1} = \Delta C_v$$

and
$$\left[\frac{\delta(\Delta H)}{\delta T}\right]_p = \left[\frac{\delta H_2}{\delta T}\right]_p - \left[\frac{\delta H_1}{\delta T}\right]_p = C_{p_2} - C_{p_1} = \Delta C_p$$

$$\therefore \quad \int \delta(\Delta E) = \int \Delta C_v \, dT$$

and
$$\int \delta(\Delta H) = \int \Delta C_p \, dT.$$

Integrating between the limits, T K and 0 K, we get,

$$\Delta E_T = \Delta E_0 + \int_0^T \Delta C_v \, dT. \quad \text{...(I)}$$

and
$$\Delta H_T = \Delta H_0 + \int_0^T \Delta C_p \, dT \quad \text{...(II)}$$

The equations (I) and (II) are called Kirchoff's equations.

For chemical reactions, the relation for ΔH is very important as most reactions take place at constant pressure.

$$\Delta H_{T_2} = \Delta C_p (T_2 - T_1)$$

Here, ΔC_p is the difference in the heat capacities of the products and the reactants constant pressure. But the C_p values often change with temperature.

Entropy

The heat change dq and temperature T are the thermodynamic quantities. Hence, fo system, the thermodynamic function $\frac{dq}{T}$ is independent of the path of transformation and denoted by S and the function has been called *entropy* by Clausius. Then by definition, $dS =$

The physical concept of entropy

If a system is left to itself, it gradually passes into a state of equilibriun equilibrium means a state of maximum disorder or chaos. Entropy has been measure of this disorder and chaos. The more a system approaches equilibriun the disorder and irreversibility and when equilibrium is reached, it has the maximum disorder. Thus, the entropy of the system goes on increasing and reaches a maximum value at equilibrium. For example, if a gas with strong odour is let loose at the corner of a room, the odour of the gas spreads all over the room randomly and equilibrium is reached when the entropy also becomes maximum.

Highlights:

- Prediction of direction of changes is possible with a thermodynamical quantity known as *entropy (S)*.
- A spontaneous change occurs in the direction leading to a total increase of entropy.
- It is convenient to calculate total entropy change in two parts. (*i*) the entropy change of the system and the entropy change of the surroundings *i.e.,*

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}.$$

- Gases generally have higher entropies than liquids.
- Entropy is a state function dependent on P, V, T and path independent.
- If system absorbs heat, entropy increases and vice-versa.
- Any irreversible process is accompanied by increase in entropy. As all spontaneous processes are irreversible, the entropy of the universe is ever increasing.
- Entropy is a measurement of randomness of a system.
- From experience we can say, disordered form is more probable than ordered form. So, increase of randomness enhances thermodynamic probability. Boltzmann expressed this idea by the relation, $S = k \ln w$, where S = entropy, k = Boltzmann constant, w = thermodynamic probability.

  As w is always greater than one, w increases when S increases.

Conversely, when an order to a system is brought, the entropy of the system decreases. For example, solidification of a liquid brings about orderly state and thereby entropy decreases.

In any system, only a part of the total energy is made available for useful work, some energy is always dissipated *i.e.,* wasted. The energy unavailable as work is proportional to the increase of entropy. The higher the entropy, the less the availability of work. Thus, entropy signifies unavailable form of energy of the system during transformation of heat into work.

Entropy of an ideal gas

In the case of a reversible expansion of an ideal gas in a container as in Fig. 4.3, the container is fitted with a frictionless movable piston at constant pressure P. The volume of the gas changes from V_1 to V_2. Since the process is reversible, the pressure on the gas is approximately equal to the external pressure P.

Hence, from 1st law of thermodynamics,

$$dq = dE + dW = dE + P\,dV. \qquad \text{...(III)}$$

Dividing both the sides of the equation (III) by T,

$$\frac{dq}{T} = \frac{dE}{T} + \frac{PdV}{T}$$

$$\therefore \qquad dS = C_v \,.\, \frac{dT}{T} + R\,\frac{dV}{V}.$$

Thus, for a change from states 1 to 2 we have,

$$\int_{S_1}^{S_2} dS = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

or,
$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}.$$

Since, for an ideal gas at constant temperature, $\frac{V_2}{V_1} = \frac{P_1}{P_2}$

$\therefore$
$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}.$$

At *constant temperature i.e.,* for isothermal expansion,

$$\Delta S_T = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}.$$

At *constant pressure P,*

$$\Delta S_p = C_p \ln \frac{T_2}{T_1}$$

At *constant volume* V,

$$\Delta S_v = C_v \ln \frac{T_2}{T_1}.$$

Entropy change in irreversible process

Entropy is a state function. The change of entropy of a given system from state 1 to state 2 is always the same and is path independent if the path is reversible. So, the change of entropy (ΔS) is given by:

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dq_r}{T}.$$

When the flow of heat is *irreversible*, let a heat reservoir at T_1 (state 1) is brought in contact with a second reservoir at T_2 (state 2) where $T_1 > T_2$, and small quantity of heat q flows from T_1 to T_2.

The decrease in entropy of state 1 = $\frac{q}{T_1}$

The decrease in entropy of state 2 = $\frac{q}{T_2}$

$\therefore$ Net change of entropy = $\frac{q}{T_2} - \frac{q}{T_1} = q \cdot \frac{T_1 - T_2}{T_1 T_2}$

The difference is a positive quantity, hence, the irreversible heat flow leads to increase in entropy.

Irreversible isothermal expansion of an ideal gas

Let n moles of an ideal gas is enclosed in a vessel of volume V_1. The vessel is connected to a vessel of volume V_2 by a tube containing stop cock, which is evacuated (Fig. 4.4). The vessels are kept in a thermostat of the temperature T. From the first law of thermodynamics, we have,

$$q = \Delta E + W$$

Now, if this expansion is carried out irreversibly at T K from volume V_1 to a volume $(V_1 + V_2)$ after opening the stop cock (Fig. 4.4). So we have,

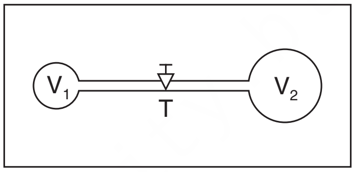


Fig. 4.4

$$q_{rev} = \Delta E + RT \ln \frac{V_1 + V_2}{V_1}$$

$$= 0 + RT \ln \frac{V_1 + V_2}{V_1}.$$

Since S is a state function, *ds* is a perfect differential, $\Delta S_{irr.}$ (system) would be same.

As there is no thermal change,

$$\Delta S_{surrounding} = 0$$

Hence, for the irreversible expansion of gas,

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding}$$

$$= R \ln \frac{V_1 + V_2}{V_1} + 0$$

$$= R \ln \frac{V_1 + V_2}{V_1} \text{ A positive quantity.}$$

Entropy change of a mixture of gases

From first law of themodynamics, we have,

$$dq = dE + PdV$$

Dividing both the sides of the above equation by T,

$$\frac{dq}{T} = \frac{dE}{T} + \frac{PdV}{T} = C_v \frac{dT}{T} + R \frac{dV}{V} \quad \text{(for 1 mol of gas)}$$

or, $$dS = C_v d(\ln T) + R d(\ln V)$$

or, $$S = C_v \ln T + R \ln V + S_0$$

where S_0 is a constant.

We know, $C_p - C_v = R$ for an ideal gas.

So, $$S = (C_p - R) \ln T + R \ln \frac{RT}{P} + S_0$$

or, $$S = C_p \ln T - R \ln P + S_0'$$

We cannot determine the absolute value of the entropy of an ideal gas. But the changes in entropy can be determined. Thus, if the temperature of an ideal gas changes from T_1 to T_2 and the volume from V_1 to V_2 for 1 mol. of the gas, we have,

$$S_1 = C_v \ln T_1 + R \ln V_1 + S_0$$
$$S_2 = C_v \ln T_2 + R \ln V_2 + S_0$$

$$\therefore \quad \Delta S = S_2 - S_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

For an isothermal change, we have

$$\Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}.$$

When two gases come in contact, they diffuse and mix-up irreversibly. Such a spontaneous irreversible process leads to an entropy increase.

Let, Moles of gas A is n_A
Moles of gas B is n_B
Temperature is T
Pressure is P

Then,

$$S_A = n_A\,[C_{P_A} \ln T - R \ln P + S_A{}^0]$$

$$S_B = n_B\,[C_{P_B} \ln T - R \ln P + S_B{}^0]$$

After mixing, the total pressure (P)

$$P = p_A + p_B.$$

The entropies of the two gases in the mixture are

$$S_A(\text{mix}) = n_A[C_{P_A} \ln T - R \ln p_A + S_A{}^0]$$

$$S_B(\text{mix}) = n_B[C_{P_B} \ln T - R \ln p_B + S_B{}^0]$$

So, change of entropy due to mixing,

$$\Delta S_{mix} = (S_{A_{mix}} + S_{B_{mix}}) - (S_A + S_B)$$

$$= S_{A_{mix}} + S_{B_{mix}} - S_A - S_B$$

or,

$$\Delta S = -\,n_A R \ln \frac{p_A}{P} - n_B R \ln \frac{p_B}{P}$$

The total moles of mixture = $n = n_A + n_B$ mol. fraction of A, $x_A = \dfrac{n_A}{n}$, $x_B = \dfrac{n_B}{n}$

Now, $\dfrac{p_A}{P} = x_A$ and $\dfrac{p_B}{P} = x_B$ (As mol. fraction = pressure fraction)

$$\therefore \quad \Delta S = -\,n_A R \ln x_A - n_B R \ln x_B.$$

or,

$$\Delta S_{mix} = -\,n\,R\left[\frac{n_A}{n} \ln x_A + \frac{n_B}{n} \ln x_B\right]$$

$$= -\,n\,R[x_A \ln x_A + x_B \ln x_B]$$

In general, for mixing any number of gases,

$$\Delta S_{mix} = -\,n\,R \sum x_i \ln x_i$$

where x_i = mol. fraction of gas i.

Work function (A)

Let us define, $A = E - TS$

For an isothermal process, $\Delta A_T = \Delta E - T\Delta S$ $(\because \quad \Delta T = 0)$

$$= \Delta E - q = -\,W_{max}$$

or,

$$-\,\Delta A_T = W_{max}$$

where W_{max} is reversible, hence, maximum work is involved. So, work function is such a thermodynamic property of the system that decreases in work function A *i.e.*, $(-\,\Delta A)$ gives the maximum amount of work available during isothermal process.

$$A = E - TS \text{ or } dA = dE - TdS - SdT = dE - dq - SdT$$
$$= -PdV - SdT.$$

So, for isochoric process $\left(\frac{\delta A}{\delta T}\right)_v = -S$, and for an isothermal process $\left(\frac{\delta A}{\delta V}\right)_T = -P$.

Free energy (G)

Two thermodynamic functions, which are very useful for physicochemical studies are:

- Gibb's free energy (G) and
- Helmholtz free energy or work function (A).

Gibb's free energy is related to enthalpy and entropy as,

$$G = H - TS.$$

$$\therefore \qquad \Delta G = \Delta H - T\Delta S. \text{ (at constant temperature).}$$

Free energy and useful work

Suppose a reversible change takes place at constant temperature T and at constant pressure P. The work of expansion of volume is expressed by PΔV and suppose the system does an additional amount of work which is denoted by useful work. Therefore, from the first law of thermodynamics, we have,

$$q = \Delta E + P\Delta V + W_{\text{useful}}$$
$$= \Delta H + W_{\text{useful}}$$

Now, since $q = T\Delta S$,

$$T\Delta S = \Delta H + W_{\text{useful}}$$
$$\therefore \qquad \Delta H - T\Delta S = -W_{\text{useful}}$$
$$= (\Delta G)_{P,\,T.}$$

or, $-(\Delta G)_{P,\,T} = W_{\text{useful}}.$

Hence, decrease in Gibb's free energy is a measure of the 'useful work' obtainable from the process.

Standard free energy change

G is a state function. To assign numerical values to free energy change of a system, it is necessary to assign a standard value for the free energy of a system at a specified state. The *standard state* is defined at constant pressure of 1 atmosphere and constant temperature *i.e.,* 25°C or 298 K.

Therefore, standard free energy change (ΔG°) is defined as the free energy change for a process taking place at standard state for the reactants and the products obtained are also in their standard states.

$$\therefore \qquad \Delta G^\circ = \Sigma G^\circ_{\text{(products)}} - \Sigma G^\circ_{\text{(reactants)}}$$

Relations of ΔG

(*i*) $\Delta G = W_{\text{useful}}$ (at constant T and P).

$= -nFE$ (n = number of electrons, F = Faraday and E = emf of a cell. This relation correlates free energy change to cell potential)

(*ii*) $\Delta G = \Delta H - T\Delta S$ (at constant T) (*iii*) $\Delta G° = -RT \ln K$

$= -2.303\ RT \log K.$

where R = gas constant, T = temperature in kelvin, K is the equilibrium constant of a reaction.

(*iv*) $\Delta G = 0$ (at equilibrium, at constant T and P).

At constant temperature and pressure always system tends to attain a position of minimum free energy which is the position of equilibrium.

Thus, for a spontaneous process, ΔG must be negative. If ΔG is negative, any change shall spontaneously occur. If ΔG is zero, the initial and the final states would be at equilibrium with each other and finally if ΔG is p*ositive,* the process will not take place spontaneously, but it may reverse.

Highlights:

- *First law* of thermodynamics states—the energy may change from one form to another, but the sum total of energy of the universe remains constant.
- Mathematical expression of first law:

$$\boxed{dE = dq - dW}$$

- Kirchoff's equation:

$$\frac{\Delta H_2 - \Delta H_1}{(T_2 - T_1)} = \Delta C_p.$$

- *Entropy* is a measure of randomness or disorder of a system. It is also defined as "unavailable energy". Entropy change, $\Delta S = \frac{q_{rev}}{T}$.
- *State function* is one which depends only on the initial and final states of the system but independent of the path followed *e.g.,* ΔG, ΔS, etc.
- *Free energy change* is a state function and is related to enthalpy change, entropy change and temperature by *Gibb's-Helmholtz equation* as

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

THERMOCHEMISTRY

All types of chemical reactions are accompanied by heat changes. The reactions in which heat is evolved are termed *exothermic* and in which heat is absorbed are *endothermic.*

The energy from chemical reactions comes from the breaking or formation of bonds. The thermal changes in chemical processes are governed by two general principles, both of which are corollaries of the first law.

A. Law of Lavoisier and Laplace. This law states that the heat change accompanying a chemical process in one direction is equal in magnitude but opposite in sign to that accompanying the same process taking place in the opposite direction.

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H = -92 \text{ kJ}$$

$$HCl(g) \longrightarrow \frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \qquad \Delta H = +92 \text{ kJ}$$

According to the first law, heat content (H) or energy content (E) of the initial reactants again returns to the same magnitude. As such, the net heat-content change or energy content change is zero *i.e.,* heat changes in the two directions must be equal in magnitude but opposite in sign.

B. Hess's Law of Constant Heat Summation. This law states that *for a chemical process the amount of heat evolved or absorbed is the same whether the process takes place in one or several steps. Let us take the example of formation of* CO_2 *in one step and two steps (a) and (b):*

$$C + O_2 = CO_2 \qquad \Delta H = -\,94.05 \text{ Kcal}$$

$$(a) \qquad C + \frac{1}{2}\,O_2 = CO \qquad \Delta H_1 = -\,26.42 \text{ Kcal}$$

$$(b) \qquad CO + \frac{1}{2}\,O_2 = CO_2 \qquad \Delta H_2 = -\,67.63 \text{ Kcal.}$$

Summing up we get, $\Delta H_1 + \Delta H_2 = (-\,26.42 - 69.63)$ Kcal

which illustrates the law $= -\,94.05$ Kcal.

From first law we find that ΔH_P and ΔE_V will be independent of the path.

The principal advantage of this law is that thermochemical equations can be treated as simple algebraic equations and the heat of formation, heat of transition, etc., which are difficult to measure experimentally can be easily found out by addition, subtraction, multiplication of the quantities *i.e.,* ΔH terms algebraically.

Highlights:

Hess's law is used to calculate:

- Enthalpy changes (ΔH) of formation from enthalpy changes of combustion.
- Enthalpy changes of reaction from enthalpy changes of formation.
- Lattice energies is the Born-Haber cycle.

(*i*) *Heat of reaction.* Heat of reaction (ΔH) is the difference between the heat contents of the products and the reactants, when molar quantities react and indicated by a balanced equation.

Example:

(*a*) $H_2 + Cl_2 = 2\,HCl$ +43,608 cals (exothermic)

(*b*) $H_2 + I_2 = 2\,HI$ –12,680 cals (endothermic)

Thus, the heat of reaction for the formation of 2 moles of HCl is 43,600 cal which is exothermic whereas for the formation of 2 moles of HI, 12,680 cal of heat is absorbed and the reaction is endothermic.

(*ii*) *Heat of combustion.* Heat change for the complete combustion of a gm-mole of the substance at a given temperature under normal pressure is called its heat of combustion. Combustion reactions are always exothermic, so heat of combustion is always negative.

In the case of organic compounds, complete combustion means when these compounds are converted finally to CO_2 and H_2O.

The heat of combustion is experimentally determined in a "bomb calorimeter" which is a pressure vessel internally enamelled with platinum (Fig. 4.5). The experimentally determined values of heat of combustion are useful.

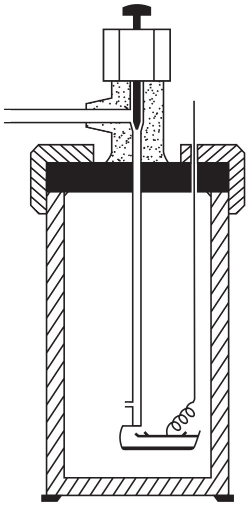


Fig. 4.5 Bomb calorimeter.

Example:

$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O \qquad \Delta H = -\,325 \text{ Kcal}$$

(*iii*) *Heat of neutralisation* of an acid or a base is defined as the amount of heat liberated (exothermic) when 1 gm equivalent of an acid is neutralized by one gm equivalent of base in large excess of water.

Example:

$$HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O \qquad \Delta H = -13.7 \text{ Kcal}$$

$$HCl(aq) + KOH(aq) \longrightarrow KCl(aq) + H_2O \qquad \Delta H = -13.7 \text{ Kcal.}$$

If the acid and base are both strong, they can be assumed to be completely dissociated, *i.e.,*

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

i.e.,

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

Therefore, the heat of neutralisation is really the heat of formation of 1 gm mole of water from 1 gm ion of hydrogen and hydroxyl ion, and this is always the equivalent of 13.7 Kcal of heat.

But when a weak acid or a weak base is neutralized, the heat of neutralisation deviates considerably from 13.7 Kcal.

(*iv*) *Heat of formation.* It is the amount of heat liberated or absorbed when one mole of the compound is formed from its constituent elements, all in their respective standard states and at a reference temperature. The standard enthalpy of formation (ΔH_f^o) is just the negative of the heat of formation.

In order to measure the change in enthalpy, it is needed to assume some arbitrary value for substances at a given state. Conventionally, the enthalpy of any element at 1 atm and 298 K is assumed to be 'zero'.

$$C_{(graphite)} + 2\,H_2\,(g) \longrightarrow CH_4(g) \qquad \Delta H_f = -74.8 \text{ kJ.}$$

The enthalpy of formation is related to the stability of compound. The lower the enthalpy of formation of a compound, the more stable is the compound. If the enthalpy of formation of a compound is positive, it means the energy content of the compound is greater than the energy content of its constituent elements and hence the compound is unstable. Whereas, when the enthalpy of formation of a compound is negative, the energy content of the corresponding compound is lower than its constituent elements and hence the compound is stable. Thus, the stability of a compound is inversely proportional to the enthalpy of formation of a compound.

Example:

ΔH_f of HI is + 26.9 kJ and ΔH_f of HF is – 161.7 kJ indicates the HF is much more stable than HI.

(*v*) *Heat of solution and heat of dilution.* The heat change taking place when 1 gm mole of the solute is completely dissolved in a solvent is called the heat of solution.

The heat of solution changes with concentration, *i.e.,* one gm mole of KCl dissolved in 50 moles of water and in 200 moles of water will cause different heat changes.

The value of heat of solution obtained graphically by extrapolating ΔH to infinite dilution is the integral heat of solution at infinite dilution.

At high dilution, the heat change becomes constant.

Example:

$$KCl(s) + 50\,H_2O = KCl\,(50\,H_2O) \qquad -4276 \text{ Cal.}$$

$$KCl(s) + 100\,H_2O = KCl\,(100\,H_2O) \qquad -4391 \text{ Cal.}$$

(*vi*) *Heat of fusion.* Heat change taking place when 1 mole of a substance changes from solid to its liquid phase at its melting point is known as the heat of fusion of the substance. Heat of fusion is always positive.

Example:

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H = 6 \text{ kJ.}$$

(*vii*) *Heat of vaporization.* It is the heat change involved in converting 1 mole of substance from liquid to the gaseous state at its boiling point. It is also positive.

Example:

$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H = 42 \text{ kJ.}$$

(*viii*) *Heat of sublimation.* It is the heat change involved in converting 1 mole of solid directly to its vapour at a temperature below the melting point of the substance.

Example:

$$I_2(s) \longrightarrow I_2(g) \qquad \Delta H = 62.4 \text{ kJ.}$$

Highlights:

- Enthalpy change is the exchange of energy between a reaction mixture (system) and its surroundings when the reaction takes place at constant pressure.
- The enthalpy change (ΔH) is calculated when starting temperature of the reactants and final temperature of the products are the same.
- The present unit of ΔH is kJ mol^{-1}.
- If ΔH is negative, the reaction is exothermic *i.e.,* the system loses energy to surroundings.
- If ΔH is positive, the reaction is endothermic *i.e.,* the system gains energy from its surroundings.
- The standard conditions for change of enthalpy (ΔH) are 298 K and 1 bar (100 kPa), the standard enthalpy change is represented by $\Delta H°_{298}$.
- It is impossible to measure $\Delta H°_{298}$ directly. Many values are determined indirectly using *Hess's law.*
- Values measured under nonstandard conditions are corrected to give the value under standard conditions.
- Enthalpy change for melting, sublimation, vaporisation are measured at m.p. or b.p.

Bond Energy

Bond energy is defined as the average energy required to break the bonds present in a molecule of gaseous compound, to atoms or radicals in gaseous form. Bond energy is also called the *heat of formation* of the bond. This energy is dependent on the nature of the atoms present as well as the environment.

Example. For water the energy of separating a H-atom is 118 Kcal, whereas this energy of separating the second H-atom from the residual OH group is 102 Kcal. This difference in bond energy is related to the more reactive nature of OH radicals than oxygen, towards H atoms to form stable molecules.

Taking average of the two bond energies we have

$$\frac{118 + 102}{2} = 110 \text{ Kcal for O—H bonds.}$$

Similarly, for CH_4 (methane) molecule, we can find the bond energy for C—H bonds by taking in average one-fourth of the total heat of formation of methane, *i.e.,*

$$\frac{396}{4} = 99 \text{ Kcal/mol.}$$

Alternatively, we can also take the average of the four different dissociation energies of C—H bond of methane.

Variation of bond energy

(*i*) Bond energy varies with the size of the atoms.

Example: bond energy for H—F and H—Cl are 56.5 and 43.1 kJ/mol, respectively.

(*ii*) Bond energy varies with the difference between the electronegativity of the two atoms. Bond energy decreases as H—F > H—H > C—C > N—N > F—F.

(*iii*) Bond energy varies with the total environment of the molecule.

Application of bond energies

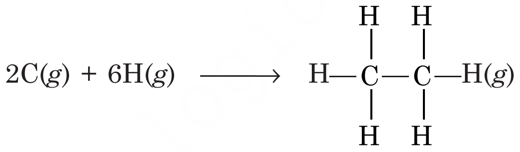
(*i*) The heat of reaction can be calculated from the bond energies since in a reaction certain bonds are formed and certain bonds are broken. So, the total enthalpy change involved in these bond breaking and making gives the heat of reaction.

i.e.,

$$\begin{aligned}\Delta H \text{ reaction} &= \Sigma\, \Delta H \text{ (bonds broken)} + \Sigma\, \Delta H \text{ (bonds formed)}\\ &= \Sigma \text{ Bond energy (reactants)} - \Sigma \text{ Bond energy (products)}\end{aligned}$$

(*ii*) Heat of formation can also be calculated from the average bond energy summation.

Example: Heat of formation of ethane is,



$$2C(g) + 6H(g) \longrightarrow H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}H(g)$$

$$\begin{aligned}\Delta H_f \text{ for ethane is} &= 1 \times \text{(bond energy for C—C)} + 6 \times \text{(bond energy for C—H)}\\ &= (1 \times 79.3 + 6 \times 98.5) \text{ Kcal.}\\ &= 670.3 \text{ Kcal mol}^{-1}.\end{aligned}$$

SECOND LAW OF THERMODYNAMICS

Heat is readily available and man is interested to convert this heat energy to useful work. Second law of thermodynamics guides the conditions under which heat and work are interconvertible. For the conversion of heat into work two conditions must be fulfilled.

1. Without the help of a "thermodynamic engine" the conversion of heat into work is impossible and the engine must work in a reversible cyclic process.

2. The engine must take up heat at higher temperature, convert a portion of it into work and give up the rest of heat to a body at lower temperature.

From the above experience, second law of thermodynamics can be stated in some different important forms,

(*a*) It is impossible to convert heat completely into an equivalent amount of work, without producing some other effects in the system.

(*b*) It is impossible for a self-acting machine unaided by any external agency, to convey heat from a body at a low to one at a high temperature.

(*c*) All spontaneous processes tend to equilibrium.

(*d*) The energy of the universe is constant, but the entropy approaches a maximum.

Effect of temperature on free energy-(Gibbs-Helmholtz equation)

We know,

$$\begin{aligned}H &= E + PV \text{ and } G = H - TS\\ &= E + PV - TS\end{aligned}$$

Differentiating, we get $dG = dE + PdV + VdP - TdS - SdT$

We know, $dq = dE + PdV$

$\therefore$ $dG = dq + VdP - TdS - SdT$

Again for reversible mechanical process $dS = \dfrac{dq}{T}$

$\therefore$ $dq = TdS$

$\therefore$ $dG = VdP - SdT$

$\therefore$ For an isobaric process $dG = -SdT$ $\quad\therefore\quad \left(\dfrac{\partial G}{\partial T}\right)_P = -S$

$$\therefore \quad \left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S.$$

We know $G = H - TS$

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

$$\therefore \quad \Delta G = \Delta H - T\left(\frac{\partial \Delta G}{\partial T}\right)_p$$

This is Gibbs-Helmholtz equation, which relates free energy and ethalpy changes at constant pressure.

Significance of Gibbs-Helmholtz equation

Gibbs-Helmholtz equation is a very useful equation in thermodynamics as it encompasses both the essence of first and second laws of thermodynamics and almost any relation of thermodynamics can be deduced from this equation.

We know that if ΔG is negative the reaction takes place spontaneously and when $\Delta G = 0$ *i.e.,* when the free energy of the reactants and the products are equal, the reaction attains equilibrium.

(*a*) When a reaction is exothermic *i.e.,* ΔH is neagtive, and ΔS is positive, ΔG has negative value and the reaction becomes spontaneous.

(*b*) In endothermic process, ΔH is positive, the reaction occurs if $T\Delta S$ is positive and greater than ΔH.

(*c*) When ΔH is negative and ΔS is also negative, the process will be spontaneous only when ΔH is greater than $T\Delta S$.

Hence, the *criteria for spontaneous processes* are:

(*a*) If ΔH is negative and ΔS is positive – ΔG becomes negative.

(*b*) If both ΔH and ΔS are negative and $\Delta H > T\Delta S$.

(*c*) If both ΔH and ΔS are positive and $T\Delta S > \Delta H$.

Application of thermodynamics to phase transition i.e., change of phase. (Clapeyron-Clausius equation)

Change of phase taking place during freezing, vaporization, etc. can be studied thermodynamically.

Let G_1 and G_2 be the free energies of a liquid and its vapour, which are in equilibrium at a temperature T. Imagine a very small change of a small amount of liquid vaporizing at equilibrium. The drop in free energy of the liquid is $-\Delta G_1$ and corresponding gain in free energy of the vapour is $+\Delta G_2$. Since the system is in equilibrium,

as net $\Delta G = 0 \quad \therefore \quad \Delta G_1 = \Delta G_2$

or, $V_1\Delta P - S_1\Delta T = V_2\Delta P - S_2\Delta T.$

or,
$$\frac{\Delta P}{\Delta T} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{V_2 - V_1}$$

Since,
$$\Delta S = \frac{q}{T}$$

$\therefore$
$$\frac{dP}{dT} = \frac{\Delta S}{V_2 - V_1} = \frac{q}{T(V_2 - V_1)}$$

where q is molar heat of transition from one phase to another.

Thus, $\frac{dP}{dT} = \frac{q}{T(V_2 - V_1)}$. This equation is the famous **Clapeyron-Clausius equation.**

Application of Clapeyron-Clausius equation

1. *Determination of latent heat.*

We know
$$\frac{dP}{dT} = \frac{q}{T(V_2 - V_1)}.$$

When two phases of liquid (Vol. V_1) and vapor (Vol. V_2) are in equilibrium, the volume V_1 of the liquid can be neglected as it is very small compared to the volume of vapor V_2.

$\therefore$
$$\frac{dP}{dT} = \frac{q}{T\,V_2} = \frac{L}{T\,V_2} \qquad (q = L = \text{latent heat of vaporization})$$

Now, for ideal gas $PV = RT$, *i.e.*, $V = \frac{RT}{P}$

$\therefore$
$$\frac{dP}{dT} = \frac{LP}{RT^2}$$

or,
$$\frac{dP}{P} = L \,.\, \frac{dT}{RT^2}$$

Assuming, latent heat is constant and on integrating,

$$\ln\frac{P_2}{P_1} = \frac{L}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \text{or,} \quad \log\frac{P_2}{P_1} = \frac{L}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

or,
$$\log\frac{P_2}{P_1} = \frac{L}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right].$$

Thus, from the vapour pressures P_1 and P_2 at different temperatures T_1 and T_2 we can determine the molar heat of vaporization with the integrated Clapeyron-Clausius equation.

2. *Effect of pressure on boiling point.* With the help of the integrated Clapeyron-Clausius equation we can determine the boiling point of a liquid at a different pressure when the boiling point of it is known at one pressure along with the latent heat of vaporization.

3. *Effect of temperature on vapour pressure of a liquid:* Again from the similar expression we can calculate the vapour pressure of a liquid at a different temperature if the vapour of it is known at a particular temperature alongwith its latent heat.

THIRD LAW OF THERMODYNAMICS

In 1912, Planck enunciated the third law of thermodynamics as "the entropy of a solid or a liquid is zero at the absolute zero of temperature".

At absolute zero temperature, kinetic energy of a substance is zero and it is present in a perfectly arranged crystalline state. So, there is no disorder and hence the entropy of all pure substances at absolute zero is zero.

- *Entropy and the third law*—Third law can be used to determine the entropy of a substance.

Absolute value of entropy can be measured by determining the heat capacities (C_p) of a substance at different temperature. These C_p values are plotted against T and can be extrapolated to T = 0. The area of the curve between T = 0 and the required temperature gives the value of absolute entropy of the substance at the required temperature.

Mathematically, we have

$$S_T - S_0 = \int_0^T \frac{C_p}{T}\, dT$$

From 3rd law, $S_0 = 0$. $\therefore$ $S_T = \int_0^T \frac{C_p}{1}\, dT = \int_0^T C_p \, d\ln T$

$$\therefore \quad S_T = \int_0^T 2.303\, C_p \, d\log T$$

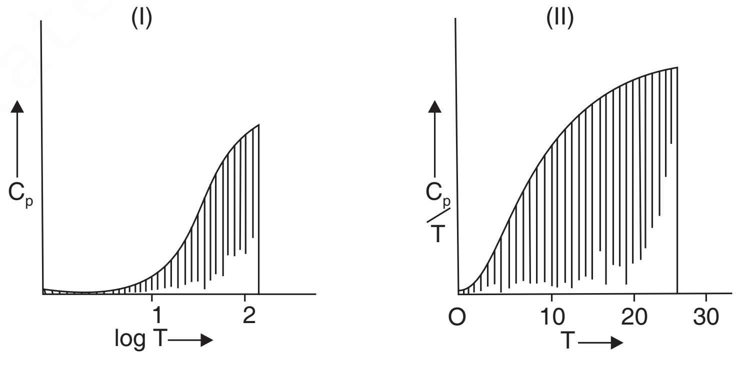


Fig. 4.6 Graphical determination of entropy.

Coupling of non-spontaneous reactions

Those chemical/biological reactions only take place spontaneously for which ΔG = negative. Many reactions occur in nature which have ΔG = positive only when they are coupled with another reaction whose ΔG is much larger negative. Hence, the energy required for the first reaction to occur is supplied by the second reaction which is coupled to it.

Example. Biochemical reaction in our body like oxidation of glucose releases large amount of energy and a part of this energy is utilised by our system to convert ADP (Adenosine diphosphates) to ATP (Adenosine triphosphate). ATP is a high energy molecule, so when in the cyclic process ATP is hydrolysed to ADP, free energy is released which can again be coupled to another biochemical reaction of our system that is non-spontaneous or requires energy. Thus, the energy of glucose oxidation can be utilised to carry out other non-spontaneous reaction via ATP.

Highlights:

- *Intensive property* is independent of the amount of substance present in the system *e.g.,* temperature, pressure, viscosity, surface tension, density, specific heat, refractive index, etc.
- *Hess's law states:* For a chemical process, the amount of heat evolved or absorbed is the same whether the process takes place in one step or in several steps.
- *Second law of thermodynamic states:* It is impossible to convert heat completely into work.
- ΔG is negative for a spontaneous reaction.
- ΔG is zero for reaction at equilibrium.
- ΔG is positive for non-spontaneous reaction.
- ΔS for a spontaneous process is $\Delta S > 0$.
- The entropy of the universe is increasing.
- *Third law of thermodynamics states:* The entropy of a solid or a liquid is zero at the absolute zero of temperature.
- *Clapeyron-Clausius equation is:*

$$\frac{dP}{dT} = \frac{q}{T(V_2 - V_1)}.$$

Spontaneity of changes of a system

- Many of the spontaneous processes are accompanied with a decrease in enthalpy but this statement is not always true, reactions with increasing enthalpy may also occur spontaneously.
- A spontaneous process always has a net increase in entropy for the computation of the change of entropy, the changes in entropy of both the system and the surrounding are to be considered when a system is in equilibrium,

$$dS_{total} = 0$$

For any spontaneous irreversible process,

$$dS_{total} > 0$$

When a reversible process is at equilibrium,

$$dS + dS' = 0$$

For a spontaneous process,

$$dS + dS' > 0$$

where dS and dS' are the changes of entropy of the system and the surroundings respectively.

- For a spontaneous process at a definite T and P, we can calculate ΔG of the system, if the ΔG is negative the change is spontaneous, if ΔG is zero the initial and final states of the system will be at equilibrium, if ΔG is positive the process is non-spontaneous.

Chemical Potential (μ)

Free energy per mole at a given temperature T and pressure (P) is called the *chemical potential* μ or $\overline{G}$.

Therefore, chemical potential, $\mu = \frac{G}{n}$ (for a pure substance).

For a species *i* which is component of a mixture we can express its chemical potential μ_i as follows.

$$\mu_i = \left(\frac{\partial G}{\partial n}\right)_{T,\,P,\,n_j}$$

where n_j represents the constant composition of a mixture.

It is to be noted that free energy is an extensive property but chemical potential is an intensive property.

Just like temperature, pressure or electric potential it tends to equalise within all parts of a system. Chemical potential also has such a tendency, that is why the study of chemical potential has become important.

Thus, chemical potential of water in ice must be same in both the phases. It can be proved easily. For the equilibrium,

$$\underset{(I)}{\text{Ice}} \rightleftharpoons \underset{(II)}{\text{Water}}$$

If *dn* moles are transferred from phase I to phase II,

$$dG = \mu(II)\,dn - \mu(I)\,dn$$

But for equilibrium, $dG = 0$, $\therefore$ $\mu(I) = \mu(II)$

Maxwell's Relations

1. $dE = TdS - PdV$
2. $dH = TdS + VdP$
3. $dA = -PdV - SdT$
4. $dG = VdP - SdT.$

Applying the cross-derivative rule, we have

(i) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$, (ii) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$,

(iii) $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$, (iv) $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$.

These four derivatives are very well known relations, which have extensive applications in both physical and chemical phenomena.

Chemical potential of an ideal gas at temperature, T.

We have,

$$dG = -Sdt + VdP$$
$$= O + VdP \text{ (at constant, T)}$$

$$\therefore \quad \Delta G = G_2 - G_1 = \int_1^2 VdP$$

Applying this to one mole of an ideal gas (PV = RT), we get,

$$G_2 - G_1 = RT \ln \frac{P_2}{P_1}$$

or, $$\mu_2 - \mu_1 = RT \ln \frac{P_2}{P_1}.$$

Since G_2 and G_1 are molar free energies μ_2 and μ_1 respectively, μ_1 becomes μ_ϕ^0 if we apply the standard conditions *i.e.,* pressure 1 atmosphere. We get,

$$\mu = \mu_\phi^0 + RT \ln P$$

or, $$G = G^0 + RT \ln P$$

where μ^0 is the standard chemical potential but not a constant, it is a function of T.

Gibbs-Duhem Relations

The free energy G of a system is a state function, that is, G depends upon P, T and V. As they are interrelated we can write for a fixed composition of a system,

$$G = f\,(P, T)$$

if we take an *open system* in which the quantities of the components may vary, the free energy then will depend upon the quantities of the components. Let us have a system containing n_1 moles of A_1, n_2 moles of A_2, etc., then the free energy (G) of the system is given by,

$$G = f\,(P, T, n_1, n_2\ , n_3 ...)$$

If all the variables vary, the complete differential will be given by,

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,\, n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,\, n_i} dT + \left(\frac{\partial G}{\partial n_1}\right)_{P,\, T,\, n_2,\, n_3} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P,\, T,\, n_1,\, n_3 ...} dn_2 + ...$$

We know, $$\left(\frac{\partial G}{\partial P}\right)_{T,\, n_i} = V \left(\frac{\partial G}{\partial T}\right)_{P,\, n_i} = -S.$$

$$dG = VdP - SdT + \left(\frac{\partial G}{dn_1}\right)_{P,\, T,\, n_2,\, n_3} dn_1 + \left(\frac{\partial G}{dn_2}\right)_{P,\, T,\, n_1,\, n_3} dn_2 ...$$

The term $\left(\frac{\partial G}{dn_2}\right)_{P,\, T,\, n_1,\, n_3 ...}$ means that P, T and all other moles are constant except n_2, this term is called the *partial molal free energy* of the component A_2, under this convention the chemical potential μ_i for the *i*th component of the mixture is given by,

$$\left(\frac{\partial G}{dn_i}\right)_{P,\, T,\, n_j}$$

At constant temperature and pressure, if we express partial molal free energies in terms of μ, we have,

$$dG_{P,T} = \mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 + ...$$
$$= \Sigma \mu_i\, dn_i \qquad ...(a)$$

Now at constant temperature and pressure, we increase the constituents by the same proportions Δx, the changed amounts of A_1 are $n_1 \Delta x$, of A_2, $n_2 \Delta x$ and A_i, $n_i \Delta x$.

Therefore,

$$dn_1 = n_1\,\Delta x,\ dn_2 = n_2\,\Delta x,\ dn_i = n_i\,\Delta x$$

Since, G is an extensive property, therefore it will increase by the amount $G\Delta x$

hence, $dG = G\Delta x$

So, we have,

$$dG = \mu_1 n_1 \Delta x + \mu_2 n_2 \Delta x + \ldots + \mu_i n_i \Delta x + \ldots$$

or, $$G\Delta x = \mu_1 n_1 \Delta x + \mu_2 n_2 \Delta x + \ldots + \mu_i n_i \Delta x + \ldots$$

Hence, $$G = \mu_1 n_1 + \mu_2 n_2 + \ldots + \mu_i n_i + \ldots = \Sigma \mu_i n_i$$

Now, complete differentiation of this equation gives us,

$$dG = (\mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \ldots) + (n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \ldots) \quad \ldots(b)$$

Subtracting equation (*a*) from (*b*)

$$n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \ldots = 0$$

We have thus three useful relations for chemical potentials with the composition of the system,

(*i*) $G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \ldots = \Sigma \mu n$

(*ii*) $dG = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \ldots = \Sigma \mu dn$

(*iii*) $0 = n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \ldots = \Sigma n d\mu$

These relations are commonly known as Gibbs-Duhem relations.

Deduction of Van't Hoff's reaction isotherm *(Application of thermodynamics to homogeneous equilibrium or thermodynamics of chemical equilibrium):*

Let us consider a general reaction

$$aA + bB \;\rightarrow\; cC + dD \quad \ldots(i)$$

We, know, $G = H - TS = E + PV - TS$ $\quad [\because\ H = E + PV]$

So, $dG = dE + PdV + VdP - TdS - S\,dT.$

Again, $dq = dE + PdV$ and $dS = dq/T$

$\therefore$ $dG = V.dP - S.dT$

At constant temperature, $(dG)_T = V.dP.$

Free energy change for one mole of any gas at a constant temperature is given by:

$$dG = V.dP = R.T\,\frac{dP}{P} \qquad \left[\because\ PV = RT \text{ or } V = \frac{RT}{P}\right]$$

Integrating both sides,

$$\int dG = RT \int \frac{dP}{P}$$

So, $$G = G^0 + RT \ln P \quad \ldots(ii)$$

where G^0 = integration constant known as standard free energy *i.e.,*

$G^0 = G$ when $P = 1$ atm.

Let the energy/mole of A, B, C and D at their respective pressures P_A, P_B, P_C and P_D are G_A, G_B, G_C and G_D, respectively. Then, free energy change for the reaction (*i*) is given by

$$\Delta G = G_{products} - G_{reactants}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \quad \ldots(iii)$$

Substituting the values of G_A, G_B, G_C and G_D from (*ii*) and (*iii*), we have

$$\Delta G = (cG_C^{\,0} + cRT \ln P_C + dG_D^{\,0} + dRT \ln P_D)$$
$$- (aG_A^{\,0} + aRT \ln P_A + bG_B^{\,0} + bRT \ln P_B)$$

$$= (cG_C^{\,0} + dG_D^{\,0} - aG_A^{\,0} - bG_B^{\,0}) + RT \ln \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

So, $$\Delta G = \Delta G^0 + RT \ln \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \qquad \ldots(iv)$$

Now, at equilibrium, $\Delta G = 0$

So, $$\Delta G^0 = -RT \ln \left[\frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}\right]_{eq}$$ $\Delta G°$ is a constant as G is a state function

$\Delta G°$ is the difference in free energy between the products and the reactants.

$$= -RT \ln K_{eq} \qquad \left[\text{where } K_{eq} = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}\right]$$

$$\therefore \qquad \Delta G^0 = -RT \ln K_{eq} \qquad ..(v)$$

Combining (*iv*) and (*v*), we have

$$\Delta G = -RT \ln K_{eq} + RT \ln \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

or, $$-\Delta G = RT \ln K_{eq} - RT \ln \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \qquad \ldots(vi)$$

This expression (*vi*) is called Van't Hoff reaction isotherm. It is of great importance as it gives a quantitative relation for free energy change accompanying a chemical reaction. $-\Delta G$ is called the **Affinity** of the reaction.

Highlights:

- $\Delta G° = -RT \ln K_{eq}$ when pressures of reactants and products are one (*i.e.,* P = 1).
- The above expression gives free energy change for a reaction.
- The above relation shows that equilibrium constant (K_{eq}) can be calculated from a table of standard free energy values.

Example 1. *One gm of water requires 536 calories of heat for conversion to steam at 100°C. Calculate the increase in internal energy per mol of water assuming water vapour to behave as an ideal gas.*

Sol. According to first law of thermodynamics

$$q = \Delta E - w$$

Here $$w = PV = RT = 2 \times 373 \text{ cals} = 746 \text{ cals}, \; q = 536 \times 18 \text{ cal mol}^{-1}$$

or, $$\Delta E = q - w = 9648 - 746 = 8902 \text{ cal mol}^{-1} = 8.902 \text{ Kcal mol}^{-1}.$$

Example 2. *The amount of work of a system is* 8.36×10^9 *ergs, after absorbing 990 cals. of heat. Calculate the internal energy change of the system.*

Sol. We have, $\Delta E = q - w$

Here $q = 990 \text{ cals} = \dfrac{990 \times 4.2}{10^3} \text{ kJ} = 4.13$

$$w = 8.36 \times 10^9 \text{ ergs} = \frac{8.36 \times 10^9}{10^7 \times 10^3} \text{ kJ} = 0.836 \text{ kJ}$$

$\therefore$ $\Delta E = 4.158 - 0.836 = 3.332$ kJ.

Example 3. *Calculate the work done by the following reaction at 27°C.*

$$\underset{1 \text{ mol.}}{Zn} + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$$

Sol. Here, $w = P(V_2 - V_1) = PV_2$ $[\because \; V_1 = 0]$

$= nRT = RT$ $[\because \; n = 1]$

$$= 8.314 \times (273 + 27) = \frac{8.314 \times 300}{1000} \text{ kJ.}$$

$= 2.4942$ kJ.

Example 4. *Calculate the heat of combustion at constant pressure of carbon. (Given* q_v *at 200°C is 97000 cals).*

Sol. $C(s) + O_2(g) = CO_2(g)$

Here $q_v = -97000$ cal.

mols of gaseous reactant, $n_1 = 1$

mols of gaseous product, $n_2 = 1$

$\therefore$ $\Delta n = n_2 - n_1 = 0.$

We have, $q_p = q_v + \Delta nRT.$

$= -97000 + 0 \times RT$

$= -97000$ cals.

So, $q_p = q_v$ (As $n_2 = n_1$)

Example 5. *Calculate the value of* ΔE *for the reaction at 500 K,* $Mg(s) + 2HCl(g) \rightarrow MgCl_2(s) + H_2(g)$ *(Given* $\Delta H = -109$ *Kcal).*

Sol. We know, $\Delta H = \Delta E + \Delta nRT.$

Here, $\Delta n = 1 - 2 = -1$, T = 500 K

$R = 2 \text{ cal deg}^{-1} \text{ mol}^{-1} = 2 \times 10^{-3} \text{ Kcal deg}^{-1} \text{ mol}^{-1}$

$\therefore$ $\Delta E = \Delta H - \Delta nRT = -109 - (-1) \times 2 \times 10^{-3} \times 500$

$= -108$ Kcal.

Example 6. *Heats of combustion of ethylene, hydrogen, and ethane are 337.2, 68.3, 372.8 Kcal* mol^{-1} *at a definite temperature. Calculate the heat of reaction of* $C_2H_4(g) + H_2(g) \longrightarrow C_2H_4(g)$ *at that temperature.*

Sol. Given,

(*i*) $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O,$ $\Delta H = -337.2$ Kcal.

(*ii*) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O,$ $\Delta H = 68.3$ Kcal.

(*iii*) $C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O,$ $\Delta H = -372.8$ Kcal

or, (*iv*) $2CO_2 + 3H_2O \longrightarrow C_2H_6 + \frac{7}{2}O_2,$ $\Delta H = +372.8$ Kcal.

Adding the equations (*i*), (*ii*) and (*iv*) we have,

$$C_2H_4 + 3O_2 + H_2 + \frac{1}{2}O_2 + 2CO_2 + 3H_2O \longrightarrow 2CO_2 + 2H_2O + H_2O + C_2H_6 + \frac{7}{2}O_2$$

($\Delta H = -32.7$ Kcal)

$\therefore$ $C_2H_4 + H_2 \rightarrow C_2H_6,$ $\Delta H = -32.7$ Kcal.

Example 7. *Calculate O—H bond energy from the following heats of reactions.*

$H_2(g) \rightarrow 2H(g),$ $\Delta H = 104$ *Kcal* ...(*i*)

$O_2(g) \rightarrow 2O(g),$ $\Delta H = 120$ *Kcal* ...(*ii*)

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g),$ $\Delta H = -58$ *Kcal* ...(*iii*)

Sol. From equation (*ii*)

$$\frac{1}{2}O_2(g) \rightarrow O(g), \quad \Delta H = 60 \text{ Kcal.}$$

From equation (*iii*), $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ $\Delta H = 58$ Kcal.

(*i*) + (*ii*) – (*iii*) gives = $H_2(g) + \frac{1}{2}O_2(g) + H_2O(g) \rightarrow 2H(g) + O(g) + H_2(g) + \frac{1}{2}O_2(g)$

i.e., $H_2O(g) \rightarrow 2H(g) + O(g),$ $\Delta H = 222$ Kcal.

We know that, there are two O—H bonds in a molecule of water, and for breaking of these two bonds energy requirement is 222 Kcal.

So, for dissociation of one O—H bond energy requirement is 222 ÷ 2 = 111 Kcal.

$\therefore$ O—H bond energy is 111 Kcal.

Example 8. *Calculate the enthalpy of formation of propane* (C_3H_8) *at 298 K. Given the standard enthalpies of combustion:*

$\Delta H^\circ_C\ (C_3H_8) = -2220\ kJ\ mol^{-1}$

$\Delta H^\circ_C\ (C) = -393\ kJ\ mol^{-1}$

$\Delta H^\circ_C\ (H_2) = -286\ kJ\ mol^{-1}.$

Sol. A thermodynamic cycle is drawn:

$$\begin{tikzcd}
3C(s) + 4H_2(g) + 5O_2(g) \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"] & & C_3H_8(g) + 5O_2(g) \arrow[dl, "\Delta H_3"'] \\
& 3CO_2(g) + 4H_2O(l) &
\end{tikzcd}$$

According to Hess's law – $\Delta H_1 = \Delta H_2 - \Delta H_3$

$$\Delta H_1 = \Delta H^\circ_f(C_3H_8)$$

$$\begin{aligned}\Delta H_2 &= 3\Delta H^\circ_C(C) + 4 \times \Delta H^\circ_C(H_2).\\ &= 3 \times (-393) + 4 \times (-286) \text{ kJ mol}^{-1}\\ &= -2323 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta H_3 = \Delta H^\circ_C = -2220 \text{ kJ mol}^{-1}$$

Hence, $\Delta H^\circ_f(C_3H_8) = (-2323) - (-2220) \text{ kJ mol}^{-1}$

$$= -103 \text{ kJ mol}^{-1}.$$

Example 9. *Calculate the enthalpy change of transition from yellow P to Red P from the given thermochemical cycle.*

Sol. Thermochemical cycle:

$$\begin{tikzcd}
\text{Yellow P} \arrow[rr, "\Delta H_T (\Delta H_1)"] \arrow[dr, "\Delta H_2", "2386 \text{ cals}"'] & & \text{Red P} \arrow[dl, "\Delta H_3"', "2113 \text{ cals}"] \\
& H_3PO_4 &
\end{tikzcd}$$

According to Hess's law – $\Delta H_T = \Delta H_2 - \Delta H_3$

$$= 2386 - 2113 \text{ cals} = 273 \text{ cals}.$$

Example 10. *The latent heat of evaporation of water at 100°C at constant pressure is 538 cal g^{-1}. If average C_p for water and steam are 1 cal g^{-1} and 8.1 cal mol^{-1}, respectively for the interval, calculate the latent heat of water at 150°C.*

Sol. Basis = 1 g.

$$\Delta H_{150^\circ} = ?; \ \Delta H_{100^\circ} = 538$$

$$C_p \text{ for water} = 1; \quad C_p \text{ for steam} = \frac{8.1}{18}.$$

$$\Delta C_p = 0.45 - 1 = -0.55.$$

$$T_2 - T_1 = 423 - 373 = 50 \text{ K}.$$

We have, $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$

$$\Delta H_{150^\circ} - \Delta H_{100^\circ} = -0.55(50)$$

$$\Delta H_{150^\circ} = \Delta H_{100^\circ} - 0.55 \times 50$$
$$= 538 - 0.55 \times 50 = 510.5 \text{ cal g}^{-1}.$$

Example 11. *Calculate the maximum work done for the isothermal reversible expansion of one mole of an ideal gas at 25°C from 2 atm to 1 atm.*

Sol. Maximum work $= 2.303 \text{ RT ln } \dfrac{P_1}{P_2}$

$$= 2.303 \times 8.31 \times 298 \log \frac{2}{1}$$
$$= 1.66 \times 10^3 \text{ J} = 1.66 \text{ kJ}.$$

Example 12. *Calculate the change of molar entropy during melting of ice. Given latent heat – 19.14 J g^{-1}.*

Sol. $dS = \dfrac{q_{rev}}{T}$

$$= \frac{19.14 \times 18}{273} = 1.26 \text{ J mol}^{-1}.$$

Example 13. *Calculate the change of molar entropy during the conversion of liquid oxygen to oxygen gas at its b.p. (– 182.9°C). Given L = 12.19 J g^{-1}.*

Sol. $dS = \dfrac{q_{rev}}{T}$

$$= \frac{12.19 \times 32}{(273 - 182.9)} = \frac{12.19 \times 32}{90.1} = 4.33 \text{ J mol}^{-1}.$$

Example 14. *Calculate change of entropy in isothermal reversible expansion of one mole of an ideal gas.*

Sol. We know that $\Delta E = 0$

Therefore, $q = W = \text{RT ln } \dfrac{V_2}{V_1}$

$$dS = \frac{q_{rev}}{T} = \text{R ln } \frac{V_2}{V_1}$$ [Positive quantity]

Example 15. *At what temperature will water boil when the atmospheric pressure is 528 mm Hg? Given latent heat of vapourisation of water is 545.5 cal g^{-1}.*

Sol. Here, $P_1 = 528$ mm of Hg; $P_2 = 1$ atm $= 760$ mm of Hg.

$T_1 = ?$; $T_2 = 100°\text{C} = 373$ K; $H_v = 545.5 \text{ cal g}^{-1}$

$= 545.5 \times 18 \text{ cal mol}^{-1}$

$= 9819 \text{ cal mol}^{-1}$.

$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$.

From the integrated form of Clausius-Clapeyron equation, we have

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\therefore \qquad \log \frac{760}{528} = 0.1582 = \frac{9819}{2.303 \times 1.987}\left[\frac{1}{T_1} - \frac{1}{373}\right]$$

or, $T_1 = 363$ K.

Example 16. *Calculate q, W, ΔE and ΔH for isothermal reversible expansion of an ideal gas at 27°C from a volume of 10 dm³ to 20 dm³ against a constant external pressure of one atmosphere?*

Sol. (*i*) Since operation is isothermal and the gas is ideal so, $\Delta E = 0$.

(*ii*) Now, from 1st law, $\Delta E = 0$ or $q = W$.

But, for a reversible process, work done by system,

$$W = P(V_2 - V_1)$$
$$= 1 \text{ atm } (20 - 10) \text{ dm}^3 = 10 \text{ atm dm}^3 = 10 \text{ atm L}$$
$$= 10 \text{ L atm} \times \left(\frac{8.314 \text{ J}}{0.0821 \text{ L atm}}\right) = 1012.7 \text{ J.}$$

(*iii*) $q = W = 1012.7$ J.

(*iv*) $\Delta H = \Delta E + P\Delta V = 0 + 1012.7 \text{ J} = 1012.7$ J.

Example 17. *A gas during expansion from 10 litre to 20 litre under 2 atmospheric pressure absorbs 300 cal. heat energy. Find the change in internal energy.*

Sol. Work done in an irreversible process is given by

$$W = P(V_2 - V_1) = 2(20 - 10) = 20 \text{ lit.atm.}$$
$$= (20 \times 24.25) \text{ cal} \qquad [\because \ 1 \text{ lit. atm} = 24.25 \text{ cal}]$$
$$= 485 \text{ cal.}$$

From the 1st law of thermodynamics,

$$q = \Delta E + W$$

or, $\Delta E = q - W = (300 - 485) \text{ cal} = -185$ cal.

So, internal energy will decrease by an amount of 185 cal.

Example 18. *The initial temperature and pressure for one mole of an ideal gas is (C_v = 5 cal) 27°C and 1 atm. Pressure is increased reversibly upto 7 atm and temperature is incremented to 90°C. Calculate the entropy change for the process.*

Sol. For one mole of an ideal gas the entropy change in a reversible process is

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

Here, $T_1 = 27°C = 300$ K; $T_2 = 90°C = 363$ K; $P_1 = 1$ atm; $P_2 = 7$ atm;
$C_p = C_v + R = (5 + 2)$ cal $= 7$ cal.

$$\therefore \qquad \Delta S = 7 \ln \frac{363}{300} + 2 \times \ln \frac{1}{7} = -2.5577 \text{ cal deg}^{-1}.$$

Example 19. *The value of K_p (equilibrium constant) of the reaction regarding ammonia synthesis at 27°C is 3.49×10^{-2} atm^{-1}. Thus find the value of K_p for the following reaction at 37°C.*

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g) + 11.2 \text{ Kcal.}$$

Consider the reaction to be independent of heat and temperature.

Sol. From Van't Hoff equation, we have

$$\ln \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Here, $T_1 = 27°C = 300\ K$; $T_2 = 37°C = 310\ K$.

$K_{P_1} = 3.49 \times 10^{-2}\ atm^{-1}$; $K_{P_2} = ?$

$\Delta H = -11.2\ Kcal = -11200\ cal$; $R = 1.987\ cal\ deg^{-1}\ mol^{-1}$.

$$\therefore \qquad \log \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{K_{P_2}}{3.49 \times 10^{-2}} = \frac{-11200}{2.303 \times 1.987}\left[\frac{310 - 300}{300 \times 310}\right]$$

or, $K_{P_2} = 1.9038 \times 10^{-2}\ atm^{-1}$.

SHORT QUESTIONS AND ANSWERS

Q. 1. State First law with mathematical expressions.

Ans. See text page 68. Alternatively, it can be stated as the net energy of the universe remains constant.

Q. 2. State intensive property of a system.

Ans. See text page 66.

Q. 3. Why is enthalpy more useful than internal energy?

Ans. Internal energy and ethalpy of a system are measured by keeping the volume and the pressure constant, respectively. Since, in most of the reactions, they occur at atmospheric pressure, so enthalpy is more useful than internal energy.

Q. 4. The molar heat of sublimation of a solid is always greater than the molar heat of vaporization of the corresponding liquid. Why?

Ans. Since the molar heat of sublimation is the summation of heat of melting and heat of vaporization so it is always greater than the heat of vaporization of the corresponding liquid.

Q. 5. When does the entropy of a substance become zero?

Ans. The entropy of a substance becomes zero when the substance is perfectly crystalline *i.e.,* ordered state and at the temperature of 0 K.

Q. 6. Derive Clapeyron-Clausius equation and mention its applications.

Ans. See text page 84.

Q. 7. Derive Gibbs-Helmholtz equation and mention its significance.

Ans. See text page 85.

Q. 8. What is enthalpy?

Ans. See text page 71.

Q. 9. What do you mean by entropy?

Ans. Entropy is the measurement of randomness *i.e.,* disorder of the system. Its change *i.e.,* dS is defined as $dS = \frac{q_{\text{reversible}}}{T}$.

Q. 10. What are the limitations of first law of thermodynamics?

Ans. The first law does not indicate:

(*i*) Whether the transformation of intrinsic energy of a substance would occur at all.

(*ii*) If it so occurs, then to what extent or in which direction would the transformation take place.

Q. 11. Apply the first law of thermodynamics for the following cases (*a*) adiabatic change, (*b*) cyclic process.

Ans. (*a*) For adiabatic change

$$q = 0$$

So, from first law, $\Delta E = q - W$ or $\Delta E = 0 - W$ $[\because \quad q = 0]$

So, $W = -\Delta E$

So, in adiabatic process, the work done by the system is equal to the decrease in internal energy.

For cyclic process the internal energy does not change at all, *i.e.,* $\Delta E = 0$.

So, from first law, $\Delta E = q - W$

or $0 = q - W$ $[\because \quad \Delta E = 0]$

or $W = q$.

So, in cyclic process the work done by the system is equal to the amount of heat absorbed by the system.

Q. 12. Define reversible and irreversible processes.

Ans. See page 69.

Q. 13. Distinguish between adiabatic and isothermal changes.

Ans.

Isothermal change	Adiabatic change
(*a*) Temperature of the system remains constant.	(*a*) Heat exchange between the system and the surrounding does not occur.
(*b*) Change in internal energy does not take place.	(*b*) Internal energy of the system changes.
(*c*) PV = Constant for such process.	(*c*) PV^{γ} = constant for such process.

Q. 14. Write down the expression for maximum work done in an isothermal reversible process.

Ans. $W = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$.

Q. 15. Write the expression for work obtained in an isothermal irreversible reversible process.

Ans. $W_{irr} = P_2(V_2 - V_1)$.

Q. 16. Define C_p and C_v. State relation between them.

Ans. See page 73.

Q. 17. Explain that Joule-Thomson experiment is isoenthalpic.

Ans. See page 71.

Q. 18. What is inversion temperature?

Ans. See page 72.

Q. 19. State with example the significance of Hess's law.

Ans. See page 81.

Q. 20. State the law of Laplace and Lavoisier.

Ans. See page 80.

Q. 21. Define (*a*) heat of formation, (*b*) heat of combustion, (*c*) heat of neutralisation.

Ans. See page 81, 82.

Q. 22. State the second law of thermodynamics.

Ans. See page 84. Alternatively it can be stated as the net entropy of the universe tends to a maximum.

Q. 23. What do you mean by a cyclic process?

Ans. See page 70.

Q. 24. State Maxwell's relations.

Ans. See page 89.

Q. 25. Define work function and free energy.

Ans. See pages 78 and 79.

Q. 26. How can you measure a spontaneous system with the help of free energy?

Ans. See text page 79.

Q. 27. What do you mean by $\Delta G°$ for the reaction $H_2 + \frac{1}{2} O_2 = H_2O$ is – 54.65 Kcal at 25°C?

Ans. It means that if a mole of H_2 and $\frac{1}{2}$ mole of O_2 both at unit pressures at constant temperature (25°C), the decrease in free energy is 54.65 Kcal.

EXERCISES

1. *Short Questions:*
    - (*i*) Derive an expression for the variation of heat of reaction with the temperature with the help of first law of thermodynamics.
    - (*ii*) Derive Clapeyron-Clausius equation and state its applications.
    - (*iii*) Define the concepts of Helmholtz free energy and Gibb's free energy. Describe a relation between the two.
    - (*iv*) What is the significance of entropy? What is the criteria for spontaneity?
    - (*v*) Derive Kirchoff's equation. It is based on which law? Explain.

(*vi*) What is Joule-Thomson effect?

(*vii*) What is bond energy? How can you calculate the bond energy of C—C bond in ethane?

(*viii*) Write notes on (*a*) Heat of formation, (*ii*) Heat of combustion.

(*ix*) State Hess's law and explain how it can be used to calculate the heats of formation.

(*x*) Why is entropy a state function?

2. *Objective Type Questions:*

(*i*) Which is a state function?

(*a*) q (*b*) W (*c*) $q - W$ (*d*) q/W.

(*ii*) Which is an extensive property?

(*a*) Temperature (*b*) Viscosity (*c*) Volume.

(*iii*) Which is an intensive property?

(*a*) Pressure (*b*) Time (*c*) Volume.

(*iv*) When is a system in equilibrium?

(*a*) ΔG is zero (*b*) ΔS is minimum (*c*) ΔG is maximum.

(*v*) Heat of neutralization of a strong acid with a strong base is constant since

(*a*) Salts are formed. (*b*) Only H^+ and OH^- ions react in each case.

(*c*) Strong acid and strong base react completely.

(*vi*) The expression of first law of thermodynamics is

(*a*) $q = \Delta H - W$ (*b*) $\Delta H + P\Delta V = \Delta E$ (*c*) $\Delta E = q - W$.

(*vii*) All naturally occurring processes proceed spontaneously to

(*a*) increase in free energy (*b*) decrease in free energy (*c*) decrease in entropy.

(*viii*) All living systems are

(*a*) adiabatic systems (*b*) Closed systems (*c*) Open system.

(*ix*) Entropy of a system changes during melting. During melting it

(*a*) decreases (*b*) increases (*c*) remains unchanged.

(*x*) On increasing pressure, boiling point of water

(*a*) remains unchanged (*b*) increases (*c*) decreases.

3. (*a*) What do you mean by thermodynamics?

(*b*) Explain the terms— (*i*) Isolated system, (*ii*) Closed system, (*iii*) Extensive properties, (*iv*) Intensive properties, (*v*) Reversible process, (*vi*) Irreversible process, (*vii*) Isothermal process, (*viii*) Adiabatic process, (*ix*) Isochoric process, (*x*) Isobaric process, (*xi*) State function.

(*c*) Give the mathematical expression for first law of thermodynamics.

4. (*a*) What is Joule-Thomson effect?

(*b*) Prove the constancy in Joule-Thomson expansion.

(*c*) What do you mean by inversion temperature?

5. Derive an expression for the work done during reversible isothermal expansion of an ideal gas.

6. (*a*) Show that for a gaseous expansion, $\Delta H > \Delta E$.

(*b*) Define molar heat capacities.

(*c*) Prove that $C_p - C_v = R$.

7. Derive Kirchoff's equation.

8. (*a*) What do you mean by entropy?

(*b*) Give physical significance of entropy.

(*c*) Give characteristics of entropy.

(*d*) Explain the relation: $S = k \ln w$.

9. Derive an expression for entropy for an ideal gas.

10. Show that entropy change in an irreversible process is positive.

11. Show that entropy change for an irreversible isothermal expansion of an ideal gas is positive.

12. Entropy change for the mixture of gases can be represented by

$$-\Delta S_{mix} = -nR\,\Sigma\,x_i \ln x_i \qquad \text{where } x_i = \text{mole fraction of gas.}$$

13. (*a*) What do you mean by work function (A)?

(*b*) What do you mean by free energy (G)?

(*c*) What is the relationship between free energy and useful work?

(*d*) What do you mean by standard free energy change?

14. (*a*) State Hess's law.

(*b*) Mention the applications of Hess's law.

(*c*) Explain the terms (*i*) Heat of reaction, (*ii*) Heat of combustion, (*iii*) Heat of neutralisation, (*iv*) Heat of formation, (*v*) Heat of solution, (*vi*) Heat of fusion, (*vii*) Heat of vaporisation, (*viii*) Heat of sublimation.

15. How can you determine the bond energy and lattice energy with the help of Hess's law?

16. (*a*) Derive Gibbs-Helmholtz equation.

(*b*) Give the significance of Gibbs-Helmholtz equation.

17. Derive Clausius-Clapeyron equation.

18. (*a*) How can you determine spontaneity of changes of a system?

(*b*) What do you mean by chemical potential (μ)?

(*c*) Show that chemical potential does not change during phase transfer of a compound.

19. Derive Maxwell's relation and state its usefulness.

20. Derive an expression for chemical potential at a temperature T in terms of P.

21. Derive Gibbs-Duhem relations.

22. What do you mean by Van't Hoff reaction isotherm? Derive an expression for the reaction isotherm of the general reaction $aA + bB + \ldots \rightleftharpoons lL + mM + \ldots$.

Long Questions

1. When ice melts at 0°C, the latent heat of fusion is 80 cals. g^{-1}. The density of ice is 0.82 and of water of unity. Calculate ΔE, ΔH, *q* and *w* per mole.

(1440.1 cals; 1440 cals; 1440; cals; – 4.01 × 10^6 ergs)

2. Calculate ΔE and ΔH if 10 litres of helium at N.T.P. are heated inside a gas cylinder to 100°C assuming it to behave ideally and having $C_v = \frac{3}{2}R$. [**Ans.** 133.8; 223.1 cals]

3. A system performs 8.36 × 10^9 ergs work after absorbing 990 cals. heat from the surrounding. Find the internal energy change of the system. [**Ans.** 790 cals]

4. The volume of a 45 g nitrogen gas is expanded from 5 litre to 10 litre at 25°C isothermally and reversibly. Considering the gas to be an ideal find out the work obtained in this case.

[**Ans.** 2.788 × 10^7 ergs]

5. During isothermal reversible expression of 4 g of helium gas at 27°C the pressure reduces from 10 atm to 1 atm. Calculate the work done in calories. Consider the gas to behave like an ideal.

[**Ans.** 1381.8 cals]

6. The heats of formation of CO_2 from diamond and graphite are – 94500 and – 94050 cal, respectively. What is the enthalpy change in the transformation of diamond to graphite? [**Ans.** – 450 cal]

7. Calculate the heat of oxidation of ethyl alcohol to carbon dioxide, when the heats of formation of carbon dioxide and liquid water are given as – 94.05 and – 68.32 Kcal. The heat of formation of ethyl alcohol is – 66.4 Kcal. [**Ans.** 326.6 Kcal]

8. Find heat of formation of caustic soda from the following data:

$$\text{Na} + \text{H}_2\text{O} = \text{NaOH}\ (aq) + \frac{1}{2}\ \text{H}_2 + 98{,}000$$

$$\text{H}_2 + \frac{1}{2}\ \text{O}_2 = \text{H}_2\text{O} + 68{,}380$$

$\text{NaOH} + \text{water} = \text{NaOH}\ (aq) + 13{,}300$. [**Ans.** 153080 cals]

9. Calculate the heat of formation of benzene given that the heats of combustion of benzene, carbon and hydrogen are 754300 cals, 94380 cals and 68380 cals, respectively. [**Ans.** – 17120 cals]

10. Isothermally at 27°C one mole of a van der Waal's gas expands reversibly from 2 litres to 20 litres. Calculate the work done if $a = 1.42 \times 10^{12}$ dynes cm^4 mol^{-1} and $b = 30$ c.c mol^{-1}.

[**Hint.** $W = RT \ln \dfrac{V_2 - b}{V_1 - b} + a\left[\dfrac{1}{V_2} - \dfrac{1}{V_1}\right]$.

$$W = 2.303 \times 8.31 \times 10^7 \times 300 \log \frac{20 - 0.03}{2 - 0.03} + 1.42 \times 10^{12}\left[\frac{2000 - 20000}{20000 \times 2000}\right] \text{ergs}$$

$= 5677 \times 10^7$ ergs.]

11. 70 g of nitrogen gas was initially at 50 atm and 25°C. It was allowed to expand isothermally against a constant external pressure of one atmosphere. Calculate ΔQ, ΔW, ΔU, ΔH.

[**Ans.** 1.5 Kcal; 1.5 Kcal; 0; 0]

12. From the following bond enthalpies calculate ΔH for the reaction, $H_2 + Br_2 \rightarrow 2\ HBr$. Bond energy H—H = 435.24 kJ mol^{-1}; Br—Br bond energy = 192.5 kJ mol^{-1}; H—Br bond energy = 368.3 kJ mol^{-1}. [**Ans.** – 108.86 kJ]

13. The heat of combustion of methyl alcohol is – 173.65 Kcal. Given, $\Delta H_{(H_2O,\ l)} = -\ 68320$ cal; $\Delta H_{f\,(CO_2,\ g)} = -\ 94050$ cal. Evaluate the heat of formation of methyl alcohol. [**Ans.** – 57040 cal]

14. Calculate ΔS, ΔA and ΔG for vaporisation of 2 moles of benzene (b.p. = 353.2 K and G = 101 cal g^{-1})

[**Ans.** $\Delta S = 44.5$ cal/°K, $\Delta G = 0$, $\Delta A = -\ 1.4$ Kcal]

15. The van der Waal's constant for CO_2, $a = 3.59$ litre^2 atm/mol^{-2} and $b = 0.043$ litre mol^{-1}. What is the inversion temperature of the gas? [**Ans.** 2036 K]

16. The sp. heat of benzene is 0.39. Find the change in entropy when 1 kg of benzene at 10°C is mixed with 4.0 kg of benzene at 30°C. [**Ans.** 0.9879 eV]

17. Calculate the entropy change in vaporisation of ether. Given, boiling point = 35°C, L = 6500 cal mol^{-1}. [**Ans.** 21.1 eV]

18. Calculate the free energy change of g mole of SO_2 at 25°C and 10 atm pressure. Given, $\Delta G°_{298} = -\ 71.8$ Kcal mol^{-1}. (**Ans.** – 70.43 Kcal/mol^{-1}]

19. ΔG and ΔH for a particular reaction at 127°C are – 12 Kcal and 17.5 Kcal. Find out ΔS.

[**Ans.** – 13.75 eV]

20. The vapour pressure of water at 90°C is 530 mm Hg. The average latent heat of vaporisation of water is 546 cal g^{-1} within the temperature range 90°C – 100°C. Calculate the vapour pressure at 100°C. [**Ans.** 760 mm Hg]

5

Reaction Dynamics/Chemical Kinetics

INTRODUCTION

From the study of chemical equilibrium involving law of mass action, we can predict how far the reaction would go. But can say nothing about how fast the equilibrium will attain. Though thermodynamics has got an enormous influence in chemical equilibrium yet has no valid application in studying the rate of reaction. The passage towards equilibrium takes some time which may be almost instantaneous or very long. The velocity of a reaction is not same even at constant temperature. Every chemical reaction has a definite velocity at a definite temperature. Modern techniques have been developed to study the reaction rate which gets completed in milliseconds or even in microseconds.

But there are several other reactions where the rate can be easily measured. As for example:

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Velocity of Reaction

From law of mass action, we know that the rate of reaction is dependent on the active masses of reacting substances. Actually active mass means 'molar concentration'.

For a reaction $\longrightarrow aA + bB \rightleftharpoons cC + dD$

rate of reaction, $(r) \rightarrow$

$$r = k\ .\ [A]^a\ .\ [B]^b$$

where [A] and [B] are the concentrations of the reactants at that instant.

k is a constant known as *rate constant* or *specific reaction rate.*

When $[A] = [B] = 1$

then, $k = r.$

In this case, the rate constant will express the rate of the reaction, *i.e.,* the rate constant is called specific reaction rate.

Highlights:

- Higher the value of k higher the reaction rate.
- Reaction rate is determined by the decreasing concentration of the reactants in unit time.
- The rate of a reaction can also be determined by the increasing concentration of the products in unit time.
- Mathematically $r = -\dfrac{dc}{dt} = \dfrac{dx}{dt}$

  where c = concentration of the reactant,
  x = concentration of the product.

To consider the rate of a reaction, we should take into account the 'order' and the 'molecularity' of a reaction.

Order of a Reaction

The rate of reaction will definitely depend on the concentration of the reactants. Therefore, the rate equation will involve the concentration of the reactants. In the experimentally determined rate equation, the powers of the concentration terms are added to get the order of a reaction. As for example, for a reaction:

$$aA + bB \longrightarrow \text{Products}$$

rate of the reaction (r) = $k \cdot [A]^a \cdot [B]^b$.

So, the order of the reaction will be = ($a + b$).

The experimentally determined rate equation for the decomposition of H_2O_2 is:

$$r = k \cdot [H_2O_2]$$

Here we see rate is proportional to the first power of the concentration of H_2O_2. So it is a **first order** reaction.

Table 5.1

Reactions	*Experimentally determined rate*	*Order*
(*i*) $2HI = H_2 + I_2$	$r = k \cdot [HI]^2$	2
(*ii*) $H_2 + I_2 = 2HI$	$r = k \cdot [H_2][I_2]$	2
(*iii*) $CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH$	$r = k[CH_3COOC_2H_5]\ [NaOH]$	2

Highlights:

- The number of molecules of the equation for the chemical change has got no relation with the order of a reaction.
- The order of a reaction will be determined by the power terms of the concentrations of the rate equation.
- The order of a reaction may be zero or fraction.

Molecularity of a Reaction

The minimum number of molecules, atoms or ions taking part in a chemical reaction is known as molecularity of the reaction. As for example

$$2HI = H_2 + I_2$$

For this reaction, minimum two molecules of HI will be required. So, the molecularity is 'two'. Again for the reaction:

$$2H_2O_2 = 2H_2O + O_2$$

But the reaction can be written as

$$H_2O_2 = H_2O + O$$

So, for decomposition of H_2O_2, one molecule is needed and hence the molecularity is one.

Highlights:

- For the reaction

$$2N_2O_5 = 4NO_2 + O_2,$$

$$\text{The observed rate} = k \,.\, [N_2O_5]$$

So, the order of the reaction is one and the molecularity is two.

- $$2NO + O_2 = 2NO_2$$

$$\text{Rate} = k \,.\, [NO]^2\, [O_2]$$

So, both the order and the molecularity of the reaction are three.

- For the reaction

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$

$$\text{The observed rate} = k \,.\, [BrO_3^-]\, [Br^-]\, [H^+]^2$$

So, the order of the reaction is four but the molecularity is twelve.

- For the reaction

$$CO + Cl_2 = COCl_2$$

$$\text{Rate} = k \,.\, [CO]\, [Cl_2]^{1.5}$$

So, the order of the reaction is 2.5 and the molecularity is 2.

Mathematical Formulation of First Order Reaction

The reactions, where the experimentally determined rate of the reaction is dependent on the first power of the concentration of the reactant, are called first order reactions.

If c be the concentration, then the rate of the reaction $= -\dfrac{dc}{dt} = kc$.

where k = rate constant.

Let the reaction be

$$\underset{(a-x)}{A} \longrightarrow \underset{x}{\text{Products.}}$$

At time 't', a = initial concentration of A.

x = concentration of the product at time t.

Therefore, the rate equation will be

$$\frac{dx}{dt} = k \,.\, (a-x)$$

or

$$\frac{dx}{a-x} = k \,.\, dt.$$

Integrating we have,

$$-\ln (a-x) = kt + z$$

where z = integration constant

when $t = 0, \quad x = 0$

Then, $-\ln a = z$

So, $-\ln (a-x) = kt - \ln a$

or

$$\ln \frac{a}{a-x} = kt$$

or
$$k = \frac{1}{t} . \ln \frac{a}{a - x}$$
$$= \frac{2.303}{t} . \log \frac{a}{a - x}.$$

- The rate equation can be written as

$$\ln \frac{(a - x)}{a} = - kt$$

or
$$\frac{a - x}{a} = e^{-kt}$$

or
$$(a - x) = a \,.\, e^{-kt}$$

or
$$x = a(1 - e^{-kt}).$$

- The above equation expresses a number of characteristics of a first order reaction—

(*i*) $\frac{a}{a - x}$ is a common ratio, it is purely a dimensionless number. So, for any unit of concentration, the value of k will be same.

(*ii*)
$$k = \frac{1}{t} \,.\, \ln \frac{a}{a - x}.$$

So, unit of k will be time^{-1}.

(*iii*)
$$k = - \frac{dc}{dt}\Big/ \text{C} = - \frac{dc/\text{C}}{dt} = \frac{\text{fraction of reactants}}{\text{time}}$$

So, k is change of fraction of reactants in unit time.

(*iv*) From the equation,

$$t = \frac{1}{k} \,.\, \ln a/(a - x)$$

The half-life of a first order reaction can be calculated

$$t_{1/2} = \frac{1}{k} . \ln \frac{a}{a - \frac{a}{2}} \quad \left[x = \frac{a}{2}\right]$$
$$= \frac{1}{k} \,.\, \ln 2$$
$$= \frac{2.303}{k} . \ \log_{10} 2 = \frac{0.693}{k}.$$

(*v*) For complete reaction $x = a$, then the equation

$x = a(1 - e^{-kt})$ will be

$$a = a(1 - e^{-kt})$$

$\therefore$ $t =$ infinity.

So, a first order reaction is never completed.

- If we put $a - x = c$ *i.e.,* concentration at any time 't' and $a = c_0$, we have, $kt = \ln \frac{c_0}{c}$

$\therefore$
$$c = c_0 \,.\, e^{-kt}$$

Therefore,
$$\log c = \frac{- k}{2.303t} + \log c_0$$

$\therefore$ log c is plotted against 't' we get a straight line with a negative slope $= \frac{- k}{2.303}$.

Examples of a First Order Reaction

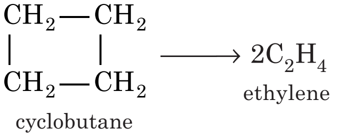
(*i*) Decomposition (gas phase)

(*a*) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

(*b*) $N_2O_4 \longrightarrow 2NO_2$

(*c*) $CH_3CH_2Cl \longrightarrow C_2H_4 + Cl_2$

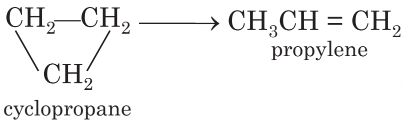
(*d*)



$$\begin{array}{c}CH_2-CH_2\\ |\qquad\ \ |\\ CH_2-CH_2\end{array} \longrightarrow 2C_2H_4$$

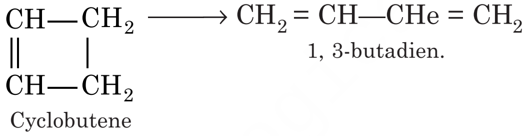
(*ii*) Isomerisation (gas phase)

(*a*)



$$CH_3CH = CH_2$$

(*b*)

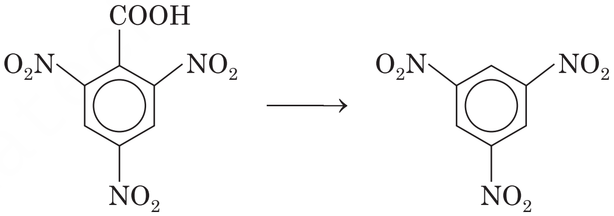


$$\begin{array}{c}CH-CH_2\\ \|\qquad\ |\\ CH-CH_2\end{array} \longrightarrow CH_2 = CH—CHe = CH_2$$

(*iii*) Decomposition (solution phase)

(*a*) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

(*b*)



(*iv*) Hydrolysis

$$\underset{\text{Cane Sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(*v*) Solvolysis

$$(CH_3CO)_2O + 2C_2H_5OH \longrightarrow 2\ CH_3COOC_2H_5 + H_2O$$

(*vi*) Radioactive disintegration:

$$Ra \longrightarrow Rn + \alpha$$

Mathematical Formulation of a Second Order Reaction

Reactions in which two molecules, identical or different, take part and the rate of the reaction is proportional to the concentration of each of them, are called second order reaction.

Let, the reaction be represented by,

$$A + B \longrightarrow C + D$$

Initial concentration of A = a

Initial concentration of B = b

Decrease in concentration of A and B at time $t = x$

Concentration of A at time $t = a - x$

Concentration of B at time $t = b - x$

Concentration C and D at time $t = x$

Rate of the reaction = k[A] [B]

or
$$\frac{dx}{dt} = k(a - x)\,(b - x)$$

or
$$k\,dt = \frac{dx}{(a - x)(b - x)} = \frac{1}{b - a}\left[\frac{1}{a - x} - \frac{1}{b - x}\right]dx$$

$\therefore$
$$\int \frac{1}{b - a}\left(\frac{1}{a - x} - \frac{1}{b - x}\right)dx = \int k\,dt$$

or
$$\frac{1}{b - a}\int\left(\frac{1}{a - x} - \frac{1}{b - x}\right)dx = k\int dt$$

or
$$\frac{1}{b - a}\left[\int \frac{1}{a - x}\,dx - \int \frac{1}{b - x}\,dx\right] = k\int dt$$

or
$$\frac{1}{b - a}\,[-\ln(a - x) + \ln(b - x)]$$
$$= kt + z \text{ (integration constant)}$$

or
$$\ln\frac{b - x}{a - x} = k(b - a)t + z$$

At $\quad t = 0,\ x = 0 \quad \therefore \quad \ln\frac{b}{a} = z$

$\therefore$
$$\ln\frac{b - x}{a - x} = k(b - a)t + \ln\frac{b}{a}$$

$\therefore$
$$-k(b - a)t = \ln\frac{b}{a} - \ln\frac{(b - x)}{(a - x)} = \ln\frac{b(a - x)}{a(b - x)}$$

or
$$k(b - a)t = -\ln\frac{b(a - x)}{a(b - x)} = \ln\frac{a(b - x)}{b\,(a - x)}$$

$\therefore$
$$k = \frac{1}{(b - a)t}\ln\frac{a(b - x)}{b(a - x)}$$
$$= \frac{2.303}{(b - a)t}\log\frac{a(b - x)}{b(a - x)}$$

If, initially, concentration of both the reactants are equal *i.e.,* $a = b$, then we can write,

$$\frac{dx}{dt} = k(a - x)^2 \quad \text{or} \quad \frac{dx}{dt} = k(b - x)^2$$

Taking

$$\frac{dx}{dt} = k(a-x)^2$$

or $$\frac{dx}{(a-x)^2} = k\,dt$$

or $$\frac{1}{a-x} = kt + z \text{ (integration constant)}$$

when $t = 0, \quad x = 0, \quad z = \frac{1}{a}$

$$\therefore \qquad kt = \frac{1}{a-x} - \frac{1}{a} \quad \text{or} \quad k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \text{ if we put } a - x = c$$

then, $$kt = \frac{1}{c} - \frac{1}{a} \quad \therefore \quad \frac{1}{c} = kt + \frac{1}{a}.$$

Characteristic of a Second Order Reaction

(*i*) *Time of half reaction*

$$t_{1/2} = \frac{1}{k} \cdot \frac{x}{a(a-x)} = \frac{1}{k}\, \frac{a/2}{a(a-a/2)} = \frac{1}{ak}$$

i.e., half decomposition time of a second order reaction is inversely proportional to the first power of initial concentration and is equal to $\frac{1}{k}$ when $a = 1$

(*ii*) *Unit of rate constant k*

$$\frac{dx}{dt} = k(a-x)^2 = kc^2 \text{ when } (a-x) = c$$

$$\therefore \qquad k = \frac{dx}{dt} \cdot \frac{1}{c^2} = \frac{\text{conc}}{\text{time}} \times \frac{1}{\text{conc}^2} = \text{conc}^{-1} \,.\, \text{time}^{-1} = l \,.\, \text{mol}^{-1}\, \text{sec}^{-1} \; [l = \text{litre}]$$

(*iii*) *Physical significance*

$$k = \frac{dx}{dt} = \text{When } c = 1$$

i.e., k is the rate of decomposition at unit concentration of the reactants.

Examples of a Second Order Reaction

(*i*) Decomposition (gas phase):

(*a*) $2HI \longrightarrow H_2 + I_2$

(*b*) $2NO_2 \longrightarrow 2NO + O_2$

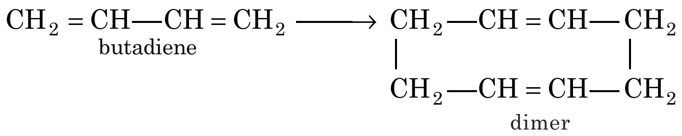
(*c*) $2NOCl \longrightarrow 2NO + Cl_2$

(*ii*) Displacement reaction (gas phase):

(*a*) $H + D_2 \longrightarrow HD + D$

(*b*) $Cl + H_2 \longrightarrow HCl + H$

(*iii*) Dimerisation (gas phase):



$$\underset{\text{butadiene}}{CH_2=CH—CH=CH_2} \longrightarrow \underset{\text{dimer}}{\begin{array}{l} CH_2—CH=CH—CH_2 \\ | \qquad\qquad\qquad\quad | \\ CH_2—CH=CH—CH_2 \end{array}}$$

(*iv*) Addition (gas phase):

$$H_2 + I_2 \longrightarrow 2HI$$

(*v*) Substitution reaction (Solution phase):

(*a*) $I^- + CH_3Br \longrightarrow CH_3I + Br^-$

(*b*) $OH^- + CH_3I \longrightarrow CH_3OH + I^-$

(*vi*) Hydrolysis of an ester:

$$CH_3COOC_2H_5 + OH^- \longrightarrow CH_3COO^- + C_2H_5OH$$

(*vii*) Esterification:

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

Comparison

Points	*First order reaction*	*Second order reaction*
Rate equation	$k = \frac{1}{t} \ln \frac{a}{a-x}$	$k = \frac{1}{t} \frac{x}{a(a-x)}$
Linearity	log c decreases linearly with time	$\frac{1}{c}$ increases linearly with time.
Unit of k	sec^{-1}	$l\ mol^{-1} \cdot sec^{-1}$
k	Independent of concentration.	Dependent on concentration.
$t_{1/2}$	Independent of initial concentration.	Inversely proportional to initial concentration.

Third Order Reaction

The rate equation for a third order reaction is

$$A + B + C \longrightarrow \text{Products}$$

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

where,

Initial concentration of A = a

Initial concentration of B = b

Initial concentration of C = c

no. of moles of each reactant decomposed at time $t = x$.

When, $a = b = c$

the rate equation becomes,

$$\frac{dx}{dt} = k(a-x)^3$$

$$= kc^3 \qquad \text{[when } a - x = \text{c]}$$

$$= kc^2(c - x) \qquad \text{[when } a = b \neq c \text{ and } (a - x) = c\text{]}$$

Again $$\frac{dx}{dt} = k(a - x)^3$$

or $$\frac{dx}{(a-x)^3} = k\,dt$$

Integrating,

$$\frac{1}{2}\cdot\frac{1}{(a-x)^2} = kt + z \qquad \text{(Integration constant)}$$

When $t = 0$, $x = 0$

$$\frac{1}{2}\cdot\frac{1}{a^2} = \text{Z} \quad \therefore \quad \text{Z} = \frac{1}{2a^2}$$

or $$\frac{1}{2}\frac{1}{(a-x)^2} - \frac{1}{2a^2} = kt$$

$\therefore$ $$kt = \frac{1}{2}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

$\therefore$ $$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] = \frac{1}{t}\,\frac{x(2a-x)}{2a^2(a-x)^2}.$$

Characteristics of a Third Order Reaction

(*i*) Where $x = \frac{1}{2}a,$

$$k = \frac{1}{t}\cdot\frac{\frac{1}{2}a\cdot\left(2a - \frac{1}{2}a\right)}{2a^2\cdot\left(\frac{1}{2}a\right)^2} = \frac{1}{t}\,\frac{a^2 - \frac{1}{4}a^2}{\frac{1}{2}a^4} = \frac{1}{t}\,\frac{\frac{3}{4}a^2}{\frac{1}{2}a^4}$$

$$= \frac{1}{t}\frac{3}{2}\cdot\frac{1}{a^2} \quad \text{or} \quad t = \frac{1}{k}\cdot\frac{3}{2}\cdot\frac{1}{a^2} = \frac{3}{2k}\cdot\frac{1}{a^2}$$

$\therefore$ $$t \propto \frac{1}{a^2}$$

So, the time required for the completion of the same fraction of the change is inversely proportional to the square of the initial concentration.

(*ii*) k is dependent on the unit of concentration.

(*iii*) Unit of k is mole^{-1} sec^{-1}.

Examples of Third Order Reaction

(*i*) $2NO + O_2 \longrightarrow 2NO_2$

(*ii*) $2NO + Cl_2 \longrightarrow 2\ NOCl$

(*iii*) $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$

Zero Order Reactions

There are certain reactions where rate of reaction does not diminish with time *i.e.,* the rate of the reaction is not dependent on the concentration of the reactant or, in other words, rate of the reaction is proportional to the zero power of the concentration of the reactant *i.e.,*

$$-\frac{dc}{dt} = k[\mathrm{A}]^0 = k \qquad [\because \quad [\mathrm{A}]^0 = 1]$$

where concentration of the reactant A = c

or
$$-\int_{c_0}^{c} dc = \int_0^t k\,dt = k\int_0^t dt$$

or
$$-[c - c_0] = k[t - 0] \quad \text{or} \quad c_0 - c = kt$$

Characteristic of a Zero Order Reaction

(*i*) We have,

$$k = \frac{c_0 - c}{t}$$

i.e., the amount decomposing in unit time is constant, which is equal to k (Zero order rate constant), independent of concentration or time, *i.e.,* the reaction velocity is constant and is independent of concentration.

(*ii*) In zero order reactions when c plotted against t would give a straight line of slope k ;

because $\frac{dc}{dt}$ is constant.

Examples of Zero Order Reactions

These reactions are controlled by catalyst. The bromination of acetone in acid solution is of zero order with respect to Br_2; since the reaction velocity is not influenced by a change in concentration of bromine.

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + HBr$$

$$HI + \xrightarrow[prs]{W} \frac{1}{2}H_2 + \frac{1}{2}I_2$$

Fractional Order Reactions

Not all reactions are of integral or zero order, many fractional order reactions are known. In those reactions, the rate of reaction is proportional to fractional power of concentration of the reactant, *i.e.,*

$$\frac{-dc}{dt} = \mathrm{K}c^{1/n}$$

where concentration of the reactant = c.

Examples of Fractional Order Reaction

(*i*) $CH_3CHO \longrightarrow CH_4 + CO; \; -\frac{dc}{dt} = \mathrm{K}c^{3/2}$

(*ii*) $2SbH_3 \xrightarrow{Sb} 2Sb + 3H_2; \; \frac{-dc}{dt} = \mathrm{K}c^{3/5}$

(*iii*) $\text{ortho-}H_2 \longrightarrow \text{para-}H_2; \; \frac{-dc}{dt} = \mathrm{K}c^{3/2}$

Usually such order involves a mechanism where atoms or free radicals are intermediates of the reaction.

Pseudo Unimolecular Reactions

Let us take the reaction

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

If we determine the rate of the reaction, we see that the reaction is of the second order. So, the reaction is dependent on the concentration of both the reactants. So, the rate equation of the reaction is

$$\frac{-dc}{dt} = k[C_{12}H_{22}O_{11}]\ [H_2O]$$

In solution the amount of water is excessively high compared to sugar. After complete hydrolysis of sugar, the change of concentration of sugar is very negligible. So $[H_2O]$ is constant. The rate equation comes to

$$\frac{-dc}{dt} = k'[C_{12}H_{22}O_{11}]$$

or $$\frac{dx}{dt} = k'(a-x)$$

or $$k' = \frac{1}{t}\,.\ln\frac{a}{a-x}$$

So, characteristics of first order reaction is seen actually in second order reaction. Due to presence of excess water, the incident so happens. Such solvolytic first order reactions are called **Pseudo unimolecular reactions**. Other pseudo unimolecular reactions are:

(*i*) $COS + H_2O \longrightarrow CO_2 + H_2S$

(*ii*) $CH_3COOCH_3 + H_2O \longrightarrow CH_3COOH + CH_3OH$

(*iii*) $(CH_3CO)_2O + 2C_2H_5OH$ (excess) $\longrightarrow 2CH_3COOC_2H_5 + H_2O$

Methods for the Determination of the Order of a Reaction

(*i*) *Substitution methods (with the help of rate equations)*

The following are the expressions of rate constants for different reactions:

First order reaction ⇒ $k = \frac{1}{t}\ln\frac{a}{a-x}$

Second order reaction ⇒ $k = \frac{1}{t}\cdot\frac{x}{a(a-x)}$

Third order reaction ⇒ $k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$

To determine the rate of a reaction a definite amount (a) of the reactant is taken and with the passage of time 't' the change in concentration (x) is determined mechanically or by chemical analysis, *i.e.*, $(a-x)$ is determined. By putting the value 'a' and $(a-x)$ the value of 'k' is determined. The order of the reaction is determined by that equation which gives the satisfactorily constant value of 'k'. The method is laborious and too complicated to give a satisfactory constant value. But is still employed for simpler reactions.

(*ii*) *Half-life method*

The half-lives ($t_{1/2}$) for reactions of different orders are as follows:

First order = $0.693/k$ (fixed)

Second order = $1/(ak)$

Third order = $1/(a^2k')$

In separate sets of experiments if different concentrations are taken and $t_{1/2}$ are measured the order can easily be determined. If $t_{1/2}$ remains constant the reaction is of the first order, if $t_{1/2}$ varies inversely as the initial concentration the reaction is of the second order, *i.e.,* plot of $t_{1/2}$ *vs.* $1/a$ will give a straight line. If the plot $t_{1/2}$ *vs.* $1/a^2$ gives a straight line, the reaction is of third order.

(*iii*) *Van't Hoff's differential method*

Let, the order of a reaction be = n.

For, the first experiment the initial concentration = c_1.

For the second experiment the initial concentration = c_2.

So, the rate equations for the two experiments will be

$$R_1 = -\frac{dc_1}{dt} = kc_1{}^n;$$

$$R_2 = -\frac{dc_2}{dt} = kc_2{}^n.$$

Taking 'log' on both the sides

$$\log R_1 = \log k + n \log c_1$$

$$\log R_2 = \log k + n \log c_2$$

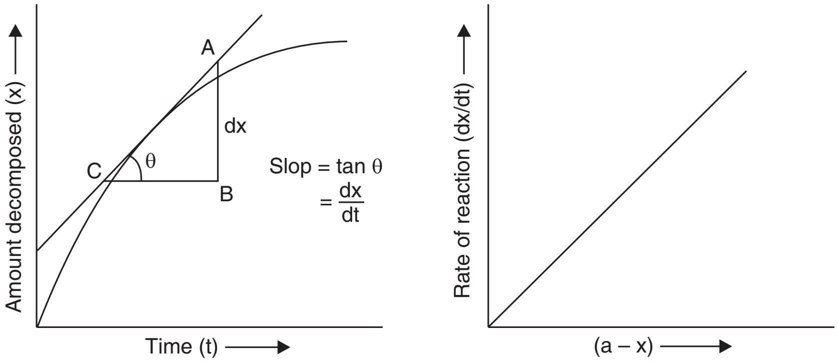
or

$$n = \frac{\log R_1 - \log R_2}{\log c_1 - \log c_2}$$

If the rates of reaction determined initially R_1 and R_2 are known, so the order can be determined.

(*iv*) *Graphical method*

If we plot 'time' *vs* 'a function of concentration', we can get the order of a reaction. By plotting $\log c$ *vs* t if a straight line is obtained the reaction is of first order. If a plot of $1/c$ *vs* 't' gives a straight line the reaction is of second order and if the plot of $1/c^2$ *vs* 't' gives a straight line the reaction is of third order (Fig. 5.1 (*a*) and (*b*)).



(*a*) (*b*)

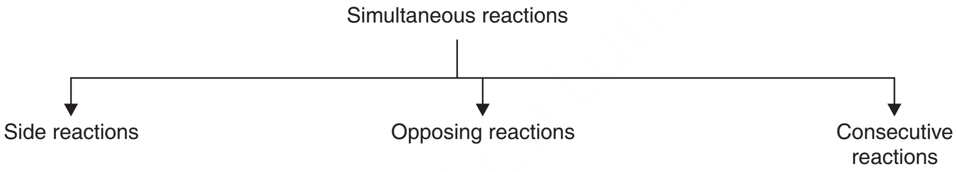
Fig. 5.1

Disturbing Factors in the Determination of an Order

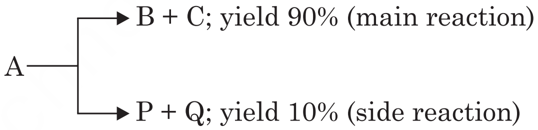
The reaction which takes a single path has no interfering influence in the main reaction. But many reactions are complicated, so the interpretation of the order of a reaction from their velocity data becomes difficult. The rate constant values are not obtained constants for a number of reactions. There are certain disturbing factors which influence the reaction and constant values for k are not obtained. Some of these factors are given below:

Simultaneous Reactions

In a simple reaction, the reactants react to give products. But many of the reactions are not so simple. The other reactions occur simultaneously. These reactions are called **simultaneous reactions.** These reactions interfere to give a constant value of k. There are three types of simultaneous reactions.

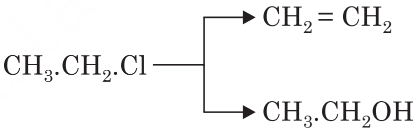


(*a*) *Side reaction:* Sometimes the reactants undergo two or more independent reactions simultaneously. Each reaction gives a set of products. The reaction which gives the major product is called main reaction and the other is called side reaction.

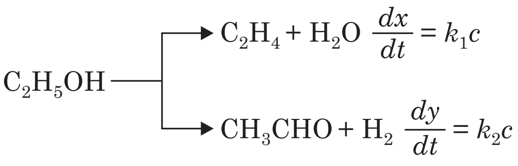


$$A \begin{cases} \rightarrow B + C;\ \text{yield 90\% (main reaction)} \\ \rightarrow P + Q;\ \text{yield 10\% (side reaction)} \end{cases}$$

Example:



$$CH_3.CH_2.Cl \begin{cases} \rightarrow CH_2 = CH_2 \\ \rightarrow CH_3.CH_2OH \end{cases}$$



$$C_2H_5OH \begin{cases} \rightarrow C_2H_4 + H_2O \quad \frac{dx}{dt} = k_1c \\ \rightarrow CH_3CHO + H_2 \quad \frac{dy}{dt} = k_2c \end{cases}$$

[k_1 and k_2 are not same]

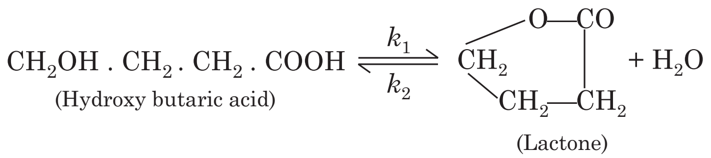
(*b*) *Opposing reaction:* The reversible reactions also interfere to give the constant value of 'k'.

$$A + B \rightleftharpoons C + D$$

So, the experimentally determined rate for this reaction is a net result for the two opposing reactions.

Example:

$$CH_3COOH + C_2H_5OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$



Rate equation for the first reaction is:

$$\frac{dx}{dt} = k_1(a - x)(b - x) - k_2x^2.$$

where k_1 = rate constant for the forward reaction

k_2 = rate constant for the backward reaction

Here the reverse reaction interferes the determination of the rate constant of the main reaction.

(*c*) *Consecutive reaction:* In many reactions, the products obtained change to a third product. These types of reactions are known as consecutive reactions.

$$\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}$$

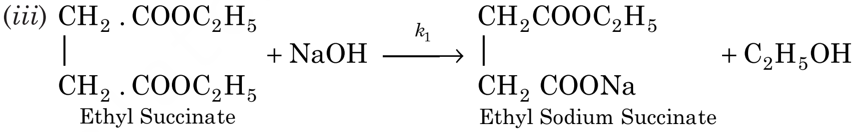
Examples:

(*i*) $(CH_3)_2O \xrightarrow{k_1} CH_{34} + HCHO \xrightarrow{k_2} CO + H_2$

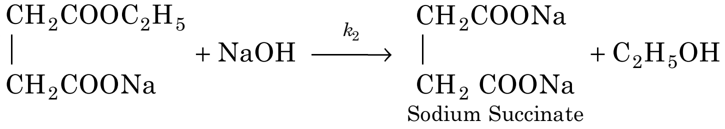
(*ii*) $2NO + H_2 \xrightarrow{k_1} N_2 + H_2O_2$

$$H_2O_2 + H_2 \xrightarrow{k_2} 2H_2O$$

(*iii*)



$$\begin{array}{l} CH_2\,.\,COOC_2H_5 \\ | \\ CH_2\,.\,COOC_2H_5 \\ \text{Ethyl Succinate} \end{array} + NaOH \xrightarrow{k_1} \begin{array}{l} CH_2COOC_2H_5 \\ | \\ CH_2\ COONa \\ \text{Ethyl Sodium Succinate} \end{array} + C_2H_5OH$$



$$\begin{array}{l} CH_2COOC_2H_5 \\ | \\ CH_2COONa \end{array} + NaOH \xrightarrow{k_2} \begin{array}{l} CH_2COONa \\ | \\ CH_2\ COONa \\ \text{Sodium Succinate} \end{array} + C_2H_5OH$$

(*iv*) $H_2O_2 + 2HI \longrightarrow 2H_2O + I_2$

$$H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$$

$$IO^- + 2H^+ + I^- \xrightarrow{k_2} H_2O + I_2$$

Of these reactions, the first proceeds very slow, which can be measured and that determines the order of the reaction.

Period of induction

Sometimes it is seen that even though the proper conditions for the reaction are maintained the reaction does not start. After some time the reaction starts and proceeds as usual with normal speed. This period of static state of reaction is known as *period of induction.* As for example—period of induction is noted during the reaction of H_2 and Cl_2 in the presence of light. Generally, induction period is observed in photochemical and polymerisation reactions. Generally, negative catalysts are responsible for this inactivity in the *period of induction* or sometimes slow production of an active intermediate.

Effect of Temperature on Reaction Rate (Arrhenius Equation)

Temperature has a great influence on reaction rate: Arrhenius studied the fact and concluded that rate of every reaction increases with increase of temperature. Rate of a reaction gets doubled when temperature increases by 10°.

Keeping concentration constant if we increase the temperature, rate of a reaction will increase *i.e.,* value of k will increase. Arrhenius first related temperature T of a reaction with k. He established that **when $\log_e k$ or $\ln k$ is plotted against $\frac{1}{T}$ a straight line is obtained** (Fig. 5.2).

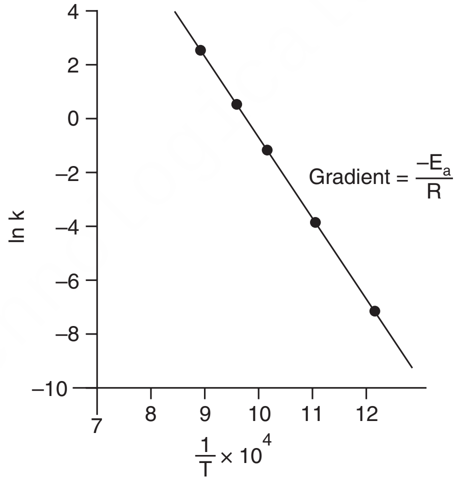


Fig. 5.2 Plot of ln *k* against 1/T for a reaction.

The relation can be expressed mathematically as follows:

$$\ln k = A - \frac{E}{RT} \quad \text{or} \quad \frac{d \ln k}{dT} = \frac{E}{RT^2}$$

where A and E are constants.

Their values are different for different reactions.

Let, rate constant of a reaction at temperature $T_1 = k_1$ and rate constant of that reaction at temperature $T_2 = k_2$.

Then, we can write,

$$\ln k_1 = A - \frac{E}{RT_1} \quad \text{and} \quad \ln k_2 = A - \frac{E}{RT_2}$$

Subtracting the above two equations we have,

$$\ln \frac{k_1}{k_2} = -\frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

or
$$\log \frac{k_1}{k_2} = -\frac{E}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

So, if we can determine the two rate constants k_1 and k_2 we can find out the value of E from the above equation. If E for a reaction is known, we can determine the value of k_2 when k_1 is known.

Highlights:

- Temperature coefficient of a chemical reaction is defined as the ratio of two rate constants of the reaction at two temperatures differing by 10°.

  Temperature co-efficient $= \dfrac{k_{25°}}{k_{35°}}$ (usually)

- Plot of ln k *vs.* $\dfrac{1}{T}$ gives a straight line so the equation of the straight line is:

$$\ln k = a - \frac{b}{T}$$

  where k is the specific reaction rate and T is the absolute temperature.

- The exponential form of the above equation is known as **Arrhenius equation**

$$k = Ae^{-E_a/RT}.$$

where, k = Rate constant E_a = Energy of activation
R = Gas constant T = Absolute temperature
A = Another constant known as *frequency factor.*

Arrhenius equation describes how the rate constant for a reaction varies with temperature and makes it possible to determine the **activation energy** for the reaction.

Energy of Activation (E_a) of a Reaction: its Significance

The molecules of reactants, which take part in a chemical reaction should get activated by gaining a minimum definite amount of energy, which is known as **energy of activation** (E_a). For every reaction, the molecules should be raised to a state of sufficient energy, otherwise the reaction will not be

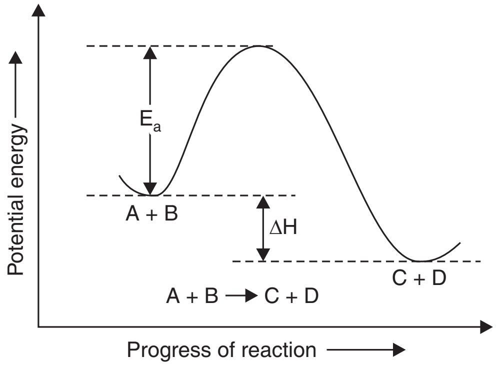


Fig. 5.3

possible. This energy state is different for different reactions. At any state, the molecules possess an average energy. Some molecules are more energised than the others. The minimum amount of energy over the average energy of a molecule required to get activated for participation in a reaction is called **energy of activation.**

These activated molecules take part in the reaction, others cannot take part in the reaction unless activated. After the reaction, this excess energy is liberated in the form of heat. When the liberated energy is less than E_a, the reaction becomes *endothermic* and when the liberated energy is greater than E_a the reaction becomes **exothermic** (See Fig. 5.3).

Highlights:

- Energy of activation (E_a) is the **critical value of energy,** which a molecule should possess to get activated to take part in a reaction.
- There is always an equilibrium between ordinary molecules and excited or activated molecules with an energy difference E_a.
- Theoretically, E_a is minimum energy which a molecule must have as a prerequisite to take part in a chemical reaction.

Collision Theory

According to this theory, the molecules of the reactants collide to take part in a reaction. When two gases A and B react, the reaction becomes possible when molecules of A and B collide. Number of collisions per second (z) in any given volume can be obtained from kinetic theory. Again the number of molecules reacted in one second can be obtained from rate constant k (experimentally determined). It is observed that the number of molecules reacted is always less than the number of molecules collided *i.e.*, every collision does not give rise to reaction. Arrhenius proposed that only the molecules attaining energy of activation E_a due to collision can take part in the reaction. According to Maxwell, at a temperature T, the ratio of total number of collisions and the number of collisions giving E to the molecules is $e^{-E/RT}$.

Let the total number of collisions be z.

$\therefore$ Number of collisions of molecules possessing $E = z \, . \, e^{-E/RT}$.

These number of molecules will react.

$$\therefore \qquad k = z \, . \, e^{-E/RT}.$$

or

$$\ln k = \ln z - E/RT = A - \frac{E}{RT}$$

This supports the experimentally derived equation. So, the theory of collision can be accepted.

Highlights:

- A simple collision between the reacting molecules does not necessarily cause reaction.
- The collisions, which lead to the reaction, are called **effective collisions.** Effective collisions are sufficiently energetic.
- Not only effective collisions are responsible for a reaction, but orientation of collision is also important.

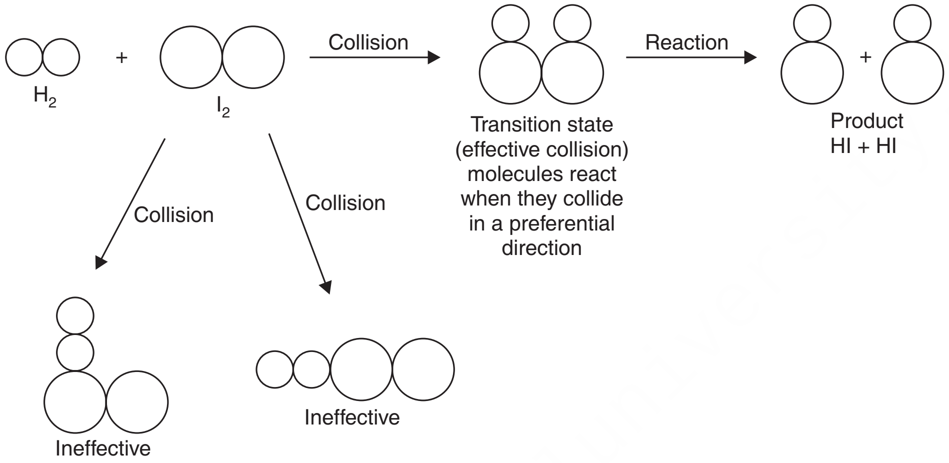


Fig. 5.4

Rate of a reaction = [No. of properly oriented molecules per unit volume per unit time]
× fraction of molecules equal to or greater than threshold energy.

SOLVED EXAMPLES

Example 1. *In an experiment, 250 cc of H_2O_2 solution of strength 2 (N) is taken. So, it is added colloidal gold and at interval of 5 minutes an aliquot (5 ml) is taken and cooled in ice cold water and titrated against standard $KMnO_4$ solution. The titre values will give the change in concentration of H_2O_2 i.e., x. Determine from the following data the value of k and establish that the decomposition is of the Ist order.*

Decomposition of H_2O_2

Time	*0*	*5*	*10*	*20*	*30*	*50*
Time value ($KMnO_4$ in cc)	*46.1*	*37.1*	*29.8*	*19.6*	*12.3*	*5.0*

Sol. For a Ist order reaction

$$k = \frac{1}{t} . \ln \frac{a}{a - x}$$

Here, $a = 46.1$

Now, putting $t = 5$

$$k = \frac{1}{5} . \ln \frac{46.1}{37.1} = 0.0434 \text{ min}^{-1}$$

at $t = 10$, $k = \frac{1}{10} \ln \frac{46.1}{29.8} = 0.0436 \text{ min}^{-1}$

at $t = 20$, $k = \frac{1}{20} \ln \frac{46.1}{19.6} = 0.0427 \text{ min}^{-1}$

at $t = 30$, $k = \frac{1}{30} \ln \frac{46.1}{12.3} = 0.044 \text{ min}^{-1}$

at $t = 50$, $k = \frac{1}{50} \ln \frac{46.1}{5.0} = 0.044 \text{ min}^{-1}$.

Since the '*k*' values are fairly constant by putting the data in the Ist order-rate equation the reaction *i.e.,* decomposition of H_2O_2 is of the Ist order.

Example 2. *A 20% sugar solution is taken. 50 cc of this solution and 50 cc of (N) HCl is mixed at constant temperature. The mixture is poured in a polarimeter tube. The optical rotation of this solution is measured at regular intervals and the final reading is taken after 24 hrs. The data is given below:*

The optical rotation of sucrose in 1(N) HCl at various times is given in the following table:

Time (in minute)	*0*	*7.18*	*18*	*27.05*	α
Rotation (degrees)	*+ 24.09*	*+ 21.4*	*+ 17.7*	*+ 15*	*– 10.74*

Show that the reaction is of the Ist order.

Sol. Here, $a = r_0 - r_\alpha$

$(a - x) = r_t - r_\alpha$

where r_0, r_t and r_α are initial rotation, rotation after time '*t*' and rotation after infinite time where the reaction is assumed to be completed.

$$r_0 - r_\alpha = 24.09 + 10.79 = 34.83$$

Time	$r_t - r_\alpha$,	$k = \frac{1}{t}\ln\frac{r_0 - r_\alpha}{r_t - r_\alpha}$
7.18	32.14	$k = \frac{1}{7.18}\log\frac{34.83}{32.14} = 0.00486 \text{ min}^{-1}$
18	28.14	$k = \frac{1}{18}\log\frac{34.83}{28.14} = 0.00519 \text{ min}^{-1}$
27.05	25.74	$k = \frac{1}{27.05}\log\frac{34.83}{25.79} = 0.00485 \text{ min}^{-1}$.

Since, the *k*-values are fairly constant by putting the data in the Ist order rate equation *i.e.,* the hydrolysis of methyl acetate is of the Ist order.

Example 3. *1 cc methyl acetate was added to a flask containing 20 ml 0.5(N) HCl kept at a temperature of 25°C. 2 ml of aliquot (reaction mixture) was withdrawn at different intervals and titrated against a standard alkali. The data are as follows:*

Time (in minutes):	*0*	*75*	*119*	*183*	α
Vol. of alkali used:	*19.24*	*24.20*	*26.60*	*29.32*	*42.03*

From the above data show that the hydrolysis is of the Ist order.

Sol. Here $a = V_\alpha - V_o$

$a - x = V_\alpha - V_t$

where V_o, V_t and V_α are the volumes of alkali initially, after a time *t* and after an infinite time, respectively.

$$V_\alpha - V_o = 42.03 - 19.24 = 22.79$$

Time	$V_\alpha - V_t$	*k*
75	17.83	$k = \frac{2.303}{75}\log\frac{22.79}{17.83} = 0.00395 \text{ min}^{-1}$
119	15.43	$k = \frac{2.303}{119}\log\frac{22.79}{15.43} = 0.00321 \text{ min}^{-1}$
183	12.71	$k = \frac{2.303}{183}\log\frac{22.79}{12.71} = 0.00316 \text{ min}^{-1}$

Since the 'k' values are fairly constant by putting the data in the Ist order rate equation *i.e.,* the hydrolysis of methylacetate is of the Ist order.

Example 4. *A Ist order reaction is 25% completed in 30 mins. Determine the time of 50% completion of the reaction.*

Sol. Time of 50% reaction, *i.e.,* $t_{1/2}$ to be determined for Ist order reaction $t_{1/2}$ is $\dfrac{0.693}{k}$

and $$k = \frac{2.303}{t} . \log \frac{a}{a - x}$$

Here, $t = 30$ min $a = 100\%$

$$a = (100 - 25)\% = 75\%$$

$$k = \frac{2.303}{30} \log \frac{100}{75} = 0.0095 \text{ min}^{-1}$$

$$\therefore \quad t_{1/2} = \frac{0.693}{0.0095} = 72.9 \text{ minutes.}$$

Example 5. *Half-life for a first order reaction is 17 mins. Calculate the rate constant and time for 75% completion of the reaction.*

Sol. We know $$t_{1/2} = \frac{0.693}{k}$$

Here, $t_{1/2} = 17$ mins.

$$\therefore \quad k = \frac{0.693}{17} \text{ min}^{-1} = 0.0407 \text{ min}^{-1}$$

Here, $a = 100\%$

$$a - x = (100 - 75)\% = 25\%$$

$$\therefore \quad k = \frac{2.303}{t} \log \frac{100}{25}$$

$$\therefore \quad t = \frac{2.303}{k} \log \frac{100}{25} = \frac{2.303}{0.0407} \log 4 = 34 \text{ minutes.}$$

Example 6. *The half-life for radium is 1600 years. Calculate the time for 80% disintegration.*

Sol. Radioactive disintegration is of the Ist order

$$\therefore \quad t_{1/2} = \frac{0.693}{k}$$

$$\therefore \quad 1600 = \frac{0.693}{k}$$

$$\therefore \quad k = \frac{0.693}{1600} \text{ year}^{-1} = 0.000433 \text{ year}^{-1}$$

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

Here $a = 100\ \%$

$$(a - x) = 100 - 80 = 20$$

$$t = \frac{2.303}{0.000433} \log \frac{100}{20} = 37.17 \text{ yrs.}$$

Example 7. *The following is the data for the hydrolysis of ethyl acetate by NaOH solution. An aliquot (25 cm) of the reaction mixture was titrated against a standard acid at regular time intervals.*

Time (in minute)	*0*	*5*	*15*	*25*	*35*
Vol. of acid (a – x)	*16*	*10.24*	*6.13*	*4.32*	*3.41*

Show that the reaction is of the 2nd order.

Sol. The 2nd order rate equation is

$$k = \frac{1}{at}\,\frac{x}{(a-x)}$$

Here $a = 16$ *c.c.*

T	$a - x$	x	k
5	10.24	5.76	$k = \frac{1}{16 \times 5} \times \frac{5.76}{10.24} = 0.007 \text{ conc}^{-1} \text{ sec}^{-1}$
15	6.13	9.87	$k = \frac{1}{16 \times 15} \times \frac{9.87}{6.13} = 0.0067 \text{ conc}^{-1} \text{ sec}^{-1}$
25	4.32	11.68	$k = \frac{1}{16 \times 25} \times \frac{11.68}{4.32} = 0.0069 \text{ conc}^{-1} \text{ sec}^{-1}$
35	3.41	12.59	$k = \frac{1}{16 \times 35} \times \frac{12.59}{3.41} = 0.0066 \text{ conc}^{-1} \text{ sec}^{-1}$

Since the k values are fairly constant by putting in the 2nd order rate equation *i.e.,* the hydrolysis of ethylacetate by NaOH is of the 2nd order.

Example 8. *Deduce the rate constant and* $t_{1/2}$ *for nth order reaction.*

Sol. Let the reaction be

$$n\text{A} \longrightarrow \text{Products.}$$

The rate equation is

$$\frac{-d[\text{A}]}{dt} = k \,.\, [\text{A}]^n$$

Let a be the initial concentration and x be the concentration which has reacted in the time 't'. So the concentration of A at time t is $(a - x)$.

$$\therefore \quad \frac{-d[\text{A}]}{dt} = \frac{-d(a-x)}{dt} = \frac{dx}{dt} = k(a-x)^n$$

$$\therefore \quad \frac{dx}{(a-x)^n} = k\,dt$$

$$\int_0^x \frac{dx}{(a-x)^n} = k\int_0^t dt$$

$$\because \quad t = 0\,,\ x = 0$$

$$\frac{1}{(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] = k\,.\,t$$

$$\therefore \qquad k = \frac{1}{t(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

$$t = \frac{1}{k(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

For $t_{1/2}$, $x = a/2$

$$\therefore \qquad t_{1/2} = \frac{1}{k(n-1)}\left[\frac{1}{(a/2)^{n-1}} - \frac{1}{(a)^{n-1}}\right]$$

$$\therefore \qquad t_{1/2} = \frac{1}{k(n-1)}\left[\frac{2^{n-1}-1}{a^{n-1}}\right]$$

unit of k is (conc)$^{-(n-1)}$ (time)$^{-1}$.

Example 9. *In a 2nd order reaction, where the initial concentration of the reactants is the same half of the reactants are consumed in 10 mins. If the specific reaction rate is* 5.2×10^{-3} *mol*$^{-1}$ *litre min*$^{-1}$*, what is the initial concentration of the reactants?*

Sol. For a 2nd order reaction

$$k = \frac{x}{at(a-x)}$$

Here, $t = 60$ mins, $x = a/2$

$k = 5.2 \times 10^{-3}$ mol^{-1} litre min^{-1}

$$\therefore \qquad 5.2 \times 10^{-3} = \frac{a/2}{60\,.\,a\,.\,a/2} = \frac{1}{60a}$$

$$a = \frac{1}{60 \times 5.2 \times 10^{-3}} = 3.2 \text{ mol litre}^{-1}.$$

Example 10. *When the initial concentration is changed from 0.5 to 1 mol l*$^{-1}$*, the time of half completion for a reaction is found to change from 50 sec. to 25 sec. Calculate the time taken for the concentration to be reduced to 20% of the initial value.*

Sol. $t_{1/2}$'s are related to initial concentrations as

$$\frac{T_1}{T_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Here, $T_1 = 50$ sec, $T_2 = 25$ sec, $a_1 = 0.5$ mol l^{-1}

$a_2 = 1$ mol l^{-1}

$$\therefore \qquad \frac{50}{25} = \left(\frac{1}{0.5}\right)^{n-1}$$

or $\qquad 2 = 2^{n-1}$

$\therefore \qquad n - 1 = 1$

or $\qquad n = 2$

So, the reaction is of the 2nd order.

$$\therefore \qquad k = \frac{1}{at_{1/2}} = \frac{1}{0.5 \times 50} = \frac{1}{25}\ l\ \text{mol}^{-1}\ \text{sec}^{-1} = .04\ l\ \text{mol}^{-1}\ \text{sec}^{-1}$$

$$t = \frac{k}{ak(a-x)} = \frac{0.8 \times 25}{0.5 \times 0.2} = 200 \text{ sec.}$$

Example 11. *In a 2nd order reaction, the initial concentration of reactants is 0.1 mol l^{-1}. The reaction is found to be 20% complete in 40 minutes. Calculate the rate constant, half-life period, time required to complete 75% of the reaction.*

Sol. Here, $a = 0.1$ mol l^{-1}

$x = 0.2\ a = 0.2 \times 0.1 = 0.02$ mol l^{-1}

$t = 40$ min.

$a - x = (0.1 - 0.2)$mol $l^{-1} = 0.08$ mol l^{-1}

For the second order reaction,

$$k = \frac{x}{at(a-x)} = \frac{0.02}{0.1 \times 40 \times 0.08}$$

$$= 0.0625\ l\ \text{mol}^{-1}\ \text{min}^{-1}$$

$$k = \frac{1}{at_{1/2}}$$

$$\therefore \qquad t_{1/2} = \frac{1}{ak} = \frac{1}{0.1 \times 0.0625} = 160 \text{ mins.}$$

$x' = 0.75a = 0.075$ mol l^{-1}, $k = 0.0625$ mol^{-1}.

$t = ?\ (a - x') = 0.025$ mol l^{-1}

$$\therefore \qquad t' = \frac{x'}{ak(a-x')} = \frac{0.075}{0.1 \times 0.0625 \times 0.625} = 480 \text{ mins.}$$

Example 12. *If one percent decomposes in the first minute in a unimolecular reaction, calculate how much would remain undecomposed at the completion of the first hour.*

Sol. For a unimolecular reaction

$$k = \frac{2.303}{1} \log \frac{a}{a-x}$$

Here, $a = 100$ $\qquad a - x = (100 - 1) = 99$

$$\therefore \qquad k = \frac{2.303}{1} \log \frac{100}{99}$$

$$= 2.303 \times 0.0044 \text{ min}^{-1}$$

$$= 0.01 \text{ min}^{-1}$$

when $t = 1$ hr $= 60$ mins

$$k = \frac{2.303}{60} \log \frac{160}{a-x}$$

or

$$0.01 = \frac{2.303}{60} \log \frac{100}{a-x}$$

or $$\frac{60 \times 0.01}{2.303} = \log \frac{100}{a - x} = \log 100 - \log (a - x)$$

or $$\log (a - x) = \log 100 - 0.2605$$
$$= 2 - 0.2605 = 1.7395$$

$\therefore$ $$(a - x) = \text{Antilog } 1.7395 = 54.89$$

$\therefore$ % undecomposed = 54.89.

Example 13. *If $k_1 = k_2 = k_3$ for three reactions being respectively of first, second and third orders when concentration is expressed in mole l^{-1}, what will be the above relation if the concentration unit is mol m^{-1}?*

Sol. For nth order reaction,

unit of k = mole^{1-n} $l^{n-1} t^{-1}$ when c = mol l^{-1}

and mole^{1-n} l^{n-1} t^{-1} = mole^{1-n} $10^{3(n-1)}$ ml^{n-1} t^{-1} when c = mol ml^{-1}

For first order reaction,

$$k_1 = t^{-1} \quad (k_1 \text{ will remain same})$$

For second order reaction,

$$k_2 = \text{mole}^{-1}\, l t^{-1}$$
$$k_2 = \text{mole}^{-1}\, 10^3 \text{ ml } t^{-1}$$

or $$10^{-3}\, k_2 = \text{mole}^{-1} \text{ ml } t^{-1}$$

For third order reaction,

$$k_3 = \text{mole}^{-2}\, l^2\, t^{-1}$$
$$= \text{mole}^{-2}\, 10^6 \text{ ml}^2\, t^{-1}$$

or $$10^{-6}\, k_3 = \text{mole}^{-2} \text{ ml}^2\, t^{-1}$$

So, the reaction will be,

$$k_1 = 10^{-3}\, k_2 = 10^{-6}\, k_3.$$

Example 14. *A certain substance A is mixed with equal moles of a substance B. At the end of one hour A is 75% reacted. How much A and B will be left increased at the end of two hours if the reaction is: (i) first order in A and independent of B, (ii) first order in A and first order in B?*

Sol. Let, initial concentration = [A] = [B] = a

$$t = 1 \text{ hrs.}$$
$$x = 0.75a$$

(*i*) When first order in $$\text{A} = \text{K} = \frac{2.303}{1} \log \frac{a}{a - 0.75a} = 2.303 \log \frac{a}{0.25a}$$
$$= 2.303 \log 4 = 1.3865 \text{ hr}^{-1}.$$

when time $t' = 2$ hrs.

$$1.3865 = \frac{2.303}{2} \log \frac{a}{a - x'}$$ [where x' = amount reacted]

$\therefore$ $$\log \frac{a}{a - x'} = \frac{1.3865 \times 2}{2.303} = 1.204 \quad \therefore \quad \frac{a}{a - x'} = \text{Antilog } 1.204 = 16$$

$\therefore$ $$(a - x') = \frac{a}{16} = \frac{100}{16} = 12.5\%$$

So, % of A left unreacted = 12.5%

% of B left unreacted = 100% ($\because$ order = 0 w.r.t. B)

(*ii*) In the second case, the over all order of the reaction is 2.

$$\therefore \quad k = \frac{x}{at(a-x)} = \frac{0.75a}{a \times 1 \times 0.25a} = 3a^{-1}\ \text{hr}^{-1} \qquad (\text{when } t = 1 \text{ hr})$$

At $t' = 2$ hrs.

$$k = \frac{x'}{at(a-x')} \text{ when } x' = \text{amount of reactants A and B reacted}$$

$$3a^{-1} = \frac{x'}{a \times 2 \times (a-x')} \quad \text{or} \quad 6 = \frac{x'}{a-x'}$$

$$\therefore \quad x' = \frac{6a}{7}$$

So, % of A and B left unreacted = $\left(a - \frac{6}{7}a\right)$

i.e.,
$$100 - \frac{6}{7} . 100 \approx 14.3.$$

Example 15. *The specific reaction rates of a chemical reaction at 273 K and 303 K are respectively 2.45 × 10^{-5} and 162 × 10^{-5}. Calculate the activation energy of this reaction.*

Sol. Rate constants at two temperatures are given by Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Here, $T_1 = 273$ K $\quad T_2 = 303$ K $\quad k_1 = 2.45 \times 10^{-5}$

$k_2 = 162 \times 10^{-5} \quad R = 1.987$ Cal K^{-1} . mole^{-1}

$$\therefore \quad \log \frac{162 \times 10^{-5}}{2.45 \times 10^{-5}} = \frac{E_a}{2.303 \times 1.987}\left[\frac{303 - 273}{273 \times 303}\right]$$

$$1.8203 = \frac{E_a}{2.303 \times 1.987} \times \frac{30}{273 \times 303}$$

$$\therefore \quad E_a = 22,\ 968 \text{ cal mole}^{-1}.$$

Example 16. *The values of Arrhenius factor and activation energy are 4 × 10^{13} s^{-1} and 98.6 kJ mol^{-1}, respectively for a first order reaction. Calculate the temperature at which its half-life is 10 mins.*

Sol. The exponential form of Arrhenius equation is,

$$k = Ac^{-E_a/RT}$$

where A is called the Arrhenius factor and E_a is the energy of activation.

As the reaction is first order, $k = \frac{0.693}{t_{1/2}}$

Here, $t_{1/2} = 10$ mins = 600 sec.

$$\therefore \qquad k = \frac{0.693}{600}$$

$$= 1.155 \times 10^{-3} \text{ sec}^{-1}$$

From Arrhenius equation we have,

$$2.303 \log_{10} (k/\text{A}) = - \text{E}_a/\text{RT}$$

$$\text{or} \qquad \text{T} = \frac{\text{E}_a}{2.303\text{R} \log(\text{A}/\text{K})}$$

Here, $\text{E}_a = 98{,}600 \text{ J. mol}^{-1}$, $\text{R} = 8.316 \text{ J mol}^{-1} \text{ K}^{-1}$, $\text{A} = 4 \times 10^{13} \text{ sec}^{-1}$

$k = 1.115 \times 10^{-3} \text{ sec}^{-1}$.

$$\therefore \qquad \text{T} = \frac{98600}{2.303 \times 8.316 \times \left(\dfrac{4 \times 10^3}{1.115 \times 10^{-3}}\right)} \text{ K}$$

$$= \frac{98600}{2.303 \times 8.316 \times 16.555} \text{K}$$

$$= 98600$$

$$= 373 \text{ K}.$$

Example 17. *A second order reaction, whose rate constant at 800°C was found to be* $5.0 \times 10^{-3}\ l \text{ mol}^{-1} \text{ s}^{-1}$ *has an activation energy of 45 kJ* mol^{-1}*. What is the value of the rate constant at 875°C?*

Sol. We have,

$$\log \frac{\text{K}_2}{\text{K}_1} = \frac{\text{E}_a(\text{T}_1 - \text{T}_1)}{2.303 \text{ RT}_1\text{T}_2}$$

Here, $\text{K}_1 = 5 \times 10^{-3}\ l \text{ mol}^{-1} \text{ s}^{-1}$, $\quad \text{E}_a = 4.5 \times 10^4 \text{ J mol}^{-1}$

$\text{T}_2 = (875 - 273) = 1148 \text{ K}$, $\text{T}_1 = (800 + 273) = 1073$

$\text{R} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$\therefore \qquad \log \frac{\text{K}_2}{\text{K}_1} = \frac{4.5 \times 10^4 \ (1148 - 1073)}{2.303 \times 8.314 \times 1073 \times 1148} = 0.1431$$

$$\therefore \qquad \frac{\text{K}_2}{\text{K}_1} = \text{Antilog } 0.1431 = 1.39$$

$$\therefore \qquad \text{K}_2 = 1.39 \times 5 \times 10^{-3}\ l \text{ mol}^{-1} \text{ s}^{-1}$$

$$= 7.0 \times 10^{-3}\ l \text{ mol}^{-1} \text{ s}^{-1}.$$

Lasers in Chemistry

Laser means "light amplification by stimulated emission of radiation". The use of lasers has initiated new types of spectroscopic experiments and has improved the precision of spectroscopic experiments.

To achieve a laser action a **Population inversion** should be generated in the system. Let, the populations be n_2 and n_1 and energies of the two states be E_2 and E_1. When $\text{E}_2 > \text{E}_1$, let us state we have a population inversion with $n_2 > n_1$, then photons of frequency $1 \rightarrow 2 = \dfrac{\text{E}_2 - \text{E}_1}{h}$ are spontaneously emitted as molecules drop from the state 2 to the state 1.

These photons will stimulate other molecules in the state 2 to emit photons of frequency 1 → 2 and drop to state 1 (Fig. 5.5).

Photons of frequency 1 → 2 will also induce absorption from state 1 to state 2 but as the system contains $n_2 > n_1$ **stimulated emission will predominate over absorption** and we will get a net amplification of radiation of frequency $\nu_{1\to2}$.

The laser system is contained in a cylindrical cavity whose ends have parallel mirrors. A few photons are spontaneously emitted when the molecules go from the state 2 to state 1. Those photons emitted at the cylindrical axes pass out of the system and have no role in the laser action. Those photons emitted along the laser axis travel forward and backward between the end mirrors and stimulate emission for further photons. The presence of end mirrors makes the laser a standing wave pattern.

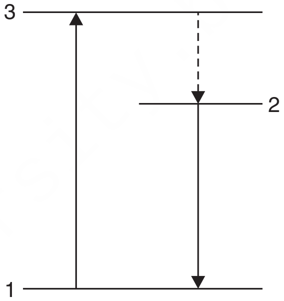


Fig. 5.5. States involved in laser action.

Let l be the distance between the mirrors and light only with wavelength = λ, such that $\frac{n\lambda}{2} = l$, where n is an integer, will resonate in the cavity. This makes the laser nearly monochromatic, the laser output is highly monochromatic and highly directional. These properties make laser useful in **spectroscopy** and **kinetics.** Thousands of different lasers exist; the material in which the laser action can be employed may be a solid, a liquid or a gas. The frequency emitted lies in the IR, visible or UV region.

Kinds of lasers

- Solid-state metal ion laser.
- Semiconductor laser or diode laser.
- Gas laser.
- Chemical laser.
- Dye laser.

An example of chemical laser: One can use the reaction:

$$H + F_2 \longrightarrow HF + F,$$

which is an elementary step of the mechanism of reaction:

$$H_2 + F_2 \longrightarrow 2HF \text{ (chain reaction)}$$

A laser in which the population inversion can be produced by a chemical reaction is called a **chemical laser.** The HF chemical laser can be used as an antimissile.

Laser Technique

A laser can be used to excite a major fraction of a reactant species to a specific vibration level in a molecular beam. Then we can study the dependence of the reaction probability on the vibrational quantum states of these reactants.

This sort of idea can be utilised to a selective excitement of a particular normal vibrational mode that involves mainly vibration of a particular bond and to break preferentially that bond. Thus, laser light can be employed to control the outcome of the reaction. For example, we can take the following two reactions:

(*i*) $H + HOD \longrightarrow OD + H_2$

(*ii*) $H + HOD \longrightarrow HO + HD.$

By using laser, one can preferentially break the O – H bond in HOD, similarly, excitation of O-D stretching vibration in HOD leads to break the O–D bond preferentially. Whether control of chemical reactions by lasers will ever have commercial applications is not clear.

The breaking of a chemical bond in a molecule occurs within a fraction of a second (10^{-13} to 10^{-12} second). By using laser light, the bond breaking process can be observed spectroscopically. This technique is called **Femtosecond Transition State Spectroscopy** (FTS) or laser femto chemistry. The experiments are done using either molecular beams or gaseous molecules in a chamber.

Unimolecular reactions are best studied by FTS.

SHORT QUESTIONS

Lasers in Chemistry:

Q. 1. What is a laser?

Q. 2. Explain why the laser radiation is monochromatic.

Q. 3. Mention various kinds of lasers.

Q. 4. Give an example of chemical laser.

Q. 5. Can you break a bond preferentially by the application of laser?

Q. 6. What do you mean by FTS?

Q. 7. Give one major application of laser.

SHORT QUESTIONS AND ANSWERS

Q.1. What do you mean by chemical kinetics?

Ans. Chemical kinetics is that branch of chemistry which deals with the rate of a chemical reaction.

Q. 2. What do you mean by rate of a reaction?

Ans. The rate of a reaction is defined as the decrease in concentration of the reactants or increase in concentration of the products at unit time. The rate of reaction is increased if the concentration of the reactants increases.

Let, the reaction be

$$A \longrightarrow B.$$

$$\text{Rate of reaction} = -\frac{\Delta A}{\Delta t} \quad \text{or} \quad +\frac{\Delta B}{\Delta t}$$

Unit = Concentration time inverse.

Q. 3. What is specific reaction rate or rate constant (k)?

Ans. It is the rate of the reaction when the concentration of the reactants are unity.

Q. 4. What are the factors that can change the value of k?

Ans. (1) Temperature, (2) Order of a reaction.

Q. 5. Differentiate average rate from instantaneous rate.

Ans. $\text{Average rate} = \dfrac{\text{Change in concentration}}{\text{Total time (involved for the change)}} = \dfrac{\Delta A}{\Delta T}$

Instantaneous rate is the rate of the reaction determined at the particular moment of time. The average rate approaches the instantaneous rate when Δt becomes smaller.

Q. 6. What do you mean by the order of a reaction?

Ans. It is equal to the total number of reacting species atoms, ions of molecules the concentration of which changes actually during the course of a chemical reaction. If we take a reaction:

$$\alpha A + \beta B + \gamma C \longrightarrow \text{Products}$$

the rate = $k \cdot A^{\alpha} \cdot B^{\beta} \cdot C^{\gamma}$

where k = rate constant and the order of the reaction $\alpha + \beta + \gamma$.

Q. 7. What is the molecularity of a reaction?

Ans. Molecularity of a reaction in equal to the sum of the coefficients of various reactants appearing in a balanced chemical equation *i.e.,* it is the sum of the stoichiometric coefficients in the simplest chemical equation. If the reaction is:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

The molecularity of the above reaction is two. So molecularity is a theoretical approach and its value is always a whole number.

Q. 8. What are unimolecular and bimolecular reactions?

Ans. When the molecularity is one it is unimolecular reaction and when it is two then the reaction is bimolecular.

Q. 9. Compare order and molecularity of a reaction.

Ans.

Order	*Molecularity*
(*i*) Order is a purely experimental fact related to the rate equation of the reactions. It is not connected with the chemical equation of the reaction.	(*i*) Molecularity is a theoretical concept. Its classical definition is connected with the overall chemical equation. In modern definition it is related to the mechanism of the reactions.
(*ii*) If a reaction is $A + B \longrightarrow \text{Products}$ the rate will be Rate = $K \cdot [A]^{\alpha} [B]^{\beta}$ experimentally observed fact.	(*ii*) It is the sum of the stoichiometric co-efficients of a chemical equation. Modern definition is—it is the number of molecules taking part in the rate determining step of the mechanism.
(*iii*) Order changes with physical conditions like → pressure, temperature, etc.	(*iii*) Molecularity does not depend on such factors.
(*iv*) Order may be a whole number, zero or a fraction.	(*iv*) Molecularity is always a whole number.

Highlight:

For elementary reaction order is necessarily equal to molecularity. For complex reactions it may or may not be equal.

Q. 10. What is a first order reaction?

Ans. If the rate of a chemical reaction varies to the first power of concentration of the single reactant, it is known as first order reaction.

$$\text{A} \longrightarrow \text{Products.}$$

$\therefore$ Rate = $\dfrac{-dA}{dt} = k\ .\ [A]$ = rate equation for a first order reaction.

Q. 11. Give examples of first order reaction.

Ans. 1. Radioactive disintegration process.

2. Rate of growth of bacterial culture.

Q. 12. What is a second order reaction?

Ans. A second order reaction is a reaction, the rate of which is directly proportional to the square of the concentration of a single reactant or equal to concentration of two different reactants. For a reaction:

$$\text{A + B} \longrightarrow \text{Products}$$

Rate = $k\ .\ [A]\ [B]$ or Rate = $k\ .\ [A]^2$ = Rate equation for second order reaction.

Q. 13. Comment on half-life of a first order and a second order reaction.

Ans. $t_{1/2}$ for a first order reaction = $\dfrac{0.693}{k}$. So, it is a constant quantity.

$t_{1/2}$ for a second order reaction = $\dfrac{1}{ak}$.

So, half-life in this case is inversely proportional to the initial concentration.

Q. 14. Is a first order or a second order reaction completed?

Ans. Integrated form for a first order rate equation is:

$$c = c_0 e^{-kt}$$

The plot of concentration *vs.* time will be asymptotic plot. Hence, concentration will be zero at infinite time. So the reaction is not completed.

For a second order reaction the integrated form of the rate equation is:

$$k = \frac{1}{t}\,\frac{x}{a(a-x)}$$

when, $x = a,\ t = \infty$

So, a second order reaction is also an incomplete reaction.

Q. 15. For a first order reaction one hour is needed for a change of concentration c to c/2. What is the time for the change from c/2 to c/4?

Ans. One hour.

Q. 16. For a second order reaction one hour is needed for a change of concentration *a* to *a*/2. What will be the time for the change from *a*/2 to *a*/4?

Ans. When concentration changes from a to $a/2$, $t_{1/2} = \dfrac{1}{ak}$.

When concentration changes from $a/2$ to $a/4$, $t_{1/2} = \dfrac{1}{a/2 \,.\, k}$

$$\therefore \qquad \frac{t'_{1/2}}{t'_{1/2}} = \frac{1}{ak}\bigg/\frac{1}{ak/2} = \frac{1}{2} \quad \text{or} \quad t'_{1/2} = 2 \,.\, t_{1/2} = 2.1 = 2 \text{ hrs.}$$

Q. 17. What is the special characteristic of a zero order reaction?

Ans. The integrated form of zero order reaction is

$$K = \frac{c_0 - c}{t}, \quad \text{where } c_0 = \text{initial concentration}$$

c = concentration at time t.

when, $\qquad c = 0;\ t = \dfrac{c_0}{k_a}$

which is a finite quantity. So, the reaction will be completed and for a zero order reaction, the rate is not at all dependent on the concentration of the reactants.

Q. 18. What is activation energy?

Ans. Activation energy of a reaction is defined as the extra energy over and above the average potential energy of the reactants, which must be supplied to the reactants to enable them to cross-over the energy barrier between the reactants and products. It is denoted by E_A.

Q. 19. What is threshold energy?

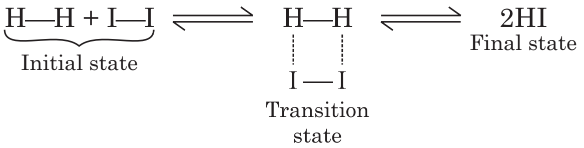
Ans. It is the minimum amount of energy from zero level of the reactant molecule which must possess in order to react. It is denoted by E_T.

Q. 20. How are the activation and threshold energies related?

Ans. $E_A = E_T - E_R$

Q. 21. What is transition state theory?

Ans. Chemical reactions occur through an intermediate stage known as transition state or activated complex (Fig. 5.6).



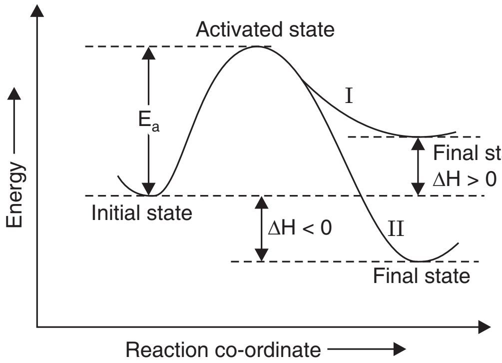


Fig. 5.6

Particles in collision react only if, upon impact, they attain impact, they attain the energy of the transition state.

$\Delta H > 0$ endothermic reaction (Curve I)

$\Delta H < 0$ exothermic reaction (Curve II)

Q. 22. What is the utility of the study of chemical kinetics?

Ans. The study of chemical kinetics helps to determine the mechanism of a chemical reaction.

EXERCISES

1. Explain the terms 'rate constant', 'order of a reaction' and 'molecularity of a reaction'.
2. What is meant by order of a reaction? Derive an expression for the velocity coefficient of a second order reaction.
3. Indicate how the specific reaction rate of a first order reaction can be evaluated. Derive the rate constant for a 1st order reaction and show that it is an incomplete reaction.
4. Discuss any two methods of determination of order.
5. Derive an expression for rate constant of zero order reaction and discuss about its (*i*) half-life, (*ii*) completion time.
6. Discuss the various factors affecting the rate of a reaction.
7. Explain the meaning of pseudo unimolecular reaction.
8. Describe an accurate method for determining order of a reaction with three reactants.
9. Distinguish between rate and specific reaction rate of a chemical reaction. Derive the rate constant expression of a 2nd order reaction:

   $A + B \xrightarrow{k} c$, the reactants A and B are at equal concentrations.
10. How does rate of a reaction vary with temperature? What is Arrhenius equation?
11. For,

    $$5\,Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

    Rate = Constant × $[Br^-]\,[BrO^-_3]\,[H^+]^2$.

    State the molecularity and order of the above reaction.
12. Briefly develop the concept of activation energy and temperature.
13. Classify the statement: "decomposition of H_2O_2 is of the 1st order".
14. Half-time change for a 1st order reaction is 40 mins. What is the rate constant of the reaction at the same temperature? [0.0173 min^{-1}]
15. The half-life period of a 1st order reaction is 15 mins. Calculate the rate constant and the time taken to complete 80% of the reaction. [34.85 mins]
16. The hydrolysis of ethyl nitrobenzoate by aqueous NaOH was followed at 25 °C, by titration of the hydroxide against standard acid at different stages in reaction. From the given data, show that the reaction is of the 2nd order.
17. During the hydrolysis of ethyl acetate by NaOH using equivalent concentration, 25 c.c. of the reaction mixture was titrated at regular intervals against standard acid. The volumes of acid used by unchanged NaOH are given below:

Time (minute)	0	5	15	25	35
Vol. of acid (c.c.)	16	10.24	6.13	4.32	3.41

Show that the reaction is of the 2nd order.

18. The half-life periods for the decomposition of ammonia (catalytically) are as follows :

Pressure in mm	50	100	200
Half-life period in hrs.	3.52	1.92	1

Find the reaction is of which order.

19. The decomposition of Cl_2O_7 at 400 K in the gas-phase to Cl_2 and O_2 is a 1st order reaction.

(*i*) After 55 seconds at 400 K the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

(*ii*) Calculate the pressure of Cl_2O_7 after 100 sec. of decomposition at this temperature.

[**Ans.** 6.236×10^{-3} sec$^{-1;}$ 0.0332 atm]

20. A 2nd order reaction, where $a = b$, is 20%, is completed in 500 seconds. How long will it take to go to 60% completion? [**Ans.** 3000 seconds]

21. The following data were obtained in the hydrolysis of ethyl acetate, using equal concentration of ester and NaOH:

Time (minutes):	0	5	15	25	35
Vol. of HCl (c.c.)	16.0	10.24	6.13	4.32	3.41

Show that reaction is of 2nd order.

22. A 1st order reaction has rate constant equal to 1.25×10^{-4} sec^{-1} at 298 K and 8.5×10^{-4} sec^{-1} at 318 K. Calculate the activation energy of the reaction. [**Ans.** 18, 050 Cal mol^{-1}]

23. Two reactions:

(*i*) A $\longrightarrow$ Products, (*ii*) B $\longrightarrow$ Products, follow first order kinetics. The rate of the reaction (*i*) is denoted when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (*ii*) is half that of reaction (*i*), calculate the rate of the reaction (*ii*) at 300 K. [**Ans.** 0.0327 min^{-1}]

24. The activation energy for the reaction

$$2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

is 209.5 kJ mol^{-1} at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy. [**Ans.** 1.462×10^{-19}]

25. When log K (velocity constant for a reaction) was plotted against $1/t$, the slope of the line was found to be – 5400 K. Calculate the energy of activation for this reaction (R = 8.314 JK^{-1} mol^{-1})

[**Ans.** 103.4 kJ mol^{-1}]

6

Catalyst

CATALYST

The Swedish chemist Berzelius in 1835 noticed that velocity of a number of reactions increased by the mere presence of a very small quantity of a foreign substance, which was not at all related to the reactants. Berzelius named the phenomenon of acceleration of the reaction as **catalysis** and the substance influencing the reaction, a **catalyst**. Since all reactions tend to attain equilibrium, it can be said that catalysts smoothen the passage towards equilibrium.

DEFINITION

A catalyst is a substance, not related to the reactants, influences the velocity of the reaction by not involving itself in the reaction. The phenomenon of influencing a reaction by a foreign substance is known as catalysis or 'a catalyst is a substance which enhances the rate of reaction approaching equilibrium but without involving itself in the process'.

A catalyst may also retard a chemical reaction. So the proper definition of a catalyst will be—**a catalyst is a substance which alters the rate of a chemical reaction without involving itself in the reaction.**

(*i*) **Positive catalysis or catalysis.** A catalyst which increases the rate of a reaction is called a positive catalyst or a catalyst and the phenomenon is catalysis.

(*ii*) **Negative catalysis.** The catalyst which retards the rate of a reaction is called a negative catalyst and the phenomenon is negative catalysis.

Examples of Catalysis

Positive Catalysis

Reaction	*Catalyst*
(*i*) $2KClO_3 \longrightarrow 2KCl + 3O_2$	MnO_2
(*ii*) $2H_2O_2 \longrightarrow 2H_2O + O_2$	Pt
(*iii*) $2SO_2 + O_2 \longrightarrow 2SO_3$	Pt or V_2O_5
(*iv*) $N_2 + 3H_2 \longrightarrow 2NH_3$	Fe
(*v*) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$	H^+ ion

Negative Catalysis

Reaction	*Catalyst*
(*i*) $2H_2O_2 \longrightarrow 2H_2O + O_2$	H_2SO_4
(*ii*) $2H_2 + O_2 \longrightarrow 2H_2O$	CO

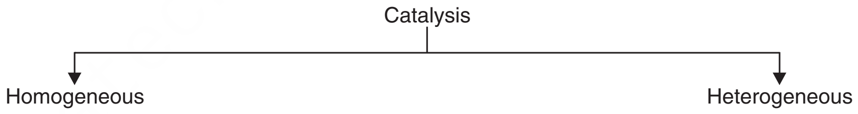
Characteristics of a Catalyst

(*i*) A small amount is effective.
(*ii*) Catalyst remains unaltered at the end of the reaction.
(*iii*) Catalyst hastens the attainment of equilibrium.
(*iv*) Catalyst has no influence on the point of equilibrium.
(*v*) Catalytic action is universal.

Highlights:

- Catalyst undergoes no chemical change in a reaction. So it has no influence on the standard free energy change $\Delta G°$ *i.e.,* on K, the equilibrium constant of the reaction as the two are related by $-\Delta G° = RT \ln K$.
- So, the point of equilibrium is independent of the catalyst.
- Catalyst only helps to attain the equilibrium rapidly.
- Catalyst merely lowers the energy barrier (E_a) of a reaction.
- So "a catalyst is a substance that makes a chemical reaction that could happen, but does not happen, happen".
- Since $K = \frac{k_1}{k_2}$, so if a catalyst changes k_1, it will also change k_2 in the same proportion so that their ratio K remains unchanged.
- This means if a catalyst accelerates the forward reaction, it also accelerates the backward reaction, it never increases the equilibrium yield.

Types of Catalysis



There is a third type of catalysis in mainly biological systems. Those catalysts are termed **Enzymes** or **Low catalysts.**

Homogeneous Catalysis

In this type of catalytic reactions, the catalyst remains in the same phase with the reactants and is evenly distributed throughout the reaction phase.

This type of catalytic reactions occur in gas or solution phase *i.e.,* in one single phase.

Examples of homogeneous catalysis in gas phase

(*a*) NO in HNO_3 vapour in the oxidation of SO_2 (Chamber process)

$$2SO_2(g) + O_2(g) + [NO(g)] \longrightarrow 2SO_3(g) + [NO(g)]$$

(*b*) $$H_2(g) + Cl_2(g) + [\text{moisture}] \longrightarrow 2HCl(g) + [\text{moisture}]$$

(*c*) $$NH_3(g) + HCl(g) + [\text{moisture}] \longrightarrow NH_4Cl(g) + [\text{moisture}]$$

Examples of homogeneous catalysis in solution phase

(*a*) Inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6 + [H^+]$$

(*b*) Decomposition of H_2O_2 in the presence of I^-

$$2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2$$

Heterogeneous Catalysis

In this type of catalytic reactions, the catalyst forms a separate phase, usually a finely divided solid either as such or supported on an inert solid such as asbestos or gas (fluidised bed). This is usually termed *contact catalysis.* This type of catalysis has a great technical importance.

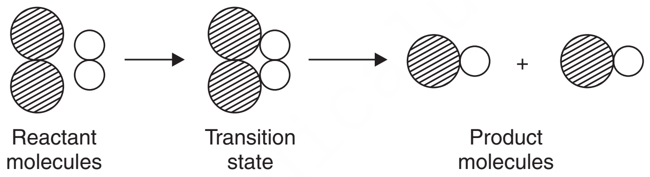
Examples of Heterogeneous Catalysis:

(*a*) $2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$ (Pt-Catalyst)

(*b*) $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$ (Fe-Catalyst)

Activation energy and Catalysis reaction

According to collision theory: the molecules of reactants collide to give products. Schematically it is represented as follows:



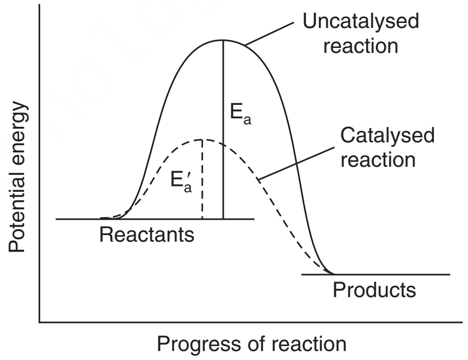


Fig. 6.1 Progress of reaction.

The minimum amount of energy required to attain transition state is called energy of activation, E_a. Catalyst lowers the energy of activation (E_a) of a reaction.

Important Applications of Catalysts

Reactions	*Examples*	*Catalyst used*
(*i*) Dehydration	$C_2H_5OH \longrightarrow C_2H_4 + H_2O$	Alumina, Zirconia
(*ii*) Hydrolysis	Vegetable oil + $H_2O \longrightarrow$ Fatty acid + glycerol	Twitchel's reagent
(*iii*) Oxidation	$2SO_2 + O_2 \longrightarrow 2SO_3$ $C_6H_6 + O_2 \longrightarrow$ Maleic anhydride $C_{10}H_8 + O_2 \longrightarrow$ Phthalic anhydride	V_2O_5
(*iv*) Hydrogenation	Oil + $H_2 \longrightarrow$ Vanaspati $N_2 + 3H_2 \longrightarrow 2NH_3$ (Haber's process) Alkene + $H_2 \longrightarrow$ Akane	Raney Ni Fe Ni, Pt, Pd

(*Contd.*)

(*v*) Dehydrogenation	$C_6H_5C_2H_5 \longrightarrow C_6H_5CH = CH_2 + H_2$ (Styrene)	Cr_2O_3/MoO_3
(*vi*) Alkylation	Friedel– Craft's reaction $C_6H_6 + RX \longrightarrow C_6H_5R + HX$	Anhydrous $AlCl_3$, BF_3, HF
(*vii*) Isomerisation	Normal paraffin ⟶ isoparaffin	Anhydrous $AlCl_3$
(*viii*) Cracking	Long chain paraffin ⟶ branched chain alkanes	Bauxite, MoO_3
(*ix*) Halogenation	Benzene + Cl_2 ⟶ Chlorobenzene	Fe or anhydrous $FeCl_3$
(*x*) Polymerisation	Ethene ⟶ Polythene Styrene ⟶ Polystyrene Vinyl chloride ⟶ PVC	Zeigler catalyst or Peroxides or Persalts

Phase Transfer Catalyst

This type of catalytic reaction may be considered as a combination of homogeneous and heterogeneous catalyses. If we take water and a non-aqueous solvent like benzene and if the reactants remain in the benzene phase and the catalyst in the water phase the reaction is accomplished at the interface provided a little surface active agent (detergent) is added to the system. This type of catalytic reaction is now widely used.

Highlights:

Two other types of catalytic reactions are to be noted.

(*i*) **Autocatalysis—**Examples of such autocatalytic reaction are:
  (*a*) Hydrolysis of ester—water formed in the reaction catalyses the reaction.
  (*b*) Decolourisation of $KMnO_4$ by oxalic acid. Mn^{+2} ion formed initially catalyses the reaction.
(*ii*) **Induced catalysis—**Sodium arsenite solution is not generally oxidised by O_2 but sodium sulphite is oxidised. If air is passed through a solution containing the two salts, both of them undergo simultaneous oxidation. This type of catalytic reaction is known as induced catalytic reaction.

Catalyst Poison

Certain foreign substances, when present in very trace amount, may damage the efficiency of the contact catalyst and may even destroy the catalytic activity. These substances are called **catalyst poisons** or **anti-catalysts.** As_2O_3 acts as a catalyst poison in the contact process for the manufacture of H_2SO_4. The poison acts very likely by blocking the active sites of the catalyst.

Catalyst Promoters

Promoters are the substances which promote the catalytic activity or enhance the activity of a catalyst by its presence. An important catalyst promoter is Al_2O_3 and alkali metal oxide, when used with iron in the Haber's process, the catalytic action increases.

Highlights:

Characteristics of catalytic reactions:

(*i*) Catalyst remains unchanged in mass and chemical composition at the end of the reaction.
(*ii*) Always a small quantity of catalyst is required.
(*iii*) A catalyst is more effective in a finely divided state.

(*Contd.*)

(*iv*) A catalyst is specific in its action.

(*v*) A catalyst cannot initiate a reaction.

(*vi*) A catalyst does not change the position of equilibrium but can only shorten the time required to attain the equilibrium.

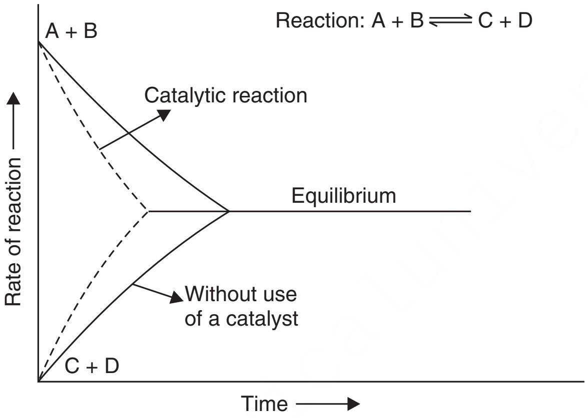


Fig. 6.2 Effect of catalyst on time to attain equilibrium.

(*vii*) Change of temperature can alter the rate of a catalytic reaction as for a non-catalytic reaction.

Mechanism of Catalytic Reactions

The following two theories have been widely accepted:

(*i*) Intermediate compound formation theory

(*ii*) Adsorption theory.

(*i*) Intermediate compound formation theory

This theory explains the catalytic reaction due to the formation of an unstable intermediate compound which is more reactive compared to the reactants. The following examples can be given in support of the above theory:

(*a*) NO_2 acts as an oxygen carrier in *Lead Chamber process.*

$$2NO + O_2 = 2NO_2 \text{ ... fast}$$

$$SO_2 + NO_2 = SO_3 + NO$$

the net reaction being

$$2SO_2 + O_2 = 2SO_3 \text{ (slow if uncatalysed)}$$

(*b*) The intermediate formation of ethyl hydrogen sulphate in the dehydration of alcohol by conc. H_2SO_4 to ether.

(*c*) In Friedel–Craft reaction, anhydrous $AlCl_3$ forms an intermediate compound with RCl and finally generates R^+ for the reaction.

$$RCl + AlCl_3 \longrightarrow \overset{\delta+}{R} \ldots \overset{\delta-}{AlCl_4} \rightleftharpoons R^+ + AlCl_4^-.$$

(*ii*) Adsorption theory (Heterogeneous catalysis)

This theory mainly explains the mechanism of a catalytic reaction between two gases catalysed by a solid. Here, the catalyst works by adsorption of the gas molecule on its surface. The adsorption theory is compared to the intermediate compound formation theory. Here, the intermediate compound is an **activated complex** formed on the catalyst surface. The adsorption theory can be explained by the following Fig. 6.3.

(*a*) Adsorption of H_2 molecule

(*b*) H–H bond weakened and broken by chemisorption

(*c*) Formation of activated complex with ethene.

(*d*) The product ethane released from catalyst surface.

Fig. 6.3 (*a*), (*b*), (*c*) and (*d*).

Biochemical Catalysts (Enzymes)

Numerous organic reactions occur in the body of living beings, either plants or animals, to maintain the life processes. These reactions are catalysed by certain organic compounds which are known as **biocatalysts** or **enzymes.**

Enzymes are invariably protein molecules. But not all protein molecules are enzymes. This statement can be explained by the fact that those protein molecules containing an active site are enzymes. The protein molecules, which do not contain those active sites cannot function as enzymes. It is assumed that enzymes act on a substrate to give products. The following figure explains the enzymatic activity:

Enzymatic activity can be explained as:

$$\text{Enzyme} + \text{Substrate} \rightleftharpoons \underset{\text{[activated complex]}}{\text{Enzyme} - \text{Substrate}} \longrightarrow \text{Products} + \text{Enzyme}$$

The reaction is abbreviated as:

$$E + S \rightleftharpoons E - S \longrightarrow P + E.$$

where E = enzyme, S = substrate (reactant),
ES = activated complex, P = products.

The reaction may be represented pictorially as follows (Fig. 6.4).

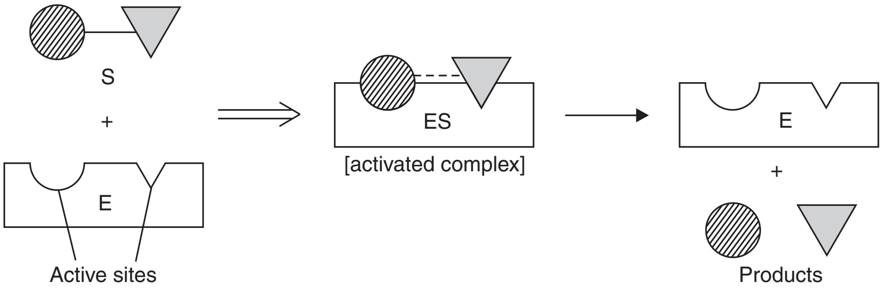


Fig. 6.4 Illustration of the lock-and-key model of enzyme catalysis.

Examples of enzymatic reactions

(*i*) Inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

(*ii*) Fermentation

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2\,C_2H_5OH + 2CO_2$$

(*iii*) $$\text{Amylose} \xrightarrow{\text{Amylase}} \text{Maltose}$$

(*iv*) $$H_2O_2 \xrightarrow{\text{Peroxidase}} H_2O + \frac{1}{2}O_2.$$

Highlights:

- Enzymatic reactions generally take place at 35°-45°C.
- Enzymes lose their activity at higher temperatures.
- Enzymes do not act in cold conditions.
- Enzymatic activity is pH dependent.
- For its full activity, enzyme needs help of another factor (compound) known as co-factor or co-enzyme.
- Enzymatic reactions are generally dependent on the concentrations of enzymes.
- Enzymatic reactions not at all depend on the concentration of the reactant *i.e.*, substrate *i.e.,* enzymatic reactions are zero order reactions.

SHORT QUESTIONS AND ANSWERS

Q. 1. What is a catalyst?

Ans. A catalyst is a substance that speeds up chemical reactions without changing itself.

Q. 2. What is the effect of a catalyst on free energy change of a reaction?

Ans. A catalyst cannot change the free energy change of a reaction.

Q. 3. What is the effect of a catalyst on the equilibrium constant of a reaction?

Ans. A catalyst does not alter the equilibrium constant of a reaction, it only shortens the time of attaining the equilibrium.

Q. 4. Mention the effect of a catalyst on activation energy (E_a) of a reaction.

Ans. A catalyst lowers the activation energy of a reaction.

Q. 5. Draw a distribution curve showing how the proportion of molecules able to react increases when a catalyst lowers the activation energy.

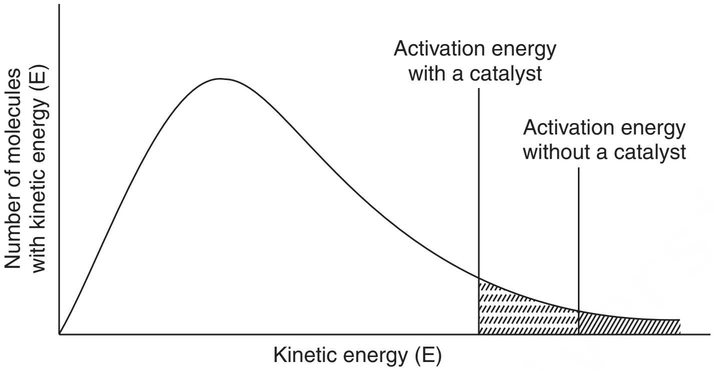


Fig. 6.5

Give experimental evidence that different catalyst has no influence on the yield of a reaction.

Ans. It has been observed that at the same temperature the yield of SO_3 is the same, whether the catalyst used be Pt, Fe_2O_3 or V_2O_5.

Q. 6. Give important uses of negative catalysts of technical importance.

Ans. An important type of negative catalyst is termed *anti-oxidants*. Aromatic amines, thiourea, etc., are used as antioxidants for prolonging the life of rubber. Widest technical use of negative catalyst is TEL as 'antiknock' compound in motor fuel. *n*-propyl gallate, lentoxy anisole are added to retard the rancidity of oil.

Q. 7. What is autocatalysis?

Ans. When one of the products of a reaction itself acts as a catalyst for that reaction the phenomenon is called *autocatalysis*.

Q. 8. Draw a graph for an autocatalytic reaction.

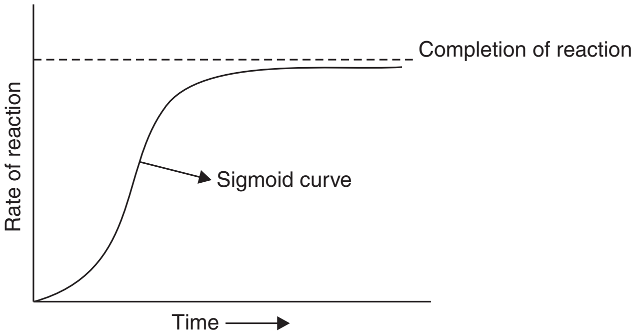


Fig. 6.6

Ans. In autocatalysis reaction as the catalytic product is gradually formed, the rate of reaction increases. The rate is maximum when the reaction is complete (Fig. 6.6).

Q. 9. Why is the hydrolysis of ethyl acetate autocatalytic?

Ans. As traces of moisture initiate the reaction, CH_3COOH is formed acts as catalyst.

$$CH_3COOC_2H_5 + H_2O \longrightarrow \underset{\text{catalyst}}{CH_3COOH} + C_2H_5OH$$

Q. 10. What are homogeneous and heterogeneous catalysts? Give examples.

Ans. If the catalyst is in the same phase as the reactants, it is a homogeneous catalyst. If the catalyst is in a different phase, it is a heterogeneous catalyst.

Example: (*i*) Homogeneous catalyst = Hydrolysis of ester, both acid and base catalysed.

(*ii*) Heterogeneous catalyst (contact catalyst) = In Haber's process for manufacture of ammonia ($Fe + Al_2O_3 + K_2O$).

Q. 11. What are enzymes?

Ans. Enzymes are proteins in nature and are the catalysts for biochemical reactions.

Q. 12. Do you know any use of enzymes in detergent?

Ans. Some washing powders contain proteases—enzymes that remove blood stains on dirty clothes.

Q. 13. Mention the main characteristics of an enzyme.

Ans. Enzymes are highly specific. Each enzyme catalyses a particular reaction. Every enzyme has an 'active site', that is, just right shape and size for the substrate molecules. Each enzyme works best at a particular temperature and pH.

CATALYTIC APPLICATIONS OF ORGANOMETALLIC COMPLEXES

Effective Atomic Number (E.A.N.)

To explain the formation of a complex of a metal with a ligand, it was suggested by Sidgwick that metal ions will tend to accept the electron pairs from donors, *i.e.,* ligand until they have obtained a sufficient number of electrons, so that a metal ion in the resulting complex has an effective atomic number of the nearest inert gas. This rule will help to understand the formation of a complex which in turn will lead to get a better explanation of complex compounds acting as catalysts in various reactions.

So, the *effective atomic number* (*E.A.N.*) of a metal is obtained by deducting the number of electrons lost in the metal ion formation, then adding the number of electrons gained by co-ordination *i.e.,* two electrons from each ligand having one co-ordination centre. The rule can be exemplified by the following table:

E.A.N. Determination

Metal ion	*Atomic no. of metal*	*Co-ordination number*	*Electrons lost in ion formation*	*Electrons added by co-ordination*	*E.A.N.*
Fe^{2+}	26	6	2	12	36 (Kr)
Co^{3+}	27	6	3	12	36 (Kr)
Cu^{+}	29	4	1	8	36 (Kr)
Ni^{2+}	28	4	2	8	34 (Se)

The 18-electron Rule

This is another way of expressing noble gas electron number rule *i.e.,* effective atomic number rule regarding complex formation. The statement of 18-electron rule is that the valence shell of metal atom will attain 18 electrons by saturation of $(n - 1)$ *d*, *ns* and *np* orbitals of metals by the ligands. Thus, the saturation will occur as follows:

10 (for $(n - 1)$ *d* subshell) + 2 (for *ns* subshell) + 6 (for *np* subshell) = 18 electrons.

To illustrate, let us cite the following examples:

Compounds	*Central metal atom with oxidation number*	*Electronic configuration of the central metal of (n–1) d subshell*	*No. of electrons donated by ligands*	*Total no. of electrons in (n – 1) d, ns and np levels*
(*i*) Ni $(CO)_4$	Ni(0)	$3d^{10}$	2 × 4 (four CO groups) = 8	10 + 8 = 18 electron valence shell configuration
(*ii*) $Fe(CO)_5$	Fe(0)	$3d^8$	2 × 5 (five CO groups) = 10	8 + 10 = 18 electron valence shell configuration

The attainment of 18 electrons in the valence shell of the metal atom or satisfying 18-electron rule is one of the useful criteria of elucidating the structure of metal carbonyls.

Structure and bonding in organometallic complexes, the 16-and 18-electrons rule:

The role of metals in catalytic cycles during some chemical reactions:

- **Hydrogenation using $(Ph_3P)_3RhCl$**

The hydrogenation of unsaturated organic compounds *i.e.,* mostly alkenes is an important industrial reaction. Almost all large scale hydrogenation processes are carried out using Raney Ni as catalyst, which acts heterogeneously. Homogeneous systems are used for pharmaceutical industries. Organometallic chemists made the process very popular. The hydrogenations of alkenes and alkynes have been studied extensively. $(Ph_3P)_3$ RhCl, which is generally known as Willkinson's catalyst, acts as a homogeneous catalyst for the hydrogenation of alkenes and alkynes. The catalyst is not able to reduce other organic functional groups, though it is a very reactive compound. It is dissociated (only 5%) into 14 electron species in pure solvents, thus:

$$(Ph_3P)_3\ RhCl \rightleftharpoons (Ph_3P)_2RhCl + PPh_3$$

The species $(Ph_3P)_2$ RhCl is of low coordinating power.

The action of the Willkinson's catalyst is represented by the following cycle. In the cycle there are four co-ordination compounds (II – V). The 14-electron species (II) is formed by dissociation of phosphene ligand from (I). The structure (II) is seen to possess a vacant coordination site shown by a square. This is because stable Rh(I) complexes are generally four coordinated (16-electron species).

The 14-electron species (II) which takes two hydrogen atoms to give (III) by oxidative addition (III) is still unsaturated and has a vacant site, so it can readily accept π electrons from the alkene to give (IV). The stage IV is very very significant in the overall hydrogenation process as in this stage, the substrates alkene, hydrogen are now bonded to the same metal atom. Next step is the rearrangement of the coordination site to give V. (V) undergoes reductive elimination to release the alkane and regenerate the 14-electron species.

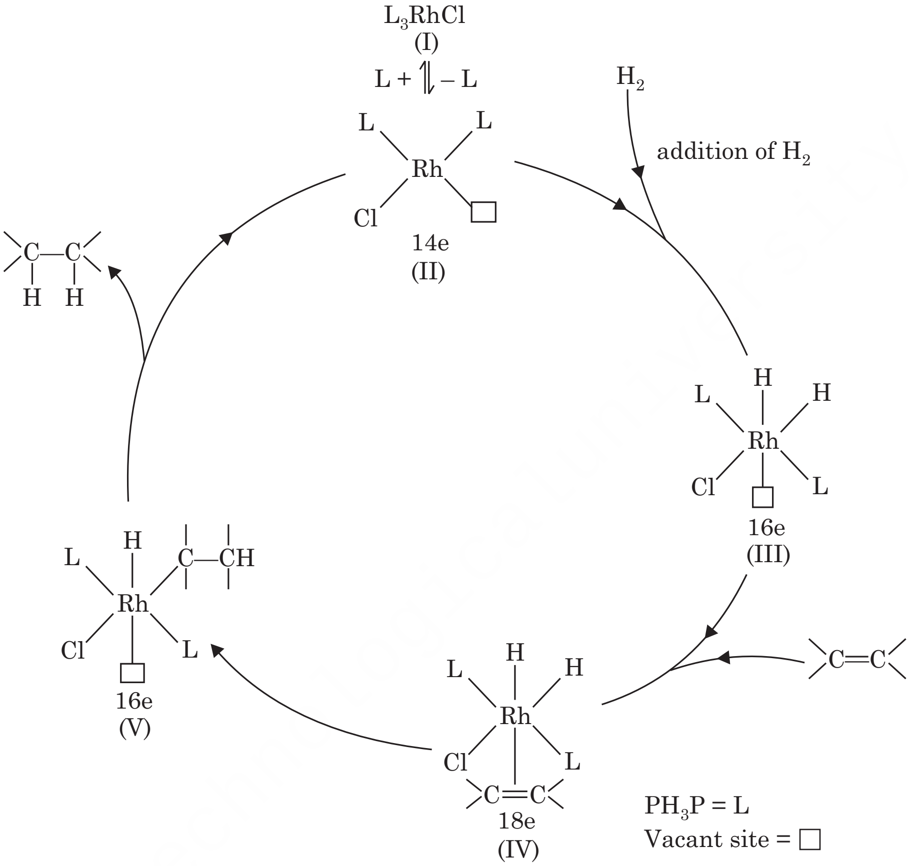


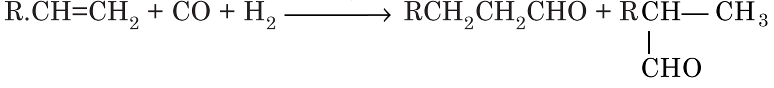
Fig. 6.7 Catalytic applications of organometallics.

Highlights:

- Oxidative addition refers to the increase in coordination site of the central metal.
- Reductive elimination refers to the decrease in coordination site of the central metal.

- **Hydroformylation**

The reaction of an alkene with synthesis gas *i.e.,* mixture of carbon monoxide and hydrogen ($CO + H_2$) to produce an aldehyde, is known as *hydroformylation.* The reaction, which takes place in presence of a catalyst is as follows:



$$R.CH{=}CH_2 + CO + H_2 \xrightarrow{\text{Catalyst}} RCH_2CH_2CHO + R\underset{\displaystyle CHO}{\underset{|}{CH}}—CH_3$$

Several transition metal compounds are used as catalyst in hydroformylation. But among them, catalysis by cobalt or rhodium compounds is of interest. Industrially cobalt carbonyl is used as catalyst at 130° – 170°C and under 200 – 300 atm pressure. As this needs high pressure reactor the initial installation cost of the plant is high for an industrial process.

The mechanism of hydroformylation using cobalt carbonyl as catalyst is shown in the scheme.

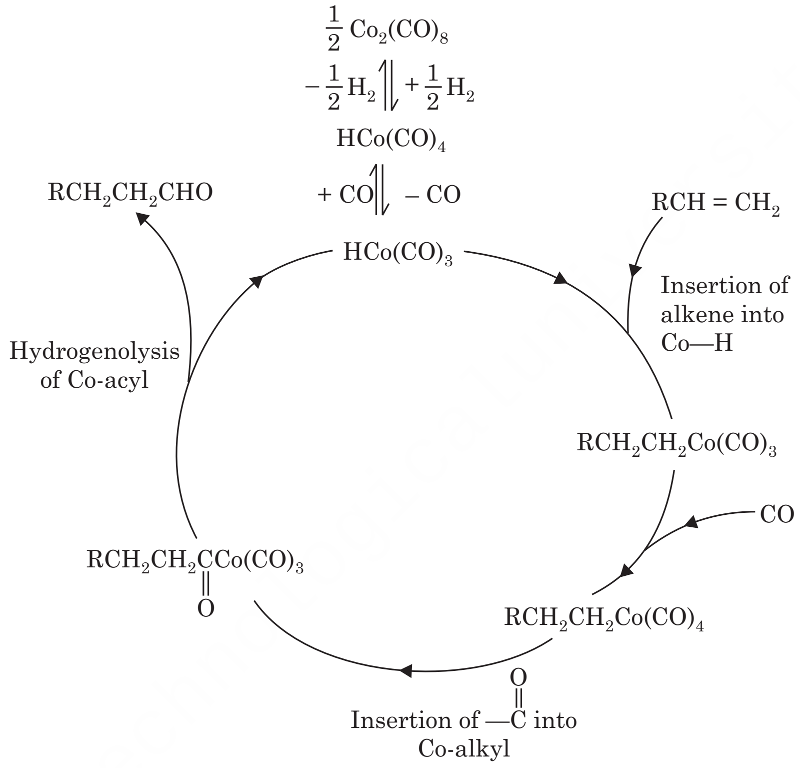


Fig. 6.8

EXERCISES

1. Define with illustrations:
   (*i*) catalysis, (*ii*) positive catalysis, (*iii*) negative catalysis.
2. What do you mean by (*i*) homogeneous and (*ii*) heterogeneous catalytic reactions?
3. What are catalyst poisons and promoters?
4. Discuss a few important catalytic processes.
5. "A catalyst doesn't affect the final state of equilibrium, although it shortens the time required to establish the equilibrium."—explain.
6. Give a brief account of the various theories of the mechanism of catalysis.
7. What will be a more effective catalyst—platinum as a lump or finely divided platinum? Give reason.
8. How does a catalyst accelerate the speed of a reaction? Explain with proper energy profile diagram.
9. Write notes on:
   (*i*) Adsorption theory of catalysis,
   (*ii*) Enzyme catalysis.

10. Give one example of an industrially important catalytic reaction, mentioning the specific catalyst used.

11. Write an account of the kinetics of heterogeneous catalytic reaction.

12. Write notes on:

(*i*) Catalyst and equilibrium point.

(*ii*) Catalyst and energy of activation.

(*iii*) Phase transfer catalysis.

13. Write briefly on acid-base catalysis.

14. What are the chief criteria of catalysis? Describe four applications of catalysis.

15. Write notes on:

(*i*) Hydrogenation catalysts and oxidation catalysts and their application in India.

(*ii*) Specificity of catalytic action.

16. Write short notes on:

(*i*) Effective atomic number

(*ii*) 18-electron rule.

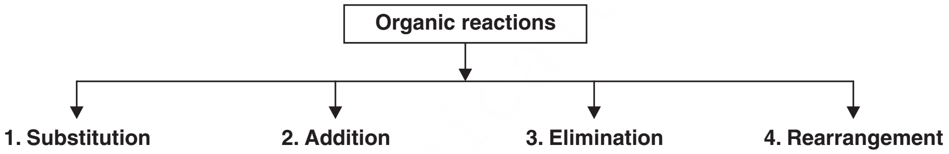
17. Discuss with suitable mechanisms—the processes of hydrogenation and hydroformylation.

7

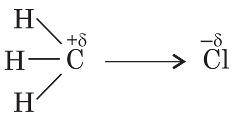
Mechanism of Organic Reactions

REACTION TYPES

Types of organic reactions may be depicted as follows:



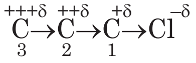
In organic compounds, the carbon atom is attached to other atoms by covalency. One covalent bond is made of a pair of electrons. If the bond is between two same atoms, *i.e.,* of the same electronegativities, then the influence of the atoms on the bond is same. If the bond is between two atoms of unequal electronegativities, then the influence of the atoms on the bond is not the same. It will depend on the elctronegativity values of the two atoms. The displacement of the bonding electrons will be towards the atom of greater electronegativity. And in this condition the bond is said to be polarised, and acquires ionic character. For example, in methyl chloride, the bond between carbon and chlorine is polarised and the bonding electron is displaced towards chlorine atom as follows:



Inductive Effect

As a result of the displacement of the bonding electrons between C—Cl, carbon atom acquires a small positive charge and the chlorine atom acquires a small negative charge. This sort of bond polarisation due to the presence of electronegative element like chlorine is known as **inductive effect**. And this effect is permanent.

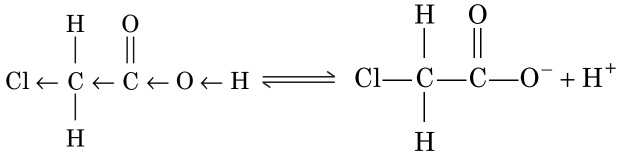
The **inductive effect** is seen to exist upto third carbon atom from the electronegative atom in the chain



$$\overset{+++\delta}{\underset{3}{C}}\rightarrow\overset{++\delta}{\underset{2}{C}}\rightarrow\overset{+\delta}{\underset{1}{C}}\rightarrow\overset{-\delta}{Cl}$$

But the charge on the carbon atoms gradually decreases, which has been indicated by +δ, ++δ, +++δ, etc.

This inductive effect has a great influence on the character of organic compounds as well as on organic reactions. As for example, chloroacetic acid is more acidic than acetic acid. This phenomenon is explained as follows: Due to inductive effect of chlorine atom the release of proton from chloroacetic acid ($K_a = 1.55 \times 10^{-3}$) molecule becomes much easier than that of acetic acid ($K_a = 1.85 \times 10^{-5}$).



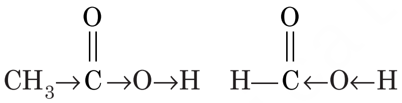
$$Cl \leftarrow \overset{\displaystyle H}{\underset{\displaystyle H}{C}} \leftarrow \overset{\displaystyle O}{\overset{\|}{C}} \leftarrow O \leftarrow H \rightleftharpoons Cl—\overset{\displaystyle H}{\underset{\displaystyle H}{C}}—\overset{\displaystyle O}{\overset{\|}{C}}—O^- + H^+$$

An example of (–I) effect

The electronegativity scale is represented as follows:

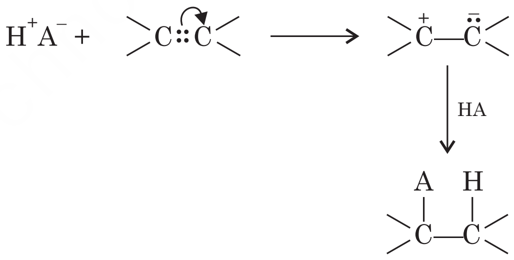
$$NO_2 > F > COOH > Cl > Br > I > OH > OCH_3$$

The electron displacement due to electronegative atom is known as **(–I) effect**, on the contrary, electron displacement by repulsion is known as **(+I) effect.** Due to (+I) effect of CH_3 group, CH_3COOH is weaker acid than HCOOH. Electron repulsion of the bonding electrons by the CH_3 group in acetic acid molecule makes H^+ release comparatively difficult. It is an example of (+I) effect.



$$CH_3 \rightarrow \overset{\displaystyle O}{\overset{\|}{C}} \rightarrow O \rightarrow H \quad H—\overset{\displaystyle O}{\overset{\|}{C}} \leftarrow O \leftarrow H$$

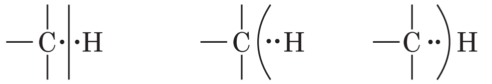
Another phenomenon is worthwhile to mention. If an organic molecule contains a double bond, then the π electrons are transferred completely to one of the bonded atoms under the influence of attacking reagents. This effect is temporary and is known as **electromeric effect**.



The effect is generally represented by a **bend arrow**. Sometimes non-polar covalent molecules like bromine get polarised under the influence of double bond. This sort of polarisation effect is the cause of many organic reactions.

Homolytic and Heterolytic Fissions of a Bond

During the occurrence of an organic reaction there is always a bond breaking and a bond making process. The bond break-up may be homolytic or heterolytic.



(*a*) homolytic bond breaking (*b*) heterolytic bond breaking (*c*) heterolytic bond breaking

This type of bond breakings give rise to **free radicals** as well as **carbocations** (C^+) and **carbanions** ($C^–$). Free radicals are generated due to homolytic fission and carbocations and carbanions are generated due to heterolytic fission of the bond. So organic reactions can take place through free radical formation or through the formation of carbocations and carbanions. When the reaction takes place through free radical formation (Fig. *a*) the mechanism of the reaction is called **free radical mechanism**. When the reaction takes place through the formation of an ion (Figs. *b* and *c* above) the mechanism is known as **ionic mechanism**.

Free Radical Mechanism

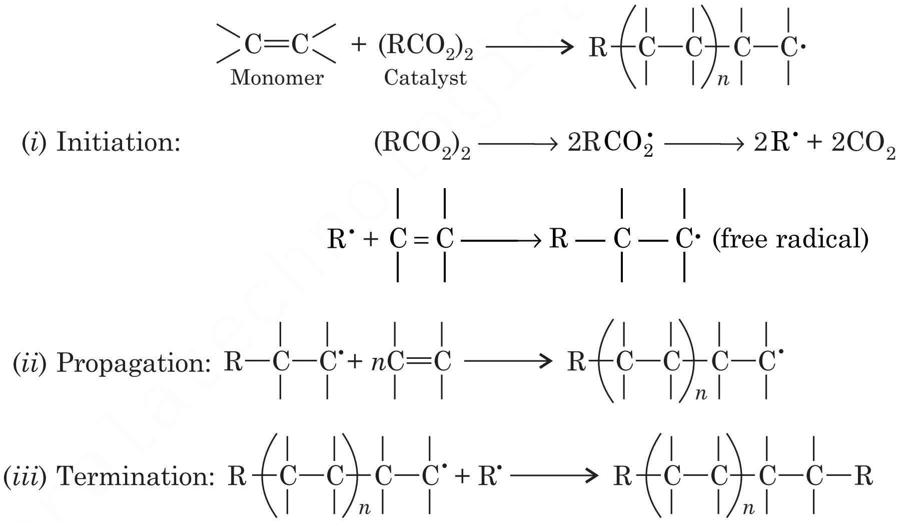
The chlorination of methane, *i.e.,* substitution of methane takes place through free radical mechanism. So it is a free radical substitution reaction. It is represented as follows:

$$Cl_2 \xrightarrow{\text{heat or } h\nu} 2Cl^\bullet \qquad \text{Initiation step}$$

$$\left.\begin{aligned} Cl^\bullet + CH_4 &\longrightarrow HCl + CH_3^\bullet \\ CH_3^\bullet + Cl_2 &\longrightarrow CH_3Cl + Cl \end{aligned}\right\} \text{Propagation step}$$

$$\left.\begin{aligned} Cl^\bullet + Cl^\bullet &\longrightarrow Cl_2 \\ CH_3^\bullet + CH_3^\bullet &\longrightarrow CH_3 - CH_3 \end{aligned}\right\} \text{Termination step}$$

Polymerisation reactions also take place through free radical mechanism.



$$\rangle C{=}C\langle \ + \ (RCO_2)_2 \longrightarrow R\left(-C-C-\right)_n-C-C^\bullet$$

Monomer Catalyst

(*i*) Initiation: $(RCO_2)_2 \longrightarrow 2RCO_2^\bullet \longrightarrow 2R^\bullet + 2CO_2$

$$R^\bullet + C=C \longrightarrow R-C-C^\bullet \text{ (free radical)}$$

(*ii*) Propagation: $R-C-C^\bullet + nC{=}C \longrightarrow R\left(-C-C-\right)_n-C-C^\bullet$

(*iii*) Termination: $R\left(-C-C-\right)_n-C-C^\bullet + R^\bullet \longrightarrow R\left(-C-C-\right)_n-C-C-R$

There are other ways of termination of a polymerisation reaction.

Classification of Reagents

The reagents which take part in *ionic reactions* are categorised as:

1. **Electrophiles or electrophilic reagents**
2. **Nucleophiles or nucleophilic reagents**

Electrophiles mean electron seeking, *i.e.,* these reagents attack at the point of highest electron density of a molecule. That means electrophiles are positively charged species. On the contrary, **nucleophiles** mean nucleus seeking, *i.e.,* they attack at the positive centre of a polarised molecule. Nucleophiles may be negatively charged or a neutral molecule having an atom with a lone pair of electrons.

Nucleophiles	**Electrophiles**
(*a*) OH^-, CN^-, Cl^-, Br^-, I^-	(*a*) H^+ and other positive ions.
(*b*) Double and triple bonds of alkenes and alkynes.	(*b*) Halogen and halogen acids.

(*c*) Compounds containing an atom with a lone pair.	(*c*) H_2SO_4, HNO_3, HNO_2, etc.
(*d*) R_2O:, :NH_3 , R_3N:, etc.	(*d*) NO_2, $AlCl_3$, BF_3, etc.

That means electrophiles are Lewis acids *i.e.,* electron pair acceptors and nucleophiles are Lewis bases *i.e.,* electron pair donors. And the reactions of electrophiles and nucleophiles may be considered as neutralisation reactions, nucleophiles donate an electron pair and the electrophiles accept it and makes a bond. Conventionally, if the attacking reagent be an electrophile, the reaction is called **electrophilic reaction** and when the attacking reagent is a nucleophile, the reaction is called **nucleophilic reaction**.

Classification of Reactions

Broadly, the reactions may be classified as follows:

1. **Electrophilic reactions**
2. **Nucleophilic reactions**

Again electrophilic reactions may be of the two types *viz.* **addition** and **substitution**. And so is the case with nucleophilic reactions.

Another type of reaction is very common in organic chemistry which is known as elimination reaction.

Some common ionic organic reactions are:

- **Electrophilic addition**
- **Electrophilic substitution**
- **Nucleophilic addition**
- **Nucleophilic substitution and**
- **Elimination reaction**

Energy Changes during the Progress of a Reaction

Energy is needed to break a bond and energy is released while making a bond. If we take chlorination of methane for example. The methane molecules must collide with chlorine molecules. The minimum amount of energy that must be provided by a collision for reaction to occur is called the **energy of activation** (E_{act}). The source of E_{act} is the kinetic energy of moving molecules. The potential energy at any stage of the reaction is indicated by the height of the curve (see Fig. 7.1).

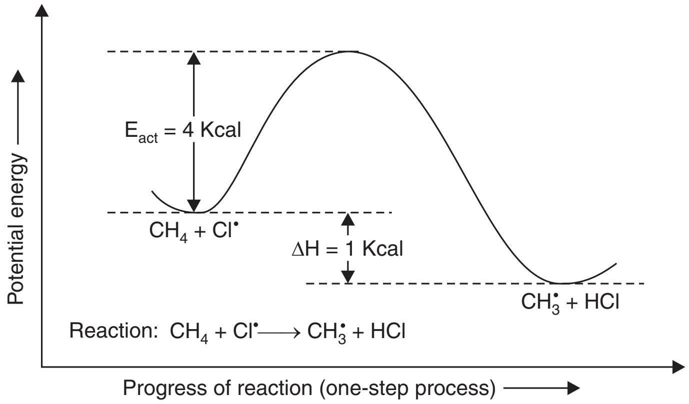
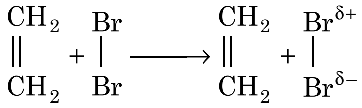


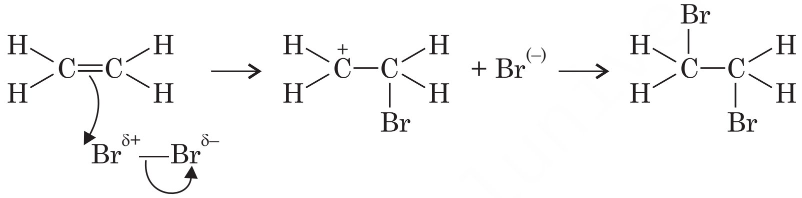
Fig. 7.1 Potential energy changes during progress of reaction: (One-step process) an exothermic reaction.

Examples:

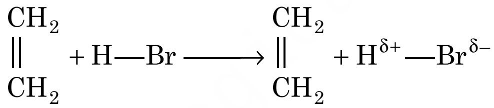
1. Electrophilic addition. Bromine molecule gets polarised when comes in close contact with a π bond. The positive bromine ion then gets attached to a carbon atom attached to a double bond making other carbon atom of the double bond a carbocation, that carbocation gets attached to the Br^- generated. Thus addition of a bromine molecule takes place to a double bond:



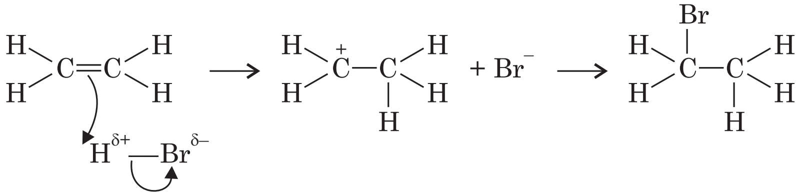
$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{c} Br \\ | \\ Br \end{array} \longrightarrow \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{c} Br^{\delta+} \\ | \\ Br^{\delta-} \end{array}$$



The addition of HBr to ethylene is also an example of electrophilic addition:



$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + H—Br \longrightarrow \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + H^{\delta+}—Br^{\delta-}$$

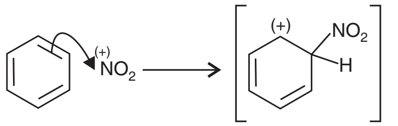


2. Electrophilic substitution. Electrophilic substitution takes place in three steps. Nitration of benzene is an example of electrophilic substitution.

Step 1. Generation of an electrophile:

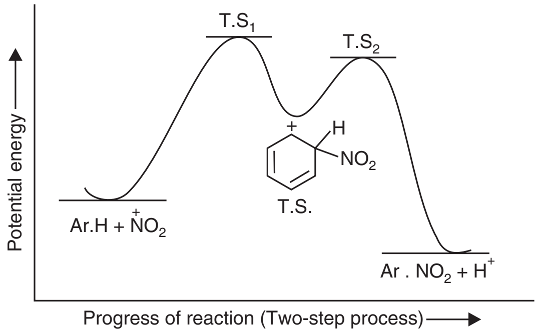
$$HNO_3 + 2H_2SO_4 \rightleftharpoons 2HSO_4^- + H_2O^+ + {}^+NO_2$$

Step 2. Formation of a transition state:

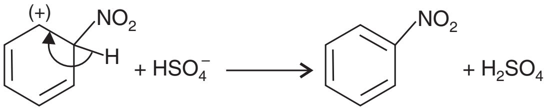


Transition state (T.S.) (I)

Potential energy diagram for nitration

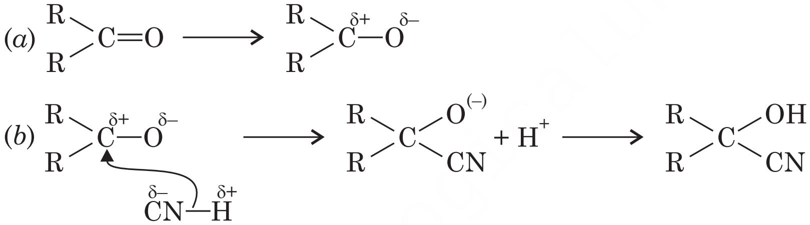


Setp 3. Back to aromaticity from the transition state (I).



Here after the attack of the electrophile the stable aromatic system is disturbed. That is why, the transition state readily goes to the stable aromatic form by releasing a proton and the release of the proton is helped by generated HSO_4^-, the base during reaction.

3. Nucleophilic addition. Addition of HCN to a ketone is an example of nucleophilic addition. Here the attack of nucleophile (CN^-) occurs on a carbonyl carbon leading to an addition reaction. The carbonyl group of the ketone polarises HCN and the addition takes place as follows:



4. Nucleophilic substitution. Nucleophilic attack on the carbon atom of C—X bond in a haloalkane or alkyl halide, RX, leads to substitution, where X = Cl, Br or I. So hydrolysis of alkyl halide is an example of nucleophilic substitution. Study of the rate equations of the reactions suggests that there are two different mechanisms:

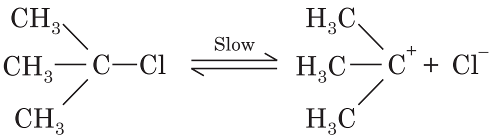
(*a*) Nucleophilic substitution unimolecular ($S_N{}^1$)

(*b*) Nucleophilic substitution bimolecular ($S_N{}^2$).

(*a*) **$S_N{}^1$ reaction.** This is a two-step process. The rate equation is:

$$\text{rate} = K[C(CH_3)_3Cl]$$

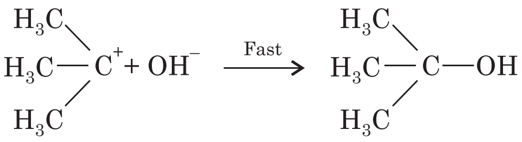
Step 1. Ionisation of the alkyl halides *i.e.,* formation of a carbocation intermediate by breaking of C—Cl bond. Then the nucleophile OH^- attacks and forms a new bond.



Tertiary butyl carbocation

Tertiary butyl carbocation is stable due to the (+I) effect of the methyl groups. This step is rate determining step of the substitution *i.e.,* this step is slow.

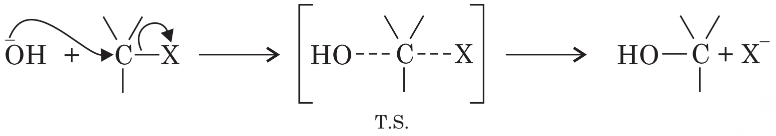
Step 2.



(*b*) **SN^2 reaction:** This is a one-step process. Here the rate equation is

$$\text{rate} = K\,[\text{alkyl halide}]\,.\,[OH^-]$$

The mechanism of the substitution can be represented as follows:



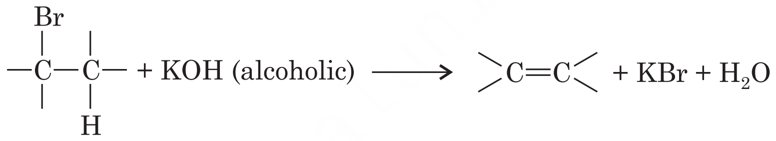
$$\overset{-}{O}H + \text{C—X} \longrightarrow [\text{HO}\cdots\text{C}\cdots\text{X}] \longrightarrow \text{HO—C} + X^-$$

T.S.

Here the mechanism shows that C—X bond breaks as the nucleophile OH⁻ forms a new bond with carbon simultaneously.

Elimination reaction. This is a reaction that splits off a simple compound from a molecule to form a double bond.

Example 1.



$$\text{—}\overset{Br}{C}\text{—}\underset{H}{C}\text{—} + \text{KOH (alcoholic)} \longrightarrow \text{>C=C<} + \text{KBr} + H_2O$$

Elimination of a hydrogen halide from an alkyl halide produces alkene.

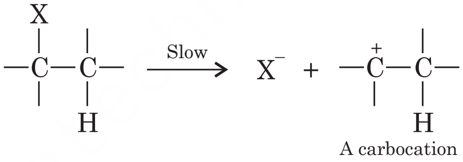
The elimination reaction is of two types and they are base catalysed elimination reactions:

(*a*) Unimolecular reaction (E^1)

(*b*) Bimolecular reaction (E^2).

(*a*) E^1 reaction. This reaction occurs in two steps:

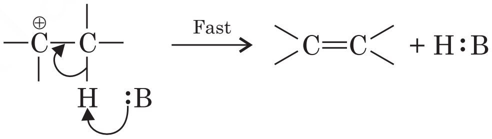
Step 1.



$$\text{—}\overset{X}{C}\text{—}\underset{H}{C}\text{—} \xrightarrow{\text{Slow}} X^- + \text{—}\overset{+}{C}\text{—}\underset{H}{C}\text{—}$$

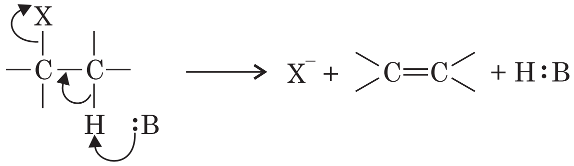
A carbocation

Step 2.



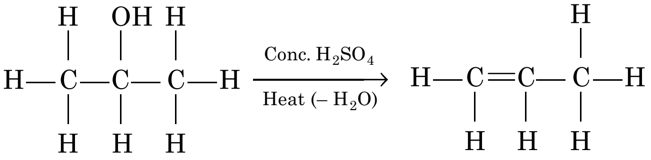
$$\text{—}\overset{\oplus}{C}\text{—}\underset{H}{C}\text{—} \;\; :B \xrightarrow{\text{Fast}} \text{>C=C<} + \text{H:B}$$

(*b*) E^2 reaction. This reaction occurs in one step process



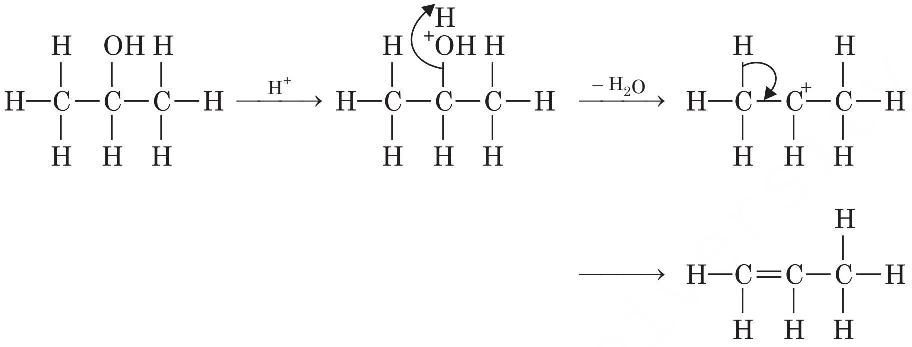
$$\text{—}\overset{X}{C}\text{—}\underset{H}{C}\text{—} \;\; :B \longrightarrow X^- + \text{>C=C<} + \text{H:B}$$

Another example of elimination reaction is the removal of water from an alcohol to form an alkene.



$$\text{H—}\overset{H}{\underset{H}{C}}\text{—}\overset{OH}{\underset{H}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{—H} \xrightarrow[\text{Heat } (-H_2O)]{\text{Conc. } H_2SO_4} \text{H—}\underset{H}{C}\text{=}\underset{H}{C}\text{—}\overset{H}{\underset{H}{C}}\text{—H}$$

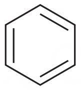
This is an example of acid catalysed elimination reaction. Thus

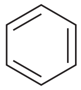


Resonance

The idea of resonance has a major role in understanding the mechanisms of reactions. So the idea needs to be discussed here:

According to Kekule the benzene molecule has following two structures (I) and (II).


(I)


(II)

The structures (I) and (II) cannot satisfactorily explain all the properties of benzene.

1. Despite having three double bonds benzene undergoes substitution reactions more easily than addition reactions.
2. Benzene is more stable than expected.
3. All the C—C bond lengths in benzene is 1.39 Å instead of 1.54 Å for a single bond and 1.34 Å for a C═C bond.

The Kekule structure is still the accepted structure for benzene. This acceptance is not for the discovery of new facts about benzene but is a result of modification of the structural theory. That theory is the concept of **resonance.** Whenever a molecule can be represented by two or more structures that differ only in the arrangement of electrons the different structures arrived at have the same arrangement of atomic nuclei, there is resonance. The primary conditions for drawing the resonating structures are:

(*a*) Position of atoms in the molecule cannot be changed and the molecule should be planar.

(*b*) Position of σ-bonds cannot be changed.

(*c*) Only π electrons and non-bonded electrons can be shifted.

Then all the structures so drawn are the structures of the molecule concerned and none of these structures can staisfactorily explain all the properties of the molecule but a **hybrid** of all these structures which cannot be represented by any one of them is the actual structure of the molecule. Each of these drawn structures contributes to the **resonance hybrid** (Fig. 7.2). The resonance hybrid structure is more stable than any of the contributing structures. The difference in energy of any of the contributing structures and the hybrid structure is called the **resonance energy** (Fig. 7.2).

Graphical representation of the idea of resonance from the heats of hydrogenation values.

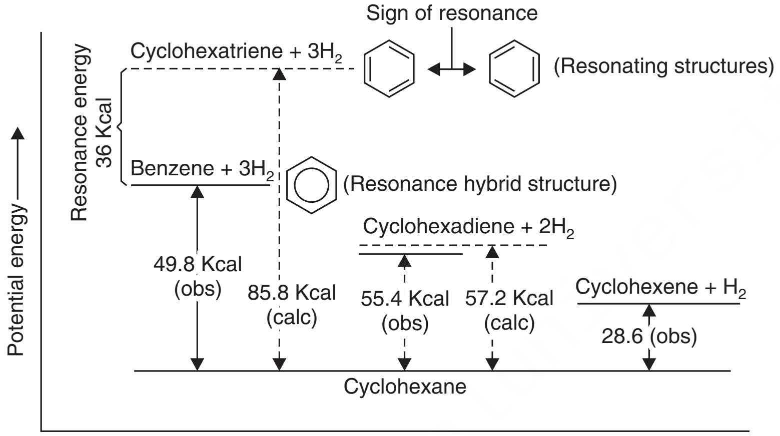


Fig. 7.2 Stability of benzene (Resonance energy).

Explanation

(*i*) We should expect from the graph that the heat of hydrogenation of cyclohexatriene *i.e.,* benzene to be 85.8 Kcal/mol but actually it is 49.8 Kcal/mole. That is, benzene is more stable by 36 Kcal/mole than expected which is **resonance energy** of benzene.

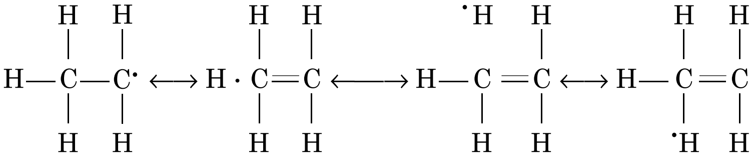
(*ii*) The resonance hybrid structure of benzene contains no single or double bond but a special type of bond that is why all C—C bonds in benzene are equal in length.

(*iii*) As a resonance hybrid benzene is more stable than either of the contributing resonating structures *i.e.,* Kekule structures, this additional stability possessed by benzene is responsible for substitution reactions of benzene and for a new set of properties called *aromatic properties* or *aromaticity.*

Hyperconjugation (*No bond resonance*)

The stabilities of tertiary, secondary and primary alkyl radicals is due to delocalisation of odd electrons through overlapping of the p orbital occupied by the odd electron and the σ-orbital of the alkyl group. For this overlapping, the three electrones *i.e.,* the odd electron and the bond pair of the C—H bond, help to bind together the three nuclei *i.e.*, two carbons and one hydrogen. This type of delocalisation involving σ-orbital is known as hyperconjugation.

In terms of resonance, the hyperconjugation may be represented as follows:

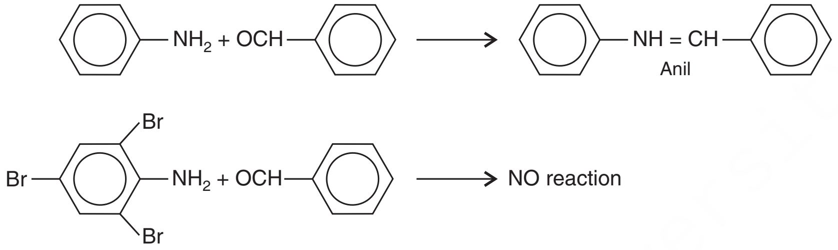


$$\begin{array}{ccccccccccccccccccccccc}
 & & H & & H & & & & H & & H & & & & {}^{\bullet}H & & H & & & & H & & H \\
 & & | & & | & & & & | & & | & & & & & & | & & & & | & & | \\
H & \text{—} & C & \text{—} & C^{\bullet} & \longleftrightarrow & H & \cdot & C & = & C & \longleftrightarrow & H & \text{—} & C & = & C & \longleftrightarrow & H & \text{—} & C & = & C \\
 & & | & & | & & & & | & & | & & & & | & & | & & & & | & & | \\
 & & H & & H & & & & H & & H & & & & H & & H & & & & {}^{\bullet}H & & H
\end{array}$$

Each of the above no-bond resonance structures appears strange. But it is apparent that the C—H bond is something less than a single bond and the odd electron is partly accommodated by the H atoms.

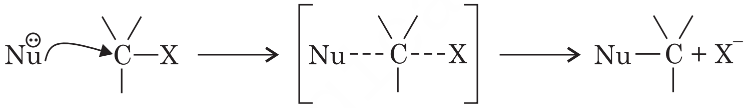
Steric Hindrance

Aniline reacts to form anil with benzaldehyde but 2, 4, 6-tribromoaniline does not. Victor Meyer attempted to explain these abnormalities by **steric hindrance** *i.e., o*–groups in 2, 4, 6-tribromoaniline mechanically interfere the attack by the reagent *i.e.,* tending to shield the molecule from the attacking reagent benzaldehyde.



The term **steric hindrance** originally considers the geometry of the molecule. When a chemical reaction occurs, it does so via **transition state**. The term spatial factor is used to denote steric hindrance, consequently, the geometry of both the initial molecule and the transition state.

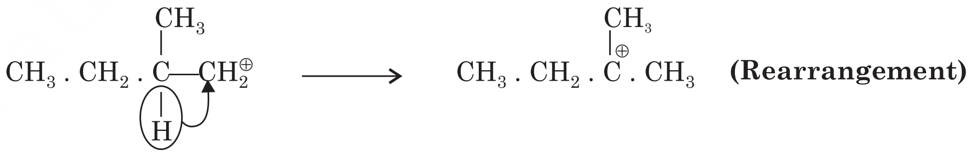
In an S_N2 reaction:



The transition state accommodates more atoms than the initial state. Also, state of hybridisation at the attacked C-atom changes sometimes and the effect of steric hindrance becomes pronounced in T.S. The effect of steric hindrance requires a knowledge of reaction mechanism.From the foregoing discussion we can say, S_N1 reactions will not be affected by the influence of steric hindrance whereas S_N2 reactions are very much affected by steric hindrance.

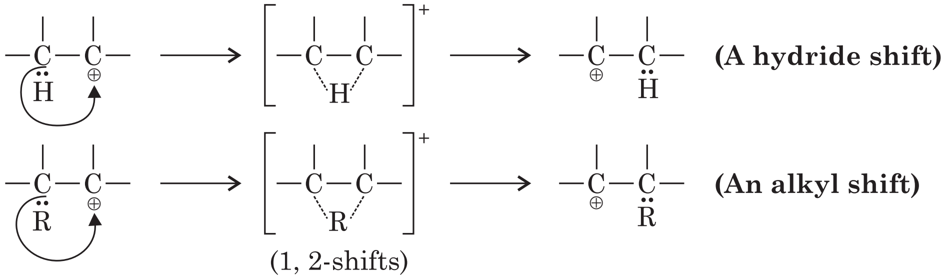
1, 2-shift

A carbonium ion (Carbocation) is formed during a reaction and and rearranges to form a stable carbonium ion (Carbocation) as for example



$$CH_3 . CH_2 . \underset{H}{\overset{CH_3}{C}}—CH_2^{\oplus} \longrightarrow CH_3 . CH_2 . \overset{CH_3}{\overset{\oplus}{C}} . CH_3 \quad \textbf{(Rearrangement)}$$

This type rearrangement takes place by migration of a hydrogen atom with a pair of electrons known as a **hydride shift** or an alkyl group with a pair of electrons known as **alkyl shift or 1, 2-shift.** These are the rearrangements in which the migrating group moves from one atom to the neighbouring next atom. This shift is very much important in understanding organic reactions.



(1, 2-shifts)

Isomerism

Different organic compounds having the same molecular formula are known as isomers. The phenomenon is known as **isomerism**.

The isomerism is of two types:

(*i*) **Structural isomerism**

(*ii*) **Stereoisomerism**.

Structural isomerism may be classified as:

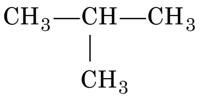
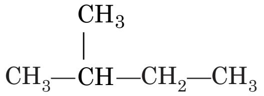
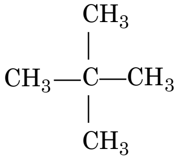
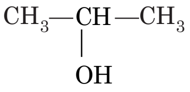
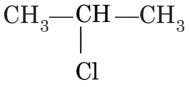
(*a*) **Chain isomerism**

(*b*) **Functional group isomerism**

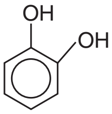
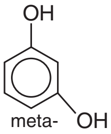
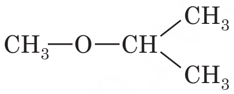
(*c*) **Position isomerism**

(*d*) **Metamerism**.

Examples are displayed in the following table.

Types of isomerism	*Molecular formula*	*Different structures (Compounds)*
(*a*) Chain isomerism	(*i*) Butane [C_4H_{10}]	(*i*) $CH_3—CH_2—CH_2—CH_3$ *n*-butane (*ii*)  $CH_3—\underset{\underset{CH_3}{\vert}}{CH}—CH_3$ Isobutane
	(*ii*) Pentane [C_5H_{12}]	(*i*) $CH_3—CH_2—CH_2—CH_3$ *n*-pentane (*ii*)  $CH_3—\overset{\overset{CH_3}{\vert}}{CH}—CH_2—CH_3$ Isopentane (*iii*)  $CH_3—\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}—CH_3$ Neopentane
(*b*) Functional group isomerism	(*i*) C_2H_6O	(*i*) CH_3CH_2OH ethyl alcohol (*ii*) $CH_3—O—CH_3$ dimethyl ether
	(*ii*) C_3H_6O	(*i*) $CH_3.CH_2.CHO$ Propanaldehyde (*ii*) CH_3COCH_3 acetone
(*c*) Position isomerism	(*i*) C_3H_8O	(*i*) $CH_3CH_2CH_2OH$ *n*-propylalcohol (*ii*)  $CH_3—\underset{\underset{OH}{\vert}}{CH}—CH_3$ isopropylalcohol
	(*ii*) C_3H_7Cl	(*i*) $CH_3.CH_2.CH_2.Cl$ 1-chloropropane (*ii*)  $CH_3—\underset{\underset{Cl}{\vert}}{CH}—CH_3$ 2-chloropropane

(*Contd.*)

	(*iii*) $C_6H_9(OH)_2$	(*i*)  ortho- (*ii*)  meta- (*ii*)  para-
(*d*) Metamerism (isomerism in the same class of organic compounds)	(*i*) $C_4H_{10}O$	(*i*) $C_2H_5—O—C_2H_5$ diethyl ether (*ii*) $CH_3—O—C_3H_7$ methyl *n*-propyl ether (*iii*)  $CH_3—O—CH(CH_3)_2$ Methyl isopropyl ether

Bond rotation (Fig. 7.3) is possible about single covalent bonds but is prevented under normal conditions by **double bonds** or **triple bonds**. The lack of rotation about double bonds gives rise to **geometric isomerism**. The topic has been treated later on.

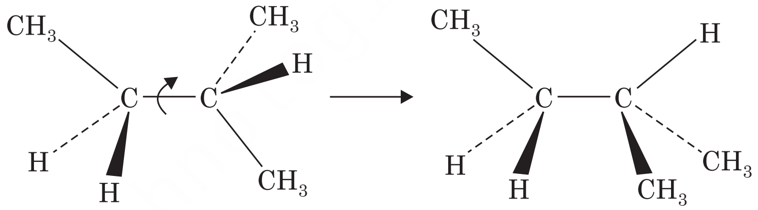
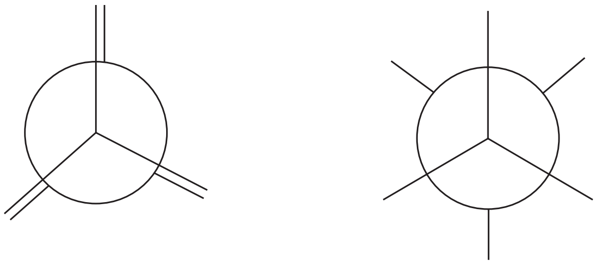


Fig. 7.3 The groups at the end of a single C—C bond can rotate freely relative to each other giving rise to different conformations of molecules.

Conformational Isomerism

The different spatial arrangements arising out of the rotation of a C—C single bond are known as conformations. The different structures obtained due to the rotation of this C—C single bond are known as **conformers**. The two conformers of ethane are given in Fig. 7.4(*a*).



Eclipsed form
(I)

Anti form or staggered form
(II)

Fig. 7.4 (*a*) Newman projection formula for ethane.

There are many other conformers between these two extremes. They are known as 'skew' or 'Gauche' forms. The rotation about $C_2—C_3$ bond of *n*-butane gives different conformers as depicted in Fig. 7.4(*b*).

$$\overset{4}{C}H_3—\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_3 \quad (n\text{-butane})$$

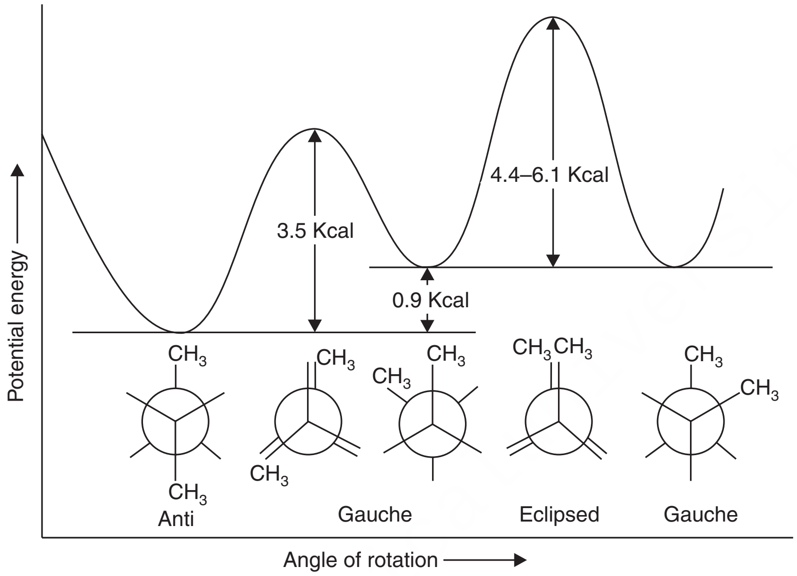


Fig. 7.4 (*b*) Potential energy changes during rotation about C_2—C_3 bond of *n*-butane.

From the potential energy diagram, we see that the anti-conformation of *n*-butane is more stable (CH_3-groups are as apart as possible, 180°). In two Gauche conformations, the —CH_3-groups are 60° apart and they are less stable than the anti-form and more stable than the eclipsed form, the eclipsed conformation is least stable due to severe crowding.

Conformations of Cyclohexane

Factors influencing the stability of conformations: To go deep into the chemistry *i.e.,* the stability of the cyclic compound and its reactivity, we must take help of conformational analysis.

- Any deviations from the normal, *i.e., sp^3* hybridised carbon (bond angle 109.5°) are accompanied by **angle strain**.
- Any pair of tetrahedral carbon attached to each other tend to have their bonds staggered (*i.e.,* ethane-like). Any deviation from the staggered conformation is accompanied by **torsional strain.**
- Any two atoms or groups that are not bonded to each other can interact. This non-bonded interaction can either be repulsive or attractive. And the result can be either destabilisation or stabilisation of the conformation.

In the case of cyclohexane the following conformations are common [Fig. 7.4(*c*)].

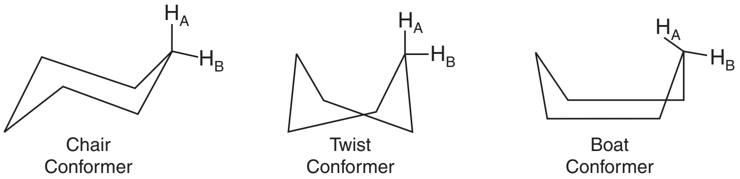


Fig. 7.4 (*c*) Conformers of cyclohexane.

Newman projection formula of **chair conformer** [Fig. 7.4(*d*)]:

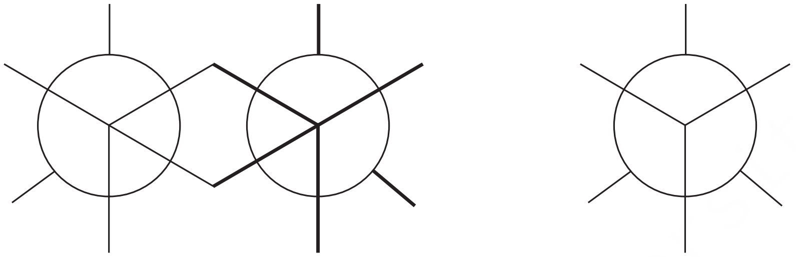


Fig. 7.4 (*d*) Cyclohexane (chair form) staggered form of ethane.

Here the three pairs of tetrahedral carbon of cyclohexane remain in staggered forms. So the chair cyclohexane is more stable conformer of the cyclohexanes. For **boat cyclohexane** the Newman projection formula is as Fig. 7.4(*e*).

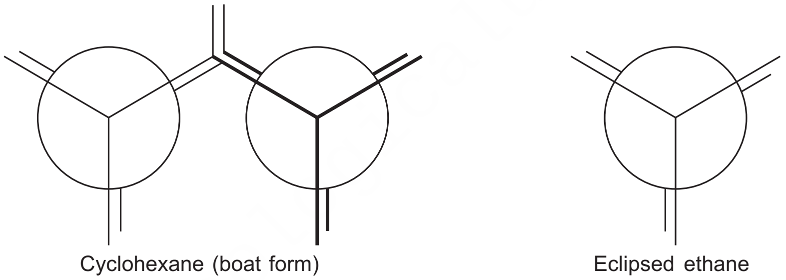


Fig. 7.4 (*e*)

The boat conformation is less stable than the chair conformation at an energy maximum, it is thus not a conformer but a transition state between two conformers. Here the three pairs of tetrahedral carbon of cyclohexane remain in eclipsed forms.

The **twist form** or **skew boat form** is a conformer lying at energy minimum. Between the chair form and twist form there are half chair forms with angle strain and torsional strain. The half chair form is a most unstable form which lies at energy maximum (see Fig. 7.5).

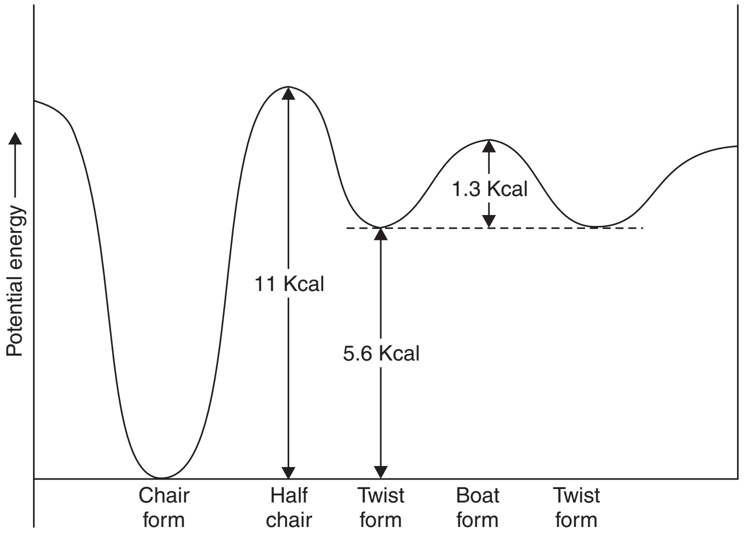


Fig. 7.5 Potential energy diagram (conformations of cyclohexane).

Stereoisomerism

Isomers that differ with respect to the arrangements of atoms or groups in space are known as **stereoisomers** and the phenomenon is known as **stereoisomerism**. This part of the science, which deals with structures in three dimensions is called **stereochemistry**. The two general types of stereoisomerism are:

(*i*) **Optical isomerism** and (*ii*) **Geometrical isomerism**.

Since conformational isomers differ from each other only in this way, that their atoms are oriented is space, they also belong to the **stereoisomers**.

(*i*) **Optical isomerism.** Optical isomerism is shown by the compound containing at least one chiral carbon atom (asymmetric). Optical isomers rotate the plane of polarised light. Generally, a chiral carbon atom is one that is attached to four different atoms or groups. Simple test of determining chirality of a three dimensional molecule is non-superimpossibility of its mirror images (Fig. 7.7). **Polarized light** is a light beam in which all the waves are vibrating in the same plane.

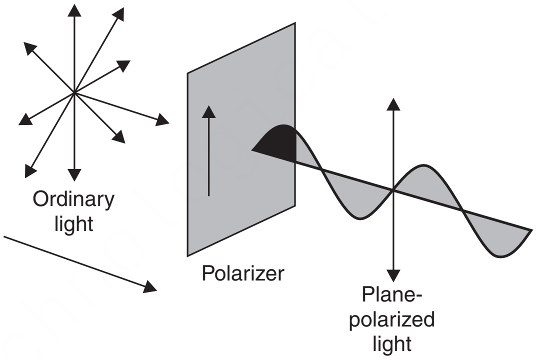


Fig. 7.6 Arrangement for producing plane polarized light.

Light is plane-polarized after passing through a sheet of Polaroid. *Optical isomers* rotate the plane of polarized light (Fig. 7.6).

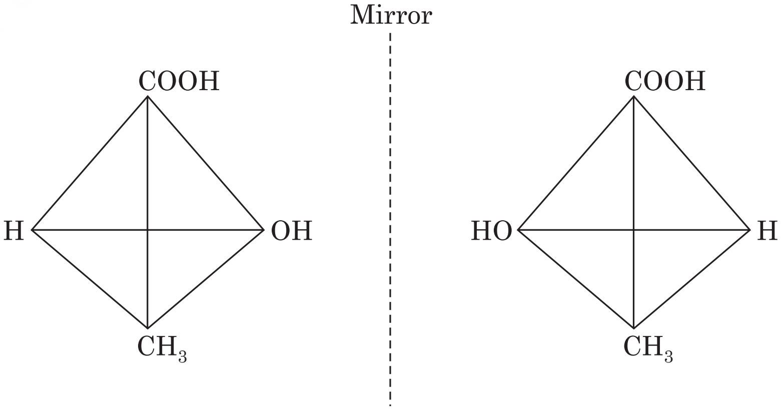


Fig. 7.7 Two configurations of lactic acid.

Two optical isomers of lactic acid (Fig. 7.7) are molecules with no centers, axes or planes of symmetry. Asymmetric molecules are chiral and can exist in distinct mirror image forms, giving rise to **optical isomerism**. Any carbon atom with four different groups or atoms attached to it is **asymmetric**.

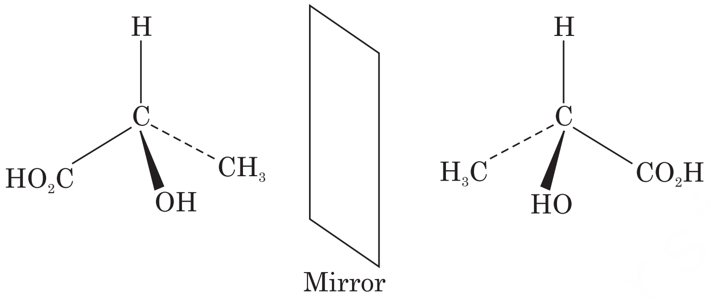
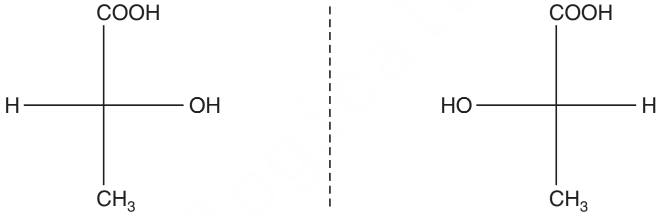


Fig. 7.8 (*a*) The mirror image forms of lactic acid.

Asymmetric Molecules

If we translate the three-dimensional molecule to a two-dimensional figure, we get **Fischer projection formula** of the molecule.



D(–)-Lactic acid mirror L(+)-Lactic acid

Fig. 7.8 (*b*)

Then the test of chirality is very simple. If we rotate Fischer projection formula of one molecule on the plane of the paper by 180° none of the configurations arrived at which is superimpossible on the other. These types of molecules rotate plane of polarised light (see Fig. 7.6) either right or left. The two configurations of lactic acid rotate plane of polarised light in the same degrees but in the opposite directions. These two forms of stereoisomers (configurations) are known as **enantiomers**.

Highlights:

- Number of possible stereoisomers = 2^n.
  where n = number of chiral carbon atoms in the molecule.
- A mixture of equal parts of enantiomers is called racemic modification. The prefix (±) is used to designate the racemic mixture. They can be separated by various physical and chemical methods.

For **compound containing two different chiral carbon atoms**, the stereoisomers (I) and (II), (III) and (IV) are pairs of enantiomers, (I) and (III), (II) and (IV) are diastereomers.

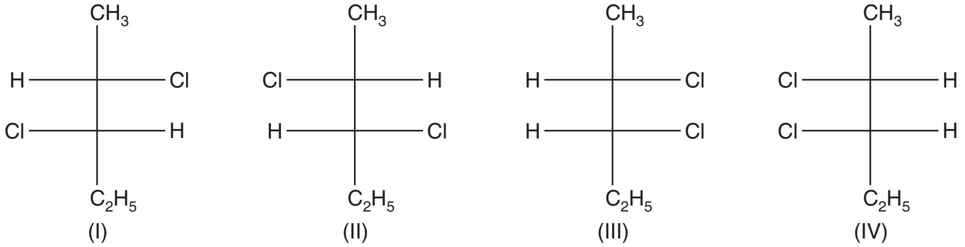


Fig. 7.8 (*c*) Stereoisomers of 2, 3-Dichloropentane.

Stereoisomers which are not pairs of enantiomers are known as diastereomers.

Another interesting phenomenon arises among the compounds containing similar chiral carbon atoms [Fig. 7.8(*d*)].

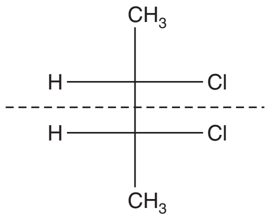


Fig. 7.8 (*d*) Optically inactive isomer (meso form).

Lower part of the molecule is mirror image of the upper part of the molecule and the molecule becomes optically inactive due to internal compensation. This type of isomer is known as **mesoform**.

Geometrical Isomerism

This type of isomerism arises out of restricted rotation about C = C bond. When similar groups are attached to the same side of the molecule, the configuration is known as *cis*-isomers (Z-isomers). When similar groups are attached or the opposite side of the C = C bond, the configuration is known as *trans* isomers (E-isomers). **The geometrical isomerism is also a case of diastereoisomerism** [Fig. 7.8(*e*)].

cis-2-butene
(Z-2-butene)

Trans-2-butene
(E-2-butene)

Fig. 7.8 (*e*)

R-S System of Nomenclature

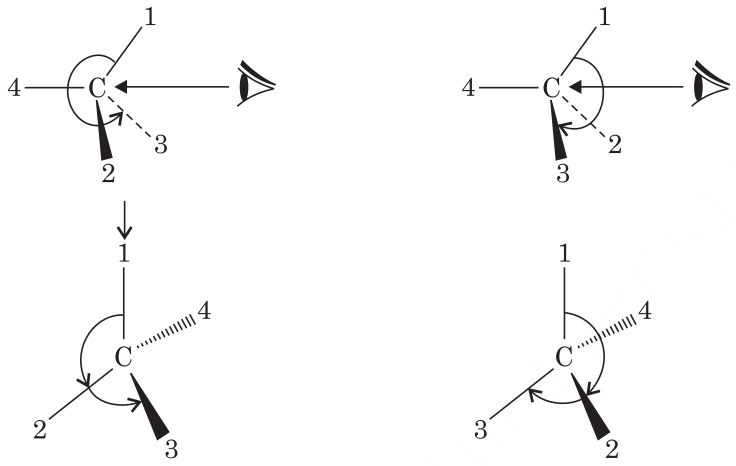
R-S system of nomenclature was developed by Cahn, Ingold and Prelog to designate the configurations of stereoisomers having chiral centres. The system is often termed as "absolute configuration" assignment as this type of specifying configuration is independent of any reference compound.

There are certain **methods of assigning R-S notations** to any chiral centre of a molecule. These are as follows:

- The number of stereocentres in the molecule are identified.
- The four different groups (ligands) attached to each of the stereocentres are found out and given priority 1, 2, 3, 4 or *a*, *b*, *c*, *d*, etc. based on '**sequence rule**', such that $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$ or $a \rightarrow b \rightarrow c \rightarrow d$.
- Then the molecule is viewed from the position far from the lowest priority group and a hypothetical path is drawn moving from $1 \rightarrow 2 \rightarrow 3$ or $a \rightarrow b \rightarrow c$.

If the path provides a clockwise motion, then the stereocentre is designated to have 'R' configuration. If the path describes a counter clockwise or anticlockwise path, then the stereocentre is said to have 'S' configuration [Fig. 7.9].

The (R) or (S) designation is written in italics within the parentheses followed by a hyphen before the name of the compound.



1 → 2 → 3 anticlockwise
(S)–Configuration

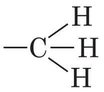
1 → 2 → 3 clockwise
(R)–Configuration

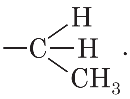
Fig. 7.9 Assigning R and S notations.

Sequence rules for determining the priority of groups or ligands

- The four different groups attached to a chiral centre get their priorities according to the atomic number of the atom of each group attached directly to the chiral centre. For example, in 1-bromo-1-chloroethane ($CH_3CHClBr$), the chiral centre is attached to CH_3, Cl, Br, H. The atomic numbers of atoms directly attached to the chiral centre show the priority order to be Br > Cl > CH_3 > H.
- When the preferences cannot be determined on the basis of the atomic number of the atoms directly attached to the chiral carbon, in this case, the atomic numbers of next sets of atoms in the unassigned groups are taken into consideration. The priorities are then determined at the first point of difference. As for example, with 2-chlorobutane ($CH_3CHClC_2H_5$), the four ligands attached to the central chiral centre are CH_3, C_2H_5, Cl, H. Among these, Cl is of highest and H is of lowest priority. For deciding the preference between —CH_3 and CH_2CH_3 decision cannot be made on the basis of first C–atom of each group attached directly to the chiral centre.

The two groups are viewed as follows:

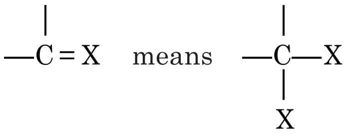
In the case of —CH_3, other three atoms are hydrogen *i.e.,*  $—C(H)(H)H$ but in the case of

—CH_2CH_3 the two atoms are hydrogen and the third one is carbon *i.e.,*  $—C(H)(H)CH_3$.

So, —CH_2CH_3 gets priority over —CH_3.

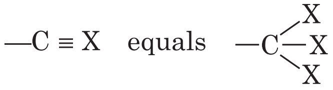
Similarly, in the case of —CH_2NH_2 and —CH_2CH_3 , the former will get priority over the latter.

- A double or triple-bonded atom X to C is considered to be equivalent to two or three X′s. For example



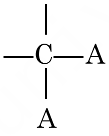
$$-\overset{|}{C}=X \quad \text{means} \quad -\underset{\underset{X}{|}}{\overset{|}{C}}-X$$

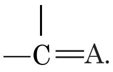
and



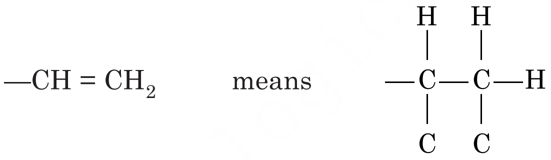
$$-C\equiv X \quad \text{equals} \quad -C\begin{smallmatrix}X\\X\\X\end{smallmatrix}$$

But one thing to be kept in memory is that a real $-\underset{\underset{A}{|}}{\overset{|}{C}}-A$ has priority over $-\overset{|}{C}=A$.

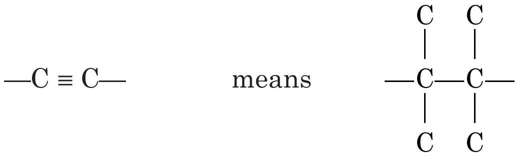




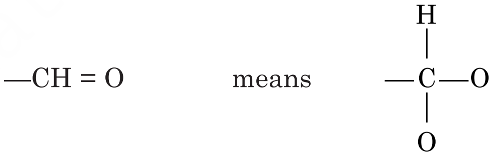
For example:



$$-CH=CH_2 \qquad \text{means} \qquad -\underset{\underset{C}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{C}{|}}{\overset{\overset{H}{|}}{C}}-H$$

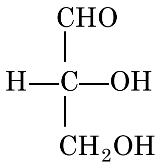


$$-C\equiv C- \qquad \text{means} \qquad -\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-$$



$$-CH=O \qquad \text{means} \qquad -\underset{\underset{O}{|}}{\overset{\overset{H}{|}}{C}}-O$$

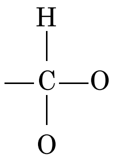
To illustrate the above phenomenon, let us consider the following examples:



$$H-\underset{\underset{CH_2OH}{|}}{\overset{\overset{CHO}{|}}{C}}-OH$$

Glyceraldehyde

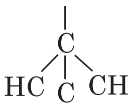
—CHO is considered as



$$-\underset{\underset{O}{|}}{\overset{\overset{H}{|}}{C}}-O$$

Here O, O, H of —CHO attains the priority over the O, H, H of $-CH_2OH$ group. The complete priority sequence is then —OH → —CHO → $-CH_2OH$ → H.

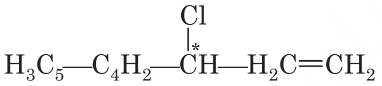
The $-C_6H_5$ group is considered as



. The priority sequence of 1-amino-2-methyl-1-phenyl-propane is $-NH_2 \rightarrow C_6H_5 \rightarrow C_3H_7 \rightarrow H$.

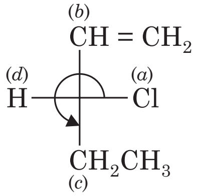
Example: (i) 3-chloro-1-pentene.

- To determine 'R' or 'S' enantiomer of the compound we are to draw the Fischer projection formula. For Fischer projection formula, the number '1' carbon should be on the top of the vertical line. Then the groups are placed across the horizontal lines and the last carbon is at the bottom of the vertical line.
- Then the asymmetric carbon atoms are to be determined. Then the sequence rule is applied to get the priority sequence.
- Then configuration is specified if priority sequence is $a \rightarrow b \rightarrow c \rightarrow d$ is clockwise and hydrogen (d) remains in the horizontal line, then the configuration of the asymmetric carbon atom is assigned to be 'S'.
- If the sequence is the same *i.e.*, clockwise and hydrogen falls on the vertical line then the configuration of the asymmetric carbon atom is assigned to be 'R' carbon atom (with asterisk is asymmetric carbon atom). Fischer projection of 3-chloro-1-pentene is:



$$H_3C_5—C_4H_2—\overset{\overset{Cl}{|}}{C^*}H—H_2C{=}CH_2$$

3-Chloro-1-pentene



Fischer projection formula

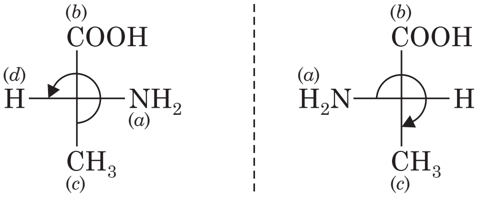
Priority sequence is: Cl→ —CH = CH$_2$ → CH$_2$CH$_3$

Rotation is anticlockwise and hydrogen is on the horizontal line. So the configuration of carbon number '3' is 'R'.

(ii) Alanine 

$—C_3H_3\overset{*}{C_2}H(NH_2)\underset{|}{COOH}$.

Fischer projection formula is:

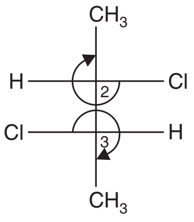


D-alanine (I) Mirror L-alanine (II)

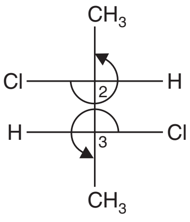
In configuration (I) hydrogen falls on the left hand side of horizontal line, by convention it is D-configuration. Its optical isomer *i.e.,* enantiomer will inevitably be L-configuration, *i.e.,* hydrogen will fall on the right hand side of the horizontal line. In D-alanine the priority sequence is NH$_2$ → COOH → CH$_3$, rotation is anticlockwise with hydrogen on the horizontal axis. So configuration is 'R'.

In L-alanine the priority sequence is same but the rotation is clockwise with hydrogen in the horizontal line. The configuration of the asymmetric carbon is 'S'.

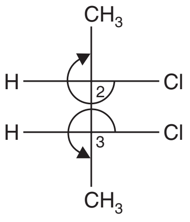
(iii) For **2, 3-dichloro butane** [$C_4H_3C_3^*H(Cl).C_2^*H(Cl).C_1H_3$] the Fischer projection is



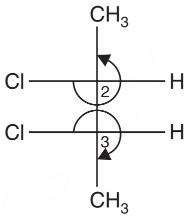
(I)



(II)



(III)



(IV)

(I) and (II) are enantiomers. (I) and (III) or (II) and (III) are diastereoisomers. (III) and (IV) are known as mesoforms. They are optically inactive due to internal compensation.

In the case of (I) the priority sequence for carbon number (2) is Cl → $CH(Cl)CH_3 \rightarrow CH_3$. So, the configuration is 'S'.

The priority sequence for carbon number '3' is Cl → $CH(Cl)CH_3 \rightarrow CH_3$.

So the configuration is 'S'.

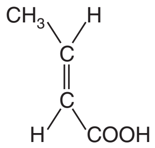
So the IUPAC nomenclature of the compound (I) is:

(2S,3S)-2,3-Dichlorobutane.

Similarly, the others are: (II) (2R, 3R); (II) (2S, 3R); (IV) (2R, 3S).

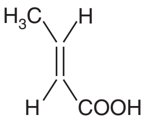
E and Z Nomenclature

For the compounds of the type *Cab* = *Cab* or *Cab* = *Cac*, the terms *cis* and *trans* are adequate but if three or four of the substituents are different then the nomenclature of these geometrical isomers or diastereomers leads to ambiguity and sometimes to confusion. Here also the sequence rule is applied. Generally E- is applied for *trans*-isomer and Z- is for *cis*-somer when the groups of higher priority are on the same side of the reference plane, *i.e.,* double bond, then the symobol (Z) is used to specify the configuration. The symbol (E) is used when the groups of higher priority are on the opposite sides of the double bond. For example: 2-Butenoic acid.



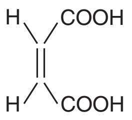
($CH_3 > H$; $CO_2H > H$)

which is represented as

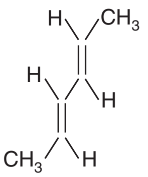


(E)-2-Butenoic acid

Similarly:



(Z)-Butene dioic acid (Haleic acid)
($CO_2H > H$; $COOH > H$)



(2E, 4E)-2, 4-Hexadiene

SHORT QUESTIONS AND ANSWERS

Q. 1. Why is the RX + KOH → ROH + KX called nucleophilic substitution?

Ans. Since the attacking reagent (OH^-) is a nucleophilic reagent, and substitution of X^- takes place by OH^-, *i.e.,* substitution of weakly basic group takes place by a strongly basic group.

Q. 2. How can you ascertain that X^- is a weakly basic group and OH^- is a strongly basic group?

Ans. X^- is a weak base as its conjugate acid HX is a strong acid; and OH^- is a strong base as its conjugate acid H_2O is very weak.

Q. 3. What are nucleophilic reagents?

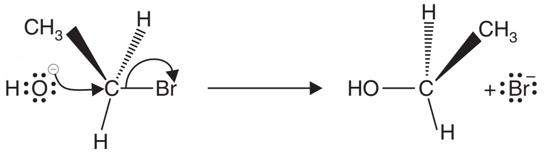
Ans. Nucleophilic reagents can supply an electron pair. Obviously a nucleophilic reagent attacks a molecule at the point of low electron density. Nucleophilic reagents may be negatively charged *viz*. OH^-, CN^- etc. and neutral molecules like H_2O, NH_3 with unshared pair of electrons.

Q. 4. Rate equations suggest that there are two different mechanisms for nucleophilic substitution—explain.

Ans. Hydrolysis of primary halogenoalkane *viz.* bromobutane is a second order reaction. The rate equation is,

$$R = K[C_4H_9Br]\,[OH^-]$$

The suggested mechanism is:

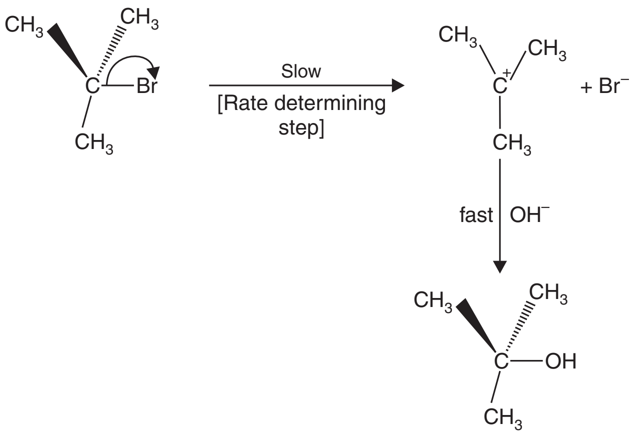


In $S_N{}^2$ reaction two molecules are involved in the rate determining step.

Hydrolysis of tertiary halogenoalkanes *viz.* 2-bromo 2-methylpropane is first order. Rate equation for the reaction is:

$$\text{Rate} = K[C_4HgBr]$$

The suggested mechanism is:

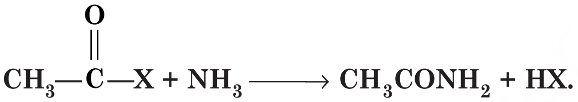


In S_N1 mechanism one molecule is involved in rate determining step.

The mechanism shows that C—Br bond breaks first to form a **carbocation intermediate**.

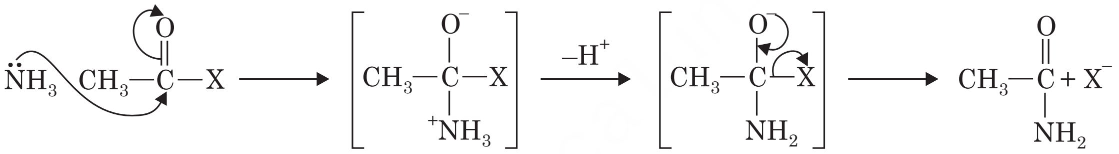
Then the nucleophile forms a bond with the carbocation formed. So, S_N2 is a one step process and S_N1 is a two step process.

Q. 5. Is the following reaction a nucleophilic substitution?



$$CH_3-\overset{\overset{\large O}{\|}}{C}-X + NH_3 \longrightarrow CH_3CONH_2 + HX.$$

Ans.



Here substitution of X^- takes place by nucleophilic NH_3, so, this is an example of nucleophilic substitution. This is an example of acyl nucleophilic substitution.

Q. 6. Of the two isomeric C_4H_9 Br, why does 2-bromo-2-methylpropane follow S_N1 path?

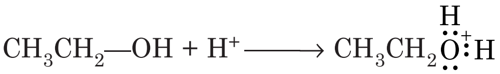
Ans. When a methyl group is attached to a carbocation (C^+), the charge is dispersed by its (+I) effect. More the number of methyl groups, more is the dispersal of charge and more the dispersal of charge, more is the stability of carbocation. So we can write the following stability sequence,

$$\overset{+}{C}H_3 < \underset{1^\circ\ \text{Primary}}{CH_3\overset{+}{C}H_2} < \underset{2^\circ\ \text{Secondary}}{(CH_3)_2\overset{+}{C}H} < \underset{3^\circ\ \text{Tertiary}}{(CH_3)_3\overset{+}{C}}$$

and see that $\overset{+}{C}H_3$ is the least stable and $(CH_3)_3C^+$ is the most stable carbocation. 2-bromo-2-methylpropane ionises to give most stable 3° carbocation whereas 1-bromomethane gives 1° carbocation. That is why the ionisation in the first case is possible and S_N1 path is followed.

Q. 7. What do you expect if ethanol is heated with conc. H_2SO_4?

Ans. At first ethanol is protonated,

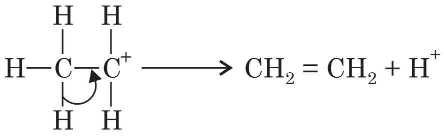


$$CH_3CH_2—OH + H^+ \longrightarrow CH_3CH_2\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot\cdot}{O}}\overset{+}{:}H$$

then a water molecule is eliminated to give a carbocation

$$CH_3CH_2—\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot\cdot}{O}}:\overset{+}{H} \longrightarrow CH_3\overset{+}{C}H_2 + H_2O.$$

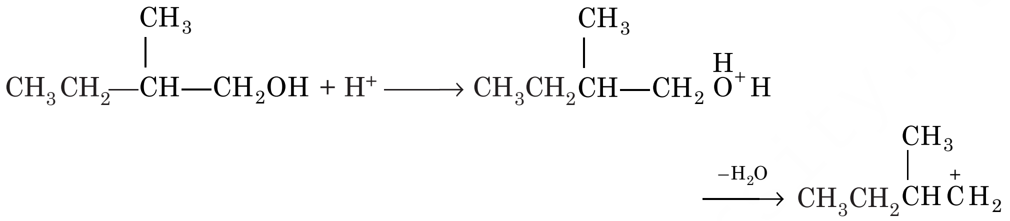
This carbocation eliminates an H^+ to give an alkene.



This reaction is an example of dehydration of an alcohol.

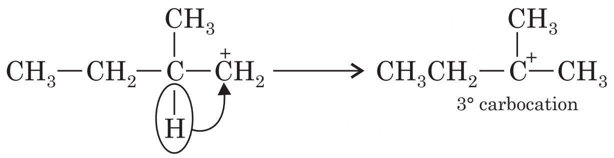
Q. 8. 2-Methylbutanol on dehydration gives 2-methyl but-2-ene—explain.

Ans.



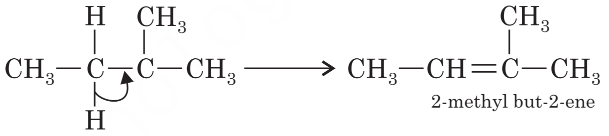
$$CH_3CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2OH + H^+ \longrightarrow CH_3CH_2\overset{CH_3}{\overset{|}{C}H}-CH_2\overset{H}{O^+}H \xrightarrow{-H_2O} CH_3CH_2\overset{CH_3}{\overset{|}{C}H}\overset{+}{C}H_2$$

The formed carbocation is 2°. This rearranges to the most stable 3° carbocation by 1,2 hydride shift.



$$CH_3-CH_2-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{+}{C}H_2 \longrightarrow \underset{\text{3° carbocation}}{CH_3CH_2-\overset{CH_3}{\overset{|}{\overset{+}{C}}}-CH_3}$$

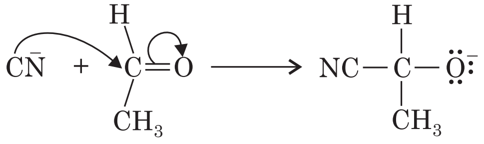
This species then eliminates a proton to give 2-methyl but-2-ene.



$$CH_3-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{CH_3}{\overset{|}{C}}-CH_3 \longrightarrow \underset{\text{2-methyl but-2-ene}}{CH_3-CH=\overset{CH_3}{\overset{|}{C}}-CH_3}$$

Q. 9. Give an example of nucleophilic addition.

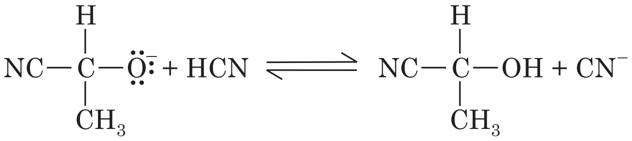
Ans. First step of nucleophilic addition HCN to ethanal:



$$\overset{-}{C}N + \underset{CH_3}{\overset{H}{C}}=O \longrightarrow NC-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\ddot{\underset{..}{O}}:^-$$

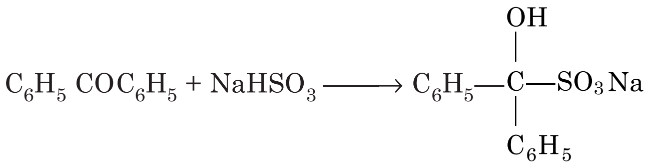
To complete the reaction, the negatively charged oxygen acts as a base and accepts an H^+ from HCN.

Second step of nucleophilic addition of HCN to ethanal:



$$NC-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\ddot{\underset{..}{O}}:^- + HCN \rightleftharpoons NC-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH + CN^-$$

Q. 10. Benzophenone does not form bisulphite compound. Explain.

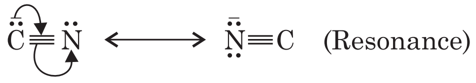


$$C_6H_5\,COC_6H_5 + NaHSO_3 \longrightarrow C_6H_5-\underset{C_6H_5}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-SO_3Na$$

Ans. The bulky group (C_6H_5) surrounding carbonyl group prevents the attack of nucleophilic (SO_3^{-2}) due to steric hindrance and hence the nucleophilic addition to form the bisulphite compound does not take place.

Q. 11. Give the products of the reaction of ethyl bromide and AgCN.

Ans. CN^- is an ambident nucleophile *i.e.,* it can attack from both the sides of the species.



$$\ddot{\bar{C}} \equiv \ddot{N} \longleftrightarrow \bar{\ddot{N}} \equiv C \quad \text{(Resonance)}$$

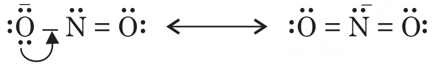
So the products of the reaction are:

$$C_2H_5\,Br + Ag\,CN \longrightarrow \underset{\text{major}}{C_2H_5\,NC} + \underset{\text{minor}}{C_2H_5CN} + Ag\,Br$$

Q. 12. Indentify the products of the following reaction:

Ans. $$R\text{—}X + KNO_2 \longrightarrow A + B + C$$

$:\bar{\ddot{O}} - \ddot{N} = \ddot{O}:$ is an ambident nucleophile.

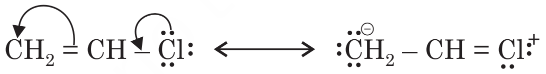


$$:\bar{\ddot{O}} - \ddot{N} = \ddot{O}: \longleftrightarrow :\ddot{O} = \bar{\ddot{N}} = \ddot{O}:$$

$$R\text{—}X + KNO_2 \longrightarrow \underset{\substack{\text{major}\\(A)}}{RONO} + \underset{\substack{\text{minor}\\(B)}}{RNO_2} + \underset{(C)}{KX}$$

Q. 13. Vinyl chloride does not undergo nucleophilic substitution—explain.

Ans.

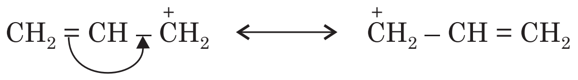


$$CH_2 = CH - \ddot{\underset{\cdot\cdot}{Cl}}: \longleftrightarrow :\overset{\ominus}{C}H_2 - CH = \overset{+}{\underset{\cdot\cdot}{Cl}}:$$

Due to resonance C—Cl bond attains a partial double bond character and C—Cl bond energy increases and no carbocation is formed. So, vinyl chloride does not undergo nucleophilic substitution.

Q. 14. Allyl Bromide undergoes nucleophilic substitution readily—explain.

Ans. Allyl carbocation is resonance stabilised



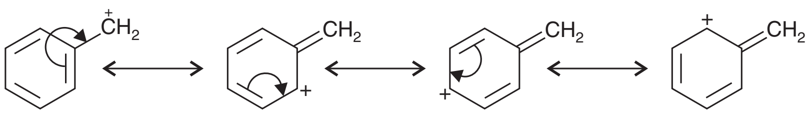
$$CH_2 = CH - \overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2 - CH = CH_2$$

and behaves as if the chlorine atom is ionic.

So, $CH_2 = CH - \overset{+}{C}H_2 + OH^- \longrightarrow CH_2 = CH\text{–}CH_2OH\ (S_N{}^1)$

Q. 15. Benzyl chloride undergoes $S_N{}^1$ reaction—explain.

Ans. $C_6H_5\,\overset{+}{C}H_2$ is resonance stabilised, so ionisation of benzyl chloride takes place and $S_N{}^1$ path is followed.



Q. 16. Find out the nucleophile from the following:

$$\overset{+}{N}O_2,\ CCl_4,\ \dot{C}H_3,\ CN^-$$

Ans. CN^-, as it has lone pairs $C \equiv \ddot{N}$.

Q. 17. Arrange the reactivity of the following towards nucleophilic reagent:

CH_3F, CH_3I, CH_3Br, CH_3Cl

Ans. $CH_3I > CH_3Cl > CH_3Br > CH_3F$

as bond dissociation energies (D) is of the order C—F > C—Cl > C—Br > C—I.

Thus C—I bond is readily broken and the reactivity of CH_3I is greatest.

Q. 18. Aqueous KOH with RX gives alcohol whereas alcoholic KOH alkene—explain.

Ans. In aqueous medium, S_N takes place,

$$RX + KOH \longrightarrow ROH + KX$$

whereas in alcoholic medium

$$C_2H_5OH + KOH \rightleftharpoons C_2H_5O^-K^+ + H_2O.$$

The $^-OC_2H_5$ is strongly basic and preferentially help elimination.

$$RCH_2CH_2X \xrightarrow{^-OC_2H_5} RCH = CH_2$$

Q. 19. Why do haloalkanes give cyanides with KCN^- and isocyanides with AgCN?

Ans. Both the reagents act as nucleophilic and release CN^-; CN^- being ambident nucleophile, there are two active sites in the CN^-

$$\underset{\cdot\cdot}{\overset{-}{C}} \equiv N \longleftrightarrow \underset{\cdot\cdot}{C} = \underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}{}^-$$

Ag^+ promotes R^+ formation from RX by precipitating AgX and reaction takes $S_N{}^1$ path.

$$R - X + Ag^+ [CN^-] \xrightarrow{\text{slow}} Ag\,X\downarrow + R^+ + [CN^-] \xrightarrow{\text{fast}} R - N^+ \equiv C^\ominus$$

In the absence of such promotion by Ag^+ *e.g.* with $Na^+ [CN^-]$ the $S_N{}^2$ reaction is found

$$N \equiv C^- + R - X \longrightarrow \underset{\text{T.S.}}{[N \equiv C\text{---}R\text{---}X]} \rightarrow N \equiv C \equiv R + X^-$$

Q. 20. What do you mean by leaving group?

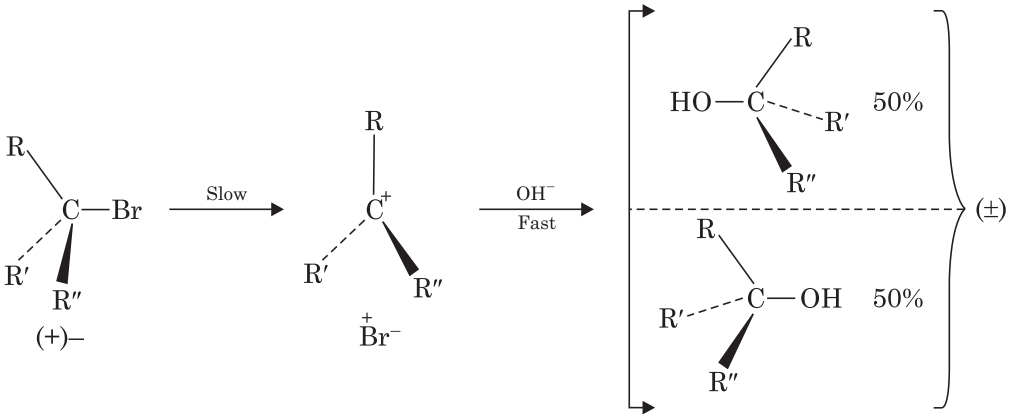
Ans. The charged species (group) that is replaced during a substitution reaction is a leaving group.

Q. 21. What is the characteristic of a better leaving group?

Ans. The stronger or harder as a base, worse as a leaving group. ^-OH, OR^-, $NH_2{}^-$ are harder bases and are the worst as a leaving group. The best leaving groups are anions of strong acids *e.g.,* halide ions (X^-).

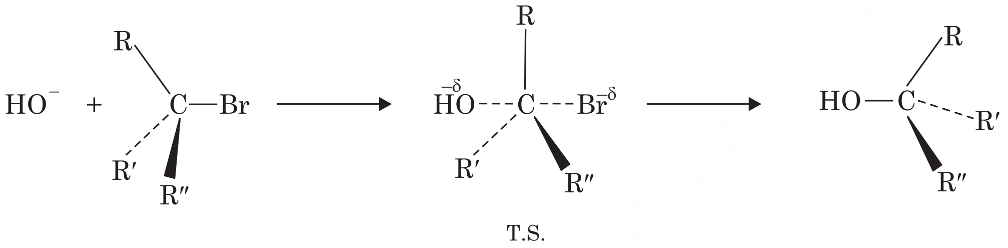
Q. 22. Discuss the stereochemistry of $S_N{}^1$ and $S_N{}^2$ reactions.

Ans. In $S_N{}^1$ reaction racemisation takes place that means (+)– and (–)–isomers form in equal amounts if we take an optically active RX.



As the planar carbocation is formed in rate determining step and the process of formation is slow, it is quite likely that attack by OH^- would take place with equal readiness from either side of planar carbocation leading to 50/50 mixture of the (+)– and (–)–forms. That is, always **racemisation** takes place during S_N1 reaction.

In S_N2 reaction:



The back side attack by the nucleophile always leads to **inversion of configuration** in S_N^2 reaction.

Q. 23. Discuss the effect of solvent on S_N^1 and S_N^2 reactions.

Ans. The change of solvent (I) affects the rate of the reaction (II) which may change the mechanistic pathway.

S_N^1 reaction becomes faster if the solvent polarity increases.

The solvolysis of $(CH_3)_3$ Br becomes 3×10^4 times faster in 50 % ethanol than in ethanol alone. Developing ion pair gets solvated easily and helps the process ionisation.

Increase in solvent polarity has little effect in S_N^2 reaction; only a slight decrease in reaction rate is observed. Change of solvent may have marked effect on S_N^2 reaction. The reaction rate becomes 4.5×10^4 fold faster than the reaction CH_3I with N_3^- if we change the solvent from CH_3OH to $HCON(CH_3)_2$ (DMF). Because in CH_3OH due to hydrogen bonding N_3^- is solvated and its nucleophilic activity is reduced. Whereas in DMF the hydrogen loading is absent and N_3^- remains unsolvated and powerful nucleophile can attack.

Increase in solvent polarity and ion solvating ability may change reaction pathway from $S_N^2 \rightarrow S_N^1$. Transfer from protic polar solvent to polar nonprotic solvent may change the reaction pathway from $S_N^1 \rightarrow S_N^2$ by increasing the effectiveness of the nucleophilic.

Q. 24. The order of reactivity of halogen acids towards an alcohol is—

HI > HBr > HCl.

Explain.

Ans. The alcohol is first protonated, there is attack by X^- to give RX. So, the reaction is nucleophilic substitution and the leaving group is H_2O.

$$ROH \xrightarrow{HX} R-OH_2^+ \xrightarrow{X^-} [X^{-\delta}\text{---}R\text{---}O^+H_2] \longrightarrow RX + H_2O.$$

Nucleophilicity of X^- decreases in order: $I^- > Br^- > Cl^-$.

Hence the order of reactivity of HX is

HI > HBr > HCl.

Q. 25. For a given HX, the order or reactivity of the alcohols follows the order 3° > 2° > 1°—explain.

Ans. Since the stability of carbocation follow the order: 3° > 2° > 1°. Hence, the reactivity of alcohols follow the order: 3° > 2° > 1° for a given HX.

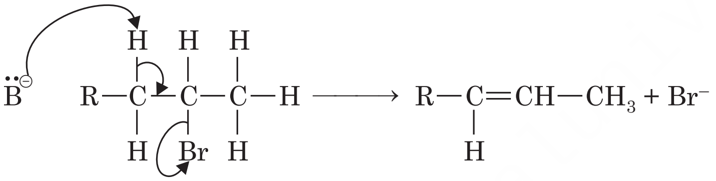
Q. 26. What do you mean by an elimination reaction?

Ans. Elimination reaction is a reaction that splits off a simple molecule of a compound *e.g.,* H_2O from a molecule of organic compound to form a double bond. Elimination of a molecule of hydrogen halide from a haloalkane produces an alkene. This reaction is known as **dehydrohalogenation**.

By far, the most common elimination mechanism is the one step E^2 pathway.

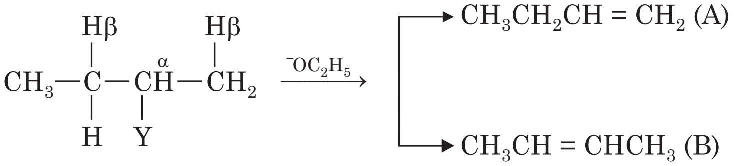
$$\text{Rate} = K[RCH_2CH_2Br][B]$$

(*i*)



$$\ddot{B}^{\ominus} \quad R-\underset{H}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H \longrightarrow R-\underset{H}{C}=CH-CH_3 + Br^-$$

(*ii*)



$$CH_3-\underset{H}{\overset{H\beta}{C}}-\underset{Y}{\overset{\alpha}{CH}}-\overset{H\beta}{CH_2} \xrightarrow{^-OC_2H_5} \begin{cases} CH_3CH_2CH = CH_2 \text{ (A)} \\ CH_3CH = CHCH_3 \text{ (B)} \end{cases}$$

In substrates which have alternative β-hydrogen available, more than one alkenes can be obtained, that is determined by two empirical rules.

Table

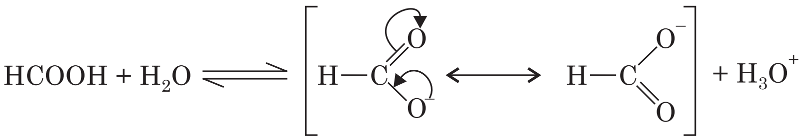
Substrate	*Y*	*Base*	*Alkenes*		*Name of the Rule*	*Rule*
			A	*B*		
$CH_3CH_2\underset{\substack{\vert \\ Y}}{CH}CH_3$	Br	$^-OEt^-$	19%	81%	Saytzev	The alkene will predominate which has **most alkyl substituents** on the double bond carbons.
	$N^+(CH_3)_3$	$^-OEt^-$	95%	5%	Hofmann	The alkene which has least alkyl substituents on the double bond carbons.

Q. 27. What is the origin of acidity in organic compounds?

Ans. (*i*) The strength of H—A bond, (*ii*) the electronegativity of A, (*iii*) factors stabilising A^-, (*iv*) the nature of the solvent.

Q. 28. HCOOH is an acid—explain.

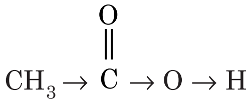
Ans. $H-\overset{\overset{O}{\Vert\uparrow}}{C}\leftarrow O\leftarrow H$ Due to electron pull, H^+ release is possible, and anion formed has got resonance stability.



So, HCOOH is an acid as the anion has resonance stability.

Q. 29. Justify the pK_a values

Acid	pK_a
CH_3COOH	4.76
$(CH_3)_2CHCOOH$	4.86
$(CH_3)_3CCOOH$	5.05

Ans. 

$$CH_3 \rightarrow \overset{\overset{O}{\|}}{C} \rightarrow O \rightarrow H$$

Acidity in CH_3COOH is somewhat reduced due to (+I)-effect of the CH_3 group and that effect is more pronounced in $(CH_3)_2CHCOOH$ and still more pronounced in $(CH_3)_3CCOOH$. So pK_a value gradually increases *i.e.,* acidity decreases.

Q. 30. Justify the pK_a values

Acid	pK_a
CH_3COOH	4.76
FCH_2COOH	2.66
$ClCH_2COOH$	2.86
$BrCH_2COOH$	2.90
ICH_2COOH	3.16

Ans. The electron withdrawing substituents with (–I) effect has got marked influence on the acidity of simple aliphatic acids.

The electronegativity order of halogens is:

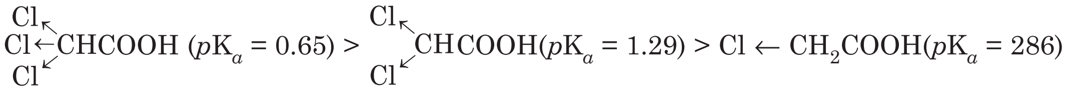
$$F > Cl > Br > I$$

So, acidity order will be,

$$F \leftarrow CH_2COOH > Cl \leftarrow CH_2COOH > Br - CH_2COOH > I\text{-}CH_2COOH:$$

pK_a values are in accordance with the above acidity order.

Q. 31. Acidity order with pK_a values of the following acids is:

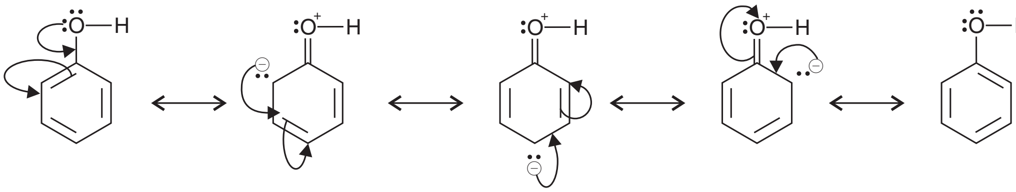


$$\begin{matrix}Cl\nwarrow \\ Cl\leftarrow \\ Cl\swarrow\end{matrix}CHCOOH\ (pK_a = 0.65) > \begin{matrix}Cl\nwarrow \\ \\ Cl\swarrow\end{matrix}CHCOOH(pK_a = 1.29) > Cl \leftarrow CH_2COOH(pK_a = 286)$$

Justify.

Ans. As the number of electron withdrawing groups increases acidity increases; pK_a value decreases.

Q. 32. Phenol is (*i*) acidic, (*ii*) o, p-orienting. Explain.

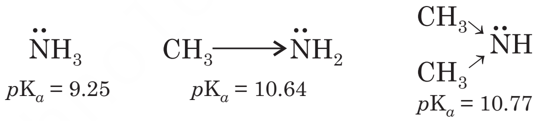


(*i*) The electronegative atom 'O' of phenol gets positively charged due to resonance. So bonding electrons of O—H bond will be pulled strongly towards O-atom making release of H^+ easier. Moreover, the anion formed on the release of H^+ by phenol molecule is resonance stabilised. So, phenol can behave as an acid.

(*ii*) Due to resonance, *o*- and *p*- positions of the benzene ring of phenol molecule become electron rich. Benzene having a delocalised π-cloud is susceptible to electrophilic substitution. When benzene ring is attached to a group containing a 'key atom' (here 'O' has lone pair of electrons) the resonance effect gives rise to increased electron densities in the *o*- and *p*- positions. This increased electron density activates the benzene ring towards electrophilic substitution S_E2. The electrophiles can attack at those positions leading to electrophilic substitution. So phenol is **o-, p-orienting***.

Q. 33. pK_a values for NH_3, CH_3NH_2, $(CH_3)_2NH$ are 9.25, 10.64 and 10.77 respectively. Justify.

Ans. $\ddot{N}H_3$ is a Lewis base, it can donate a pair of electrons. When this donation capacity is increased by any effect, the basicity is increased. The (+I)-effect of CH_3 groups increases the electron density of N atom in CH_3NH_2 and this effect is more pronounced in $(CH_3)_2$ NH due to two CH_3 groups performing as stronger bases than NH_3.

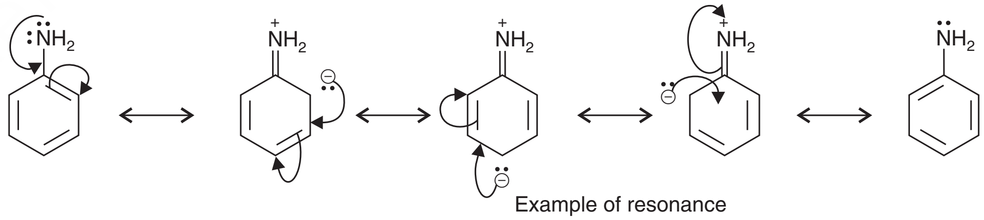


$$\ddot{N}H_3 \quad pK_a = 9.25 \qquad CH_3 \longrightarrow \ddot{N}H_2 \quad pK_a = 10.64 \qquad (CH_3)_2\ddot{N}H \quad pK_a = 10.77$$

Q. 34. pK_a values of NH_3, CH_3NH_2 and $PhNH_2$ are 9.25, 10.64 and 4.62 respectively. Justify.

Ans. NH_3 is basic, CH_3NH_2 is more basic, due to the (+I) effect of the $-CH_3$ group. The pK_a values are in accordance with the above fact. But we see that pK_a of aniline is 4.62 *i.e.,* it is less basic than NH_3.

The resonating structures of aniline is:



Example of resonance

Due to resonance, the electron density over 'N' atom becomes less than that over NH_3. So aniline (pK_a = 4.62) becomes less basic than NH_3.

Q. 35. Do you expect that *p*-nitroaniline is less basic than aniline?

Ans. Yes, the electron withdrawing effect of $-NO_2$ group in *p*-nitroaniline makes electron density of 'N' atom less than that in aniline and that is why *p*-nitroaniline becomes less basic.

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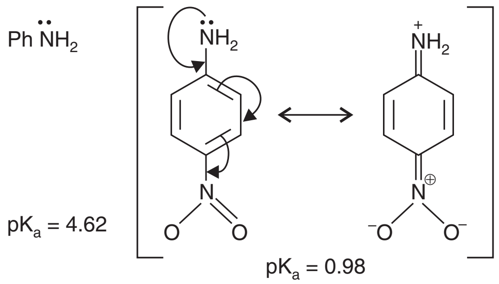
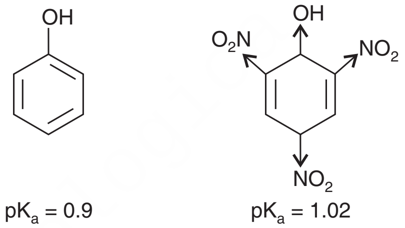
*This property common to other groups, like $\ddot{N}H_2, :\ddot{O}R$, helps electrophilic substitution and are *o*-, *p*-orienting.



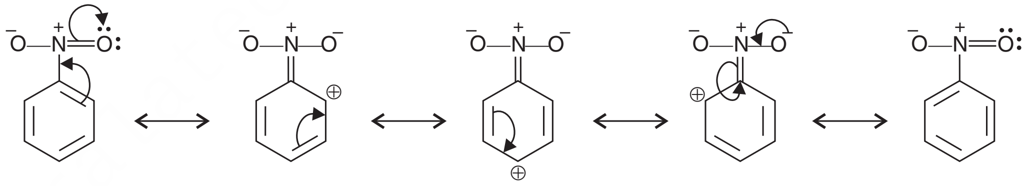
Q. 36. 2, 4, 6-Trinitrophenol (picric acid) is a very strong acid—explain.

Ans. Introduction of an —NO_2 group in the phenol molecule increases its acidity due to (–I) effect of the —NO_2 group. The three —NO_2 groups in 2, 4, 6-trinitrophenol exercise pronounced (–I) effect making the phenol molecule total acidic. That is why, it is known as picric acid.



Q. 37. —NO_2 group is m-orienting—explain.

Ans. The resonating structures of nitrobenzene are:



Due to resonance, *o*- and *p*- positions of benzene ring of nitrobenzene become electron deficient. For electrophilic attack, electron-rich centre is necessary. The *m*-position of the benzene ring is comparatively electron-rich, that is why electrophile attacks there and *m*-substitution takes place. So, —NO_2 group is *m*-orienting.

Q. 38. Nitration of phenol is easier than that of nitrobenzene—explain.

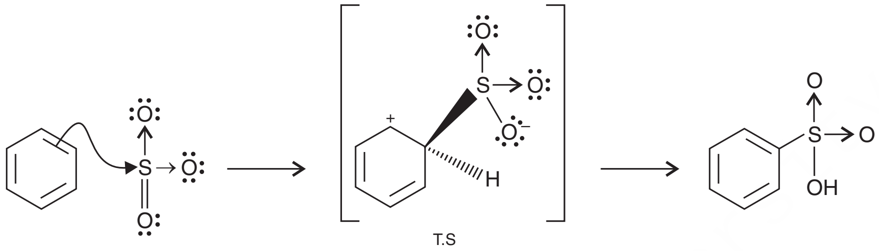
Ans. In phenol —OH group activates the benzene ring towards further electrophilic substitution by enriching the electron density at *o*- and *p*- positions due to resonance. Nitration is an electrophilic substitution and takes place easily in the case of phenol. On the contrary, —NO_2 group in nitrobenzene deactivates the benzene ring by withdrawing electrons from the benzene ring and making *o*- and *p*- positions positively charged. So, further electrophilic attack at nitrobenzene molecule becomes difficult. So, nitration of nitrobenzene molecule becomes difficult.

Q. 39. Show that sulphonation of benzene is an elctrophilic substitution.

Ans. The sulphonating agent is Oleum *i.e.*, SO_3 dissolved in conc. H_2SO_4. The eletrophile SO_3 is generated as follows:

$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$$

Second step is attack by electrophile SO_3 and the formation of a transition state.



So, sulphonation of benzene is an electrophilic substitution.

Q. 40. What are the electrophiles for (*i*) halogenation and (*ii*) alkylation reactions of benzene?

Ans. (*i*) For halogenation *viz.* chlorination, the reagents are anhydrous $FeCl_3$ and Cl_2. Electrophile is thus generated.

$$Cl_2 + FeCl_3 \rightleftharpoons FeCl_4^- + Cl^+$$

So, Cl^+ acts as an electrophile during chlorination of benzene.

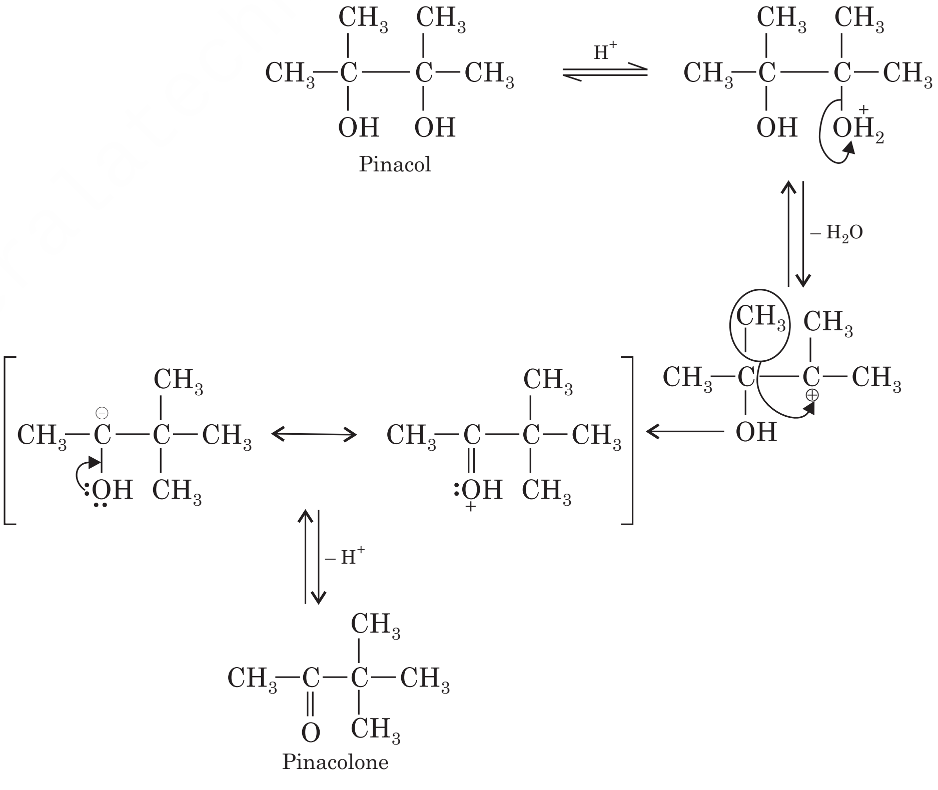
(*ii*) For alkylation the reagents are anhydrous $AlCl_3$ and RCl. Electrophile is thus generated.

$$RCl + AlCl_3 \rightleftharpoons AlCl_4^- + R^+$$

So, R^+ acts as an electrophile during alkylation *i.e.,* in Friedel–Craft's reaction.

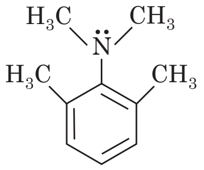
Q. 41. Mention an organic reaction where rearrangement takes place.

Ans. Pinacol-pinacolone rearrangement (example of 1, 2-alkyl shift)

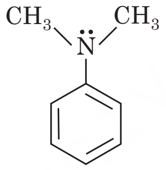


Q. 42. What do you mean by steric inhibition of resonance?

Ans. 2, 6-Dimethyl –N, N-dimethyl aniline (I) is more basic than N, N-dimethylaniline (II). Due to crowding in (I), —$N(Me)_2$ group goes out of plane of the benzene ring by free rotation about the single bond. So primary condition of resonance, the planarity, is affected and resonance is inhibited. So lone pair over —$N(Me)_2$ group in (I) is available to be accepted by a proton (H^+). This is an example of *steric inhibition of resonance.* But in (II) lone pair over —$N(Me)_2$ comes into resonance with benzene ring and not so much available for an H^+.



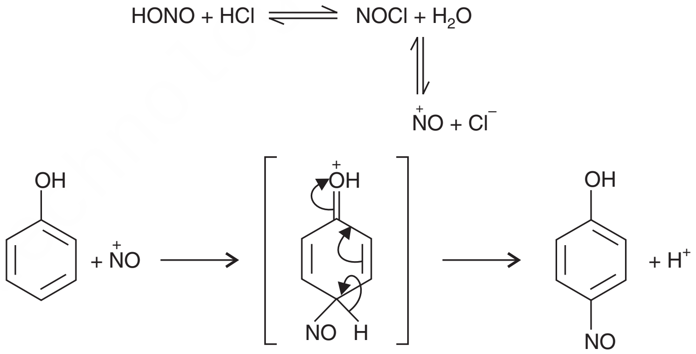
(I)



(II)

Q. 43. When Phenol is treated with $NaNO_2$ and HCl at 0–5°C, *p*-nitrosophenol is obtained. Is this reaction an electrophilic substitution?

Ans. Yes, here the electrophile is NO^+



$$HONO + HCl \rightleftharpoons NOCl + H_2O \rightleftharpoons \overset{+}{N}O + Cl^-$$

EXERCISES

1. Classify the different organic reactions.
2. What do you mean by polarisation? What is the reason behind it?
3. What do you mean by inductive effect? How does it play an important role in organic reactions?
4. Compare the acidity among

CH_3COOH, $CH_2Cl.COOH$, $CH.Cl_2COOH$, CCl_3COOH.

5. What is electromeric effect? Is it permanent?
6. State the origin of a carbocation, carbonium ion and free radical.
7. State the products obtained during the chlorination of CH_4 in diffused sunlight. Mention the mechanism.
8. What is polymerisation reaction? Give an example of such type of reaction with plausible mechanism.
9. What do you mean by electrophiles and nucleophiles?

10. Electrophiles are in general Lewis acids–explain.

11. Draw the energy profile of the following reaction:

$$A + B \longrightarrow A \text{ --- } B \longrightarrow AB$$

12. Write notes on electrophilic addition and electrophilic substitution.

13. Write a short note on nucleophilic addition reaction.

14. What do you mean by S_N^1 and S_N^2 reactions. Explain with proper mechanism involved with examples.

15. What is elimination reaction? Describe different types of elimination reactions.

16. What is resonance? State the important features of it.

17. What are the significances of the terms:

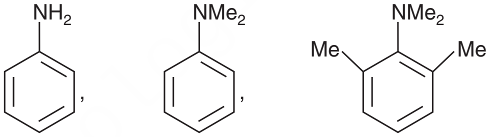
(*i*) Resonance hybrid and (*ii*) Resonance energy.

18. Heat of hydrogenation value of 1, 3, 5-cyclohexatriene is 85.8 kcal/mole while that of benzene is 49.8 kcal/mole—explain.

19. Write a short note on hyperconjugation.

20. What do you mean by 1, 2-shift.

21. Compare the basicity among the following:



22. What do you mean by dehydrohalogenation? Explain with proper mechanism and example.

23. What does the term 'isomerism' refer to? Give different classifications of isomerism.

24. Draw Fischer projection formula of D- and L-glycine (NH_2CH_2COOH). Name them as per R—S nomenclature.

25. Draw the resonance structures of:

(*i*) phenate ion (*ii*) acetate ion

(*iii*) chlorobenzene (*iv*) butadiene.

26. Draw all the Fischer projection formulae of:

(*i*) glyceraldehyde (*ii*) lactic acid

(*iii*) tartaric acid (*iv*) 2, 3-dibromopentane.

Name them as per R, S-nomenclature.

8

Ionic Equilibrium

Law of Mass Action and Ionisation

Law of mass action is applicable to electrolytic dissociation, when the electrolyte is weak. In a solution a weak electrolyte dissociates reversibly.

$$\mathrm{AcOH} \rightleftharpoons \mathrm{H^+ + O\bar{A}c}; \qquad K_a = \frac{[\mathrm{H^+}]\,[\mathrm{OAc^-}]}{[\mathrm{AcOH}]}$$

$$\mathrm{NH_4OH} \rightleftharpoons \mathrm{NH_4{}^+ + OH^-}; \qquad K_b = \frac{[\mathrm{NH_4^+}]\,[\mathrm{OH^-}]}{[\mathrm{NH_4OH}]}$$

K_a = Ionisation constant of an acid (Acid dissociation constant)

K_b = Ionisation constant of a base.

If for a weak acid 'the degree of dissociation' is α, then

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+ + A^-}$$

At equilibrium, $C(1-\alpha) \qquad C\alpha \quad C\alpha$

When C = concentration of HA

$$K_a = \frac{[\mathrm{H^+}]\,[\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{C\alpha \,.\, C\alpha}{C\,(1-\alpha)} \approx \alpha^2 C \qquad \text{[as } \alpha \text{ is negligible]}$$

$$\therefore \qquad \alpha = \sqrt{\frac{K_a}{C}} \qquad \text{...(1)}$$

If V litre of solution contains one gm. mol. of HA, then $C = \dfrac{1}{V}$

and
$$K_a = \frac{\dfrac{\alpha}{V} \cdot \dfrac{\alpha}{V}}{\dfrac{1-\alpha}{V}} = \frac{\dfrac{\alpha^2}{V^2}}{\dfrac{1-\alpha}{V}}$$

Then K_a comes to :

$$K_a = \frac{\alpha^2}{(1-\alpha)\,V}$$

$$\therefore \qquad \alpha = \sqrt{K_a V} = K'\sqrt{V} \qquad \text{...(2)}$$

The expression which relates the variation of degree of dissociation (α) of a weak electrolyte with dilution is known as *Ostwald's dilution law.* The equation implies that a weak electrolyte will dissociate completely at infinite dilution.

Putting C = 1 we get $\alpha = \sqrt{K_a}$

i.e., the degree of dissociation of a normal solution of a weak electrolyte is approximately equal to the square root of its ionisation constant.

Common Ion Effect

If we add NaOAc to a solution of AcOH, the ion ($OA\bar{c}$) becomes common. Let us see its effect on ionisation of AcOH.

$$AcOH \rightleftharpoons H^+ + OA\bar{c}, \; NaOAc \longrightarrow Na^+ + OA\bar{c}$$

$$K_a = \frac{[H^+]\,[OAc^-]}{[AcOH]} \qquad ...(3)$$

Now, NaOAc being a salt dissociates completely in solution. So concentration term [$OA\bar{c}$] increases in the equation (3), to maintain the value k_a constant, [H^+] will decrease *i.e.,* undissociated [AcOH] will increase. As a result, the dissociation of AcOH will be suppressed. This phenomenon is known as *Common ion effect.* In general, we can say, that common ion effect suppresses the dissociation of a weak electrolyte in solution.

ACIDS AND BASES

Arrhenius Theory of Acids and Bases

According to this theory an acid is a substance which when dissolved in water gives H^+ ions and a base is a substance which when dissolved in water gives OH^- ions. It is well known that in neutralisation reactions, acids react with alkalies to form salts and water. In the Arrhenius concept neutralisation may be explained as follows:

$$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow NaCl + H_2O$$

$$(2H^+ + SO_4^{=}) + ZnO \longrightarrow ZnSO_4 + H_2O$$

The indication of neutralisation is:

$$H^+ + OH^- \longrightarrow H_2O$$

i.e., the formation of water.

Bronsted and Lowry Concept

Arrhenius theory is suitable in explaining the reactions of acids and bases in aqueous solutions but it fails to explain the following reactions, specially in non-aqueous solvents. As for example, $NaNH_2$ dissolves in liquid ammonia and behaves as NaOH in water as is implied from the following equations.

$$2NaNH_2 + MgSO_4 = Mg(NH_2)_2\downarrow + Na_2SO_4 \text{ (in liq. } NH_3\text{)}$$

$$2NaOH + MgSO_4 = Mg(OH)_2\downarrow + Na_2SO_4 \text{ (in water)}$$

So, behaviours of NH_2^- and OH^- ions are same and OH^- is derived from a base, so we can say $NaNH_2$ is a base *i.e.,* a substance can behave as an acid or a base by not producing H^+ or OH^- ions. The definition of acids and base needs to be extended.

Bronsted and Lowry defined: *Acid as a species which can donate a proton and base as a species which can accept a proton.* These species may be neutral or charged. Whether the species will behave as an acid or a base will depend upon the nature of the solvent. The strengths of the acids or bases may be determined by their tendencies to donate or accept a proton in a definite solvent. For every acid, there is a base known as *conjugate base* and for every base there is an acid known as *conjugate acid.*

As for example, Cl^- is a conjugate base of the acid HCl and HCl is the conjugate acid of the base Cl^-. Some Acid/Base conjugate pairs are shown in the following table.

Acid		*Conjugate base*
$HClO$	$\rightleftharpoons$	$H^+ + ClO^-$
H_2O	$\rightleftharpoons$	$H^+ + OH^-$
HSO_4^-	$\rightleftharpoons$	$H^+ + SO_4^=$
HCO_3^-	$\rightleftharpoons$	$H^+ + CO_3^=$
NH_4^+	$\rightleftharpoons$	$H^+ + NH_3$
$[Cr(H_2O)_6]^{+3}$	$\rightleftharpoons$	$H^+ + [Cr(H_2O)_5OH]^{+2}$

Role of Solvent

Solvent makes to act the substances to behave as an acid or a base. Solvent behaves as a base towards acid and vice versa.

Acid_I	+	Base_II		Acid_II	+	Base_I
CH_3COOH	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CH_3COO^-
HCl	+	CH_3COOH	$\rightleftharpoons$	$CH_3COOH_2^+$	+	Cl^-
CH_3COOH	+	NH_3	$\rightleftharpoons$	NH_4^+	+	CH_3COO^-
HF	+	CH_3COOH	$\rightleftharpoons$	$CH_3COOH_2^+$	+	F^-
H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-

(Autoprotolysis of water)

Acid_I and Base_I are conjugate pair and Acid_II and Base_II are conjugate pair.

Highlights:

- $HClO_4$, HBr, H_2SO_4, HCl and HNO_3 are of same strengths in water; but in glacial acetic acid their strengths are as follows:
  $$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$
  This phenomenon in water is known as *levelling effect of water*.
- Neutralisation reaction can be explained with the help of the equation:
  $$\text{Acid}_\text{I} + \text{Base}_\text{II} \rightleftharpoons \text{Acid}_\text{II} + \text{Base}_\text{I}$$
  $$CH_3COOH + OH^- \rightleftharpoons H_2O + CH_3COO^-$$
- Hydrolysis reaction is explained as follows according to Bronsted Lowry concept: Aqueous solution CH_3COONa is alkaline because CH_3COONa ionises completely in solution as it is a salt and water being weak electrolyte ionises incompletely.
  $$CH_3COONa \longrightarrow CH_3COO^- + Na^+; \quad H_2O \rightleftharpoons H^+ + OH^-$$
  According to Bronsted, *CH_3COO^- is a strong base as its conjugate acid, acetic acid is weak*. Therefore, CH_3COO^- ions will readily accept protons from water molecules setting OH^- ions free. As a result, the solution will get enriched with OH^- ions and will behave alkaline. And water will remain undissociated being a weak electrolyte.

Classification of Solvents

Solvent	*Example*
(*i*) Protophilic (Proton seeking)	H_2O, NH_3
(*ii*) Protogenic (Proton generating)	H_2O, CH_3COOH, HF
(*iii*) Amphiprotic (Both proton seeking and generating)	H_2O, $EtOH$
(*iv*) Aprotic (Independent of proton seeking and generating)	C_6H_6, CCl_4.

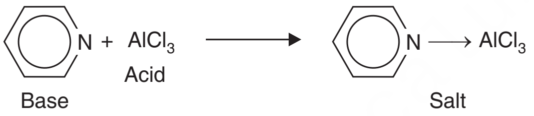
Lewis Concept

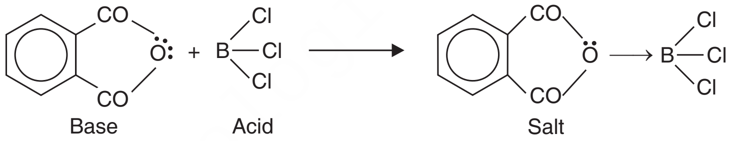
An acid is a substance which can accept a pair of electrons and a base is a substance which can donate a pair of electrons.

$$\text{Acid} + \text{Base} \rightleftharpoons \text{Neutralisation effect}$$
$$F_3B + :NH_3 \rightleftharpoons F_3B \leftarrow NH_3$$
$$H^+ + :NH_3 \rightleftharpoons NH_4^+$$
$$Cu^{++} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{++}$$

Highlights:

- Neutralisation of $AlCl_3$ (Lewis acid) with pyridine (Lewis base) in C_6H_5Cl solvent or neutralisation of BCl_3 with phthalic anhydride can only be explained in the light of Lewis concept of acids and bases.





- A substance can behave as an acid even though it does not donate a proton, this phenomenon can only be explained by the Lewis concept.

Ionic Product of Water

Water is very much inferior as an electrolyte. It ionises as follows:

$$H_2O \rightleftharpoons H^+ + OH^-$$

or more correctly, $2H_2O \rightleftharpoons H_3O^+ + OH^-$. So dissociation constant (K) of water is,

$$K = \frac{[H^+]\,[OH^-]}{[H_2O]} \quad \text{or} \quad \frac{[H_3\,O^+]\,[OH^-]}{[H_2O]^2}$$

$[H_2O]$ is constant because of very feeble ionisation of water. Therefore,

$$K[H_2O] = [H^+][OH^-]$$

or $$K_w = [H^+][OH^-] \qquad (\because \quad [H_2O] = \text{constant})$$

K_w is known as *ionic product of water,* its value at 25°C is 1×10^{-14}.

Highlights:

- We arrive at an important conclusion that in any aqueous solution, the product $[H^+]\,[OH^-]$ is constant, its value is 10^{-14} at 25°C.
- Dissociation constant of water and ionic product of water are not same.

pH Scale

For various experiments, we need to know hydrogen ion concentration of a solution. It is worthwhile to mention that an aqueous solution always contains H^+ and OH^- ions. Even strong acid solution contains OH^- ions, though negligibly small. Again an alkaline solution contains

H^+ ions though in small concentration. Because $[H^+] \times [OH^-]$ is constant in aqueous medium and its value is 10^{-14}.

1 (N) solution of a strong acid contains an $[H^+]$ of 10^{-1} g.ion l^{-1}. As strong acid dissociates completely in aqueous solution, so $[OH^-]$ of the solution will be 10^{-13} g.ion l^{-1}. Again 0.01 (N) strong alkali solution contains $[OH^-]$, 10^{-2} g.ion l^{-1} which is completely dissociated in aqueous solution. Therefore, hydrogen ion concentration of the solution will be 10^{-12} g.ion l^{-1}. In pure water $[H^+] = [OH^-] = 10^{-7}$. So in an aqueous solution when $[H^+]$ exceeds that of $[OH^-]$, the solution becomes acidic. And in the solution where the $[H^+]$ becomes less than that of $[OH^-]$, the solution becomes alkaline.

Let us consider an acid solution of concentration $\frac{N}{6000}$, so its hydrogen ion concentration will be 1.66×10^{-4} g.ion l^{-1}. It is somewhat inconvenient to express the concentration of the solution in such a manner. S.P.L. Sorensen (1909) simply applied negative logarithm of hydrogen ion concentration to remove this sort of difficulty for expressing such concentrations. A simple operation like this made an easy expression for hydrogen ion concentration of the solution. He defined pH as negative logarithm of hydrogen ion concentration:

$$pH = -\log_{10} [H^+]$$

A more convenient scale for expressing concentration of H^+ ion in aqueous solutions is thus developed.

pH scale

pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$[H_3O^+(aq)]/mol\ dm^{-3}$	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
	increasingly acidic				⟵			neutral		⟶	increasingly alkaline				

Now applying this idea in the case of pure water,

where $[H^+] = 10^{-7}$

$\therefore \quad -\log_{10}[H^+] = -\log_{10}(10^{-7})$

$\therefore \quad pH = 7$

Again in pure water, $[OH^-] = 10^{-7}$

$-\log_{10}[OH^-] = -\log_{10}(10^{-7})$

$\therefore \quad pOH = 7.$

Therefore, in any aqueous solution pH + pOH = 7 + 7 = 14

Highlight:

$$[H^+] \times [OH^-] = K_w.$$

or, $-\log_{10}[H^+] + (-\log_{10}[OH^-]) = -\log_{10}K_w$

$\therefore \quad pH + pOH = pK_w = 14 \quad$ where $-\log_{10}K_w = pK_w$.

Pure water is neutral because in pure water, $[H^+] = [OH^-] = 10^{-7}$.

So, all acidic solutions will have pH less than 7, and all alkaline solutions will have pH greater than 7.

Highlight:

Following such conventions we express K_a and K_b as follows:

$$pK_a = -\log_{10} K_a, \quad \text{and} \quad pK_b = -\log_{10} K_b$$

As for example: K_a for salicylic acid $= 10^{-3}$.

$\therefore \quad pK_a = 3.$

Example 1. *Calculate pH of the following solutions:*

(*a*) *4.9×10^{-4} (N) acid,* (*b*) *0.0016 (N) base.*

Sol. Both acid and base are strong.

As the acid and base are strong, the dissociation is complete. So,

(*a*) $[H^+] = 4.9 \times 10^{-4}$ g-ion l^{-1}

$-\log_{10}[H^+] = -\log_{10}(4.9 \times 10^{-4})$

$\therefore$ $\text{pH} = 4 - \log_{10} 4.9 = 4 - 0.69 = 3.31$

(*b*) $[OH^-] = 1.6 \times 10^{-3}$ g-ion l^{-1}

$-\log_{10}[OH^-] = -\log_{10}(1.6 \times 10^{-3})$

$\therefore$ $\text{pOH} = 3 - \log_{10} 1.6 = 3 - 0.2041$

$= 2.7959$ or 2.76

$\therefore$ $\text{pH} = 14 - p\text{OH} = 14 - 2.76 = 11.24.$

Example 2. *Calculate $[H^+]$ of a solution of pH 3.63.*

Sol. $\text{pH} = 3.63$

$-\log_{10}[H^+] = 3.63$

$\log_{10}[H^+] = -3.63 = -3 - 0.63 = 4 - 0.37 = \bar{4}.37$

$[H^+] = \text{antilog } \bar{4}.37 = 2.34 \times 10^{-4}$

$\therefore$ $[H^+] = 2.34 \times 10^{-4}$ g-ion litre^{-1}.

Example 3. *Calculate $[H^+]$, $[OH^-]$ and pH of a weak base [0.1(N)].*

Given: $\alpha = 0.013$.

Sol. $[OH^-] = 0.013 \times 0.1 = 1.3 \times 10^{-3}$ g-ion litre^{-1}.

$$[H^+] = \frac{10^{-14}}{1.3 \times 10^{-3}} = 7.7 \times 10^{-12} \text{ g-ion litre}^{-1}.$$

$$\text{pH} = -\log_{10}(7.7 \times 10^{-12}) = 12 - \log 7.7$$

$$= 12 - 0.8865 = 11.1135.$$

Relative Strengths of Acids and Bases

Tendency of donating protons in any aqueous solution is a measure of acidity of the solution. If concentrations of two acids A and B are C_A and C_B respectively, ratio of strengths should be $C_A : C_B$. There are several other processes for comparing strengths of acids. One such method is by comparing dissociation constants of the acids.

Let, degree of dissociation of acid $A_1 = \alpha_1$

Degree of dissociation of acid $A_2 = \alpha_2$

The concentrations of the acids were same (C).

So, their strengths S_1 and S_2 are represented by,

$$\frac{S_1}{S_2} = \frac{\alpha_1 C}{\alpha_2 C} = \frac{\alpha_1}{\alpha_2} = \frac{\sqrt{K_1 C}}{\sqrt{K_2 C}} \sqrt{\frac{K_1}{K_2}}$$

So, the ratio of dissociation constants of two acids compare their strengths.

Buffer Solutions

Some solutions do not change their pH on addition of little acid or alkali. Such solutions are known as buffer solutions. The arrest of pH changes of these solutions is known as *buffer action.*

Mechanism of buffer action: A buffer solution is generally a mixture of solutions of a weak acid HA and its salt BA.

So we have,

$BA \longrightarrow B^+ + A^-$ (Completely dissociated in aqueous solution as it is a salt)

$HA \rightleftharpoons H^+ + A^-$ (Incomplete dissociation in aqueous solution as the acid is weak)

A^- is a strong base as its conjugate acid HA is weak. So A^- will readily accept H^+ from solution which comes from the added acid to the solution.

$$H^+(\text{external}) + A^- \longrightarrow HA$$

The undissociated molecules of HA will be generated more and more, again whose dissociation is almost prevented due to common ion effect of A^-. So the change of pH will be arrested.

If we add a little base to such a buffer solution the external KH^- will be removed by the acid HA, as OH^- is a strong base:

$$OH^-(\text{external}) + HA \longrightarrow H_2O + A^-\ .$$

So, pH of such solution will not change on addition of little acid or alkali and that is the buffer action of the solution.

Again, a weak base BOH and its salt will give a buffer solution.

As in this case, $BA \longrightarrow B^+ + A^-$ (complete dissociation)

$BOH \rightleftharpoons B^+ + OH^-$ (incomplete dissociation)

On addition of acid to such solution, external H^+ will be removed by BOH

$$H^+(\text{external}) + BOH \longrightarrow B^+ + H_2O.$$

Again on addition of alkali to such solution OH^- ions are removed as follows:

$$OH^- + B^+ \longrightarrow BOH$$

B^+ is an acid, according to Bronsted concept.

So the pH of the solution will not change on the addition of a little acid or alkali.

pH of a Buffer Solution

(*i*) **Buffer solution (prepared from weak acid and its salt)**

Let, the acid be HA and its salt be BA, here the common ion is A^-

$$HA \rightleftharpoons H^+ + A^- \text{ (weak acid)}$$

$$\therefore \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\log_{10} K_a = \log [H^+] + \log_{10} [A^-] - \log_{10} [HA]$$

$$\log_{10} K_a = \log_{10} [H^+] + \log_{10} \frac{[A^-]}{[HA]}$$

or,
$$-\log_{10} [H^+] = -\log_{10} K_a + \log_{10} \frac{[A^-]}{[HA]}$$

or,
$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$$

Due to common ion effect, the dissociation of acid HA is very poor,

So, we can write $[A^-] = [\text{Salt}]$ as all the A^- in the solution are due to ionisation of BA.

$$\therefore \quad pH = pK_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

This is the famous *Henderson equation.*

The acidity or alkalinity of mixed solution, *i.e.,* pH depends upon the ratios of the concentration of salt and acid. The buffer action is favourable in pH ranges $pK_a \pm 1$ *i.e.,* when concentration of salt becomes 10 times the concentration of acid and vice versa.

(*ii*) **Buffer solution (prepared from a weak base and its salt)**

In this case:

$$BOH \rightleftharpoons B^+ + OH^- \text{ (weak)}$$

$$K_b = \frac{[B^+]\,[OH^-]}{[BOH]} = \frac{[B^+]}{[BOH]} \times \frac{K_w}{[H^+]} \qquad \left[\because\ [OH^-] = \frac{K_w}{[H^+]}\right]$$

$$\therefore \qquad [H^+] = \frac{K_w}{K_b} \cdot \frac{[B^+]}{[BOH]}$$

As entire B^+ ions in the solution is due to complete ionisation of BA and BOH is weak

$$\therefore \qquad pH = pK_w - pK_b - \log \frac{[B^+]}{[BOH]} = pK_w - pK_b - \log \frac{[Salt]}{[Base]}$$

where [Salt] = [Base], then $pH = pK_w - pK_b$.

Highlights:

- Buffer solution almost invariably consists of a mixture of a weak acid HA and its salt BA or a mixture of weak base BOH and its salt BA.
- The buffer capacity of a solution is defined by db/d_{pH}, where d_{pH} is the increase of pH resulting from the addition of *db* of base, the addition of acid decreases the pH and is equivalent to a negative amount of base.

Different Buffer Solutions

Component conjugate acid–base pair	*pH ranges*
(*i*) Glycine/Glycine hydrochloride	1.0-3.7
(*ii*) Phthalic acid/Potassium hydrogen phthalate	2.2-3.38
(*iii*) Acetic acid/Sodium acetate	3.7-5.6
(*iv*) NaH_2PO_4/ Na_2HPO_4	5.8-8
(*v*) Boric acid/Borax	6.8-9.2
(*vi*) NH_4OH/NH_4Cl	10
(*vii*) Na_2HPO_4/Na_3PO_4	11-12

Example 1. *Prepare a buffer solution of pH 5. [Given* $pK_a CH_3COOH$ *at 25° is 4.76].*

Sol.
$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$= 4.76 + \log \frac{[Salt]}{[Acid]}$$

$$\therefore \qquad \log \frac{[Salt]}{[Acid]} = pH - 4.76 = 5.00 - 4.76 = 0.24.$$

$$\therefore \qquad \frac{[Salt]}{[Acid]} = \text{antilog}\ (0.24) = 1.738$$

Therefore, when 1.738 g-moles of CH_3COONa is mixed with 1 g-mole of CH_3COOH and the volume of the solution is made upto one litre, the desired buffer solution of pH 5 is obtained.

Solubility Product

The law of mass action cannot be successfully applied to the process of electrolytic dissociation except to the cases of weak electrolytes. But it can be successfully applied to the saturated solutions of sparingly soluble salts, because a heterogeneous equilibrium is set up as follows.

$$BA(s) \rightleftharpoons BA\text{ (solution)} \rightleftharpoons B^+ + A^-$$

Applying law of mass action,

$$K = \frac{[B^+]\,[A^-]}{[BA(s)]}$$

or $$K[BA(s)] = [B^+][A^-]$$

The concentration of solid salt [BA (s)] is constant. By convention it is unity. So [BA (s)] = 1.

Therefore, $[B^+]\ [A^-] = \text{constant} = K_{sp}$.

The constant K_{sp} is called the solubility product of the salt BA. The above equation signifies that the product of concentrations of B^+ and A^- of a salt is constant independent of the individual concentrations of B^+ and A^- ions when temperature is constant.

If S is the solubility of BA, then $[B^+] = S$ g.mol l^{-1} and $[A^-] = S$ g.mol.l^{-1}.

$$K_{sp} = [B^+]\ [A^-] = S^2$$

For a salt like B_xA_y:

$$B_xA_y(s) \rightleftharpoons B_xA_y\text{ (Solution)} \rightleftharpoons xB^+ + yA^-$$

If the solubility is S mol l^{-1} then $[B^+] = x$S, $[A^-] = y$S

$$\therefore \quad K_{sp} = [B^+]^x\ [A^-]^y = (xS)^x\ (yS)^y = x^xy^y.S^{x+y}$$

It is a universally applicable equation.

Highlights:

- When the solubility of $Mg_3(PO_4)_2$ is C mol. l^{-1}

$$Mg_3(PO_4)_2(s) \rightleftharpoons Mg_3(PO_4)_2\text{ (Solution)} \rightleftharpoons 3Mg^{+2} + 2PO_4^{-3}$$

  its K_{sp} is $[Mg^{+2}]^3\ [PO_4^{-3}]^2 = (3C)^3 \times (2C)^2 = 108\ C^5$.
- The solubility product of a sparingly soluble binary electrolyte is simply the square of its solubility in pure water expressed in mol l^{-1}.
- It is customary to express the concentrations of the ions in g. ion l^{-1} *i.e.,* formula weight per litre and not in g. equiv. per litre.

The solubility product of a salt may be defined as the greatest possible product of concentrations of its constituent ions in its saturated solution expressed in g.ion l^{-1}, each concentration term being raised to a power representing the number of gm. ions of each type formed by dissociation of one molecular formula weight of the salt.

Example 1. *The solubility of chalk is 0.0305 gl^{-1}. Calculate its solubility product. (mol. wt. of $CaCO_3$ = 100)*

Solubility $S = 0.0305\ gl^{-1} = 3.05 \times 10^{-4}$ mol l^{-1}

$$K_{sp} = S^2 = (3.05 \times 10^{-4})^2 = 9.3 \times 10^{-8}.$$

Example 2. *The solubility of CaF_2 is 0.0002 mol l^{-1}. Calculate K_{sp} of CaF_2.*

$$CaF_2 \rightleftharpoons Ca^{+2} + 2F^-$$

$$[Ca^{+2}] = 0.0002 \text{ g ion } l^{-1} \, . \, [F^-] = 2 \times 0.0002 \text{ g ion } l^{-1}.$$

$$K_{sp} = [Ca^{+2}] \, [F^-]^2 = 0.0002 \times (0.0004)^2 = 3.2 \times 10^{-11}.$$

Effect of Common Ion on Solubility

We know that, for a saturated solution of a sparingly soluble salt BA,

$$K_{sp} = [B^+] \, [A^-]$$

If we add to the solution a substance, which has an ion common to the above salt then concentration of that ion will increase. As a result, the concentration of other ion will decrease otherwise the constant K_{sp} will change. Therefore, B^+ and A^- will combine to give the solid BA(*s*) and the solubility of BA will decrease.

Highlights:

- It is almost invariably true that addition of a common ion at first diminishes the solubility of a sparingly soluble salt but when relatively large amounts are added the solubility starts to increase.
- The presence of a neutral salt without a common ion often results in an increase of solubility of a sparingly soluble salt.

Example. 3. *(a) At 25° the solubility of $BaSO_4$ is 0.00233 gl^-. Calculate the solubility product of the salt, taking complete dissociation.*

(b) Calculate the solubility of $BaSO_4$ in a solution of $(NH_4)_2SO_4$ containing 13.2 gl^- at 25°C. [Ba = 137]

Sol. (*a*) $$[Ba^{++}] = [SO_4^{=}] = \frac{0.00233}{137 + 96} = 10^{-5} \text{ g.ion } l^{-1}$$

∴ $$K_{sp} = [Ba^{++}] \, . \, [SO_4^{=}] = 10^{-5} \times 10^{-5} = 10^{-10}.$$

(*b*) $$[(NH_4)_2SO_4] = \frac{13.2}{132} = 0.1 \text{ (M)}$$

∴ $$[SO_4^{=}] = 0.1 \text{ g.ion } l^{-1}.$$

Let, the changed solubility of $BaSO_4$ = S′.

∴ $$K_{sp} = S' \times (S' + 0.1) = 10^{-10}.$$

∴ $$S' = \frac{10^{-10}}{10^{-1}}$$ [S′ is negligible compared to 0.1]

$$= 10^{-9} \text{ mol. } l^{-1}.$$

∴ $$S' = 2.33 \; gl^{-1}.$$

Example 4. *A litre of a solution contains 0.01 mole NH_4OH and 0.001 g.ion Mg^{+2}. To arrest the precipitation of $Mg(OH)_2$. What will be concentration of NH_4^+ ion from NH_4Cl? Given $K_{b \, NH_4OH} = 1.8 \times 10^{-5}$ and $K_{sp \, Mg(OH)_2} = 1.12 \times 10^{-11}$.*

Sol. We know that $K_{sp} = [Mg^{+2}] \, [OH^-]^2 = 1.12 \times 10^{-11}$

∴ $$[OH^-] = \left[\frac{1.12 \times 10^{-11}}{0.001}\right]^{1/2} = 1.1 \times 10^{-4} \text{ g.ion } l^{-1}.$$

So, $[OH^-]$ should not exceed 1.1×10^{-4} g.ion l^{-1} to arrest the precipitation of $Mg(OH)_2$. For doing so, we are to suppress the dissociation of NH_4OH by adding common ion NH_4^+.

So, $$K_b = \frac{[NH_4^+] \, [OH^-]}{[NH_4 \, OH]} = 1.8 \times 10^{-5}.$$

or $$= \frac{[NH_4^+] \times 1.1 \times 10^{-4}}{0.01} = 1.8 \times 10^{-5} \quad \therefore \quad [NH_4^+] = 1.6 \times 10^{-3} \text{ g.ion } l^{-1}.$$

Effect of a Salt without a Common Ion on Solubility

For the correct expression for solubility product we should use activity (a) in place of concentration: *i.e.*, $K_{sp} = a_{Ag^+} \cdot a_{Cl^-}$

So, true expression is $K_{sp} = \gamma_{Ag^+} \cdot [Ag^+] \cdot \gamma_{Cl^-} [Cl^-]$ where γ = activity coefficient.

$\because$ activity (a) = Concentration (c) × activity coefficient (γ)

$\therefore$ $a = c\gamma$.

For a very dilute solution $\gamma = 1$ then $a = c$.

If we add KNO_3 to a saturated solution of AgCl the γ-term of the expression of K_{sp} decreases. So, $[Ag^+] \cdot [Cl^-]$ increases in order to keep the true K_{sp} value constant.

Therefore, solubility of a sparingly soluble salt increases on addition of any salt without a common ion. This effect is known as *salt effect.*

Highlights:

- Many proteins, which are sparingly soluble in water, are soluble in salt solutions due to this salt effect.
- The effect of common ion on solubility is utilised in qualitative inorganic analysis to separate the ions present in a solution.

Application of Common Ion Effect and Solubility Product in Qualitative Inorganic Analysis

General Group Separation of Basic Radicals:

Precipitation of a salt takes place when its ionic product exceeds its solubility product. A salt may not get precipitated even when its ionic product exceeds its solubility product. It may remain in saturated solution for sometime. That is why, for precipitation in chemical analysis, the value of solubility product of the salt should always be higher than its ionic product.

Group I. *The chlorides of Group I metals (Hg_2^{+2}, Pb^{+2}, Ag^+) are insoluble, on addition of dil. HCl, ionic product ($C_M^+ \times C_{Cl^-}$) easily exceeds the solubility products and the cations are precipitated. Only $PbCl_2$ has higher solubility product and for that reason it is not completely precipitated here. It is also precipitated in Group II.*

Group II. *The reagent is H_2S in presence of dil. HCl. The common ion H^+ suppresses the ionisation of H_2S. So concentration of sulphide ion $C_S^=$ remains low. The metallic ions (Hg^{+2}, Cu^{+2}, Pb^{+2}, Bi^{+3}, As^{+3}, Sb^{+3}, Sn^{+2}), whose solubility product of sulphides are low, get precipitated here i.e., despite low $S^=$ ion concentration, the ionic products ($C_M^{+2} \times C_S^{-2}$) of metal ions exceed the solubility products because of low value of solubility products. IIIB metallic ion (Co^{+2}, Mn^{+2}, Ni^{+2}, Zn^{+2}) sulphides have higher values of solubility products, so their precipitation is arrested here, CdS and PbS have comparatively higher values of solubility products, so $C_S^=$ should be high for them. To increase the ionisation of H_2S, low acidity or higher pH is necessary; to reduce acidity of the medium water is added to dilute the medium. Again diluted acid medium precipitates colloidal As_2S_3 and SnS which creates difficulty in filtration. So in more or less concentrated acid medium they (Gr II) are precipitated and filtered and then filtrate is diluted with water and passed H_2S to precipitate CdS and PbS.*

Group III A. *Here reagent is NH_4Cl/NH_4OH. The common NH_4^+ suppresses the dissociation of weak base NH_4OH thereby C_{OH^-} remains low. As a result Fe^{+3}, Al^{+3}, Cr^{+3} get precipitated as hydroxides because their solubility products are exceeded. The precipitation of*

Zn^{+2}, Mg^{+2} and Mn^{+2} as hydroxides are arrested as their solubility product values for hydroxides are comparatively higher.

Group IV. *Here reagents are NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$. Group IV metals i.e., Ba^{+2}, Ca^{+2}, Sr^{+2} are precipitated as carbonates.*

SOLVED EXAMPLES

Example 1. *Calculate the pH of 0.005M $Ca(OH)_2$ solution assuming complete dissociation.*

Sol. $[OH^-] = 2 \times 0.005 = 10^{-2}$ mol. l^{-1}.

$\therefore$ pOH = 2.

$\therefore$ pH = 14 – 2 = 12.

Example 2. *Calculate $[H^+]$, $[OH^-]$ and pH of a solution prepared by diluting 20 ml of 0.1 M HCl to 1 litre.*

Sol. $$[H^+] = \frac{20 \times 0.1}{1000} = 0.002 = 2 \times 10^{-3} \text{ mole } l^{-1}.$$

$$\therefore \quad pH = -\log_{10}[H^+] = -\log_{10}[2 \times 10^{-3}]$$
$$= 3 - \log 2 = 3 - 0.3010$$
$$= 2.6990 \sim 2.7$$
$$\therefore \quad pOH = 14 - 2.7 = 11.3$$
$$-\log_{10}[OH] = 11.3$$
$$[OH] = 10^{-11.3} = 5.01 \times 10^{-12} \text{ g.ion } l^{-1}.$$

Example 3. *Calculate the pH of (a) 1.0×10^{-8} (M) HCl solution.*

(b) 1×10^{-8} (M) NaOH solution.

Sol. (*a*) When the $[H^+]$ is 10^{-6} or greater the ionisation of water is negligible due to common ion effect. But when it exceeds 10^{-6}, the contribution of H^+ ions is to be counted during calculation of pH.

Let the contribution of $[H^+]$ from water = x.

So, the $[H^+]$ of the solution = $(1 \times 10^{-8} + x)$ and $[OH^-] = x$

$$\therefore \quad K_w = [H^+][OH^-]$$
$$= (1 \times 10^{-8} + x) \times x = 10^{-14}.$$

or $$x^2 + 10^{-8}x - 10^{-14} = 0$$

$$\therefore \quad x = \frac{-10^{-8} \pm \sqrt{(10^{-8})^2 + 4\,.\,1\,.\,10^{-14}}}{2 \times 1}$$
$$= 9.5 \times 10^{-8} \text{(M)}$$
$$[H^+] = (1.0 \times 10^{-8} + x) = (1.0 \times 10^{-8} + 9.5 \times 10^{-8})$$
$$= 10.5 \times 10^{-8}$$
$$\therefore \quad pH = -\log_{10}[H^+] = -\log_{10}(10.5 \times 10^{-8})$$
$$= 8 - \log_{10} 10.5 = 6.98.$$

(*b*) Here let the contribution of OH^- ions from water be x.

$$\therefore \quad \text{total } [OH^-] = (1 \times 10^{-8} + x)$$

So, $$[H^+][OH^-] = K_w = 10^{-14}$$

$$\therefore \quad (1 \times 10^{-8} + x) \times x = 10^{-14}$$

$$\therefore \quad x^2 \times 1.0 \times 10^{-8}x - 10^{-14} = 0$$

$$\therefore \quad x = 9.5 \times 10^{-8} \text{ (M)}$$

$$\therefore \quad [\text{OH}^-] = 9.5 \times 10^{-8} \text{ g. ion } l^{-1}$$

$$\therefore \quad \text{pOH} = 8 - \log 9.5 = 6.98$$

$$\therefore \quad \text{pH} = 14 - 6.98 = 7.02.$$

Example 4. *(a) Calculate the molar concentration of an CH_3COOH solution.* (*Given $K_a = 1.8 \times 10^{-5}$. $\alpha = 0.02$*)

(b) Calculate the degree of dissociation of 0.01 (M) AcOH.

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

at equilibrium: $C(1 - \alpha)$ $C\alpha$ $C\alpha$

$$\therefore \quad K_a = \frac{[H^+]\,[CH_3\,COO^-]}{[CH_3\,COOH]}$$

$$= \frac{0.02C \times 0.2C}{C(1-0.02)} = \frac{0.0004 \times C}{0.98}$$

$$\therefore \quad c = \frac{1.8 \times 10^{-5} \times 0.98}{0.004} \text{ molar}$$

$$= 0.044 \text{ molar.}$$

$$(b) \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.01}} = 4.24 \times 10^{-2}.$$

Example 5. *A buffer solution contains 0.1 mole CH_3COOH and 0.1 mole of CH_3COONa per litre. Calculate the pH of buffer solution. ($pK_a = 4.74$).*

Sol. According to Henderson equation pH of a buffer solution

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 4.74 + \log \frac{0.1}{0.1} = 4.74.$$

Example 6. *pH of blood is 7.4. Calculate the ratio of HCO_3^- and H_2CO_3. Given K_a of $H_2CO_3 = 4.5 \times 10^{-7}$.*

Sol. $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$,

$$\therefore \quad K_a = \frac{[H^+]\,[HCO_3^-]}{[H_2\,CO_3]}$$

$$\therefore \quad \frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_a}{[H^+]} = \frac{4.5 \times 10^{-7}}{[H^+]} = \frac{4.5 \times 10^{-7}}{3.98 \times 10^{-8}} \simeq 11$$

$$\text{pH} = 7.4$$

$$\therefore \quad -\log_{10}[H^+] = 7.4 \quad \therefore \quad [H^+] = 10^{-7.4} = 3.98 \times 10^{-8} \text{ g.ion } l^{-1}$$

Example 7. *The solubility product of CaF_2 in water at 18°C is 3.45×10^{-11}. Calculate the solubility of CaF_2 in water.*

Sol. $K_{sp} = [Ca^{+2}]\,[F^-]^2$

$= [S] \times [2S]^2$ where, S = solubility.

$= 4S^3$

$$\therefore \qquad 4S^3 = 3.45 \times 10^{-11}$$

$$S = \frac{\sqrt[3]{3.45 \times 10^{-11}}}{4} \text{ mole } l^{-1}$$

$$= 2.05 \times 10^{-4} \text{ mole } l^{-1}.$$

Example 8. *Calculate the solubility SrF_2 in 0.1M NaF solution. Given, K_{sp} of SrF_2 = 8×10^{-12}.*

Sol.

$$SrF_2 \rightleftharpoons \underset{\text{S mole}}{Sr^{+2}} + \underset{\text{2S mole}}{2F^-}$$

Initially = in 0.1 M NaF Solution = S mole (2S + 0.1) mol.

$$\therefore \qquad K_{sp} = 8 \times 10^{-10} = [Sr^{+2}] \times [F^-]^2$$

$$= S \times (0.1)^2 = 0.01S$$

$$\therefore \qquad S = \frac{8 \times 10^{-10}}{0.01} = 8 \times 10^{-8} \text{ mol } l^{-1}.$$

SHORT QUESTIONS AND ANSWERS

Q. 1. Give an expression for the ionisation constant.

Ans.

$$K = \frac{\alpha^2 C^2}{C(1-\alpha)}$$

where, K = ionisation constant, α = degree of dissociation of a weak electrolyte,

C = concentration of the weak electrolyte, mol l^{-1}.

For weak electrolytes, α is negligibly small,

So, $1 - \alpha \approx 1$

$$\therefore \qquad K = \alpha^2 C \quad \therefore \quad \alpha = \sqrt{\frac{K}{C}}.$$

Q. 2. What is the Arrhenius concept of acids and bases?

Ans. An acid is a substance which in aqueous solution gives H^+ ions.

A base is a substance which in aqueous solution gives OH^- ions.

Thus, HCl is an acid and NaOH is a base.

Q. 3. What is the Lowry and Bronsted concept of acid and base?

Ans. An acid is a species (neutral or charged) which can donate a proton and a base is a substance or species (neutral or charged) which can accept a proton.

Thus HCl and HSO_4^- are acids as both of them can donate a proton and Cl^- and $SO_4^=$ and HSO_4^- are bases as they can accept a proton.

Q. 4. What are conjugate acid-base pairs?

Ans. Every acid has a conjugate base and every base has a conjugate acid, differing by a proton. This sort of pairs are known as conjugate acid-base pairs. Cl^- is a conjugate base of acid HCl. HSO_4^- is a conjugate base of H_2SO_4.

Again HCl is the conjugate acid of Cl^- and H_2SO_4 is the conjugate acid of the base HSO_4^-.

Some conjugate acid-base pairs are:

$HSO_4^-/SO_4^=$, HNO_3/NO_3^-, H_2O/OH^-, H_3O^+/H_2O.
NH_4^+/NH_3 and so on.

If the acid is strong, its conjugate base will be weak and vice-versa.

Q. 5. Show that solvent acts as a base or an acid according to Lowry Bronsted concept.

Ans. According to Lowry Bronsted concept acid–base reaction always follows the equation:

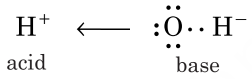
$$\begin{array}{ccccccc} \text{Acid}_I & + & \text{Base}_{II} & \rightleftharpoons & \text{Acid}_{II} & + & \text{Base}_I \\ CH_3COOH & + & H_2O & \rightleftharpoons & H_3O^+ & + & CH_3COO^- \\ HF & + & CH_3COOH & \rightleftharpoons & CH_3COOH_2^+ & + & F^- \\ H_2O & + & H_2O & \rightleftharpoons & H_3O^+ & + & OH^- \end{array}$$

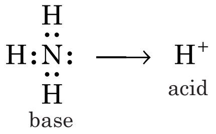
So, every acid–base reaction proceeds according to the equation *i.e.,* conjugate acids and bases are formed during the reaction,

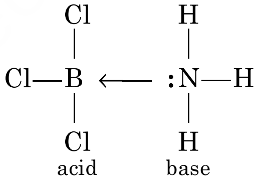
$$\text{Acid}_I + \text{Base}_{II} \rightleftharpoons \text{Acid}_{II} + \text{Base}_I$$

Q. 6. Give Lewis concept of acids and bases.

Ans. An acid is a species which can accept a pair of electrons and a base is a species which can donate a pair of electrons.







Q. 7. Show that ionic product of water (K_w) is 1×10^{-14}, given K for water = 1.8×10^{-16}.

Ans. $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

or $H_2O \rightleftharpoons H^+ + OH^-$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]} \quad \text{or} \quad \frac{[H^+][OH^-]}{[H_2O]}$$

$$[H_2O] = \frac{1000}{18} = 55.5555 \text{ moles } l^{-1}.$$

$$K_w = K[H_2O] = [H^+][OH^-] = 1.8 \times 10^{-16} \times 55.5555$$
$$= 100 \times 10^{-16} = 1.00 \times 10^{-14}.$$

Q. 8. In pure water, what will be the $[H^+]$ or $[OH^-]$?

Ans. As, $[H^+][OH^-] = 10^{-14}$ and in pure water, $[H^+] = [OH^-]$

$\therefore$ $[H^+] = [OH^-] = 10^{-7}$ g.ion l^{-1}.

Q. 9. What is pH?

Ans. It is negative logarithm of hydrogen ion concentration, *i.e.*,

$$pH = -\log_{10} [H^+] \quad \text{or} \quad [H^+] = 10^{-pH}$$

The acidity or alkalinity of a solution is generally expressed by pH.

Q. 10. Explain the pH scale.

Ans. The pH scale is a logarithmic scale for measuring the concentration of hydrogen ions in aqueous solutions.

In acidic solutions, $[H^+]$ range $= 10^0 - 10^{-6}$ g . ion l^{-1}

In neutral solutions, $[H^+] = [OH^-] = 10^{-7}$ g . ion l^{-1}.

In alkaline solutions, $[H^+]$ range $= 10^{-8} - 10^{-14}$ g . ion l^{-1}.

$$pH = -\log_{10} [H^+]$$

pH =	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
[H⁺] =	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}

acidic ⟵ neutral ⟶ alkaline

Q. 11. What is the pH of 0.02 mol dm^{-3} HCl?

Ans.
$$\begin{aligned} pH &= -\log_{10} [H^+] \\ &= -\log_{10} [2 \times 10^{-2}] \quad \text{(as the acid is strong)} \\ &= -\log_{10} 2 + 2 \log_{10} 10 \\ &= 2 - 0.3010 = 1.699 \approx 1.7. \end{aligned}$$

Q. 12. What is the hydrogen concentration of coca cola with pH 2.37?

Ans. $pH = 2.3$

or $-\log_{10} [H^+] = 2.3$

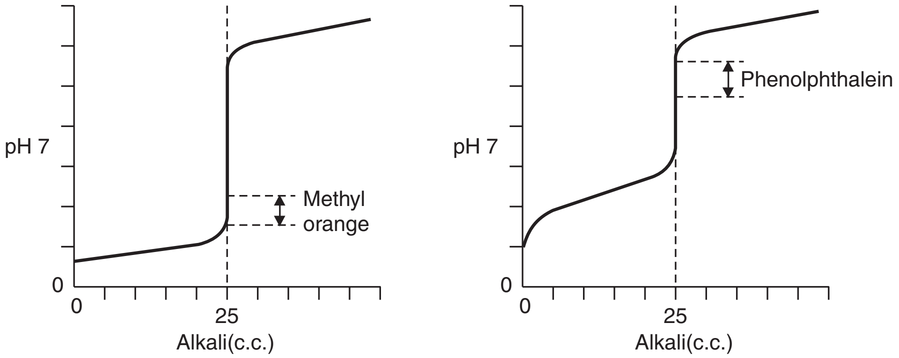
or $\log_{10} [H^+] = -2.3$

or $[H^+] = 10^{-2.3}$

$= 5 \times 10^{-3}$ mol dm^{-3}.

Q. 13. Explain the pH changes during acid–base titration.

Ans. Addition of an alkali from a burette to 25 ml of an acid in a conical flask and plotting a graph give a shape determined by the nature of the acid and the base.



Strong acid–strong base

Weak acid–strong base

Fig. 8.1 Neutralisation Curves.

The graphs show the pH range for the colour change of an acid/base indicator for detecting the end point of the titration.

The indicator chosen to detect the end point must change colour completely in the pH range of the near vertical part of the curve (Fig. 8.1). It is to be noted that, at the equivalence point, when exactly equal amounts of acid and alkali have been added, the pH is not always neutral.

Q. 14. Neutralisation reactions do not always produce neutral solutions—explain.

Ans. At the equivalence point, a salt is formed; if acid and base both are strong, hydrolysis of salts does not take place and the solutions remain neutral at the equivalence point (pH = 7). When a salt formed at the equivalence point has either a 'parent acid' or a 'parent base' weak, it hydrolyses to give a solution that is not neutral. The 'strong parent' in the partnership wins.

Weak acid/strong base end point is alkaline (pH > 7)

Strong acid/weak base end point is acidic (pH < 7).

Q. 15. Neutralisation is essentially a reaction between H^+ and OH^- ions in aqueous solution—explain.

Ans. $$H_3O^+ + OH^- \longrightarrow 2H_2O\ (l)$$

Enthalpy change of neutralisation is same for all acid-base partners, strong or weak. This experimental evidence supports the above view.

Q. 16. What is pK?

Ans. pK is the logarithmic form of an equilibrium constant, useful for pH calculations.

$$-\log_{10} K_a = pK_a, \quad -\log_{10} K_b = pK_b, \quad -\log_{10} K_w = pK_w$$

Taking logarithms produces a convenient small scale of values.

Q. 17. How can you use pK values for pH calculations?

Ans. We know that,

(*i*) $$pK_w = pH + pOH = 14$$

$$\therefore \quad pH = 14 - pOH$$

(*ii*) pH of a weak acid $= pH = \frac{1}{2} pK_a - \frac{1}{2} \log c$

when K_a = ionisation constant of weak acid.

c = concentration of undissociated acid.

(*iii*) pH of a weak base $= 14 - \frac{1}{2} p\,K_b + \frac{1}{2} \log c$

where c = concentration of undissociated base.

K_b = dissociation constant of weak base.

Q. 18. What is the pH of a 0.02 mol. dm^{-3} solution of NaOH?

Ans. NaOH is a strong base

$$[OH^-] = 0.02 \text{ mole dm}^{-3}$$

$$pOH = -\log 0.02 = 1.7$$

$$pH = 14 - pOH = 14 - 1.7 = 12.3.$$

Q. 19. H_3PO_4 has three K_a values–explain.

Ans. There are three dissociations for H_3PO_4 and accordingly k_a values.

(*i*) $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_{a_1} = \dfrac{[H^+]\,[H_2\,PO_4^-]}{[H_3\,PO_4]}$

(*ii*) $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}$; $K_{a_2} = \dfrac{[H^+]\,[H_2PO_4^{-2}]}{[H_3PO_4^-]}$

(*iii*) $HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}$; $K_{a_3} = \dfrac{[H^+]\,[PO_4^{-3}]}{[HPO_4^{-2}]}$

$$K_{a_1} > K_{a_2} > K_{a_3}.$$

Q. 20. Relate K_a, K_b and K_w.

Ans. (*i*) $\underset{\text{acid}}{HA} + H_2O \rightleftharpoons H_3O + \underset{\text{base}}{A^-}$

Conjugate pair

$$K_a = \frac{[H_3\,O^+]\,[A^-]}{[HA]}$$

(*ii*) $A^- + H_2O \rightleftharpoons HA + OH^-$

Conjugate pair

$$K_b = \frac{[HA]\,[OH^-]}{[A^-]}$$

Now, $K_a \times K_b = \dfrac{[H_3\,O^+]\,[A^-]}{[HA]} \times \dfrac{[HA]\,[OH^-]}{[A^-]} = [H_3O^+]\ [OH^-]$

$= K_w = 10^{-14}.$

$\therefore \quad K_a \times K_b = K_w$

or $\quad -\log K_a - \log K_b = -\log K_w$

$\therefore \quad pK_a + pK_b = pK_w = 14.$

Q. 21. Mention the importance of pH.

Ans. (*i*) The pH value of soil helps to decide the type of fertiliser to be used in agriculture.

(*ii*) A small variation of pH of human blood (6.7) causes bodyache.

(*iii*) pH value helps to determine the condition of reactions in laboratory and in industry.

Q. 22. What is common ion effect?

Ans. The change in equilibrium position due to addition of an ionic compound that contains one of the ions involved in the equilibrium is known as common ion effect.

(*i*) The common ion effect can change the ionisation of weak acids and weak bases.

(*ii*) The common ion effect influences the behaviour of buffer solution.

(*iii*) The common ion effect alters the solubility of a sparingly soluble salt.

Q. 23. What is a buffer solution?

Ans. Buffer solutions are mixtures of a weak acid and its salt or a weak base and its salt, which help to keep pH of a solution more or less constant.

Q. 24. What is the pH of a buffer solution containing 0.4 mol dm^{-3} methanoic acid and 1.0 mol dm^{-3} sodium methanoate? pK_a(HCOOH) = 3.8.

Ans.
$$\text{pH} = \text{p}K_a + \log\frac{1.00}{0.40}$$
$$= 3.8 + 0.4 = 4.2.$$

Q. 25. Will $\left(\frac{N}{10}\right)$ Mn^{+2} containing $\left(\frac{N}{100}\right)$ H$^+$ be precipitated by passing H_2S?

Ans.
$$H_2S \rightleftharpoons 2H^+ + S^{-2};\ K = \frac{[H^+]\,[S^{-2}]}{[H_2S]} = 1.1 \times 10^{-22}$$

$$\therefore \quad 1.1 \times 10^{-22} = \frac{(0.01)^2 \times [S^{-2}]}{[H_2S]} = \frac{(0.01)\,[S^{-2}]}{0.1} \qquad [\because\ S_{H_2S} = 0.1M]$$

$$\therefore \quad [S^{-2}] = 10^{-19}. \quad \therefore \quad [Mn^{+2}]\,[S^{-2}] = 0.1 \times 10^{-19} = 10^{-20}$$

$$K_{sp}\,.\,(MnS) = 1.4 \times 10^{-15}$$

So, ppt. will not be obtained.

EXERCISES

1. Deduce Ostwald's dilution law and state its limitations.
2. Deduce the relation between solubility and solubility product of CaF_2 at room temperature.
3. Explain the terms: (*i*) Buffer solution (*ii*) Buffer capacity and (*iii*) Buffer action.
4. Explain the following–Aqueous solution of NaCl conducts electricity while chlorine water does not conduct electricity.
5. Which are the strongest Lewis acids in the series? (*a*) BF_3, BCl_3, BI_3; (*b*) $BeCl_2$, BCl_3.
6. Tricovalent phosphorus compounds can serve as Lewis bases and also as Lewis acids–comment.
7. The reaction HCl (*aq*) + KOH (*aq*) → KCl (*aq*) + H_2O is neutralisation according to:
   (*a*) Bronsted-Lowry concept, (*b*) Lewis theory and (*c*) Solvent system concept. Elucidate.
8. Deduce the Hendersen equation and state its utility.
9. What do you mean by common-ion effect? How is it utilized in qualitative chemical analysis?
10. What do you mean by autoprotolysis of water?
11. Derive an expression for ionic product of water. Show that it is different from dissociation constant of water.
12. Give the Bronsted-Lowry concept of acids and bases.
13. What is the basic equation for acid-base reaction of Bronsted theory?
14. Explain (*a*) neutralisation, (*b*) hydrolysis, in the light of Bronsted theory.
15. What is a buffer solution? Explain buffer action.
16. Derive an expression for pH of the buffer solutions:
    (*a*) Weak acid and its salt.
    (*b*) Weak base and its salt.
17. What is pH? Give its importance and usefulness.
18. What do you mean by solubility product? What is true solubility product?
19. Give an expression for the solubility product of the salt $A_x\,B_y$.
20. Discuss the effect of common ion on solubility product.

21. What will be the pH of a solution obtained by mixing 800 ml of 0.05 (N) NaOH and 200 ml of 1N HCl? [**Ans.** 12.3]

22. Calculate the pH and pOH of .1N HCl. [**Ans.** 1, 13]

23. Find α for NH_4OH in a solution of .1M. Given $K_b = 2 \times 10^{-5}$. [**Ans.** .014]

24. What will be the pH of a solution obtained by mixing 5g. of CH_3COOH and 7.5 g. of CH_3COONa, making a volume equal to 500 ml? [**Ans.** 4.78]

25. pH of a solution is 10.57. Calculate the $[H^+]$. [**Ans.** 2.69×10^{-11} moles l^{-1}]

26. Calculate the pH and pOH of:

(*a*) 0.00345 (N) acid (*b*) 0.000775 (N) acid

(*c*) 0.00886 (N) base [**Ans.** (*a*) 2.46, 11.54 (*b*) 3.11, 10.89 (*c*) 11.95, 2.05]

assuming complete dissociation.

27. Solubility of $PbSO_4$ is 0.038 g-l^{-1}. Calculate its solubility product. [**Ans.** 1.6×10^{-8}]

28. Solubility of Ag_2CrO_9 g-l^{-1}. Calculate its solubility product. [**Ans.** 1.4×10^{-12}}

29. $[Ag^+]$ in a solution is 4×10^{-3} g-in l^{-1}. Calculate the minimum concentration of Cl^- to precipitate AgCl. Given K_{sp} of AgCl = 1.8×10^{-10}. [**Ans.** 5×10^{-8} g-in l^{-1}]

30. Calculate the concentration of H_2S required to arrest the precipitation of PbS from a solution of 0.001 (M) $Pb(NO_3)_2$. Given $K_a(H_2S) = 1.1 \times 10^{-23}$, $K_{sp}(PbS) = 3.4 \times 10^{-28}$. [**Ans.** 5.6 (M)]

9

Electrochemistry

INTRODUCTION

Substances behave differently towards electric current. Some conduct it and some do not. Substances which conduct electricity are **conductors,** as for example, metals, acids, bases etc. and which do not conduct electricity are **nonconductors** as for example, wood, asbestos etc. Again conductors can be divided into two subdivisions: (*i*) **electrolytes** and (*ii*) **non-electrolytes**. Electrolytes dissociate when they conduct electricity *i.e.,* a chemical change occurs then, whereas when non-electrolytes conduct electricity there is no such chemical change. Substances which conduct electricity and get dissociated in solution or in the fused states were termed electrolytes by Faraday. Salts, acids, alkalies are examples of such electrolytes.

Table 9.1: Comparison

Metallic conductors	*Non-metallic conductors (electrolytes)*
• Flow of electrons takes place during the passage of electricity through them. • It involves no chemical change during conduction of current. But some physical changes may occur.	• Flow of ions takes place during the passage of electricity through them. • Chemical change takes place *i.e.,* new products are obtained during conduction of current.

Electrolysis

Dissociation of a compound by passing electric current through a compound in solution or in fused state is known as **electrolysis.** An arrangement for electrolysis is shown in Fig. 9.1. The current is always passed into and out of the electrolyte by means of metal foils or plates

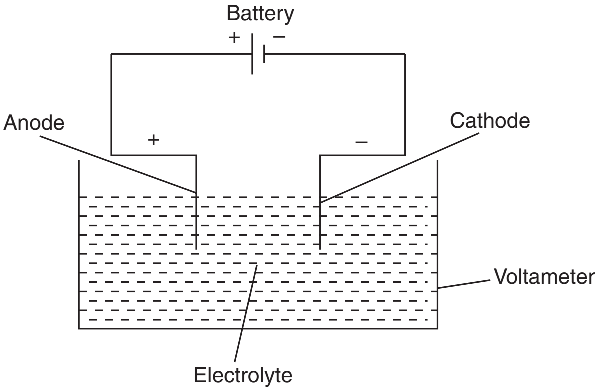


Fig. 9.1 Set-up for electrolysis.

kept immersed in it. They are electrodes (cathode and anode). **An ion is an atom or a group of atoms carrying positive or negative charge of electricity.** When an electrolyte (electrically neutral) is dissolved in water (or in fused state), it breaks up into two or more ions of two different kinds, positive and negative, the amount of positive charge being exactly equal to the amount of negative charge. The ions produced exist in equilibrium with the undissociated electrolyte molecules.

$$\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-, \quad \text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^- \text{ etc.}$$

Such a dissociation of an electrolyte is called **ionic or electrolytic dissociation**. This dissociation is complete at infinite dilution. It is the ions, not the undissociated molecule, which conduct electricity. The anions migrate towards the anode and cations migrate towards the cathode. The liberation of the ions at the electrodes depends upon their **discharge potentials**. This theory of electrolytic dissociation was first put forward by Arrhenius, that is why the theory is known as **Arrhenius ionic theory**.

Faraday's Laws of Electrolysis

First law: *The mass of an ion liberated during electrolysis is directly proportional to the quantity of electricity which has passed through the electrolyte.*

If W = the mass of ion liberated in gms,
c = the current strength in amperes,
t = the time in secs,
Q = the quantity of electricity in coulombs,

then according to first law:

$$W \propto Q \quad \text{but} \quad Q = c \times t$$

$$\therefore \quad W \propto ct$$

$\therefore$ W = Zct where Z is a constant.

When Q = 1 *i.e.,* $c = 1$ and $t = 1$, W = Z

i.e,. **Z is mass of ion liberated by unit quantity of electricity. Z is called electrochemical equivalent (E.C.E.).**

Second law: *When the same quantity of electricity is passed through different electrolytes, the relative masses of ions liberated are proportional to their chemical equivalents.*

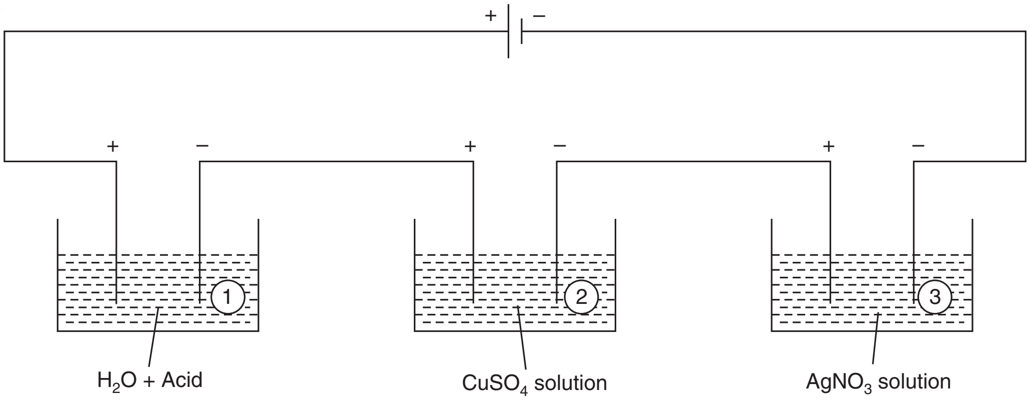


Fig. 9.2 Different voltameters containing different electrolytes.

That is to say, when 1 g of H_2 is liberated in cell (1), 63.5/2 g Cu will be liberated in cell (2) and 108 g Ag will be liberated in cell (3) (Fig. 9.2).

Let, the quantity of electricity = Q coulomb

the quantity of Cu deposited = W_1 g

the quantity of Ag deposited = W_2 g

Then, according to Faraday's second law:

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1 Q}{Z_2 Q} \qquad \text{(from the first law)}$$

$$\therefore \qquad \frac{E_1}{E_2} = \frac{Z_1}{Z_2} \quad \text{or} \quad \frac{E_1}{Z_1} = \frac{E_2}{Z_2} \quad \text{or} \quad E \propto Z$$

So chemical equivalent of an element is proportional to its electrochemical equivalent.

If one of the elements is H, then,

$$\frac{E}{E_H} = \frac{Z}{Z_H} \quad \text{or} \quad Z = \frac{E \times Z_H}{E_H}$$

Chemical equivalent of hydrogen = E_H, chemical equivalent of any element = E

E.C.E. of hydrogen = Z_H, E.C.E. of any element = Z

$$\therefore \qquad Z = \frac{E \times Z_H}{1.008} \approx \frac{E \times Z_H}{1}$$

So, E.C.E. of any element = Chemical equivalent of the element × E.C.E. of hydrogen.

Combination of First and Second Laws of Faraday

From first law, $W \propto Q$ (where E is constant)

From second law, $W \propto E$ (where Q is constant)

$$\therefore \qquad W = KQE \text{ (where E and Q vary)}$$

$$\text{or} \qquad Q = \frac{W}{KE} \text{ (K = Constant)}$$

$$\text{When} \qquad W = E, \quad Q = \frac{1}{K}$$

Therefore, to liberate 1 gm equiv. of any element during electrolysis, the quantity of electricity is fixed. This quantity of electricity is called one faraday (F).

$$\therefore \qquad F = Q = \frac{1}{K} \quad \text{(for 1 gm. equiv.)}$$

$$\therefore \qquad W = KQE = \frac{QE}{F}$$

From first law, W = ZQ

$$\text{or} \qquad E = ZQ \quad \text{(for 1 gm. equiv.)}$$

$$= ZF$$

$$\text{or} \qquad F = \frac{E}{Z}$$

for one gm equivalent of different elements

$$\frac{E_1}{Z_1} = \frac{E_2}{Z_2} = \ldots\ldots = \frac{E_n}{Z_n} = F$$

Therefore, we can accept that, 1 F = 96500 coulomb.

Table 9.2: Displaying the constancy of E/Z for different elements

Element	*E*	*Z*	*F = E/Z (Coulomb)*
H	1.008	0.0000104	96496
Ag	107.88	0.0001118	96495
Cu	31.78	0.0003294	96494 96495
O	8.0	0.0000829	≈ 96500

The concept of transport number. Ions of an electrolyte *i.e.*, cations and anions present in the solution conduct current. If 100 cations cross the barrier from left to right, then current is wholly carried by cation. We can say that the cation transport number is hundred per cent and the anion transport number is zero per cent. The case may be totally reversed, in that case, the transport number of anions is hundred per cent and that of cations is zero per cent. It is to be noted that deposition at the electrodes in the above two cases will be same (Fig. 9.3).

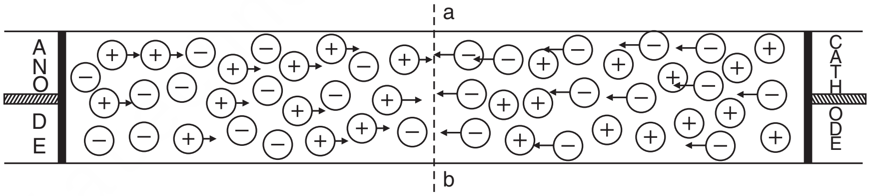


Fig. 9.3 Concept of transport number.

Usually both cations and anions cross the barrier (*ab*) but in unequal numbers owing to their unequal speeds; so their transport numbers are unequal. For example, if 80 cations cross the barrier (*ab*) towards cathode compartment and 20 anions cross the barrier (*ab*) towards anode compartment, the total quantity of the current passed will remain same as above *i.e.,* 100 units but the current carried by cations is 80 per cent and the current carried by anions is 20 per cent. So we can define **transport number** as the fraction of the current carried by an ion. So,

$$\text{transport number } (t) = \frac{n_i Z_i}{\Sigma n_i Z_i}$$

where, n_i = number of the ions and Z_i = valency of the ions which cross the barrier.

Transport number is proportional to speeds of the ions.

So, $t_+ \propto u$ and $t_- \propto v$ and $(t_+ + t_-) \propto (u + v)$

But $t_+ + t_- = 1$

$$\therefore \qquad t_+ = \frac{u}{u+v} \quad \text{and} \quad t_- = \frac{v}{u+v}$$

where u and v are the speeds of cations and anions respectively.

Transport number or transference number of an ion is dependent on the speed of the ions.

Let the two electrodes, A and B, are kept inside an electrolyte and their potential difference is E. The current I is flowing, the solution contains $n(\pm)$ number of ions per millilitre and the valency of ions is $z(\pm)$. The number of ions liberated at the positive and negative electrodes per unit area are given by $n_+ u$ and $n_- v$. If unit of the charge is 'e' (Fig. 9.4)

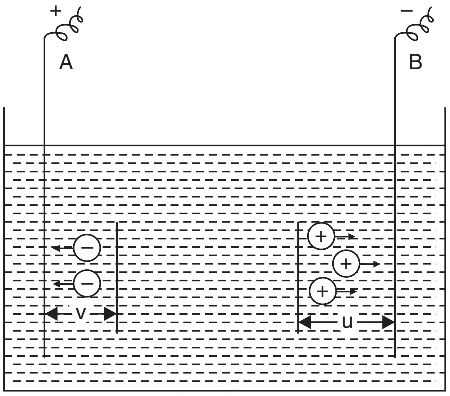


Fig. 9.4 Voltameter.

Current carried by the positive ions = $I_+ = (n_+u)z_+e$

Current carried by the negative ions = $I_- = (n_-v)z_-e$.

The total current carried by the positive and negative ions = $I = I_+ + I_-$

$$= (n_+u)z_+e + (n_-v)z_-e.$$

As every part of the electrolyte is electrically neutral, therefore, $n_+z_+ = n_-z_-$

So,
$$t_+ = \frac{I_+}{I} = \frac{n_+z_+eu}{n_+z_+eu + n_+z_+ev} = \frac{n_+\ z_+eu}{n_+z_+e(u+v)} = \frac{u}{u+v}$$

Similarly,
$$t_- = \frac{I_-}{I} = \frac{n_-z_-ev}{n_+z_+eu + n_+z_+ev} = \frac{n_+z_+ev}{n_+z_+e(u+v)} = \frac{v}{u+v}$$

∴
$$t_+ = \frac{u}{u+v} \quad \text{and} \quad t_- = \frac{v}{u+v}$$

It is obvious that, $t_+ + t_- = 1$

or
$$t_+ = 1 - t_-$$

Relative Speeds of Ions During Electrolysis (Transport Number)

It has been noted that the ions are liberated in equivalent amounts at the two electrodes, this phenomenon creates an idea that perhaps the ions move at the same rate during electrolysis, but it is not so, ions are always discharged in equivalent amounts but their speeds are different. The following model will make the idea clear (Fig. 9.5).

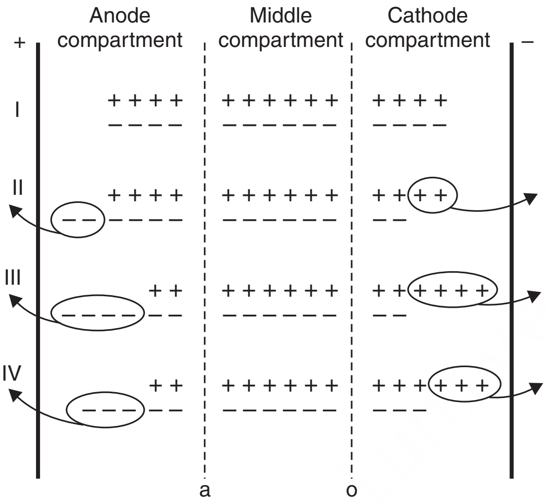


Fig. 9.5 Scheme showing the equivalence of discharge for any relative rate of motion of the two ions.

The '+' sign represents a cation and '–' sign represents an anion. Let there be total 14 molecules in the electrolyte.

(*i*) 4 molecules each in the anode and cathode compartments and 6 molecules in the middle compartment.

(*ii*) **When only the anions move.** Let two anions have crossed diaphragm towards the anode, we get the picture (II). The cations did not move at all. The concentration in the anode compartment has not altered while the concentration of the cathode compartment has fallen by two molecules due to deposition of ions at the respective electrode.

(*iii*) **When the anions and cations move at the same rate.** Let two cations and two anions have crossed the diaphragms towards cathode and anode, we get the picture (III). In this case also, the number of anions and cations discharged is the same *i.e.,* four, but the concentration of both the compartments has fallen to the same extent *i.e.,* by two molecules due to deposition of ions at the respective electrodes.

(*iv*) **When the ions move at the different speeds.** Let when two cations have crossed the diaphragm towards the cathode, one anion passes towards anode. We get the picture (IV). The total number of cations and anions discharged is again the same three. Although concentration in the cathode compartment has fallen by one molecule and that of anode compartment has fallen by two molecules.

It is evident from the above discussion that the fall of concentration around an electrode is proportional to the speed of the ions moving away from it.

$$\frac{\text{Fall round anode}}{\text{Fall round cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}} = \frac{u}{v}$$

$$= \frac{\text{Number of equivalence of electrolyte lost from anode compartment}}{\text{Number of equivalence of electrolyte lost from cathode compartment}}$$

The total gm. equivalence liberated from both the compartments is proportional to $(u + v)$.

So,
$$t_+ = \frac{\text{The number of electrolytes lost from anode compartment}}{\text{Total number of equivalence of the electrolyte liberated on the electrode}}$$

$$t_- = \frac{\text{The number of electrolytes lost from cathode compartment}}{\text{Total number of equivalence of the electrolyte liberated on the electrode}}.$$

Determination of Transport Number (Hittorf's Method)

Two broad vertical glass tubes A, B are connected in the middle by a 'U' tube '*e*'. The three tubes are fitted with stopcocks. The tubes are fitted with silver plates which act as anode and cathode which are introduced into A and B. A dilute $AgNO_3$ solution (N/20) is taken for electrolysis. A current 0.01 to .02 amp. is passed for a period of 2–3 hours through the $AgNO_3$ solution. A milliammeter M, coulometer X are connected in series. After a definite time, the current is stopped. The solution from the anode compartment is taken for analysis (Fig. 9.6).

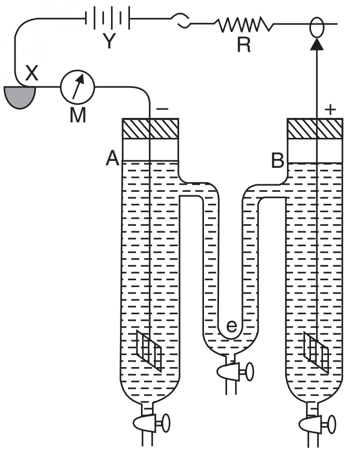


Fig. 9.6. Transference number determination by Hittorf's method.

Let,

The solution collected from anode (anolyte) = x g

The amount of $AgNO_3$ in x g anolyte = y g

The amount of water containing y g . $AgNO_3$ = $(x - y)$ g

$AgNO_3$ present in $(x - y)$ g of water before electrolysis = z g.

Weight of silver deposited on cathode in the coulometer = w g.

The increase in weight of $AgNO_3$ in anode compartment due to dissolution of silver from the anode = $\frac{w \times 170}{108}$ = Wg.

If no migration would have taken place, the total weight of $AgNO_3$ should have been present $(x - y)$ g of water in the anode compartment = $(W + z)$ g.

Actual weight of $AgNO_3$ present = y g

so, loss due to migration, $= (W + Z) - y = \{W - (y - Z)\}$g.

$$t_{Ag^+} = \frac{\text{No. of equiv. of } AgNO_3 \text{ lost from anode compartment due to migration}}{\text{No. of equiv. of silver deposited in the coulometer}}$$

$$t_{Ag^+} = \frac{W - (y - Z) \times 108}{170 \times w}$$

$$\therefore \quad t_{NO_3^-} = 1 - t_{Ag^+}$$

Highlight:

- **Abnormal transport number:** the transport number of Cd^+ ion is normal in CdI_2 solution but it decreases abnormally with increase in concentration of CdI_2.

Concentration (N)	0.01	0.02	0.05	0.10	0.20	0.50
$t_{Cd^{+2}}$	0.444	0.442	0.396	0.296	0.127	0.003

It is obvious that Cd^{+2} is moving towards anode in larger amounts than the cathode and that is the cause of decrease of $t_{Cd^{+2}}$. It can only be explained by the formation of complex ions.

Let, CdI_2 ionises as follows in a concentrated solution:

$$2CdI_2 \rightleftharpoons Cd^{+2} + [CdI_4]^{-2}$$

i.e., Cd^{+2} ion is moving towards both cathode and anode and towards anode due to above complex ion formation. This abnormal transport number does indicate the formation of complex ion. This is true for other complex compounds too.

Example 1. In an electrolysis of $CuSO_4$ between copper electrodes the total mass of copper deposited at cathode was 0.153 g and masses of Cu per unit volume of the anode liquid before and after electrolysis were 0.79 and 0.91 g respectively. Calculate the transport number of the Cu^{++} and SO_4^{--} ions.

Before electrolysis the amt. of Cu^{+2} in the liquid per unit vol. surrounding anode = 0.79 g.

After electrolysis the amt. of Cu^{+2} in the liquid per unit vol. surrounding anode = 0.91 g.

Increase in wt. due to dissolution of Cu anode during electrolysis = (0.91 – 0.79) g = 0.12 g.

Increase in wt. of Cu-cathode in the coulometer = 0.153 g.

If no Cu^{++} had migrated from the anode, increase of wt. would have been 0.153 g.

But actual increase = 0.12 g.

Fall in concentration due to migration of Cu^{+2} ions = (0.153 – 0.12) g = 0.033 g.

$$\therefore \quad \text{Transport number of } Cu^{++}\ (t_{Cu^{++}}) = \frac{0.33}{0.153} = 0.215$$

and Transport number of $SO_4^{--} = (1 - t_{Cu^{++}}) = (1 - 0.215) = 0.785$.

Example 2. Calculate the transport number of Ag^+ and NO_3^- ions when the speed ratio of the two ions is 0.916 during electrolysis of a silver nitrate solution.

$$\frac{\text{Speed of } Ag^+}{\text{Speed of } NO_3^-} = \frac{u}{v} = \text{ratio } (r) = 0.916$$

$$r = \frac{u}{v} = \frac{1-n}{n}\,(n = t_{NO_3^-}) \quad \text{or} \quad n = \frac{1}{1+r}$$

$$n = t_{NO_3^-} = \frac{1}{1+0.916} = 0.521$$

$$t_{Ag^+} = 1 - t_{NO_3^-} = 1 - n = (1 - 0.521) = 0.479.$$

Specific Conductance

The resistance (R) of a conductor is proportional to its length '*l*' and is inversely proportional to its area of cross-section '*a*'.

$$\therefore \qquad R = \rho \, . \, \frac{l}{a} \quad \text{or} \quad \rho = \frac{Ra}{l}$$

where ρ = constant, its value is dependent on material of the conductor and is known as specific resistance.

When, $l = 1$ and $a = 1$, $R = \rho$

Therefore, the specific conductance of an electrolyte is the resistance in ohm which is offered by a cm^3 of the conductor during the passage of electricity.

The reciprocal of specific resistance is termed **specific conductance** or **specific conductivity** (K, Kappa).

$$K = \frac{1}{\rho} = \frac{l}{a} \cdot \frac{1}{R} = \frac{cm \times 1}{cm^2 \times ohm} = ohm^{-1}\, cm^{-1} = mho\ cm^{-1}$$

If a solution acts as an electrolyte, the specific conductivity of the solution is known as K_v, *i.e.,* it is the conductivity of 1 cm^3 of the solution.

Equivalent Conductance

If one *g*-equivalent of an electrolyte is dissolved in V ml of the solution, the conductivity of all the ions of the electrolyte present in the solution is known as equivalent conductance and is abbreviated as λ_v

i.e., $\lambda_v = K_v V.$

If C is the concentration of the solution in g-equivalent l^{-1}, the volume of the solution containing 1 *g*-equivalent will be 1000/C.

then, $$\lambda_v = K_v \times \frac{1000}{C}$$

We know that, $\lambda_v = K_v V.$

$$= \frac{l}{a} \cdot \frac{1}{R} \cdot V \qquad \left[\because \; K_v = \frac{l}{a} \cdot \frac{1}{R}\right]$$

$$= \frac{cm \times 1 \times cm^3}{cm^2 \times ohm \times g\,.\,equivalent}$$

$$= ohm^{-1}\, cm^2\ g\ .\ equivalent^{-1}.$$

Molar Conductivity (λ_m)

It is defined as the conductance of all the ions present in one mole of the electrolyte in a solution. If M is the concentration in moles l^{-1}, then

$$\lambda_m = \frac{1000\,K}{M}$$

The unit of λ_m is $ohm^{-1}\, cm^2\, mole^{-1}$.

Effect of Dilution on Conductance

The value of specific conductance (K) is expected **to fall with dilution of an electrolyte** solution; as the number of current carrying ions per ml of the solution should gradually decrease. But the value of λ_v **or** λ_m **actually increases with dilution** as it is the product $K_v \times V$ and on dilution more and more of the electrolyte ionises. After a certain dilution there remains no more electrolyte molecule to ionise and then there is no change *i.e.,* no increase of λ_v or λ_m with dilution. The maximum value of equivalent conductance λ_v or molar conductivity λ_m is known as equivalent conductance at infinite dilution or molar conductivity at infinite dilution and abbreviated as λ_∞ or μ_∞.

Table 9.3

Normality	*Specific conductivity (K)*			*Equivalent conductivity (λ_v)*		
	KCl	*CH_3COONa*	*CH_3COOH*	*KCl*	*CO_3COONa*	*CO_3COOH*
1.0	0.0982	0.0412	0.00132	98.2	41.2	1.82
0.5	0.05115	0.0247	0.001005	102.3	49.4	2.01
0.1	0.01119	0.00611	0.00024	111.9	61.1	2.30
0.01	0.001225	0.000702	0.000143	122.5	70.2	14.3
0.001	0.0001276	0.0000752	0.000041	127.6	75.2	41.0
0.0001	0.0000129	0.00000768	0.0000107	129.5	76.8	107.0

Classification of Electrolytes

(*i*) **Strong electrolytes:** Strong acid HCl, strong alkali NaOH have high conductances even at low dilutions and there is no sharp increase in their equivalent conductances on dilution. Such electrolytes are called **strong electrolytes**.

(*ii*) **Weak electrolytes:** Weak acid like acetic acid has a low value of λ_v at higher concentration and there is rapid increase of λ_v with dilution. Such electrolytes whose λ_v values increase with dilution are known as **weak electrolytes** (see Fig. 9.7).

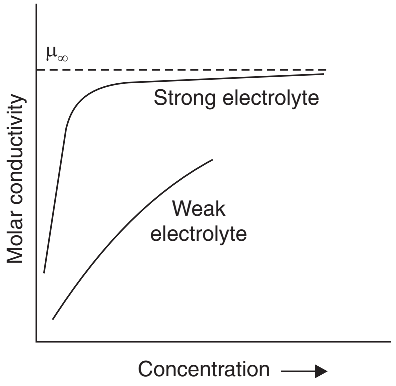


Fig. 9.7 Change of equivalent conductivity with dilution.

Experimental Determination of Specific Conductance (K)

The arrangement of apparatus adopted for the determination is modified Wheatstone's meterbridge arrangement (see Fig. 9.8). The modification is necessary as the passage of current will electrolyse the electrolyte. The products of electrolysis will accumulate on the electrodes which will change the effective resistance. The use of A.C. is necessary to avoid this difficulty.

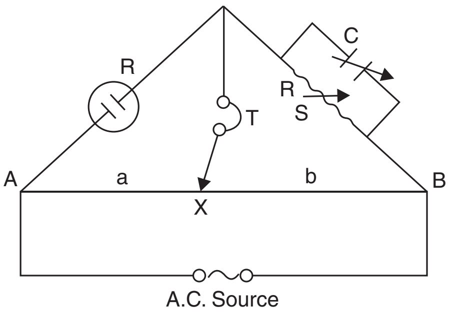


Fig. 9.8 Determination of conductivity of solutions; C is a compensating condenser (adjustable).

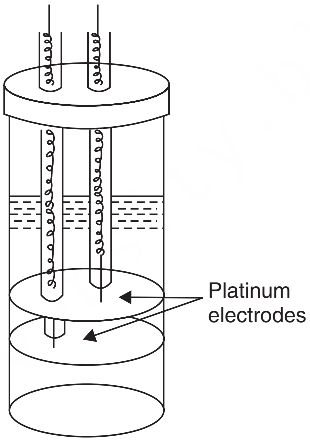


Fig. 9.9 Conductivity cell.

The modifications are: (*a*) the use of A.C., (*b*) the use of telephone detector or magic eye indicator, (*c*) the electrolyte is taken in a cell containing platinised Pt electrodes (Fig. 9.9).

The solution whose conductance is to be measured is put into the conductivity cell (see Fig. 9.9). When the sound in the telephone is minimum or zero reading on the appropriate meter, specific resistance ρ is given by the following equation:

$$\frac{\rho}{R} = \frac{a}{b}$$

Since the conductivity of a solution rapidly increases with temperature, the cell should be placed in a thermostat. Conductivity water (double distilled water) should be used throughout. Different cells are in use, the common form is shown in Fig. 9.9. Connections are made by Pt wires.

Calculation of Specific Conductance (K)

If necessary ρ is calculated from the observed resistance, if the area of the electrodes and the distance between them are accurately known. But the procedure is to calculate a factor for each cell known as **cell constant** (x).

Specific conductance = Observed conductance × Cell constant

When l is the distance between the electrodes and s, the area of cross-section of the electrode, the resistance R of liquid enclosed between the electrodes is:

$$R = \rho \times \frac{l}{s} = \rho \times x$$

where $l/s = x$ is **cell constant.**

The cell constant is known by determining the conductance of $\left(\frac{N}{50}\right)$ KCl solution. The K value of the solution has been accurately determined by Kohlrausch to be 0.002768 $\text{ohm}^{-1} . \text{cm}^{-1}$ at 25°C.

Specific conductance K = x × Observed conductance.

$$= x \times \frac{1}{\rho} = x \times \frac{b}{a} \times \frac{1}{R}$$

If the observed resistance with $\left(\frac{N}{50}\right)$ KCl be l_1 the cell constant (x) = $\rho_1 \times 0.002768$. The cell constant being known it is easy to obtain the specific conductance of any solution by using the above relation.

Highlights:

- It should be noted that cell constant (x) = $\frac{l}{s}$ where l is the distance between the electrodes and s is the mean area of the electrodes.
- According to equation:

$$K = x \times \text{observed conductance.}$$

The lower the cell constant, the higher is the observed conductance and so for weak electrolytes a conductivity cell having a small cell constant should be used.

Kohlrausch's law (Law of independent migration of ions)

At 25° the equivalent conductance at infinite dilution (λ_∞) values for some electrolytes are given in the table below:

Table 9.4

Ionic Conductance and Ionic Mobilities of some Ions at Infinite Dilution at 25°C.

Cation	λ_c	*Mobility, U cm²/sec. volt*	*Anion*	λ_a	*Mobility, V cm²/sec volt*
H^+	349.8	0.00362	OH^-	197.6	0.00205
K^+	73.5	0.00076	$\frac{1}{2}SO_4^-$	79.8	0.00083
NH_4^+	73.4	0.00076	Cl^-	76.3	0.00079
Ag^+	61.9	0.00064			
$\frac{1}{2}$ Ca^{++}	59.5	0.00062	NO_3^-	71.4	0.00074
$\frac{1}{2}$ Mg^{++}	53.1	0.00055	HCO_3^-	44.5	0.00046
Na^+	50.1	0.00052	CH_3COO^-	40.9	0.00042

It is evident from the table that each ion contributes a certain definite quantity towards λ_∞ of the solution. This regularity was first observed by Kohlrausch and was put in the form of a law which is known as **Kohlrausch's law**. The law may be stated as follows:

The equivalent conductance at infinite dilution (λ_∞) of an electrolyte is equal to the sum of ionic conductances of its constituent ions, *i.e.,*

$$\lambda_\infty = \lambda_c + \lambda_a$$

where, λ_c = Ionic conductance of cation.

λ_∞ = Ionic conductance of anion.

Highlight:

Kohlrausch's law can be stated in another way: At infinite dilution, when the dissociation of an electrolyte is considered complete, each ion makes a definite contribution towards the molar conductance of the electrolyte irrespective of its association with other ions. Thus, $\lambda_m^{\infty} = r_+ . \lambda_+^{\infty} + r_- . \lambda_-^{\infty}$

where r_+ and r_- are numbers of cations and anions and λ_+^{∞} and λ_-^{∞} are molar conductances of cations and anions respectively. Examples are: $\lambda_m^{\infty}(\text{KCl}) = \lambda_{\text{K}}^{\infty} + \lambda_{\text{Cl}^-}^{\infty}$ and $\lambda_m^{\infty}(\text{K}_3\text{PO}_4) = 3\lambda_{\text{K}^+}^{\infty} + \lambda'^{\infty}_{\text{PO}_4^{-3}}$

Ionic Conductance of Some ions at 25°C

$\text{Na}^+ = 50.11 \text{ ohm}^{-1}$ $\text{Br}^- = 78.4 \text{ ohm}^{-1}$
$\text{K}^+ = 53.22 \text{ ohm}^{-1}$ $\text{Cl}^- = 76.34 \text{ ohm}^{-1}$
$\text{NH}_4^+ = 73.40 \text{ ohm}^{-1}$ $\text{NO}_3^- = 71.44 \text{ ohm}^{-1}$

Applications of Kohlrausch's law

(*i*) **Determination of ionic conductances.** Ionic conductance possesses a constant value at a definite temperature. Its unit is ohm^{-1} cm^{-2} and is directly proportional to the speeds of the ions.

$$\lambda_c \propto u \quad \text{or} \quad \lambda_c = ku$$
$$\lambda_a \propto v \quad \text{or} \quad \lambda_a = kv$$

where k is a constant.

And $$\lambda_{\infty} = \lambda_c + \lambda_a = ku + kv = k(u + v)$$

$$\therefore \quad \frac{\lambda_c}{\lambda_{\infty}} = \frac{kv}{k(u+v)} = \frac{u}{u+v} = t_+$$

And $$\frac{\lambda_a}{\lambda_{\infty}} = \frac{kv}{k(u+v)} = \frac{v}{u+v} = t_- = (1 - t_+)$$

So, the ionic conductances of cations and anions can be determined from their experimentally determined transport numbers from the above relations.

(*ii*) **Determination of λ_{∞} of weak electrolytes:** λ_{∞} for weak electrolytes cannot be determined experimentally, because they do not ionise to a sufficient extent in solution, except at a infinite dilution. But λ_{∞} for weak electrolytes can be calculated from Kohlrausch's law.

Example: The λ_{∞} values for CH_3COONa, HCl and NaCl are x, y and z, respectively. Calculate λ_{∞} for CH_3COOH.

We have

(*i*) $\lambda_{\text{Na}^+} + \lambda_{\text{CH}_3\text{COO}^-} = x$

(*ii*) $\lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} = y$

(*iii*) $\lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = z.$

So, $(\lambda_{\text{Na}^+} + \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-}) - (\lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-}) = (x + y - z) = (\lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{H}^+})$ $\lambda_{\infty}(\text{CH}_3\text{COOH})$

(*iii*) **Ionic mobility (Absolute velocity of ions)**

We have,

$$\text{A}h = t_+ \frac{\text{I}t}{\text{F}} \cdot \frac{1000}{\text{C}}$$

where, A = Cross-section of the tube through which current passes.

h = The distance through which cation moves.

C = Concentration (equiv. dm^{-3})

It = amp × sec = Q = quantity of current (coulomb)

F = Faraday.

when, A = 1, Potential gradient = 1 V cm^{-1}

$$\text{Specific conductance } K = \frac{1}{\rho} = \frac{1}{V/I} = I \qquad [\because \quad V = 1 \text{ V cm}^{-1}]$$

Let, U = Mobility of cation in cm sec^{-1} under unit potential gradient of 1 V/cm

$$\text{So,} \quad U = \frac{\text{distance}}{\text{time}} = \frac{h}{t}$$

For very dilute solutions,

$$U = \frac{h}{t} = t_+\left(\frac{K \times 1000}{C}\right) \times \frac{1}{F} = \left(t\lambda_\infty\right)\frac{1}{F}$$

$$= \lambda_c \times \frac{1}{F} = \frac{\lambda_c}{F} \qquad [\because \quad t_+\lambda_\infty = \lambda_c]$$

Similarly, $V = \dfrac{\lambda_a}{F}$, where V = mobility of anion in cm sec^{-1} under potential gradient 1 V cm^{-1}.

So, Ionic conductance = Ionic mobility × F

or $$\text{Ionic mobility} = \frac{\text{Ionic conductance}}{F}$$

Therefore, Ionic mobilities can easily be calculated.

Highlights:

- The ions move very slowly.
- The speeds of most ions (except H^+ and OH^-) lie in the range 4×10^{-4} to 8×10^{-4} cm sec^{-1} under 1 volt cm^{-1}.
- The H^+ ions are about five times and OH^- ions are three times faster.

Conductometric Titration

During a titration, the conductivity of the solution changes depending on the relative mobility of the ions added from the burette or removed from the solution due to reaction. And the use of this conductivity change is made to determine the equivalent point of reactions involving neutralisation reactions or precipitations. The conductance of the solution is measured after each addition of titrant and the results are expressed graphically (conductance *vs* volume of titrant). And the end point is determined. Ideally two straight lines are obtained which intersect at the equivalence point [Fig. 9.10(*a*)].

Highlights:

- The change in volume throughout the course of titration must be kept small by using a titrant which is at least 100 times more concentrated than the solution being titrated.
- Measurements of conductance in the region of equivalence point are of little value due to hydrolysis, dissociation or solubility of the reaction products. For this reason, the graph shows a curvature rather than a clear intersection of the two straight lines [Fig. 9.10(*b*)].

(a) Neutralisation Reactions

In the titration of a strong acid with a strong base, there is always an initial decrease in conductance. The conductance then rises beyond the equivalence point. In the titration of NaOH with HCl, the decrease in conductance is due to the replacement of OH^- ions (molar ionic conductivity = 199) by Cl^- ions (molar ionic conductivity = 76). Beyond the equivalence point, the increase in conductivity is due to excess of H^+ ions with very high ionic molar conductivity (350).

In the titration of HCl with NaOH, the initial fall in conductance is due to the replacement of H^+ ions (350) with Na^+ ions (50) and the rise beyond equivalence point is due to excess OH^- ions (199) [Fig. 9.10(*a*)].

Highlight:

The stronger the solution used for the titration, the sharper is the end point (Fig. 9.10).

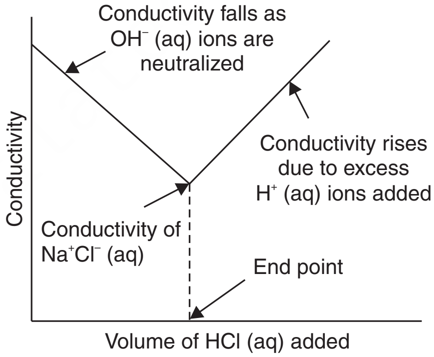


Fig. 9.10 (*a*) Changes in conductivity during titration of NaOH(*aq*) with HCl(*aq*). In water $H^+(aq)$ and $OH^-(aq)$ ions are very mobile, so they conduct electricity very well.

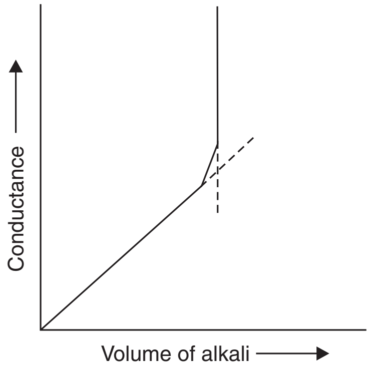


Fig. 9.10 (*b*) Changes in conductivity during titration of a weak acid (CH_3COOH) (*aq*) with a strong base (NaOH) (*aq*).

(b) Precipitation Reactions

Conductometric titrations of this type may be performed if the reaction product is sparingly soluble salt. The precipitate should be formed fairly rapidly and should not have strong adsorbent properties. The titration of KCl solution *vs* $AgNO_3$ solution satisfies the above conditions. The nature of the titration curve is as in Fig. 9.10 (*c*).

The point of intersection of the two curves is sharp. So, end point of the reaction can be determined easily.

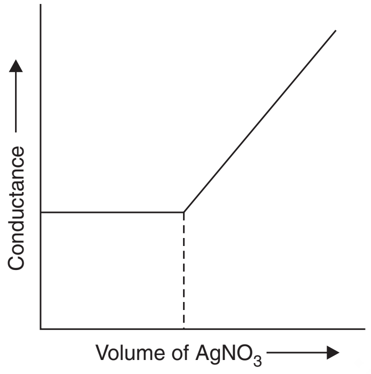


Fig. 9.10 (*c*) Titration curve of KCl solution by AgNO$_3$ solution.

Titration of a very weak acid with strong base or a very weak base with strong acids results in a small initial conductance. The conductance increases as the concentration of the salt increases. In the region of the equivalence point, due to hydrolysis the titration curve shows a marked curvature (Fig. 9.10(*b*)). The equivalence point is located by extrapolating the straight lines.

SOLVED EXAMPLES

Example 1. *A conductivity cell contains two electrodes of area of cross-section 1.25 cm^2. They are 10.5 cm. apart. If the cell is filled with an electrolyte and offers a resistance of 1996 ohm, calculate the cell constant and specific conductivity.*

Sol. Cell constant $= \dfrac{l}{a} = \dfrac{10.5}{1.25} = 8.4 \text{ cm}^{-1}$

Observed conductivity $= \dfrac{1}{1996} \text{ ohm}^{-1}$.

Specific conductivity = Cell constant × observed conductivity.

$$= 8.4 \times \frac{1}{1996} = 8.4 \times \frac{1}{1996}$$

$$= 4.2 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}.$$

Example 2. *Specific conductivity of an $\frac{N}{50}$ KCl solution at 25°C is 0.0002765 mhos cm^{-1}. If the resistance of cell containing this solution is 500 ohms, what is the cell constant?*

Sol. Cell constant $= \dfrac{l}{a}$ and $R = \rho \dfrac{l}{a}$

or $$\frac{l}{a} = \frac{R}{\rho} = R \times \frac{1}{\rho} = R \times K$$

$\therefore$ $$\frac{l}{a} = 500 \times 0.0002765 \text{ cm}^{-1}$$

$$= 0.138 \text{ cm}^{-1}.$$

Example 3. *Specific conductivity of a conductivity cell containing 0.2 (N) KCl is 2.767 × 10^{-3} ohm^{-1} cm^{-1}, the observed resistance of the cell is 4364 ohm. Calculate the cell constant. If the cell is filled with another solution the observed resistance is 3050 ohm. Calculate specific resistance of the solution.*

Sol. $$\text{Cell constant} = \frac{l}{a} \quad R = \rho\frac{l}{a}$$

or $$\frac{l}{a} = \frac{R}{\rho} = R \times \frac{1}{\rho} = R \times K$$

∴ $$\frac{l}{a} = R \times K = 4364 \times 2.767 \times 10^{-3}\ \text{cm}^{-1} = 12.075\ \text{cm}^{-1}$$

$$\rho = \frac{R}{l/a} = \frac{3050}{12.075}\ \text{ohm. cm.}$$

$$= 252.58\ \text{ohm. cm.}$$

Example 4. *A conductivity cell containing 0.02 N KCl solution offers a resistance of 550 ohm at a definite temperature. The specific conductivity of 0.02 N solution at that temperature is 0.002768 ohm^{-1} cm^{-1}. If the cell is now filled with 0.2 N $ZnSO_4$, the observed resistance of the cell is 72.18 ohm. Calculate the equivalent and molar conductivities of the $ZnSO_4$ solution.*

Sol. Cell constant = R × K

$$= 550 \times 0.002768 = 1.5224\ \text{cm}^{-1}$$

Again, $$K = \text{cell constant} \times \text{observed conductivity}$$

$$= 1.5224 \times \frac{1}{72.18} = 0.02109\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

$$\lambda_v(\text{equivalent conductivity}) = K_v \times \frac{1000}{C}$$

$$= 0.02109 \times \frac{1000}{0.2}$$

$$= 105.45\ \text{ohm}^{-1}\ \text{cm}^2$$

$$\lambda_m(\text{molar conductivity}) = \frac{1000\,K}{M} = \frac{1000 \times 0.02109}{0.1}$$

$$= 210.9\ \text{ohm}^{-1}\ \text{cm}^2.$$

Example 5. *The resistance of a decinormal solution of a salt occupying a volume between two Pt electrodes 1.80 cm apart and 5.4 cm^2 in area was found to be 32 ohms. Calculate the equivalent conductance (λ_v) of the solution.*

Sol. $$R = \rho\frac{l}{a} \quad \text{or} \quad \frac{1}{\rho} = \frac{1}{R}\frac{l}{a} = \frac{1}{32} \times \frac{1.8}{5.4}$$

$$K = 0.010416\ \text{ohm}^{-1}\ \text{cm}^{-2}$$

$$\lambda_v = \frac{1000\,K}{C} = \frac{1000 \times 0.010416}{0.1} = 104.166\ \text{ohm}^{-1}\ \text{cm}^{-2}.$$

Example 6. *The equivalent conductance of* 1.028×10^{-3} *(N) acetic acid is 48.15* $ohm^{-1}\ cm^{-2}\ eq^{-1}$ *at 298 K. Its equivalent conductance at infinite dilution is 390.6* $ohm^{-1}\ cm^{-2}\ eq^{-1}$*. Calculate the degree of dissociation of acetic acid.*

Sol.
$$\alpha = \frac{\lambda_v}{\lambda_v^{\infty}} = \frac{48.15}{390.6} = 0.1233.$$

Example 7. *The equivalent conductances at infinite dilution of various electrolytes are given:* $\lambda_{\infty}HCl = 426.1 \quad \lambda_{\infty}AcONa = 91.0\lambda_{\infty}\ NaCl = 126.5$*. Calculate* $\lambda_{\infty}(AcOH)$*.*

Sol. $\lambda_{\infty}\text{HCl} + \lambda_{\infty}\text{AcONa} - \lambda_{\infty}\text{NaCl}$

$$= (\lambda_{H^+} + \lambda_{Cl^-}) + (\lambda_{Na^+} + \lambda_{OAc^-}) - (\lambda_{Na^+} + \lambda_{Cl^-})$$

$$= \lambda_{H^+} + \lambda_{OAc^-} = \lambda_{\infty}\text{AcOH}$$

$\therefore \quad 426.1 + 91.0 - 126.5 = \lambda_{\infty}\ \text{AcOH} = 390.6\ \text{Ohm}^{-1}\ \text{cm}^2.$

Example 8. *Equivalent conductance of acetic acid at 25°C is 0.0018* $ohm^{-1}m^2\ eq^{-1}$*. If ionic conductance of* H^+ *ions and* CH_3COO^- *ions at infinite dilution are 0.0348* $ohm^{-1}\ m^2\ eq^{-1}$ *and 0.004* $ohm^{-1}\ m^2 eq^{-1}$*, respectively. Calculate the degree of dissolution of acetic acid.*

Sol. $\lambda_{\infty}(\text{CH}_3\text{COOH}) = \lambda_{\infty}\text{H}^+ + \lambda_{\infty}\text{CH}_3\text{COO}^-$

$$= 0.0348 + 0.004\ \text{ohm}^{-1}\ \text{m}^2\ \text{eq}^{-1} = 0.0388$$

$$\therefore \quad \text{Degree of dissolution} = \frac{\lambda_v}{\lambda_{\infty}} = \frac{0.0018}{0.0388} = 0.046.$$

Example 9. *If 3g of acetic acid is added to enough water to make one litre solution, what will be the concentration of acetate ion. Calculate the percentage ionisation of acetic acid.* $(K_a = 1.8 \times 10^{-5})$*.*

Sol. Strength of CH_3COOH solution $= \frac{3}{60}$ g equiv. $l^{-1} = 0.05(\text{N})$

	$\text{CH}_3\text{COOH} \rightleftharpoons$	CH_3COO^- +	H^+
Initially	= 0.05	0	0
Degree of ionisation	=	α	
At equilibrium	$= .05(1 - \alpha)$	$.05\alpha$	$.05\alpha$

$$K_a = \frac{[\text{CH}_3\text{COO}^-]\,[\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{0.05\alpha \times 0.05\alpha}{0.05\,(1-\alpha)} = \frac{(0.05)^2\alpha^2}{0.05}$$

[α being negligible, $1 - \alpha \approx 1$]

$$= 0.05\alpha^2$$

$$\therefore \quad \alpha = \sqrt{\frac{Ka}{0.05}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.05}} = \sqrt{\frac{18 \times 10^{-6}}{0.05}} = 18.9 \times 10^{-3}$$

$$= .01898.$$

Example 10. *The specific conductivity of saturated solution of AgCl is* 1.24×10^{-6} *mho* cm^{-1}*. The mobilities of* Ag^+ *and* Cl^- *ions are 53.8 and 65.3 mho* $eq^{-1}\ cm^2$*. Calculate the solubility of AgCl in* gl^{-1} *(At. wt, Ag = 108, Cl = 35.5).*

Sol. According to Kohlrausch's law,

$$\lambda_\alpha = \lambda_+ + \lambda_-$$

i.e.,
$$\lambda_\alpha(\text{AgCl}) = \lambda(\text{Ag}^+) + \lambda(\text{Cu}^-)$$
$$= 58.3 + 65.3 = 119.1 \text{ mhos eq}^{-1}\text{ cm}^2$$
$$\lambda_v = \text{K}_v\text{V}$$

$$\therefore \quad \text{V} = \frac{\lambda_\infty v}{\text{K}_v} = \frac{119.1}{1.24 \times 10^{-6}} = 9.6 \times 10^5 \text{ cm}^3 \text{ eq}^{-1}$$
$$= 9.6 \times 10^2\ l \text{ eq}^{-1}$$

$$\therefore \quad \text{Solubility} = \frac{1}{9.6 \times 10^2} \text{ eq } l^{-1} = 0.00104 \text{ eq } l^{-1}$$
$$= (0.0104 \times 143.5) \text{ g } l^{-1}$$
$$= 0.1495 \text{ g } l^{-1}.$$

Example 11. *The speed ratio of Ag^+ and NO_3^- ions in a solution of $AgNO_3$ electrolysed between Ag-electrodes is 0.916. Find the transport number of Ag^+ and NO_3^- ions.*

Sol.
$$\frac{\text{Speed of Ag}^+}{\text{Speed of NO}_3^-} = \frac{u}{v} = \frac{0.916}{1.000}$$

$$\therefore \quad t_{\text{Ag}^+} = \frac{u}{u+v} = \frac{0.916}{0.916+1} = \frac{0.916}{1.916} = 0.478$$

Hence,
$$t_{\text{NO}_3^-} = 1 - t_{\text{Ag}^+} = 1 - 0.478 = 0.522.$$

Example 12. *A dilute solution of $CuSO_4$ was electrolysed, using Pt-electrodes. The amount of Cu in the anodic solution was found to be 0.6350 g, and 0.6236 g before and after electrolysis, respectively. The weight of Ag deposited in a silver coulometer, placed in series, was found to be 0.1351 g. Calculate the transport number of Cu^{+2} and SO_4^{-2} ions.*

[At. wts. = Ag(107.88), Cu(63.6)]

Sol. Wt. of Cu in anodic solution after electrolysis is = 0.6236 g.

Wt. of Cu in anodic solution before electrolysis = 0.6350 g.

∴ Loss in wt. of Cu from anodic solution (anolyte) = (0.6350 – 0.6236) g = 0.0114 g

Wt. of Ag deposited in voltameter = 0.1351 g.

∴ Amt. of Cu deposited equivalent to 0.1351 g of Ag.

$$= \frac{\text{wt. of Cu}(x)}{\text{Eq. wt. of Cu}} = \frac{\text{wt. of Ag}}{\text{Eq. wt. of Ag}}$$

$$= \frac{x}{\frac{63.6}{2}} = \frac{0.1351}{107.88}$$

$$\therefore \quad x = \frac{0.1351 \times 31.8}{107.88} = 0.0398 \text{ g}$$

$$\therefore \quad t_{\text{Cu}^{+2}} = \frac{\text{Loss at anode}}{\text{Total loss}} = \frac{0.114}{0.0398} = 0.286$$

$$\therefore \quad t_{\text{SO}_4^{\infty}} = 1 - t_{\text{Cu}^{+2}} = 1 - 0.286 = 0.714.$$

SHORT QUESTIONS AND ANSWERS

Q. 1. What is electrochemistry?

Ans. Electrochemistry is the study of interrelations of electrical energy and chemical energy and interconversions of the two energies. This statement applies for both generation of e.m.f. of a cell as well as electrolysis.

Q. 2. What are electrochemical reactions?

Ans. Electrochemical reactions are the reactions which involve the flow of current.

Q. 3. Mention the types of electrochemical reactions.

Ans.

(*i*) *Electrolysis:* Electrolysis requires electrical energy from some external source to bring about a chemical change *i.e.,* in this type of reaction, electrical energy is consumed.

(*ii*) *Electrochemical cell reactions:* Electrochemical cell reactions are mainly redox reactions, involved in the cell where electrical energy is produced due to a chemical change.

Q. 4. What is electrolysis?

Ans. Electrolysis is a process where electric current is used to decompose a molten ionic compound or a solution of ions into elements.

Q. 5. Why are the molten compounds or solutions used as electrolytes?

Ans. Ions can only conduct electricity when they are free to move, which is only possible in molten state or in solution.

Q. 6. Mention some important uses of electrolysis process.

Ans.

(*i*) Extraction of Na, Al etc.

(*ii*) Electrolysis of brine to produce NaOH and Cl_2

(*iii*) Electroplating

(*iv*) Copper refining.

Q. 7. What are the products of electrolysis of molten salts?

Ans. Metals are deposited at the cathode and the nonmetals are liberated at the anode.

Q. 8. What are the products of electrolysis of an aqueous solution of a salt?

Ans. During electrolysis of a solution of a salt in water, the deposition at the cathode depends on the type of metal ion in the salt. If the metal is in lower position of electrochemical series, it gets deposited at the cathode *viz.* Cu^{+2}

$$Cu^{+2}(aq) + 2e \rightleftharpoons Cu^{\circ}(s)$$

But if the metal is in higher position in electrochemical series, the product at the cathode is hydrogen, from hydrogen ions produced by the ionisation of water

$$2H^{+}\ (aq) + 2e \rightleftharpoons H_2(g)$$

During the electrolysis of a salt solution, the liberation at the anode depends on the type of electrode. If the anode is graphite or platinum, the products are halogens from metallic halides (Cl^-, Br^-, I^-)

$$2X^{-}\ (aq) \longrightarrow X_2(g) + 2e\ (X = Cl, Br, I)$$

Otherwise oxygen is liberated from water. If the anode is a metal (Cu, or Ag), atoms of electrode turn into ions.

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e.$$

Q. 9. What is the effect of concentration of a salt solution during electrolysis?

Ans. The concentration of a salt solution has an effect on the product of electrolysis at the anode. Chlorine is liberated at the anode during electrolysis of a concentrated solution of NaCl. In electrolysis of a dilute solution of NaCl increasing amounts of oxygen are liberated.

Q. 10. (a) Draw a neat sketch of an electrolytic cell.

(b) Sodium is extracted by the electrolysis of a mixture of a molten NaCl and $CaCl_2$. In a commercial cell the current is 30,000 A. What mass of Na is formed in an hour at the steel cathode?

Ans. (*a*)

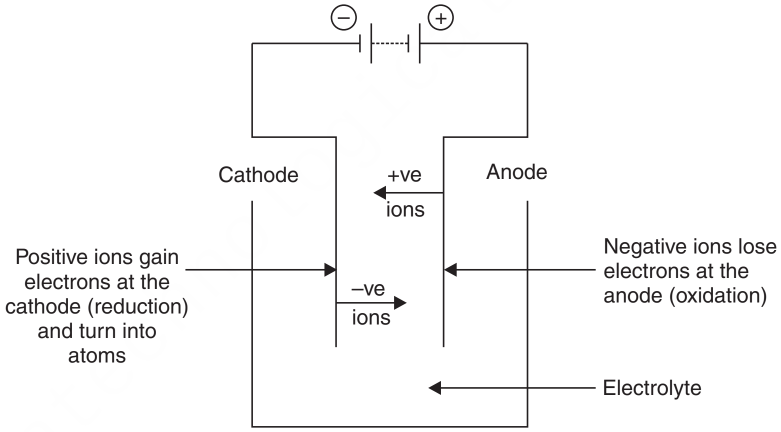


Fig. 9.11. Electrolytic cell.

(*b*) The equation for liberation at the cathode is

$$Na^+ + \bar{e} \longrightarrow Na$$

Time of electrolysis = 3600 sec.

Quantity of electricity in an hour = 30000 C/S × 3600 s.

= 108,000,000 C.

Amount of Na formed per hr. $= \dfrac{108,000,000}{96,480}$ mol

Mass of Na formed per hr. $= \dfrac{108,000,000}{96,480} \times 23 = 25,750$ g

= 25.75 kg.

Q. 11. What is the utility of electrolysis of brine?

Ans. Electrolysis of brine is the basis of the alkali and chlorine industry—a well known **electrochemical industry**. Brine is a solution of NaCl in water. Electrolysis of brine is used to manufacture chlorine, hydrogen and sodium hydroxide. During electrolysis chlorine is liberated at the anode, hydrogen is liberated at the cathode and bubbles off, while the solution turns to NaOH.

The cell to be used for electrolysis should be carefully designed so that chlorine can be kept apart from NaOH, otherwise they will react. Two types of cell are in use: (*a*) *mercury cell* (*b*) *membrane cell.*

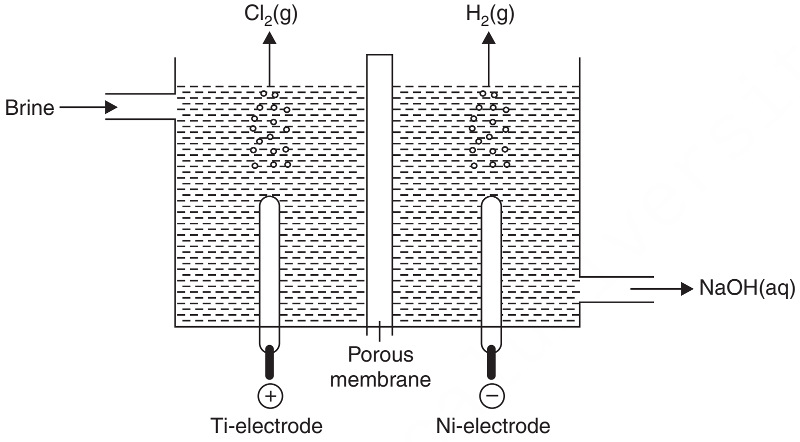


Fig. 9.12 Membrane cell.

A membrane cell is shown in Fig. 9.12. The membrane permits the solution to pass and prevents mixing of NaOH and Cl_2. The membrane has ion-exchange properties, it allows positive ions to pass but not the negative ions.

Q. 12. What do you mean by resistance?

Ans. Resistance (R) of any conductor is the obstruction offered to the flow of current.

$$R \propto \frac{l}{a}; \quad \text{where} \quad l = \text{length}, \quad a = \text{area of cross-section of the conductor}$$

or

$$R = \rho \frac{l}{a}$$

where, ρ = proportionality constant and is known as specific resistance or resistivity.

$$\therefore \qquad \rho = \frac{R.a}{l}; \text{ unit of R = ohms.}$$

Q. 13. What do you mean by specific resistance or resistivity?

Ans. Specific resistance or resistivity is the resistance offered by the conductor of 1 cm length and 1 cm^2 area of cross-section. Thus it is resistance offered by a conductor of 1 cm^3.

From,

$$\rho = \frac{R.a}{l}$$

$$\rho = R; \qquad \text{where } a = 1 \text{ cm}^2, l = 1 \text{ cm}.$$

unit of ρ = ohm-cm.

Q. 14. What is conductance?

Ans. The conductance (C) is the reciprocal of R

$$C = \frac{1}{R}$$

Unit of conductance = ohm^{-1} or mho

It is a measure of ease with which current flows through a conductor.

Q. 15. What is specific conductance?

Ans. The specific conductance (K) is the reciprocal of specific resistance (ρ).

$$K = \frac{1}{\rho} = \frac{1}{R}\left(\frac{l}{a}\right)$$

It is defined as the conductance of 1 cm^3 of a conductor

unit of K = $ohm^{-1}\ cm^{-1}$

Q. 16. What do you mean by equivalent conductivity of an electrolytic solution?

Ans. It is the conducting power of all the ions present in a solution of an electrolyte containing 1 g equiv.

Equivalent conductivity $\lambda_{eq} = \dfrac{1000\,K}{C}$

C = normality of the solution.

Unit of $\lambda_{eq} = ohm^{-1}\,cm^2\,equiv^{-1}$.

Q. 17. What do you mean by molar conductivity of an electrolyte?

Ans. It is the conductivity of all the ions produced in a solution containing one gm mole of the electrolyte. *i.e.,* molar conductivity $\lambda_m = \dfrac{1000\,K}{M}$

where, M = molarity of the solution

K = specific conductance.

Q. 18. Give the relationship of molar conductivity with concentration.

Ans. The relation is

$$\lambda_m = \lambda_m^{\infty} - b\sqrt{c}$$

where, b = constant c = concentration

λ_m^{∞} = molar conductivity at infinite dilution

λ_m = molar conductivity at a given dilution

As $c \to 0$ $\lambda_m = \lambda_m^{\infty}$.

Q. 19. What is the effect of dilution on molar conductivity?

Ans. Molar conductivity increases with dilution.

Q. 20. What do you mean by degree of dissociation of an electrolyte?

Ans. The degree of dissociation (α) is the fraction of the electrolyte that dissociates into ions. For weak electrolytes it is related to λ_m and λ_m^{∞} as follows:

$$\alpha = \frac{\lambda_m}{\lambda_m^{\infty}}.$$

Q. 21. What is transport number?

Ans. It is the fraction of total quantity of electricity, carried by cations or anions.

Q. 22. Define Kohlrausch's law.

Ans. The molar conductance, at infinite dilution of an electrolyte, is equal to the sum of ionic conductances of cations and anions.

Q. 23. What are the applications of conductance measurement?

Ans. (*i*) Measurement of degree of dissociation.

(*ii*) Determination of solubility and solubility product.

(*iii*) Conductometric titration.

Q. 24. All conductance measurements are done with the help of A.C.—explain.

Ans. D.C. will help electrolysis of the electrolytic solution bringing about a change in concentration of the electrolyte which in turn will affect the conductance of the solution.

Q. 25. In all conductometric titrations, we plot conductance vs. volume of titre and not resistance vs volume of titre—explain.

Ans. Conductance varies linearly with the volume of titre, but resistance $\left(R = \frac{1}{C}\right)$ does not vary linearly with the volume of titre, so plot of resistance vs. volume will not give straight line. That is why resistance cannot be plotted against volume of titre.

Q. 26. Equivalent conductivity of a weak electrolyte increases with dilution—explain.

Ans. Equivalent conductivity of a weak electrolyte depends on the number of ions of the electrolyte present in solution with dilution of a weak electrolyte, degree of dissociation increases, so is the number of ions. That is why equivalent conductivity of weak electrolyte increases with dilution.

Q. 27. Why equivalent conductivity at infinite dilution cannot be directly determined experimentally?

Ans. Kohlrausch pointed out that at high dilution the equivalent conductivity (λ) is plotted against the square root of concentration (c) gives a straight line which meets the zero axis of concentration at λ^{∞}, the equivalent conductance at infinite dilution, *i.e.,* at high dilution λ^{∞}, and c are related by the equation.

$$\lambda = \lambda^{\infty} - K\sqrt{c}$$

So, λ^{∞} can be determined by **extrapolation of the curve** λ vs. $\sqrt{c}$ (Fig. 9.13) for strong electrolytes to zero concentration. However λ are not so related in case for weak electrolytes. So λ^{∞} for weak electrolytes cannot be experimentally determined by the above equation.

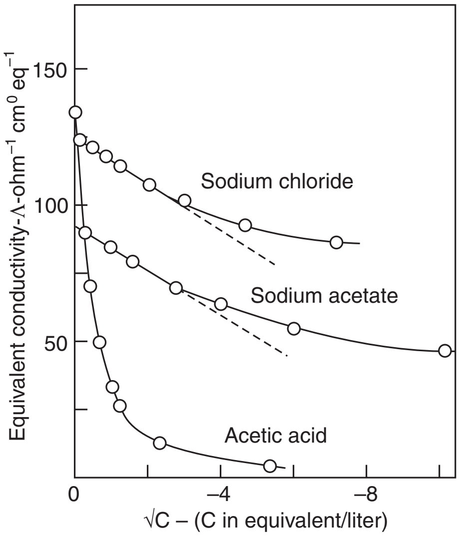


Fig. 9.13 Extrapolation of λ versus $\sqrt{c}$.

Q. 28. Specific conductances decreases with dilution while the equivalent conductance increases—explain.

Ans. When an electrolyte is diluted, degree of dissociation increases and also the total volume increases. As a result, the number of ions per millilitre decreases. But it outweighs the minor increase in conductance due to increase in degree of dissociation. *i.e.,* specific conductance decreases with dilution. But equivalent conductance increases because the total number of ions per gram equivalent increases with dilution for the increased value of degree of dissociation.

EXERCISES

1. What is an electrolyte? Give examples. What do you mean by electrolysis?

2. (*a*) Explain the terms : (*i*) Faraday (*ii*) E.C.E.

(*b*) Relate C.E. and E.C.E.

3. (*a*) State the Faraday's laws of electrolysis.

(*b*) Prove that $\frac{E_1}{Z_1} = \frac{E_2}{Z_2} = \ldots \frac{E_n}{Z_n} = F$.

4. (*a*) Define the terms:

(*i*) Specific conductance (*ii*) Equivalent conductance.

(*b*) Discuss the effect of change in concentration of the solution on specific conductance and equivalent conductance.

5. (*a*) Define the terms (*i*) specific conductance and (*ii*) equivalent conductance. With the aid of a plot, explain the variation of equivalent conductance of KCl and CH_3COOH on dilution.

(*b*) State and explain Kohlrausch's law of independent mobilities of ions.

6. What is meant by the transport number of an ion? How is it determined? A molar solution of CdI_2 showed an anion transport number 1.2. How would you account for the result?

7. (*a*) Define the specific resistance of a solution. Mention its units.

(*b*) State and explain Kohlrausch's law. Discuss its significance and applications.

8. (*a*) Define transport number. How will you determine transport number?

(*b*) Specific conductance of an electrolyte decreases, while equivalent conductance increases on dilution—explain.

(*c*) State Kohlrausch's law. Explain a few applications of this law.

9. (*a*) Write Kohlrausch's empirical equation.

(*b*) Define specific conductance.

(*c*) Write the shortcomings of the theory of electrolytic dissociation.

(*d*) Define Faraday's second law.

(*e*) Give the applications of the theory of electrolytic dissociation.

10. (*a*) State the relationship between the cell constant, conductivity and conductance.

(*b*) State Kohlrausch's experimental equation.

(*c*) Define the absolute ionic mobility.

11. What is meant by equivalent conductivity of an electrolyte? Describe the method you would adopt to measure equivalent conductivity as also its value at infinite dilution for KCl and acetic acid.

12. Write short notes on :

(*i*) Cell constant (*ii*) Absolute velocity of an ion

(*iii*) Conductometric titration

(*iv*) Kohlrausch's extrapolation method of determining λ_v.

13. Discuss all types of conductometric titrations. Also explain the nature of the graph between conductance and volume of titrant used.

14. Define Kohlrausch's law and discuss its applications.

15. Why does the equivalent conductivity of a NaCl solution increase with dilution? How can the electrolytic conductance be measured?

16. Specific conductivity of an $\frac{N}{50}$ KCl solution at 25°C is 0.000275 mhos cm^{-1}. If the resistance of cell containing this solution is 500 ohms, what is the cell constant? [**Ans.** 0.138 cm^{-1}]

17. The resistance of 0.098 (N) KCl was found to be 214.4 ohms at 298 K. Calculate the equivalent conductance (λ_v) of the solution at the same temperature, if the cell constant is 0.878 cm^{-1}.

[**Ans.** 42.18 ohm^{-1} cm^{-1}]

18. The resistance of a conductivity cell filled with 0.1 (N) solution of NaCl is 210 ohm at 18°C. Calculate the equivalent conductance (λ_v) of the solution (cell constant = 0.88 cm^{-1}).

[**Ans.** 41.9 ohm^{-1} cm^2]

19. The resistance of a cell filled with 0.02 (N) KCl solution at 25°C is 225 ohms. The specific conductance of 0.02 M KCl solution at this temperature was 0.00277 ohm^{-1} cm^{-1}. The cell was then washed out and filled with 0.1 M of $CuSO_4$; and its resistance was found to be 37.5 ohms. Calculate the equivalent and molar conductances of $CuSO_4$ solution.

[**Ans.** 83.0 ohm^{-1} cm^2, 166.0 ohm^{-1} cm^2]

20. The resistances of 0.1 N KCl solution and 0.02 N of an electrolytic solution in a conductivity cell were found to be 310 ohms and 2,000 ohms respectively at 298 K. The specific conductance of 0.1 N KCl solution is 0.0128 ohm^{-1} cm^{-1}. Calculate the equivalent conductance of the given solution. [**Ans.** 99.2 ohm^{-1} cm^2]

21. The equivalent conductance at infinite dilution of NH_4Cl, NH_4NO_3 and $AgNO_3$ are 149.74×10^{-4}, 144.84×10^{-4} and 133.36×10^{-4} Sm^2 eq^{-1} respectively. Calculate the equivalent conductance of AgCl at infinite dilution. [**Ans.** 1.382×10^{-2} S m^2 eq^{-1}]

22. The equivalent conductance of 0.01 N acetic acid is 16.30 ohm^{-1} cm^2 eq^{-1}. The ionic conductances of H^+ and CH_3COO^- ions at infinite dilution are 349 and 40 ohm^{-1} cm^2 eq^{-1}, respectively. What is the percentage dissociation of acetic acid at this concentration? [**Ans.** 4.19%]

23. During the electrolysis of $CuSO_4$ solution, loss of Cu in the anode compartment was 0.420. In a voltameter connected in series, 1.058 g of Cu was deposited. Find the transport no. of Cu^{+2} ion.

[**Ans.** $t_{Cu^{+2}} = 0.215$]

24. A 2.84% $CuSO_4$ solution was electrolysed using Pt cathode and Cu-anode. After electrolysis, the cathode solution contained 0.409 g Cu in 54.7 g solution. The increase in the weight of cathode was 0.804 g. Calculate the transport number of Cu^{+2} and SO_4^{--} ions [At. wt. = Cu(63.6), S(32) and O(16)]. [**Ans.** $t_{Cu^{+2}} = 0.215$, $t_{SO_4^{=}} = 0.785$]

25. A 0.80% $AgNO_3$ solution was electrolysed using Ag-electrodes. After electrolysis 51.0 g of the anode solution (anolyte) was found to contain 0.519 g of $AgNO_3$. A one amp. current was passed for 2 mins. What is the transport no. of Ag^+ in $AgNO_3$. [**Ans.** $t_{Ag^+} = 0.46$]

10

Electrochemical Cells

ELECTRODE POTENTIAL

Oxidation is a process where electrons are lost by a substance and reduction is a process where electrons are gained by a substance. As for example in the reaction:

$$2FeCl_3 + SnCl_2 \rightleftharpoons 2FeCl_2 + SnCl_4$$

i.e.,
$$Fe^{+3} + Sn^{+2} \rightleftharpoons Fe^{+2} + Sn^{+4}$$

For 1 g. atom of Fe^{+3}, 55.85 g. Avogadro's number of electrons are gained to get reduced to 1 g. atom of Fe^{+2}. And for every g. atom of Sn^{+2}, twice the Avogadro's number of electrons is lost.

If we make an arrangement as shown in Fig. 10.1 after sometime, we get Sn^{+4} in the vessel B and Fe^{+2} in vessel A. And we get deflection in milliammeter. There is a clear sign of flow of electrons through the metallic wire connected and this arrangement is considered as a cell which generates electric current at the cost of oxidation and reduction reactions occurring simultaneously. We take oxidation as a half cell reaction and reduction as another half cell reaction and the total reaction is redox reaction and becomes the source of e.m.f. of the cell.

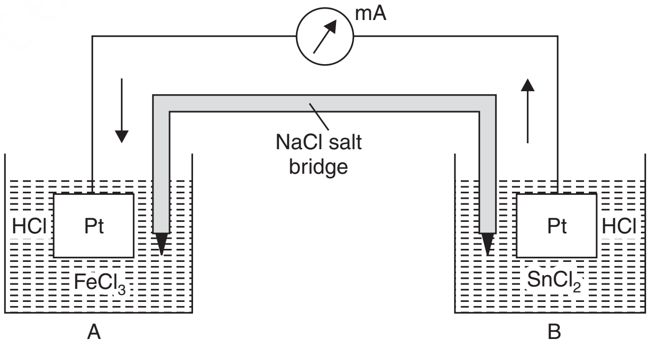


Fig. 10.1 Construction of a cell.

Reaction in vessel A : $2Fe^{+3} + 2e \rightleftharpoons Fe^{+2}$ [reduction]

Reaction in vessel B : $Sn^{+2} - 2e \rightleftharpoons Sn^{+4}$ [oxidation]

$$2Fe^{+3} + Sn^{+2} \rightleftharpoons Fe^{+2} + Sn^{+4} \text{ [cell reaction]}$$

So, a cell is constructed of two electrodes and the e.m.f. of the cell is obtained from the algebraic sum of the two electrode potentials.

Nernst Solution Pressure Theory for Electrode Potential

If a metal rod (M) is dipped into a solution containing its ions (M^{+n}) the metal shows a tendency to send ions into solution. Nernst called this tendency as "solution pressure". By sending the ions, the metal rod accumulates electrons and as a result, metal rod becomes negatively charged. On the contrary, the solution has a tendency to send M^{+n} ions to the metal rod due to "osmotic pressure". When "solution pressure" equalises "osmotic pressure" there is no net effect. But when one exceeds the other the metals get either positively or negatively charged. As for example, in the case of Zn/Zn^{+2}, the solution pressure exceeds osmotic pressure, Zn rod sends Zn^{+2} ions into the solution and gets negatively charged and attracts positive charges towards the rod and, as a result, an electrical double layer is set up and a potential is established between the metal rod (Zn) and its ions (Zn^{+2}). And so is the case with Cu/Cu^{+2}, but in this case, osmotic pressure exceeds solution pressure and Cu rod gets positively charged. Here also a electrical double layer is set up and electrode potential is established. This established potential is called **electrode potential**.

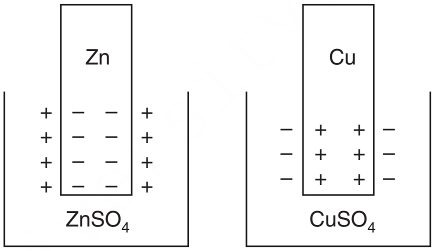


Fig. 10.2 Electrode potential.

The electrode potential is also established in the case of every electrode where electrical double layer is set up by exchange of electrons. For example, the system

$$\text{(Pt) } Fe^{+2} \rightleftharpoons \text{(Pt) } Fe^{+3} + e$$

sets up an electrical double layer where an inert metal platinum is dipped into a mixture containing Fe^{+2} and Fe^{+3} and an electrode potential is established.

So, an electric cell is composed of two electrodes. To consider the electrodes separately, we call each of them as **single electrode**. And each electrode has a potential which is known as **single electrode potential (∈)**. E.M.F. of the cell is algebraic sum of the two electrode potentials.

$$E = \in_1 + \in_2$$

Single Electrode Potential (∈)

The electrode potential for an electrode reaction:

$$M^{+n} + ne \rightleftharpoons M \text{ (metal)}$$

is given by Nernst equation $\in = \in^\circ + \frac{RT}{nF} \ln a_{M^{+n}}$ where $\in^\circ$ is a constant dependent upon the metal.

$n \Rightarrow$ Valency of metal

$R \Rightarrow$ Gas constant

$T \Rightarrow$ Absolute temperature

$F \Rightarrow$ Faraday constant

$a \Rightarrow$ Activity of M^{+n}.

At 25°C the equation comes to :

$$\in = \in^\circ + \frac{2.303 \times 8.341 \times 298}{n \times 96500} \log_{10} a_{M^{+n}}$$

$$= \in^\circ + \frac{0.059}{n} \log_{10} a_{M^{+n}}$$

For general purpose, $a_{M^{+n}} = C_{M^{+n}}$

So, then the expression is : $\in\ = \in° + \dfrac{0.059}{n} \log_{10} C_{M^{+n}}$ [A form of Nernst equation]

When $a = 1$, then $\in\ = \in°$

$\in°$ is known as **Standard electrode potential** of metal M.

If we construct the following cell:

$$Zn^{(-)} \mid Zn^{+2} \parallel Cu^{+2} \mid^{(+)} Cu,\ E_{cell} = 1.015 \text{ V}$$

For this cell Zn/Zn^{+2} is anode and Cu/Cu^{+2} is cathode and at anode, Zn is ionised to Zn^{+2} *i.e.,* oxidation takes place at anode and at the cathode Cu^{+2} is neutralised *i.e.,* reduction takes place at the cathode.

Total cell reaction is:

$$Zn + Cu^{+2} \rightleftharpoons Zn^{+2} + Cu.$$

Highlights:

According to IUPAC convention,

- The single vertical lines denote electrical contact.
- The double vertical lines denote the junction of the two solutions and this liquid junction potential is eliminated or minimised by the use of a salt bridge.
- A complete cell consists of two half cells. The right hand half cell is regarded as the positive electrode and the left hand half cell is regarded as negative electrode.
- Electrons flow through the external wire from the negative electrode to the positive electrode. So reduction takes at the right hand electrode and oxidation takes place in the left hand electrode.
- E.m.f. of the cell $E = \in_{right} - \in_{left}$ (when both are reduction potentials)

  $$E = \in_{red} + \in_{ox}.$$
- Oxidation potential may be taken as reduction potential with a minus sign.

Determination of Standard Potential $\in°$ of a Metal Electrode

The electrode potentials cannot be determined straight. We are to assign a definite value of electrode potential for a definite electrode. For example, to determine the electrode potential, we take the $\in°$ value for hydrogen electrode to be 'zero' *i.e.*, a solution of acid with ($[H^+] = 1$) and to which hydrogen gas is bubbled at one atmosphere and platinum foil is dipped. We have a zero potential for this electrode. Now if we want to determine standard electrode potential of zinc ($\in°_{Zn}$) we are to construct the following cell. (See page 227)

$$\begin{array}{c} Zn \mid ZnSO_4\,(\text{solution}) \\ (a_{Zn^{+2}} = 1) \end{array} \Bigg\| \begin{array}{c} H_2SO_4\,(\text{solution}) \mid H_2\ (\text{Pt}) \\ (a_{H^+} = 1) \end{array}$$

Table. 10.1: Standard Electrode Potentials (Reduction), 25°C

	Electrode	*Electrode reaction (Reduction)*	*E°(Volts)*
Oxidants *i.e.,* electronegative	F_2, F^-	$\frac{1}{2}F_2 + e = F^-$	2.80
	$Pt, Cl_2(g); Cl^-$	$Cl_2 + e = Cl^-$	1.360
	$Pt, O_2; H^+$	$\frac{1}{2}O_2 + 2H^+ + 2e = H_2O$	1.23
	Au, Au^{+++}	$Au^{+++} + 3e = Au$	1.06
	Hg, Hg_2^{++}	$Hg_2^{++} + 2e = 2Hg$	0.799
	Ag, Ag^+	$Ag^+ + e = Ag$	0.798
	$Pt; Fe^{+++}, Fe^{++}$	$Fe^{+++} + e = Fe^{++}$	0.771
	Cu, Cu^{++}	$Cu^{++} + 2e = Cu$	0.344
	Calomel electrode	$\frac{1}{2}Hg_2Cl_2 + e = Hg + Cl^-$	0.268
Reductants *i.e.,* electropositive	**(Pt)** $\mathbf{H_2, H^+}$	$\mathbf{H^+ + e = \frac{1}{2}H_2}$	**0.000**
	Pb, Pb^{++}	$Pb^{++} + 2e = Pb$	– 0.122
	Sn, Sn^{++}	$Sn^{++} + 2e = Sn$	– 0.136
	Zn, Zn^{++}	$Zn^{++} + 2e = Zn$	– 0. 762
	Mg, Mg^{++}	$Mg^{++} + 2e = Mg$	– 1.866
	Na, Na^+	$Na^+ + e = Na$	– 2.715
	Li, Li^+	$Li^+ + e = Li$	– 2.959

The e.m.f. of the cell will be

$$E° = \in°_H + \in°_{Zn} = \in°_{Zn} \qquad [\because \quad \in°_H = 0]$$

The e.m.f of a cell is measured by potentiometer, and we get standard e.m.f. E° of the above constructed cell which is $\in°_{Zn}$.

Likewise, the electrode potential of other metals are determined similarly and listed in table. This list with $\in°$ values are known as **electrochemical series**. (Table 10.1)

Example 1. *Calculate the e.m.f. of the cell*

$$Zn \left| \begin{matrix} ZnSO_4(solution) \\ (a_{Zn^{+2}} = 1) \end{matrix} \right\| \begin{matrix} CuSO_4(sol^n) \\ (a_{Cu^+} = 1) \end{matrix} \right| Cu$$

Sol. = Standard reduction potential of Cu + std. oxidation potential of Zn.

= 0.344 + 0.762

= 1.106.

Typical calculation of e.m.f. of a cell

Liquid junction potential

Daniel cell: $Zn \mid ZnSO_4(C_1) \parallel CuSO_4(C_2) \mid Cu$

Cell reaction is: $Zn + Cu^{+2} \rightleftharpoons Zn^{+2} + Cu$

$$E = \in_{right} - \in_{left} \qquad \text{[when both are reduction potentials]}$$

$$\in_{right} = \overset{\circ}{\in}_{Cu} + \frac{RT}{2F} \ln \frac{[Cu^{+2}]}{[Cu]}$$

or $$= \overset{\circ}{\in}_{Cu} + \frac{RT}{2F} - \ln [Cu^{+2}] \qquad [\because \quad [solid] = 1]$$

Likewise,

$$\in_{left} = \overset{\circ}{\in}_{Zn} + \frac{RT}{2F} \ln [Zn^{+2}] \qquad [\because \quad [solid] = 1]$$

$$E_{cell} = \left\{\overset{\circ}{\in}_{Cu} + \frac{RT}{2F} . \ln [Cu^{+2}]\right\} - \left\{\overset{\circ}{\in}_{Zn} + \frac{RT}{2F} . \ln [Zn^{+2}]\right\}$$

$$\therefore \qquad E_{cell} = (\overset{\circ}{\in}_{Cu} - \overset{\circ}{\in}_{Zn}) + \frac{RT}{2F} \ln \frac{[Cu^{+2}]}{[Zn^{+2}]} .$$

Interpretation of the Electrochemical Series (Table 10.1)

1. The higher the standard electrode potential (reduction) of an element, higher is the electronegativity of that element. Lower position in the table of an element indicates its higher tendency of ionisation.

2. If a cell is constructed with the two elements as the electrodes then the e.m.f. of the cell is obtained from the oxidation potential of anode and reduction potential of cathode.

Let Fe and Cu are used as electrodes, then e.m.f. of the cell,

E = Reduction potential of Cu + Oxidation potential of Fe.

= 0.344 + 0.441

= 0.785 volt.

3. The higher electropositive metal *i.e.*, possessing lower standard electrode potential (reduction) will displace the metal from the solution of its ions with a higher standard electrode potential (reduction) value.

For example – Zn($\in°_{Zn}$ = – .762) will displace Cu from its solution ($\in°_{Cu}$ = .344)

Likewise, the non-metals with the higher electronegativity displace the elements possessing lower electronegativity.

For example:

$$2KI + Cl_2 \longrightarrow 2KCl + I_2\uparrow$$

Redox-electrodes

A mixture of Fe^{+2}/Fe^{+3} salt in a solution or Ce^{+3}/Ce^{+4} salt in a solution can act as an electrode if a platinum wire is dipped into either of the solutions. Any oxidised or reduced form of an element behaves so. These electrodes are known as redox electrodes. Electrode potential ($\in$) is given by:

$$\text{Oxidant} + ne \rightleftharpoons \text{Reductant}$$

$$\text{Ox} + ne \rightleftharpoons \text{Red.}$$

$$\in\, = \in°_{Red-ox} + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}} = \in°_{Red-ox} + \frac{0.059}{n} \log_{10} \frac{[Ox]}{[Red]} \quad \text{(for general purpose)}$$

Here also $\in°$ values are determined against standard hydrogen electrode.

Table 10.2: Normal potentials ($\in°$) of some redox system (Hydrogen scale)

Electrode	*Electrode reaction*	*Electrode potential* $\in°$*(volts)*
(Pt) Cr^{+2}/Cr^{+2}	$Cr^{2+} + e \rightleftharpoons Cr^{2+}$	0.41
(Pt) V^{+2}/V^{+2}	$V^{+3} + e \rightleftharpoons V^{+2}$	– 0.21 – 0.25
(Pt) $H^+/\frac{1}{2}H_2$	$H^+ + e \rightleftharpoons \frac{1}{2}H_2$	0.00
(Pt) Sn^{+4}/Sn^{+2}	$Sn^{+4} + 2e \rightleftharpoons Sn^{+2}$	+ 0.15
(Pt) Cu^{+2}/Cu^{+1}	$Cu^{+2} + e \rightleftharpoons Cu^{+1}$	+ 0.16
(Pt) $[Fe(CN)_6]^{2-}/[Fe(CN)_4]^{4-}$	$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$	+ 0.36
(Pt) MnO_4^-/MnO_4^{2-}	$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$	+ 0.54
(Pt) $\frac{1}{2}I_2/I^-$	$\frac{1}{2}I_2 + e \rightleftharpoons I^-$	+ 0.535
(Pt) Fe^{+2}/Fe^{+2}	$Fe^{+3} + e \rightleftharpoons Fe^{+2}$	+ 0.77
(Pt) $\frac{1}{2}Br_2/Br^-$	$\frac{1}{2}Br_2 + e \rightleftharpoons Br^-$	+ 1.065
(Pt) $IO_2^-/\frac{1}{2}I_2$	$IO_3^- + 6H^+ + 5e \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$	+ 1.20
(Pt) MnO_2/Mn^{+2}	$MnO_2 + 4H^+ \ 2e \rightleftharpoons Mn^{+2} + 2H_2O$	+ 1.23
Tl^{+3}/Tl^{+2}	$Tl^{+3} + 2e \rightleftharpoons Tl^{+1}$	+ 1.25
$\frac{1}{2}Cl_2/Cl^-$	$\frac{1}{2}Cl_2 + e \rightleftharpoons Cl^-$	+ 1.36
$Cr_2O_7^{2-}/2Cr^{+3}$	$Cr_2O_7^{2-} + 14\ H^+ + 6e \rightleftharpoons 2Cr^{+3} + 7H_2O$	+ 1.36
MnO_4^-/Mn^{+2}	$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{+2} + 4H_2O$	+ 1.52
$BrO_2^-/\frac{1}{2}Br_2$	$BrO_3^- + 6H^+ + 5e \rightleftharpoons \frac{1}{2}Br_2 + 3H_2O$	+ 1.52
Ce^{+4}/Ce^{+3}	$Ce^{+4} + e \rightleftharpoons Ce^{+2}$	+ 1.61
MnO_4^-/MnO_2	$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$	+ 1.69
Co^{+2}/Co	$CO^{+2} + e \rightleftharpoons CO^{+2}$	+ 1.82
$S_2O_4^{2-}/2SO_4^{2-}$	$S_2O_4^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$	+ 2.01
$\frac{1}{2}F_2/F^-$	$\frac{1}{2}F_2 + e \rightleftharpoons F^-$	+ 2.65

The pair which occupies lower position in the table can oxidise the pair which occupies a higher position in the table.

Latimer Diagram

The redox potential of different oxidation states for a particular element can be summarised with the help of EMF diagram and the simplest type of such diagram is the **Latimer diagram**.

A Latimer diagram in a compact form explains a great deal of information and shows the relationships between the various species in a simple and lucid form.

We know that Mn exists in different oxidation states and in acidic medium preferably at zero pH, the different oxidation states are represented by the corresponding $\in°$ values as follows:

$$\begin{aligned}
Mn^{2+} + 2e + &\rightleftharpoons Mn, & \in° &= -1.18\text{ V}\\
Mn^{+3} + e &\rightleftharpoons Mn^{2+}, & \in° &= 1.52\text{ V}\\
MnO_2 + 4H^+ + e &\rightleftharpoons Mn^{3+} + 2H_2O, & \in° &= .95\text{ V}\\
MnO_4^{2-} + 4H^+ + 2e &\rightleftharpoons MnO_2 + 2\ H_2O, & \in° &= 2.26\text{ V}\\
MnO_4 + e &\rightleftharpoons MnO_4^{2-}\ , & \in° &= +.56\text{ V}\\
MnO_2 + 4H^+ + 2e &\rightleftharpoons Mn^{2+} + 2H_2O, & \in° &= 1.23\text{ V}
\end{aligned}$$

$$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O, \quad \in^\circ = 1.70 \text{ V}$$
$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O, \quad \in^\circ = 1.51 \text{ V}$$

The whole information can be summarised in the compact manner in a collinear diagram as follows.

$$MnO_4^- \xrightarrow{0.56\text{ V}} MnO_4^{2-} \xrightarrow{2.26\text{ V}} MnO_2 \xrightarrow{0.95\text{ V}} Mn^{3+} \xrightarrow{1.52\text{ V}} Mn^{2+} \xrightarrow{-1.18\text{ V}} Mn$$

In this diagram, the oxidation states of Mn decrease gradually from left to right. The species H^+, H_2O etc. are not included in the diagram. The couple such as MnO_4^-/MnO_2 or MnO_4^-/Mn^{2+} or MnO_2/Mn^{2+} etc. are called **skip couples** and the corresponding potentials are called **skip-step potentials**.

A **Latimer diagram** helps us to derive the standard potentials of such non-adjacent couples. We know that ΔG° values corresponding to different steps can be added but the $\in^\circ$ values cannot be so added. Again ΔG° is related to $\in^\circ$ as follows, $\Delta G^\circ = -nF\in^\circ$. The overall ΔG° of two successive steps will be the sum of the individual $\in^\circ$ values to ΔG° values by multiplying by the relevant $-nF$ factor, adding them together and converting the sum back to $\in^\circ$ for the non-adjacent couple dividing by $-nF$ for the overall electron transfer. Since the nF factor cancels in this way, we can write

$$\in^\circ_{1\to 3} = \frac{n_1 \in^\circ_{1\to 2} + n_2 \in^\circ_{2\to 3}}{n_1 + n_2}$$

Besides calculating the $\in^\circ$ values of non-adjacent couples, the **Latimer diagram** is also helpful in predicting whether a particular species will undergo disproportionation or comproportionation.

A species will disproportionate into its neighbour species if the potential on the left is lower than that of the right species. On the other hand, a species will undergo comproportionation if the potential on the left is higher than that of the right species in the diagram. For example, we know that H_2O_2 disproportionates into H_2O and O_2 under acidic conditions.

$$O_2 \xrightarrow{0.70\text{ volt}} H_2O_2^{-1} \xrightarrow{1.76\text{ volt}} H_2O^{-2}$$

The **feasibility of disproportionation of H_2O_2** can be predicted by considering the change in the $\in^\circ$ values for the following reactions:

Overall reaction:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

(*a*) Oxidation: $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e \qquad \in^\circ_{Ox} = -.70 \text{ V}$

$\therefore \qquad \Delta G^\circ_1 = -nF\in^\circ = -2F \times (-.70) = 1.4 \text{ F}$

(*b*) Reduction: $H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O \qquad \in^\circ_{Red} = 1.76 \text{ V}$

$\therefore \qquad \Delta G^\circ_2 = -nF\in^\circ = -2F \times 1.76 = -3.52 \text{ F}$

Adding (*a*) and (*b*),

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad \Delta G^\circ = -2.12 \text{ F}$$

Since the process is accompanied by decrease in Gibbs free energy, therefore disproportionation will be spontaneous. On the other hand, for the change $Ag^{2+} \xrightarrow{1.98\text{ V}} Ag^+ \xrightarrow{0.80\text{ V}} Ag$ it can be shown by similar calculation that disproportionation of Ag^+ will not take place because it will be accompanied by increase in ΔG° value. Hence, in this case the comproportionation reaction $Ag^{2+} + Ag = 2Ag^+$ will take place.

Frost Diagram

A Frost diagram for an element M is a plot of $n\epsilon°$ for the couple M^{n+}/M against its oxidation number n where n gives the change of oxidation number from n to zero. On the basis of this diagram, it can be predicted whether the oxidant or the reductant will show greater tendency for a reaction. When the line joining two points in the diagram is quite steep, the potential of the corresponding couple is higher. Hence, we can make thermodynamic predictions about the reaction between any two couples by comparing the steps of the corresponding lines. The oxidising agent of a redox couple will show tendency to reduction if the slope is more +ve. The reducing agent of the couple with less +ve slope will tend to undergo oxidation. The **Frost diagram** for nitrogen in various oxidation states is as given in Fig. 10.3(*a*) and 10.3(*b*).

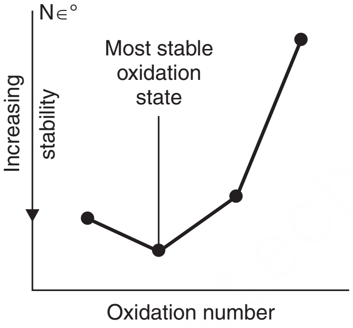


Fig. 10.3 (*a*)

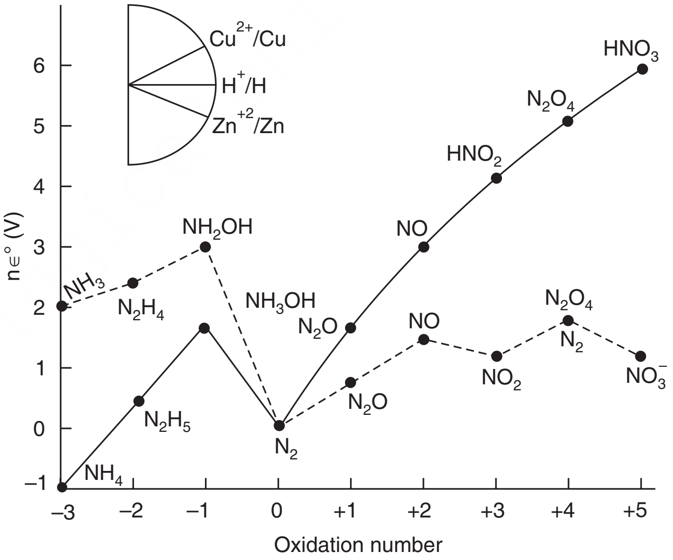


Fig. 10.3 (*b*) Frost diagram for nitrogen (N).

An examination of this plot shows that the slope of the line connecting HNO_3 to lower oxidation numbers is quite steep and hence HNO_3 will function as a good oxidising agent under standard conditions *i.e.,* (at pH = 0). A comparison of the slope of the Cu^{2+}/Cu couple with that of the HNO_3/NO couple shows that it is more +ve for the latter and hence HNO_3 will oxidise Cu to Cu^{2+}. The diagram also indicates that the slope remains steep all the way to N_2 indicating that N_2 should be the product of reduction of HNO_3 if excess Cu is present in the reaction. Cu, however, does not reduce HNO_3 to N_2 due to kinetic limitations and NO is commonly the gas which is evolved when Cu is heated with dilute HNO_3.

An ion or a molecule in a Frost diagram will be unstable with respect to disproportionation if it lies above the line connecting two adjacent species. This is due to the fact that, the average free energy of the intermediate species is larger than the mean free energy of the two adjacent species. From the diagram it is seen that since NH_2OH lies above the line joining NH_3 and N_2 it will undergo disproportionation. The disproportionation is, however, not spontaneous as it is not kinetically favoured.

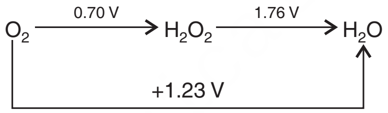
A substance that lies below the line connecting two adjacent neighbours in a Frost diagram is more stable than they are because its average free energy is lower. Under such circumstances comproportionation will be thermodynamically favoured *e.g.,* in NH_4NO_3, NH_4^+ ion contains N in –3 oxidation state and in NO_3^- ion N is present in +5 oxidation state, on the other hand N_2O has an oxidation state of +1, which is intermediate between – 3 and + 5 and its position in the Frost diagram is lower than that of NO_3^- ion and NH_4^+ ion and so NH_4NO_3 undergoes comproportionation, $NH_4^+ + NO_3^- \longrightarrow N_2O + 2H_2O$. When the line joining three adjacent species becomes approximately a straight line, then no one species will be the exclusive product *e.g.,* oxidation of NH_3 by Ostwald process to NO and then to NO_2 followed by dissolution in H_2O produces HNO_3 and also NO as well as HNO_2. This is due to the fact that NO, HNO_2 and HNO_3 lie approximately on a straight line in the Frost diagram.

$$NO + NO_2 + H_2O \longrightarrow 2\ HNO_2$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO_2 + 2H_2O$$

$$3NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

A Frost diagram can be constructed from a Latimer diagram *e.g.,* let us consider the Latimer diagram.



The oxidation numbers of 'O' atom in O_2, H_2O_2 and H_2O are 0, – 1 and – 2, respectively. When 'O' changes from O_2 to H_2O_2, oxidation number of 'O' changes from 0 to –1, Hence, change in oxidation number = – 1. $\therefore$ $\in^\circ = -1 \times .70 = -.70$ volt, when O changes to H_2O its oxidation number changes from 0 to – 2 and in this case, $n = -2$. Therefore, $n\in^\circ$ for the formation of $H_2O = -2 \times 1.23 = -2.46$ volt. When these values of $n\in^\circ$ are plotted against the corresponding oxidation numbers, we get the required Frost diagram as follows.

The potential corresponding to reduction of H_2O_2 to H_2O can be calculated as follows from the examination of the line it is obvious that at the point corresponding to – 1 oxidation number $n\in^\circ = -.70$ volt and $n\in^\circ$ corresponding to oxidation number of – 2 is – 2.46 volt. The difference is, therefore, $-2.46 - (-.70) = -1.76$ volt.

The change in oxidation number from H_2O_2 to H_2O is –1. Therefore, the $\in^\circ$ for the couple H_2O_2/H_2O is equal to $\dfrac{-1.76}{-1} = +1.76$ volt.

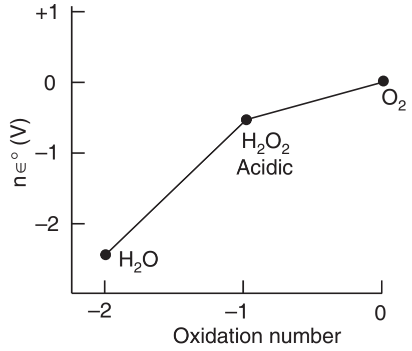


Fig. 10.4 Frost diagram for the system $O_2 \rightarrow O_2^{-2} \rightarrow 2O^{-2}$.

This is in accordance with the Latimer diagram.

Highlights:

Uses of standard potential (reduction) values:

1. Prediction of an oxidation-reduction reaction.
2. Prediction regarding liberation of hydrogen by a metal from a hydracid.
3. Prediction of feasibility of a chemical reaction.

Example. Predict whether the reaction will occur spontaneously or not.

$$Zn^{+2} + Cu \rightleftharpoons Zn + Cu^{+2}$$

$$\in^{\circ}_{Zn^{+2}/Zn} = -0.762 \quad \in^{\circ}_{Cu^{+2}/Cu} = 0.344$$

The two half cell reactions are:

$$Zn^{+2} + 2e \rightleftharpoons Zn \ [\in^{\circ} = -0.762]$$

$$Cu - 2e \rightleftharpoons Cu^{+2} \ [\in^{\circ} = 0.344]$$

Adding $Zn^{+2} + Cu \rightleftharpoons Zn + Cu^{+2} \ [E^{\circ}_{Cu} = -1.106]$

Since, $E^{\circ}_{cell} = -$ ve.

So, the reaction will not occur spontaneously.

Example. Find whether Cu^{+} disproportionate in aqueous solution into Cu^{+2} and Cu° *i.e.,* cell reaction is

$$2Cu^{+} \rightleftharpoons Cu^{+2} + Cu^{\circ}, \text{ Given, } \in^{\circ}_{Cu^{+2}/Cu^{+}} = +0.15 \text{ V}$$

$$\in^{\circ}_{Cu^{+}/Cu^{\circ}} = 0.52 \text{ V}$$

The two half cell reactions are:

$$Cu^{+} + e \rightleftharpoons Cu^{\circ} \ [\in^{\circ} = 0.52 \text{ V}]$$

$$Cu^{+} - e \rightleftharpoons Cu^{+2} \ [\in^{\circ} = 0.15 \text{ V}]$$

Adding $Cu^{+} + Cu^{+} \rightleftharpoons Cu^{+2} + Cu^{\circ} \ [E^{\circ}_{cell} = 0.37 \text{ V}]$

Since E°_{cell} is positive, Cu^{+} will disproportionate spontaneously in aqueous solution into Cu^{+2} and Cu°.

Example. Ag will not displace hydrogen from HCl, given $\in^{\circ}$ $Ag^{+}/Ag = 0.798$.

Sol. Cell reaction: $2Ag + 2H^{+} \longrightarrow 2Ag^{+} + H_2$

The two half cell reactions are:

$$2Ag - 2e \rightleftharpoons 2Ag^{+} \ [\in^{\circ} = -0.798]$$

$$2H^{+} + 2e \rightleftharpoons H_2 \ [\in^{\circ}H^{+}/H = 0.00 \text{ V}]$$

Adding $2Ag + 2H^{+} \rightleftharpoons 2Ag^{+} + H_2 \ [E^{\circ}_{cell} = -0.798]$

Since, the E°_{cell} value is negative, Ag cannot displace H_2 from HCl.

Concentration Cell

When a metal is dipped into two solutions of one of its salts of different concentrations, a very interesting situation arises:

$$\text{Ag} \mid \text{AgNO}_3(\text{C}_1) \parallel \text{AgNO}_3(\text{C}_2) \mid \text{Ag}$$

Ag	$AgNO_3(C_1)$ (Dilute)	Salt bridge of satd. NH_4NO_3	$AgNO_3(C_2)$ [Concentrated]	Ag

or $$\text{Ag} \mid \text{AgNO}_3(\text{C}_1\text{M}) \parallel \text{AgNO}_3(\text{C}_2\text{M}) \mid \text{Ag} \qquad (\text{C}_2 > \text{C}_1)$$

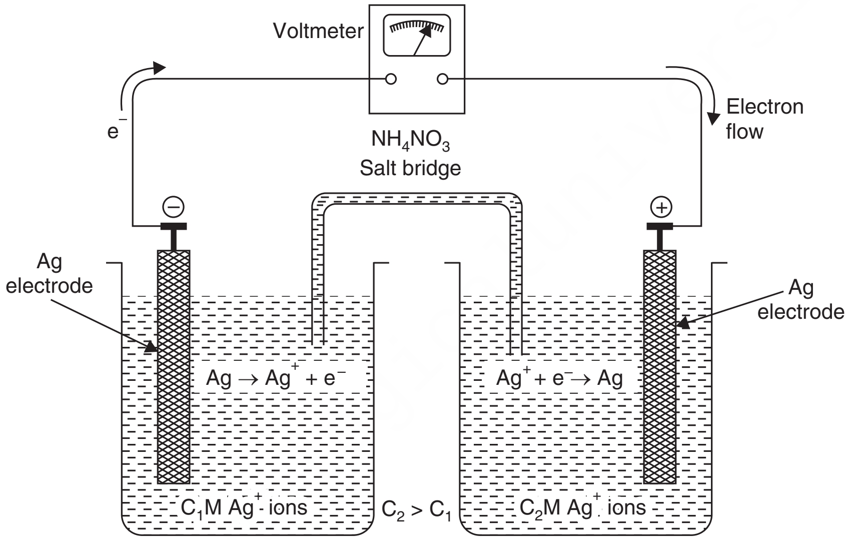


Fig. 10.5 Concentration cell.

Imagine that current passes through the external wire as shown by the arrow. We shall get silver deposited on the right hand electrode and dissolution of silver from the left hand electrode as if silver being transported from concentration C_2 to concentration C_1^-.

So, the cell reaction is

Half cell reaction (left) oxidation $\quad \text{Ag} - e \rightleftharpoons \text{Ag} + (\text{C}_1)$

Half cell reaction (right) $\quad \text{Ag}^+(\text{C}_2) + e \rightleftharpoons \text{Ag}°$

Total: $\quad \text{Ag}^+ (\text{C}_2) = \text{Ag}^+ (\text{C}_1)$

$$\in°_R = \in°_L \text{ and } \quad n = 1$$

$$E = 2.303 \frac{RT}{nF} \log \frac{C_2}{C_1} = \frac{2.303 \times 8.138 \times (298)}{n \times 96500} \log \frac{C_2}{C_1}$$

So, $$E = \frac{0.059}{1} \log \frac{C_2}{C_1} \qquad [\because \quad n = 1]$$

Therefore, e.m.f. of such cell depends on the relative concentration and not on the absolute values.

If $\frac{C_2}{C_1} = 10$, the observed e.m.f. is 59 mV.

The stronger solution acts as positive electrode.

This type of concentration cell is known as **electrolyte concentration cell.**

Another type of concentration cell is **electrode concentration cell**, one such cell is:

$$\text{Pt} \mid \text{H}_2\,(p_1) \mid \text{H}^+ \mid \text{H}_2\,(p_2) \mid \text{pt}$$

p_1 and p_2 are unequal pressures of H_2

The cell reaction is:

$$\begin{array}{ll} \text{Oxidation:} & \text{H}_2\,(p_1) - 2e \rightleftharpoons 2\text{H}^+ \\ \text{Reduction:} & 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\,(p_2) \\ \hline \text{Overall:} & \text{H}_2(p_1) \longrightarrow \text{H}_2(p_2) \end{array}$$

e.m.f. of the cell is: $E = \dfrac{RT}{2F} \ln \dfrac{p_1}{p_2}$.

Application of the Concentration Cells H_2

Determination of solubility of sparingly-soluble salts.

If we want to determine the solubility of AgCl, we are to measure e.m.f. of the following cell.

$$\text{Ag} \mid \text{Ag NO}_3\ (0.01\text{N}) \;\vdots\; \begin{array}{c}\text{Saturated solution}\\ \text{of KNO}_3\\ \text{salt bridge}\end{array} \;\vdots\; \text{Saturated AgCl} \mid \text{Ag}$$

e.m.f. of the cell is given by,

$$E = \frac{0.059}{n} \log \frac{C_2}{C_1}$$

Here $n = 1$, concentration of Ag^+ in 0.01(N) $AgNO_3$ solution is 0.01 g. ion l^{-1} is (C_2).

So, $$E = \frac{0.059}{1} \log \frac{0.01}{C_1}$$

So, C_1 *i.e.,* Ag^+ in AgCl can be calculated.

Example 1. Calculate (*i*) Solubility product of AgI, (*ii*) Solubility of AgI in water at 25°. Given e.m.f. of the cell is 0.788 V at 25°C. The activity coefficient (*f*) is 0.9 each.

Cell: Ag/AgI/ in 0.05 (M) KI) | NH_4NO_3 | $AgNO_3$(0.05M) | Ag.

The concentration of Ag^+ in $AgNO_3$ is $0.05 \times 0.9 = 0.045$ M

The concentration of I^- in KI is $0.05 \times 0.9 = 0.045$ M

Let C_1 be the concentration of Ag^+ in AgI solution.

$$\therefore \qquad E = \frac{0.059}{1} \log \frac{0.045}{C_1}$$

or $$0.788 = 0.059 \log \frac{0.045}{C_1}$$

or $$\log \frac{0.045}{C_1} = \frac{0.788}{0.059} = 13.33$$

or $$\frac{0.045}{C_1} = \text{Antilog } 13.33$$

$$= 2.138 \times 10^{13}$$

$$\therefore \qquad C_1 = \frac{0.045}{2.138 \times 10^{13}} = 2.105 \times 10^{-15} \text{ mol l}^{-1}.$$

$$\therefore \qquad K_{sp} \text{ of AgI} = [Ag^+]\,[I^-]$$
$$= 2.105 \times 10^{-15} \times 0.045$$
$$= 9.472 \times 10^{-17}$$

$$\text{Solubility of AgI} = \sqrt{K_{sp}}$$
$$= \sqrt{9.472 \times 10^{-17}}$$
$$= 9.732 \times 10^{-9} \text{ mol l}^{-1}$$
$$= 9.732 \times 10^{-9} \times 143.5 \text{ g l}^{-1}$$
$$= 1.396 \times 10^{-6} \text{ gl}^{-1}$$

Determination of valency

$$\text{Hg} \parallel \underset{C_2}{Hg_2(NO_3)_2}\ 0.5(N) \parallel \underset{C_1}{Hg_2(NO_3)_2}\ (0.05)\ (N)/Hg$$

The e.m.f. of the above cell = 0.029 V

We have, $E = \frac{0.059}{n} \log \frac{C_2}{C_1} = \frac{0.059}{n} \log \frac{0.5}{0.05}$ where n is valency.

$$= \frac{0.059}{n} \log 10 = \frac{0.059}{n}$$

or $$0.029 = \frac{0.059}{n} \qquad \therefore \quad n = \frac{0.059}{0.029} \approx 2.$$

INDICATOR ELECTRODES

Hydrogen Electrode

It consists of a small piece of platinum foil electroplated with platinum black, over which hydrogen gas is passed. The platinum black surface exhibits a strong absorption power towards hydrogen gas, as a result, the metal surface remains in continuous contact with the hydrogen gas. The electrode will act as if it were an electrode of metallic hydrogen. When in use, therefore, only a part of the foil is immersed in 1(N) HCl; the remainder is surrounded by pure hydrogen gas at 1 atm. pressure. This is **standard hydrogen electrode.** The e.m.f. of this electrode has been arbitrarily assigned to be zero.

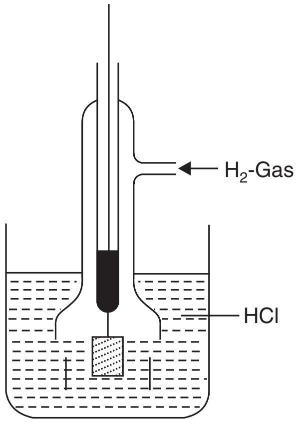


Fig. 10.6 Hydrogen Electrode.

The pH of a solution can be determined with the help of a hydrogen electrode in that case, the platinum electrode is dipped into the solution whose pH is to be determined, instead of 1(N) HCl and H_2 gas at 1 atm passed over the platinum electrode.

The electrode reaction is

$$H^+(aq) + e \rightleftharpoons \frac{1}{2} H_2(g)$$

The electrode potential is given by,

$$\in\ = \in^\circ + \frac{RT}{F}\log\frac{[H_2]^{1/2}}{[H^+]}$$

$$\in\ = \in^\circ + 0.059\log\frac{1}{[H^+]} \quad (n = 1)$$

$$\in\ = 0 - 0.059\log[H^+]$$

$$= 0.059\ \text{pH at } 25°\text{C}.$$

A full cell is constructed by coupling the above half cell with a standard hydrogen electrode. The e.m.f. E of the cell is then determined potentiometrically. Since electrode potential of standard hydrogen electrode is zero, the observed e.m.f. of the cell gives directly the electrode potential (∈) of the half cell. So,

the cell is: (Pt) H_2 | $H^+(a = 1)$ || H^+ (a = unknown) | H_2(Pt)

$$E_{Obs} = \in\ = 0.059\ \text{pH}$$

$$\therefore \qquad \text{pH} = \frac{E_{Obs}}{0.059}$$

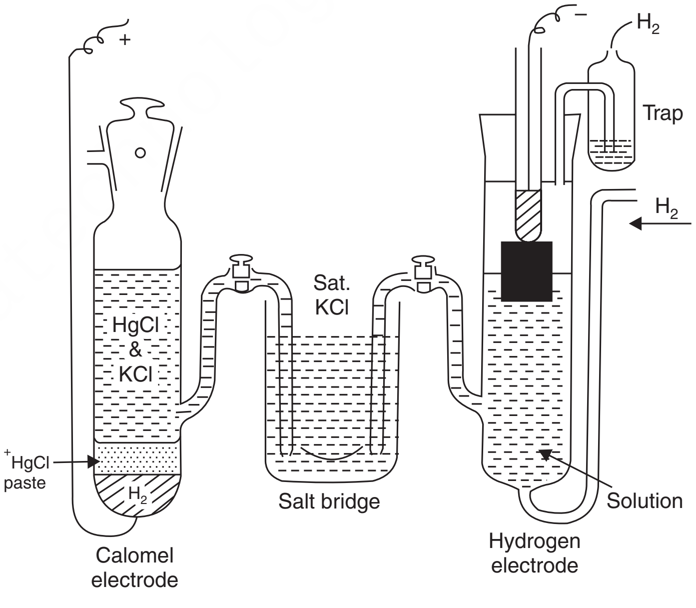


Fig. 10.7 Determination of pH by Hydrogen Electrode.

Reference Electrodes

For determination of standard electrode potentials (∈°), standard hydrogen electrode is used as reference. But there are some difficulties with hydrogen electrode. Maintaining 1 atm. pressure of hydrogen and to make $a_{H^+} = 1$ is very difficult. To overcome this difficulty another electrode which is known as secondary reference electrode is used for determining standard electrode potential. One of such electrodes is **calomel electrode**. To determine pH of a solution the cell constructed with the calomel electrode will be: (Pt) H_2 | H^+ (a) || Normal calomel electrode (Fig. 10.7).

Calomel Electrode

This electrode possesses certain advantages. It can be prepared easily and can be used for a long time. The standard electrode potential of this electrode is determined against standard hydrogen electrode.

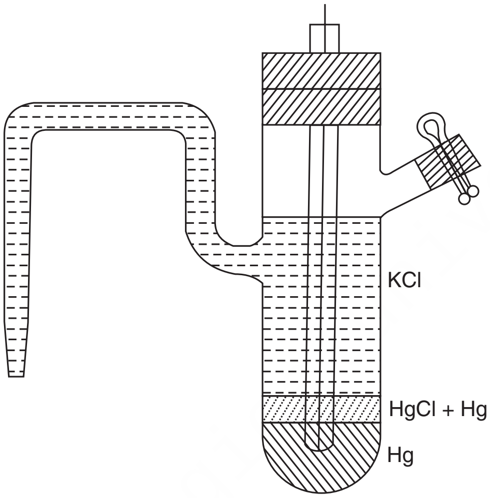


Fig. 10.8 Calomel Electrode.

The bottom of the electrode is filled with mercury. Mercury layer is covered with a paste of Hg_2Cl_2 (0.1N) and over it there is a saturated solution of KCl with some crystals of KCl. The electrode reaction is:

$$\frac{1}{2}\,Hg_2Cl_2(s) \rightleftharpoons Hg + Cl^- \,(a_{Cl^-})$$

The electrode potential $\in$ is given by

$$\in \;=\; \in^\circ + \frac{RT}{F}\ln a_{Cl^-} \quad (\because\; n = 1).$$

The standard electrode potential (reduction) of calomel electrode

For 1.0(N) KCl = + 0.28 V

Saturated KCl = + 0.2422 V

Any electrode whose standard potential is to be determined is connected to calomel electrode by means of KCl salt bridge. The e.m.f. of the set-up cell is determined potentiometrically from which the standard electrode potential of the electrode is calculated. To determine pH of a solution, we have,

$$\begin{aligned} E_{Obs} &= \in\text{ (calomel)} - \in\text{ (}H_2\text{ electrode)} \\ &= \in\text{ (calomel)} - 0.059\log[H^+] \\ &= 0.28 + 0.059\text{ pH} \end{aligned}$$

$$\text{or} \qquad pH = \frac{E_{Obs} - 0.28}{0.059}$$

Ag-AgCl Electrode

The use of this reference electrode is very common. The electrode consists of a silver wire, coated electrolytically with silver chloride and is dipped into a solution KCl of definite strength. The potential of this electrode

$$\text{Ag/AgCl}(s)\ \text{Cl}^- \ (a_{\text{Cl}^-} = 1) \parallel \text{HCl}\ (a = 1),\ \text{H}_2\ (1\ \text{atm})/\text{Pt}$$

$$\in° = -\,0.2224\ \text{V at } 25°$$

has been accurately determined against a standard hydrogen electrode.

Glass Electrode

A glass electrode consists of a very thin bulb or membrane of specially prepared and pH responsive glass and which is fused on to a piece of thick high resistance glass. The thick glass membrane serves as a solid electrode whose potential changes with pH of the solution with which it remains in contact. For good electrical contact the bulb contains a silver–silver chloride electrode immersed in a standard HCl solution. A platinum wire may be used in place of the Ag–AgCl electrode (Fig. 10.9).

For pH determination with the help of glass electrode the electrode is dipped into the solution where pH is to be determined and is usually combined with a reference electrode—generally calomel electrode—to form a complete cell. The potential of the glass electrode varies linearly with pH (Fig. 10.10).

$$\begin{aligned} \in_{\text{glass electrode}} &= \in° + \frac{\text{RT}}{\text{F}} \ln\,[\text{H}^+] \\ &= \in° - \frac{2.303\,\text{RT}}{\text{F}}\,\text{pH} \\ &= \in° - 0.059\ \text{pH at } 25°. \end{aligned}$$

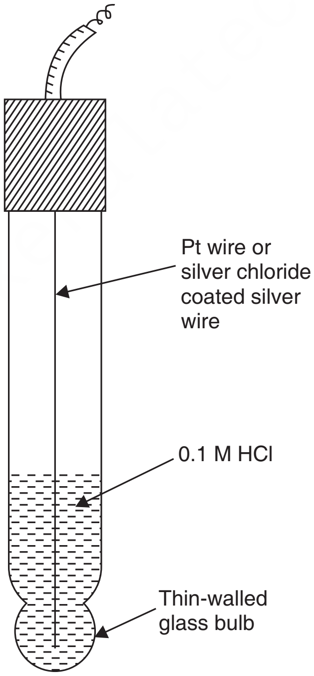


Fig. 10.9 Glass Electrode.

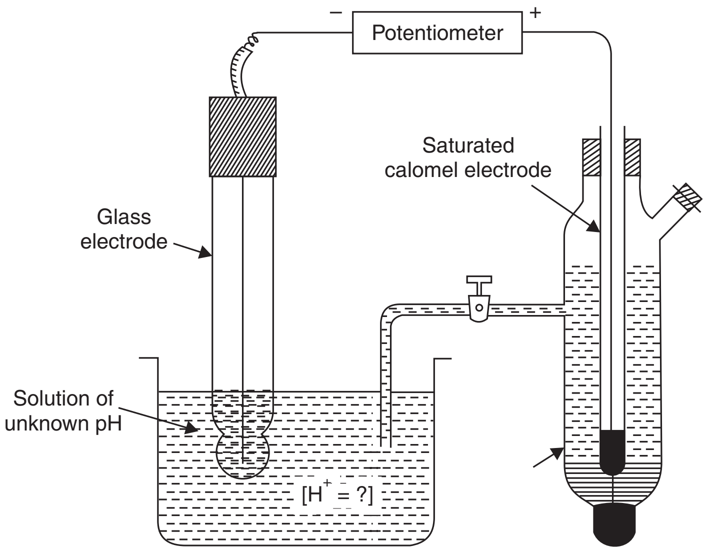


Fig. 10.10 Determination of pH by Glass Electrode.

Highlights:

- e.m.f. of the cell comprising of glass electrode and calomel electrode gives the pH of the solution from the equation, $\in = \in^\circ - 0.059$ pH
- Glass electrode is virtually hydrogen electrode.
- $\in^\circ$ value is not zero in the case of a glass electrode.
- $\in^\circ$ value of glass electrode can easily be determined by calibration using buffers of known pH.
- Glass electrode is the most extensively used electrode for pH determination.

The advantages of glass electrode. (*a*) Its rapid response, (*b*) remains unaffected by the presence of oxidising and reducing agents.

The disadvantages of glass electrode. (*a*) Its fragility and (*b*) its inability in the presence of high concentrations of alkali.

Only lithium silica glasses enable pH measurements to be valid over practically the entire pH range.

pH and millivolt meters

A linear relationship exists between the pH of a solution, at a given temperature, and the e.m.f. of a cell (E) constructed of a **reference electrode** and an **indicator electrode.**

Since, $$E = K - 0.0592 \text{ pH}$$

i.e., $$\frac{\Delta E}{\Delta pH} = -0.0592$$

Thus a calibration in mV can be converted into pH units when divided by 0.059. **In practice, however, pH meter scales are calibrated in pH units and in millivolts (mV) and the appropriate scale and range is selected by a simple control.**

Polarisation

When a simple cell drives a current, the following is the cell reaction:

At Copper plate:

$$Cu \rightleftharpoons Cu^{+2} + 2e$$
$$2H^+ + 2e \rightleftharpoons H_2\uparrow$$

At Zinc plate:

$$Zn \rightleftharpoons Zn^{+2} + 2e$$
$$Zn^{+2} + SO_4^{-2} \rightleftharpoons ZnSO_4$$

Total cell reaction:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

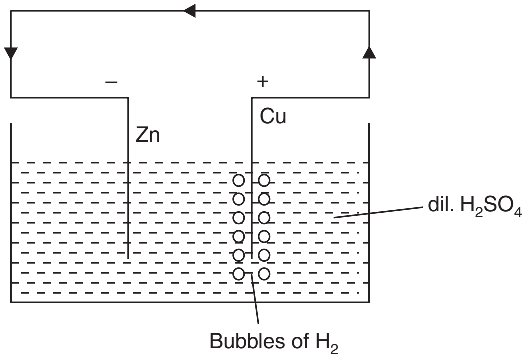


Fig. 10.11

When current flows from Cu-plate to Zn-plate, a layer of hydrogen bubbles is found to be formed on the surface of the Cu-plate. The effect of accumulation of hydrogen is two-fold:

(*i*) Hydrogen layer increases the resistance offered to the flow of current by covering the Cu-plate.

(*ii*) The layer of H_2 in contact with the acid solution is found to acquire a potential lower than that of Zn. The Zn-plate, therefore, behaves as positive electrode and H_2 accumulated as negative electrode, so, an additional e.m.f. is generated, which is called **polarisation e.m.f.** or **back e.m.f.** and which tends to drive a current opposite to the direction of the main current flow; and hence this back e.m.f. opposes the main e.m.f. As the hydrogen bubble is generated more and more, the polarisation e.m.f. increases and ultimately it comptetely neutralises original e.m.f. and the current stops totally. This phenomenon is known as **polarisation**.

Polarisation effect is also seen during electrolysis: when an electric current is passed through dil. H_2SO_4 using Pt-electrodes, H_2 and O_2 are evolved.

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

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

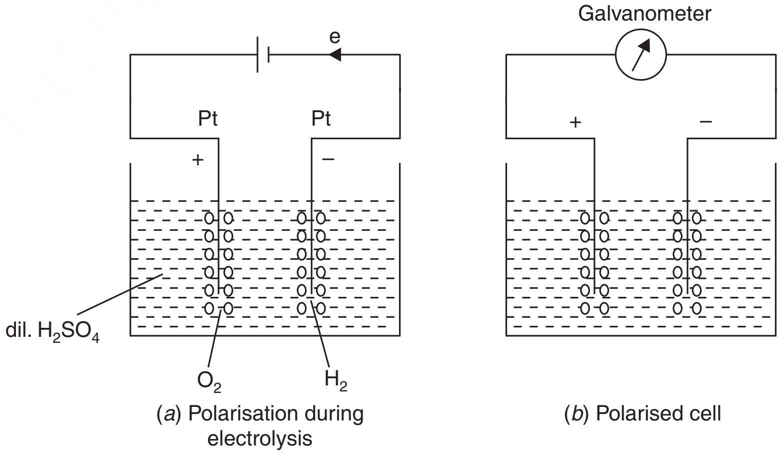
At anode: The reaction is,

$$2O^{-2} - 4e \rightleftharpoons O_2\uparrow$$

At cathode: The reaction is,

$$2H^+ + 2e \rightleftharpoons H_2\uparrow$$

If, after some time, the battery is removed and a galvanometer is fitted in the outer circuit, a current is seen to pass between the two electrodes, but in opposite direction to that during electrolysis. Hydrogen and oxygen gases covering the two Pt-electrodes become the source of this e.m.f. (back e.m.f.). **This phenomenon of back e.m.f. developed by products of electrolysis is known as polarisation** (Fig. 10.12).



(*a*) Polarisation during electrolysis

(*b*) Polarised cell

Fig. 10.12 Development of polarisation by the products of electrolysis.

Decomposition Potential

If we start electrolysis of dil. H_2SO_4 using Pt electrodes applying an e.m.f. of one volt, it will soon come to an end due to back e.m.f. developed during electrolysis. So, to keep the electrolysis going on, we are to apply an e.m.f. which can overcome the effect of back e.m.f. **The minimum voltage, which is just sufficient to overcome the back e.m.f. or polarisation e.m.f. is called decomposition potential of the given electrolyte** (Fig. 10.13).

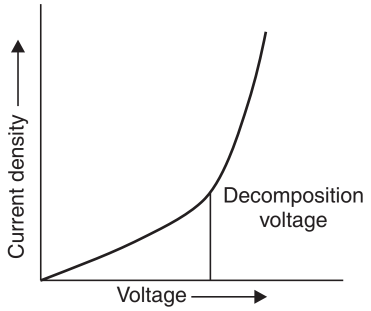


Fig. 10.13 Decomposition Potential.

At this stage, if the applied e.m.f. is gradually increased, electrolysis continues uninterrupted. So, a minimum voltage must always be applied to start the electrolysis process.

Highlights:

- The decomposition potential is different for different electrolytes.
- The decomposition potential of $CuSO_4$ is 1.5 V with Cu-electrodes and that of $ZnSO_4$ is 2.55 V with Zn-electrodes. When an e.m.f. of less than 2-5 V is applied between Cu-electrodes only Cu will get deposited at the cathode while Zn will remain in solution if a mixture of $CuSO_4$ and $ZnSO_4$ is used as electrolyte.

Overvoltage

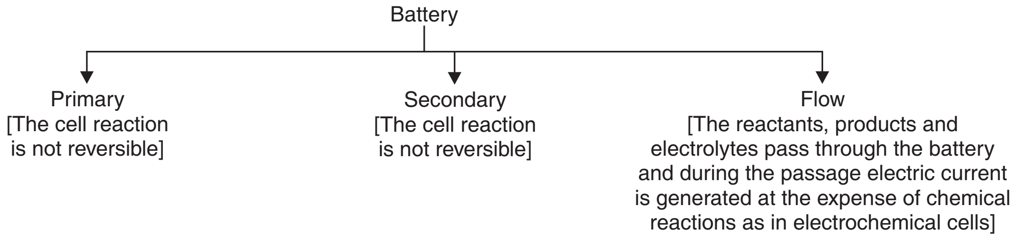
Theoretical voltage required for the decomposition of an acid solution should be equal to the e.m.f. of the reversible cell constructed with H_2 (*g*) at 1 atm. But it is seen that the value of applied e.m.f. is always higher than this theoretical value. Electrolysis of dil. H_2SO_4 with Pt-electrodes requires 1.7 V in place of 1.23 V (theoretical value). **This difference between the theoretical voltage and actual applied voltage necessary for electrolysis is known as overvoltage.**

Battery

Cells are devices where electric current is generated at the cost of some physicochemical processes going inside the cell. In order to apply exact thermodynamic principles to cell reaction it is customary to distinguish between reversible and irresversible cells. Because the thermodynamic principle is only applicable to reversible cells. It is well known that any chemical reaction conducted reversibly can yield some external work and the useful work available from the process, provided the process has been conducted reversibly at constant temperature and under a given pressure is equal to (the decreasing Gibbs free energy $-\Delta G$). Since electrical work is equal to nFE, where F = faraday and E = e.m.f. of the cell
so, we have

$$-\Delta G = nFE \quad \text{or} \quad \Delta G = -nFE$$

A battery is an electrochemical cell which is used as the source of direct current of a constant voltage. Battery works on the above thermodynamic principle.



Primary Cells

(*a*) **Leclanche cell.** (Fig. 10.14) This type of cell was devised by Georges Leclanche. The cell consists of a glass vessel B, which contains a saturated solution of NH_4Cl as an active liquid. The cathode is an amalgamated Zn-rod (Z) dipped partially in NH_4Cl solution. The anode is made of gas carbon (C) placed within a porous pot P which is also dipped partially in NH_4Cl solution. The space between the carbon rod and the pot is filled with a mixture of powdered charcoal and MnO_2 which serves as a depolariser. Since MnO_2 is a very poor conductor, charcoal is added to increase the conductivity. The top of the pot is sealed with pitch. The seal has a hole to allow the escape of NH_3 gas. The e.m.f. of the cell is 1.4 V.

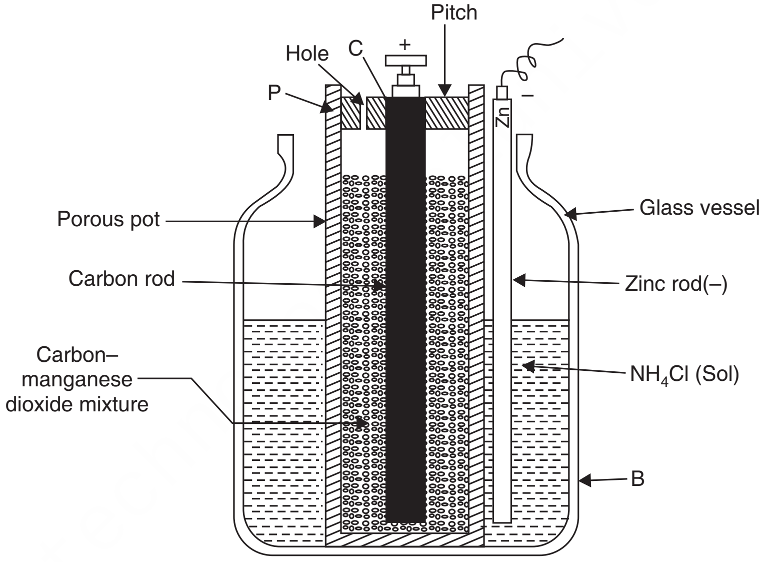


Fig. 10.14 Leclanche cell.

Cell reaction: $Zn + NH_4Cl = ZnCl_2 + 2\ NH_3 + H_2$

H_2 is oxidised by MnO_2 as $H_2 + 2\ MnO_2 = Mn_2O_3 + H_2O$.

When current is drawn from the cell, Zn rod is used up and the MnO_2 is reduced. The resulting Mn_2O_3 is slowly oxidised by air to MnO_2.

$$2Mn_2O_3 + O_2 = 4\ MnO_2$$

(*b*) **Dry cell.** (Fig. 10.15) It is essentially a Leclanche cell. Instead of NH_4Cl solution, NH_4Cl paste is used here. The paste contains NH_4Cl, MnO_2 and C (graphite). The cell is not really dry.

A zinc vessel serves as negative electrode. A carbon rod is placed at the centre to act as a positive electrode. It is filled at the top with a brass cap. The carbon rod is insulated at the bottom from Zn-vessel with a cardboard washer. The inside of the Zn-vessel is lined up with a thin sheet

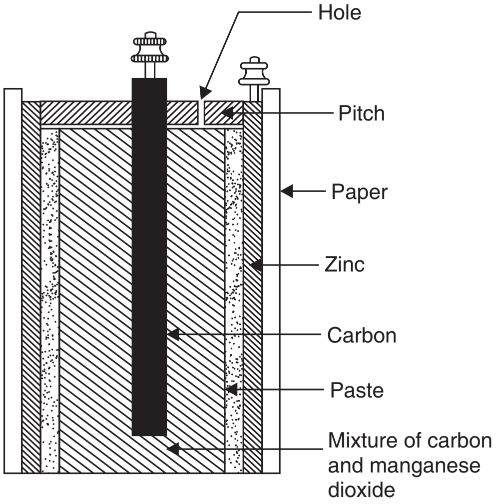


Fig. 10.15 Dry cell.

of blotting paper. To prevent drying of the paste, the top of the cell is sealed with pitch. A small hole is at the seal. The e.m.f. of the cell is 1.45 V.

This type of cell is widely used in torches, transistors, signalling equipments, telephone etc.

Alkaline Battery

It is a modification of dry cell where NH_4Cl has been replaced by KOH and acts as an electrolyte. In this type of battery, zinc is used in powder form and makes a gel with KOH. And the graphite-rod is kept surrounded by a paste of MnO_2. The cell reaction is

Anode: $Zn(s) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s) + 2e^-$

Cathode: $2MnO_2(s) + H_2O(l) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$

Net reaction: $Zn(s) + 2MnO_2(s) + H_2O(l) \longrightarrow Zn(OH)_2(s) + Mn_2O_3(s)$

Advantage. The life of alkaline battery is longer than the dry cell because zinc does not corrode.

Use. It is mainly used in camera, calculators, watches etc.

Nickel-Cadmium Battery

These battery is constructed of cadmium anode and a paste of NiO(OH)(*s*) cathode. The cell reaction is

Anode: $Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$

Cathode: $2NiO\,.\,OH(s) + 2H_2O(l) + 2e^- \longrightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

Net reaction: $2NiO.OH(s) + Cd(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$

Here the reaction products adhere to the electrode surfaces and the reaction can be easily reversed. This type of battery is portable and reachargeable. The main advantage of this battery is that, it undergoes no deterioration as no gases are produced during charging and discharging.

Use: It is used in calculators, electronic flash units etc.

Mercury Battery

This type of battery is constructed of zinc-amalgam (a solution of Zn in mercury) as anode and a paste of KOH, $Zn(OH)_2$ and HgO as cathode. The anode and the cathode are divided by a paper. The paper permits the migration of ions. The cell reaction is:

Anode: $\text{Zn-amalgam(s)} + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode: $HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-(aq)$

Net reaction: $\text{Zn-amalgam}(s) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

The entire cell is covered in a stainless steel case. The size is small. It is expensive.

Use: It finds its use in pacemakers, hearing aids, digital watches etc.

Fuel Cells

In these cells combustion of the fuel is employed as chemical reaction to generate electricity.

$$\text{Fuel} + O_2 \longrightarrow \text{Combustion products} + \text{electricity}$$

Aluminium-Air battery

It may be considered as a combination of a battery and a fuel cell. The cell reaction is:

At anode:

$$\mathrm{Al}(s) \longrightarrow \mathrm{Al}^{3+}(aq) + 3e^- \text{ (Oxidation)}$$

$$\mathrm{Al}^{3+}(aq) + 3\mathrm{OH}^-(aq) \longrightarrow \mathrm{Al(OH)}_3(s)$$

$$\mathrm{Al}(s) + 3\mathrm{OH}^-(aq) \longrightarrow \mathrm{Al(OH)}_3(s) + 3e^-$$

At cathode:

$$\mathrm{O}_2(g) + 2\mathrm{H}_2\mathrm{O}(l) + 4e^- \longrightarrow 4\mathrm{OH}^-\ (aq) \text{ (Reduction)}$$

Net reaction is: $$4\ \mathrm{Al}(s) + 3\mathrm{O}_2(g)\ 6\mathrm{H}_2\mathrm{O}(l) \longrightarrow 4\mathrm{Al(OH)}_3(s)$$

In such a battery the anode is very very pure aluminium and air is bubbled through the solution at **cathode**. The electrolyte is aqueous solution of NaCl (or NaOH).

It is expected that this type of battery will find its application in automobiles as source of energy replacing fuels.

Storage Cells

A storage cell can operate both as a voltaic cell and as an electric cell. The common example of storage cell is lead-acid storage cell.

It is constructed of electrodes made of lead and the other electrode in $\mathrm{PbO_2}$. The two types of electrodes are separated by strips of wood or glass fibres. The electrodes are totally immersed in 20% dilute $\mathrm{H_2SO_4}$. The cell reaction is

At anode:

$$\mathrm{Pb} \longrightarrow \mathrm{Pb}^{2+} + 2e^-$$

$$\mathrm{Pb}^{2+} + \mathrm{SO}_4^{2-} \longrightarrow \mathrm{PbSO}_4\downarrow$$

At cathode:

$$\mathrm{PbO}_2 + 2\mathrm{H}^+ + 2e^- \longrightarrow \mathrm{Pb}^{2+} + 2\mathrm{H}_2\mathrm{O}$$

$$\mathrm{Pb}^{2+}\ \mathrm{SO}_4^{2-} \longrightarrow \mathrm{PbSO}_4\downarrow$$

Net reaction: $$\mathrm{Pb} + \mathrm{PbO}_2 + 4\mathrm{H}^+ + 2\mathrm{SO}_4^{2-} \longrightarrow 2\mathrm{PbSO}_4\downarrow + 2\mathrm{H}_2\mathrm{O} + \text{Energy}$$

It is worthwhile to mention that $\mathrm{PbSO_4}$ gets precipitated at both the electrodes.

The cell can be again charged when both the anode and the cathode get covered with $\mathrm{PbSO_4}$. The cell loses its function as a voltaic cell. The positive pole of the generator is joined to the positive pole of the battery and the negative terminal is attached to the negative pole of the battery.

Reaction at cathode:

$$\mathrm{PbSO}_4 + 2e^- \longrightarrow \mathrm{Pb} + \mathrm{SO}_4^{-2}$$

Reaction at anode:

$$\mathrm{PbSO}_4 + 2\mathrm{H}_2\mathrm{O} - 2e^- \longrightarrow \mathrm{PbO}_2 + 2\mathrm{H}^+ + \mathrm{SO}_4^{-2}$$

Net reaction: $$2\mathrm{PbSO}_4 + 2\mathrm{H}_2\mathrm{O} + \text{Energy} \longrightarrow \mathrm{Pb} + \mathrm{PbO}_2 + 4\mathrm{H}^+ + 2\mathrm{SO}_4^{2-}$$

After charging the cell restores its original condition and is again used.

Use: This type of battery is used in electrical vehicles, automobiles, power stations etc.

Solar Battery

In this type of battery, solar energy is utilised to generate electric current in a photovoltaic cell. In this type of photovoltaic cell, *p*-type semiconductor is connected with *n*-type semiconductor. Due to this contact, a limited number of electrons can flow and cross the junction between the two types of semiconductors.

SOLVED EXAMPLES

Example 1. *Calculate the standard potential of* Cu^{+2}/Cu *if the electrode potential at 25° is 0.296 V when* $[Cu^{+2}] = 0.015$ *M.*

Sol.

$$\in\ = \in^\circ + \frac{0.0592}{n} \log [M^{+n}]$$

$$= \in^\circ + \frac{0.0592}{2} \log [Cu^{+2}]$$

$$\therefore \qquad \in^\circ = \in - \frac{0.0592}{2} \log 0.015$$

$$= [0.296 - 0.0296 \times (-1.8239)] \text{ V}$$

$$= [0.296 + 0.05398] \text{ V}$$

$$= 0.34998 \text{ V.}$$

Example 2. *Calculate the single electrode potential of copper metal in contact with 0.15 (M)* Cu^{+2} *solution.* $\in^\circ$ *for copper* $= +0.34$ *V* $(R = 8.314 \text{ J. } K^{-1} \text{ mol}^{-1},\ T = 298 \text{ K})$.

Sol.

$$\in\ = \in^\circ + \frac{RT}{nF} \ln [M^{+n}]$$

$$= 0.34 + \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log [Cu^{+2}]$$

$$= 0.34 + \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log 0.15$$

$$= 0.3156 \text{ V.}$$

Example 3. *Calculate the voltage at 25°C of a cell formed by dipping silver in silver nitrate (0.1 M) and zinc in zinc sulphate (0.2 M) and connecting them without liquid junction potential.*

Sol. (–) (+)

The cell ⇒ $Ag/AgNO_3$ (0.1 M) || $ZnSO_4$ (0.2 M)/Zn

The cell reaction ⇒ $Zn^{+2} + 2e \rightleftharpoons Zn$ ($E_{cell} = \in_R - \in_L = \in_+ - \in_-$, R = Right hand electrode and Reduction L = Left hand electrode undergoing oxidation)

$$2Ag - 2e \rightleftharpoons 2Ag^+$$

$$\overline{\quad Zn^{+2} + 2Ag \rightleftharpoons Zn + 2Ag^+ \quad}$$

$$\therefore \qquad E_{cell} = \left(\in^\circ_{Zn} + \frac{RT}{2F} \ln [Zn^{+2}]\right) - \left(\in^\circ_{Ag} + \frac{RT}{2F} \ln [Ag^+]^2\right)$$

$$= \left(\in^\circ_{Zn} + \frac{RT}{2F} \ln [Zn^{+2}]\right) - \left(\in^\circ_{Ag} + \frac{RT}{F} \ln [Ag^+]\right)$$

$$= (-0.762 + 0.0296 \log 0.2) - (0.798 + 0.059 \log 0.1)$$

$$= -1.522 \text{ V.}$$

Highlights:

- If after calculation of E_{cell} it comes negative, half cells are to be reversed to get positive value of E_{cell}. Here if Ag-electrode is made positive electrode (one half cell) and Zn-electrode is made (negative electrode) (the other half cell) then E_{cell} would become positive.
- If we cannot make right choice during construction of a cell, E_{cell} would come out negative, but the table of $\in^\circ$ values and the above procedure will help to calculate E_{cell} of any reversible cell.

Example 4. *Calculate the e.m.f. of a Daniel cell at 25°C, when the concentrations of $ZnSO_4$ and $CuSO_4$ are 0.001 M and 0.1 M, respectively. The standard potential of cell is 1.1 volts.*

Sol. We can write $E_{cell} = (\overset{\circ}{\in}_+ - \overset{\circ}{\in}_-) + \dfrac{RT}{nF}\ln\dfrac{[Cu^{+2}]}{[Zn^{+2}]}$

$$= E^\circ_{Cell} + \frac{0.0592}{2}\log\frac{0.1}{0.001} \qquad [\because \quad E^\circ_{cell} = \in^\circ_+ - \in^\circ_-]$$

$$= 1.1 + 0.0296 \log 100$$

$$= 1.1 + 0.0296 \times 2$$

$$= 1.1592 \text{ V.}$$

Example 5. *Calculate the e.m.f. of the cell:*

$$Ni \mid Ni^{+2}\ 1(M) \parallel Pb^{+2}\ 1(M) \mid Pb$$

at 25°C. Write down its cell reaction. Given $\in^\circ_{Ni} = -0.24$ V and $\in^\circ_{Pb} = -0.13$ V at 25°C.

Sol. $E^\circ_{cell} = \in^\circ_{right} - \in^\circ_{left}$

$$= (-0.13) - (-0.24)$$

$$= 0.11 \text{ V.}$$

Cell reaction:

At anode: $Ni - 2e \rightleftharpoons Ni^{+2}$ (Ox)

At cathode: $Pb^{+2} + 2e \rightleftharpoons Pb$ (Red)

$$Ni + Pb^{+2} \rightleftharpoons Ni^{+2} + Pb$$

Example 6. *Sketch the electrochemical cell and write down the cell reaction, if Zn and Ag electrodes are dipped in respective solutions. Also find out the standard emf of the cell, given that $\in^\circ_{Zn/Zn^{+2}} = 0.76$ V and $\in^\circ_{Ag/Ag^+} = 0.8$ V at 25°C.*

Sol. $\in^\circ_{Ox} = \in^\circ_{Zn/Zn^{+2}} = 0.76$ V *i.e.,* $\in^\circ_{Red} = \in_{Zn^{+2}/Zn} = -0.76$ V

$\in^\circ_{Ox} = \in^\circ_{Ag/Ag^+} = -0.8$ V *i.e.,* $\in^\circ_{Red} = \in^\circ_{Ag^+/Ag} = 0.8$ V.

So here S.R.P of Ag-electrode is higher than that of Zn-electrode. So, Ag-electrode will form right hand half cell *i.e.,* +ve electrode.

$$Cu = Zn/Zn^{+2}\ (a = 1)/Ag^+\ (a = 1)/Ag^+$$

According to '2R' convention reduction will take place at right hand electrode (cathode).

Cell reaction ⇒

At cathode: $2Ag^+ + 2e \rightleftharpoons 2Ag$ (Reduction)

At anode: $Zn - 2e \rightleftharpoons Zn^{+2}$ (Oxidation)

$$2Ag^+ + Zn^{+2} \rightleftharpoons 2Ag + Zn^{+2}$$

$$E^\circ_{cell} = \in^\circ_{Right} - \in^\circ_{Left}$$
$$= 0.8 - (-0.76) = 1.56 \text{ V.}$$

Example 7. *Two copper rods are placed in copper sulphate solution of concentration 0.1 M and 0.01 M separately in the form of a cell. Write the scheme of the cell and calculate its e.m.f. at 298 K.*

Sol.

$$\text{Cell} = \text{Cu/Cu}^{+2}\ (0.01\text{ M}) \parallel \text{Cu}^{+2}\ (0.1\text{ M})/\text{Cu}$$

$$E_{cell} = \frac{0.0592}{n} \log \frac{C_2}{C_1}, \text{ here } C_2 = 0.1 \text{ M and } C_1 = 0.01 \text{ M}$$

$$E_{cell} = \frac{0.0592}{2} \log \frac{0.1}{0.01} = \frac{0.0296}{\log 10} = 0.0296 \text{ V.}$$

Example 8. *Calculate the equilibrium constant for Daniel cell at 25°C from the following data,*

R = 8.316 J. *F = 96,500 C. S.E.P. (Ox) for Zn electrode.*
= 0.765 V and S.E.P. (Ox) for Cu electrode = – 0.337

Sol. $\in^\circ_{Zn/Zn^{+2}} = 0.765$ V *i.e.,* $\in^\circ_{Zn^{+2}/Zn} = -0.765$ V

and $\in^\circ_{Cu/Cu^{+2}} = -0.337$ V *i.e.,* $\in^\circ_{Cu^{+2}/Cu} = 0.337$ V

$$\text{Cell} = \text{Zn/Zn}^{+2} \parallel \text{Cu}^{+2}/\text{Cu}$$

Half cell reactions $\text{Cu}^{+2} + 2e \rightleftharpoons \text{Cu} \quad .....\in^\circ = 0.337 \text{ V}$

$\text{Zn} - 2e \rightleftharpoons \text{Zn}^{+2} \quad .....\in^\circ = 0.765 \text{ V}$

Cell reaction: $\text{Zn} + \text{Cu}^{+2} \rightleftharpoons \text{Zn}^{+2} + \text{Cu}\ (E^\circ_{cell} = \in^\circ_{Red} + \in^\circ_{OX}) = 1.102$ V.

$$\therefore \qquad K = \frac{[\text{Zn}^{+2}]\,[\text{Cu}]}{[\text{Zn}]\,[\text{Cu}^{+2}]}$$

$$\in_{Zn^{+2}/Zn} = \in^\circ_{Zn^{+2}/Zn} + \frac{0.0592}{2} \log \frac{[\text{Zn}^{+2}]}{[\text{Zn}]}$$

$$\in^\circ_{Cu^{+2}/Cu} = \in^\circ_{Cu^{+2}/Cu} + \frac{0.059}{2} \log \frac{[\text{Cu}^{+}]}{[\text{Cu}]}$$

At equilibrium, these two electrode potentials will be equal. Therefore,

$$\in^\circ_{Zn^{+2}/Zn} + \frac{0.0592}{2} \log \frac{[\text{Zn}^{+2}]}{[\text{Zn}]} = \in^\circ_{Cu^{+2}/Cu} + \frac{0.0592}{2} \log \frac{[\text{Cu}^{+2}]}{[\text{Cu}]}$$

$$\in^\circ_{Cu^{+2}/Cu} - \in^\circ_{Zn^{+2}/Zn} = \frac{0.0592}{2} \log \frac{[\text{Zn}^{+2}]}{[\text{Zn}]} - \frac{0.0592}{2} \log \frac{[\text{Cu}^{+2}]}{[\text{Cu}]}$$

or
$$0.337 - (-0.765) = \frac{0.0592}{2} \log \frac{[\text{Zn}^{+2}]/[\text{Zn}]}{[\text{Cu}^{+2}]/[\text{Cu}]}$$

$$1.102 = 0.0296 \log \frac{[\text{Zn}^{+2}]/[\text{Cu}]}{[\text{Cu}^{+2}]/[\text{Zn}]}$$

$$= 0.0296 \log K$$

$$\therefore \qquad \log_{10} K = \frac{1.102}{0.0296} = 37.2297$$

$$K = \text{Antilog } 37.2297$$

$$= 1.697 \times 10^{37}.$$

Highlight:

- The high value of K indicates the spontaneity of the reaction.

Example 9. *Calculate the potential of an Ag-electrode in a solution that is saturated with AgI and has an iodide concentration of exactly unity.*

$$K_{sp}\,(AgI) = 8.3 \times 10^{-17}, \quad \in^\circ_{Ag^+/Ag} = +\,0.799 \text{ V}.$$

Sol.

$$[Ag^+] = \frac{K_{sp}}{I} = \frac{8.3 \times 10^{-17}}{1} = 8.3 \times 10^{-17} \text{ (M)}.$$

Example 10. *The potential of a hydrogen gas electrode in a solution of an acid of unknown strength is 0.29 V at 298 K as measured against normal hydrogen electrode. Calculate the pH of the solution.*

Sol.

$$E_{cell} = \in^\circ_H - \in_H$$

$$= 0 - (-\,0.0592 \text{ pH})$$

$$= 0.0592 \text{ pH}$$

$$\therefore \qquad \text{pH} = \frac{E_{cell}}{0.0592} = \frac{0.29}{0.0592} \approx 4.9.$$

Example 11. *Find out the pH of a solution in a quinhydrone half cell, which is coupled with standard calomel electrode. The e.m.f. of the combined cell was determined to be 0.123 V at 25°C.* $E_{calomel} = 0.2415$, $\in_Q/H_2Q = 0.6990$.

Sol.

$$E_{cell} = \in_{Q/H_2Q} - \in_{calomel}$$

$$0.123 = (0.6990 - 0.0592 \text{ pH}) - 0.2415$$

or $$-\,0.0592 \text{ pH} = 0.123 + 0.2415 - 0.6990 = -\,0.3345$$

or $$\text{pH} = \frac{0.3345}{0.0592} = 5.65.$$

Example 12. *Calculate* K_{sp} *of AgCl from the following data:*

$$\in^\circ_{Ag\text{–}AgCl(s)} = 0.2223 \qquad \in^\circ_{Ag^+/Ag} = 0.798 \text{ at } 25°C.$$

Sol. Cell reaction

$$Ag^+ + e \rightleftharpoons Ag \qquad \in^\circ = 0.798$$

$$Ag + Cl^- \rightleftharpoons AgCl(s) + e \qquad \in^\circ = -\,0.2223$$

$$\overline{Ag + Cl^- \rightleftharpoons AgCl(s). \qquad E^\circ_{cell} = 0.5757}$$

We have, $$-\,\Delta G^\circ = nFE^\circ$$

$$nFE^\circ = -\,RT \ln K$$

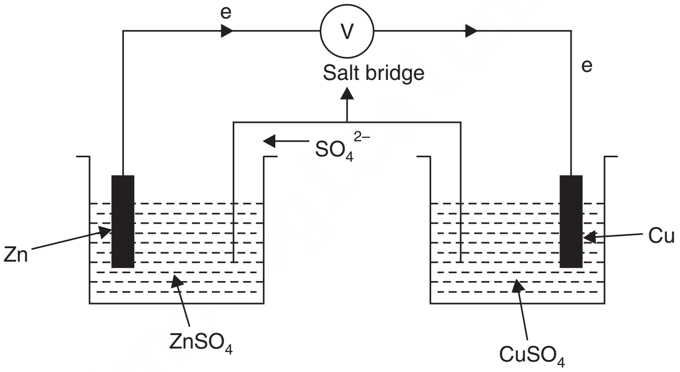
or $$\log K = -\frac{nFE^\circ}{2.303\,RT} = -\frac{1\times 0.5757}{0.0592} = -9.7246 = -10 + 0.2754$$

or $$\text{Here } K = K_{sp} = \text{Antilog } \overline{10}.2754 = 1.886 \times 10^{-10}\ \text{mol}^2\,\text{l}^{-2}.$$

SHORT QUESTIONS AND ANSWERS

Q. 1. What is galvanic cell or voltaic cell?

Ans. It is a simple device of producing electrical energy by chemical reaction, *e.g.,* Daniel cell. Such a cell is also known as **electrochemical cell**.



$$Zn \longrightarrow Zn^{+2} + 2e^- \quad \text{(oxidation)}$$
$$Cu^{2+} + 2e \longrightarrow Cu \quad \text{(reduction)}$$

Fig. 10.16

In the above cell Zn-electrode is anode and Cu-electrode is cathode.

Q. 2. What is an electrolytic cell?

Ans. It is a device used for converting electrical energy into chemical energy.

Q. 3. What do you mean by electrode potential (E)?

Ans. It is the tendency of an electrode in a half cell to lose or gain electrons when it is in contact with the solution of its own ions.

Q. 4. What are reduction and oxidation potentials?

Ans. Reduction potential is the tendency of an electrode in a half cell to gain electrons and oxidation potential is the tendency of an electrode in a half cell to lose electrons.

Q. 5. What do you mean by standard electrode potential (E°)?

Ans. It is the electrode potential of a metal in contact with its ions when the concentration of ions is 1 M (1 molar).

Q. 6. What is a salt bridge?

Ans. It is an inverted U-tube containing an electrolyte (*e.g.,* KCl, KNO_3). It connects (acts as a bridge) the solutions of the two half cells.

Q. 7. What is the E.M.F. of a cell?

Ans. It is defined as the potential difference between the two terminals of the cell when no current is drawn from it.

Q. 8. Define normal hydrogen electrode.

Ans. It is a reference or standard reference electrode. Its electrode potential is taken as zero at all temperatures. A normal hydrogen electrode generally consists of a Pt-foil coated with platinum, dipped in solution having 1 M H^+ ion concentration and hydrogen gas at 1 atmospheric pressure constantly bubbled over it. It can be represented as:

$$\text{Pt, } H_2 \text{ (1 atm)} \parallel H^+ \text{ (1 M)}$$

Reaction: $$H^+(aq) + e^- \longrightarrow \frac{1}{2} H_2(g)$$

or $$\frac{1}{2} H_2(g) \longrightarrow H^+(aq) + e^-$$

Q. 9. How is electrode potential measured?

Ans. Apparatus for measuring the standard electrode potential of a redox system is given in Fig. 10.17.

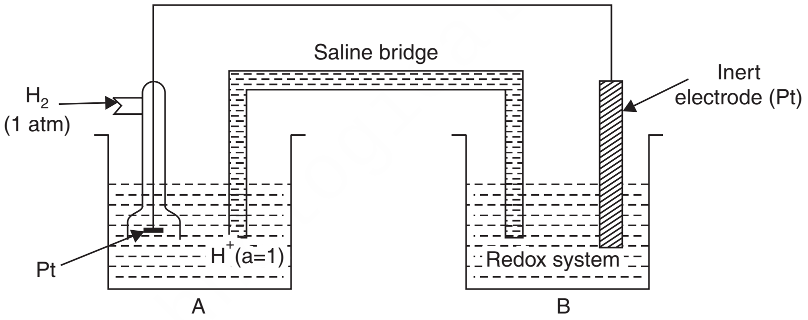


Fig. 10.17 A cell constructed with standard hydrogen electrode.

A = Solution of H^+ ions of unit activity

B = Redox solution of unit activity.

Saline bridge has the function of bringing into physical contact the two solutions without mixing them; it consists of a strong electrolyte (*e.g.,* KCl).

Q. 10. How is the E.M.F. of a cell measured?

Ans. E.M.F. of a cell is measured by means of a device, named **potentiometer**.

$$\Delta\in = \in^\circ_{\text{Redox}} - \in^\circ_{H_2/H^+}$$

$\therefore$ $$\in^\circ_{H_2/H^+} = 0$$

$\therefore$ $$\Delta\in = \in^\circ_{\text{Redox}}$$

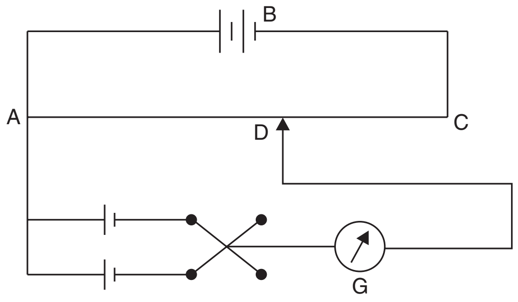


Fig. 10.18 Diagram for Potentiometer.

Q. 11. What do you mean by potentiometry?

Ans. Potentiometry is an electrochemical method of analysis based on measuring the potential difference (e.m.f.) between two half cells, one of which is an indicating electrode and the other is a reference electrode.

Q. 12. What is an indicating electrode?

Ans. It is an electrode in balance with an redox couple, the potential of which is given by Nernst equation.

Q. 13. Give the hemistry the different indicating electrodes.

Ans. (*a*) First Class ⇒ Metallic electrodes in contact with a solution of their own ion (an electrode which is reversible in relation to the cation)

$$M^{n+} + ne^- \rightleftharpoons M; \text{ where, } [M^{n+}] \Rightarrow \text{ conc. of cation in moles dm}^{-3}$$

$$\in \; = \; \in^\circ_{M/M^{n+}} + \frac{0.059}{n} \log [M^{n^+}]$$

(*b*) Second class ⇒ Metallic electrodes in contact with one of their not readily soluble salts and with the anion of this salt:

$$M \mid MA(s), A^{-n}$$

where, $M \Rightarrow$ Metal

$MA(s) \Rightarrow$ the salt which is not readily soluble.

$[A^{-n}]$ = Conc. of the anion in moles dm^{-3}.

And, $$\in \; = \; \in^\circ_{M/M^{n+}} + \frac{0.059}{n} \log K_{sp} - \frac{0.059}{n} K_{sp} [A^{-n}]$$

where K_{sp} = solubility product of the salt which is not readily soluble.

(*c*) Redox = Electrodes which are inert in contact with a redox couple in solution.

Pt/Ox, Red

And, $$\in \; = \; \in^\circ_{Redox} + \frac{0.059}{n} \log [Ox]/[Red]$$

Pt ⇒ Platinum

[Ox] = Conc. of the oxidised form in moles dm^{-3}.

[Red] = Conc. of the reduced form in moles dm^{-3}.

(*d*) Membrane type = Selective electrodes specific to certain ions. They consist of a membrane which in presence of particular ions assumes a potential which is dependent on the activity of the ions in relation to those of which the electrode is selective. The best known of this type is glass electrode.

$$\in \; = \; \in_r + \frac{0.059}{n} \log a$$

where, $\in_r \Rightarrow$ Constant potential linked to the choice of the reference electrode and the internal solution, $a \Rightarrow$ activity of the ion in relation to which the electrode is selective.

Q. 14. What are reference electrodes?

Ans. These are the electrodes whose potential is constant and independent of the composition of the contacting solution.

The most widely used are saturated calomel electrodes ($\in \; = +\, 0.246$ V) and the silver-silver chloride electrode ($\in \; = +\, 0.222$ V).

Highlight:

The potential of reference electrodes is determined as referred to the standard hydrogen electrode.

Q. 15. Define the electrochemical series?

Ans. When the standard reduction potentials of the electrodes are arranged in an increasing order, the series so obtained is known as electrochemical series.

Q. 16. What is Nernst equation?

Ans. Nernst proposed the fundamental electrode relation between the formal (or observed) potential and the standard electrode potential for the redox reaction:

$$\in_{\text{Red}} = \in^{\circ}_{\text{Red}} - \frac{2.303\,\text{RT}}{n\text{F}} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

where, R ⇒ molar gas constant.

T ⇒ absolute temperature.

n ⇒ number of electrons involved in the redox reaction.

$\in^{\circ}$ = standard reduction electrode potential.

$\in_{\text{Red}}$ = observed reduction electrode potential.

F = Faraday (96500 Coulombs)

At 25°C the value of the term 2.303 RT/F comes out as equal to 0.059.

So at 25°C

$$\in = \in^{\circ} - \frac{0.059}{n} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

Highlight:

The concentration of metal is taken as unity.

Q. 17. What is lead storage battery?

Ans. It consists of six voltaic cells connected in series.

Reactions:

$$\begin{array}{ll} \textit{Anode:} & \text{Pb} + \text{SO}_4^{2-} \longrightarrow \text{PbSO}_4 + 2e^- \\ \textit{Cathode:} & \text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \\ \hline \textit{Net reaction:} & \text{Pb} + \text{PbO}_2 + 4\text{H}^+ + 2\text{SO}_4^{2-} \longrightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}. \\ \hline \end{array}$$

Reaction during recharging the battery

$$\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \Leftrightarrow \text{Pb}(s) + \text{PbO}_2(s) + 4\text{H}^+ + 2\text{SO}_4^{2-}$$

Q. 18. What is the reaction in nickel-cadmium battery?

Ans. *Anode:*

$$\text{Cd}(s) + 2\text{OH}^-(aq) \longrightarrow \text{Cd(OH)}_2(s) + 2e^-$$

Cathode:

$$\text{NiO}_2 + 2\text{H}_2\text{O} + 2e^- \longrightarrow \text{Ni(OH)}_2 + 2\text{OH}^-\,(aq)$$

Q. 19. What are fuel cells?

Ans. Fuel cells are the devices that convert chemical energy of a fuel directly into electrical energy.

Q. 20. Give the reaction in H_2–O_2 fuel cell.

Ans. *Anode:* $\{H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-\} \times 2$

Cathode:

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

Net reaction: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Highlight:

Such a cell is used to generate electrical power such as in Apollo space programme.

Q. 21. What do you mean by corrosion?

Ans. It generally refers to the slow and continuous deterioration of metals and alloys by chemical or electrochemical actions of environments, *e.g.,* rusting of iron.

Q. 22. Classify corrosion.

Ans. (*a*) Chemical corrosion ⇒ it involves direct chemical action between metals and gases.

(*b*) Electrochemical corrosion ⇒ it involves deterioration of metal due to flow of electric current from one point to another.

(*c*) Dry corrosion ⇒ it refers to the corrosion of metals involving direct chemical action between metals and dry gases.

(*d*) Wet corrosion ⇒ it involves flow of electric current from one point to another through some perceptible distance in the presence of liquid or moisture in air.

Q. 23. State the electrochemical theory of rusting.

Ans. Reaction:

Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$

Cathode: $2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$.

The Fe^{+2} ions formed at anode are oxidised by O_2 to Fe^{+3} ions which then combine with OH^- ions to form hydrated ferric oxide, *i.e.,* rust.

$$2Fe^{+2} + H_2O + O \longrightarrow 2Fe^{+3} + OH^-$$

$$2Fe^{+3} + 6OH^- \longrightarrow 2Fe(OH)_3 \quad \text{or} \quad Fe_2O_3.3H_2O \text{ (rust)}$$

Q. 24. What measures ought to be taken to prevent corrosion?

Ans. (*a*) Barrier protection.

(*b*) Sacrificial protection.

(*c*) Electrical protection.

(*d*) Use of anti-rust solutions.

Q. 25. Given (*i*) $Fe^{+2} + 2e \longrightarrow Fe$, $\epsilon° = -0.44$ V

(*ii*) $Fe^{+3} + e \longrightarrow Fe^{+2}$, $\epsilon° = 0.77$ V

Represent the data in the form of Latimer diagram.

Ans. We have $\Delta G^\circ_{(i)} = -nFE^\circ = -2F(-0.44) = 0.88\ F$

$$\Delta G^\circ_{(ii)} = -nFE^\circ = -F(0.77) = -0.77\ F$$

Adding the above two equations,

$$\Delta G^\circ_{(iii)} = \Delta G^\circ_{(i)} + \Delta G^\circ_{(ii)} = 0.88 + (-0.77)\ F = +0.11\ F$$

So $\Delta G^\circ_{(iii)}$ is the value for the reaction,

$$Fe^{+3} + 3e \longrightarrow Fe$$

$$\in^\circ = \frac{\Delta G^\circ}{-nF} = \frac{+0.11\ F}{-3\ F} = -0.04\ V$$

The Latimer diagram of the above system is Fig. 10.19.

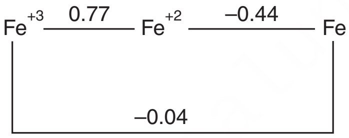
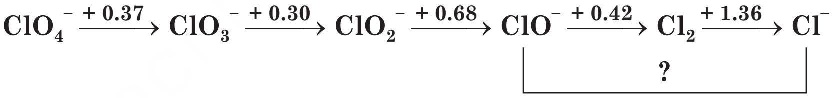


Fig. 10.19 Latimer diagram for Fe species.

It is conventional to put highly oxidised form of the element on the left and the elements with lower oxidation state are put successively in the Latimer diagram.

Q. 26. In alkaline solution (pH = 14) the Latimer diagram for chlorine is



$$ClO_4^- \xrightarrow{+0.37} ClO_3^- \xrightarrow{+0.30} ClO_2^- \xrightarrow{+0.68} ClO^- \xrightarrow{+0.42} Cl_2 \xrightarrow{+1.36} Cl^-$$

$$ClO^- \xrightarrow{?} Cl^-$$

Calculate from the above diagram $\in^\circ$ value for the reaction,

$$\mathbf{ClO^- \longrightarrow Cl^-.}$$

Ans. $ClO^- \xrightarrow{+e} \frac{1}{2} Cl_2, \qquad \in^\circ = +0.42\ V; \qquad \Delta G^\circ_I = -(+0.42)\ F = -0.42\ F$

$$\frac{1}{2} Cl_2 \xrightarrow{+e} Cl^-, \qquad \in^\circ = +1.36\ V; \qquad \Delta G^\circ_{II} = -(+1.36)\ F = -1.36\ F$$

Adding total ΔG for the reaction $= -1.78\ F$

From the relation, $\Delta G^\circ = -nFE^\circ$

$$\in^\circ (ClO^-/Cl^-) = \frac{\Delta G_I + \Delta G_{II}}{-nF} = \frac{-1.78\ F}{-2\ F} = 0.89\ V$$

Q. 27. Use the following data to draw a Frost diagram.

$$\mathbf{\in^\circ(Mn^{+2}, Mn) = -1.18\ V, \qquad 2\in^\circ = -2.36\ V}$$

$$\mathbf{\in^\circ(Mn^{+3}, Mn^{+2}) = 1.51\ V.}$$

Ans. $\in^\circ(Mn^{+2}, Mn) = -1.18\ V$

$$\in^\circ(MnO_2, Mn^{+3}) = 0.95\ V$$

$$3\in^\circ(Mn^{+3}, Mn) = -0.85\ V$$

$$4\in^\circ(MnO_2, Mn) = 0.10\ V$$

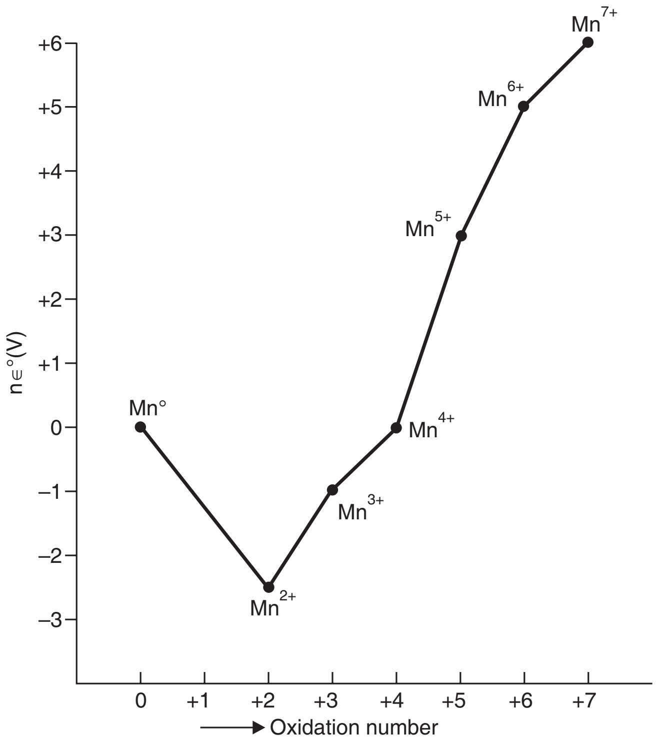


Fig. 10.20 Frost diagram for Mn in acidic pH.

Highlights:

- Plot of $n\in°$ *vs* n for Mn (n = oxidation state) such diagram are called Ebsworth diagram or Frost diagram.
- The steeper the line joining two points, the higher the potential of corresponding couple.
- A state is unstable with respect to disproportionation if it lies above the line connecting two adjacent oxidation states.
- Mn^{+3} is likely to disproportionate to Mn^{+2} and MnO_2. Since both these products involve one electron transfer, the process is likely to be rapid.
- The point for Mn(VI) similarly suggests disproportionation to Mn(VII) and Mn(IV).
- MnO_2 is also a strong oxidizing agent—its slope to Mn^{+2} is greater than the slopes to higher oxidation states. Most species that reduce MnO_4^- should also reduce MnO_2.
- The minimum at Mn^{+2} suggests this to be the common product of reduction of MnO_4^- [Mn(VII)] in acidic solution and it is the most stable oxidation state of Mn.

Q. 28. Construct a Frost diagram from the Latimer diagram for *Tl*.

$$\begin{tikzcd}
Tl^{+3} \arrow[r, "+1.25"] \arrow[rr, bend right, "+1.23"'] & Tl^{+} \arrow[r, "-0.34"] & Tl
\end{tikzcd}$$

Ans. The oxidation states of *Tl* are + 3, + 1 and 0, in the three species. For the change of oxidation number from + 1 to 0 *i.e.,* $Tl^{+1} \rightarrow Tl^0$, $\in° = -0.34$ V, here $n = 1$, so, $n\in° = -0.34$ V.

For the change of oxidation number from + 3 to 0

$$(Tl^{+3} \longrightarrow Tl^{0}) \quad \in^{\circ} \text{ value} = +\ 1.23 \text{ V}$$

So, for $n = 3$, $n\in^{\circ} = 3 \times 1.23$ V = **+ 3.69 V**.

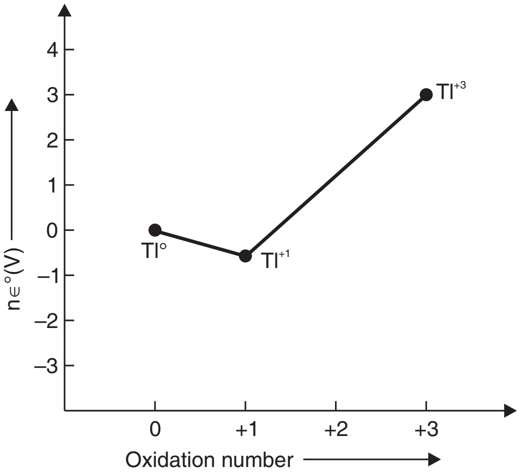


Fig. 10.21 Frost diagram for *Tl* species.

Tl^{+1} is the most stable oxidation state of *Tl* as the species lies lowest in the Frost diagram.

EXERCISES

1. Distinguish between electrolytic and electrochemical cells.
2. Define the electrode potential.
3. Prove that $\in_{ox} = -\in_{red}$.
4. What is a standard hydrogen electrode? What is its potential?
5. What is overvoltage? What is the cause of overvoltage?
6. Give the reason: the hydrogen overpotential falls with rising temperature.
7. What is standard electrode potential?
8. State the peculiarity of a concentration cell.
9. Why is a voltmeter is not used for the measurement of e.m.f. of a cell?
10. What is a storage cell? Name some of its types.
11. What is a calomel electrode? Describe its construction: Why it is used as reference electrode in place of a standard hydrogen electrode?
12. What is an electrochemical series?
13. Why are standard potentials of Zn/Zn^{+2} and Cu/Cu^{+2} electrodes opposite in sign?
14. Describe the construction and working of $H_2 - O_2$ fuel cell.
15. Give the cell rotation for a concentration cell.
16. Describe the construction of a glass electrode. Explain how the pH of a solution is determined using the glass electrode.
17. What are primary and secondary reference electrodes?
18. Write a note on decomposition potential.
19. Write notes on: (*i*) Weston standard cell, (*ii*) significance of standard electrode potential.

20. Distinguish: (*i*) a reversible cell from an irreversible cell

(*ii*) a galvanic cell from a concentration cell.

21. What is Nernst equation? State its utility.

22. Derive an expression for electrode potential of an M/M^{n+} electrode?

23. What is fuel cell? Give detail of one such cells.

24. What are reversible and irreversible cells?

25. Explain the construction of Ni-Cd cell.

26. Give the cell reaction of the following:

(*i*) Zn^{+2}/Zn, (*ii*) $AgCl(s), Cl^-/Ag$, (*iii*) Fe^{+3}/Fe^{+2} Pt, (*iv*) $2H^+/H_2(g)$ Pt.

27. Give the use of Ag-AgCl electrode.

28. Describe the construction and working of Daniel cell.

29. Explain the construction and working of lead storage battery.

30. How is single electrode potential measured experimentally?

31. Write down the electrode reactions and overall cell reactions for the following cells. Also give the expression for their e.m.f.

(*i*) $Zn \mid ZnSO_4 \parallel CuSO_4/Cu$

(*ii*) $(Pt)\ H_2\ (1\ atm) \mid HCl/AgCl(s), Ag$

32. Describe the potentiometric methods for

(*i*) Determination of pH of a solution.

(*ii*) Calculation of solubility product of AgCl.

33. The reaction $H_2 + Cl_2 + 2H_2O \rightleftharpoons 2H_2O + 2Cl^-$ has an equilibrium constant $K = 10^{46}$ at 25°C. Calculate E° at 25°C for cell: $(Pt)\ H_2/HCl\ (aq)/Cl_2\ (Pt)$.

34. The standard potentials of Cu/Cu^{+2} and Cu/Cu^+ system are 0.337 and 0.530 V, respectively. Give the equilibrium constant for the reaction,

$$2Cu^+ \rightleftharpoons Cu^{2+} + Cu$$

35. Zinc rod is dipped in 0.01 (M) $ZnSO_4$ solution at 25°C. Give the single electrode potential of Zn-half cell, if

$$E^\circ_{cell} = +\ 0.763\ V\ (0.8192\ V)$$

36. Calculate the e.m.f. of voltaic cell: $Fe \mid Fe^{+2}\ (aq) \parallel Cu^{+2}(aq) \mid Cu$. Given the electrode potentials of Cu and Fe are 0.34 V and –0.44 V, respectively. (0.78 V).

37. Will a reaction take place if an Ag-bar is placed in a solution of $FeSO_4$? Explain using the following data:

$$\in^\circ_{Ag^+/Ag} = 0.799\ V, \text{ and } \in^\circ_{Fe^{+2}/Fe} = 0.44\ V\ (-\ 1.239\ V)$$

38. Calculate the e.m.f. of a Daniel cell at 25°C, when the concentrations of $ZnSO_4$ and $CuSO_4$ are 0.001 M and 0.1 M respectively. The standard potential of the cell is 1.1 V (1.13 V).

39. Calculate the e.m.f of the following concentration cell:

$$Ag/Ag^+\ (0.1\ M) \parallel Ag^+\ (1M) \mid Ag$$

[**Ans.** 0.0592 V]

40. The e.m.f. of the cell at 25°C

$$Hg(l) \mid Hg_2Cl_2(s), KCl(sol)\ (1.0\ N) \mid Quinhydrone \mid Pt$$

is 0.212 V. Calculate the pH of the solution. The potential of the normal calomel electrode is 0.2812 V and E° for the quinhydrone electrode is 0.6996 V, both at the same temperature.

[**Ans.** 6.5]

41. Calculate the valency of mercurous ions with the help of the following cell:

$$\text{Hg} \mid \text{HgNO}_3 \text{ (0.001 N) in 0.1 N HNO}_3 \mid \text{HgNO}_3 \text{ (0.01)} \mid \text{Hg}^+$$ [**Ans.** 2]

42. Find the equilibrium constant of the reaction at 25°C.

$$2\ \text{Fe}^{+3} + \text{Sn}^{+2} \rightleftharpoons 2\ \text{Fe}^{+2} + \text{Sn}^{+4}$$

from $\in^\circ$ values given in the Table 10.2. [**Ans.** $K = 10^{21}$]

43. Calculate the equilibrium constant of the reaction at 25°C.

$$\text{Fe}^{+3} + \text{I}^- \rightleftharpoons \text{Fe}^{+2} + \frac{1}{2}\ \text{I}(s)$$

from the $\in^\circ$ (reduction) values

$$\in^\circ_{\text{Fe}^{+2}/\text{Fe}} \Rightarrow 0.44\ \text{V}, \quad \in^\circ_{\text{Fe}^{+3}/\text{Fe}} \Rightarrow 0.036\ \text{V}$$

$$\in^\circ_{\text{I}(s)/\text{I}^-} \Rightarrow 0.5355\ \text{V}.$$ [**Ans.** $K = 166$]

44. Suggest a cell, to calculate ionic product of water. [**Ans.** H_2-electrode || O_2-electrode]

45. When calomel electrode is connected to H_2-electrode at 18°C, gives e.m.f. value ⇒ 0.5622 V. Calculate the pH of the solution. [**Ans.** 5.4]

46. E.m.f. of the cell, which is constructed by connnecting H_2-electrode to normal calomel electrode, at 25°C in 0.664 V. Calculate its (*i*) pH and (*ii*) H^+ concentration. [**Ans.** (*i*) 6.5, (*ii*) 3.16×10^{-7}]

11

Phase Rule

INTRODUCTION

The phase rule was deduced by Willard Gibbs (who introduced the free energy function, G in thermodynamics) in 1876, and it was later on developed by Ostwald, Van't Hoff and others. We all know that a homogeneous system is one in which both the reactants and products are of one phase (*i.e.,* solid, liquid or gas) and a heterogeneous system is one in which they are in different phases. Before stating the rule, the terms—phases, components and degrees of freedom—need to be explained.

1. **Phase.** "Phase is defined as any physically distinct portion of matter which itself is homogeneous and uniform in composition, mechanically separable from other parts by definite boundary surfaces".

(*a*) Thus, gases being mutually miscible in all proportions will constitute one phase only. Thus mixture of H_2 and O_2 constitutes single phase.

(*b*) Mixture of two completely miscible liquids has single phase.

(*c*) Solution of a solute in a solvent constitutes single phase such as salt solution in water.

(*d*) If two liquids are immiscible, they form two phases such as chloroform and water.

(*e*) Except solid solutions all different kinds of solids form different phases.

(*f*) If we keep a mixture of miscible liquids in a closed vessel, above the liquid mixture, there will be some vapors of the liquids, so the system will have two phases.

(*g*) At freezing point, water consists of three phases:

$$\text{Ice}(s) \rightleftharpoons \text{Water}(l) \rightleftharpoons \text{Water vapor}(g)$$

(*h*) A heterogeneous mixture of the type

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

consists of three phases—two solid and one gaseous.

2. **Component.** Component is defined as the smallest number of independently variable constituents, in terms of which the composition of each phase can be expressed in the form of a chemical equation.

This concept of component can be explained in connection with phase rule with the help of the following examples.

(*a*) In ice-liquid water-water vapor system, the composition of each phase can be expressed by a single component *i.e.,* H_2O. So, it is a one-component system.

(*b*) A salt solution will be a two-component system.

(*c*) In the thermal decomposition of $MgCO_3$,

$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g).$$

The composition of each of the three phases can be expressed in terms of at least any two of the three constituents, then the composition of any one phase can be represented as

Phase: $MgCO_3 = MgCO_3 + OMgO$

Phase: $MgO = O\,MgCO_3 + MgO$

Phase: $CO_2 = MgCO_3 - MgO$

So it is a two-component system.

(*d*) Suppose a solid dissociates into a number of gaseous substances in a closed vessel

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

The overall composition of the dissociated vapour (NH_3, HCl) is exactly the same as that of the undissociated substance (NH_4Cl). Thus, the number of component is one. However, if NH_3 or HCl is introduced in the system in excess, the system becomes a two-component system.

(*e*) In the system of sodium sulfate-water, various phases may exist like Na_2SO_4; Na_2SO_4, $7H_2O$; Na_2SO_4, $10H_2O$; ice; solution and vapor. The composition of each phase can be expressed in terms of Na_2SO_4 and H_2O, so the system is a two-component system.

(*f*) In the equilibrium,

$$Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2$$

the minimum number of components required to express the composition is three and hence is a three-component system.

3. **Degrees of Freedom or Variance.** The number of degrees of freedom of a system is the minimum number of the independent variables of a system, such as temperature, pressure and concentration, which can completely define the equilibrium of a system.

(*a*) A system consisting of pure gas or gas mixture. It is a one component, one-phase system. If the temperature and pressure are specified, the volume of the gas is known. Hence the degree of freedom is two.

(*b*) The system ice(s) $\rightleftharpoons$ Water(l) $\rightleftharpoons$ vapor(g) is one-component, three-phase system and all these three phases can co-exist at the freezing point of water at a particular temperature and pressure. So this system will have no degree of freedom *i.e.,* it is a non-variant or invariant system. If temperature or pressure is altered, one of the phases will disappear and the three phases will not be in equilibrium.

(*c*) For the system, NaCl(s) $\rightleftharpoons$ NaCl-Water(aq) $\rightleftharpoons$ $H_2O(g)$ the solubility at the saturation point is fixed by either temperature or pressure, so the system is univariant.

(*d*) For the simple system water (l) $\rightleftharpoons$ Water vapor (g) temperature or the pressure is required to define the system, hence the system is univariant.

The Phase Rule

The rule can be stated as "the sum of the number of phases and the degrees of freedom of any system exceeds the number of components by two, provided that the only significant external factors acting are temperature, pressure and concentration and not influenced by gravity, surface action, magnetic or electric forces.

$$\boxed{F = C - P + 2}$$

where C is the number of components, P the number of phases and F is the degree of freedom.

Examples 1.

(*a*) Water(l) $\rightleftharpoons$ Vapor (g)

$C = 1, P = 2.$ Hence $F = 1 - 2 + 2 = 1.$

(*b*) For water at critical point

Ice (s) $\rightleftharpoons$ Water (l) $\rightleftharpoons$ Vapor (g)

$C = 1, P = 3.$ Hence $F = 1 - 3 + 2 = 0.$

(*c*) For $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

$C = 2, P = 3.$ Hence $F = 2 - 3 + 2 = 1.$

Advantages of phase rule

1. Phase rule is applicable to both physical and chemical equilibria.
2. The nature or quantities of the components do not have any role.
3. Different systems behave in a similar fashion if they have same degrees of freedom.
4. The nature of the system can be predicted under different sets of variable conditions like whether different substances can co-exist or be interconverted under different sets of conditions.
5. The equilibrium system requires no information regarding its molecular nature or micro structure.

Limitations of phase rule

1. This rule can be applied only to systems that have attained equilibrium, so it is of no value for systems which may attain equilibrium very slowly.
2. The rule considers only the number of phases and not their amounts present, hence if a trace amount of a phase is present and not taken into account, the rule is inapplicable.
3. It states that all the phases must be present under the identical conditions of temperature and pressure.

Phase diagram

The conditions of equilibrium between different phases of a substance can be shown by plotting temperature and pressure as variables and the diagram is called the phase diagram. From the phase diagram, the properties like melting point, boiling point, triple point can be found.

The Water System

This system consists of three phases—ice, water, vapor and one-component H_2O.

From Fig. 11.1, we find that curve BO is the vapor pressure curve of ice which indicates that ice has a small but definite vapour pressure. The point B has a natural limit of – 273°C, beyond which the two phases merge.

OA is the vapour pressure curve of water, also called the vaporisation curve. The OA curve terminates at A, the critical temperature of +374°C above which distinction between liquid and vapor vanishes.

For both of these curves OA and OB, they are one-component systems with two phases (C = 1, P = 2).

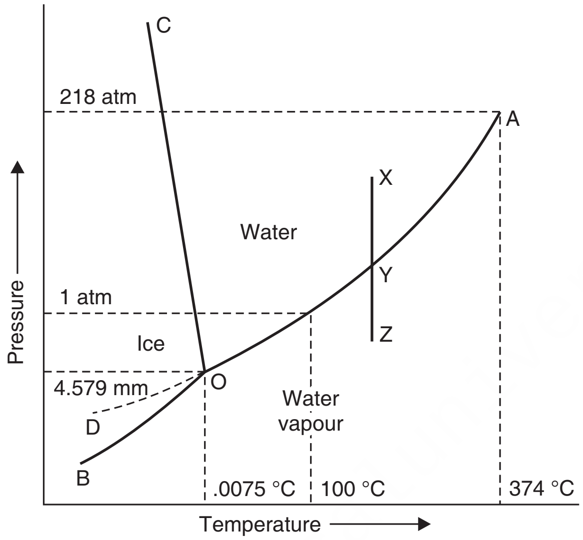


Fig. 11.1 The phase-diagram for water (not to scale).

Since F = 1 there is only one degree of freedom *i.e.,* if the temperature is fixed, all other properties are also fixed.

The point of intersection of these two curves is point O, called the triple point, because the three phases, ice-water-vapour are in equilibrium, *i.e.,* it is actually the melting point of ice *i.e.,* 0.0098°C under 4.579 mm pressure and at this point C = 1, P = 3, Hence F = 0 *i.e.,* at this point neither temperature nor pressure can be altered without the disappearance of one of the three phases. The curve OC represents the change of melting point of ice with pressure. The inclination of OC towards the pressure axis shows that melting point of ice is decreased by increasing pressure.

The curves OA, OB and OC divides the whole region into three portions AOC, BOC and AOB in which only one phase is present and so the system becomes bivariant and to locate any point in these areas, temperature as well as pressure is to be known because the degree of freedom $F = 1 - 1 + 2 = 2$.

The dotted portion OD, which is the continuation of the curve AO below 0°C is the vapor pressure curve of supercooled water below 0°C. This curve represents a metastable system. This curve OD runs above the vapor pressure curve for ice for the above reason and on slight disturbance the supercooled water immediately changes to the stabler form *i.e.*, ice.

Sulfur System. Sulfur system is another one-component system with a slight more complexity. Sulfur at low temperature is in the rhombic form and at high temperature in the monoclinic form. The other two modifications are liquid sulfur and sulfur vapor.

In the phase diagram for sulfur (Fig. 11.2), AB is the vapor pressure curve of rhombic sulfur which is stable upto 95°C (0.006 mm) at B. BC is the similar curve of monoclinic sulfur and the point B is the transition point between the two allotropes of sulfur. At B, rhombic and monoclinic sulfur have same vapor pressure and co-exist with sulfur vapor.

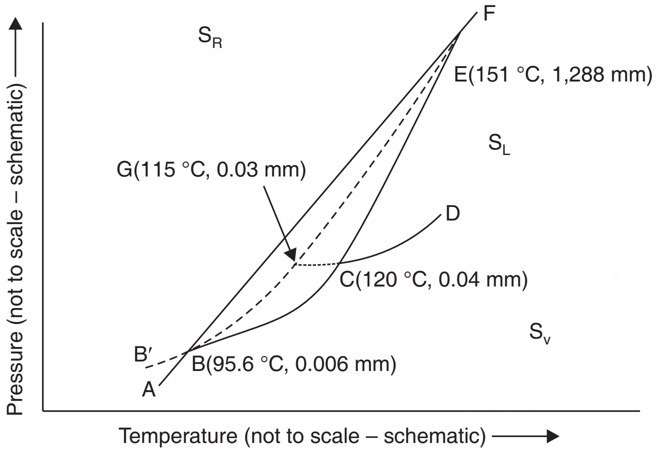


Fig. 11.2 The sulphur system.

Hence, B is actually the triple point. Again at C (120°C, 0.04 mm) monoclinic sulfur melts and CD is the vapor pressure curve of liquid sulfur. The lines BE and CE represent changes in transition temperature and melting point, respectively, with pressure. These two lines meet at E (151°C, 1288 atm) which is again a triple point where rhombic, monoclinic and liquid sulfur co-exist in equilibrium.

Highlights:

The Phase rule: "The sum of the number of phases and the degrees of freedom of any system exceeds the number of components by two provided that the only significant external factors acting are temperature, pressure and concentration."

$$\boxed{F = C - P + 2}$$

Phase (P): Phase is defined as any physically distinct portion of matter which is itself homogeneous and uniform in composition, mechanically separable from other parts by definite boundary surfaces.

Component (C): Component is defined as the smallest number of independently variable constituents in terms of which the composition of each phase can be expressed in the form of a chemical equation.

Degrees of freedom (F): It is the minimum number of independent variables of a system, which can completely define the equilibrium of a system, such as temperature, pressure, concentration.

The conversion of rhombic to monoclinic is slow and hence if rhombic sulfur is heated quickly it bypasses the transition point B without change and finally melts to liquid sulfur at G. Curve BG is the metastable vapor pressure curve of rhombic sulfur. These metastable systems are represented by dotted curves. There are three stable and one unstable triple points and four phases co-exist nowhere in the curve in equilibrium.

At the triple point $F = C - P + 2 = 1 - 3 + 2 = 0$ *i.e.*, zero variant and three phases coexist.

Along the lines AB, BC, CD, BE, CE and EF two phases co-exist and $F = C - P + 2 = 1 - 2 + 2 = 1$, *i.e.,* the system is univariant and either temperature or specific volume determines the system completely.

From the diagram it is also found that under ordinary pressure, cooling of liquid sulfur leads to solid monoclinic variety along CE but under high pressure, rhombic sulfur separates on cooling liquid sulfur along EG.

Thus actual observation can be explained perfectly in terms of phase rule.

Phase Rule for Two-Component Alloy Systems

For a two component system, the highest degree of freedom $F = C - P + 2 = 2 - 1 + 2 = 3$ *i.e.,* the behaviour of a system may be represented by a three-dimensional diagram of pressure, temperature and composition which cannot be drawn on a paper.

In the case of a two component alloy system there is a solid-liquid equilibrium of the alloy and the vapor phase is practically absent and hence the effect of pressure can be considered to be negligible. Thus now the system is present at atmospheric pressure and it remains constant, which will reduce the degrees of freedom by one *i.e.,* $F = C - P + 1$ and the system is called **condensed system**. The variables reduce to temperature and composition and hence the diagrams are represented on temperature-composition equilibrium.

Eutectic Systems

The cooling curve of a pure substance can be represented as Fig. 11.3 (*a*). When the pure liquid is cooled it reaches its freezing point *b* when the pure solid makes its appearance and the temperature remains constant until the total liquid is solidified (*bc*) and then again temperature falls along *cd*.

The cooling curve of a mixture of solid is represented by Fig. 11.3 (*b*). When a solid solution is cooled at freezing point, a solid phase appears, the rate of cooling is altered and there is a break in the cooling curve. The temperature decreases continuously but at different rate than before freezing point. If the mixture becomes eutectic the temperature falls until the eutectic point is reached. The system becomes invariant, temperature remains constant until total solidification occurs (along *cd*) and again temperature falls uniformly along *de*.

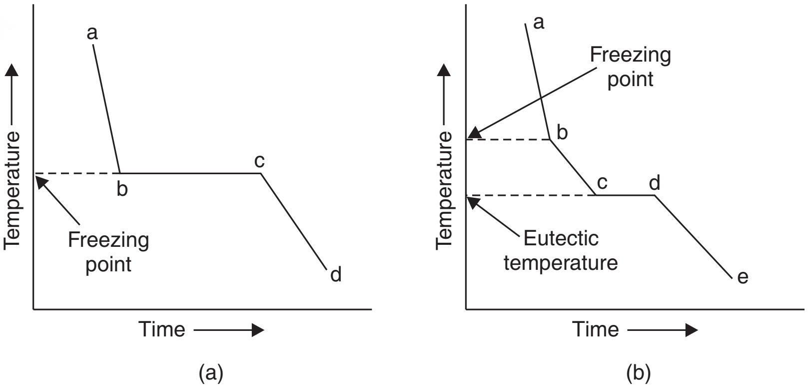


Fig. 11.3 Cooling curves.

From the cooling curve of any mixture of definite composition freezing point and eutectic temperature both can be obtained.

The freezing point of a system varies with the composition but the eutectic point remains constant.

If the composition of the mixture coincides with the eutectic composition, there is no double break but the curve mimicks that of pure component.

By plotting freezing point against composition, T-C curve is obtained for alloy system. It is also necessary to know the freezing points of the pure components.

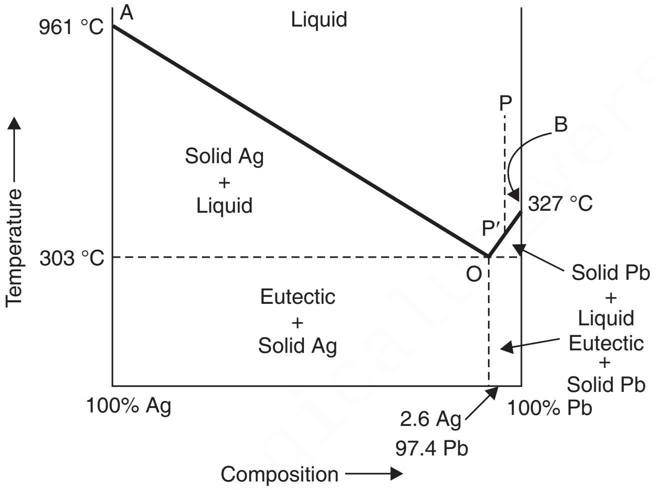


Fig. 11.4 T-C diagram of Pb-Ag system.

The composition corresponding to a freezing point gives the composition of the alloy.

A binary system consisting of two substances which do not react chemically but is miscible in all proportions in liquid phase is called "eutectic system".

A solid solution of two or more substances having lowest freezing point than all the mixture of the components is called "eutectic mixture" and the minimum freezing point attainable corresponding to the eutectic mixture is "eutectic point".

The eutectics are applied for constructing safety devices in boilers, automobiles etc.

Lead-Silver-Sample (Eutectic System)

It is a two-component system with four possible phases—solid Ag, solid Pb, solution of Ag + Pb and vapor. At constant atmospheric pressure, the vapour phase is absent and the condensed phase rule is applicable as F = C – P + 1.

Curve AO represents the freezing point curve of Ag. A is the melting point (961°C) of Ag. AO represents the curve along which the melting point of Ag falls gradually on addition of Pb till the lowest point (303°C) is reached when the solution gets saturated with Pb and hence any extra Pb added gets precipitated as solid phase and so also melting point of Ag cannot be lowered any further. This point O is the eutectic point (2.6 % Ag and 97.4 % Pb) and the whole mass at this point crystallizes out with the above fixed composition.

Similarly, another curve BO is obtained starting from the melting point of pure lead (327°C) at B, as Ag is added the melting point gradually falls till the lowest point O is reached with the above mentioned composition. According to reduced phase rule equation, the system is univariant along AO and BO and at point O, F = 3 – P = 3 – 3 = 0 *i.e.,* invariant, which is the eutectic temperature and a lead-silver mixture can never have a melting point below the eutectic temperature.

The region above the curve AO and BO represents solution of Pb and Ag and below the curve AO represents solid eutectic with crystalline Ag and below the curve BO represents solid eutectic with crystalline Pb.

Tin-Magnesium System

The equilibrium diagram of tin (Sn) and magnesium (Mg) is shown in Fig. 11.5. When Mg is added to Sn, the melting point of Sn (232°C) lowers along PQ. At O (210°C) a new solid phase of a compound of Sn and Mg begins to separate alongwith Sn. So Q is the invariant eutectic point. Further addition of Mg raises the melting point along QR and the maximum is reached at R. Thus along QR from molten alloy only solid compound crystallizes out in equilibrium with the liquid. At R the composition of the liquid and the solid phase is the same. This temperature (783°C) is the congruent melting point of the compound, which is Mg_2Sn.

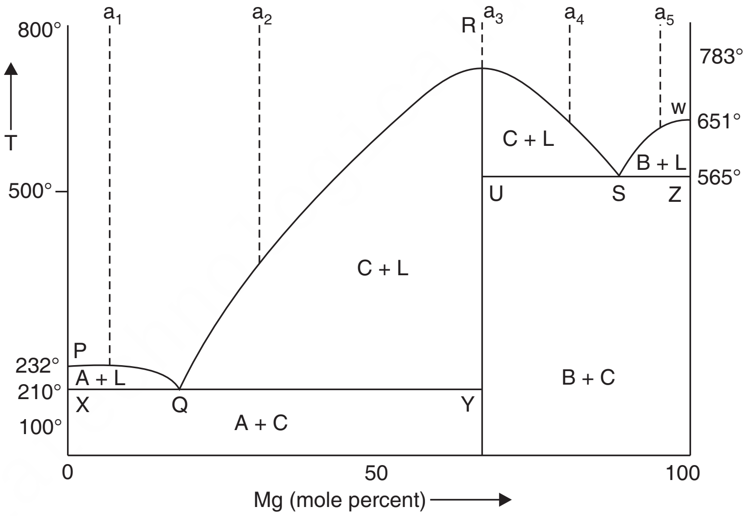


Fig. 11.5 Phase diagram of the system Sn-Mg: A—Sn crystals, B—Mg crystals, C—compound Mg_2Sn, L—liquid.

Further increasing the magnesium, the freezing point decreases along RS and reaches the second eutectic point S (565°C). Again on increasing the Mg the freezing point rises along SW. At the eutectic points the solid compound is in equilibrium with either solid tin or solid Mg. The hump in the diagram indicates the formation of a compound. The compound formed is stable and has its melting point at the maximum. The melting points and the eutectic points P, R, W, Q, S are invariant and the areas in between the lines are univariant.

Iron-Carbon Alloy System

The equilibrium diagram of Fe-C is especially useful to understand the heat treatment of steel. The phase-diagram of iron-iron carbide system is used upto 6.67% weight of carbon. Pure iron exists in three allotropic modifications α, γ and δ. C atoms being small compared to iron atoms form only interstitial solid solutions and the solubility of C in these allotropes is quite different.

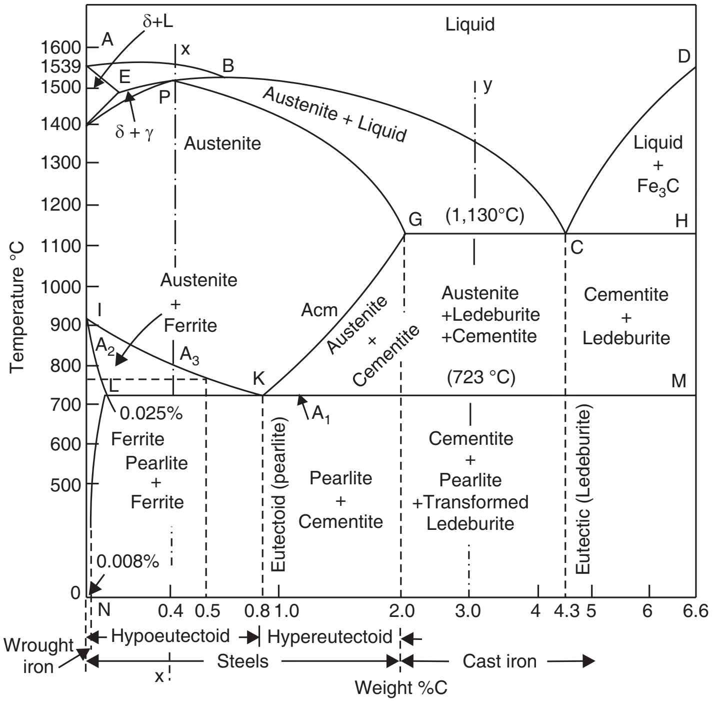


Fig. 11.6 Equilibrium diagram for Fe-C system.

In the phase diagram, the curve ABCD is the liquidus line and AEPGCH is the solidus line. Above the liquidus there is only liquid phase whereas below the solidus there is only solid phase and between the two lines both phases are present. On dissolving C in molten iron (δ form at 1535°C) the freezing point is lowered until at eutectic temperature of 1130°C corresponding to 4.3% C by weight. On further addition of C, freezing point increases upto 6.67% C content and it is called cementite.

Pure iron changes from δ to α form at a temperature of 910°C. The phase diagram indicates that upto 0.088% C is commercially pure iron, whereas 0.088% to 2% C content is steel and C content above 2% represents cast iron.

From the curve, AEB area represents δ-iron and liquid. Area DCH represents cementite and liquid. Area BCGP represents austenite and liquid and finally PGKI represents δ-iron (*i.e.* austenite) only.

The transformation of one solid phase into another takes place at the critical temperatures indicated on the diagram.

For an iron-C alloy (cast iron) containing 3% C, freezing begins at 1270°C. On further cooling, austenite separates out from the liquid, then at 1130°C, the mixture is austenite containing 2% C and liquid has eutectic composition. Hence further removal of heat leads to total solidification of the liquid to ledeburite, a mixture of austenite and cementite. Cooling further leads to the decomposition of the eutectic mixture of cementite and finally at 723°C the residual austenite transforms to pearlite and at temperature below 723°C, all the ledeburite is transformed into pearlite and cementite mixture.

The Fe-C phase diagram shows the phases, which are formed when the cooling rate is slow *i.e.,* when equilibrium is attained. But with faster cooling rates metastable phases like martensite and bainite are formed which are not shown in the phase diagram.

Highlights:

Condensed phase rule. For two-component alloy systems it is considered that there is practically no gas phase and the effect of pressure is negligible. So the system is considered to be under atmospheric pressure which reduces the degrees of freedom by one and hence,

$$\boxed{F = C - P + 1}$$

Triple point. It is the point of a system at which the gaseous, liquid and solid phases of a substance can co-exist in equilibrium. At triple point the system is non-variant.

Eutectic point. A solid solution of two or more substances having lowest freezing point is the eutectic mixture and the minimum freezing point attained is the eutectic point.

Congruent melting point. A compound possesses congruent melting point if it melts to give a liquid having the composition same as the solid.

SOLVED PROBLEMS

Problem 1. *An alloy of Cd and Bi contains 25% Cd. Find the mass of eutectic in 1 kg of the alloy, if the eutectic system contains 40% Cd.*

Sol. In the eutectic system, 40 % is Cd and hence 60 % is Bi.

In 1 kg alloy content of Cd is 25%, *i.e.*, 250 gm.

∴ Corresponding to 250 gm Cd, the content of Bi in eutectic is $\frac{250 \times 60}{40}$ gm = 375 gms.

∴ The mass of eutectic in 1 kg alloy is (250 + 375) gm = 625 gm. **Ans.**

Problem 2. *An alloy AB contains 40% A in 1 kg. AB on cooling forms eutectic containing 60% A and 40% B and the rest of B. What is the amount of B formed during eutectic formation?*

Sol. In 1 kg of AB, A = 40 % = 400 gm and B = 60% = 600 gm.

The eutectic mixture contains 60 % A and 40 % B.

∴ Corresponding to 400 gm A, the content of B = $\frac{400 \times 40}{60}$ = 266.7 gm

∴ Amount of B separated out = (600 – 266.7) gm = 333.3 gm. **Ans.**

SHORT QUESTIONS AND ANSWERS

Q. 1. State Phase rule.

Ans. See page 267.

Q. 2. What is condensed phase rule?

Ans. See page 272.

Q. 3. Define the following terms:

(a) Phase (b) Component (c) Degrees of freedom.

Ans. (*a*) See page 266.

(*b*) See page 266.

(*c*) See page 267.

Q. 4. What is triple point?

Ans. See page 269.

Q. 5. What is an invariant system? Give an example.

Ans. A system in which the degree of freedom is zero is called an invariant system. This signifies that no condition is required to define the system at that point.

Example: Triple point of water is where ice, water and water vapour are in equilibrium.

Q. 6. What is the significance of triple point?

Ans. A triple point for a system is invariant. It is constant for a substance at a set of temperature and pressure conditions. If temperature or volume is altered, one phase of the substance disappears and the system becomes univariant from invariant.

Q. 7. State two important merits of phase rule.

Ans. (*i*) Phase rule is applicable to both physical and chemical equilibria.

(*ii*) Phase rule helps to predict the behaviour of a system under different sets of conditions.

Q. 8. State limitations of phase rule.

Ans. (*i*) Phase rule can be applied only for a system which is in equilibrium.

(*ii*) Phase rule conditions that all phases of the system must be present simultaneously under similar set of conditions.

Q. 9. What do you mean by eutectic? What is the eutectic composition of Pb-Ag System? Give one application of eutectics.

Ans. Eutectic is a solid solution of two or more substances having the lowest freezing point of all the possible mixture of those components.

Eutectic composition of Pb-Ag system → 97.4 % Pb, 26% Ag. By suitable choice, very low melting alloys can be selected for preparing safety devices like fire sprinklers, plugs in automobiles etc.

Q. 10. State (i) number of phases and (ii) number of components for

$$\mathbf{Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g).}$$

Ans. (*i*) There are two solid phases—Fe and FeO— and one gaseous phase of a mixture of $H_2O(g)$ and $H_2(g)$. So there are three phases in equilibrium.

(*ii*) The minimum number of components required to express the composition of each phase is three.

Q. 11. How many degrees of freedom are there for the following systems?

(i) Water(l) $\rightleftharpoons$ Water vapour(g)

(ii) Gaseous mixture of H_2 and O_2

Ans. (*i*) For Water(l) $\rightleftharpoons$ Water vapour(g) system either temperature or pressure is to be specified to define the system completely. Hence degree of freedom is **one**.

(*ii*) For the gaseous mixture of H_2 and O_2 both the pressure and the temperature are to be specified to define the system completely, so the system has **two** degrees of freedom.

Q. 12. For a two-component alloy system of Pb and Ag, state the degrees of freedom (i) as per phase rule and (ii) as per condensed phase rule.

Ans. (*i*) For a two-component alloy system of Pb and Ag when P = 1, degree of freedom according to phase has the highest value of F = C – P + 2 = 2 – 1 + 2 = 3.

(*ii*) As per condensed phase rule:

For solid-liquid equilibrium of alloy, practically no gas is present and hence at atmospheric condition the pressure remaining constant, degrees of freedom reduces by one and F becomes F = C – P + 1 = 2 – 1 + 1 = 2.

EXERCISES

1. State phase rule.
2. Define the following terms:
phase, component, degrees of freedom.
3. What is condensed phase rule?
4. What is triple point?
5. Write a brief note on: eutectic point, metastable state.
6. Write down the limitations of phase rule.
7. What is "phase diagram"? Explain (*a*) triple point and (*b*) eutectic point with reference to phase diagram.
8. Draw and explain the phase diagram of ice-water-water vapor system and show the variation of melting-point of ice with pressures.
9. What are the merits and the limitation of phase rule?
10. Discuss the application of phase rule to sulfur system with special reference to triple points and metastable equilibrium.
11. What are meant by invariant and bivariant degrees of freedom?
12. Draw and explain the phase diagram of a binary alloy system with simple eutectic formation.

Objective Type Questions MCQ

1. Gibbs phase rule is:
(*a*) F + P = C + 2 (*b*) F – C = P + 2 (*c*) P + C = F + 2.
2. Condensed phase rule equation is:
(*a*) F = C – P + 2 (*b*) F = C – P + 1 (*c*) F = C + P – 2.
3. The maximum number of degrees of freedom for a two-component alloy system is
(*a*) 3 (*b*) 1 (*c*) 2.
4. The composition of the eutectic mixture of Pb-Ag system is
(*a*) 2.6% Pb, 97.4% Ag (*b*) 2.6% Ag, 97.4 % Pb (*c*) 26% Pb, 74% Ag.
5. In the thermal decomposition of $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ the system is a
(*a*) one component (*b*) two component (*c*) three component.
6. Heterogeneous mixture of $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ consists of
(*a*) one phase (*b*) two phases (*c*) three phases
7. In the water system at triple point, the system is
(*a*) univariant (*b*) trivariant (*c*) invariant.
8. Condensed phase rule has two variables, namely
(*a*) temperature and concentration.
(*b*) temperature and pressure
(*c*) pressure and concentration
9. Eutectic mixture has:
(*a*) highest melting point. (*b*) variable composition (*c*) lowest melting point.
10. Number of components of the system $Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$
(*a*) two (*b*) three (*c*) four.

12

Colloids

INTRODUCTION

Thomas Graham (1861) while doing his classical researches on liquid diffusion observed two classes of substances.

Solution of some substances could readily pass through animal and vegetable membranes. To this class belonged almost all inorganic acids, bases and salts and many organic compounds like urea, sugar etc. Graham called them **crystalloid** as most of them were crystalline.

The other class of substances are diffused very slowly in solution and the solution could not pass through the membrane, they were called colloids (from the Greek word *Kolla* meaning glue, which is a member of this class). Other members are starch, gelatin, albumin, proteins and other amorphous substances.

Graham's view has undergone changes since it has been seen that every substance can exhibit colloidal properties under suitable conditions. Thus we now define colloidal state as: a two phase heterogeneous system in which one phase is dispersed in a fine state of subdivision having diameter of 10^{-4} to 10^{-7} cm in another medium termed the continuous or dispersion medium. In a colloidal solution there exists a discontinuous phase called the dispersed phase and the continuous dispersion medium, and also a stabilizing agent which does not allow the dispersed phase to coalesce and settle.

Classification of Colloids

(*a*) **Classification based on dispersed phase and dispersion medium** which may be either solid or liquid or gas and so the following types (Table 12.1) of colloids are formed.

Table 12.1 Types of colloidal systems

Dispersion medium	*Dispersed phase*	*Colloidal system*	*Examples*
Gas	Liquid	Liquid aerosol	Mist, Fog, Cloud, Insecticide spray,
	Solid	Solid aerosol	Smoke, Fume
Liquid	Gas	Foam	Foam, Froth, Whipped cream, Lemonade
	Liquid	Emulsion	Milk, Cream, Mayonnaise,
	Solid	Sol	Glue, Paints, Starch paste, Milk of Magnesia, Gold sol, As_2O_3, S, FeO_3 or AgCl sol in water
Solid	Gas	Solid foam	Pumice stone, bread dough, Lava, Styrene foam, Rubber.
	Liquid	Gel	Curd, Jelly, Cheese, Butter, Shoe polish, Pearl ($CaCO_3$ with water).
	Solid	Solid sol	Gems, Alloys, Minerals

(*b*) Classification based on affinity for solvent

When there is a strong affinity between the dispersed phase and the dispersion medium the colloid is known as **lyophilic colloid,** while if there is no apparent affinity it is called **lyophobic colloid.** The main differences between these two classes of colloids are summarised in Table 12.2.

Table 12.2 Characteristics of lyophilic and lyophobic sols

Lyophilic sol	*Lyophobic sol*
(*i*) Stable	(*i*) Unstable
(*ii*) The particles may or may not migrate in an electrical field.	(*ii*) The particles are charged and hence move towards electrode in an electrical field.
(*iii*) Viscosity is much higher than that of the medium.	(*iii*) Viscosity is same as that of the medium.
(*iv*) They are reversible sols.	(*iv*) They are irreversible.
(*v*) They are self-stabilized due to the strong attraction between two phases.	(*v*) They are much less stable, stabilizer is reqd. for stabilization.
(*vi*) Surface tension is much lower than that of the medium.	(*vi*) Surface tension is same as that of the medium.
(*vii*) They are not easily precipitated by the addition of electrolytes.	(*vii*) They are coagulated easily by adding electrolyte.
(*viii*) Starch gelatin, gum, albumin are lyophilic colloids.	(*viii*) Colloidal metals, metallic sulfides are lyophobic colloids.
(*ix*) Not visible under ultramicroscope.	(*ix*) Visible under ultramicroscope.
(*x*) Prepared simply by direct dissolving.	(*x*) Prepared by indirect methods.

(*c*) Classification based on nature of dispersed phase

(*i*) *Multimolecular colloids:* When the dispersed phase consists of aggregates of atoms or molecules and the main attractive force between them is the van der Waals force of attraction. They are lyophobic in nature.

Examples: Gold sol and Sulfur sol.

(*ii*) *Macromolecular colloids:* A large number of small molecules combine to form a giant molecule held by covalent bonds having a colloidal dimension are called macromolecular colloids. They are lyophilic and have gold numbers.

Examples: Proteins, Polysaccharides, Gums, Synthetic rubber, Nylon etc.

(*iii*) *Association colloids:* On increasing concentration, the solute molecules or ions come closer to form aggregate spontaneously of colloidal dimensions, called micelles are associated colloids. *Example:* Soaps and synthetic detergents.

Sodium oleate forms micelles and contains a lyophobic group ($C_{17}H_{33}^+$) and a lyophilic group (—COONa), the hydrocarbon portion inside the micelle, while the ionised groups are at the surface. They move freely in an electric field and the solution has high conductivity. The minimum concentration at which the micellization begins is called the **critical micellization concentration** (cmc). These colloids play very important role in solubilizing solvent repellant substances, such as water insoluble dyes are solubilized in soap solutions.

Preparation of Colloidal Solutions

The main methods of preparation of colloidal solutions are (*a*) Condensation method (*b*) Dispersion method.

(A) **Condensation Method:** In this method, a large number of particles of molecular size are allowed to coalesce or condense to form bigger particle of colloidal dimension. The various processes used are:

(*i*) *By exchange of solvent:* Sulfur or phosphorus is not directly soluble in water. If an alcohol solution of S or P is poured into water, colloidal solution of S or P is formed.

(*ii*) *By changing physical state:* Hg or S sols are produced by allowing their vapours to pass through cold water. Ammonium citrate is added to stabilize the solution.

(*iii*) *By controlled condensation:* Prussian blue sol is obtained by precipitating it in presence of a protective colloidal system like starch.

(*iv*) *Chemical methods:* (*a*) by double decomposition, colloidal solution of arsenious sulfide is made by passing H_2S gas, through a suspension of As_2O_3 in water, until saturation.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O.$$

Sols of insoluble inorganic salts are prepared in this way.

(*b*) *By reduction:* Colloidal solutions of metals such as Ag, Au, Pt in water can be prepared by reducing aqueous solution of their salts by reductants like formaldehyde, carbon monoxide, hydrazine etc.

Thus gold sol is obtained by treating a solution of gold chloride with formaldehyde (0.3 %).

$$2AuCl_3 + 3HCHO + 3H_2O \longrightarrow 2\,Au(sol) + 3HCOOH + 6HCl$$

The liberated acid is neutralized by K_2CO_3 to stabilize the sol.

(*c*) *By hydrolysis:* Colloidal solutions of many oxides and hydroxides of iron, aluminium can be prepared by this method. On adding a freshly prepared saturated solution of $FeCl_3$ dropwise on boiling water, hydrolysis of $FeCl_3$ takes place with the formation of deep red colloidal sol of ferric hydroxide.

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3\,(sol) + 3HCl$$

(*d*) *By oxidation:* Sulfur sol is prepared by passing H_2S through a solution of SO_2 in water until the smell of SO_2 is removed. The solution on boiling with saturated NaCl solution precipitates out S, on filtration, which is washed free of Cl^- and finally dissolves on further addition of water.

(B) **Dispersion method:** In this method, the bigger or large particles are broken down to colloidal dimension and dispersing them in a medium to form colloidal solution. The methods used are:

(*i*) *By mechanical dispersion*: Many substances of large size are ground and dispersed in a medium to get a coarse suspension which is then passed through a colloid mill, which is essentially two metal discs rotating in opposite directions at high speed with a very narrow clearance.

The space in between the metal discs breaks down the particles to colloidal size. Black ink, paints, varnishes, ointments dyestuffs are prepared by this method.

(*ii*) *Bredig's arc method or electro dispersion:* (Figure 12.1) Colloidal solution of metals like Au, Ag, Cu, Pb, Pt etc. are obtained by this method. An electric current is passed through water containing traces of alkali, when an electric arc is produced between the tips of two closely placed electrodes of these metals. The heat of the spark converts the ends of the metal rods to form vapours of metal which immediately condense to give metal colloids. The trace of alkali stabilizes the colloidal solution and finally the solution is cooled by cooling mixture.

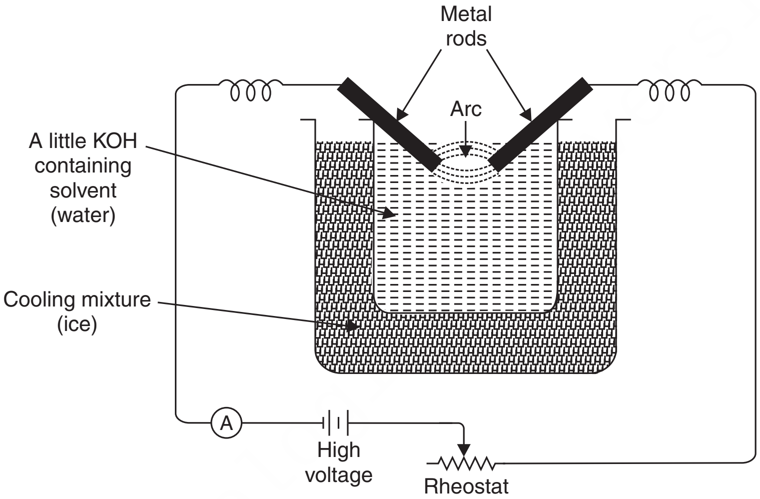


Fig. 12.1 Bredig's arc method.

(*iii*) *Mechanical dispersion method:* (Fig. 12.2) this technique consists of finely pulverising the substances to be dispersed in the medium, which constitutes the dispersion phase. This coarse suspension is then passed through colloid-mill which mechanically grinds the coarse particles. The colloid-mill consists of two discs made of metal, which rotates in opposite direction at a very high speed. The clearance between the discs is very small that apparently determines the size of the colloidal particle. The coarse particles which come in between the two rotating discs get teared to smaller colloidal particles, which are finally stabilized by addition of a suitable protective colloid.

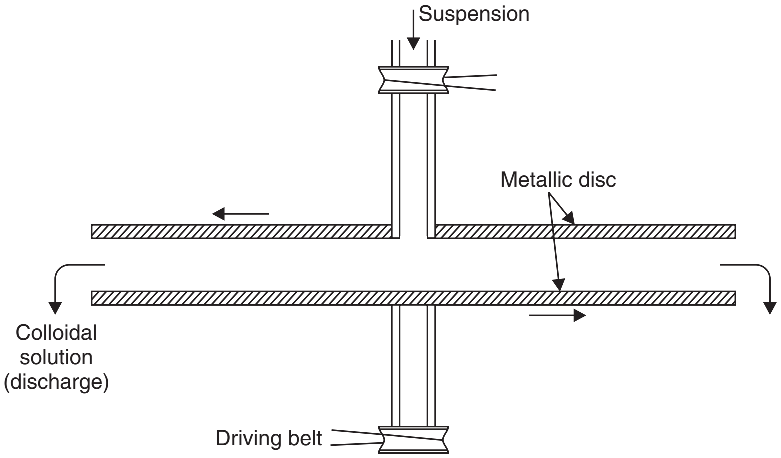


Fig. 12.2 Colloidal mill.

(*iv*) *Peptization:* A freshly prepared precipitate such as AgCl, $Fe(OH)_3$, $Al(OH)_3$ etc. can be converted into colloidal state by the addition of small amount of a foreign electrolyte solution. The foreign electrolyte is known as the **peptizing agent** and the process is called **peptization**.

(*a*) Thus freshly precipitated $Fe(OH)_3$, if shaken with a dilute solution of $FeCl_3$, would give rise to ferric oxide sol.

$$\underset{\text{Precipitate}}{Fe(OH)_3(s)} + \underset{\text{Peptizing agent}}{Fe^{3+}} \longrightarrow \underset{\text{(Colloid/Sol)}}{Fe(OH)_3 \,.\, Fe^{3+}}$$

(*b*) Freshly precipitated AgCl can be peptized by shaking with a dilute aq sol. of $AgNO_3$

$$\underset{\text{Precipitate}}{AgCl(s)} + \underset{\text{Peptizing agent}}{Ag^+} \longrightarrow \underset{\text{(Sol/Colloid)}}{AgCl \,.\, Ag^+}$$

(*c*)

$$\underset{\text{Precipitate}}{Al(OH)_3} + \underset{\text{Peptizing agent}}{H^+} \longrightarrow \underset{\text{(Colloid)}}{Al(OH)_3 \,.\, H^+}$$

Though there is no rule, but it is common that the peptizing agent which are most effective contains a common ion with the precipitate forming colloid.

Dispersion is also sometimes carried out by the use of an atomiser *e.g.,* in the dispersion of a liquid in a gas.

Purification of Colloidal Solutions

The colloidal solutions prepared by the above methods contain several impurities of electrolytes and other soluble substances. So, they become unstable. Hence, it is essential to purify these colloidal sols. The following methods are commonly used for purification.

(*i*) **Dialysis.** The semipermeable membranes like cellophane parchment paper, animal membrane have pore sizes which allow the free passage of only the dissolved molecules or ions of a true solution but retains the bigger colloidal particles. Thus, the process of separation of crystalloids from colloids by diffusion through the animal or vegetable membrane is called **Dialysis**.

The sol to be purified is taken in a parchment or cellophane bag, which is partly immersed in water or the dispersion medium. The crystalloids from the sol move out through the cellophane while some amount of water or solvent from outside may enter the bag. The solvent is renewed from time to time. The process is allowed to continue until most of the ions are eventually removed and the retained colloid gets stabilized. In certain sols such as Al_2O_3 hydrosol, the disperse phase is too small to be retained by cellophane and hence the system needs controlled heating whereby the particles grow bigger in size.

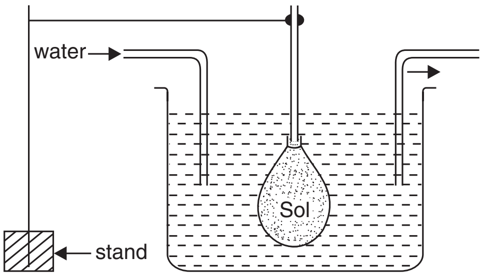


Fig. 12.3 Dialysis.

To accelerate this slow process of purification and also to achieve a higher degree of purity the dialysis is carried out in a direct current electric field, and the process is called **electrodialysis**. Electrodialysis is of no use in separating non-electrolytic impurities.

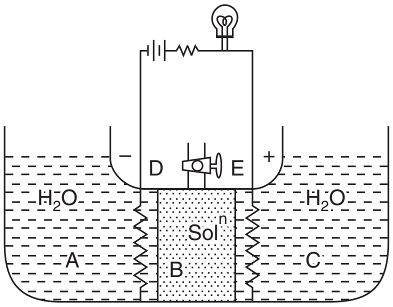


Fig. 12.4 Electrodialyser (diagrammatic).

(*ii*) **Ultra-filtration.** Colloidal particles can pass through ordinary filter papers. But when ordinary filter paper is impregnated with a solution of gelatin or collodion and hardened by formaldehyde the pores become smaller, so that colloidal particles cannot pass through it. Such a filter paper is called ultrafilter paper. The sol when poured over the ultrafilter, electrolytes can pass through, but the colloidal particles are retained and form a slime over it. The slime when brought in contact with water, disperses freely and forms colloidal solution. This process of purifying colloids from the crystalloids using ultrafilters is called ultrafiltration.

By using impregnating solutions of different concentration graded ultrafilters can be prepared which is capable of separating impurities of different sizes.

Properties of Colloidal Solutions

Colloidal solutions possess some characteristic properties. Important ones are described below:

(*i*) **Physical properties**

(*a*) Colloidal systems are heterogeneous, intermediate between true solution and suspension and contain two phases—dispersed phase and dispersion medium.

(*b*) *Colour.* Colour and appearance depend on the size, shape, refractive index and some other properties of the dispersed phase. Gold sol of very fine particles is red and of coarser particles is blue in colour; sulfur sols may be colorless to faint and deep yellow in reflected light and reddish in transmitted light.

(*c*) *Shape.* Although the most common shape of the particles are spherical; but highly asymmetrical shape is also found. Vanadium pentoxide particles are rod-shaped, RBCs (red blood corpuscles) normally are double concave plates and give red color, but in sickle-cell anaemia they become new-moon shaped. Colloidal particles are readily filterable through ordinary filter paper.

(*d*) *Adsorption.* Generally colloidal particles are either positively or negatively charged, so they attach to a variety of molecules on their surfaces.

This property of colloid has been utilized in dyeing fabrics where the fabrics are first treated with colloidal suspension which adsorbs dye.

(*ii*) **Colligative properties.** High molecular weight is the characteristic of colloidal particles and hence in a solution, the number of moles present is very low. Colligative properties like osmotic pressure, depression of freezing point, lowering of vapour pressure depend on the molarity of the solution and hence these values are very low for colloidal solution.

(*iii*) **Mechanical properties**

(*a*) *Brownian movement.* Robert Brown, an English botanist, in 1927, observed under a microscope that pollen grains dispersed in water executed a ceaseless random motion. This random zigzag motion is also executed by all colloidal particles, including colloidal particles suspended in a gaseous medium, independent of their nature, smaller particles executing a more rapid and brisk motion than the larger ones. This perpetual zigzag motion is called **Brownian motion.** This motion is described by Perrin as "they go and come, stop, start again, mount, descent, remount again, without in the least tending towards immobility".

The true cause of Brownian movement was suggested by Wiener in 1863 as molecular collision of colloidal particles with liquid molecules. The colloidal particles are constantly hit from all sides of the surrounding molecules. The colloidal particles after impact with solvent molecule move in a straight line until its speed and direction are not altered by another impact. The intensity of Brownian motion is less with increase in size of the colloidal particles and also with the increase in viscosity of medium.

Brownian motion also increases with increase in temperature. Large particles do not show Brownian movement.

(*b*) *Diffusion.* In a colloidal solution, colloidal particles move from a region of higher concentration to a region of lower concentration until uniformity is attained. But the diffusion process is slower than diffusion in true solution due to higher mass and lower speed of colloidal particles. Diffusion is used to separate colloidal particles of different size.

(*c*) *Sedimentation.* Colloidal particles constantly exhibit Brownian motion and remain suspended in solution, thereby stabilizing the colloidal solution. Larger colloidal particles settle slowly by the effect of gravity and is called sedimentation. Svedberg increased the rate of sedimentation with centrifugal sedimentation by employing a high-speed centifuge called ultracentrifuge. In this machine sedimentation is effected under enormous centrifugal force of rotation.

(*iv*) **Optical properties or Tyndall effect.** When a beam of light is passed through a colloidal solution, the path of light becomes illuminated due to the scattering of light by the colloidal particles. This phenomenon is called Tyndall effect, which does not happen for true solution. These colloidal particles can be viewed through a microscope placed at right angles to the path of light and is called the ultramicroscope. The phenomenon of Tyndall effect can be explained by the scattering of light by the colloidal particles. The particles absorb the incident light energy, becomes self-luminous and scatter this absorbed light. The intensity of the scattered light depends on the difference between the refractive indices of particle and medium.

Tyndall effect was first studied by Zeigmondy in 1903 and this effect can be applied for viewing the colloidal particles quantitatively.

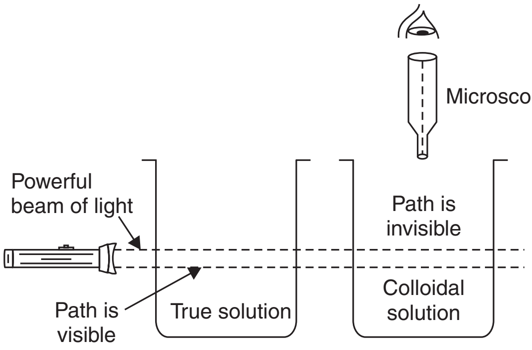


Fig. 12.5 Tyndall effect exhibited by a colloidal solution.

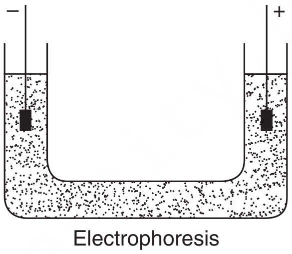


Fig. 12.6 Electrophoresis.

(*v*) **Electrical properties**

(*a*) *Electrophoresis.* Lyophilic and lyophobic colloid particles are either positively or negatively charged. In a U-tube, containing a colloidal solution, when a potential gradient is applied the colloidal particles move towards oppositely charged electrode. After reaching the electrode, they lose their charge and coagulate there. The movement of the colloidal particles in an electric field is called electrophoresis. When the negatively charged particles like CdS, As_2S_3 metallic sols, organic sols move towards cathode, the phenomenon is called cataphoresis. Positively charged particles are $Fe(OH)_3$, $Al(OH)_3$, basic dyes etc. The speed of the colloidal particle under the potential gradient of 1 volt/cm is called electrophoretic mobility.

(*b*) *Electro-osmosis.* When electric current is passed through a colloidal solution such that the dispersed phase is prevented from movement, the dispersion medium begins to move in the electric field. This phenomenon is called electro-osmosis (Fig. 12.7).

(*c*) *Isoelectric Point.* The colloidal sols of protein are either positively or negatively charged in acidic or alkaline solution and hence when electrolysed in a medium, pH of the medium will dictate the migration of the colloidal particle to any electrode. Hence the pH of the dispersion medium at which the dispersed particles are neutral and hence they do not migrate when subjected to an electric field is called **isoelectric point**. The isoelectric point of protein depends on pH and ionic strength in the medium. Proteins are least soluble in isoelectric point and hence coagulate at isoelectric point.

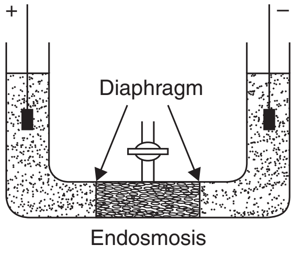


Fig. 12.7

Coagulation of Colloids

Colloid particles are electrically charged, so they repel each other and become stable. When the charge is neutralised, the particles approach each other to form aggregates and settle down. The precipitation of colloidal solution is called 'coagulation' or flocculation. This can be achieved by

(*i*) *Adding oppositely charged:* Two oppositely charged colloidal solutions when mixed, mutual coagulation of the two sols takes place.

(*ii*) *Electrophoresis:* In electrophoresis the electrically charged colloidal particles migrate towards the oppositely charged electrode and finally coagulate.

(*iii*) *Adding electrolytes:* By addition of oppositely charged ion *i.e.,* by adding electrolytes the charges of the colloidal particles are neutralised and precipitated. Coagulating power of an ion increases with the increasing valency of the coagulating ion. The higher the valency of the ion, greater is the coagulating power—this is known as Schulze-Hardy law. Thus, the coagulating power increases in the series

$$Na^+ < Ba^{+2} < Al^{3+} \quad \text{or} \quad Cl^- < SO_4^{2-} < PO_4^{3-}.$$

Generally, the coagulating power of trivalent ion is 500–1000 times greater than bivalent ion which is 100-500 times greater than monovalent ion.

Protection of Colloid

The stability of colloids can be achieved by any of the following:

(*i*) **Electrical charge.** All the colloidal particles of a colloidal solution bear similar charges and hence they repel each other. This mutual repulsion prevents them from coalescing and coagulating.

(*ii*) **Solvation.** Colloidal particles are surrounded by a layer of solvent molecules which resists the dispersed phases from forming large aggregates and coagulate. Thus, the solvent layer forms a protective envelope. These sols are very stable.

(*iii*) **Protective agents.** Protective agents are added to some colloidal systems, which get adsorbed on the surface of the colloidal particles and by coating them prevents coagulation.

(*iv*) **Protective colloids.** Lyophilic colloids are much more stable than the lyophobic colloids—since the former are extensively solvated. When a lyophilic colloid is added to a lyophobic colloid, the latter becomes more stable even to the action of electrolytes. The process by which lyophilic colloid protects the lyophobic sol is called protection and the lyophilic colloid is called the **protective colloid**. Thus, if a little albumin (lyophilic colloid) is added to a gold sol (lyophobic sol), the former acts as protective colloid and prevents coagulation of the latter even against addition of high concentration of an electrolyte, like NaCl. This protection is due to the formation of a protective thin layer surrounding the particles of the lyophobic colloid, through which the oppositely charged ion of the electrolyte cannot penetrate to neutralize the charge for coagulation. Zsigmondy introduced the term 'gold number' to measure the protective power of lyophilic colloids. It is defined as "the minimum weight in mg of a protective colloid, which when added to one ml of standard gold sol (containing 0.0053 to 0.0058 % gold) containing also 1 ml of 10 % NaCl solution to just prevent its coagulation. This is indicated by the change of colour from red to blue. The smaller the gold number the greater is the protective power of lyophilic colloid.

Table 12.3 Gold numbers

Protective colloid	*Gold number*
Gelatin	0.005 to 0.015
Casein	0.01 to 0.02
Albumin	0.1 to 0.2
Gum	0.1 to 0.2
Starch	10 to 15
Sodium oleate	0.40
Haemoglobin	0.003 to 0.07

Emulsion and Gel

Emulsions are colloidal systems in which both dispersed phase and dispersion medium are liquids (immiscible). The familiar examples are–milk, which consists of liquid fat dispersed in water (oil in water type); butter, which consists of water dispersed in liquid fat (water in oil type).

Emulsions are prepared merely by shaking one liquid with the other, and hence they are not stable and easily separate into two immiscible layers. Emulsions are stabilized by adding a third substance (emulsifier) as stabilizer. This substance forms a thin layer around the dispersed phase thereby preventing it from coalescing and coagulating. The emulsifier also decreases the surface tension of the two liquids.

Albumin, casein, gum, agar-agar, soaps and detergents are the common emulsifiers. Emulsifiers are selected according to the type of emulsion, *e.g.,* soaps of alkali metals, gelatin etc. are more soluble in aqueous phase, hence they are used as stabilizers for oil-in-water-type of emulsion whereas heavy metal soaps of palmitic and oleic acid are soluble in fat and hence used in water-in-oil-type emulsion.

Emulsions have properties similar to those of lyophobic colloids like Tyndall effect, Brownian movement etc.

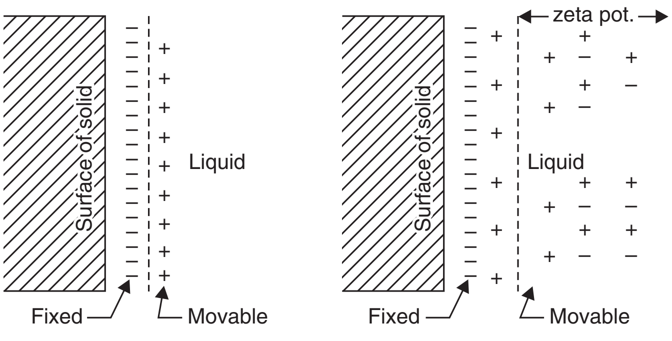
Gel: Many lyophilic sol and few lyophobic sol when coagulated under certain conditions form semi-solid mass. Such a product is called gel and the process is called gelation, *e.g.,* jam, jelly, cheese, curd etc. This is formed by entrapment of the dispersion medium inside the loose network of the dispersed particle. Gels have high viscosity and swell if placed in the dispersion medium and some shrink in volume.

Gel formation is utilized for preparation of shoe polish, cheap soaps, curds, jellies, solid fuel of alcohol with calcium oxalate.

Reversible colloid. When a colloid can be reversibly converted from a sol to gel and vice versa, it is called a reversible colloid, *e.g.,* solution of gelatin can be reconverted into sol by heating. Other colloids which cannot be reversibly transformed are called irreversible colloid, *e.g.,* normal Au colloid.

(*v*) **Zeta potential.** In lyophobic colloids, particles are of similar charge, which do not allow the particles to come closer and coalesce and hence bring stability to the system.

The charge is embedded in the colloidal particle and an equivalent amount of opposite charge remains outside and these two layers form a **double layer**. A part of this opposite charge is fixed on the particle and another part is mobile and distributed throughout the medium.



Helmholtz double layer

Diffuse double layer

Fig. 12.8 Zeta potential.

Hence, there is a potential difference between the particle and the medium. This potential is called the zeta potential which is responsible for the stability of the colloid.

Application of Colloids

(*i*) **Purification of water.** Impure water is treated with alum. Al^{3+} ions of alum precipitate negatively charged clay particles, bacteria, colloidal particles and the impurities.

(*ii*) **Purification of polluted air.** Suspended particles, smoke etc., polluted air. Smoke is negatively charged colloidal suspension consisting of carbon particles. Air is passed through Cottrell precipitator where the charge is neutralised and carbon settles down while the hot air passes out through chimney.

(*iii*) **Removal of dirt from sewage.** Sewage contains charged dirt particles, which is passed through tanks fitted with oppositely charged electrodes. By neutralizing the charge, dirt is coagulated.

(*iv*) **Leather tanning.** The raw material skin is positively charged colloidal system, which is treated with negatively charged colloidal solution of tannin, whereby mutual coagulation of oppositely charged colloids takes place.

(*v*) **Laundry.** Soaps in water form colloidal solution, which adsorb greasy materials, dirt by emulsion formation and remove dirt from clothes.

(*vi*) **Medicine.** Colloidal system of medicines are better assimilated. Blood coagulation is effected with alum or $FeCl_3$.

(*vii*) **Cosmetics.** Different types of colloidal systems and emulsion are used in cosmetics.

(*viii*) **Analysis.** Noble metals are detected by formation of their colloidal solutions and observing their colours.

(*ix*) Artificial rain are made by throwing charged sand on clouds.

(*x*) **Delta formation.** Negatively charged sand particles of the river water and Na^+, K^+, Ca^{2+} present in the sea water are responsible for the deposition of colloidal particles where river meets sea.

Highlights:

Dimension of colloidal particles range from 10^{-4} to 10^{-7} cm.

Purification of colloidal solutions can be done by dialysis, ultrafiltration.

Brownian motion. The random zigzag motion of the colloidal particles in the suspending medium is called Brownian motion. The motion is rapid for smaller particles and also for a less viscous medium.

Tyndall effect. When a beam of light is passed through a colloidal solution, the path of light becomes illuminated due to the scattering of light by the colloidal particles. This phenomenon is called Tyndall effect.

Schulze-Hardy Law. The coagulating power of an electrolyte depends predominantly on the valency of the ion bearing a charge opposite to that of the colloidal particles, and higher the valency of the active ion, the greater is its precipitating action. This is called Schulze-Hardy law.

Gold number. It is the minimum weight in mg of a protective colloid, which when added to 1 ml of standard gold sol (containing 0.0053 to 0.0058% gold) also containing 1 ml of a 10% NaCl solution to just prevent its coagulation.

Bancroft rule. The phase in which the emulsifier is more soluble becomes the outer phase.

SHORT QUESTIONS AND ANSWERS

Q. 1. Describe a colloidal system. What are the sizes of particles forming a solution and a colloidal solution?

Ans. A colloidal system is a two-phase heterogeneous system in which one phase is dispersed in a fine state of subdivision (from 1 to 50 mμ) in another medium termed the continuous or dispersion medium.

The solute particles in true solution are of dimension 1 to 10 Å.

Particles of colloidal system have dimension in the range from 10 to 1000 Å.

Q. 2. What is the difference between sol and emulsion?

Ans. Sol is a colloidal solution of a solid dispersed in a liquid medium whereas emulsion is a liquid dispersed in another immiscible liquid in the form of droplets.

Q. 3. Why are "Brownian movement" and "Tyndall effect" shown by colloidal solutions but not the true solution?

Ans. Large particles of the colloid solution do not settle down and scatter the light falling on the solution, whereas in true solution there are no such particles.

Q. 4. Write short notes on the following:

(*a*) **Brownian movement**

(*b*) **Tyndall Effect**

(*c*) **Dialysis**

(*d*) **Gold number.**

Ans. (*a*) See page 284

(*b*) See page 284

(*c*) See page 282

(*d*) See page 286.

Q. 5. Explain the action of gelatin as protective colloid.

Ans. Gelatin is a lyophilic colloid and when it is added to lyophobic sol, it forms a very thin protective shell, surrounding each particle of the lyophobic colloid and protects the penetration of oppositely charged ions, which neutralize the charge and precipitate the lyophobic colloid.

Q. 6. Write notes on

(*i*) **Electrophoresis**

(*ii*) **Peptization**

(*iii*) **Zeta potential**

(*iv*) **Protection of hydrophobic colloids.**

Ans. (*i*) See page 285

(*ii*) See page 282

(*iii*) See page 287

(*iv*) See page 286.

Q. 7. Which of the following electrolytes will be most efficient for the precipitation of As_2S_3 sol and why?

(*i*) **KCl**

(*ii*) **$CaCl_2$**

(*iii*) **$AlCl_3$.**

Ans. As_2S_3 sol is a negatively-charged sol and it can be precipitated by positively charged ions of the added electrolyte. From the above three electrolytes, the positive ions obtained are K^+, Ca^{2+}, and Al^{3+}. Since Al^{3+} possess highest positive valency, $AlCl_3$ will be the most efficient electrolyte to ppt As_2S_3 sol, as per Schulze-Hardy rule.

Q. 8. Explain how deltas are formed where rivers meet the sea.

Ans. See page 288.

Q. 9. Why is alum used to remove impurities from water?

Ans. See page 288.

Q. 10. Smoke coming out from the chimneys of different factories is led to charged metallic plate—explain.

Ans. See page 288.

Q. 11. Mention some important applications of colloid chemistry to industries.

Ans. See page 288.

Q. 12. Differentiate between lyophilic and lyophobic solutions.

Ans. See page 279.

Q. 13. State Schulze-Hardy law.

Ans. See page 286.

Q. 14. What do you mean by isoelectric point?

Ans. The pH of the medium at which the dispersed colloidal particles are neutral and hence do not migrate when an electric field is applied to the colloidal solution.

Q. 15. What happens when a sol is filtered through a filter paper?

Ans. If a sol is filtered through an ordinary filter paper, the colloidal particles will pass through the pores of the filter paper since the pore-size of ordinary filter paper is larger than the size of the colloidal particles.

EXERCISES

1. What are lyophilic and lyophobic sols?

2. Explain the following:

(*a*) Tyndall effect. (*b*) Brownian movement.

(*c*) Gold number (*d*) Protective colloids.

3. Write a note on application of colloid chemistry in (*i*) pollution control and (*ii*) industries.

4. Explain: Electrophoresis and Electro-osmosis.

5. What are the different ways of protecting a colloidal solution from coagulation?

6. State Schulze-Hardy rule and explain with an example.

OBJECTIVE QUESTIONS

1. The sizes of the colloidal particles fall in the range

(*a*) 10^{-2} to 10^{-4} cm (*b*) 10^{-4} to 10^{-7} cm

(*c*) 10^{-7} to 10^{-9} cm.

2. Light passing through a colloidal solution is

(*a*) Reflected (*b*) Absorbed completely

(*c*) Scattered.

3. Which one is the most efficient in coagulating a ferric hydroxide sol?
(*a*) K_4 $[Fe(CN)_6]$ (*b*) $K_3[Fe\ (CN)_6]$
(*c*) KCl.

4. Which process is used for the purification of a colloidal solution?
(*a*) Dialysis (*b*) Peptization
(*c*) Dissolution.

5. The random zig-zag movement of colloidal particles in a dispersion medium is called
(*a*) Tyndall effect (*b*) Brownian movement
(*c*) Dialysis.

6. Which is a protective colloid?
(*a*) $K_4[Fe(CN)_6]$ (*b*) NaCl
(*c*) Gelatin.

7. Haemoglobin in blood is
(*a*) Hydrophobic colloid (*b*) Hydrophilic colloid
(*c*) Gel.

8. Colloidal particles are electrically charged. This can be demonstrated by
(*a*) Peptization (*b*) Electrophoresis
(*c*) Dialysis.

9. Smoke is a colloidal sol of
(*a*) Solid dispersed in gas (*b*) Gas dispersed in solid
(*c*) Liquid dispersed in gas.

10. Milk is an emulsion of
(*a*) Casein dispersed in water. (*b*) Lactose dispersed in water.
(*c*) Fat globules dispersed in water.

11. Bancroft rule states that
(*a*) Colloidal particles are always charged
(*b*) Light falling in the medium is scattered by the colloidal particles.
(*c*) The phase in which the emulsifier is more soluble is the outer phase.

12. Soaps and detergents act as
(*a*) Stabilizers (*b*) Emulsifiers
(*c*) Coagulating agents.

13

Transition Metal Chemistry

TRANSITION METALS

Transition metals are *d*-block elements having partially filled *d*-energy levels in one or more oxidation states. In the *d*-block series from scandium ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$) to zinc ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$), the definition holds good for all the element excepting scandium and zinc. Scandium is excluded because it only produces compounds in the +3 state and it loses all its three outer electrons when it forms Sc^{+3} cation. Zinc is excluded because all its compounds are in the +2 state. Zn on losing two electrons produces Zn^{+2} cation with an electron configuration ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$) in which all the *d*-energy levels are full.

Transition metals have a number of common features. They are stated below:

- All are metals with useful mechanical properties with high melting points.
- All form compounds in more than one oxidation states.
- All form coloured compounds.
- All form a variety of complex ions.
- All act as catalysts, as metals or as compounds.

Many transition metal salts are paramagnetic because of the presence of unpaired electrons in the partially-filled inner *d*-energy levels.

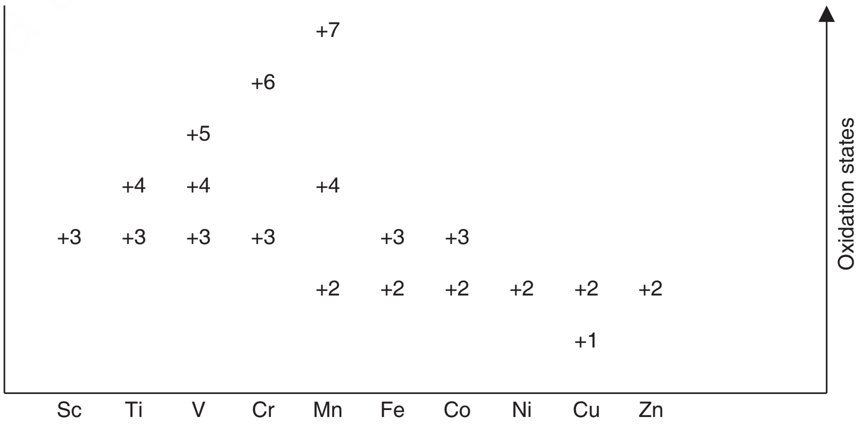


Fig. 13.1 Main oxidation states of the elements Sc to Zn (first transition series).

It is to be noted that Sc and Zn form ions in one oxidation state *i.e.,* + 3 and + 2, respectively. The chemistry of titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), cobalt (Co), iron (Fe) and copper (Cu) provide many examples of the above-mentioned features.

Double Salts and Complex Salts

A **double salt** is formed generally when molar proportions of a monovalent cation sulphate solution in water is mixed with trivalent cation sulphate solution in water and evaporated to remove excess water, and the salt crystallises as $X_2SO_4Y_2(SO_4)_3.24H_2O$ which is the general formula of a common alum, where 'X' is monovalent cation, like NH_4^+, K^+, Na^+, and 'Y' is trivalent cation as Al^{+3}, Cr^{+3}, Fe^{+3} etc. Another important double salt is Mohr's salt, $(NH_4)_2\ SO_4.FeSO_4.6H_2O$. A double salt exists as a distinct entity only in the solid crystalline state, it loses its entity in solution. The double salt is characterised by complete dissociation in solution and gives the reactions of all the ions formed by the salts in solutions, *viz.*

$K_2SO_4.Al_2(SO_4)_3.24H_2O$ in solution gives the reactions of K^+, Al^{+3} and SO_4^{-2} ions.

A complex salt does not give all the ions of its constituents in solution. A complex salt $K_4[Fe(CN)_6]$ is prepared by adding KCN solution of $FeSO_4$ solution and boiling.

$$FeSO_4 + 2KCN = Fe(CN)_2 + K_2SO_4$$
$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6]$$

The solution of $K_4[Fe(CN)_6]$ does not respond to the tests for Fe^{+2} or CN^- ions, but responds to a test for a new ion $[Fe(CN)_6]^{-4}$ (ferrocyanide ion). **This ion remains intact** even in solution

$$K_4\ [Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{-4}$$

and gives its distinctive reactions. So, it can be said, the complexions, like ferrocyanide ion, are quite stable in the solid state as well as in solution. A complex salt is different from a double salt in respect of its distinctive character even in solution.

Examples of complex salts

$$[Ag(NH_3)_2]Cl \rightleftharpoons [Ag(NH_3)_2]^{++} + Cl^-$$
$$[Cu(NH_3)_4]SO_4 \rightleftharpoons [Cu(NH_3)_4]^{++} + SO_4$$
$$K[Ag(CN)_2] \rightleftharpoons K^+ + [Ag(CN)_2]^-$$

Instability Constants of Complex Salts

The dissociation of a complex ion, like ionisation of weak electrolyte, follows the law of mass action. The dissociation constant is called instability constant (K_{ins}) and is a measure of stability of a complex, the lower the value of K_{ins}, the higher is the stability of the complex and vice versa.

$$K_{ins} = \frac{[M^+]\,[L^-]}{[ML]}$$

Complex ions	*Instability constant*
$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$	6.8×10^{-8}
$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$	1.0×10^{-21}
$[Cu(CN)_4]^{-3} \rightleftharpoons Cu^+ + 4CN^-$	5.0×10^{-28}
$[Cd(CN)_4]^{-2} \rightleftharpoons Cd^{+2} + 4CN^-$	1.4×10^{-17}

Werner's Theory for Formation of Complex Compounds

Werner put forward a theory for the formation of complex compounds. The theory is known also as **co-ordination theory**. The postulates of his theory may be summarised as follows:

- Metals possess two types of valencies: (*i*) **Primary** or *principal* or ionisable valencies (*ii*) *Secondary* or **subsidiary** or non-ionisable valencies.

- Every metal atom has a fixed number of secondary valencies or co-ordination number (C.N.). The maximum number of ions or molecules thereby the central atoms could form co-ordinate bonds is known as **co-ordination number** (C.N.).

Ligands

The ions or molecules thus attached to the central metal atom by co-ordinate bonds are called ligands. The ligands may be unidentate, bidentate, tridentate etc. depending upon the number of co-ordination centres in the ligand.

Types of Ligands

Unidentate ligands—F^-, Cl^-, H_2O

Bidentate ligands—$H_2NCH_2CH_2NH_2$ (en stands for ethylene diamine)

Cu (II) has C.N. = 4 ; Co (III) and Pt (IV) has C.N. = 6.

- Primary valencies of the metal are satisfied by negative ions, but secondary valencies may be satisfied by negative groups (CN^- , Cl^-, etc.), neutral molecules (H_2O, NH_3 etc.) or even sometimes some positive groups. **In every complex formation the co-ordination number (C.N.) of the central metal atom must be fulfilled**.
- The secondary valencies are directed in space about the central metal ion. For metals with co-ordination number (C.N. = 6), the six valencies are directed to the apices of a regular octahedron. Again, for metals, with C.N. = 4, the four such valencies are either directed to the apices of a regular tetrahedron or a square (planar).

This gives rise to various types of isomerism. Werner could isolate even *optical isomers.*

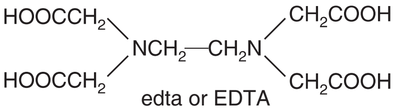
The main drawback for Werner's theory is: there is no theoretical reason to have a central atom of the complex ion to possess two kinds of valencies.

Chelate Compounds

Chelate compounds are complex compounds containing a ring structure in which a ligand molecule or ion forms more than one dative covalent bonds (co-ordinate bonds) with the central metal ion. Chelates are formed by bidentate and polydentate ligands. Chelation increases the stability of co-ordination complex *i.e.,* chelate complexes are generally more stable than complexes formed by monodentate ligands. Powerful chelating agents trap metal ions and effectively trap them in solution, as for example en (ethylene diamine), edta (ethylene diamine tetra-acetic acid). This type of ligands are known as complexones.

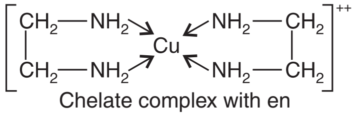
$H_2N—CH_2—CH_2—NH_2$

en



edta or EDTA

The ligand molecules which occupy two or more co-ordination centres are usually organic molecules.



Chelate complex with en

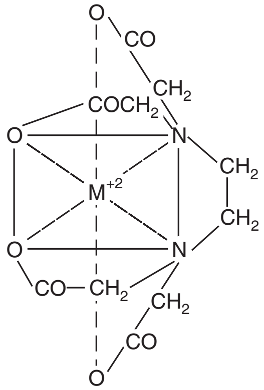


Fig. 13.2 Chelate complex of edta with a bivalent metal.

It is to be noted in chelate complexes that the rings formed are five or six membered.

Inner Metallic Complexes

Many well-known organic ligands, which act as chelating agents, possess a neutral donor atom as well as an acidic group. They form very stable cyclic complexes, which have very low solubility in water but high solubility in organic solvents. Generally, the acid group of the ligand satisfies the primary valency of the central metal ion (which therefore does not appear as an ion *i.e.,* net charge on the complex molecule is zero). Such non-electrolytic cyclic complexes are known as **inner metallic complexes** or simply **inner complexes**.

Nomenclature of Coordination Compounds (IUPAC)

Complex compounds are of the following types:

(*i*) Cationic, (*ii*) anionic, (*iii*) non-ionic and (*iv*) a combination of cationic and anionic complexes.

(*i*) In naming cationic complexes like $[Co(NH_3)_5Cl]Cl_2$, the name of the cation is considered first and then the name of the anion.

(*ii*) In naming the anionic complexes like $K_2[PtCl_6]$ the K^+ is written first then the name of the complex anion.

(*iii*) If the complex compound is non-ionic (neutral) the name of the complex compound like $[Pt\ (NH_3)_4Cl_2]^0$ is written as one word.

(*iv*) In $[Pt^{IV}(NH_3)_4Cl_2]^{2+}$ $[Pt^{II}(Cl)_4]^{2-}$, the name of the complex cation is written first then the complex anion is named.

Naming of the ligands

Neutral ligands

$(C_2H_5)_3N$	—	Triethylamine	CO	—	Carbonyl
NH_2-NH_2	—	Hydrazine	CS	—	Thiocarbonyl
CH_3NH_2	—	Methylamine	H_2O	—	Aquo or aqua
NO	—	Nitrosyl	NS	—	Thionitrosyl
$(CH_3)_2NH$	—	Dimethylamine	NH_3	—	Amine

Anion ligands

F^-	—	Fluoro	CH_3COO^-	—	Acetato
Br^-	—	Bromo	NH^{2-}	—	Imido
Cl^-	—	Chloro	OH^-	—	Hydroxo or hydroxyl
I^-	—	Iodo	S^{2-}	—	Thio
NH_2^-	—	Amido	CN^-	—	Cyano
NC^-	—	Iso-Cyano	NO_2^-	—	Nitro
ONO^-	—	Nitrito	SCN^-	—	Thiocyanato
$S_2O_3^{2-}$	—	Thiosulphato	NO_3^-	—	Nitrato

Ambident ligands

Ambidentate or ambident ligands are those which have two or more different donor atoms in their structures. These ligands can co-ordinate to the metal atom through any of the their donor atoms.

Example:

(*i*) NO_2^- ion → $O—N—\overset{(-)}{O}$ named as Nitro-O or Nitrito when donor atom is 'O'

$\bar{O}_2N$ named as Nitro-N or Nitrato when donor atom is 'N'

(*ii*) SCN^- ion → Thiocyanato-S (SCN^-)

Thiocyanato-N (NCS^-)

Indication of the Number of ligands

- If a complex contains two or more simple ligands like Cl^-, Br^- etc. their number is indicated by di- for two; tri- for three; tetra- for four before the names of the ligands.
- If a complex contains two or more complex ligands or organic molecules and which already have di-, tri- in their names their number is indicated by putting the prefixes bis- for two; tris- for three; tetrakis- for four. The name of the ligands or organic molecule is written in the bracket. Examples of complex ligands are—Ethylene diamine (en) etc.

Order of Naming the Ligands

If the co-ordination sphere of a given complex compound contains various types of ligands, these ligands are named alphabetically.

For example: $[Co(NH_3)_4Cl(NO_2)]^+$ ion is named as tetra-amine chloro nitro cobalt (III) ion.

For anionic complexes the name of central metal atom ends in *'ate'* and the oxidation state of the metal is written in Roman numerals (0, I, II).

For example:

Cr — Chromate
Cu — Cupreate
Pt — Platinate

Co — Cobaltate
Al — Aluminate
Ni — Nicklate

Examples of Cationic Complexes

$[Ag(NH_3)_2]Cl$ — Diamine silver (I) chloride.
$[Cr(H_2O)_4Cl_2]^+$ — Tetraaquodichloro chromium (III) cation.
$[Co(NH_3)_5H_2O]Cl_3$ — Pentamine mono aquo cobalt (III) chloride
$[Co\ (NH_3)_4Cl_2]Cl$ — Tetraamine dichloro cobalt (III) chloride

Examples of Anionic Complexes

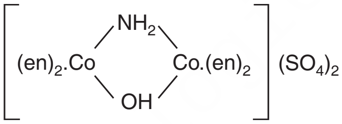
$K_4[Fe(CN)_6]$ — Potassium hexacyano ferrate (II).
$[Co(Cl)_6]^{3-}$ — Hexachloro cobaltate (III) ion.
$[Pt(NH_3)_2Cl_4]$ — Diamine tetrachloro platinum (IV).

Bridging Ligands

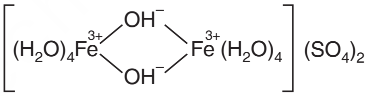
A bridging ligand, which links two metal atoms, is denoted by the prefix μ- before its name. For example

1. $[(NH_3)_5Co—NH_2—Co(NH_3)_4(H_2O)]Cl_5$ is named as:

Pentammine cobalt (III)-μ-amido-tetrammine aquo cobalt (III) chloride.

2.  is named as:

Bis-(ethylene diamine) cobalt (III)-μ-amido-μ-hydroxo-bis (ethylene diamine) cobalt (III) sulphate.

3.  is called:

Tetra-aquo iron (III)-μ-dihydroxy tetraquo iron (III) sulphate.

Isomerism in Metal Complexes

Isomerism in complex molecules arises due to difference in attachment of the groups or ions to the central metal iron or due to their different spatial arrangements about the central metal ion. Generally, two types of isomerisms are exhibited by metal complexes.

(*i*) **Structural isomerism.** This is also classified under six heads, namely (*a*) ionisation isomerism, (*b*) linkage isomerism, (*c*) co-ordination isomerism, (*d*) ligand isomerism, (*e*) hydrate isomerism.

(*ii*) **Stereoisomerism or space isomerism.** When two compounds containing the same ligands are co-ordinated to the same central metal ion, but differ in the arrangement of ligands in space, they are said to be stereoisomers of each other and the isomerism of this type is called **space-isomerism** or **stereoisomerism**. This is of two types:

(*a*) Geometrical or cis-trans isomerism
(*b*) Optical or mirror image isomerism.

Ionisation Isomerism

In this case, positions of groups inside and outside of the co-ordination sphere are interchanged and so the compound yields different ions in the solution. For example, the complex $[Co(NH_3)_5\ Br]SO_4$ (I) gives white precipitate of $BaSO_4$ when treated with $BaCl_2$ solution and indicates that SO_4^{2-} ion is outside the co-ordination sphere. And the complex $[Co(NH_3)_5SO_4]$ Br (II) gives a light yellow precipitate of AgBr when treated with $AgNO_3$ solution, indicating the Br^- ion is outside the coordination sphere.

$$[Co(NH_3)_5Br]\ SO_4 + BaCl_2 \longrightarrow [Co(NH_3)_5\ Br]^{2+} + BaSO_4 \downarrow + 2Cl^-$$

Pentaamine monobromo cobalt (III) sulphate (red-violet) (White)

$$[Co(NH_3)_5\ SO_4]Br + AgNO_3 \longrightarrow [Co(NH_3)_5\ SO_4]^+ + AgBr \downarrow + NO_3^-$$

Pentaamine monosulphato cobalt (III) bromide (Red) (Light yellow)

Other examples for the same are:

$[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt\ (NH_3)_4Br_2]Cl_2$

$[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4(NO_2)Cl]Cl$

$[Co(en)_2.(NO_2).Cl]SCN$ and $[Co.(en)_2.(NO_2).(SCN)]Cl$

Linkage Isomerism

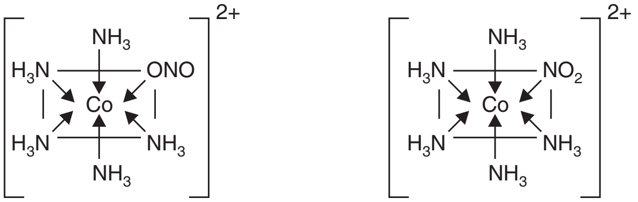
This type of isomerism is exhibited by those molecules in which the ligands can co-ordinate with the central metal ion either of its two atoms. The ligands of this type are nitro (NO_2^-), thiocyanate (SCN^-), thiosulphate ($S_2O_3^{2-}$) ions. The complexes with NO_2^- ion as with ligand NO_2^- may get attached to the central metal ion either through O-atom or N-atom acting as donor. Similarly, in case of SCN^- ion as ligand, the donor site may either be through N^- or through S-atom. With $S_2O_3^{-2}$ acting as ligand the central ion may be coordinated with the ion either through S-atom or O-atom. The names of the above ions *i.e.,* ligands when coordinated through different atoms are given below:

Nitro-O or Nitrito (ONO^-)
Nitro-N or Nitrito (NO_2^-) — NO_2^- ion

Thiocyanato-S (SCN^-)
Thiocyanato-N (NCS^-) — SCN^- ion

Thiosulphato-S
Thiosulphato-O — $S_2O_3^{-2}$ ion

For example:



Pentaamine nitrito (or Nitro-O) cobalt (III) ion (red)

Pentaamine nitrato (or nitro-N) cobalt (III) ion (Yellow)

Fig. 13.3

Co-ordination Isomerism

This type of isomerism arises from the difference in distribution of the co-ordinating groups in the cations and anions of two compounds of identical composition.

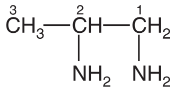
For example:

(*i*) $[Cr(NH_3)_6]^{3+}$ $[Cr(SCN)_6]^{3-}$ and $[Cr(NH_3)_4(SCN)_2]^+$ $[Cr(NH_3)_2(SCN)_4]^-$ are co-ordination isomers.

(*ii*) $[Co(en)_3]^{3+}$ $[Cr(C_2O_4)_3]^{-3}$ and $[Co(en)_2(C_2O_4)]^+$ $[Cr(en)(C_2O_4)_2]^-$ are co-ordination isomers.

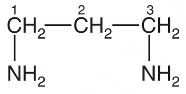
Ligand Isomerism

Some ligands themselves may exist as isomers and are so co-ordinated in the complexes. Thus, propane-1,2-diamine (pn) and propane-1,3-diamine (tn) also called trimethylene diamine have the structures:



$\overset{3}{C}H_3-\overset{2}{C}H(NH_2)-\overset{1}{C}H_2NH_2$

(pn)



$\overset{1}{C}H_2(NH_2)-\overset{2}{C}H_2-\overset{3}{C}H_2NH_2$

(tn)

They form isomeric complexes as $[Co(pn)_2Cl_2]Cl$ and $[Co(tn)_2Cl_2]Cl$

Hydrate Isomerism

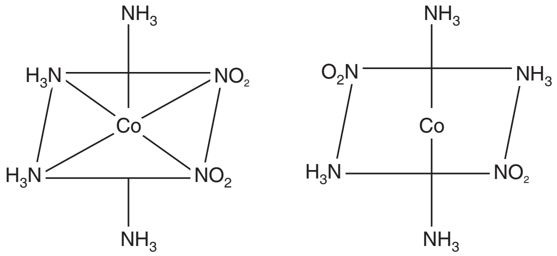
Water molecule is a very effective co-ordinating agent and may replace NH_3, Cl_2 etc. and thus enters into the co-ordination sphere of a metal ion, forming aquo-complex. Hydrate isomers are generated due to variation in number of water molecules in the co-ordination sphere. For example: three isomers of $CrCl_3.6H_2O$ are

$[Cr(H_2O)_6]Cl_3$; $[Cr(H_2O)_5.Cl].Cl_2.H_2O$; $[Cr(H_2O)_4.Cl_2].Cl.2H_2O$

Geometrical Isomerism

Geometrical isomerism originates due to the different arrangements of the co-ordinated groups in space around the central atom in a definite geometrical pattern.

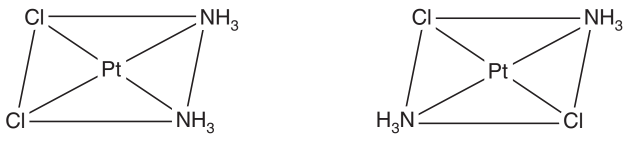
In **six co-ordinated complexes** the six groups are arranged about the central metal ion in a regular hexagonal pattern or at the six corners of an octahedron. The number of possible isomers is different for these two spatial arrangements. Thus for $[Co(NH_3)_4(NO_2)_2]NO_3$ two types of geometrical isomerisms may develop (Fig. 13.4).



(a) cis-form (b) trans-form

Fig. 13.4

Diamine dichloro platinum $[Pt(NH_2)Cl_2]$ exists in two isomeric forms (Fig. 13.5). *Cis*-form is known as **cisplatin** and is an anticancer drug.



(a) cis-form (b) trans-form

Fig. 13.5

Optical or Mirror Image Isomerism

Optical isomerism of 6- and 4-co-ordination complex compounds is shown in Fig. 13.6 and 13.7.

The complex $[Cr(en)_2Cl_2]$ with co-ordination number 6 exhibits optical isomerism.

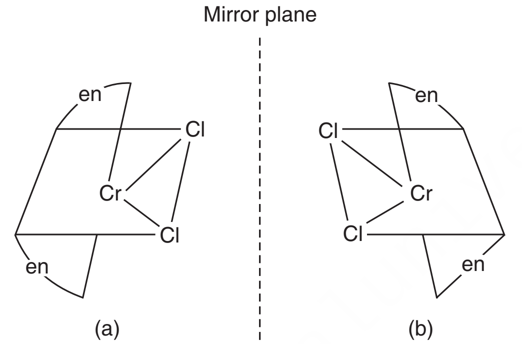


Fig. 13.6

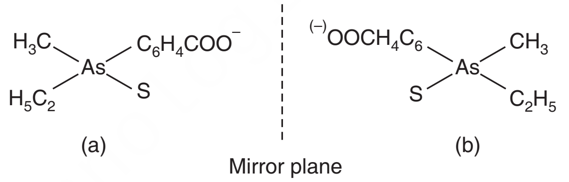


Fig. 13.7 Optically active arsenic compound with co-ordination **number 4**.

Theories of Bonding in Co-ordination Compounds

There are four distinct approaches to the theoretical treatment of bonding in co-ordination compounds. These are: (*i*) Valence bond theory, (*ii*) Crystal field theory, (*iii*) Molecular orbital theory and (*iv*) Ligand field theory.

In this context, the first two theories have been discussed.

Valence Bond Theory

This theory was developed by Pauling and deals with hybridisation of the complex. It depends on the following assumptions:

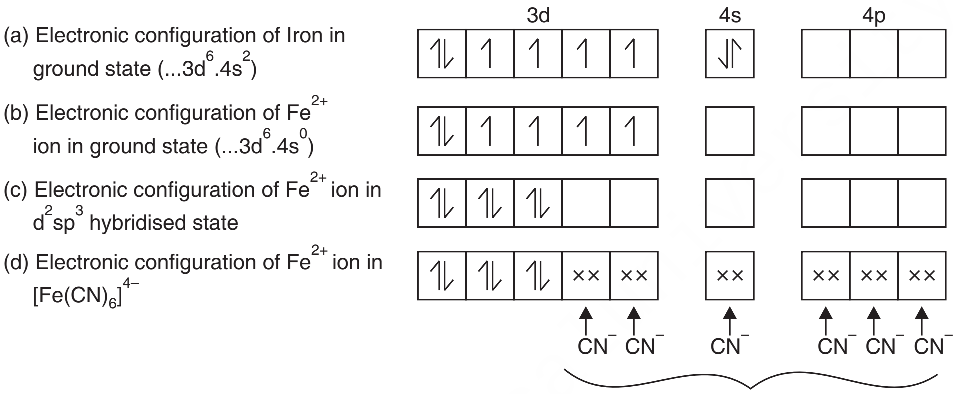
- The central metal atom provides a number of empty orbitals that are equal to its co-ordination number for forming the covalent bonds with ligand orbitals.
- The empty orbitals of the metal ion hybridise to give an equal number of equivalent hybrid orbitals.
- Ligands are groups which can donate electron pairs to metal ions which appear as electron pair acceptors.

$$Ag^+ + 2\ddot{N}H_3 \longrightarrow [Ag(NH_3)_2]^+$$

- An orbital of the ligand containing an unshared electron pair overlaps the hybridised orbitals of the metal ion and this is regarded either as partial donation of the ligand electrons to the metal ion or a sharing of that pair of electrons between the metal ion and the ligand. This overlapping results in a σ-bond or possibly a π-bond.

Octahedral complexes result from d^2sp^3 or sp^3d^2 hybridizations.

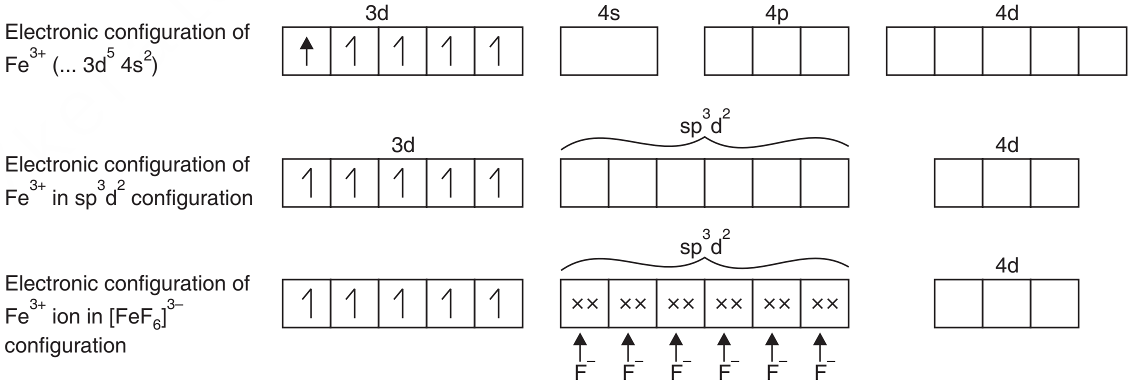
Let us site an example of an octahedral complex $[Fe(CN)_6]^{4-}$. The complex formation is as follows:



The ground state electronic configuration of Fe is ... $3d^6 4s^2$. In Fe^{2+} ion, the two 4*s* electrons move out leaving 4*s* orbital vacant. In d^2sp^3 hybridisation, six d^2sp^3 hybrid orbitals are generated which are filled by electron pairs donated by six CN^- ions acting as ligands, hence $[Fe(CN)_6]^{4-}$ complex is formed.

The shape of the complex molecule is octahedral and due to the absence of unpaired electrons, the complex is diamagnetic. This complex uses the inner *d*-orbitals. So, this is often called inner orbital complex. This is often referred to as spin paired complex.

Another example of sp^3d^2 configuration is $[FeF_6]^{3-}$ complex. The formation of this ion is as follows:

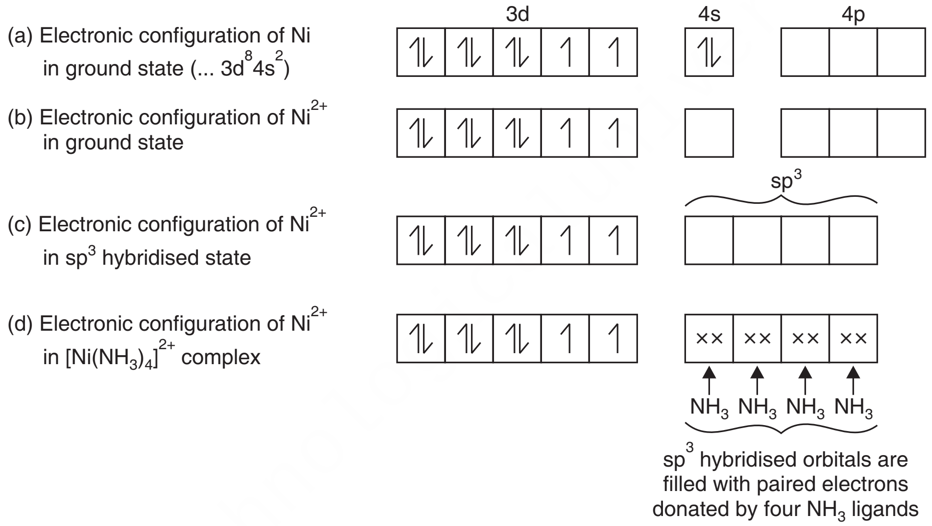


Six sp^3d^2 hybridised orbitals having lone pairs of electrons donated by six F^- ligands.

Such complex is octahedral in shape and since outer *d*-orbitals are involved, it is called outer orbital complex. Because of presence of five lone electrons in 3*d* level the compound is highly paramagnetic and often referred to as *sp* high spin complex.

Tetrahedral Complex

As is implied the tetrahedral complexes are s*p*^{3} hybridised. The formation of such complexes can be illustrated by the formation of tetramine nickel (II) sulphate complex. Atomic number of Ni is 26. Complex cation is produced from Ni^{2+} ion. The co-ordination of nickel is four. So four lone pairs are donated of four ammonia molecules. On the basis of VBT $[Ni(NH_3)_4]^{2+}$ is formed as follows:



The shape of the molecule is tetrahedral, it is paramagnetic in nature and the tetrahedral structure is shown below in Fig. 13.8.

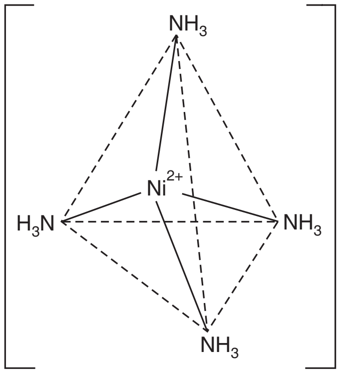
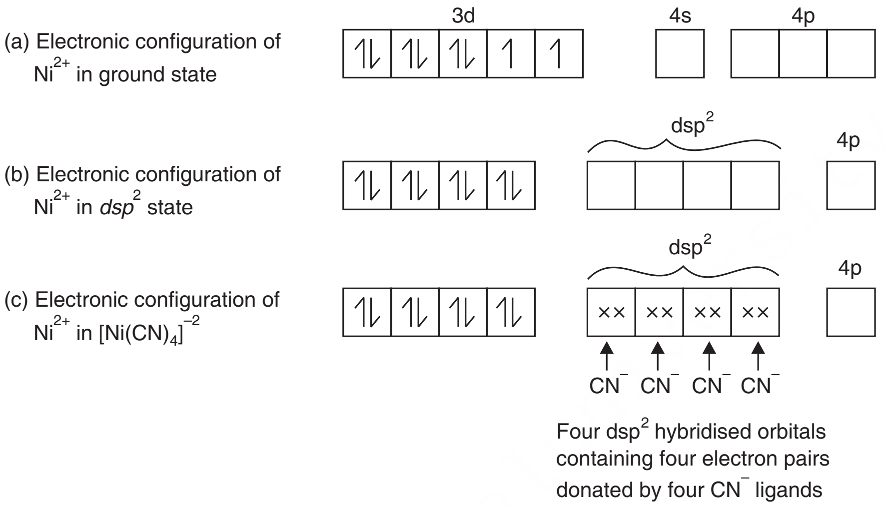


Fig. 13.8 Tetrahedral shape of $[Ni(NH_3)_4]^{2+}$ ion resulted from *sp*^{3} hybridisation.

$[Zn(NH_3)_4]^{2+}$; $[Ni(Co)_4]^0$ are also the examples of tetrahedral complexes.

Square Planar Complexes

These are formed by *dsp*^{2} hybridisation. Example is $[Ni(CN)_4]^{-2}$. The formation of the complex is shown below:



The structure of the complex is square planar, complex is diamagnetic in nature. The shape of $[Ni(CN)_4]^{-2}$ is given below in Fig. 13.9.

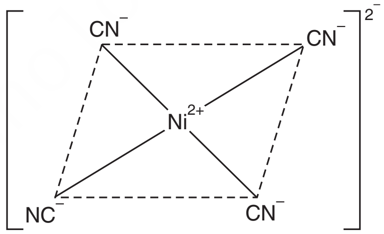


Fig. 13.9 Square planar complex resulted from *dsp*^{2} hybridisation.

CRYSTAL FIELD THEORY (CFT)

The postulate of this theory is: bonding between a central metal ion and its ligands simply arises from purely electrostatic force of attraction. That is an attraction between a positively charged metal ion (μ^{n+}) and the negative charge of the ligand or the partial negative charge of the ligand. If the ligand (L^{-n}) is neutral molecule (L) the negative end of the dipole is attracted towards the central positive metal ion. This theory does not consider the ligand electrons to enter into the orbital of the metal ion.

Crystal Field Splitting of d Orbitals

This theory considers only the effect of the ligands on the energy of outermost *d*-electrons in the central metal ion. In an octahedral complex, the central metal ion is hexa co-ordinated *i.e.,* six ligands occupy the six corners of an octahedron.

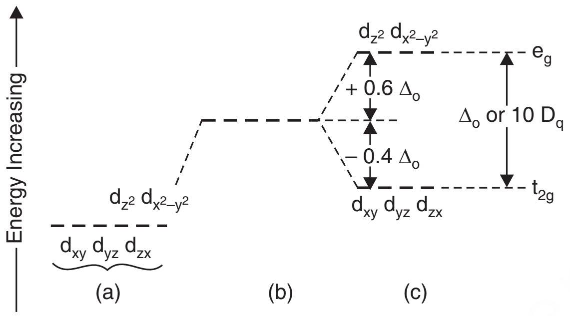


Fig. 13.10 Crystal Field Splitting in an octahedral complex. (*a*) The five degenerate *d*-orbitals in the isolated central metal ion. (*b*) Hypothetical degenerate *d*-orbitals at a higher energy level if all the ligands approach the metal ion at an equal distance from each of the *d*-orbitals. (*c*) Crystal field splitting of *d*-orbitals into t_{2g} and e_g sets by electrostatic field of the six approaching ligands.

In the free metal ion all the five *d*-orbitals are degenerate (orbitals of same energy) as shown in Fig. 13.10 (*a*). When the six ligands approach the central metal atom along the axes they exert an electrostatic force of repulsion on the *d*-electrons of outermost shell *i.e.,* the *d*-electrons are repelled by lone pair of electrons of the ligands. This repulsion force raises the degenerate *d*-orbitals of the metal to a higher energy state as shown in Fig. 13.10 (*b*) which is considered as a hypothetical state. Since the lobes of d_{z^2} and $d_{x^2-y^2}$ orbitals called as e_g set of orbitals fall directly at the path of the approaching ligands, the electrons in these orbitals experience a greater force of repulsion exerted by the electrons of the ligands than that by the electrons of the d_{xy}, d_{y_2} and d_{zx} orbital called as t_{2g} set of orbitals which are directed in space along *x*, *y* and *z* axes. Hence, under the influence of the approaching ligands the orbitals $d_{x^2-y^2}$ and d_{z^2} exist in the higher energy levels compared to d_{xy}, d_{yz} and d_{zx}. The separation of five *d*-orbitals in the t_{2g} and e_g sets of different energy states is known as **crystal field splitting**. The energy difference between e_g and t_{2g} sets of orbitals is denoted by Δ_o or $10D_q$ where '*o*' indicates an octahedral arrangement of ligands around the central metal ion. Δ_o is called **crystal field stabilisation energy (CFSE)**. It can be shown that when an octahedral complex is formed the energy of the t_{2g} set is decreased $0.4\Delta_o$ while that of e_g set is increased by $0.6\Delta_o$ as shown in Fig. 13.10.

Strong and Weak Ligands

Strong ligands can split the five *d*-orbitals into t_{2g} and e_g sets strongly *i.e.,* there splitting power is high whereas the weak ligands can split the set of orbitals weakly *i.e.*, there splitting power is weak. Strong ligands confer higher value of Δ_o and weak ligands confer lower values to Δ_o. The following is the arrangement of ligands with the splitting power of increasing order. This order is known as **spectrochemical series**.

C-donor > N-donor > O-donor > X-donor

Examples of C-donor = CN^-
N-donor = NO_2^-, NH_3
O-donor = H_2O, OH^-
X-donor = $F^- > Cl^- > Br^- > I^-$

Distribution of *d*-electrons in t_{2g} and e_g sets of orbitals—low spin and high spin complexes.

- The strong ligands *i.e.*, Δ_o when high, force the electrons to form a pair in the lower t_{2g} set of orbitals and thus the number of unpaired electrons is reduced, so the resultant spin '*s*' is also reduced. So, the complexes formed with strong ligands have minimum number of unpaired electrons, so the spin value '*s*' gets lowered. These types of complexes are known as **low spin** (L.S.) or **spin paired complexes.**

- The weak ligands *i.e.*, Δ_0 when lower, first force the electrons to occupy all the five *d*-orbitals singly and then get paired. Thus weak ligands produce higher number of unpaired electrons and so the higher value of '*s*'. These types of complexes produced by weak ligands are known as **high spin** (H.S.) or **spin free complexes**.

Table 13.1: Distribution of *d*-electrons in t_{2g} and e_g sets in strong octahedral ligand field (*n* = number of unpaired electrons, S = resultant spin)

d^z^ ion	*Distribution of d-electrons in*		*n*	*S = n/2*
	t_{2g} set	*e_g set*		
d^1	↑ – –	– –	1	1/2
d^2	↑ ↑ –	– –	2	2/2 = 1
d^3	↑ ↑ ↑	– –	3	3/2
d^4	↑ ↑ ↑	– –	2	1
d^5	↑↓ ↑↓ ↑	– –	1	1/2
d^6	↑↓ ↑↓ ↑↓	– –	0	0
d^7	↑↓ ↑↓ ↑↓	↑ –	1	1/2
d^8	↑↓ ↑↓ ↑↓	↓ ↑	2	1
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	1	1/2
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0	0

CFT and Magnetic Properties of the Complex Formed

One of the greatest achievements of **CFT** is: with the help of this theory prediction of the magnetic properties of the complexes formed is possible. The complexes having no unpaired electrons should not exhibit any magnetic property, so therefore are diamagnetic. The complexes having one or more unpaired electrons should show magnetic properties, so they are paramagnetic complexes. The magnetic moment μ is related to the unpaired electrons *n* by the relation

$$\mu = \sqrt{n(n+2)}\ .\ \mathrm{B}\mu$$

Table 13.2: Distribution of *d*-electrons in t_{2g} and e_g sets in weak octahedral ligand field

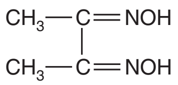
d^x ion	*Distribution of d-electrons in*		*n*	*S = n/2*
	t_{2g} set	*e_g set*		
d^1	↑ – –	– –	1	$1 \times \frac{1}{2} = \frac{1}{2}$
d^2	↑ ↑ –	– –	2	1
d^3	↑ ↑ ↑	– –	3	3/2
d^4	↑ ↑ ↑	↑ –	4	2
d^5	↑ ↑ ↑	↑ ↑	5	5/2
d^6	↑↓ ↑ ↑	↑ ↑	4	2
d^7	↑↓ ↑↓ ↑	↑ ↑	3	3/2
d^8	↑↓ ↑↓ ↑↓	↑ ↑	2	1
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	1	1/2
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0	0

Application of Ligands

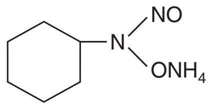
Ligands are widely used in different fields of chemistry. Some of these are given below:

(*i*) **In gravimetric analysis.** Nickel ion in alkaline medium can be estimated as well as identified with **dimethyl glyoxime** acting as chelating ligand.

Cupferron gives a precipitate with ferric ion in acid medium. The ferric cupferron complex is ignited to ferric oxide and weighed.

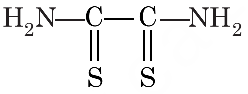


Dimethylglyoxime



Cupferron (ammonium salt of nitroso phenyl hydroxylamine)

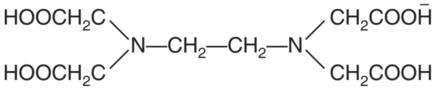
(*ii*) **In qualitative analysis.** Copper ion in faintly acidic or ammoniacal medium is detected with Rubeanic acid or dithioxamide as chelating complex.



$$\mathrm{H_2N{-}\underset{S}{\underset{\|}{C}}{-}\underset{S}{\underset{\|}{C}}{-}NH_2}$$

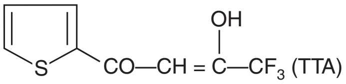
Rubeanic acid

(*iii*) **In complexometric titrations.** Using EDTA (ethylenediamine tetraacetic acid) as complexing agent many metal ions like calcium, magnesium, aluminium, etc., are estimated by complexometric titration.



EDTA

(*iv*) **In the separation of metal ions and solvent extraction.** Some metal ions like zirconium and hafnium can be separated from solution by chelation with thionyltrifluoro-acetone (TTA).



A combination of chelating agent and a masking agent *e.g.*, oxin and EDTA, greatly increases the selectivity of extraction processes.

(*v*) **For medicinal purpose:**

(*a*) EDTA is used to inhibit heavy metal poisoning.

(*b*) Thiosulphate is used as a preventing agent of cyanide poisoning.

(*c*) Vitamin B_{12} itself is a chelate compound in which the central metal ion is cobalt.

(*d*) Cisplatin is an anticancer drug.

SHORT QUESTIONS

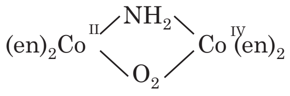
1. What are transition metals?
2. Mention the common features of the transitional metals.
3. Mention the main oxidation state of the first transition series.
4. Differentiate between double salt and complex salt.

5. Give an expression for K_{ins} and state its significance.
6. Give main postulates of Werner's theory.
7. What is a ligand?
8. What is co-ordination number?
9. Mention main drawback of co-ordination theory.
10. What are chelate compounds? Give examples.
11. What are inner metallic complexes?
12. What do you mean by ambident ligands?
13. Give examples of each:
(*a*) Cationic complex (*b*) Anionic complex.
14. Give an example of bridging ligand complex.
15. Mention the types of isomerism found in complex compounds. Give one example of each type.
16. Show the hybridisation of an octahedral complex.
17. Give the state of hybridisation of a square planar complex.
18. What is the main postulate of CFT?
19. What do you mean by crystal field splitting of *d*-orbitals?
20. What is CFSE?
21. What is spectrochemical series?
22. What are low spin and high spin complexes?
23. What is the main outcome of CFT?
24. Give some uses of ligands.
25. Calculate the magnetic moment μ for one unpaired electron. [**Ans.** 1.732 Bμ]
26. Calculate the magnetic moment μ for 2, 3, 4, 5, 6 and 7 unpaired electrons.
[**Ans.** 2.83; 3.87; 4.9; 5.92; 6.93 and 7.93 Bμ respectively]

EXERCISES

1. State the postulates of Werner's co-ordination theory and discuss the structure of $K_4Fe(CN)_6$ on the basis of this theory.
2. Explain geometrical and optical isomerisms of octahedral complexes.
3. Discuss the geometrical as well as optical isomerism in complexes with co-ordination number 4 and 6.
4. State the postulates of crystal field theory. On the basis of this theory predict whether the complexes $[CoF_6]^{-3}$ and $[Co(NH_3)_6]^{+3}$ are paramagnetic or diamagnetic.
5. Explain with example the valence bond theory regarding complex molecules.
6. Cite some fields of application of ligands in our daily lives.
7. Give IUPAC nomenclature of the following:

(*a*) $CoCl_2.6NH_3$, (*b*) $Pt(NH_3)_2Cl_2$, (*c*) $[Co(en)_2Cl_2]^+$ (*d*)



(*e*) $[Fe(CN)_6]^{-3}$. (*f*) $[Cr(H_2O)_5\ Cl]^{2+}$ (*g*) $[Cr(H_2O)_4\ Cl_2]^+$ (*h*) $[Cr(H_2O)_6]Cl_3$
(*i*) $[Pt(NH_3)_4Cl_2]Br_2$ (*j*) $[Pt(NH_3)_4\ Br_2]Cl_2$ (*k*) $[Co(NH_3)_4Cl_2]NO_2$

8. Draw the structures of the following:
(*a*) Tetraaquo dihydro aluminium ion.
(*b*) Ammonium diamine tetrathiocyano chromate (III)
(*c*) Triamine aquo dichloro cobalt (III) chloride
(*d*) Sodium hexa nitrito cobaltate (III).

14

Metallurgy

INTRODUCTION TO THE STUDY OF METALS

The gold and silver among the metals are probably the first used by man. The art of reducing copper ores and tin ores, and producing bronze dates back to 300 B.C. In history we find 'stone age' followed by 'bronze age' and 'bronze age' followed by 'iron age'.

Today we find the metals are very extensively used in art and industry. Iron in the form of steel, wrought iron and cast iron is used in constructing bridges, dams, pipes, tubes and machine parts. Copper is another important metal being used mainly in electrical articles. Nowadays almost all the metals have some specific uses.

Metals

Metals are the elements, which occupy the left hand side of the periodic table with one, two or three electrons in the outermost shell that takes part in **bonding** and **chemical reactions**.

Physical Properties of Metals

Metals are:

- Shiny when freshly polished and free of corrosion.
- Good conductors of heat and electricity.
- Malleable and ductile.
- Generally solids are with high m.p. and b.p. (only six metals melt below 100 °C—Hg which is a liquid and four group I metals: Na, K, Rb, Cs).

Major Chemical Properties of Metals

Chemically, metals tend to:

- Lose electrons to form cations or positive ions *i.e.,* metals are reducing agents.
- Form basic or amphoteric oxides.
- Form solid ionic chlorides.

The more an element exhibits these properties, the greater is its "**metallic character**".

Metallic Bonds

Metallic bonds are strong bonds in metal crystals. Each metal atom in a metal crystal contributes electrons from its outermost shell to form a "sea of delocalised electrons". Only elements with low first ionisation potential form metallic crystals. When a metal atom looses electron it becomes positively charged. So, it is quite likely that a metal crystal consist positively charged metal atoms embedded in a sea of shared electrons.

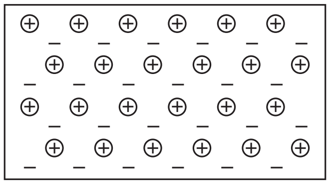


Fig. 14.1 Simplified picture of metallic bonding.

Metals conduct electricity because these shared bonding electrons can drift through the crystal structures from atom to atom when there is an electrical potential difference between the two ends. Metals can bend without breaking because metallic bonding is not highly directional. Lines or layers of metal atoms can shift their positions in a crystal without breaking the metallic bonds.

Mineral Resources of India

The sound economy of a country depends upon its mineral wealth. The most important among the mineral products in India is **coal**, about 58% of the total output is available from Jharia and Raniganj. **Iron ores** occur abundantly in India. The deposits of huge iron ore are in Singhbhoom, Keonjhar and Mayurbhanj. The next important mineral is manganese. Manganese ores are found in Chotanagpur, Mysore, Mumbai and Tamil Nadu. Copper is chiefly found in Chotanagpur and Sikkim. The bauxite deposits are largest in India. Chromite is found in Mysore and Orissa. India occupies the first place in producing mica in the world. Borax, kaoline, limestone, gypsum, pitch-blende, monazite sand are other minerals, which are found in India.

Occurrence of Metals in Nature

Some metals occur in nature in 'native' or 'free state'. A metal is said to occur native or free when it is found in nature in the metallic state. As for example gold and platinum occur in nature in the metallic state. We can say that these metals are not readily attacked by the moisture, oxygen, and carbon dioxide of the air. While those metals which are readily attacked by moisture, oxygen and carbon dioxide occur in the **combined state** or as a compound. These metallic compounds generally occur in the form of hard stones either in the underneath or in the earth surface. **These naturally occurring inorganic compounds are known as minerals**. Minerals are always associated with sand, soil or other impurities. These impurities are known as **Gangue**. The percentage of gangue in a mineral is always higher than the mineral itself.

Common Minerals

- Oxide — [Bauxite, Al_2O_3 $2H_2O$] for Aluminium
  [Hematite, Fe_2O_3] for Iron
- Carbonate — [Limestone, $CaCO_3$] for Calcium
  [Magnesite, $MgCO_3$] for Magnesium
- Sulphide — [Zinc blende, ZnS] for Zinc
  [Galena, PbS] for Lead
- Sulphate — [Gypsum, $CaSO_4.2H_2O$] for Calcium
- Nitrate — [Chile saltpetre, $NaNO_3$] for Sodium

- Halide — [Fluospar, CaF_2] for calcium
- Silicate — [Mica, $KHMg_2Al_2(SiO_4)_3$] for Magnesium
- Phosphate — [Phosphorite, $Ca_3(PO_4)_2$] for Calcium

Some minerals of common metal are listed below in tabular form:

Form	*Metal*	*Name of ores and minerals*
Oxides and hydrated oxides	(*i*) Aluminium (Al)	(*i*) Claysilicate ($Al_2O_3.2SiO_2.2H_2O$) Diaspore ($Al_2O_3.H_2O$)
	(*ii*) Copper (Cu) IB (Coinage metal)	(*ii*) Cuprite (Cu_2O)
	(*iii*) Zinc (Zn) IIB (Amphoteric metal)	(*iii*) Zincite (ZnO)
	(*iv*) Manganese (Mn) VIIB (Transition metal)	(*iv*) Pyrolusite (MnO_2) Braunite (Mn_2O_3)
	(*v*) Chromium (Cr) VIB (Transition metal)	(*v*) Chromechre (Cr_2O_3)
	(*vi*) Tin (Sn) IVA (Amphoteric metal)	(*vi*) Tin stone or cassiterite (SnO_2)
	(*vii*) Potassium (K) (Alkali metal)	(*vii*) Felspar ($K_2O.Al_2O_3.6SiO_2$)
Sulphides	(*i*) Copper (Cu) IA (Coinage metal)	Copperglance (Cu_2S); Copperpyrite (CuS, FeS)
	(*ii*) Zinc (Zn)	Zinc blende (ZnS)
	(*iii*) Lead (Pb) IVA (Amphoteric metal)	Galena (Pbs)
	(*iv*) Mercury (Hg) IIB (Liquid metal)	Cinnabar (HgS)
	(*v*) Tin (Sn)	Stannite (Cu_2S, FeS, SnS_2)
	(*vi*) Iron (Fe)	Iron pyrite (FeS_2)
	(*vii*) Silver (Ag) IB (Best conducting metal)	Silver glance (Ag_2S); Rubby silver $3Ag_2S.Sb_2S_3$
Carbonates	(*i*) Iron (Fe)	Siderite ($FeCO_3$)
	(*ii*) Copper (Cu)	Malachite ($CuCO_3$ $Cu(OH)_2$)
	(*iii*) Calcium (Ca) IIA (Alkaline earth metal)	Calcite ($CaCO_3$); Dolomite ($CaCO_3.MgCO_3$)
	(*iv*) Magnesium (Mg) IIA (Bridge metals)	Magnesite ($MgCO_3$); Dolomite ($MgCO_3CaCO_3$)
	(*v*) Manganese (Mn)	Manganese spar ($MnCO_3$)
	(*vi*) Lead (Pb)	Cerussite ($PbCO_3$)
	(*vii*) Zinc (Zn)	Calamine ($ZnCO_3$)
Sulphates	(*i*) Calcium	Gypsum ($CaSO_4.2H_2O$) Anhydrite ($CaSO_4$)
	(*ii*) Lead	Anglesite ($PbSO_4$)
	(*iii*) Aluminium	Alum (K_2SO_4; Al_2 $(SO_4)_3.24H_2O$)
	(*iv*) Barium IIA (Alkaline earth metal)	Heavy spar ($BaSO_4$)

	(*v*) Magnesium	Epsomite ($MgSO_4.7H_2O$) Kisserite ($MgSO_4.H_2O$)
Halides	(*i*) Sodium	Rocksalt (NaCl)
	(*ii*) Potassium	Sylvine (KCl)
	(*iii*) Silver IB (Conductive metal)	Horn silver (AgCl)
	(*iv*) Calcium	Fluoropalite ($3CaF_2$ $Ca_3(PO_4)_2$); Chloropative ($3COCl_2.Ca_3(PO_4)_2$)
	(*v*) Magnesium	Carnallite KCl, $MgCl_2$ $6H_2O$
	(*vi*) Aluminium	Cryolite (3NaF, AlF_3)
Silicates	(*i*) Sodium	Sodium silicate (Na_2SiO_3)
	(*ii*) Potassium	Felspar ($K_2O.Al_2O_3.6SiO_2$)
	(*iii*) Zinc	Willemite ($ZnSiO_2$)
	(*iv*) Aluminium	Felspar ($K_2O.Al_2O_3.6SiO_2$)

Ores

Generally all minerals cannot be considered important for extraction of metal from them. The process of extraction though costly may not be impossible from these minerals. **Particularly, the minerals from which metals can be extracted easily and cheaply are known as ores**. As for example, haematite is the ore of iron, bauxite is the ore for aluminium etc.

Metallurgy

The process by which the metals are extracted from their respective ores is known as metallurgy. An ore is naturally occurring substance or mineral from which the metal can be extracted economically.

Concentration of the Ore

Almost all ores are associated with gangue or matrix. Before the proper extraction of the metal the ore is freed from gangue or matrix to get it in the concentrated form. As a matter of fact, the ore is enriched with the desired metallic compound. This process of removal of gangue is known as the concentration of the ore. There are several processes of the concentration of ores, which are described below. This process of concentration of ore makes the extraction of the metal easier and cheaper. The main steps for the extraction of metals are generally as follows:

1. **Crushing and grinding**
2. **Concentration of the ore**
3. **Calcination/Roasting**
4. **Reduction**
5. **Purification**

Crushing and Grinding. This is one of the crucial steps of concentration process. The step provides breaking of big masses of rocks containing the ore into small lumps by conventional crushing and grinding with machines *viz.*, Jaw crusher, Gyratory crusher etc.

Sometimes, the concentration and further treatment of some ores demand their reduction of size into a very fine state of division. This is effected in **grinding** and **pulverising mills** (Figs. 14.2 and 14.3).

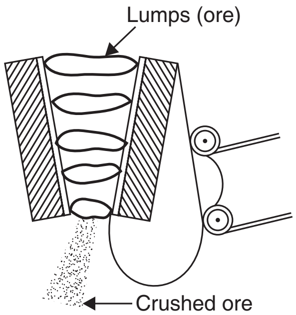


Fig. 14.2 Crushing.

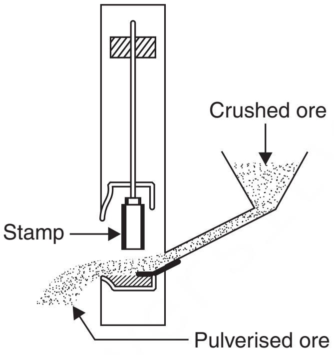


Fig. 14.3 Pulverisation.

Concentration of the Ore

(*i*) *Washing.* This process includes all methods of concentrations in which water in motion is used. From the pulverised ore in stream of water the lighter particles float away with water and thus some gangues are removed.

(*ii*) *Floatation.* Here concentration of the pulverised ore is effected by taking the advantage of the difference in its behaviour towards oil or water. Sulphide ores, as a rule, do not get wet as do silica and most oxides when treated with water. Therefore, sulphide ores will float on the surface while silica and other materials will sink.

(*iii*) *Oil floatation process.* Oils have just the opposite effect, they are attracted by sulphide ores. Oils form a film over the sulphide ore. The pulverised sulphide ore is taken in a tank and some pine oil and water are used. Generally some xanthates are used with pine oils. Air is made to bubble through a perforated pipe from the underneath of the tank. A foam is produced and floats along with the sulphide ore over the surface of water. But the sand and soil are settled down. The concentrated ore is collected from foam (Fig. 14.4).

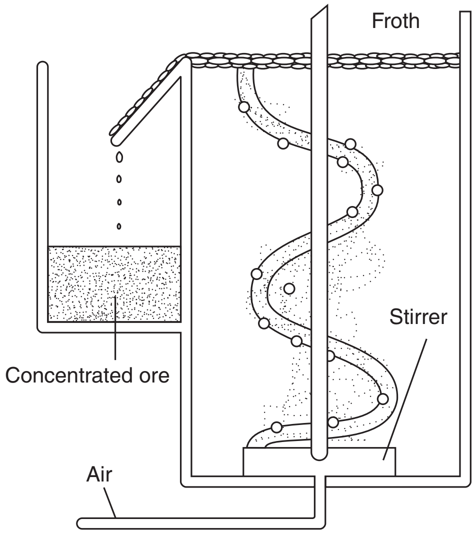


Fig. 14.4 Concentration of ore by oil floatation.

(*iv*) *Magnetic separation.* Ferromagnetic ores can be separated by passing the ore through a strong magnetic field, whereby ferromagnetic substances are separated from the ore. The tungsten or tin ore is separated by this method.

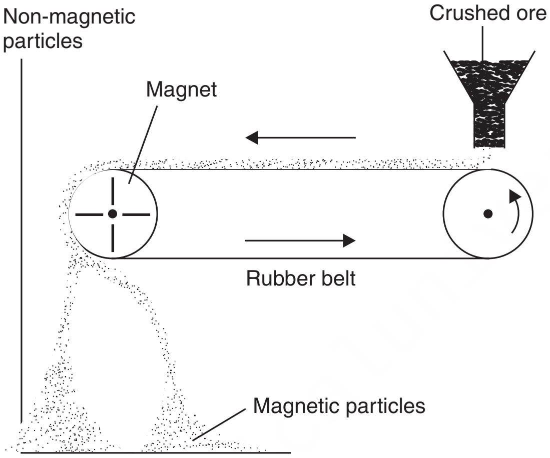


Fig. 14.5 Magnetic separation.

Calcination and roasting. These two terms are used, somewhat interchangeable, among the metallurgists, though a distinction exists between them.

- **Roasting:** To roast a material is to heat it at a temperature insufficient to melt it *i.e.,* below the point of fusion but **always in presence of air** with a view to oxidising the material. The term is usually applied in case of oxidising the ores. As for example, metallic sulphides are roasted to oxides before reduction to extract the metal.

$$2MS + 3O_2 = 2MO + 2SO_2$$
$$MS + 2O_2 = MSO_4$$

- **Calcination:** To calcine a material is to heat it very strongly but at **a temperature insufficient to melt it**; with a view to driving of volatile matters leaving some pores on the rocky ore to facilitate the reduction process, so that reducing gas *viz*., CO can enter into pores and make reduction complete. As for example,

$$M_2O_3.x\,H_2O \xrightarrow{\Delta} \underset{\text{(Calcined)}}{M_2O_3} + x\,H_2O\uparrow$$

$$MCO_3 \xrightarrow{\Delta} \underset{\text{(Calcined)}}{MO} + CO_2\uparrow$$

Fluxes

Before the extraction of metals from their ores and in their subsequent purification, the impurities (gangue) present in the ores are to be removed. They are often refractory in nature and remain unfused which may disturb efficient extraction of the metal. So, gangue must be removed. They become easily fusible when heated with other substances, those substances are known as **fluxes**.

So, **flux is a material, which when added to an ore and heated gives a fusible mass known as slag.**

$$\text{Gangue + Flux} \xrightarrow{\text{heat}} \text{Slag (fusible)}$$

Selection of Flux

The nature of flux to be used depends on the nature of gangue. If it is acidic, basic flux is to be used *viz*. lime, magnesia etc. If the gangue is basic in character, then an acid flux like sand (SiO_2) must be employed.

There are three kinds of fluxes:

- **Acidic** (SiO_2)
- **Basic** (CaO, MgO)
- **Neutral** (fluorspar)

Fuels

Almost all industries require a fuel. Large scale industries, like metal extraction, need economy of fuel consumption.

Furnaces

- **Reverberatory furnace.** This is a special type of furnace much used in metallurgy. In this furnace, the material is heated not directly over fire, but by the hot gases produced in the fire place (Fig. 14.6).

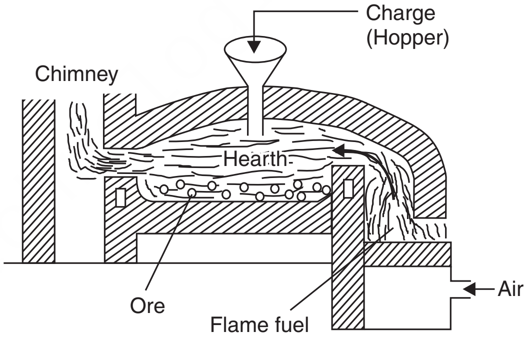


Fig. 14.6 Reverberatory furnace.

- **Muffle furnace.** It is a type of furnace consisting of an enclosed chamber, made of refractory materials, from which the fuel and its products of combustion cannot come in contact with the materials heated in it (Fig. 14.7).

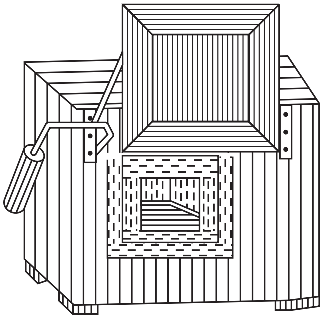


Fig. 14.7 Muffle furnace.

- The other furnaces are **blast furnace** (for iron extraction), **open hearth furnace** (for steel manufacture) and **electric furnace** (for Phosphorus extraction).

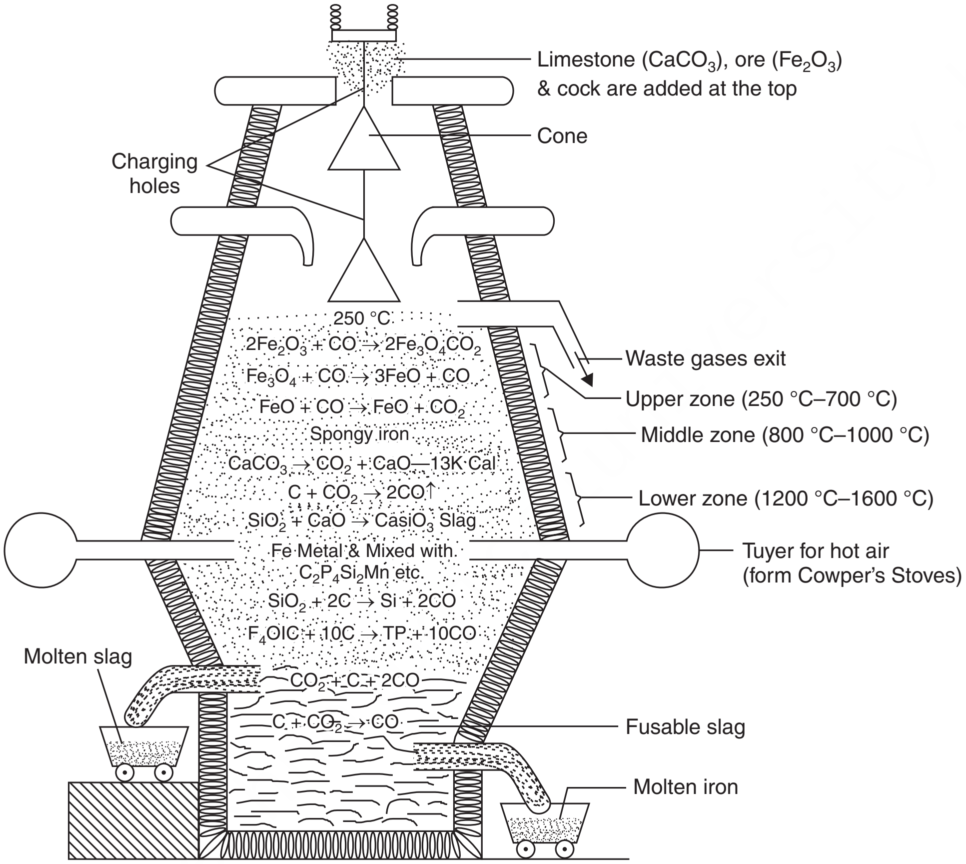


Fig. 14.8 Blast furnace (displaying reactions of iron extraction in various zones of the furnace).

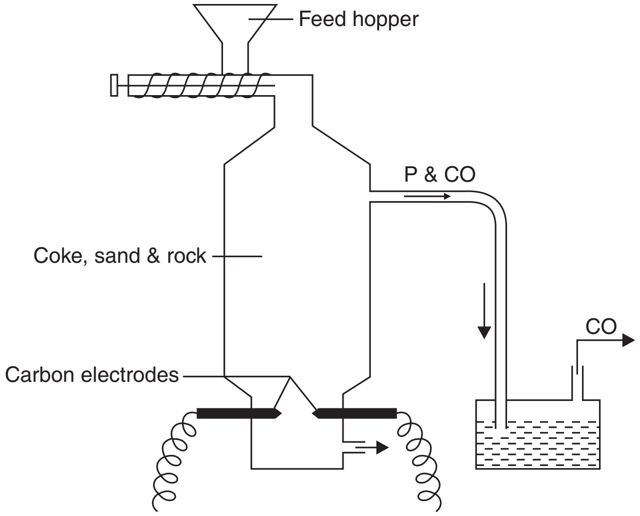


Fig. 14.9 Electric arc furnace.

Smelting. The process by which a metal is extracted in the fused state is called smelting.

Welding. It is the operation of joining the two pieces of a metal either by pressure or by fusion to one compact mass.

Alloy. An alloy is a mixture or compound or both of two or more metals. When one of these metals is mercury, the alloy is called an **amalgam**. So, an alloy may be considered as solid solution or an intermetallic compound or both. Steel is an alloy of iron and carbon, a non-metal. An alloy is often more useful than a pure metal. Controlling the composition of an alloy makes it possible to vary its properties. Generally, alloys are classified as:

- **Non-ferrous alloys**
- **Ferrous alloys**

Non-ferrous alloys do not contain iron as one of the constituents of the alloys, *e.g.*, Brass which is composed of Zn and Cu. Whereas ferrous alloys always contain iron as one of the constituents of the alloys, *e.g.,* Stainless steel contains Fe, Ni, Cr.

Importance of alloy preparation

- to increase the hardness and tensile strength
- to improve the casting property
- to increase the resistance to corrosion
- to decrease the thermal and electrical conductivities.
- to lower the melting and boiling points of individual metal.

General methods of preparation of alloys

- **By fusion.** Component metals are mixed together in the desired ratio and melted followed by cooling.
- **By compression.** Finely divided metals are compressed in the desired ratio.
- **By reduction** of the mixture of oxides to get mixture of metals in the proper ratio.

Examples of important alloys are

- **Mild steel.** An alloy of iron with carbon (0.1-0.25%). It is relatively cheap, can be easily rolled into sheets, and can be pressed into shape.
- **Stainless steel** (Chromium steel) (10-15% Cr, 90-85% Fe). It is mainly used in making utensils as well as reactors in industries.
- **Manganese steel** contains Mn 12-14% and the rest is iron. It is used in making rolls.
- **Molybdenum and Tungsten steel or High speed tool steel** are mainly used for high speed machines.
- **Wrought iron** (C = 0.1-0.25%), is mainly used in making household furnitures.
- **Ferro-titanium** is used as deoxidisers to avoid formation of 'blow holes' from molten steel.
- **Brass,** an alloy of copper (Cu:Zn = 60:40), has a gold colour and does not corrode.
- **Bronze,** an alloy of copper with upto 12% tin (Sn), a strong, hard wearing and resistant to corrosion.
- **Solder.** An alloy of Pb and Sn that melts at low temperature, can be used to join metals.
- **Duralumin.** An alloy of 95% Al with 4% Cu and smaller amounts of Mg, Fe, Si, it is stronger, harder, more resistant to corrosion than pure Al, used mainly in making the body of aeroplanes.

- **Magnalium.** An alloy of Al and Mg (98:2) used in making light machine parts.
- **Alnico.** (Composition—Steel:Al:Ni:Co = 5:2:2:1) Used for making permanent magnets.

Cementation

When a metal is heated in contact with a powder, the powder is slowly absorbed by the metal without melting whereby the property of the metal changes to a certain extent. This process is called **cementation** and the powder is called the **cement**.

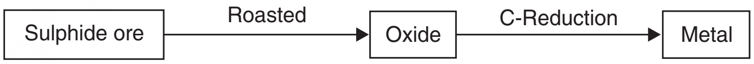
General Methods of Extraction of Metals from their Ores

- Metals like gold (Au), platinum (Pt) etc., are obtained in nature in the free state. So their method of extraction practically consists of separating them efficiently from the rocky and other impurities.
- But, most of the metals occur as their compounds such as oxides, hydroxides, carbonates, sulphides, halides etc. Then we can say, there are two broad steps in their extraction process:

  (*i*) Preliminary **calcination** and **roasting**

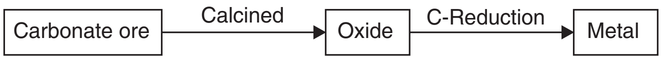
  (*ii*) Reduction.
- When the ore is an oxide, hydroxide, or carbonate it is first calcined to get porous oxides and then the calcined ore is reduced to the metal, generally, by **carbon reduction process**. The principle and processes of reduction will be discussed later on.
- When the ore is a sulphide, it is first heated in the presence of air *i.e.,* roasted to get metallic oxide and then reduced to get the metal.

Scheme I:



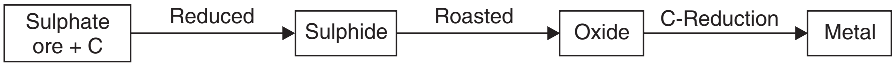
- When the ore is a carbonate or hydroxide:

Scheme II:



- When the ore is a sulphate:

Scheme III:



- When the ore is a halide or metallic oxide or is not reducible by carbon, electrolytic process of reduction is followed.

Methods of Reduction of the Processed Ore

Metal extraction involves two main types of processes for the reduction of the metallic compounds.

(*i*) **Pyrometallurgy:** It means **reactions at high temperature often above 1000°C.**

(*a*) Electrolytic reduction at high temperatures of the fused salts especially halides (for example Na, Al).

(*b*) Chemical reduction by coke at high temperatures (for example, iron, lead)

$$MO + C \xrightarrow{\Delta} M + CO$$

(*c*) Chemical reduction by a more reactive *i.e.,* electropositive metal (for example, chromium and titanium extraction).

$$Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Cr \text{ (Goldschmidt Thermit process)}$$

(*ii*) **Hydrometallurgy:** It means, **reactions at low temperature in solution in water.**

(*a*) Electrowinning at low temperature in solution in water (for example, Zn extraction for $ZnSO_4$ solution).

(*b*) Cementation using a displacement reaction (for example, using iron to displace copper from a solution of $CuSO_4$)

$$CuSO_4 + Fe = Cu + FeSO_4$$

Goldschmidt Thermit Process

The metallic aluminium has a strong affinity for oxygen at 1000°C. The combination of oxygen with aluminium at that temperature evolves much heat, which is utilised in **Goldschmidt Thermit process** or **Aluminothermic process** for the reduction of metallic oxides *e.g.,* MnO_2 or Cr_2O_3 and for the separation of molten metals.

Goldschmidt Thermit process is nowadays mostly used for welding rails and machine parts (Fig. 14.10). Thermite, a mixture of aluminium powder and iron oxide in the ratio 3:1 by weight, is ignited in a crucible by a ribbon of magnesium, when a violent reaction takes place producing molten iron at 2500°C.

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe + 199 \text{ kcal}$$

The liquid iron is dropped on the two pieces directly to the joint to be welded.

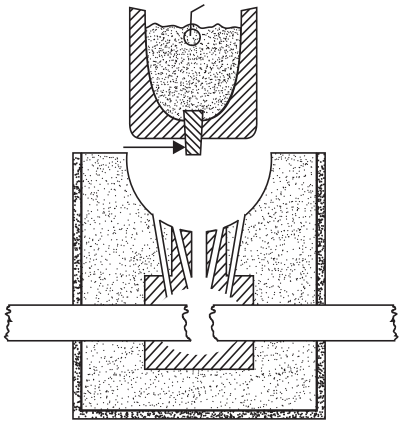


Fig. 14.10 Goldschmidt Thermit process.

Purification of the Metals Extracted

Almost all metals obtained by reduction processes contain some impurities. The impurities are to be removed to get the pure form of metal. The purification processes are:

1. Thermal refining and
2. Electro-refining

1. **Thermal refining**

- *Oxidation of impurities by air poling.* The impure metal is melted and a stream of air is purged through the bottom, as a result of which the easily oxidisable impurities are converted to oxides. The volatile oxides escape and a non-volatile oxide forms a scum over the molten metal, which is removed with the help of a laddle.
- *Fractional distillation.* Easily volatile metals can be removed with the help of fractional distillation. The crude zinc, which is known as spelter, contains about 2% of lead and traces of iron, cadmium, arsenic as impurities. The spelter is at first heated in a retort at a temperature slightly above the boiling point of zinc (920°C). When zinc together with cadmium distils over leaving behind lead (b.p. 1620°C) and iron (b.p. 2800°C). The distillate *i.e.,* molten mixture of zinc and cadmium is redistilled in another retort at a temperature slightly above 767°C when more volatile cadmium (b.p. 767°C) distils out and 99.9% of zinc is left in the retort.
- *Liquation.* An easily fusible metal such as tin or lead can be refined by this process. The impure metal containing infusible impurities is heated on the sloping hearth of a special type of furnace (Fig. 14.11), as a result the metal melts and the molten metal flows down the sloping hearth leaving behind the infusible impurities on the top.

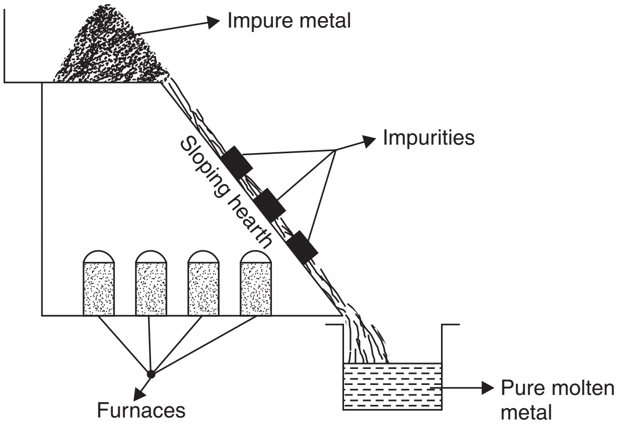


Fig. 14.11 Refining of metal by Liquation.

- *Zone refining* (Fig. 14.12). This process of purification is employed effectively in some special cases. The advantage is taken out of the fact that the impurities are more soluble in the molten metal than the solid metal and the molten metal on resolidification crystallises out as a pure metal. The actual process is: a narrow rod of impure metal is taken and a small portion of it at one end is almost melted by application of heat. This small molten zone is gradually and slowly shifted to the other end of the rod by gradual shifting of the source of heat. At last the molten zone containing all the impurities reach the other end. The rod is allowed to cool and the impure zone is cut off and removed. The remaining portion of the rod consists of the pure metal.

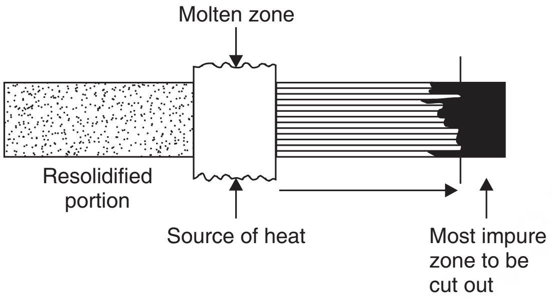


Fig. 14.12 Zone refining.

2. **Electro-refining.** This method is widely used. Usually an electrolytic cell is set up using thin sheets of pure metal as the cathode and comparatively thick impure metal slag as anode. The electrolyte used is an aqueous solution of a suitable salt. During electrolysis, pure metal from the electrolyte gets deposited on the cathode and the equivalent amount of metal from the anode passes into the solution. The impurities either remain in solution or are deposited down the anode. This deposit is known as **anode mud**. Sometimes some valuable metals are recovered from anode mud. A typical example of electrolytic refining is of copper (Fig. 14.13).

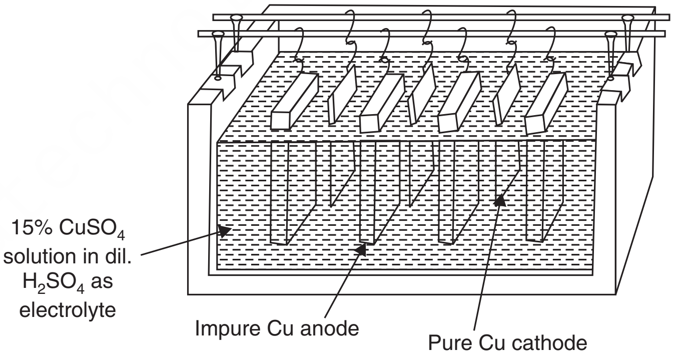


Fig. 14.13 Electrolytic refining of copper.

POWDER METALLURGY

Powder metallurgy (Fig. 14.13) is a technique or operation or process to produce metallic or alloy articles. In this technique, the metal powders or alloy constituents are compacted in a die with melting or no melting followed by sintering. The simultaneous method of compacting and sintering is called *pressure sintering.*

The article is made into the desired shape by powder metallurgy in the following steps:

(*i*) *Pulverisation of metallic powders*
(*ii*) *Mixing and blending*
(*iii*) *Compacting*
(*iv*) *Pre-sintering, and*
(*v*) *Sintering*
(*vi*) *Finishing operation.*

(*i*) **Pulverisation of metallic powders.** For pulverisation of metals techniques adopted are:

(*a*) *Mechanical:* This method may be adopted in the case of Mg, Al, Zn, and Pb. For pulverisation ball mills can be employed.

(*b*) *Atomisation:* This method involves forcing molten metal through a nozzle or spinnerette in a stream of water or compressed air, when fine powder of metals are obtained. This method requires control of pressure and temperature and the oxidation of metal into an atmosphere of inert gas. This method is commonly employed for metals like Mg, Cd, Zn, Pb, Sn etc.

(*c*) *Chemical:*

1. By reduction,

$$WO_2 + 2H_2 \xrightarrow{\Delta} W + 2H_2O$$

2. By decomposition,

$$Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO\uparrow$$

The metals are obtained in a state of fine powders in both cases.

(*ii*) **Mixing and blending.** This operation is required when a combination of metallic powders are used. They are uniformly mixed in right proportions. Lubricants may be added if necessary.

(*iii*) **Compacting.** The metal powder in right proportions is then taken in a die into the cavity (female joint) of accurate dimensions and then compressed (100–1000 N/m^2) by the male joint of the die. The solid in this stage is known as '*green compact*'.

(*iv*) **Pre-Sintering.** It involves heating the green compact to a temperature below the sintering temperature. This step increases the strength of green compact as well as removes the lubricant if used. This step is essential for tungsten.

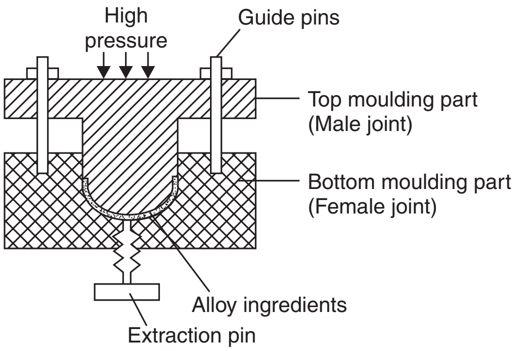


Fig. 14.14 Technique of powder metallurgy adopted in a die.

(*v*) **Sintering.** Compacted pieces are heated to a temperature below and very close to the melting point of the metal in a furnace, preferably in an atmosphere of hydrogen, whereby metal particles sinter to a coherent mass. Time and temperature of sintering depend upon the nature of the metal.

(*vi*) **Finshing operations.** The sintered articles require operations like machinery, plating etc., to get accurate shape of the work pieces.

Uses

In making:

(*i*) Porous bearings ; (*ii*) Tungsten filaments for electric bulbs ; (*iii*) Sewing machines (*iv*) Gears ; (*v*) Clutches, breaks etc.

Advantages

(*i*) Articles of any intricate shape can be produced with desired accuracy and smooth finish.

(*ii*) Clean and smooth operations.

(*iii*) Metals and non-metals can be mixed to give the desired property to the article as for example W and C can be mixed to produce W_2C (tungsten carbide) for cutting tools.

(*iv*) Articles with impregnated lubricants can be produced which would be self-lubricating for ever.

(*v*) 100% raw material is consumed with no loss.

Disadvantages

(*i*) Dies of desired precision are required which are very much expensive.

(*ii*) Ejection of the articles from the die is necessary, which limits the production of very very intricate articles.

SOME SPECIFIC EXAMPLES OF EXTRACTION OF METALS

Titanium (Ti)

Titanium is a very strong metal and has a density much less than that of steel. It melts at a very high temperature of 1675 °C. The metal is being protected like aluminium by a thin oxide layer formed on the surface of the metal.

Titanium is an element of *d*-block in the periodic table and its electronic configuration is [Ar] ... $3d^2.4s^2$. It can exhibit three oxidation states +2, +3 and +4, but only +4 oxidation state is common. Titanium (IV) chloride is a colourless liquid produced as an intermediate in titanium extraction and is used in the manufacture of titanium (IV) oxide.

Smoke grenades produce dense clouds of titanium (IV) oxide due to rapid hydrolysis of titanium (IV) chloride.

Extraction

The ores of titanium used for extracting metal are *rutile* (TiO_2) and *ilmenite* ($FeTiO_3$). Among the most abundant metals in the earth's crust Titanium achieves the fourth place. But as the extraction process is difficult and expensive, it is not widely used.

After the purification of the ore, it is heated with carbon in a steam of chlorine gas at about 1100 K.

$$TiO_2 + C + 2Cl_2 \longrightarrow TiCl_4 + CO_2$$

In **Kroll process**, the titanium (IV) chloride condenses as a liquid that can be purified by fractional distillation.

The chloride of the metal is then allowed to react with molten sodium or magnesium at 800 K in an inert argon atmosphere, the reaction is exothermic and so temperature rises.

$$TiCl_4 + 4Na \longrightarrow Ti + 4NaCl$$

The reactor is kept hot for about two days then the mass is removed from the furnace and is allowed to cool. The solid product is then crushed and leached with dilute hydrochloric acid, which dissolves the sodium chloride, leaving behind the metal Ti which is then washed and dried. Extremely pure Ti can be obtained by decomposition of TiI_4 vapour on an electrically heated tungsten (W) filament in vacuum.

Uses

(*i*) Titanium is used mainly for making aircraft engines and airframes.

(*ii*) Other major uses are the production of chemical components of chemical plants such as heat exchangers.

Chromium (Cr)

Chromium is mainly extracted from Cr_2O_3 *i.e.,* Chromium (III) oxide in a batch process employing aluminium as the reducing agent. **The commercial ore is chromite**. Chromite contains other metals like iron besides chromium. The first step is to convert the ore to pure Cr_2O_3. A mixture of the oxide with powdered aluminium is then ignited in a reaction vessel. The **exothermic reaction** produces pure metal (99 %).

$$Cr_2O_3(s) + 2Al(s) \longrightarrow 2Cr_2(s) + Al_2O_3(s)$$

Carbon can reduce Cr_2O_3 but the produced metal then contains carbon as impurity. The presence of carbon in the metal makes the metal brittle and less resistant to corrosion.

Chromium, like aluminium, is protected from corrosion by a thin layer of oxide on the metal surface. The main use of chromium is to make **alloys** with iron (**stainless steels**).

Electroplating with chromium gives a shiny, corrosion resistant finish to metals.

Uses

(*i*) The chief uses of chromium are in the manufacture of chrome steel and chromium plating.

(*ii*) Chrome steels are employed in the form of alloy "ferrochrome" containing 60–70% Cr. This is very hard and used in making cutting tools. Stainless steel is ordinary steel with 14% Cr. Steels with 18% Cr and 7–8% Ni are superior corrosion resistant. Chromium-vanadium steel is very hard and is used in axle, shafts, locomotive wheels etc.

(*iii*) Chromium plating unlike nickel plating is resistant to sulphur compounds of the atmosphere.

Nickel (Ni)

Nickel is a hard, grayish but shiny *d*-block metal with the electronic configuration ... $3d^8.4s^2$ [Ar]. The common oxidation state of nickel is +2. Nickel (II) salts, like nickel sulphate ($NiSO_4$) are green.

Uses

(*i*) Nickel is so unreactive that it is used to make spatulas and crucibles.

(*ii*) Nickel is a constituent of many alloys including some alloy steels and the ferromagnetic alloy and also of Alnico which is used in making permanent magnet.

(*iii*) Nickel in finely divided form acts as a good catalyst in hydrogenation reactions.

(*iv*) It is a heterogeneous catalyst and is used to harden unsaturated vegetable oils by addition of hydrogen across the double bond.

Manganese (Mn)

Manganese is a hard, gray, brittle d-block metal having electronic configuration ...$3d^5.4s^2$ [Ar]. The main oxidation states of manganese are:

+7 in MnO_4^- — the purple manganate (VII) ion, which is a strong oxidising agent in acid medium.

+4 in MnO_2 — an insoluble black compound and acts as an oxidising agent in acid solution.

+2 as Mn^{2+} — the pink manganese (II) ion in salts such as manganese (II) sulphate.

Uses

(*i*) Manganese is added in steel to modify its mechanical characteristics.

(*ii*) The metal is mainly used in steel industry in making alloy steels and as a deoxidant.

(*iii*) Manganese steel containing 13% Mn is extremely hard and tough and is used in making jaws or rock crushers.

(*iv*) An alloy of copper, aluminium and manganese (Heusler's alloy) is ferromagnetic.

(*v*) An alloy of copper, manganese and nickel, known as Manganin, is used for resistance coils since its electrical resistance is very slightly affected by temperature.

Cobalt (Co)

Cobalt is a hard, shiny d-block metal and is less reactive than iron. It has the electronic configuration ... $3d^7.4s^2$ [Ar].

In solution cobalt forms ions in the +2 and +3 oxidation states. Cobalt (II) is a more stable state.

Uses

(*i*) Cobalt is used in making the so called 'hard alloys' which are superior to high speed tool steel as regards the life of the tools.

(*ii*) Steels containing about 35% cobalt is used for permanent magnet.

(*iii*) Cobalt may be used for electroplating iron, steel and brass etc.

(*iv*) Cobalt oxide is used as a colouring agent in the glass and ceramic industry *i.e.*, in making blue glass and blue enamels for coating iron.

(*v*) Some cobalt salts with organic acids are used as driers in paints and varnishes.

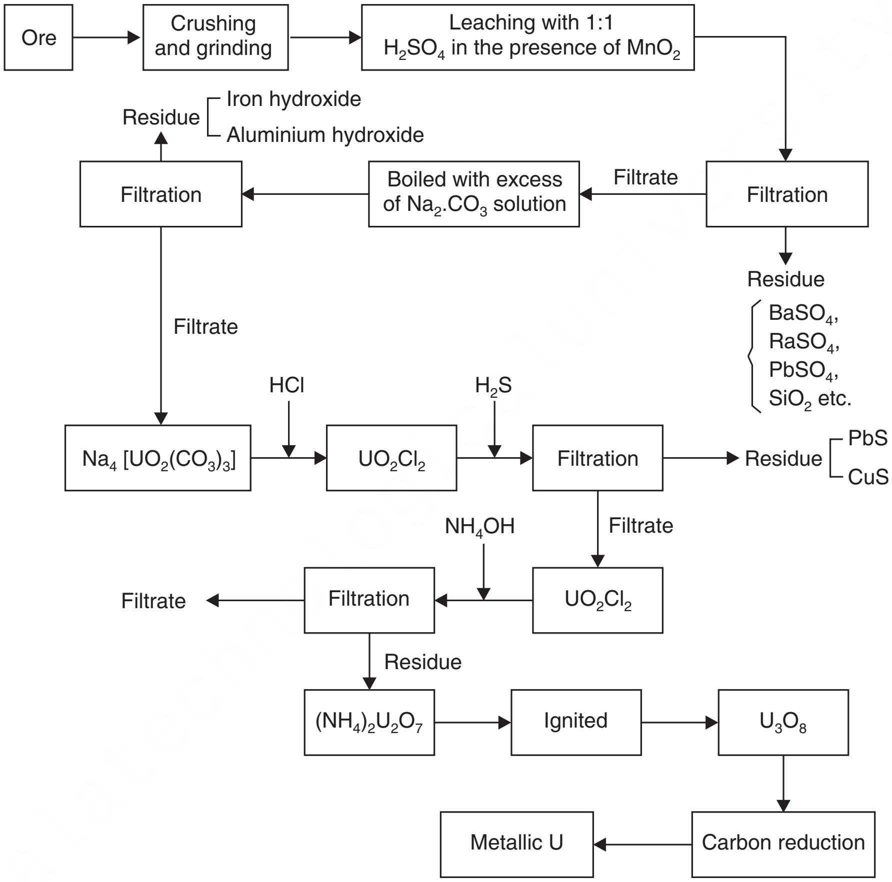
(*vi*) The radio-active isotope Co-60 is a strong γ-radiation emitter. Cobalt-60 capsules are used to kill cancer tissues by radiation.

Uranium (U)

Uranium is not obtained in free state in nature. It occurs in the form of compounds. The important ores of uranium are:

(*i*) Pitchblende (uranite—U_3O_8) (*ii*) Carnolite—$K_2O.2UO_3.V_2O_5.3H_2O$.

Uranium is extracted from pitchblende and a flow diagram for the extraction of uranium is shown below:



Uses

(*i*) Its principal use is as atomic fuel in nuclear reactors. U^{235} releases 200 meV per fission with neutrons.

$$U^{235} + {}^{1}_{0}n = Ba^{140} + Kr^{92} + 200 \text{ meV.}$$

(*ii*) In ceramics uranium compounds are sometimes used to form coloured glasses (yellow or orange).

(*iii*) Uranium steels are also important technically.

Zirconium (Zr)

Occurrence

The main ores of zirconium are:

(*i*) *Zircon—Zr* SiO_4

(*ii*) *Baddeleyite* (ZrO_2)

The ores are found in the USA, Brazil and Australia. Zirconium also occurs in alluvial sands of Kerala and Sri Lanka.

Extraction

(*i*) Zirconium is produced commercially by Kroll process. (See extraction of Titanium.)

(*ii*) *Van Arkel-de Boer process.* In this process, crude zirconium is heated with a little iodine under vacuum at 200 °C when ZrI_4 volatilizes. A tungsten or Zirconium filament is heated to 1300 °C in the same vessel. This filament decomposes ZrI_4 to pure Zr which is deposited on the filament.

$$ZrI_4 = Zr + 2I_2$$

Properties

Zirconium is a lustrous, silvery metal with m.p. 1857 °C. Zirconium is a good conductor of heat and electricity. The traces of impurities like O, N and C make the metal brittle.

Chemical: If heated to high temperatures, zirconium reacts directly with most non-metals *viz.*, O_2, H_2; when finely divided, the metal is pyrophoric. So, care should be taken during machining and the production waste chips should be avoided. Despite this inherent reactivity, the metal has got outstanding resistance to corrosion, which is due to the formation of a dense, self-heating oxide film over the metal surface. With the exception of HF, other mineral acids react at elevated temperatures with the metal. The most important oxidation state of the metal is +4.

Uses

(*i*) Zirconium has a high corrosion resistance and it is sometimes preferable to stainless steel in certain chemical plants.

(*ii*) It is used in a variety of alloy steels; a notable superconducting alloy is with niobium which retains its superconductivity even in strong magnetic fields.

(*iii*) The small percentage of hafnium (Hf), which is almost always present with zirconium, is not detrimental at all and may even improve the property of Zr. Zirconium's major use is as a cladding for uranium dioxide fuel rods in water-cooled nuclear reactors for its low absorption of 'Thermal' neutrons. Here the presence of Hf is disadvantageous, as Hf is a powerful absorber of 'Thermal neutrons'. So Hf content of Zr is reduced to less than 100 ppm.

EXERCISES

1. Define metal and mention some of its characteristics.
2. What do you mean by metallic bonds? Explain electrical conductivity of metal in the light of metallic bonds.
3. What do you mean by minerals and gangue? Give relations between them.
4. Distinguish between ores and minerals.

5. What do you mean by the study of metallurgy?

6. What is the concentration of ore?

7. Write down the different steps involved in the extraction of metals from corresponding ores.

8. Write short notes on:
(*i*) Crushing and Grinding
(*ii*) Oil floatation process
(*iii*) Calcination
(*iv*) Roasting

9. Briefly discuss the stages involved in concentration of ores.

10. What is flux? State the factors on which the selection of flux is based.

11. Describe different types of furnaces with their uses in metallurgy.

12. Write short notes on:
(*i*) Smelting
(*ii*) Welding

13. What is an alloy? Write (*a*) the importance of preparation of an alloy (*b*) general methods of preparation of alloys. Give the composition and uses of the following alloys:
(*i*) Mild steel
(*ii*) Stainless steel
(*iii*) Manganese steel
(*iv*) Duralumin
(*v*) Alnico
(*vi*) Wrought iron
(*vii*) Magnelium
(*viii*) Brass
(*ix*) Bronze
(*x*) Solder

14. What is cementation?

15. Give general method of extraction of metals from their ores.

16. Write notes on:
(*i*) Pyrometallurgy
(*ii*) Hydrometallurgy
(*iii*) Goldschmidt thermit process
(*iv*) Electro-refining
(*v*) Zone refining

17. Briefly describe the methods involved in purification of metals extracted.

18. Write a short review on powder metallurgy.

19. Mention four advantages of powder metallurgy.

20. Discuss the various steps involved in powder metallurgy and mention its application.

21. (*a*) How is metal powder prepared? Describe any two applications of powder metallurgy.
(*b*) What is sintering in powder metallurgy?

22. (*a*) State the electronic configuration of titanium. Indicate its position in the periodic table.

(*b*) Describe the extraction procedure of titanium from its ore.

(*c*) Give some uses of titanium.

23. (*a*) How is chromium extracted from Cr_2O_3?

(*b*) Give some uses of chromium.

24. Write notes on:

(*i*) Nickel

(*ii*) Manganese

(*iii*) Cobalt

25. (*a*) Write down some of the ores of uranium with chemical formula.

(*b*) With a net flow chart represent the process of uranium metal extraction.

(*c*) State some uses of uranium.

26. Give an account of zirconium with special reference to its important ores and one method of extraction.

15

Adhesives

Adhesives

Adhesive is defined as a material that is capable of joining bodies together by surface adhesion and internal strength without the structures of the bodies undergoing any changes. The process of this adhesion is called **bonding** and the bodies are called **adherends**.

Bonding has several advantages

1. The common feature of all adhesive joints is the highly uniform distribution of forces over the entire joint area and free from any residual stresses which leads to optimal utilization of material strength compared to rivet and screw joints.
2. Adhesives are capable of joining numerous materials which cannot be joined by other techniques even those differing widely in type such as glass and metal, metal and plastic etc.
3. The process of adhesion can be carried out very rationally, quickly and economically.
4. Many adhesives can be applied at room temperature hence the adherends are not exposed to high temperature as in the welding of plastics with metals.
5. The after-finishing process in case of bonding is not required as in the case of welding, soldering etc.
6. Some adhesives set even in relatively thick layers, so any unevenness of the adherends can be smoothed out during bonding.
7. Bonding of dissimilar metals with adhesives prevents galvanic corrosion as the metal to metal contact is avoided.
8. The adhesive layer of an adhesive joint can have a vibration-dampening effect.
9. Adhesives can introduce electrical and heat insulating layers between the adherends.
10. Better composite materials having improved properties than the adherends can be designed by the adhesive bonding *e.g.,* metal-faced plywood.
11. Adhesive bonding can be utilised to make the material leak-proof for liquids and gases.

Limitation and Restrictions of Adhesive Bonding

1. The usability of adhesives can be restricted when stringent requirements are imposed on the thermal stability on adhesive point.
2. Adhesives based on organic polymers show a dependence on temperature in their strength, properties and their bond strength decreases with rise in temperature.

3. Some adhesives when subjected to heavy static stress for long periods show a tendency to creep even at room temperature.
4. Adhesives are generally susceptible to higher humidities.
5. Bonding strength is low compared to other joining methods like rivetting, welding etc.
6. There is not available any single adhesive for joining all types of materials and hence judicial selection is of great importance in bonding process.
7. Adhesives require appreciable time for developing their full strength bonding for better performance.

Adhesion Theories

Several different theories have been developed that explain the mechanism of adhesion.

Mechanical theory of adhesion is based on the anchorage of the adhesive in the porous rough surface of the adherends and hold the surface by interlocking action.

Electrostatic theory explains that by contact of the adherend and the adhesive, transfer potentials are build up which sets up an electrical double layer and the corresponding coulombic attraction forces develop between the two components.

Adsorption theory regards adhesion as essentially a special property of phase interfaces. The forces that are responsible for adhesion are the so called secondary valence or van der Waal's forces.

Diffusion theory explains that adhesion is obtained by the mutual penetration of adhesive and substrate. None of the above theories explain all the aspects of bonding. Latest theories consider that bonding of adherend and adhesives takes place due to the chemical or physical forces of attraction. By wetting the surface of the adherend with the adhesive, contact in molecular dimensions takes place; when the interfacial boundary energy is lower than the sum of the surface energies of the adhesive and the adherend, permanent adhesion occurs.

Adhesive Strength Development

1. *By chemical reaction:* The reactive low molecular wt. mono and/or oligomeric ingredients of thermosetting adhesives are converted by chemical reaction into high mol. wt., crosslinked three-dimensional polymers with high bond strength.

2. *By solvent evaporation:* The adhesive is dissolved or dispersed in a solvent and applied to the surfaces to be bonded and they are brought in contact with each other. The solvent gets evaporated and thereby gelling and finally hardening takes place leading to strong bonding between the surfaces.

3. *By pressure application:* Tacky substances in solvent-free form adhere spontaneously to the surfaces of most materials, only under pressure.

4. *By cooling:* Thermoplastic materials are applied to the adherend surfaces in a molten and hot condition which on cooling solidifies developing bonding strength.

Physical factors influencing adhesive strength:

1. *Smoothness of the adherend surfaces:* For wood surfaces smoothness of the surfaces adds to the bonding strength of adhesives. In the case of other porous materials like paper, leather etc., the large number of capillaries preferentially enclose the liquid portion of the adhesive and disturb the equilibrium distribution of the adhesive on the adherend surface leading to weak joint formation.

2. *Surface tension:* The wetting characteristics of an adhesive depend on its (*a*) viscosity and (*b*) surface tension. The bonding between the surfaces is better when the surfaces can be

uniformly wetted by the adhesive sol which is guided by the interfacial tension between the two. When this tension becomes minimum, the surface is better wetted.

3. *Thickness of the adhesive film:* Very viscous adhesives produce thick film but do not wet the surfaces properly leaving many voids and hence the bonding becomes weak. This bond strength can be improved by applying pressure. The bonding strength can also be increased by adding solvent and/or plasticizer to decrease the viscosity.

4. *Physical characters of the adhesive film:* The bonding strength of the adhesive film is influenced by the following physical characteristics of the film.

(*a*) Tensile strength, shear strength and compressive strength of the film: These three characteristics influence the bonding strength in a positive way.

(*b*) Creep rate—Highly plasticized adhesives have higher creep rates under stress conditions than the rigid thermosetting materials. Creep rate under stressed condition should be lower for better adhesives.

(*c*) Difference in thermal coefficients of expansion of adherends and adhesive—When this difference is high the bonding strength weakens under temperature variations. Substance can be added to the adhesive to alter the thermal coefficient of expansion to match with that of the adherend and hence increasing the bond strength.

5. *Application modes of adhesives:* The mode of application of adhesive on the surface to be joined also influences the bonding strength. Pressure, temperature and time are the factors that affect this strength after the application of the adhesive. Sufficient time is to be allowed so that the curing time be enough to establish a strong bonding. Similarly, temperature also affects the process of bonding by allowing the solvent to evaporate. Less pressure is required in case the adherend surfaces are smooth but in the case of porous surfaces, pressure should be applied to join the surfaces together.

Chemical Factors Affecting the Adhesive Strength

1. *Degree of polymerization:* Bond strength of the adhesive is affected by the extent of polymerization of the monomers. Degree of polymerization best suited for adhesive action is different for different adhesives *e.g.,* for cellulose derivatives partially degraded low molecular weight products give higher adhesive action.

2. *Polarity of adhesives:* For organic contacting surfaces polar-group containing adhesives provide better bond strength than non-polar adhesives. Thus, addition of polar molecules to the non-polar adhesives increases the adhesive power.

3. *Complexity of the adhesive molecule:* Complexity and chain length influence the adhesive action. In the case of phenol-aldehyde resin the higher mol. wt. products have greater adhesive action. Similarly, in the case of cellulose esters the optimum chain length of fatty acid is from 6 to 14 for better bond strength.

4. *pH:* Strong acids and strong alkalies affect the bond strength of adhesives negatively. But the effects of pH are different in the case of different type of adhesives, *e.g.,* slightly alkaline pH gives better bond strength in the case of Glue which are protein in nature, whereas acidic pH increases the bond strength of vulcanized rubber.

Technique of Bonding

Different type of adherend surfaces, different type of adhesives, differing bonding processes give rise to different types of bonding. There are certain general steps involved in common bonding processes.

Cleaning and Pretreatment of Adherend Surfaces

Layers of grease, oil and lubricant are removed by solvent washing or immersion in acid or alkali bath or electrolytic methods.

Loose dirt and oxide layers can be removed by brushing. Very uneven surfaces and others are rubbed with emery paper or sand blasted to remove firmly anchored layers that may interfere with the bonding process. For certain plastics, pretreatment processes are used to increase the affinity for bonding.

For metals, acidic pickling baths are used to remove low cohesive strength materials.

For plastics which are difficult to bond, surfaces are modified by chemical treatment to increase the surface tension and wettability. Sometimes pressure and temperature are also used for these plastics.

For wooden surfaces, the adherend surfaces are machined to bring smoothness for better bond strength.

Adhesive Application

Adhesives are dissolved in proper solvents. Solid adhesives are melted, very viscous adhesives are thinned with solvent, plasticizers, catalysts, hardners etc. added in proper proportion.

Uniform addition of calculated quantity of adhesive is required for proper bonding strength, so the method of application is very important. Developing on the size and nature of the surface and rheologic properties of the adhesive, different methods of application are used as follows:

(*a*) By manual application with brushes, casting knives, spatulas, blades etc.

(*b*) Thin-flowing sprayable adhesives are distributed uniformly over large areas with spray guns (Fig. 15.1).

(*c*) By rollers.

(*d*) Highly viscous adhesives applied as coatings.

(*e*) Dry adhesives are laid as film or sheet.

(*f*) For chemically reactive systems, one component is the thermosetting resin, which is applied to one surface and the other being the catalyst applied to the other surface to be bonded.

(*g*) For immediately reacting and hardening adhesives, the components are applied to the adherend surfaces immediately before joining by double spray.

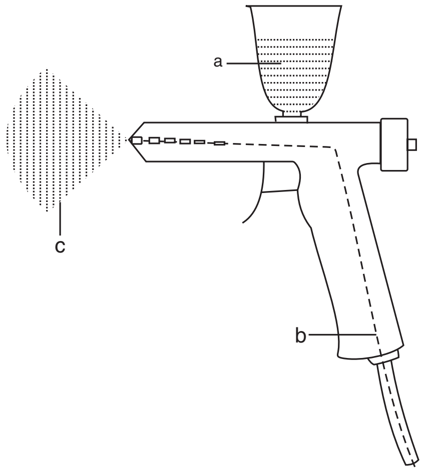


Fig. 15.1 Adhesive application by means of a spray gun (*a*) Adhesive (*b*) Compressed air (*c*) Atomized adhesive.

(*h*) Cyanoacrylate adhesives and anaerobic reactive adhesives are applied by means of special metering units that delivers small metered quantities at specified time intervals.

Joining, Fixing of Adherends

Following application of adhesives, the adherends are joined by different methods which vary with the type of adhesive applied and the surfaces to be joined.

(*a*) For immediately drying type of adhesives the adherends are held close to each other immediately completing the assembly.

(*b*) Adhesives or rubber solutions in organic solvents require longer period for air-drying. Thus to allow the time for evaporation of the solvent and tackiness to develop the assembly is to be kept for a long period.

(*c*) For bonding of the metal surfaces, the assembly of the adherend metal surfaces is required to be heated in an oven which is called 'pre-curing'.

(*d*) For chemically reacting adhesives the adherend surfaces are kept in contact and the joint is allowed to remain for the required period to allow the chemical reaction to be complete to obtain high bond strength.

Drying and Hardening

After assembling the adhesive-applied adherend surfaces some pressure is to be applied to ensure the uniform distribution of the adhesive on the whole surface and also to keep the whole surface in close contact for the appropriate time to develop highest bond strength.

(*a*) For slow reacting and setting adhesives the time of application of pressure is longer to ensure completion of the chemical reaction or complete evaporation of the solvent to develop bond strength.

(*b*) For pressure sensitive adhesives, the applied pressure is to be released immediately after the bonding. The necessary pressure is generally applied by using presses, pressure rolls.

Similarly, heat treatment is also necessary for selective adhesives.

For warm-setting adhesives heating is required for a specified period.

Polycondensation adhesives must be heated with the application of external pressure higher than the vapour pressure of the cleavage products formed during condensation. For molten adhesive, cooling under pressure is required. The heat required for the hardening processes are supplied by recirculating-air ovens, drying cabinets, radiant heaters, heating-presses etc.

Classification of Adhesives

Adhesives may be classified on the basis of chemical nature, setting mechanisms, adhesion mechanism etc. Here we classify them on the basis of their chemical nature:

1. *Thermosetting synthetic resins.* This class has high adhesive properties by forming a network of three dimensional cross-linked structures. The bonding of these are moisture, heat and fungi proof. Some members of this class are:

(*a*) *Phenol-formaldehyde resins.* This is a pressure sensitive type of adhesive. The adherend surfaces after being coated with this adhesive is subjected to curing by heat and pressure.

Use: This is available as solid, liquid or impregnated film and used for bonding wood and metal.

(*b*) *Urea-formaldehyde resin.* It is a transparent, syrupy compound, used in the form of aqueous solution or spray dried powders, generally with acid hardness to improve reactivity for bonding. Addition of water to this resin helps in forming continuous film with cross linkages and with rapid setting properties. Though this adhesive forms bond which is resistant to temperature, moisture etc., it deteriorates by acids and alkalies.

Uses. Bonding wood, particularly to produce plywood and chipboard, laminates, for aircraft and in ship industries. Modified urea resins are important for labeling adhesives.

(*c*) *Polyesters.* Unsaturated polyesters dissolved in styrene or methacrylates are used as reactive adhesives. They possess good moisture resistance but low heat resistance.

Uses. Used for making laminated glass and cloth.

(*d*) *Epoxy resins.* Epoxy compounds are available both in liquid and solid forms. Usually they are used in combination with amines, dicarboxylic acid anhydrides etc. Epoxy resins are also combined with phenolic resins and poly vinyl acetate resins and used as adhesion promoters. The thin film of epoxy resin remaining after the evaporation of the solvent acts as good adhesive having good chemical and electrical resistance. It can also be cured without the application of heat. On frequent contact with skin liquid epoxy resin causes irritation and allergies.

Uses. Used for bonding metal in aircraft industry and also for silicate containing materials and plastics. Araldite which is available in the market comes under this class of resin.

(*e*) *Silicon resins.* They set under the effect of atmospheric moisture, resistant to temperature, fungi, insects and chemicals.

Uses. For bonding of silicate containing materials, plastics, rubbers, metals etc.

2. *Thermoplastic synthetic resins:*

(*a*) *Cellulose derivatives.* Cellulose nitrate is used as a raw material for solvent adhesives. Cellulose nitrate mixed with alcohol is well known as 'collodion'. The adhesive film developed by cellulose nitrate is resistant to water but affected by strong acids and alkalies and aging. It is inflammable and in recent years it is replaced by others.

Uses. As multipurpose adhesive, shoe adhesive.

Cellulose ethers and cellulose esters. Cellulose acetate has less adhesive strength than cellulose nitrate but it is more resistant to heat.

Ethyl cellulose/methyl cellulose are used as aqueous solution with plasticizers, modifiers. The film is moisture resistant but inflammable.

Uses. For wall paper paste and also as thickener.

(*b*) *Acrylics.* Polyacrylates are used both in the form of solutions and in the form of synthetic resin emulsions and are important raw materials for pressure sensitive adhesives. Copolymers of various esters (polymethyl, polyethyl, polybutyl-acrylate) contain functional groups like $—NH_2$, —COOH, OH etc., which are utilized for cross-linking and form better adhesives. They are stable to all conditions but costly.

Uses. For bonding of paper, glass, leather etc.

(*c*) *Polyvinyls.* Polyvinyl acetate, polyvinyl chloride, polyvinyl propionate form hard films resistant to atmospheric conditions and chemicals. Polyvinyl acetate in combination with phenolic resins forms special adhesives.

Uses. For bonding of glass, metals etc. smooth surfaces and also in sealing of food materials.

3. *Natural resin adhesives:*

(*a*) *Shellac*–Hot shellac sol is an oldest known adhesive, which is hard.

Use. For making conveyer belts.

(*b*) *Asphalt*–Used for bonding metal, paper etc.

4. *Starch and dextrin adhesives.* The raw materials used for various types of starch and dextrin based adhesives are potato starch, corn starch etc. A suspension of starch is heated for sometime to obtain the adhesive which is cheap, can be applied in cold and hot states but bond strength is low and susceptible to moisture.

Uses. For making envelopes, stamps, books etc.

5. *Vegetable glue.* These protein glues are obtained from soyabean, corn, casein, albumin etc. The oily or the fatty matter is extracted or precipitated from soyabean or milk and then the protein is treated with lime and the water solution form a jelly-like adhesive. They are very cheap but of poor bond strength.

Uses. Similar to starch adhesive.

6. *Animal glue.* Animal wastes obtained from slaughterhouses etc. and hide scraps from leather industries are degreased with solvent, treated with lime. The product obtained is hydrolysed with hot water to form liquid glue. This is bleached and mixed with preservatives and concentrated to form solid glue. The solid cake or powder is boiled with water to form the adhesive solution. The bonding strength of the adhesive is high but susceptible to heat and moisture.

Uses. For manufacturing cardboard boxes and furnitures.

7. *Inorganic adhesives.* Sodium silicate alongwith litharge (lead monoxide) and MnO_2 etc. forms gel when suspended in water. This gel has adhesive properties. The bond is moisture and high temperature sensitive but fungus resistant.

Uses. For cardboard boxes making.

Testing of Adhesives

Testing of adhesives mainly encompasses:

- Solid content
- Rheologic properties
- Shelf life
- Flammability and inflammability
- Risks involved in transport and application
- Measurement of the mechanical properties like tensile strength, breaking elongation of the films or test specimens made with the adhesives.

Growth Rates of Different Adhesives

The highest growth rate is expected in automotive industry, transport and electronics.

Continued growth is expected in construction adhesives, solvent free adhesives whereas reduction in demand is expected for solvent containing adhesives and animal and vegetable glues.

SHORT QUESTIONS AND ANSWERS

Q. 1. What is an adhesive?

Ans. Adhesive is defined as a substance capable of joining bodies together by surface attachments.

Q. 2. What are the different theories that explain the mechanism of adhesion?

Ans. The theories explaining the mechanism of adhesion are:

(*a*) Mechanical theory (*b*) Electrostatic theory

(*c*) Adsorption theory (*d*) Diffusion theory

3. Mention the types of adhesives used for joining

(i) Wooden surfaces (ii) Glass and cloth (iii) Metals

(iv) Papers (v) Plastics and rubbers

Ans. (*i*) Urea-formaldehyde and phenol-formaldehyde resins are used for joining wooden surfaces.

(*ii*) Polyesters dissolved in styrene etc. are used for joining glass and cloth.

(*iii*) Epoxy resins are used for joining metals in aircraft industry.

(*iv*) Cellulose ethers, esters and also acrylics are used for binding paper.

(*v*) Silicon resins are used for bonding of plastics, rubber etc.

EXERCISES

1. What are adhesives?

2. Explain the different mechanisms of adhesive action.

3. Discuss the physical and chemical factors that influence adhesive action.

4. Write a brief note on natural and synthetic adhesives.

5. Mention a few important advantages and limitations of adhesives.

6. Describe the different steps of the bonding processes of adhesives.

7. (*i*) Adhesive action of a polymeric adhesive is influenced by

(*a*) Polar character (*b*) Degree of polymerization

(*c*) Complexity of molecule (*d*) All these

(*ii*) Adhesive used for bonding metals is

(*a*) Epoxy resin (*b*) Polyesters

(*c*) Acrylics (*d*) All these

(*iii*) Adhesive used for bonding leather for shoes

(*a*) Phenol formaldehyde resin (*b*) Acrylics

(*c*) Polyvinyls (*d*) Polyesters

(*iv*) Adhesives used for manufacturing furnitures of wood

(*a*) Urea-formaldehyde resin (*b*) Polyesters

(*c*) Silicon resins

(*v*) Natural adhesive used for stamps and envelops etc.
(*a*) Araldite
(*b*) Starch
(*c*) Polyesters
(*d*) Polyvinyl

(*vi*) Adhesive used in aircraft industry is
(*a*) Starch
(*b*) Asphalt
(*c*) Shellac
(*d*) Araldite

(*vii*) Araldite is
(*a*) Animal glue
(*b*) Cellulose derivative
(*c*) Thermosetting resin
(*d*) Polyester

8. Which of the following is fungus resistant?
(*a*) Inorganic adhesives
(*b*) Vegetable glue
(*c*) Animal glue
(*d*) Starch adhesives

9. Adhesive bonding can be utilized to make a material
(*a*) Leak proof
(*b*) Heat insulating
(*c*) Electrically insulating
(*d*) All these

10. Adhesive having least bonding strength is
(*a*) Starch
(*b*) Cellulose derivatives
(*c*) Epoxy resin
(*d*) Acrylics

16

Explosives and Propellants

Explosives

Explosives are pure substances or mixtures which on being subjected to specific stimulus like mechanical impact, frictional forces, electrical discharge and other sources of heat, high pressure shock waves initiate an oxidation reaction producing large volume of hot gases.

Once initiated, the heat evolved is sufficient to cause the reaction to continue and become self-sustaining. The minimum quantity of energy required for initiation has a characteristic value that depends on the chemical and physical properties of the material.

The reactions of explosives are exothermic. The products at hot and high pressure and when confined to a closed space lead to explosion but if the reaction is controlled at slower rate, this energy can be utilized to propel a projectile. The amount of power available from a given weight of explosive is known as "power to weight ratio".

Characteristics of Explosives

Following are the characteristics required for an explosive.

1. The decomposition rate of an explosive should be very fast and large volume of hot gases should be liberated exothermally leading to large increase in volume.
2. The explosive molecule should have a low energy of dissociation.
3. The oxygen-balance of an explosive molecule should be higher which indicates that more oxygen is available in the molecule to oxidize C and H to CO_2 and H_2O.
4. The explosive should be sensitive towards specific impacts. It should explode immediately after the application of the stimulus. The lesser the stimulus required better is the sensitivity of the explosion.
5. Explosives should not be volatile or hygroscopic but should be stable chemically so that they do not decompose on keeping or react with the storage container.
6. Lastly, explosives should be cheap.

Uses of Explosives

The principal non-military use of explosives is in mining. In coal mines, only very safe explosives with lowest possible detonation temperature are used. These explosives usually contain a large amount of NH_4NO_3 and NaCl. In industry explosives are used for blasting ores of different metals, **quarrying** limestone to be used in road construction, for blasting holes in mountains for tunnels and roads, digging earth, seismic prospecting, blasting rocks and other social and useful works.

The other main area is in military and ammunition for war as well as tackling regular social problems, as well as in the preparation of torpedos, grenades, bombs etc. Another area is in the launching of rockets, spacecrafts etc.

Classification of Explosives

Explosives are classified under three broad groups, namely primary, low and high explosives.

(A) *Primary explosives.* Primary explosives are the most sensitive to heat, friction, impact, shock and electrostatic energy. They should be handled with great care. They are used to initiate the explosion of high explosives which consist of explosives of increasing mass and decreasing sensitivity. Only few compounds can act as primary explosives for military and industrial requirements, they are dense, metallo-organic compounds. They are:

1. *Mercury fulminate.* Mercury fulminate or mercuric cyanate is a grey-white powder. It is prepared by mixing of solution of one part of mercury with eleven parts of 57% nitric acid and poured into ten parts of 95% ethyl alcohol when mercury fulminate forms as fine crystals of 99% purity. It is the most sensitive of initiating agents to impact and friction. It decomposes when stored at elevated temperature, reacts with metals in presence of water. It is slightly toxic and its use is limited.

2. *Lead azide.* The azides are among the very few useful explosive compounds that do not contain oxygen. It is extensively used as primary explosive in military detonators.

Lead azide is made in small batches buffered by the reaction solutions of lead nitrate or acetate with highly toxic sodium azide.

$$Pb(NO_3)_2 + 2NaN_3 \longrightarrow 2NaNO_3 + PbN_6$$

Nucleating agents like polyvinyl alcohol (PVA), sodium carboxy methyl cellulose (CMC) or dextrin may be added during precipitation to yield free flowing crystals or rounded agglomerates. Lead azide is less sensitive to ignition than mercury fulminate. Of the four polymorphic forms (α to δ) the α is the most common. Lead azide tends to hydrolyse at high humidity and forms hydrazoic acid, which reacts with Cu and its alloys to produce very sensitive cupric azide.

3. *Lead styphnate.* Lead 2, 4, 6-trinitro resorcinate is used to start ignition process in the explosive sequence. It is stable and non-corrosive. Addition of graphite improves its electrical conductivity in systems using electrical initiation.

4. *Diazo dinitrophenol.* It is an orange-yellow compound and prepared from picramic acid [$NH_2(NO_2)C_6H_2OH$], with sodium nitrite and HCl. The product obtained is washed and recrystallized from hot acetone. It is non-hygroscopic and sensitive to friction and impact. It is more effective than lead azide and is used as an initiator in commercial blasting caps.

5. *Tetrazene.* It is pale-yellow crystalline compound. It is prepared by treating 1-aminoguanidine hydrogen carbonate in dilute acetic acid with sodium nitrate. The compound is stable upto 75°C. It has high explosion energy and is used as a detonator.

(B) *Low explosives or propellants.* Low explosives do not explode but burn and produce large volume of gas at controlled, predetermined rates. The burning proceeds from the surface inwards at a slow rate. They are applicable wherever a well controlled force is to be generated for a short period. Typical examples are:

1. *Black powder or gun powder.* It is a mixture of 74% potassium nitrate, 15.6% carbon and 10.4% sulphur. Black powder ignites and burns fast and has reproducibility and high heat flux. It deteriorates at humidity. It can be stored many years if dry. The hygroscopicity of it is due to the presence of carbon and impurities in KNO_3. It is prepared by intimate mixing of the thoroughly milled powdered ingredients. The decomposition reaction is

$$10KNO_3 + 3S + 8C \longrightarrow 2K_2SO_4 + 2K_2CO_3 + 6CO_2\uparrow + 5N_2\uparrow$$

This excess carbon and sulphur undergo slower reduction leading to more gaseous products

$$4K_2CO_3 + 7S \longrightarrow K_2SO_4 + 2K_2S_2 + 4CO_2\uparrow$$
$$4K_2SO_4 + 7C \longrightarrow 2K_2CO_3 + 2K_2S_2 + 5CO_2\uparrow$$

This large volume of gaseous products is responsible for its explosive action. It is used for blasting of coal. Other uses include blasting in shells, igniters and primer assemblies for propellants etc.

2. *Nitrocellulose or smokeless powder:* It is prepared by treating purified cellulose with mixed acid, having an approximate composition of 63% H_2SO_4, 22% HNO_3 and 15% H_2O. When nitration is complete, the nitrocellulose and the spent acid are centrifuged. The acid is sent to mixing tanks for fortification and subsequent re-utilisation. The nitrocellulose so formed is dissolved in alcohol and ether and the solvent evaporated when it forms a jelly-like mass. It is stabilized by adding a stabilizer like diphenyl amine which can react with the liberated acid. This product is stored as pressed cylindrical rods. It produces CO, CO_2, N_2, water vapour and no smoke. So, it is known as smokeless powder.

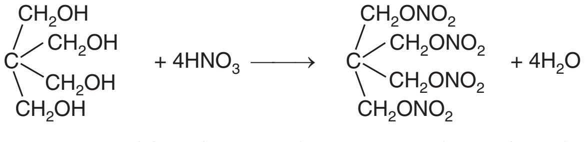
(C) *High explosives:* This group consists of six types of compounds.

1. *Single compound explosives.* Consist of only one chemical compound such as:

(*i*) *Ammonium nitrate:* It is a powerful explosive compound when once initiated by an external detonation impulse of sufficient magnitude and in sufficient amount. It is very safe to handle under ordinary condition, stable and cheap. It is readily prepared by the neutralisation of HNO_3 with NH_3, two universally available cheap raw materials. It is used to prepare binary explosives. It is also used as an explosive salt to replace a portion of the nitroglycerine used previously. It cannot be stored near inflammable materials and contact with alloys of copper is to be avoided as it detonates.

(*ii*) *Picric acid:* Chemically picric acid is trinitrophenol. It is a high explosive and used as self-filling explosives. It is largely replaced by TNT, because of its objectionable character as it reacts with metals to form picrates which are dangerously sensitive.

(*iii*) *Pentaerythritol tetranitrate (PETN):* It is obtained by the nitration of the irregular tetrahydric alcohol pentareythritol, which in turn is made by condensation of formaldehyde with acetaldehyde.



This explosive compound has become important since the First World War as powerful military explosive.

(*iv*) *2, 4, 6, Trinitrotoluene (TNT):* This high explosive is prepared by nitration of toluene. The raw material toluene is derived from coal tar or synthetically from petroleum products. TNT is widely used as shell-firing explosive and under-water explosions. Because of its low melting point (80.8°C) it is suited for loading in containers. Its comparative excellence has made it useful for military consumption, in the aspects like (*a*) being safe explosive for manufacture, storage and transportation, (*b*) non-hygroscopic, (*c*) violent-disruptive explosive, and (*d*) non-reactive towards metals to form unstable compounds.

(*v*) Cyclotrimethylene trinitroamine RDX or cylonite : This highly powerful explosive has become important for military use as well as industrial use since World War II. Its advantages are less toxicity but greater sensitivity than TNT.

(*vi*) Tetryl or tetranitromethylaniline. It is made by nitration of dimethylaniline and its melting point is around 130°C. Tetryl has important use as commercial explosive as a base charge for blasting caps. Because of its too much sensitivity, it is used as a booster charge intermediate between ignition charge and bursting charge for military use but not used for main shell firing.

2. *Binary explosives.* These are mixtures of TNT with other explosives. TNT is the most important ingredient due to its lower melting point. Binary explosives are made by mixing, heating to liquify and pouring into containers to solidify. The most important ones are:

(*i*) **Amatol.** It is an explosive mixture of TNT with ammonium nitrate. TNT is deficient in oxygen so the combustion is incomplete. The detonation products can undergo further combustion. But 80:20 mixture of ammonium nitrate and TNT is an evenly balanced composition with respect to oxygen with resulting increased strength and improved fumes. The disadvantage compared to TNT is its hygroscopicity. It is used as blasting charges in large caliber shells.

(*ii*) **Tetrytol.** It is a mixture of 70% tetryl and 30% TNT.

(*iii*) **Pentolite.** It is a mixture of 1:1 TNT and PETN.

(*iv*) **Tropex.** It is a mixture of 40% RDX, 40% TNT and 20% Al powder.

(*v*) **Titronal.** It is a mixture of 80% TNT and 20% Al flakes.

All these mixtures have some advantages over TNT alone by having higher energy or by being cheaper.

3. *Plastic explosives.* These are combinations of explosives having a plastic state with many different shapes that can be produced without risk by hand moulding or press loading. The combination includes a high explosive mixed with wax oil (that gives the plastic nature) and lower sensitivity. They can be made into flexible sheets, which can finally be cut into pieces, fixed to a metal with adhesives and made to special shapes. They are used for both industrial and military applications.

4. *Dynamites.* The term dynamite has been limited to those commercial explosives, which contain nitroglycerine as the principal ingredient. Nitroglycerine is an oily liquid, which detonates by shock or pressure above 50°C. The invention of dynamite dates back to 1866, by Alfred Nobel, who conceived the idea of mixing the nitroglycerine with highly absorbent materials. In this way, he converted a liquid, which is dangerous to handle and transport, to a solid which is relatively insensitive to ordinary shock but capable of detonating by a blasting cap. The amount of absorbent added varies the relative strength of dynamite.

$$\underset{\text{1 vol.}}{4C_3H_5\,(NO_3)_3} \longrightarrow \underset{\text{10,000 vol. of explosion}}{10H_2O\uparrow + 6H_2\uparrow + 12CO_2\uparrow + O_2\uparrow}$$

The various types of dynamites are:

(*i*) *Straight dynamites.* 15 to 60% nitroglycerine are absorbed in combustible materials like wood pulp, starch and other low-density fibres. Sodium nitrate is added as an oxidising agent that adds on good fume properties and good blasting execution. Antacid material like $CaCO_3$ to neutralize the acidity of nitroglycerine is to be added also. Important uses of this class are blasting of hard rocks, coal, minerals etc.

(*ii*) *Gelatin dynamites.* Gelatin dynamites are made by partly gelatinising the nitroglycerine by nitrocotton. The strongest known industrial explosive is the 'blasting gelatin', belonging to this class. Composition is approx. 91.5% nitroglycerin, 8% nitrocotton and 0.5% $CaCO_3$. Blasting gelatin is a solid, elastic material. Lower ratio of nitrocotton in nitroglycerin gives viscous liquid instead of the solid mass. They excell others by four important properties—high bulk density, highest water resistance among dynamites, stick well to holes into which they are loaded because of their plastic nature and lastly they excell from the point of view of fumes. They are not sensitive to shock and hence are preferred for use under wet conditions. They are mainly used for submarine blasting, blasting of hard rocks, underground blasting like deep-well shooting, tunnel driving etc. Disadvantage is that they are costly compared to others.

(*iii*) *Gun cotton or cellulose nitrate.* It is prepared by steeping cotton for 30 minutes in a cooled mixture of conc. H_2SO_4 and conc. HNO_3

$$C_6H_7O_2(OH)_3 + 3HNO_3 \longrightarrow C_6H_7O_2(NO_3)_3 + 3H_2O$$

Dry gun cotton can be ignited by shock. It explodes very sharply if set on fire. Dry gun cotton is used in torpedos, submarines, as a propellant in rifles, artillery shells. Rate of explosion of it can be controlled by mixing other substances.

(*iv*) *Ammonia dynamites.* These are dynamites in which a portion of the nitroglycerin has been replaced by ammonium nitrate. Their strengths are equivalent to straight dynamite but of lower velocity.

They possess some attractive properties for which they have wide use. These are—effectiveness, cheapness, insensitiveness to shock and friction, non-inflammability. The only disadvantage is their low water resistance, so they are not fit to be used in wet condition.

(*v*) *Cordite.* It is made by 65 parts of gun cotton, 30 parts of nitroglycerine and 5 parts of vaseline in acetone. This paste is rolled and cut into pieces of different sizes Vaseline acts as a stabilizer and cooling agent on the powder. After the evaporation of the acetone, the horny cordite remains. Gun cotton controls the explosive reaction of nitroglycerine and it can be safely used for large caliber naval guns.

(*vi*) *Gelignite.* This powerful explosive is a mixture of 65% blasting gelatine and 35% absorbing powder. It is used for under-water works.

Permissible dynamites. These are high explosives specially used for gasy coal mines etc. where inflammable gases are present.

The common permissible contain (*a*) about 80% ammonium nitrate, (*b*) low percentage of nitroglycerine as sensitizing agent, dynamites, (*c*) fibrous combustible material to utilize the excess oxygen of ammonium nitrate and absorbing nitroglycerine.

The gelatinous type of permissible dynamites contains a higher percentage of nitroglycerine and lower content of ammonium nitrate along with a small percentage of nitrocotton. This is mainly used for blasting in wet conditions.

Commercial High Explosives Containing No Nitroglycerine

(*i*) **Ammonium nitrate explosives.** This type of explosive, called Notramon, is a safe but high-velocity agent. It is incapable of detonating under the influence of blasting cap but once initiated by booster charge it can propagate explosion indefinitely. Ammonium nitrate is highly deliquescent salt, but this disadvantage can be overcome by enclosing the material in a waterproof metallic container. Because it is not sensitive to impact, friction and shock, it is the safest high-velocity agent.

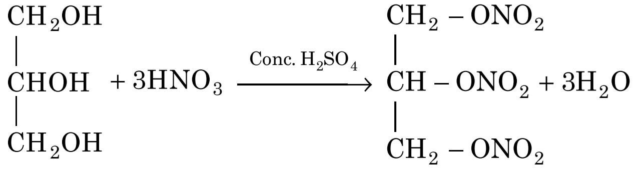
(*ii*) **Chlorate explosive.** Sodium or potassium chlorate mixed with oxidisable materials like sugar, charcoal, sulfur etc., becomes highly inflammable and sensitive to impact. Recently, a desensitizing material or liquid ingredient is added to this mixture to overcome the above disadvantage. But though being cheap, they are not popular.

(*iii*) **Liquid oxygen explosives.** Carbonaceous absorbent materials like lampblack or other carbon black are packed in a porous container and this cartridge is dipped into liquid oxygen to get saturated. These liquid oxygen explosives are of high strength and velocity but they have several disadvantages. They are highly sensitive to shock. The strength does not remain constant since the liquid oxygen steadily evaporates and hence they cannot be stored for long.

Manufacture of Important Explosives

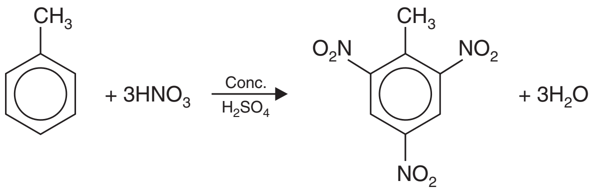
(*i*) *Nitroglycerine:* The raw materials are 99% pure glycerine, HNO_3 and H_2SO_4.H_2SO_4 is taken in slight excess of HNO_3 and is absolutely free from water. In a steel nitrating vessel, which is cooled externally by brine, the mixed acid is taken and nitroglycerine is added and nitration is done at a very low temperature under stirring. The resulting nitroglycerine and spent acid, having a composition of 76% H_2SO_4, 7% HNO_3 and 17% H_2O are run to a separator. After about 3/4 of an hour, they form separate layers, nitroglycerine being on the top. The nitroglycerine is drawn off, washed with water, the acid is neutralised with a weak solution of Na_2CO_3 under vigorous stirring. The yield is around 230, calculated on the basis of glycerine as 100.

In recent years, continuous process has been developed. It is very important that to avoid any accidental explosion a close control of the temperature is to be done during nitration. This nitroglycerine is then converted to dynamites by absorbing in different inert materials.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HNO_3 \xrightarrow{\text{Conc. } H_2SO_4} \begin{array}{l} CH_2-ONO_2 \\ | \\ CH-ONO_2 \\ | \\ CH_2-ONO_2 \end{array} + 3H_2O$$

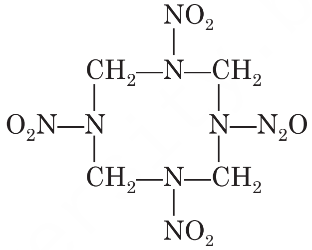
(*ii*) *Trinitrotoluene (TNT):* TNT is prepared by nitration of toluene using 1:1 mixtures of H_2SO_4 and HNO_3 in a stirred tank reactor. Either a two or a three-step process is used, the former separating out the mono-nitro compound first, then preparing bi and tri compounds in one step.



Six isomers are possible for the trinitro compound. The formation of these isomers and oxidation products leads to the formation of undesirable impurities. The liquid product containing TNT is taken out, washed with ammoniacal solution of Na_2SO_3 and finally with cold water. TNT is crystallized and the purified material melts at 80.8°C, which is finally dried and stored.

(*iii*) *RDX: Bechman process:* (80% yield)

$$\text{Hexamine} + HNO_3(98\%) + NH_4NO_3 + (CH_3CO)_2O \longrightarrow$$



Fuses

Fuses are of two types:

(*a*) *Safety fuse:* Safety fuse is employed where electrical firing is not used. It consists of a small-diameter core of black powder enclosed in a wrapper of water-proof fabric. It has an approximate burning speed of 30 or 40 sec per ft. So when a fuse is used for blasting, a sufficient length is used so that the shot-firers get time to reach to a point of safety.

(*b*) *Detonating fuse.* Detonating fuse has a velocity of detonation over 5000 metres per sec. It consists of a charge of high velocity explosive like TNT in a small diameter lead tube. The line of the fuse (cordean) is in contact with the charge throughout its length and hence causes instantaneous detonation of the whole charge. A recent type of detonating fuse contains pentaerythritol tetranitrate in a non-metallic wrapping and the velocity is as high as 7000 metres per sec. These fuses are used for exploding charges of explosive in deep holes.

Squibs

When deflagrating explosives like black powder are used, application of flame is insufficient for firing. Squibs are used for this purpose. Squibs may be in metal or cardboard tubes and may be open or closed at the firing end. Preferably, electric squibs are used.

Blasting Caps

Blasting caps are small cylindrical shells of copper or aluminium containing a detonating charge of explosives. Blasting caps are used for initiating the explosion of dynamites and are inserted into the explosive at the time of use.

There are three types of blasting caps as shown in Fig. 16.1. In ordinary fuse cap, a length of safety fuse is inserted into the open end and the metal wall is crimped about the fuse. The end of the fuse which is away from the cap is lighted and the spit of flame from the fuse in the cap fires the ignition charge leading to detonation.

In electric blasting cap, two leading wires are connected within the cap by a fine wire of high electrical resistance. On passing electric current this bridge wire is heated and becomes incandescent and fires the ignition charge.

In the delay electric blasting cap, there is a delay charge of a slow burning composition, inserted in the cap to delay the detonation of the cap charge.

This time interval can be varied from 15 to 20 sec. by using these delays. The composition of the delays has been improved so that no gas is given off on combustion.

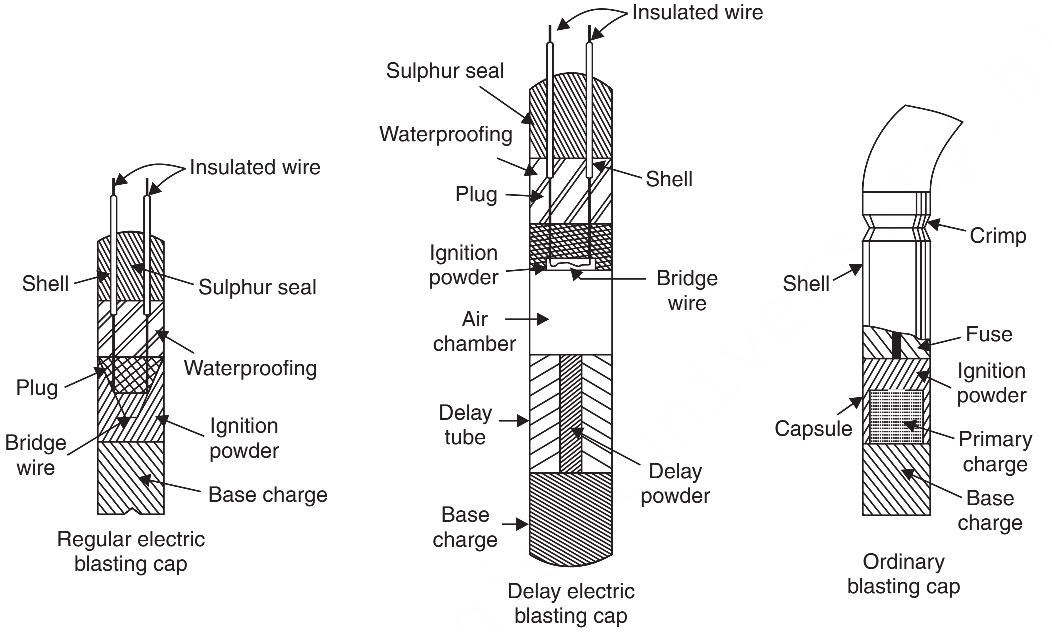


Fig. 16.1 Three types of blasting caps.

Handling and Storage of Explosives

There are many rules to be observed in handling and storing of explosives to avoid different hazards.

(*i*) Explosives should be treated with care.

(*ii*) They should be handled only by experienced and properly instructed persons.

(*iii*) They should be stored under favourable conditions and at positions sufficiently isolated from any working furnace or kiln.

(*iv*) The boundary of the explosive store should be protected by fencing and watchman with proper 'Caution Boards'.

(*v*) Smoking/fire should be strictly prohibited within 50-m radius from explosive store.

(*vi*) Jerks and drops of explosives are prohibited.

(*vii*) All electrical fitting of the store should be properly insulated and only torch light allowed inside in case of power failure.

(*viii*) Different explosives to be stored separately.

(*ix*) Nitroglycerine explosives should not be handled in unwrapped condition as it causes headache etc. on contact.

(*x*) Contact or inhalation of vapors of aromatic nitrocompounds should be avoided due to their inherent toxicity.

(*xi*) Magazines containing explosives should have lightning conductors, and they should not be handled during thunder storm.

(*xii*) Magazines should be at safe distance from buildings, rail roads and highways.

Propellants

Propellants are defined as substances or mixtures of substances of an explosive nature in a solid to liquid state that burn exothermally without contact with atmospheric oxygen and form a large volume of gas. Since propellants burn without atmospheric oxygen, the propellant system must contain the oxidizer along with the fuel. The fuel burn and the large vol. of hot gases exit through a small opening at a large velocity (as per Newton's third law of motion) which can be used for several purposes like charges for guns, rockets, gas generators, propelling rockets, launching missile. The generated gases can also be used to drive pumps, empty tanks, actuate valves, inflate air bags etc.

Classification of propellants

Propellants can be classified into solid and liquid propellants broadly.

(A) *Solid propellants.* Solid propellants may be again categorized into 'homogeneous' and 'composite'.

1. *Homogeneous solid propellants* are mixed homogeneously in a colloidal state—it is homogeneous solid propellant

(*a*) *Single-base propellants.* It is a type of homogeneous solid propellant consisting of mainly plasticized nitrocellulose. They contain stabilizers like diphenylamine, plasticizers like dibutyl phthalate. They can be used only as gun propellants or in bulk powder fillings for gas generators.

(*b*) *Double-base propellants.* General composition is 50–55% nitrocellulose and 40–45% nitroglycerine, 5% diethyl pthalate as plasticizer giving a smooth mass, 1% diphenylamine is also added as stabilizer. Flame temperature reaches about 2700°C and gases liberated at about 1500 times the original volume.

Other compositions are 65% nitrocellulose, 30% nitroglycerine, 5% petroleum jelly, where the last one functions as plasticizer.

(*c*) *Triple-base propellants.* Nitroguanidine, having a low flame temperature is used as 'cold powders' for triple-base propellants to reduce the flame temperature. In these propellants, nitroglycerine is replaced by explosive plasticizers like diethylene glycol dinitrate or butanetriol trinitrate which have low heat of explosion. They are used as gun propellants and rocket propellants. For rocket propellant, lead or copper salts are used as ballistic modifiers to reduce pressure.

2. *Composite propellants.* Heterogeneously formulated solid propellants that consist of a polymeric binder in which crystalline oxidizers are incorporated in amounts upto about 90% by weight. Composite propellants are used as gun and rocket propellants. Propellants for larger gas generators are generally of the composite type. For small charges, single and double-base propellants are used. Composite type have low binder content and the crystalline fillers on burning produces lager amount of gases and also the flame temperature is comparatively low. Gun powder is the oldest composite propellant. It gives of a flame temperature of 800-1500°C and the volume of gases is 400 times the volume of the original. Different composite solid propellants contain 75% potassium perchlorate + 25% asphalt oil, 80% ammonium perchlorate + 20% resin binder. The oxidizers are selected which should be stable, non-hygroscopic and should not produce any corrosive or objectionable product on combustion, *viz*; ammonium perchlorate produces HCl on combustion which is corrosive, Aluminium powder in rocket propellant produces large amount of smoke due to Al_2O_3 formation.

Ammonium perchlorate is replaced by ammonium nitrate to reduce HCl generation. Energetic substances (RDX or HMX), explosive plasticizers (nitroglycerine etc.) and energy-rich binders (GAP) are used to improve the performance.

(B) *Liquid propellants.* Liquid propellants contain the fuel and oxidizer as a single substance or mixture of substances (mono) or in two separate phases (bipropellants). They are more advantageous for use than the solid propellants and so their uses are more versatile. Solid propellants are located in a chamber for combustion but the liquid propellants are injected into the combustion chamber from a storage tank by metering device and hence the engines using liquid propellants are more delicate. Type of liquid propellants are:

(*i*) **Monopropellants.** Monopropellant has fuel and oxidizer as the same compound or a solution containing both. Examples of monopropellants are 80-99% H_2O_2, hydrazine and its derivatives, nitromethane, ethylene oxide, propyl nitrate etc. Monopropellant for guns have compositions like 63.2% hydroxylammonium nitrate (HAN), 20% triethylammonium nitrate (TEAN) and 16.8% water; mixtures of nitromethane and isopropyl nitrate or methanol. Monopropellants should be stable on storage and smooth on burning. But unfortunately H_2O_2 is highly reactive and decomposition occurs though stabilizers are added. Metallic storage tanks are generally avoided for H_2O_2 as metal oxide catalyzes its decomposition.

(*ii*) **Bipropellants.** Bipropellants consist of an oxidizer and a fuel that are injected in two separate phases to the combustion chamber. Commonly used oxidizers are ozone, liquid O_2, liquid fluorine or a mixture of fluorine and oxygen (FLOX). Common fuel used are hydrazine, liquid H_2, ethyl alcohol, aniline, kerosene, amines.

Conventional rocket propellants contain H_2O_2, conc. HNO_3, NO_2 or liquid O_2 as oxidizer and hydrocarbons, alcohols, amines, hydrazines and alkyl derivatives as fuel. Liquid fluorine or FLOX is used in aerospace application with improved performance.

There are several problems with these combination. Ozone and liquid fluorine, though powerful oxidizers, are toxic and explode at high concentration. Also they are difficult to handle and store.

Production

Propellants are energetic materials and hence are to be manufactured and transported with great care. A remote control is necessary with all processes in which explosive materials are involved and exposed to thermal or mechanical stresses. The production processes are:

(*a*) Solvent process

(*b*) Solventless process—Role and extrusion process

(*c*) Screw extrusion process

(*d*) Ball powder process

(*e*) Casting process

Testing for propellant includes

(*a*) Burning behaviour (Ballistic Bomb)

(*b*) Burning rate (Crawford Bomb)

(*c*) Heat of explosion

The environmentally-safe disposal and toxicological effects of propellants are also of concern and are coming under strict regulations.

Highlights:

Explosive: Explosives are pure substances or mixture, which when subjected to specific stimulus initiate an oxidation reaction producing large volume of hot gases.

Primary explosives: They are highly sensitive explosives, which explode on receiving a slight shock or fire.

High explosives: High explosives have higher energy content compared to primary explosives but they are quite insensitive to external stimuli.

Propellants: Propellants are pure substances or mixtures in liquid or solid state that burn exothermally *without contact with atmospheric oxygen* and form large volume of gaseous products.

Fuses: Fuse is a thin water-proof canvas length of tube which contains gun-powder that burn at a given speed for setting off charges of explosives.

Dynamites: Explosives containing nitroglycerine as the principal ingredient.

RDX: Powerful explosive consisting of cyclotrimethylene trinitroamine.

SHORT QUESTIONS AND ANSWERS

Q. 1. What are explosives?

Ans. Explosives are substances or mixtures, which when subjected to mechanical or thermal shock, lead to rapid oxidation exothermally to produce large amount of gaseous products of greatly increased volume and also a large amount of energy.

Q. 2. What is a rocket propellant?

Ans. Rocket propellant is either a high oxygen containing fuel or a fuel with an oxidant which is burnt under controlled condition with the evolution of a large volume of gas.

Q. 3. What are dynamites?

Ans. Dynamites are high explosives containing nitroglycerine as the principal ingredient. Nitroglycerine is usually mixed with an inert absorbent like wood pulp, starch meals, saw dust etc. with varying amount of nitroglycerine that determines its relative strength.

Q. 4. What are fuses?

Ans. Fuses are thin water-proof canvas length of tube containing gun-powder or TNT, which burn at a given speed for setting-off the charges of explosive. Fuses are of two types: (*i*) safety fuse, (*ii*) detonating fuse.

Q. 5. What do you mean by "oxygen-balance of an explosive"?

Ans. Positive oxygen balance is an important characteristic of a good explosive. It indicates the oxygen contained in the molecule, which will be utilized to oxidize the C and H of the molecule to form CO_2 and H_2O, respectively. It is expressed as the difference between the oxygen contained in the molecule and the oxygen actually required to oxidise the total C and H contained in the molecule.

EXERCISES

1. What are explosives? What are rocket propellants?
2. How are explosives classified?

3. Name two for each class:
(*a*) Primary explosive
(*b*) Two low explosive
(*c*) High explosive
(*d*) Monopropellants and bipropellants

4. What are the requirements of a good explosive?

5. Why are detonators required for high explosive? What are the uses of explosives?

6. What are propellants? How are propellants classified? State the requirements of a good propellant?

7. What is gun-cotton? What is RDX? What are fuses?

8. Explain the term "oxygen-balance of an explosive".

9. What are dynamites? State the procedure of its manufacture.

10. Write notes on the following:
(*a*) Modern explosives
(*b*) Nitroglycerine
(*c*) Rocket propellant
(*d*) Cordite
(*e*) TNT

11. (*i*) RDX is
(*a*) Trinitrotoluene
(*b*) Cyclotrimethylene trinitroamine
(*c*) Lead azide
(*d*) Nitrocellulose

(*ii*) TNT is a compound of
(*a*) Cellulose
(*b*) Glycerol
(*c*) Toluene
(*d*) Phenol

(*iii*) Characteristic of a good explosive is
(*a*) High energy of oxidation
(*b*) Slow and controlled oxidation rate
(*c*) Positive oxygen balance
(*d*) Decomposition rate should be slow

(*iv*) Example of high explosive is
(*a*) TNT
(*b*) Gun powder
(*c*) Lead azide

(*v*) Example of primary explosive is
(*a*) Ammonium nitrate
(*b*) TNT
(*c*) Lead azide

(*vi*) Gum powder is
(*a*) Primary explosive
(*b*) Low explosive
(*c*) High explosive

(*vii*) Smokeless powder is
(*a*) Tetracene
(*b*) Nitrocellulose
(*c*) Picric acid

(*viii*) Binary explosives are mixtures of other explosives with
(*a*) TNT
(*b*) Dynamite
(*c*) Nitrocellulose

(*ix*) Burning speed of safety fuse is
(*a*) 1 m $\sec^{-1}$
(*b*) 1 cm $\sec^{-1}$
(*c*) 100 m $\sec^{-1}$

(*x*) Black powder is
(*a*) Nitrocellulose
(*b*) Mercury fulminate
(*c*) Gun powder

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Water Treatment

The nature's most abundant supply *i.e.,* water is essential for the survival of all the living beings on earth *i.e.,* man, animals and plants. Water is not only essential for the survival of life, but it is also used for the operation in a large number of industries as coolant, solvent, for steam generation, for air conditioning, fire-fighting etc. Water is also used for all domestic purposes like bathing, drinking, washing, sanitary, irrigation etc.

Sources of Water

1. **Rainwater.** It is the purest form of natural water. But unfortunately it dissolves the toxic gases like CO_2, SO_2, NO_2 etc. and other solids, which pollute the atmosphere.

2. **Sea water.** It is the most impure form of water containing about 3.5% dissolved salts of which about 2.6% is sodium chloride. Other salts present include sulfates, bicarbonates, bromides of sodium, potassium, magnesium etc. Other impurities are carried to sea through rivers.

3. **River water.** The sources of river water are the springs and the rainwater. River water while flowing through the land collects lots of organic matters from falling trees and nearby habitats and also other soluble and suspended matters from the lands, soils etc. The dissolved matters include the salts like sulfates, bicarbonates and bromides of sodium, potassium and magnesium.

4. **Lake water.** It is much purer than river water, dissolved impurities are less but contains lots of organic matter.

5. **Underground water.** The rainwater and other surface water percolate down through the soil and rocks and get filtered and finally collected on rocky surface or again come out as spring. Though it contains less suspended matter but the dissolved mineral content is quite high and is of high organic purity.

Thus we can say that the surface water collects lots of suspended materials, micro-organisms and other pollutants from the habitats and become unsuitable for direct human consumption and other usage.

Effect of Water on Rocks

Water, while percolation, gets contaminated by the following processes:

(*a*) **Dissolution.** Sodium chloride, gypsum ($CaSO_4.2H_2O$) and other soluble salts get directly dissolved in the percolated water.

(*b*) **Hydration.** While percolation, water causes hydration of the minerals like anhydrite, olivine which leads to increase in volume and disintegration of such rocks, *viz.*

$$\underset{\text{Anhydrite}}{CaSO_4} + 2H_2O \longrightarrow \underset{\text{Gypsum}}{CaSO_4.2H_2O}$$

$$\underset{\text{Olivine}}{Mg_2SiO_4} + xH_2O \longrightarrow \underset{\text{Serpentine}}{Mg_2SiO_4.xH_2O}$$

(*c*) **Oxidation.** Dissolved oxygen brings about oxidation alongwith hydration.

$$\underset{\text{Magnetite}}{2Fe_3O_4} \xrightarrow{\text{Oxidation}} \underset{\text{Haematite}}{2Fe_2O_3} \xrightarrow{\text{Hydration}} \underset{\text{Limonite}}{2Fe_2O_3\,.2H_2O}$$

(*d*) **Action of carbon dioxide.** Insoluble carbonates of Ca, Mg and Fe alongwith silicates of Na, K, Ca, and Fe are converted into soluble bicarbonates and soluble carbonates, *viz.*

$$\underset{\text{(Insoluble)}}{CaCO_3} + CO_2 + H_2O \longrightarrow \underset{\text{(Soluble)}}{Ca(HCO_3)_2}$$

$$K_2O.Al_2O_3.6SiO_2 + CO_2 + 2H_2O \longrightarrow Al_2O_3.2SiO_2.2H_2O + K_2CO_3 + 4SiO_2$$

Hardness of Water

Hardness of water is the characteristic of preventing lather formation of water with soap. Generally salts like chlorides, bicarbonates and sulfates of Ca^{2+}, Mg^{2+} and Fe^{2+} make water hard. This hard water on treatment with soap which is stearic or palmitic acid salts of sodium or potassium causes white precipitate formation of calcium or magnesium stearate or palmitate.

$$\underset{\substack{\text{Sodium stearate}\\\text{(soap)}}}{2C_{17}H_{35}\,COONa} + CaCl_2 \longrightarrow \underset{\substack{\text{Calcium stearate}\\\text{(insoluble)}}}{(C_{17}H_{35}COO)_2Ca} + 2NaCl$$

Thus the cause of hardness is the precipitation of the soap and hence prevents lathering at first. When the hardness causing ions are removed as insoluble soaps, water becomes soft and forms lather.

The hardness is of two types:

(*i*) *Temporary hardness* is due to the bicarbonates of Ca^{2+} and Mg^{2+} and carbonate of Fe^{2+}. Since bicarbonates readily get precipitated on boiling the water, the temporary hardness can be easily removed, *viz.*

$$Ca(HCO_3)_2 \xrightarrow{\text{heat}} \underset{\text{insoluble}}{CaCO_3\downarrow} + H_2O + CO_2$$

(*ii*) *Permanent hardness* is due to the presence of chlorides and sulfates of Ca, Mg, Fe, etc. Permanent hardness cannot be removed easily on boiling.

Units of Hardness

Both temporary and permanent hardnesses are expressed in ppm as $CaCO_3$. The choice of $CaCO_3$ is due to the fact that its mol. wt. is 100 and equivalent weight is 50 and it is *the most insoluble salt* in water. Equivalent of $CaCO_3$

$$= \frac{(\text{Mass of hardness producing substance}) \times (\text{Chemical equivalent of } CaCO_3)}{\text{Chemical equivalent of hardness producing substance}}$$

$$= \frac{\text{Mass of hardness producing substance} \times 50}{\text{Chemical equivalent of hardness producing substance}}$$

Hardness is principally expressed in ppm unit. Other limits include French degree of hardness, English degree of hardness or Clark, USA degree of hardness and German degree of hardness.

$$1 \text{ ppm} = \frac{1 \text{ part of hardness}}{10^6 \text{ parts of water}}$$

$$1 \text{ Fr. degree of hardness} = \frac{1 \text{ part of hardness}}{10^5 \text{ parts of water}}$$

$$1 \text{ Clark} = \frac{1 \text{ grain of hardness}}{1 \text{ gallon or } 70{,}000 \text{ grains}} = \frac{1}{7 \times 10^4}$$

$$1 \text{ USA degree of hardness} = \frac{1 \text{ grain}}{1 \text{ USA gallon}} = \frac{1 \text{ grain}}{58{,}300 \text{ grains}} = \frac{1}{5.83 \times 10^4}$$

$$1 \text{ German degree of hardness} = \frac{1 \text{ grain}}{1 \text{ German grain}} = \frac{1 \text{ grain}}{56{,}000 \text{ grains}} = \frac{1}{5.6 \times 10^4}$$

Relation between various units of hardness

1 ppm	= 1 mg/l	= 0.1° Fr	= 0.07° Cl
1 mg/l	= 1 ppm	= 0.1° Fr	= 0.07° Cl
1° Cl	= 1.43° Fr	= 14.3 ppm	= 14.3 mg/l
1° Fr	= 10 ppm	= 10 mg/l	= 0.7° Cl.

Disadvantages of Hard Water

(*a*) *In domestic uses*. For *washing* and *bathing,* hard water creates difficulties, since it does not form lather freely with soap. It also creates sticky precipitates that deposit on bath tub, body, clothes etc. until all the Ca/Mg salts get precipitated. Thus a lot of soap get wasted also.

For *cooking* hard water creates similar difficulties by producing scum on the bottom of the vessels. Due to the presence of hardness producing salts in hard water, boiling point gets elevated and during cooking a lot of fuel is wasted. Pulses etc. do not cook in hard water. Taste of tea, coffee becomes unpleasant. *Drinking* of hard water is also problematic since it affects the digestive system and at the same time the possibility of deposition of calcium oxalate crystals in the urinary tract is alarming.

(*b*) *In industrial uses*. For *textile industry* and *dyeing industry*, hard water causes the usual problem of deposition of insoluble salts that interfere with the proper dyeing and printing of the fabrics. The stains of iron salts also are undesirable on fabrics. Hard water also hampers the economy by wastage of soap as it does not form good lather.

- For *sugar industry,* the salts responsible for hardness create difficulties in sugar refining and crystallization of sugar and the sugar becomes deliquescent.
- Calcium and magnesium salts also interfere with the smooth and glossy finish of the papers in the *paper industry.* Iron salts interfere with the colour of the paper.
- In *laundry,* hard water causes wastage of costly soap and also interferes with the coloration due to the staining of iron salts.
- The hydration of cement and final hardening of cement are affected by use of hard water in *concrete making.*
- Hard water is not suitable for preparing drug solutions in *pharmaceutical industry*.
- For *steam generation in boilers,* hard water creates many problems like (*i*) scale formation, (*ii*) corrosion, (*iii*) priming and foaming and (*iv*) caustic embrittlement.

Sludge and Scale Formation in Boilers

When hard water is used for boilers, on continuous evaporation, the salts present in the hard water gets saturated and are finally deposited in the areas where the flow is slow. When these precipitates are loose and slimy in nature, it is called *sludge* whereas when these precipitates are hard and they adhere strongly to the inner surface of the boilers, they are called *scale*.

Sludge can be easily removed by scrapping with a brush. Sludge is formed by the presence of $MgCO_3$, $MgSO_4$, $MgCl_2$, $CaCl_2$ etc. These salts are more soluble in hot water.

Disadvantages of sludge formation are (*i*) poor heat conduction due to the presence of sludge on the surface; (*ii*) difficulty in the operation of the boiler; (*iii*) if sludge is formed along with the scale and is trapped within the scale formed and so it is difficult to remove and (*iv*) it clogs the pipe lines and other connections to the vessel near the places where water circulation rate is slow.

Removal of sludges. Sludge formation can be prevented by (*i*) using soft water for boiler operation and (*ii*) removing the concentrated salty water from time to time so that deposition of sludge is prevented.

Scales are the hard deposits on the inner surface of the boilers which are difficult to remove. This scale formation takes place due to the following reasons:

(*a*) In low pressure boilers scale formation occurs due to the formation of $CaCO_3$ from $Ca(HCO_3)_2$.

i.e.,

$$Ca(HCO_3)_2 \longrightarrow \underset{\text{Scale}}{CaCO_3\downarrow} + H_2O + CO_2$$

(*b*) In high pressure boilers this $CaCO_3$ gets converted to soluble $Ca(OH)_2$. But here $CaSO_4$ forms the hard scale. Since the solubility of $CaSO_4$ decreases with increase in temperature, and at high temperature the precipitated $CaSO_4$ forms hard scale.

Similar hard scales are formed when SiO_2 is present in the hard water. It deposits as $CaSiO_3$ or $MgSiO_3$. These calcium or magnesium silicate scales are very difficult to remove.

Dissolved magnesium salts also precipitate as $Mg(OH)_2$ forming soft type of scale.

Disadvantages of scale formation are similar to sludge formation but the severity is more, since its removal is more difficult.

Disadvantages include

(*i*) *Poor heat transfer* from boiler to water leading to increase in fuel consumption. The increase in thickness of the scale from 1.25 mm to 12 mm leads to increase in fuel consumption from over 50% to 150%.

(*ii*) Due to the overheating of the boiler, different parts of the boiler become weak and distorted and so the operation of the boiler becomes *unsafe,* particularly the high pressure boilers.

The thick scales may sometimes lead to *explosion* due to sudden development of high pressure.

(*iii*) Valves and condensers of the boilers are chocked due to scale formation and *boiler efficiency decreases.*

Removal of scales can be done by:

(*i*) Wooden scraper or wire brush, suitable for removing loose scales.

(*ii*) Blow down operations for loose scales. The operation actually involves the removal of very hard water from a tap at the bottom of the boiler and replenishing the water with softened water called ‘make up’ water.

(*iii*) Giving thermal shocks, which involve alternate heating and cooling to make the scales brittle.

(*iv*) Chemical treatment with 5-10% HCl for carbonates and EDTA treatment for Ca/Mg salts forming complexes.

These are methods for the removal of the scales, when they are formed. There are also some methods for the *prevention of scale* formation by *internal* or *external* treatment.

Internal treatment

Internal treatment involves addition of chemical to the boiler water either to (*i*) precipitate the scale forming impurities in the form of sludges, which can be easily removed or (*ii*) convert the impurities to soluble compounds, so that scale formation can be avoided. Important internal treatments involve.

(*a*) *Colloidal Conditioning:* Organic substances like kerosene, tannin, agar-agar are added to form gels and form loose non-sticky deposits with scale-forming precipitates, which can be easily removed by blow-down operations in low pressure boilers.

(*b*) Different sodium phosphates like NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 are added to high pressure boilers to react with the hardness forming impurities to form soft sludge of calcium and magnesium phosphates and finally this can be removed by blow down operation.

$$3CaCl_2 + Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6NaCl$$

(*c*) *Carbonate conditioning:* Sodium carbonate is added to the water of low pressure boiler whereby the scale forming $CaSO_4$ gets converted to loose sludge of $CaCO_3$, which can be easily removed by blow-down operation.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

(*d*) *Calgon conditioning:* Calgon *i.e.*, sodium hexa meta phosphate when added to boiler water, reacts with scale forming $CaSO_4$ and forms soluble complex compound.

$$2CaSO_4 + [Na_4P_6O_8]^{2-} \longrightarrow [Ca_2P_6O_{18}]^{2-} + 2Na_2SO_4$$

(*e*) *Sodium aluminate conditioning:* Sodium aluminate is hydrolysed yielding NaOH and gelatinous $Al(OH)_3$. The NaOH formed reacts with magnesium salts to precipitate $Mg(OH)_2$. This $Mg(OH)_2$ and $Al(OH)_3$ are flocculent and entraps the colloidal as well as the finely divided impurities like silica in the boiler water and the loose precipitate is finally removed by blow down operation.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3\downarrow$$
$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2\downarrow + 2NaCl$$

(*f*) *Electrical conditioning:* Rotating mercury bulbs on heating by the boiling water emit electrical discharges that prevent scale formation by the particles.

(*g*) *Radioactive conditioning:* Tablets of radioactive salts placed inside a boiler emit radiations, which prevent scale formation.

Caustic Embrittlement

Embrittlement is the name that has been given to boiler failures due to development of certain types of crack resulting from excessive stress and chemical attack. In steam boiler operation, the chemicals that are believed to be responsible are NaOH and silica. During softening processes, Na_2CO_3 are added and it gives rise to NaOH at elevated temperature according to the following reaction.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

Steam boilers are made by rivetting constructions rather than welding and are particularly liable to damage by caustic alkali solutions. This cracking is not due to corrosion and the cracks appear like brittle fracture and hence called caustic embrittlement. NaOH attacks and dissolves out iron of boiler forming sodium ferroate. This finally causes the stressed parts like bends, joints, rivets to lead to the boiler failure.

Concentration cell develops between the boiler and the NaOH of different concentrations as

+ Fe at rivets, joints etc.	Concentrated NaOH Solution	Dilute NaOH Solution	Fe at – plane Surfaces

Prevention of Caustic Embrittlement

(*i*) Addition of sodium phosphate as softening agent instead of Na_2CO_3.

(*ii*) Addition of sodium sulfate to ensure a weight ratio $Na_2SO_4/NaOH > 2.5$, whereby the deposition of Na_2SO_4 prevents the penetration of NaOH into the cracks and stops caustic embrittlement in high pressure boilers.

(*iii*) Addition of organic agents like tannin, lignin, querbracho etc. also prevents cracking similar to sodium sulfate in low pressure boilers.

(*iv*) Use of crack-resisting steels: Certain steels containing Al added during manufacture appear to be resistant against caustic cracking.

Corrosion in Boilers

Boiler corrosion occurs by chemical or electrochemical attack of the contents of water. Main types are of chemicals:

(*a*) *Dissolved oxygen:* Oxygen is dissolved in water to the extent of 8 ml/*l* at room temperature and it is responsible for corrosion in the boiler. Greater the pressure, higher the dissolved O_2 content. As the water is heated in the boiler the dissolved oxygen is liberated and iron is corroded.

$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2 \downarrow$$
$$4Fe(OH)_2 \downarrow + O_2 \longrightarrow 2[Fe_2O_3.2H_2O]$$

Dissolved oxygen can be removed by:

(*i*) Mechanical deaeration methods using distillation, steam scrubbing, desorption, flash-type deaeration, which reduce O_2 concentration to about 0.01 ppm.

(*ii*) Chemical treatment–oxygen concentration is virtually made zero by using reducing agents like hydrazine, sodium sulfite etc.

(*iii*) Ion exchange techniques also reduce oxygen concentration to very low level.

(*b*) *Dissolved* CO_2: Water contains some CO_2 and the decomposition product of bicarbonates present in water also produces CO_2. This CO_2 dissolves in water forming carbonic acid which causes local corrosion called **pitting**.

$$Fe + CO_2 + H_2O \longrightarrow FeCO_3 + H_2$$
$$4FeCO_3 + O_2 + 10H_2O \longrightarrow 4Fe(OH)_3 + 4H_2O + 4CO_2$$
$$4Fe(OH)_3 \longrightarrow 2Fe_2O_3 + 6H_2O$$

Removal of CO_2 ***is done by:***

(*i*) Mechanical deaeration.

(*ii*) Adding lime or NH_3.

(*iii*) Heating.

(*c*) *Mineral acids:* Water from industrial areas contains acidic wastes or inorganic salts which on hydrolysis produce acids. These acids cause corrosion in boilers. The acids react with iron in chain reactions producing acids again and again and also produce H_2 causing hydrogen embrittlement which leads to boiler failure.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$
$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$
$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 \downarrow + 2HCl$$

Priming and Foaming

During rapid steam production, some liquid water drops are also carried along with the steam. This wet-steam formation is called *priming*.

Priming occurs due to (*i*) presence of large amount of dissolved solids, (*ii*) high steam velocities, (*iii*) sudden boiling and (*iv*) sudden increase in steam production. Priming can be controlled by (*i*) maintaining low water level in boiler, (*ii*) avoiding rapid change in steam rate, (*iii*) softening of boiler water and (*iv*) using mechanical device for steam purification.

Foaming is the production of bubbles and foams which do not break easily. Foaming occurs due to the presence of oil in the water.

Foaming can be reduced by (*i*) removing oil from boiler-feed water and (*ii*) adding anti-foaming agents.

Priming and foaming occur together and they are undesirable since they wet other mechanical parts of the boiler and reduce their efficiency. Actual height of the water column cannot be judged due to foaming hence creating difficulty in the maintenance.

Highlights:

- Chief sources of water: Sea water, rainwater, ground water and surface water.
- Impurities present in water:
  (*i*) Suspended, (*ii*) Colloidal, (*iii*) Dissolved impurities
- Temporary hardness is due to $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ and can be removed by boiling.
- Permanent hardness is due to chlorides and sulfates of Ca^{2+}, Mg^{2+}, Fe^{2+} and other heavy metals.
- Hardness expressed in equivalent amount of $CaCO_3$

$$= \frac{\text{Mass of hardness producing substances} \times 50}{\text{Chemical equivalent of hardness producing substances}}$$

- 1 ppm hardness ≡ 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water.
- Hard water cannot be used for steam generation in boilers due to the problems like scale and sludge formation, priming and foaming, boiler corrosion and failure.

Softening of Water

Softening of water means the removal of calcium, magnesium, iron salts and similar other metallic ions, which would form insoluble metallic soaps. The three important industrial methods employed for softening of water are:

1. Cold and hot lime-soda process.
2. Permutit or zeolite process.
3. Ion-exchange or demineralization process.

1. *Lime-soda process.* By this process, soluble calcium and magnesium salts are rendered insoluble by adding calculated amount of lime [$(CaOH)_2$] and soda [Na_2CO_3]. The insoluble precipitates of $CaCO_3$ and $Mg(OH)_2$ are removed by filtration. By this method, both temporary and permanent hardness are removed.

For the removal of temporary hardness the reactions are:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + MgCO_3 + 2H_2O$$
$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow$$

Hence, to remove equivalent quantities of Ca and Mg hardnesses the amount of lime necessary is in the ratio of 1:2.

Again for the removal of permanent hardness. The reactions are:

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2SO_4$$
$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$$
$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow$$

Hence, for the removal of permanent hardness due to Ca-salts, lime is not necessary, but it is necessary for Mg salts. Extra addition of $Ca(OH)_2$ causes hardness. So calculated quantities of lime and soda are to be added after the determination of actual hardness.

In the actual process the water is thoroughly mixed with the chemicals and allowed to react for sufficient time. Activated charcoal is added as activator, alum etc. are added as coagulants. To avoid after-precipitation of $CaCO_3$, sludge of the previous operation is added, which supplies the nuclei for the precipitation.

Cold Lime-Soda Process

In this method, calculated quantity of chemicals and water, along with accelerators and coagulators are added to a tank fitted with a stirrer (Fig. 17.1). On vigorous stirring, thorough mixing takes place. After softening the soft water rises upwards and the heavy sludges settle down. The softened water passes through a filtering media ensuring complete removal of the sludge and finally the filtered water flows out through the top. Cold lime soda process is used for partial softening of municipal water, for softening of cooling water etc. In actual purpose, magnesium hardness is brought down to almost zero but calcium hardness remains about 40 ppm.

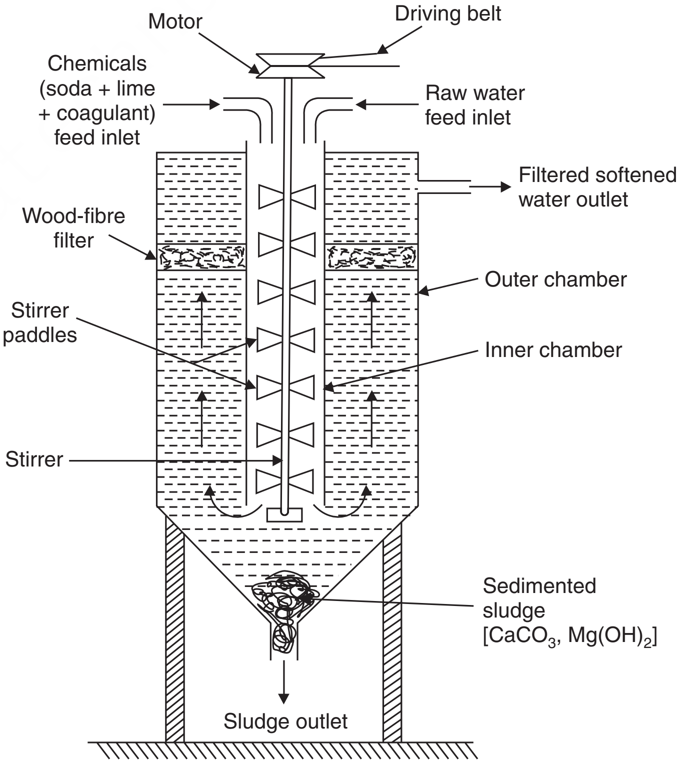


Fig. 17.1 Continuous cold lime-soda softener.

Hot Lime-Soda Process

This process is similar to the cold lime-soda process. Here the chemicals alongwith the water are heated near about the boiling point of water by exhaust steam. As the reaction takes place at high temperature, there are the following advantages:

(*i*) the precipitation reaction becomes almost complete.
(*ii*) the reaction takes place faster.
(*iii*) the sludge settles rapidly.
(*iv*) no coagulant is needed.
(*v*) dissolved gases (which may cause corrosion) are removed.
(*vi*) viscosity of soft water is lower, hence filtered easily.
(*vii*) Residual hardness is low compared to the cold process.

Hot lime-soda process consists of three parts:

(*a*) 'Reaction tank' in which complete mixing of the ingredients takes place.
(*b*) 'Ionical sedimentation vessel' where the sludge settles down and
(*c*) 'Sand filter' where sludge is completely removed.

The soft water from this process is used for feeding the boilers (Fig. 17.2).

Advantages Include:

(*i*) Lime soda process is economical.
(*ii*) The process improves the corrosion resistance of the water.
(*iii*) Mineral content of the water is reduced.
(*iv*) pH of the water rises, which reduces the content of pathogenic bacteria.

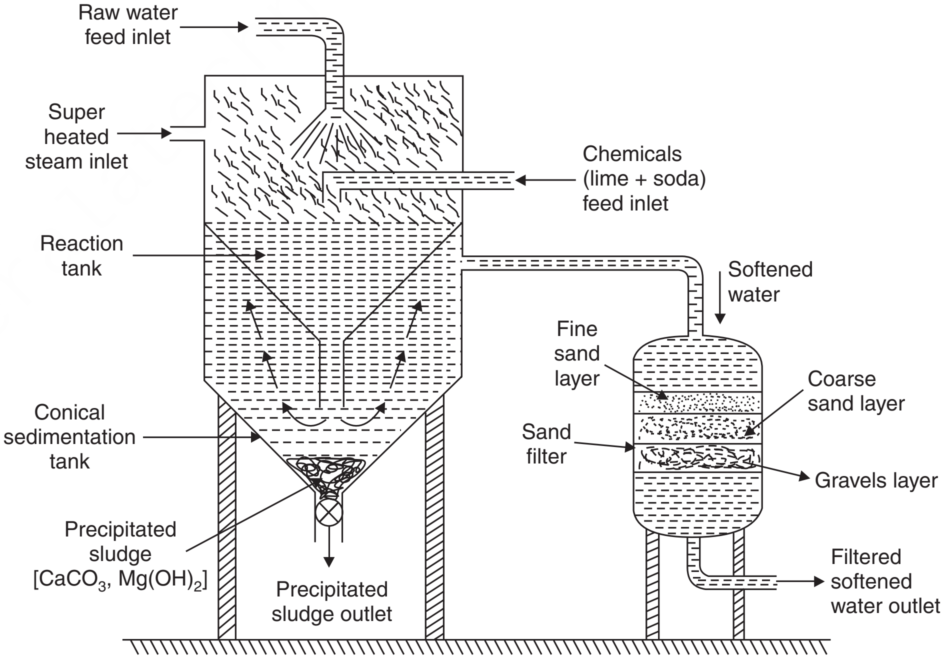


Fig. 17.2 Continuous hot lime-soda softener.

Disadvantages Include:

(*i*) Huge amount of sludge is formed and disposal is difficult.
(*ii*) Due to residual hardness, water is not suitable for high pressure boiler.

Permutit or Zeolite Process

Zeolite is hydrated sodium alumino silicate capable of exchanging reversibly its sodium ions for Ca^{2+} and Mg^{2+}, having the general formula $Na_2O.Al_2O_3.xSiO_2.yH_2O$. Common zeolite is $Na_2O\ Al_2O_3.3SiO_2.2H_2O$ and is known as natrolith. Others gluconites, green sand etc. are used for water softening.

Artificial zeolite used for softening purpose is permutit. These are porous and glassy and have greater softening capacity than green sand. They are prepared by heating together with china clay, feldspar and soda ash.

Method of Softening: Hardwater is passed through a bed of zeolite at a specific rate at ordinary temperature; the hardness causing cations *i.e.,* Ca^{2+} and Mg^{2+} are exchanged for Na and it is converted to CaZe and MgZe.

Reactions taking place are:

$$Na_2Ze + Ca(HCO_3)_2 = 2Na\ HCO_3 + CaZe$$
$$Na_2Ze + Mg(HCO_3)_2 = 2NaHCO_3 + MgZe$$
$$Na_2Ze + CaSO_4 = Na_2SO_4 + CaZe$$
$$Na_2Ze + CaCl_2 = 2NaCl + CaZe$$

Regeneration of Zeolite: The process is also commercially successful since the Ca/Mg zeolites formed by passing hard water through the bed can be easily regenerated into Na_2Ze by passing brine through the bed of inactivated zeolite.

$$CaZe \text{ or } MgZe + 2NaCl = Na_2Ze + CaCl_2 \text{ (Or } MgCl_2)$$

The washings containing $CaCl_2$ or $MgCl_2$ are wasted. The water softened by this process can be used for laundry purposes.

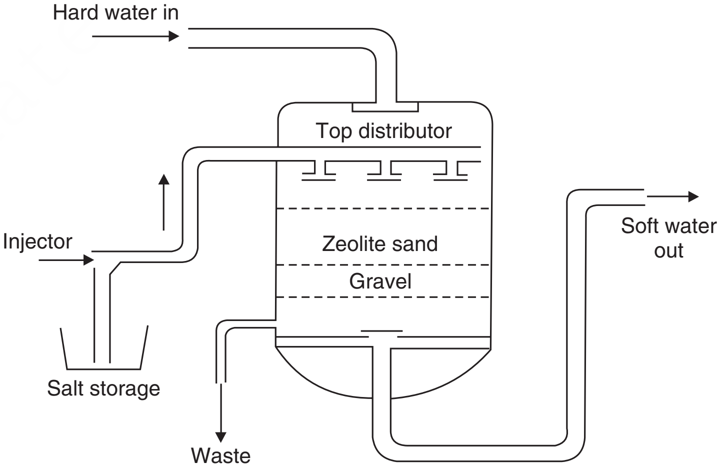


Fig. 17.3 Softening of hard water by permutit process.

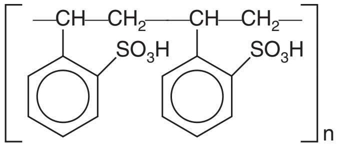
Advantages. (*i*) Hardness of water can be removed completely upto about 10 ppm; (*ii*) The equipment used is small and easy to handle; (*iii*) It requires less time for softening; (*iv*) There is no sludge formation, hence the process is clean; (*v*) Easy to regenerate; (*vi*) Any hardness can be removed without any adjustment of the process.

Disadvantages. (*i*) Coloured water or water containing suspended impurities cannot be used before filtration; (*ii*) Water containing acid cannot be used for softening since acid may destroy the zeolite; (*iii*) Since on removal of Ca^{2+} and Mg^{2+} the soft water contains large amount of $NaHCO_3$, this on heating liberates CO_2, which causes corrosion in the boilers and hence this soft water is not suitable for boilers.

Ion Exchange or Demineralization

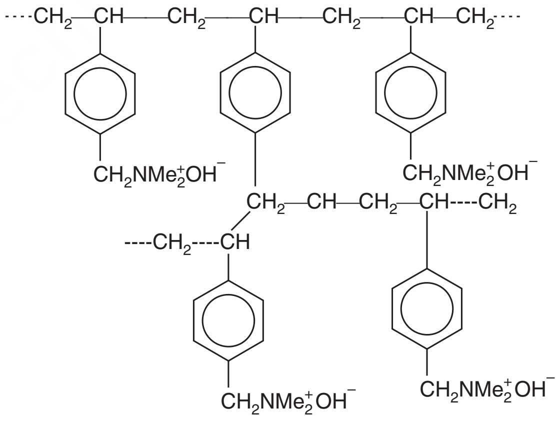
Ion exchange resins are organic polymers which are crosslinked having microporous structure and the functional groups are attached to the chains which are responsible for the ion exchange properties.

(*i*) *Cation exchange resins (RH^+)* are phenol-sulfonic acid-formaldehyde resin, styrene-divinyl benzene copolymers which exchange their H^+ ions with the cations present in the water *i.e.,* Ca^{2+} and Mg^{2+}.



cation exchange resin

(*ii*) *Anion exchange resins (ROH^-):* The styrene divinyl benzene or amine formaldehyde copolymers contain quaternary ammonium tertiary sulphonium or amino group in the resin. The resin on treatment with NaOH solution is capable of exchanging the OH^- with different anions of water *i.e.,* Cl^-, SO_4^{2-} etc.



Anion exchange resin

Method: The hard water is passed first through cation exchange resin similar to the permutit process whereby the cations like Ca^{2+}, Mg^{2+} are removed from the hard water and exchanged with H^+ as follows:

$$2RH^+ + Ca^{2+}/Mg^{2+} \longrightarrow R_2Ca^{2+}/R_2Mg^{2+} + 2H^+$$

After this the hard water is again passed through anion exchange column, which exchanges all the anions like SO_4^{2-}, Cl^- etc. present in the water with OH^-

$$ROH^- + Cl^- \longrightarrow R^+Cl^- + OH^-$$

These H^+ and OH^- combine to form water molecule. Thus the water coming out finally from the two exchangers is ion free and called *deioinized* or *demineralized* water.

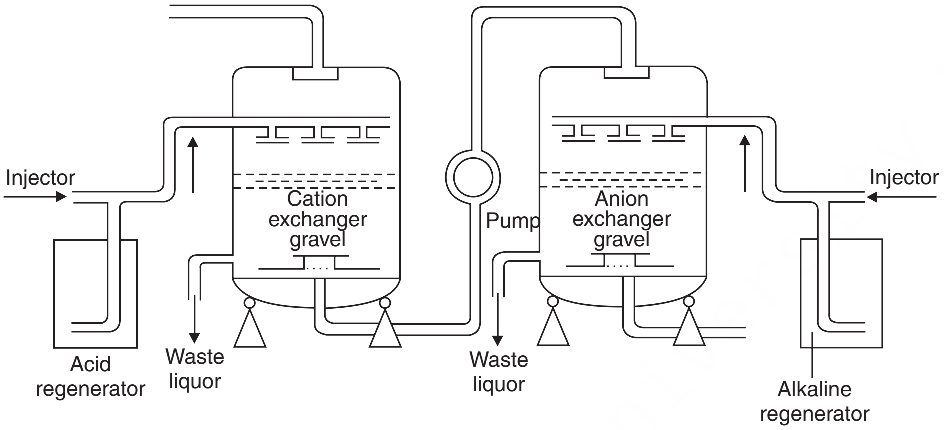
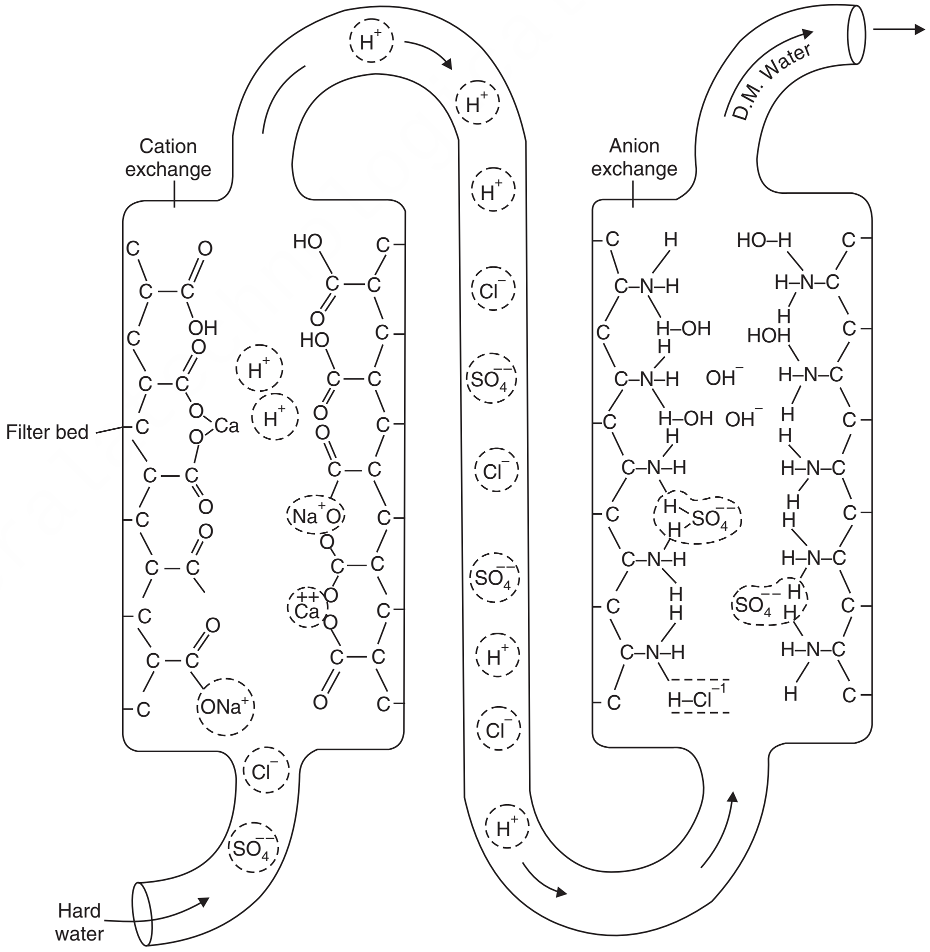


Fig. 17.4 Demineralisation of water.



Cation exchange reaction:

$2R^-H^+ + Ca^{+2} \rightleftharpoons CaR_2 + 2H^+$

Anion exchange reaction:

$RNH_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3OH^-$

$R\overset{+}{N}H_3OH^- + Cl^- \rightleftharpoons R\overset{+}{N}H_3Cl^- + OH^-$

Fig. 17.5 Demineralisation of water showing the ion exchanges.

Regeneration: The inactivated or exhausted cation exchange resin is regenerated by dil. H_2SO_4/HCl.

$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+}$$

Similarly, the exhausted anion exchange resin is regenerated by dil. NaOH

$$R_2SO_4^{2-} + 2OH^- \longrightarrow 2ROH^- + SO_4^{2+}$$

The columns are finally washed with deionized water and the washings are discarded.

Mixed Bed Deionizer

It is actually a single cylinder containing and intimate mixture of cation exchanger and strongly basic anion exchanger. Hence, water while passing through the column comes in contact with the two exchangers for a large number of times and the hardness is reduced to a very low level (1 ppm). Thus, it is actually equivalent to a series of cation and aninon exchangers.

Advantages of ion exchangers include (*i*) Easy regeneration; (*ii*) both acidic and alkaline water can be softened; (*iii*) residual hardness is very low and hence the water is suitable for high pressure boilers also.

Disadvantages are (*i*) the equipment and the process is costly and (*ii*) turbid water cannot be directly charged for softening. It needs prior filtration.

Treatment of Water for Domestic Use

Municipalities supply *potable water,* which is suitable for drinking and it must satisfy the following requirements:

Requirements for Drinking Water:

- It should be clear and odourless.
- It should be devoid of any unpleasant taste.
- Suspended matter should not exceed 10 ppm.
- It should be devoid of heavy metals and arsenic.
- pH should be about 8.
- Content of dissolved salts should not exceed 500 ppm.
- Lastly, it should be free from pathogenic (disease causing) microorganisms.

Natural water from river, lakes, canals are treated for the domestic purpose. The steps are as follows:

- Aeration of the raw water by passing compressed air to remove mainly the obnoxious odour and iron as $Fe(OH)_3$.
- Settling in a large tank to remove suspended impurities.
- Sedimentation through coagulation of the colloidal particles by adding a suitable coagulant. Chemical coagulants are generally (*i*) Alum [K_2SO_4, $Al_2(SO_4)_3.24H_2O$] (*ii*) Green vitriol [$FeSO_4.7H_2O$].
- Coagulants or flocculants are generally added in the form of solution and mixing is carried out by stirring.
- The gelatinous precipitates mainly contain aluminium hydroxide, ferrous and ferric hydroxides (ferrous hydroxides are converted to ferric hydroxide by the dissolved oxygen of water).
- These heavy flocculant precipitates contain also some bacteria making the water free of some of the microorganisms.
- These partially clarified water is filtered through sand gravity filters.

- These filters are rectangular tanks, which contain layers of fine sand at the top of one meter thick, at middle of coarse sand of 0.5 meter thick and at bottom a gravel of 0.5 meter thick.

Sterilization

(*i*) *By addition of bleaching powder (1 kg per 1000 kiloliters).*

Here sterilization is effected by the HOCl generated by the following reaction:

$$Ca(OCl)Cl + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

and this HOCl kills the germs.

Disadvantages of this process:

(*i*) Bleaching powder makes water unnecessary hard and sometimes imparts a bad taste to the water.

(*ii*) *By direct chlorination:* Here also the generated HOCl kills the pathogenic bacteria. Liquid chlorine is the most effective reagent, 0.3-0.5 ppm chlorine is sufficient.

Advantage of using Chlorine. It is effective and economical; chlorine does not make water hard and requires a little space for storage.

Disadvantages. Excess chlorine imparts unpleasant taste and odour to the treated water. Dissolved chlorine causes irritation to mucus membrane and lowers the pH of water below 6.5. The treated water should contain chlorine less than 0.2 ppm.

(*ii*) Break-point Chlorination

It is seen that when liquid chlorine is added or chlorine gas is passed through water the consumption of chlorine makes the available chlorine less and after some time the available chlorine increases. This is due to the consumption of chlorine in oxidising some oxidisable organic matter present in water at first. Then available chlorine again increases due to decomposition of chloro-organic compounds.

This free chlorine is responsible for destruction of pathogenic bacteria in water. The point at which the residual chlorine begins to appear is known as *break point* and at this point water is devoid of bad taste and odours and is bacteria free.

Advantages of break point chlorination

- Organic matters present in water are completely oxidised leaving behind odour-free water and sometimes colour-free water.
- Pathogenic bacteria are destroyed completely.
- It prevents the growth of weed in water in future.

(*iii*) Sterilization by Chloramine

When chlorine and ammonia are mixed in the ratio 2:1 of volume chloramine is formed.

$$Cl_2 + NH_3 \longrightarrow Cl.NH_2 + HCl$$

Chloramine is much more effective than chlorine in its bactericidal (bacteria killing) action. Here also HOCl is liberated.

$$Cl.NH_2 + H_2O \longrightarrow HOCl + NH_3$$

HOCl itself is bactericidal and here the liberated nascent oxygen is also bactericidal

$$HOCl \longrightarrow HCl + [O].$$

The use of chloramine for sterilization is gaining importance as it does not impart any irritating odour and does not affect the taste of the treated water.

(*iv*) Sterilization by Ozonization

Ozone is an unstable gas and decomposes to give nascent oxygen. This nascent oxygen kills bacteria and oxidises the organic matter present in the water. The ozone treatment plant consists of a tower made of enamelled iron, separated by perforated celluloid partition into a large number of compartments, ozone is passed through bottom and the water is allowed to percolate through the celluloid partition. The perforated partition makes the water into minute bubbles resulting in a counter-current contact with ozone. This makes the treatment most effective.

Advantages of ozone sterilization are

(*a*) Sterilization, bleaching, decolourisation and deodourisation take place at the same time.

(*b*) Ozone does not impart any unpleasant taste or odour to the treated water and does not change its pH appreciably as it simply decomposes into oxygen. So it does not cause any irritation to the mucus membrane as is the case with chlorine or bleaching powder treatment.

(*c*) Time of contact is only 10-15 minutes and dose strength is only 2-3 ppm.

The only *disadvantage* of this process is that it is comparatively costly.

Sterilization through Physical Methods

(*i*) Boiling, (*ii*) Exposure to the sunlight, (*iii*) Sterilization with UV light.

Dechlorination

When during chlorination, break point chlorination is reached, it becomes sometimes necessary to remove the excess chlorine from the treated water, this process is known as *dechlorination.* Sulphur dioxide is very common as an antichlor. Other common antichlors are: sodium bisulphite, sodium thiosulphate and hydrogen peroxide.

$$Cl_2 + H_2O = HOCl + HCl$$

$$H_2O + SO_2 = H_2SO_3 \qquad SO_2 + Cl_2 + 2H_2O = 2HCl + H_2SO_4$$

$$HOCl + H_2SO_3 = HCl + H_2SO_4 \qquad H_2O_2 + Cl_2 = 2HCl + O_2\uparrow$$

Dechlorination is needed to avoid the harmful effects of treated water.

Desalination of Brackish Water

The water containing dissolved salts and having very salty taste is called *brackish water,* like the sea water and it is not suitable for drinking. The process of removal of common salt from this brackish water is called *desalination.* Desalination can be done by the following methods.

(*a*) *Electrodialysis.* This method involves the removal of ions from the brine solution by applying direct current and employing pair of plastic membranes through which ions can pass. From Fig. 17.6 we can find that when direct current is passed through saline water, the Na^+ ions move towards the cathode while Cl^- ions move towards the anode through the membrane and collect in the two side compartments while the central compartment contains pure desalinated water.

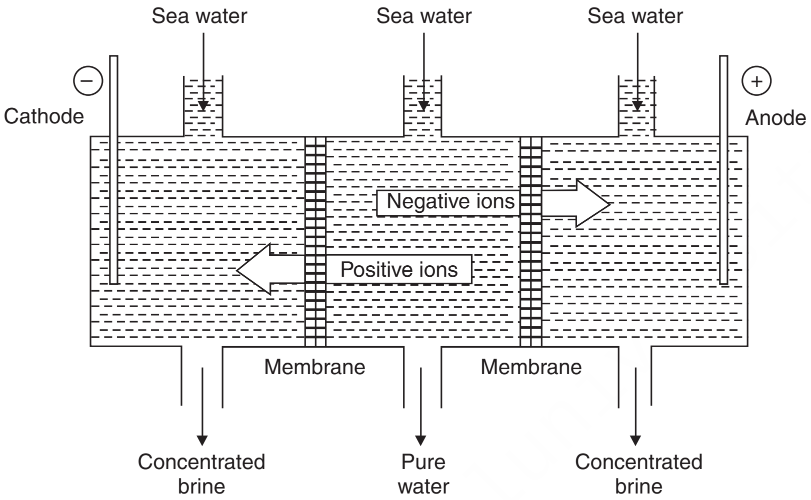


Fig. 17.6 Line diagram of electrodialysis.

To make this process more effective, ions sensitive membranes are used that allow the passage of either specific cations or specific anions. These membranes are selective as they are made up of materials containing fixed functional groups.

An electrodialysis cell as shown in Fig. 17.7 contains a large number of pair of membranes and saline water is passed under pressure in electric field applied perpendicular to the direction of flowing water. Cations and anions pass through the membrane pairs and we obtain alternate streams of pure water and concentrated salt solution.

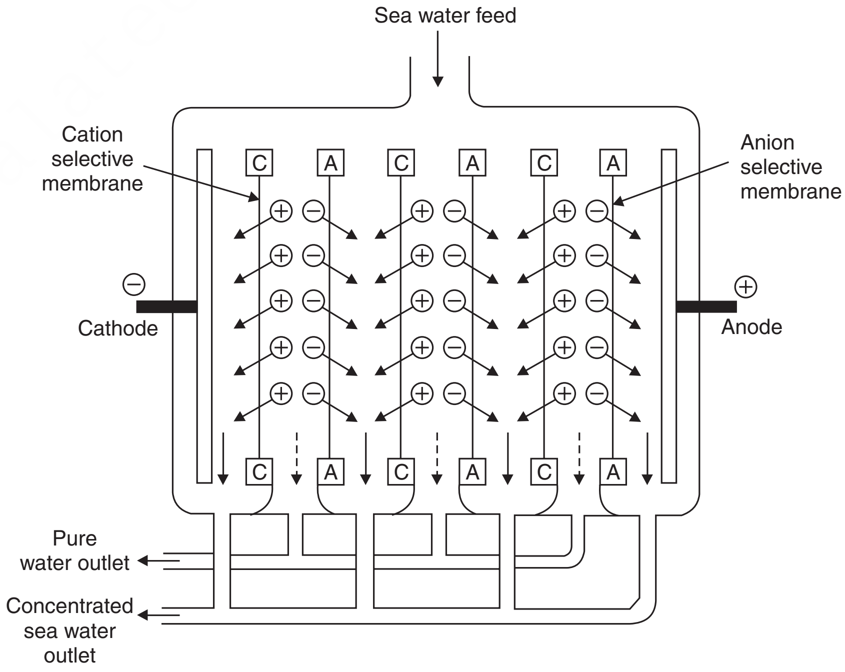


Fig. 17.7 Electrodialysis cell.

(*b*) *Reverse osmosis.* Osmosis describes the flow of solvent from dilute to concentrated solution through a semipermeable membrane. Whereas reverse osmosis describes the flow of solvent in opposite direction *i.e.,* from concentrated solution to dilute solution across a semipermeable membrane by applying hydrostatic pressure in excess of osmotic pressure.

The cellulose acetate and the more recently used polymethacrylate and polyamide membranes do not allow the solute pass, while the solvent is forced through and collected as a pure solvent in a direction as shown in Fig. 17.8. There are many *advantages* of using reverse osmosis as the purification process for water which include (*i*) removal of ionic, non-ionic, colloidal and high molecular weight solutes from water, (*ii*) regeneration of the process involves the easy replacement of the semipermeable membrane, (*iii*) easy maintenance and economical, as the membrane lifespan is high, (*iv*) uninterrupted supply of large volume of water for industrial or domestic purpose can be obtained. Reverse osmosis is largely used for purification of sea water for domestic use.

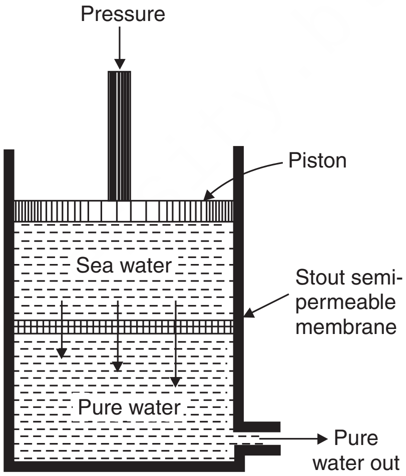


Fig. 17.8 Reverse osmosis cell.

Chemical Analysis of Water

1. **Estimation of free chlorine.** The residual free chlorine remaining after the municipal processing of domestic water is injurious to health and hence estimation of this free chlorine is essential. The principle is the treatment of water containing free chlorine with KI solution. The chlorine present liberates an equivalent amount of iodine which can be estimated with standard thiosulfate solution using starch as an indicator.

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

$$I_2 + \text{Starch} \longrightarrow \text{Deep-blue complex}$$

Method: To 50 ml of water sample in a iodine flask, 10 ml of 10% KI solution added, shaken and waited for some time in the dark and finally titrated with N/50 sodium thiosulfate solution using starch solution as indicator towards the end. The end point indicates a change from deep-blue to just colorless solution.

Calculation:

Volume of N/50 $Na_2S_2O_3$ required = V ml

$$\therefore \quad \text{Strength of free chlorine} = \frac{V \times 35.5 \times 10^6}{2500 \times 1000} \text{ ppm.}$$

2. **Alkalinity.** The alkalinity of water is estimated by estimating (*a*) OH^- and CO_3^{2-} ions and (*b*) HCO_3^- ions.

(*a*) $OH^- + H^+ \longrightarrow H_2O$

$CO_3^{2-} + H^+ \longrightarrow HCO_3^-$

(*b*) $HCO_3^- + H^+ \longrightarrow H_2O + CO_2$

These estimations are done by (*a*) titrating against standard acid solution using phenolphthalein as an indicator and (*b*) using methyl orange as an indicator.

Method: 100 ml of water sample is taken in a flask and few drops of phenolphthalein added and titrated against N/50 H_2SO_4 solution to colorless end point. The same solution is further titrated with 2 to 3 drops of methyl orange indicator.

Calculation: Vol. of acid upto phenolphthalein end point = V_1

Extra volume of acid added to get methyl orange end point $\longrightarrow V_2$ ml.

$\therefore$ Phenolphthalein alkalinity (equivalent $CaCO_3$)

$$P = \frac{V_1 \times 50 \times 10^6}{50 \times 100 \times 1000} \text{ ppm}$$

Methyl orange alkalinity (equivalent $CaCO_3$)

$$M = \frac{(V_1 + V_2) \times 50 \times 10^6}{50 \times 100 \times 1000} \text{ ppm.}$$

3. **Hardness**

(*a*) *Estimation of temporary hardness.* Temporary hardness is due to $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ which cause alkalinity in water. Temporary hardness is determined by finding the alkalinity of water before and after boiling, since temporary hardness is removed on boiling.

$$Ca(HCO_3)_2 \xrightarrow{\text{Boiling}} CaCO_3 + CO_2 + H_2O$$
$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 + CO_2$$

Method: Into 50 ml of water sample taken in a conical flask, add 2 to 3 drops of methyl orange and titrate with N/50 HCl. Let the volume of acid be V_1. Now take 100 ml of water sample in a beaker, evaporate to dryness. Add 100 ml of distilled water to the beaker and dissolve the residue left. Then, take 50 ml of this water sample and titrate with N/50 HCl using a few drops of methyl orange as an indicator. Let the volume of acid required be V_2 ml.

$\therefore$ alkalinity due to temporary hardness in $CaCO_3$ equivalent

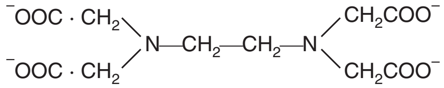
$$= \frac{(V_1 - V_2) \times 10^6}{50 \times 1000} \text{ ppm}$$

(*b*) (*i*) **Determination of permanent hardness.** The estimation is done by adding excess of standard Na_2CO_3 solution to a given volume of boiled water containing permanent hardness. The chlorides and sulfates form insoluble carbonates. The residual Na_2CO_3 is titrated against standard acid and the difference of Na_2CO_3 equivalent gives permanent hardness.

Method: 50 ml of the water sample is taken in a beaker. 50 ml of N/50 Na_2CO_3 solution is added and boiled for 15 minutes. Cool and filter the solution, wash the residue on filter paper and add it to the filtrate and titrate the N/50 Na_2CO_3 left in the flask with N/50 HCl using methyl orange as indicator. Let titre vol. be V.

$$\therefore \text{ Permanent hardness} = \frac{(50 - V) \times 10^6}{50 \times 1000} \text{ ppm.}$$

(*ii*) **Complexometric determination of permanent hardness.** Disodium salt of ethylene diamine tetra acetic acid (EDTA) is used as a complexing agent for Ca^{2+}, Mg^{2+}.



Erichrome black T is used as an indicator and pH is maintained at pH 10 using NH_4OH/NH_4Cl buffer. Erichrome black T forms unstable complex with Ca^{2+}, Mg^{2+} giving wine red colour. When EDTA added and the total Ca^{2+}, Mg^{2+} forms complex with it and the indicator becomes free, the colour of the solution changes from wine red to blue at the end point.

Method: Indicator solution 0.5 gm. Erichrome black T dissolved in 100 ml alcohol.

Standard EDTA solution (N/100): 4 gm of EDTA dissolved with 0.1 gm of $MgCl_2$ in 1000 ml water.

An aliquot $\approx \frac{M}{100}$ Zinc acetate solution (primary standard) is taken, to it 5 ml of NH_4Cl–NH_4OH buffer and a few drops of EBT indicator are added and titrated to blue end point with EDTA and the strength of EDTA is calculated.

This same procedure is repeated with 50 ml water sample. Let the volume of titrant be V ≈ (*f*) M/100 EDTA solution.

$$\therefore \quad \text{Permanent hardness} = \frac{0.001 \times V \times f \times 10^6}{50} \text{ ppm.}$$

The EDTA method for the determination is preferred to other methods since the method has greater accuracy, simplicity and rapidness.

Buffer solution: A mixture of 142 ml of conc. NH_4OH and 17.5 gm NH_4Cl is diluted to 250 ml distilled water.

Highlights:

- Softening methods include:
  (*i*) Hot and cold lime soda process.
  (*ii*) Zeolite or permutit process.
  (*iii*) Ion exchange or demineralization.
- Micro-organisms from potable water can be removed by:
  (*i*) Boiling for 10 to 15 minutes
  (*ii*) Bleaching powder treatment
  (*iii*) Chlorination with Cl_2
  (*iv*) Chloramine treatment
  (*v*) Ozonization.
- Desalination of brackish water done by:
  (*i*) Electrodialysis
  (*ii*) Reverse osmosis.
- Exhausted ion-exchange resins are regenerated by:
  (*i*) Cation exchangers regenerated by passing strong acid solution through the bed
  (*ii*) Anion exchangers regenerated by passing strong base solution through the bed.
- Hardness of water can be estimated by:
  (*i*) Permanent hardness determined by titrating with standard Na_2CO_3 solution.
  (*ii*) Complexometric titration by EDTA
- Units of hardness are:
  (*i*) ppm
  (*ii*) mg/litre (1 ppm = 1 mg/litre)
  (*iii*) Clark's degree (1 ppm = 0.07° Cl)
  (*iv*) degree French (1 ppm = 0.1° Fr).

(*Contd.*)

- Hard water does not easily lather with soap, instead it forms a greasy scum.
- Water is hard if it contains calcium or magnesium ions.
- Scum is a precipitate formed when soap comes in contact with hard water containing above mentioned ions.

$$Ca^{2+}(aq) + C_{17}H_{35}CO_2^-(aq) \longrightarrow \underset{\text{insoluble precipitate}}{Ca(C_{17}H_{35}CO_2)_2 \downarrow}$$

- Temporary hard water contains bicarbonates or hydrogen carbonates of calcium or magnesium.
- Temporary hardness is removed by boiling.

$$Ca(HCO_3)_2(aq) \xrightarrow[\text{boiling}]{\Delta} CaCO_3 \downarrow + H_2O(l) + CO_2\uparrow.$$

- The solid calcium carbonate is precipitated as scale, which affects heating element of boilers and gradually blocks the pipes in heating system.
- Permanent hardness is not removed by boiling.
- The mineral gypsum ($CaSO_4$) is slightly soluble in water and makes water permanently hard.
- Ion exchange resin and other methods of softening of water by removing calcium and magnesium ions is known as *water treatment.*

PROBLEMS

Problem 1. *Calculate temporary hardness and total hardness of a sample of water containing:*

$$Mg(HCO_3)_2 = 7.5\ mg/l\ .\ Ca(HCO_3)_2 = 16\ mg/l$$
$$MgCl_2 = 9\ mg/l\ .\ CaSO_4 = 13.6\ mg/l$$

Sol. Temporary hardness $= \left[7.5 \times \frac{100}{146} + 16 \times \frac{100}{162}\right] mg/l$

Permanent hardness $= \left[9 \times \frac{100}{95} + 13.6 \times \frac{100}{136}\right] mg/l.$

Problem 2. *How many mg. of $FeSO_4$ dissolved per litre gives 200 ppm of hardness?*

Sol. $(56 + 16 + 64)g$ of $FeSO_4 \equiv 100$ g $CaCO_3$

For 100 ppm hardness $FeSO_4$ required per 10^6 parts of water is 136 parts.

$\therefore$ For 200 ppm hardness, $FeSO_4$ required $= \frac{136 \times 200}{100}$ ppm

$= 272$ mg/l.

Problem 3. *A sample of water has a CO_3^{2-} concentration of 15.6 ppm. What is the molarity of CO_3^{2-} in the sample of water?*

Sol. $15.6 \text{ ppm} = 15.6 \times 10^{-6} \text{ g}/l \text{ of } CO_3^{2-}$

$$\therefore \quad CO_3^{2-} \text{ molarity} = \frac{15.6 \times 10^{-6}}{60} \text{ mol}/l.$$

$$= 2.6 \times 10^{-5} \text{ M.}$$

Problem 4. *A sample of water has been found to contain the following salts:*

$Ca(HCO_3)_2$ = 10.5 ppm; $Mg(HCO_3)_2$ = 12.5 ppm; $CaCl_2$ = 8.2 ppm; $MgSO_4$ = 2.6 ppm; $CaSO_4$ = 7.5 ppm.

Calculate (i) temporary and permanent hardness and (ii) the vol. of $\frac{M}{100}$ EDTA required for titration of the 100 ml of the sample to determine the total hardness of the sample.

Sol. (*i*) $Ca(HCO_3)_2 = 10.5 \text{ ppm} = 10.5 \times \frac{100}{162} = 6.481 \text{ ppm } CaCO_3$

$$Mg(HCO_3) = 12.5 \text{ ppm} = 12.5 \times \frac{100}{146} = 8.562 \text{ ppm } CaCO_3$$

$$CaCl_2 = 8.2 \text{ ppm} = 8.2 \times \frac{100}{111} = 7.387 \text{ ppm } CaCO_3$$

$$MgSO_4 = 2.6 \text{ ppm} = 2.6 \times \frac{100}{120} = 2.167 \text{ ppm } CaCO_3$$

$$CaSO_4 = 7.5 \text{ ppm} = 7.5 \times \frac{100}{136} = 5.515 \text{ ppm } CaCO_3$$

∴ Temporary hardness = (6.481 + 8.562) ppm

= 15.043 ppm

Permanent hardness = (7.387 + 2.167 + 5.15) ppm = 15.069 ppm

∴ Total hardness = (15.043 + 15.069) = 30.112 ppm

(*ii*) The volume of sample taken = 100 ml.

$$\therefore \quad \text{Volume of M/100 EDTA required} = \frac{30.112 \times 100}{1000} = 3.11 \text{ ml.}$$

Problem 5. *Calculate the amount of lime and soda required for softening 50,000 litres of hard water containing*

$MgCO_3$ = 144 ppm; $CaCO_3$ = 25 ppm; $MgCl_2$ = 95 ppm;
$CaCl_2$ = 111 ppm; Fe_2O_3 = 25 ppm; Na_2SO_4 = 15 ppm.

Sol. $MgCO_3 = 144 \text{ ppm} = 144 \times \frac{100}{84} = 171.4 \text{ ppm } CaCO_3$

$CaCO_3 = 25$ ppm.

$$MgCl_2 = 95 \text{ ppm} = \frac{95 \times 100}{95} = 100 \text{ ppm } CaCO_3$$

$$CaCl_2 = 111 \text{ ppm} = \frac{111 \times 100}{111} = 100 \text{ ppm } CaCO_3$$

$\therefore$ Lime required = $\frac{74}{100}$ [2 × $MgCO_3$ + $CaCO_3$ + $MgCl_2$] × volume of water

$= \frac{74}{100}$ [2 × 171.4 + 2500 + 100.0] × 50,000 mg

= 17,309,000 mg = 17.31 kg.

Problem 6. *A water sample on analysis gives the following data : Ca^{2+} = 20 ppm, Mg^{2+} = 25 ppm, CO_2 = 30 ppm, HCO_3^- = 150 ppm, K^+ = 10 ppm. Calculate the lime (87% pure) and soda (91% pure) required to soften 1 million litres of water sample.*

Sol. $$Ca^{2+} = 20 \text{ ppm} = \frac{20 \times 100}{40} = 50 \text{ ppm } CaCO_3$$

$$Mg^{2+} = 25 \text{ ppm} = \frac{25 \times 100}{24} = 104.65 \text{ ppm } CaCO_3$$

$$CO_2 = 30 \text{ ppm} = \frac{30 \times 100}{44} = 68.18 \text{ ppm } CaCO_3$$

$$HCO_3^- = 150 \text{ ppm} = \frac{150 \times 100}{122} = 122.95 \text{ ppm } CaCO_3$$

$\therefore$ Lime requirement = $\frac{74}{100}$ [Mg^{2+} + CO_2 + HCO_3^-] × vol. of water

$= \frac{74}{100}$ [104.65 + 68.18 + 122.95] × 10^6

= 218.9 × 10^6 mg = 218.9 kg.

Soda requirement $= \frac{106}{100}\left[Ca^{2+} + Mg^{2+} - HCO_3^-\right]$ × vol. of water.

$= \frac{106}{100}[50 + 104.65 - 122.95] \times 10^6$

= 33.6 × 10^6 mg = 33.6 kg.

Problem 7. *An exhausted zeolite softener was regenerated by passing 150 litres of NaCl sol. having a strength of 150 g/l of NaCl. If the hardness of water is 600 ppm, calculate the total volume of water that has been softened in the softener.*

Sol. 150 litres of NaCl solution contain = 150 × 150 = 22,500 gm NaCl

$= 22,500 \times \frac{100}{117}$ $CaCO_3$

= 1.932 × 10^4 g $CaCO_3$

If the hardness of water is 600 ppm

$\therefore$ Vol. of water $= \frac{1.932 \times 10^4 \times 1000}{600}$ litres

= 3.129 × 10^4 litres

Problem 8. *10 ml of 0.85 $\left(\frac{M}{100}\right)$ Zn $(OAC)_2$ required mol of an EDTA solution for standardization. 50 ml of a water sample required 20 ml of the above EDTA solution. Calculate the total hardness of water in ppm.*

Sol. Strength of EDTA solution = $\frac{10 \times 0.85}{9} = 0.94\left(\frac{M}{100}\right)$

1000. ml $\left[\frac{M}{100}\right]$ EDTA solution ≡ 1 g $CaCO_3$

$\therefore$ 20 ml of $\left(\frac{M}{100}\right)$ EDTA solution = $\frac{1}{1000} \times 20 \times 0.94$ g $CaCO_3$ = 0.019 g $CaCO_3$.

$\therefore$ 50 ml of the water sample contains 0.019 g $CaCO_3$

$\therefore$ 10^6 ml of the water sample contains = $\frac{0.019 \times 10^6}{50}$ = 377.8 gm $CaCO_3$

$\therefore$ Hardness of water = 377.8 ppm.

Problem 9. *A sample on water on analysis has been found to contain the following :*

$Ca(HCO_3)_2$ = *10.5 ppm.* $Mg(HCO_3)_2$ = *12.5 ppm*
$CaSO_4$ = *7.5 ppm* $CaCl_2$ = *8.2 ppm* $MgSO_4$ = *2.6 ppm.*

Calculate the temporary and permanent hardness in degree French.

Sol. $Ca(HCO_3)_2 = 10.5 \text{ ppm} = \frac{10.5 \times 100}{162} = 6.481 \text{ ppm}$

$Mg(HCO_3)_2 = 12.5 \text{ ppm} = \frac{12.5 \times 100}{146} = 8.562 \text{ ppm}$

$CaSO_4 = 7.5 \text{ ppm} = \frac{7.5 \times 100}{136} = 5.515 \text{ ppm}$

$CaCl_2 = 8.2 \text{ ppm} = \frac{8.2 \times 100}{111} = 7.387 \text{ ppm}$

$MgSO_4 = 2.6 \text{ ppm} = \frac{2.6 \times 100}{120} = 2.167 \text{ ppm}$

$\therefore$ Temporary hardness = (6.481 + 8.562) = 15.043 ppm
= 15.043 × 0.1° Fr = 1.504° Fr

Permanent hardness = (5.515 + 7.387 + 2.167) ppm
= 15.069 ppm
= 1.5069° Fr.

SHORT QUESTIONS AND ANSWERS

Q. 1. What is the need for "Desalination of water" programme?

Ans. Virtually there is population explosion in the modern world. So for drinking, domestic and irrigation purposes river water and other sweet water sources seem to be insufficient. So for the exploitation of the vast source of sea water, desalination programme is required, specially in the sea-side area.

Q. 2. What are the causes of corrosion of boilers?

Ans. The causes of corrosion are:

- Oxygen corrosion if boiler water is not properly deaerated.

- Electrochemical corrosion, also known as out of service corrosion, when boiler is shut down.

Q. 3. What are the disadvantages of scale formation in a boiler?

Ans.

- Scales and sludges are bad conductors of heat, as a result fuel consumption increases.
- Tubes and plates are clogged as a result the efficiency of the boiler is decreased.
- Tubes of the boiler are corroded by the scales deposited and they may crack and lead to boiler failure.

$$MgCl_2 + Fe + H_2O = Mg(OH)_2 + FeCl_2 + H_2$$

Q. 4. Why is demineralisation preferred to zeolite softening?

Ans. Demineralized water is practically free from all the ions whereas the zeolite softened water contains sodium salts which are sources of caustic embrittlement.

Q. 5. Why is chloramine preferred to Cl_2 for sterilization of drinking water?

Ans. It is because chloramine does not impart any repulsive odour to the treated water.

Q. 6. What are the criteria for drinking water?

Ans. It should be devoid of any suspending matter, and harmful dissolved matter of organic or inorganic matter and pathogenic organisms.

Q. 7. Why is UV radiation superior to other methods of sterilization of water?

Ans. UV radiation does not impart any unpleasant taste or odour to the water and the process is simple.

Q. 8. What is pitting?

Ans. Pitting is corrosion of the boiler. Dissolved gases like O_2, CO_2 , H_2S corrode the iron surface of the boiler particularly near the rivet, bends and leads to leak or boiler failure.

Q. 9. What are boiler compounds?

Ans. When the boiler water is difficult to soften or purify, some chemical substances are added to the boiler water that makes the scale in the boiler loose and easily removable. These compounds are called *boiler compounds* and examples of these are flour, kerosene, tannin, agar-agar etc.

Q. 10. What is plumbo solvancy? How can it be prevented?

Ans. Water transported through lead pipes are contaminated with Pb^{2+} due to solubility of metallic lead in water.

$$2Pb + 2H_2O + O_2 = 2Pb(OH)_2$$

The hydrolysis of Ca^{2+} and Mg^{2+} salts dissolved in water may lead to the formation of lead salts like $PbSO_4$ and $PbCl_2$.

$$MgSO_4 + 2H_2O = Mg(OH)_2 + H_2SO_4 \qquad 2Pb + H_2SO_4 + O_2 = 2PbSO_4 + 2H_2O$$

$$MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl \qquad 2Pb + 4HCl + O_2 = 2PbCl_2 + 2H_2O$$

These lead salts are somewhat soluble in water. This phenomenon is known as *plumbo solvancy*.

The Pb^{2+} salts are poisonous and is the source of *lead poisoning*.

Lead poisoning can be prevented by treatment of the water with alkali silicate and phosphate followed by filtration.

Q. 11. Differentiate between sludge and scale.

Ans. Sludge is soft, loose, slimy deposit formed inside the boiler, which is easier to remove, while scale is a hard, sticky, adherent deposit on the inner surface of the boiler which is difficult to remove.

Q. 12. What is break-point chlorination?

Ans. See text page 362.

Q. 13. State the harmful effects of silica present in water.

Ans. Presence of silica in the water leads to the formation of calcium and magnesium silicates and these silicates form sticky scales in the boiler which are very difficult to remove.

Q. 14. What is the difference between hard water and soft water?

Ans. See text page 350-355

Q. 15. Alkalinity of water cannot be due to the simultaneous presence of OH^-, CO_3^{2-} and HCO_3^-. Why?

Ans. OH^- and HCO_3^- ions react to form CO_3^{2-} ions: $OH^- + HCO_3^- = CO_3^{2-} + H_2O$.

Q. 16. Why do we express hardness of water in terms of $CaCO_3$ equivalent?

Ans. This mode permits easy addition and subtraction of concentration of hardness-causing constituents, since its mol. wt. is 100. Moreover, it has also been adopted as standard for expressing hardness.

Q. 17. What are the salts responsible for temporary and permanent hardness of water?

Ans. Temporary hardness ⇒ $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$

Permanent hardness ⇒ Chloride and sulphate of Ca^{2+} and Mg^{2+}.

Q. 18. Mention the units of hardness. Define them.

Ans. (*i*) ppm, (*ii*) degree.

ppm is defined as the parts of hardness salt present in 10^6 parts of water expressed in terms of calcium carbonate.

Degree hardness is defined as the parts of hardness salt present in 10^5 parts of water expressed in terms of calcium carbonate.

Q. 19. A water sample contains lithium chloride or zinc acetate as dissolved solids. Do you think that water will be hard?

Ans. Yes, as Li^+ and Zn^{2+} both form insoluble soaps.

Q. 20. Calculate the hardness of $\left(\frac{M}{1000}\right)$ $MgSO_4$ solution.

Ans. $MgSO_4 = CaCO_3$

$120 \text{ g} = 100 \text{ g}$

$\left(\frac{M}{1000}\right)$ $MgSO_4$ solution contains $= \frac{120}{1000}$ g, $MgSO_4 = \frac{100}{1000}$ $CaCO_3$ in 1000 ml water.

So, hardness in ppm $\frac{0.1}{1000} \times 10^6 = 100$ ppm.

Again, hardness in degree $= \frac{0.1}{1000} \times 10^5 = 10$

Q. 21. The presence of carbon dioxide is avoided in boiler feed water. Explain.

Ans. Dissolved carbon dioxide forms carbonic acid and attacks boiler pipes and corrodes.

Q. 22. Why does hard water consume a lot of soap?

Ans. When hard water comes in contact with soap Ca^{2+} and Mg^{2+} ions react with soap and scum is formed when the reaction is overconsuming much of soap, lather is then formed. That is why hard water consumes a lot of soap.

Q. 23. Why is calgon conditioning better than phosphate conditioning?

Ans. Calgon conditioning forms soluble complex salt

$$\underset{\text{Calgon}}{Na_2[Na_4(PO_3)_6]} + CaSO_4 = \underset{\text{Soluble complex}}{Na_2[Na_2\,Ca(PO_3)_6]} + Na_2SO_4$$

whereas phosphate conditioning *i.e.,* treatment with sodium phosphates, precipitates calcium and magnesium phosphates causing scale in boiler pipes.

Q. 24. Why is water softened before using in boiler?

Ans. Natural or hard water when fed in boiler produces scale, sludge and causes priming and foaming and boiler corrosion. That is why water is softened before using in boiler.

Q. 25. Why is caustic embrittlement controlled by adding sodium sulphate to boiler-feed water?

Ans. Sodium sulphate when used blocks hair cracks thus prevents infiltration of caustic soda through the cracks. Thus sodium sulphate prevents embrittlement in boilers.

Q. 26. State two harmful effects of silica in water.

Ans. Silica reacts with Ca^{2+} and Mg^{2+} ions forming calcium silicate and magnesium silicate in boiler. This type of scales are difficult to remove.

EXERCISES

1. Explain the various steps for the purification of water for municipal supply.
2. What is desalination? Name the different methods of desalination and describe any one.
3. What are boiler troubles? Why are they caused? What are the methods of their elimination?
4. Distinguish between:
   (*a*) Temporary and permanent hardness.
   (*b*) Sludge and Scale.
   (*c*) Softening and demineralization.
5. Write notes on: (*i*) Caustic embrittlement, (*ii*) Reverse osmosis, (*iii*) Priming and foaming, (*iv*) Hot lime-soda process, (*v*) Boiler corrosion.
6. What is the principle involved in the determination of total hardness of water by EDTA method?
7. What are the functions of lime and soda in hot lime-soda process? Give equations. Why coagulants are not used in hot lime-soda process?
8. Why does hard water consume more soap?
9. During deionization process, water is first passed through cation exchanger and then through anion exchanger, why?
10. Describe the methods of disinfection of water. Why is chloramine better than chlorine for sterilization of water?

OBJECTIVE TYPE QUESTIONS

1. Temporary hardness of water can be removed by
(*a*) Filtration (*b*) Boiling (*c*) Coagulation

2. Permanent hardness of water is caused by
(*a*) Calcium chloride (*b*) Magnesium sulfate (*c*) Both.

3. Hard water can be softened by passing through
(*a*) Calgon (*b*) Sodium silicate (*c*) Ion exchange resin.

4. Calgon is the trade name of
(*a*) Sodium hexametaphosphate
(*b*) Sodium zeolite
(*c*) Calcium silicate.

5. Pure water can be obtained by
(*a*) Lime-soda process (*b*) Boiling (*c*) Demineralization.

6. Brackish water can be purified by
(*a*) Reverse osmosis method
(*b*) Lime-soda process
(*c*) Calgon treatment.

7. The chemical that gets dissolved in high pressure boilers
(*a*) $MgSiO_3$ (*b*) $CaCO_3$ (*c*) $CaSO_4$.

8. A semipermeable membrane allows the flow of
(*a*) Solute molecules (*ii*) Solvent molecules
(*b*) Both solute and solvent molecules.

9. The most ideal disinfectant in water works is
(*a*) Chlorine (*b*) Bleaching powder (*c*) Chloramine.

10. A sample of water containing NaCl is
(*a*) Hard water (*b*) Soft water (*c*) Pure water.

11. Write a short note with a proper sketch diagram on “reverse osmosis” process for desalination of brackish water.

12. Why treatment of water is essential?

13. Write down the possible sources of water?

14. Give reasons for why water becomes hard.

15. Correlate the various units of the hardness.

16. Write down the disadvantages associated with using of hard water.

17. (*a*) What are scales? What are the ill-effects of scales?
(*b*) How can scale formation be prevented by (*i*) Phosphate conditioning and (*ii*) Calgon conditioning?

18. Distinguish between:
(*a*) Purification and softening of water
(*b*) Boiler scales and sludges
(*c*) Internal and external treatment of water.

19. What do you mean by caustic embrittlement? What measures can be taken to control the caustic embrittlement?

20. What factors are responsible for boiler corrosion. How can the factors can be eliminated?

21. Describe the process of water softening by permutit process.

22. Briefly discuss the process of softening of water by means of ion-exchange process.

23. Write down the requirements for drinking water.

24. Briefly describe the different steps involved in the treatment of water for domestic purpose.

25. What is desalination? Name the different methods involved in desalination? Describe any one in detail.

26. Write short notes on break point chlorination.

27. (*a*) What do you mean by carbonate and non-carbonate hardness of water?
(*b*) State harmful effects of silica present in water.
(*c*) Write short notes on aeration.

28. Write different methods of sterilization.

29. How free chlorine in water can be estimated?

30. Write down the method for determination of alkalinity of water.

31. What are the methods involved for determination of temporary and permanent hardness of water?

PROBLEMS

1. The hardness of 1,00,000 litres of a sample of hard water was completely removed by passing through a zeolite softener. The bed on exhaustion required 500 litres of NaCl solution containing 15 g l^{-1} of NaCl on regeneration. Calculate the hardness of the sample water. [**Ans.** 64.10 ppm]

2. A sample of hard water has a hardness of 510 ppm. Express its hardness in °Clark and °French.

[**Hints** → 1 ppm = 0.07° Clark = 0.1° French]

[**Ans.** 35.7° Clark and 51° French]

3. 200 ml of a sample of water required 5 ml of (N/20) sodium carbonate solution for complete precipitation of calcium ion (Ca^{2+}) and calcium carbonate. Calculate the hardness in ppm.

[**Ans.** 62.5 ppm]

4. In an experiment for the determination of hardness of a sample of water, the following results are obtained:

Volume of sample water = 100 cc.

$\left(\frac{N}{50}\right)$ Na_2CO_3 solution is added to it = 20 cc.

$\left(\frac{N}{50}\right)$ H_2SO_4 required the back titre the unreacted Na_2CO_3 = 10 cc.

From these data calculate the hardness of water in grains per gallon.

Given, 1 g = 15.4 grain. [**Ans.** 6.99 grain of $CaCO_3$]

5. A precipitate of 0.110 of calcium oxalate ($CaC_2O_4.H_2O$) was obtained from a 250 ml of water sample. Express the content of calcium in ppm. [**Ans.** 120 ppm]

6. Analysis of a sample of water revealed the content of dissolved salts in the following data:

$Mg(HCO_3)_2$ = 22 mg l^{-1}
$MgCl_2$ = 30 mg l^{-1}
$CaCl_2$ = 85 mg l^{-1}
$CaSO_4$ = 28 mg l^{-1}.

Find the temporary and permanent hardness of the water sample.

[**Ans.** 15.07 ppm; 128.75 ppm]

7. 1,00,000 litres of water contain the following:
$HCl = 7.3$ mg l^{-1}; $Al_2(SO_4)_3 = 34.2$ mg l^{-1}; $MgCl_2 = 9.5$ mg l^{-1}; $NaCl = 29.25$ mg l^{-1}.
Calculate the amounts of lime and soda to be required for softening the water.
[**Ans.** Lime = 3.7 kg; Soda = 5.3 kg]

8. The total hardness of 1,000 litres of water was completely removed by a zeolite softener. The zeolite softener required 30 litres of NaCl solution, containing 15 g l^{-1} of NaCl for regeneration. Calculate the hardness of water. [**Ans.** 384.6 ppm]

9. Calculate the lime and soda required to soften 10,000 litres of water sample having calcium hardness = 450 mg l^{-1} as $CaCO_3$; magnesium = 150 mg l^{-1} as $CaCO_3$ and total alkalinity = 400 mg l^{-1} as $CaCO_3$. [lime = 1.11 kg soda = 10.6 kg]

10. Calculate the hardness of a water sample, whose 10 ml required 20 ml of EDTA, 20 ml of calcium chloride solution, whose strength is equivalent of 1.5 g of calcium carbonate per litre required 30 ml of EDTA solution. [200 ppm]

11. Calculate the cost of lime and soda required for softening 1 million litres of a water sample containing. $Mg(HCO_3)_2 = 73$ mg l^{-1}; $MgSO_4 = 120$ mg l^{-1}; $CaSO_4 = 68$ mg l^{-1}; $CaCl_2 = 111$ mg l^{-1}. The cost of lime of 80% purity is Rs. 200 per metric ton and that of soda of 90% purity is Rs. 12,000 per metric ton.

18

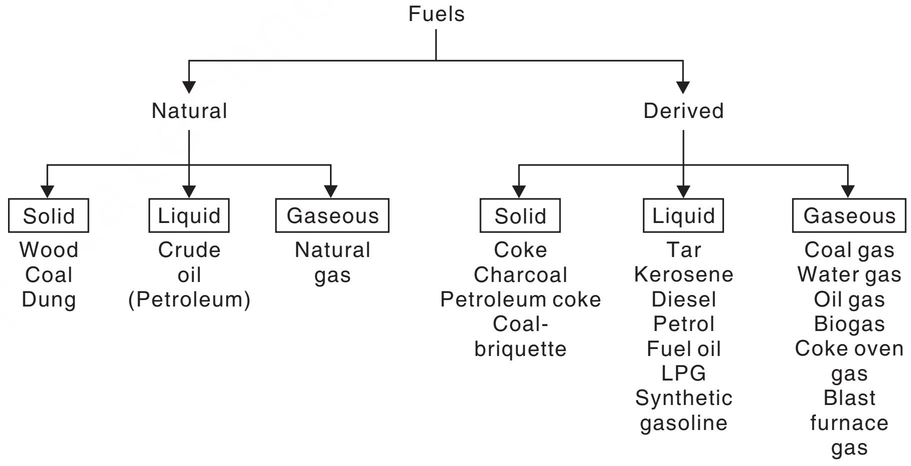
Fuels and Combustion

INTRODUCTION

Fuel is a combustible substance, which on combustion produces a large amount of heat, which can be used for various domestic and industrial purposes. The fuels commonly used contain carbon as the main constituent and some common fuels are wood, charcoal, kerosene, diesel, producer gas etc. *Fossil fuels* are non-renewable energy resources which were stored up millions of years ago by photosynthesis. The fossil fuels are coal, crude oil and natural gas.

The process of combustion involves oxidation of carbon, hydrogen etc. of the fuels to CO_2, H_2O, and the difference in the energy of reactants and the products are liberated as large amount of heat energy which is utilized.

Classification of fuels



CALORIFIC VALUE

There are different expressions for calorific values:

(*i*) The quantity of heat evolved by the combustion of unit quantity of fuel is its gross *calorific value* (GCV). Gross or higher calorific value is the quantity of heat liberated by combusting unit mass of fuel in oxygen, the original material and the final product of combustion being at a reference temperature of 25°C and the water obtained in the liquid state, represented by GCV or HCV.

(*ii*) *Net calorific value* (NCV) is the quantity of heat evolved when a unit quantity of fuel is burnt in oxygen, the original material and the final products of combustion being at a reference temperature of 25°C and the water obtained from the fuel being at the vapor state. The net calorific value is hence always less than the gross calorific value by the amount corresponding to the heat of condensation of water vapours *i.e.,* 587.0 kcal/kg.

$\therefore$ NCV = HCV – Latent heat of water vap. formed

= HCV – Mass of hydrogen × a × Latent heat of steam

since 1 part by mass of hydrogen produces 'a' part by mass of water.

Units of calorific value. The calorific value is expressed in either calorie/gm (cal/gm) or kilocalorie/kg (kcal/kg) or British thermal unit/lb (B.T.U/lb) in the case of a solid and a liquid fuel.

In the case of gaseous fuels, the units are kcal/m^3 or B.T.U./ft^3.

Determination of Calorific Value

Bomb calorimeter. The apparatus which is used to determine the calorific value of solid and liquid fuels is known as Bomb calorimeter (Fig. 18.1).

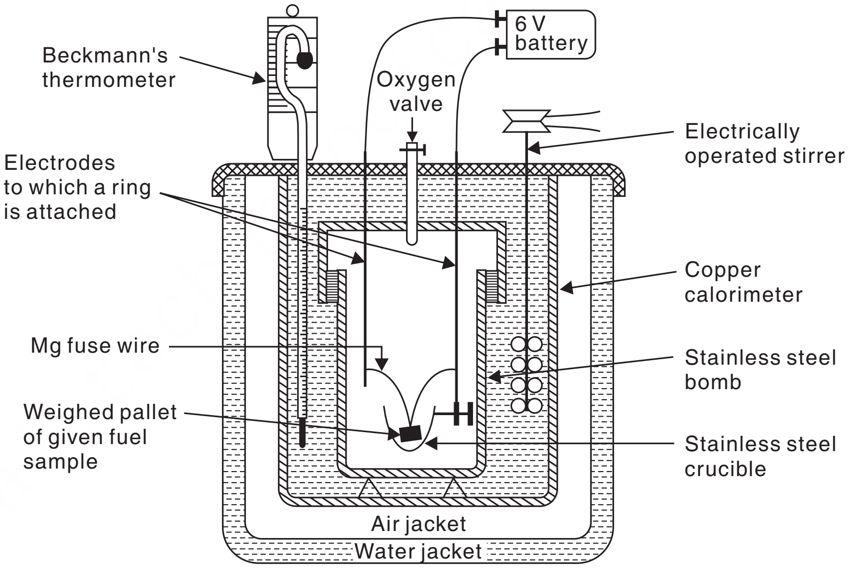


Fig 18.1 Bomb calorimeter.

The apparatus consists of a cylindrical stainless steel bomb, the lid of which is screwed to the body to make it air-tight. Through the lid there is one oxygen inlet valve and two electrodes. In the bomb there is nickel crucible attached to a ring. The sample of fuel is placed in the crucible. An electrically heated magnesium wire touches the sample. The bomb is placed in a copper calorimeter, which is surrounded by an air jacket and water jacket which minimises the heat loss due to radiation. There is a stirrer and a Beckmann's thermometer which can accurately measure the temperature upto $n/100^{th}$ of a degree.

A weighed mass of a fuel placed in the crucible is allowed to burn in oxygen by electric spark across the electrode and the heat liberated is measured by the principle of calorimetry *i.e.,* the heat liberated is taken by calorimeter and water. The initial and final temperatures of the calorimeter are noted.

Calculation: m = mass of fuel pellet (g)

W = mass of water in the calorimeter (g)

w = water equivalent of calorimeter (g)

t_1 = initial temperature of calorimeter.

t_2 = final temperature of calorimeter.

HCV = gross calorific value of fuel.

$$\text{L} = \text{HCV} = \frac{(\text{W} + w)\,(t_2 - t_1)}{m}\ \text{cal/gm.}$$

The water equivalent of calorimeter is determined by burning a fuel of known calorific value and using the above equation. The fuels used in the above purpose are benzoic acid (GCV = 6325 kcal/kg) and naphthalene (GCV = 9688 kcal/(kg). The correction factors used to get accurate results include:

(*i*) *Fuse wire correction*. Heat liberated during sparking should be subtracted from heat liberated.

(*ii*) *Acid correction.* Fuels containing Sulphur and Nitrogen if oxidised, the heats of formation of H_2SO_4 and HNO_3 should be subtracted (as the acid formations are exothermic reactions).

(*iii*) *Cooling correction*. The rate of cooling of the calorimeter from maximum temperature to room temperature is noted. From this rate of cooling (*i.e., dt*°/min) and the actual time taken for cooling (*t* min) then correction (*dt* × *t*) is called cooling correction and is added to the ($t_2 - t_1$) term.

$$\therefore \qquad \text{L} = \frac{(\text{W} + w)\,(t_2 - t_1 + \text{Cooling correction}) - (\text{Acid} + \text{fuse correction})}{m}.$$

The approximate calorific value of a fuel can be determined by knowing the amount of constituents present: Gross or higher calorific value (HCV) from elemental constituents of a fuel.

H = 34500 kcal/kg; C = 8080 kcal/kg; S = 2240 kcal/kg

Oxygen present in the fuel is assumed to be present as water (fixed hydrogen). Available H in combustion of the fuel is

= Total hydrogen – Fixed hydrogen

$$= \text{Total hydrogen} - \frac{1}{8}\ \text{mass of oxygen in fuel.}$$

Dulong's formula for calorific value from the chemical composition of fuel is,

$$\text{HCV} = \frac{1}{100}\left[8080\ \text{C} + 34500\left(\text{H} - \frac{0}{8}\right) + 2240\ \text{S}\right]\text{kcal/kg}$$

where C, H, O, S are the percentages of carbon, hydrogen, oxygen and sulfur in the fuel. Oxygen is assumed to be present in combination with hydrogen as water,

$$\therefore \qquad \text{LCV} = \left[\text{HCV} - \frac{9}{100}\ \text{H} \times 587\right]\ \text{kcal/kg.}$$

$$= [\text{HCV} - 0.09\ \text{H} \times 587]\ \text{kcal/kg.}$$

($\because$ 1 part of H gives 9 parts of water and the latent heat of steam is 587 kcal/kg).

Example 1. *A coal has the following composition by weight C = 90%, O = 3%, S = 0.5%, N = 0.5% and ash = 2.5%. Net calorific value of the fuel was found to be 8490.5 kcal/kg. Calculate the percentage of H and GCV.*

Sol.

$$\text{HCV} = \text{net calorific value} + (0.09\text{ H} + 587)\text{ kcal/kg}$$
$$= (8490.5 + 0.09\text{ H} + 587)\text{ kcal/kg} \qquad [\because\ \text{H} = \%\text{ of hydrogen}]$$
$$= (8490.5 + 52.8\text{ H})\text{ kcal/kg.}$$
$$\text{HCV} = \frac{1}{100}\left[8080 \times 90 + 34500\left(\text{H} - \frac{3}{8}\right) + 2240 \times 0.5\right]\text{ kcal/kg.}$$
$$= 7754.8 + 345\text{ H} = \text{kcal/kg.}$$
$$= 7754.8 + 345\text{ H} = 8490.5 + 52.8\text{ H.}$$
$$\therefore \quad 7754.8 + 345\text{ H} = 8490.5 + 52.8\text{ H.}$$

or
$$292.2\text{ H} = 1335\%$$
$$\therefore \quad \text{H} = 4.575\%$$
$$\therefore \quad \text{HCV} = (8490.5 + 52.8 \times 4.575) = 8731.8\text{ kcal/kg.}$$

Example 2. *On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3500 g of water was increased from 26.5°C to 29.2°C; water equivalent of calorimeter and latent heat of steam are 385 and 587 cal/g, respectively. If the fuel contains 0.7% H, calculate HCV and NCV.*

Sol.

$$\text{HCV} = \frac{(\text{W} + w)\,(t_2 - t_1)}{m} = \frac{(385 + 3500)\,(29.2 - 26.3)}{0.83}$$
$$= 12{,}638\text{ cal/g.}$$
$$\text{NCV} = (\text{HCV} - 0.9\text{ H} \times \text{L})\text{ cal/g}$$
$$= (12{,}638 - 0.9 \times 0.7 \times 587)\text{ cal/g}$$
$$= 12{,}601\text{ cal/g.}$$

Boy's Gas Calorimeter. It is used for measuring the calorific value of gaseous and liquid fuels (Fig. 18.2).

In the apparatus (Fig. 18.2) known volume of gas is burnt at a uniform rate by a burner. Around the burner there is a chimney containing coils wherein water at a constant rate is passed. Separate thermometers measure the incoming and outgoing water temperatures (t_1 and t_2) .

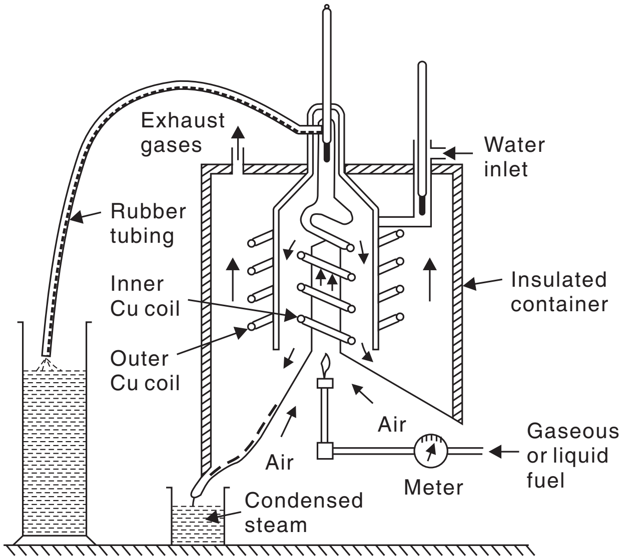


Fig. 18.2 Boy's gas calorimeter.

Let V = volume of gas burning.

W = mass of cooling water used in time t.

t_1 and t_2 = Incoming and outgoing water temperatures

m = mass of steam condensed in time t.

L = HCV.

We get $L = \dfrac{W(t_2 - t_1)}{V}$

Mass of H_2O condensed per m^3 of gas = m/v kg.

Latent heat of steam per m^3 of gas

$$= \frac{m \times 587}{V} \text{ kcal}$$

$$\therefore \qquad \text{NCV} = \left[L - \frac{m \times 587}{V}\right] \text{kcal/m}^3.$$

Example 3. *Calculate the volume of air required for complete combustion of 1 m^3 of a gaseous fuel having the composition: CO = 46%, CH_4 = 10%, H_2 = 40%, C_2H_2 = 2%, N_2 = 1% and the remaining being CO_2.*

Sol. Let the gaseous fuel be 1 m^3

$$CO + \frac{1}{2} O_2 = CO_2$$

Volume of O_2 required = $0.46 \times \dfrac{1}{2} = 0.23 \text{ m}^3$

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Volume of O_2 required = $0.1 \times 2 = 0.2 \text{ m}^3$

$$H_2 + \frac{1}{2} O_2 = H_2O$$

Volume of O_2 required = $0.4 \times \dfrac{1}{2} = 0.2 \text{ m}^3$

$$C_2H_2 + 2\frac{1}{2} O_2 = 2CO_2 + H_2O$$

Volume of O_2 required = $0.2 \times \dfrac{5}{2} = 0.05$

Total O_2 required = $(0.23 + 0.2 + 0.2 + 0.05) \text{ m}^3 = 0.68 \text{ m}^3$

$\therefore$ Volume of air required = $0.68 \times \dfrac{100}{21} \text{ m}^3 = 3.238 \text{ m}^3$.

SOLID FUELS

Wood

Wood is derived from trunks and branches of trees. It contains about 15% moisture after airdrying. Wood contains lignocellulose—wood pulp mainly consists of α cellulose and a very small amount of β cellulose, resins and proteins. The average composition of wood on moisture-free basis is C = 55%, H = 6%, O = 43% and ash = 1%. Wood is largely used as domestic fuel, its use as engineering fuel is restricted. Calorific value varies from 4000 to 6400 Btu/lb.

Coal

Coal is the most important solid fuel and derived from prehistoric plants. Coal is highly carbonaceous and composed of C, H, N, and O and non-combustible inorganic matter.

Origin. Vegetable matter is first transformed into peat, then to lignite then into bituminous coal and finally to anthracite. The transformation period extends over millions of years through a continuous process. The continuity can be proved graphically by plotting oxygen and C percentages of coal at different stages of formation.

Classification of coal. Various types of coal are ranked according to the degree of coalification from the parent material wood as follows:

$$\text{Wood} \longrightarrow \text{Peat} \longrightarrow \text{Lignite} \longrightarrow \text{Bituminous coal} \longrightarrow \text{Anthracite}$$

With the progressive transformation of wood, the moisture, H, O, N, S, volatile matter content decrease whereas carbon content, calorific value and hardness increase.

1. *Peat* is regarded as the first stage of coalification of coal. The composition and properties of peat widely vary from place to place, depending on nature of the original plant material. It is extracted by hand cutting. It is an uneconomical fuel since it contains about 80–90% moisture. It is used as domestic fuel, in steam boilers, power stations and gas producers. Peat is also used as a fertiliser. Low temperature carbonisation of peat is used for getting peat coke and byproducts. Peat is easy to ignite and burns freely to give a long pleasant flame .

2. *Lignite* or brown coals are soft, brown coloured coal. Lignite is compact in texture, containing 20–60% moisture. Airdried lignite contains C = 60–70%, O = 20%. Its calorific value is 6500–7000 kcal/kg. It burns with a smoky flame. It is powdered, dried and pressed into briquettes and used for domestic purpose, for boilers and for production of producer gas.

3. *Bituminous coals* are black and usually banded with alternate very bright and dull layers. On the basis of carbon content bituminous is classified as:

(*a*) *Sub-bituminous coals.* (C content 70–78%, H 4–5% and O 20%). The airdried material has moisture content of 10–20%. Calorific value is 6800–7600 kcal/kg. It ignites easily and if low in S content, used for gaseous fuel production.

(*b*) *Bituminous coal* (C content 78–90%, calorific value is from 8000 to 8500 kcal/kg). Its chief use is for combustion in household, industrial furnaces and boilers, railway locomotives and thermal power stations. By carbonisation and gasification it is converted to coke, gaseous fuels like producer gas, water gas, coal gas, liquid fuels like coal tar fuels.

(*c*) *Semi-anthracite* is intermediate between bituminous coals and anthracite. It ignites more easily than anthracite. When air-dried moisture content is 1–2%, volatile matter = 10–15%. Calorific value is 8500–8800 kcal/kg.

4. *Anthracite* is the highest rank coal having highest percentage of C (92–98%), lowest volatile matter and moisture. Calorific value is 8400–8600 kcal/kg. It burns without smoke but ignites with difficulty, possesses no coking power. Its chief uses are in boilers, domestic ovens and metallurgical furnaces.

Occurrences. Peat deposits are found in Nilgiri hills, lignites occur in Assam, Kashmir, Rajasthan and Tamil Nadu. Bituminous coals are found in Bihar, Bengal, Madhya Pradesh,Chhattisgarh and Orissa. Anthracites are found in Kashmir and eastern Himalayas.

Analysis of Coal

Ranking of coal is done on:

(*a*) *Proximate analysis:* It consists of determination of percentages of (*i*) volatile carbonaceous matter, (*ii*) fixed carbon, (*iii*) ash and (*iv*) moisture of the airdried coal.

(*b*) *Ultimate analysis:* Consisting of determination of percentages of C, H, O, N and S.

(*c*) *Calorific value:* The coking properties are of importance for bituminous coals only. Other chemical and physical properties are specific gravity, surface area and porosity, refractive index etc.

(a) ***Proximate Analysis:***

(*i*) *Moisture:* 1 g of finely powdered airdried sample taken in a crucible and heated in an electrically heated hot air oven at 105°C–110°C for 1 hr. and again weighed after desiccation till constant weight.

$$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100.$$

(*ii*) *Volatile matter:* The dried sample left in the crucible along with the lid is heated in a muffle furnace at a 250°C ± 20°C for 7 minutes and then cooled, weighed after desiccation till constant weight.

$$\text{Volatile matter percentage (V.M.)} = \frac{\text{Loss in weight}}{\text{Wt. of coal sample taken}} \times 100.$$

(*iii*) *Ash:* The residual sample after the two above experiments in the crucible is heated in the furnace at 700°C ± 50°C for 1 or 2 hours without the lid. Then it is cooled, left in the desiccator and weighed till constant weight.

$$\therefore \quad \text{Percentage of ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of coal taken}} \times 100.$$

(*iv*) *Fixed carbon:* Percentage of fixed carbon =

100 – % of (moisture + volatile matter + ash)

Significance: By taking away the latent heat of evaporation *moisture content* lowers the calorific value of coal. Hence, lower the moisture content, better the quality of coal. Similar is the effect of *volatile matter content,* which escapes unburnt so volatile matter content lowers with better quality of coal. Low volatile matter also reduces coking property of coal. *Ash* being non-combustible, reduces the calorific value of coal. Ash deposition also causes problems in the furnace walls and the ultimate disposal of ash is also a problem.

Higher the percentage of *fixed carbon,* higher is the calorific value and better is the quality of coal.

(b) ***Ultimate Analysis:***

(*i*) *Carbon and hydrogen:* Accurately weigh 1–2 gm of the coal sample and burn in a current of O_2 in combustion apparatus whereby CO_2 and H_2O are formed. CO_2 and H_2O are absorbed by previously weighed tubes containing KOH and anhydrous $CaCl_2$. The increase in weight gives the C and H content as follows:

$$\underset{12}{C} + O_2 \longrightarrow \underset{44}{CO_2} \quad \text{and} \quad \underset{112\text{ g}}{2KOH} + CO_2 \longrightarrow \underset{138\text{ g}}{K_2CO_3} + H_2O.$$

$$\underset{2}{H_2} + \frac{1}{2}O_2 \longrightarrow \underset{18}{H_2O} \quad \text{and} \quad \underset{111\text{ g}}{CaCl_2} + 7H_2O \longrightarrow \underset{237\text{ g}}{CaCl_2.7H_2O}.$$

$$\therefore \quad \text{Percentage of C} = \frac{\text{Increase in wt. KOH} \times 12 \times 100}{\text{Wt. of coal sample} \times 44}.$$

$$\text{and percentage of H} = \frac{\text{Increase in wt. } CaCl_2 \times 2 \times 100}{\text{Wt. of coal sample} \times 18}.$$

(*ii*) *Nitrogen:* About 1 g of accurately weighed coal sample taken in a Kjeldahl's flask along with conc. H_2SO_4, K_2SO_4 and heated. Then it is treated with excess of KOH and the liberated NH_3 is absorbed in known excess of standard acid solution. The excess acid is back-titrated with standard NaOH solution. From the volume of acid consumed N content is calculated as follows:

$$\text{Percentage of N} = \frac{\text{Volume of acid consumed} \times \text{Normality} \times 1.4}{\text{Wt. of coal taken}}.$$

(*iii*) *Sulfur:* While determining the calorific value of a coal sample in a bomb calorimeter, the S in the coal is converted to sulfate. Finally the washings containing sulfate is treated with dil. HCl and $BaCl_2$ solution, which precipitates $BaSO_4$ which is filtered in a sintered glass crucible, washed with water and heated to a constant weight.

$$\text{Percentage of S} = \frac{\text{Wt. of } BaSO_4 \times 32 \times 100}{\text{Wt. of coal sample in bomb} \times 233}.$$

(*iv*) *Ash content:* Ash content is determined similar to proximate analysis.

(*v*) *Oxygen content* = 100 – % of (C + H + S + N + ash)

Significance: Higher percentage of C and H increases the calorific value of coal and hence better is the coal. Higher the percentage of O, lower is the calorific value and lower is the coking power. Also, O when combined with H in the coal, H available for combustion becomes unavailable. S, although contributes to calorific value, is undesirable due to its polluting properties as it forms SO_2 on combustion.

Coke

Carbonisation or coking bituminous coal leads to the formation of coke. Coke obtained from coal with high volatile matter forms swelling coke which is soft coke, and from a mixture of high and low volatile coking bituminous coal (non-swelling) in coke ovens hard coke is obtained. Both soft and hard cokes are obtained by *high temperature carbonisation*. A smokeless fuel or semicoke is obtained from *low temperature carbonisation*.

Coke and Coal

- Coke possesses much strength and porosity compared to coal.
- By coking the undesirable sulfur content of coal is removed from coke and due to lower volatile matter content of coke it burns with a short flame. All these properties of coke make it suitable for metallurgical processes compared to coal.

Carbonisation of Coal

Depending on the operation temperature there are mainly two types of carbonisation processes, namely,

(*i*) Low temperature carbonisation (LTC) and (*ii*) High temperature carbonisation (HTC). Coarsely powdered coal taken in a closed retort and heated out of contact with air leads to the breakdown of coal with the formation of water, ammonia, other volatile matters, gases and coke. This process is called the *carbonisation of coal* or *coking of coal.*

Table 18.1: By-products of carbonisation of coal

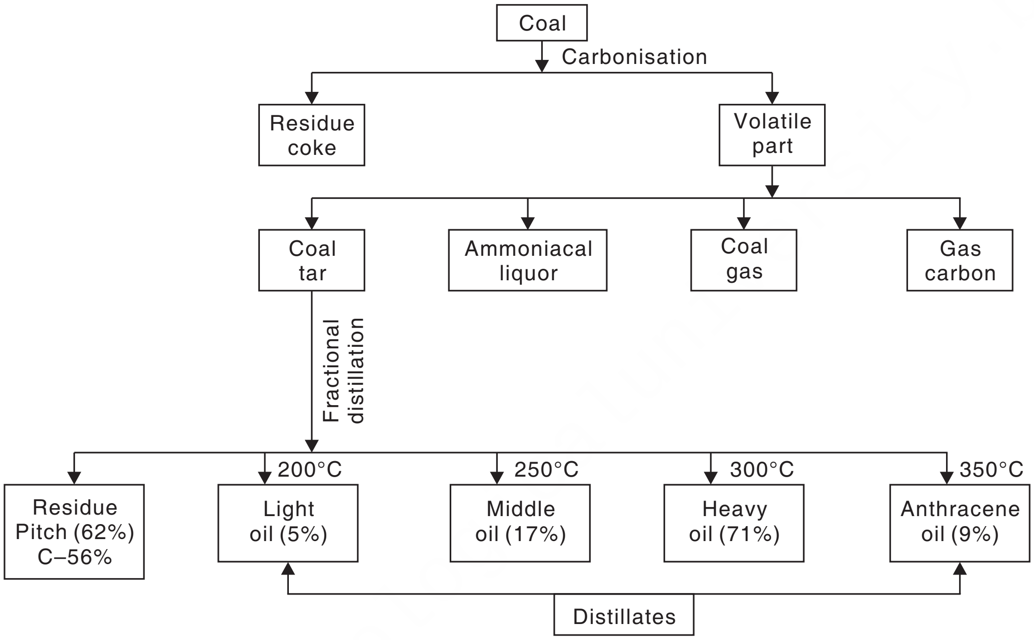


Table 18.2: Products (by fractional distillation)

Light oil	Benzene, Toluene, Xylene, Cumene etc.
Middle oil	Naphthalene, Phenol, Cresol, Pyridine etc.
Heavy oil	Cresol, Xylene, Naphthalene etc.
Anthracene oil	Phenanthrene, Anthracene, Quinoline etc.

(*i*) *Low temperature carbonisation (LTC).* In this process, coal is heated in steel retorts at 500°C–700°C. The yield of coke is 75–80% and it contains 8–12% volatile matter. The coke obtained is not mechanically strong but highly reactive and can be easily ignited to give smokeless flame and used as a domestic fuel. Low temperature carbonisation yields a very complex mixture of higher phenols, substituted aromatic hydrocarbons and other N and O containing compounds. Disinfectants are made from this tar. The coal gas obtained has calorific value of 6500 kcal/m^3 and is richer in hydrocarbons and poorer in hydrogen compared to the gas produced by HTC. The crude spirit corresponds to crude benzol of HTC but contains greater amount of paraffins, naphthalene and olefin.

(*ii*) *High temperature carbonisation (HTC).* It is carried out at 900°C–1200°C producing coke of good porosity, hardness, purity and strength and can be used in metallurgy. As all the volatile matters are driven off, the yield of coke is 65–75% containing 1–3% volatile matter. The retorts used are made of brick. The gas and tar yields are lower. The calorific value is lower, about 4500 kcal/m^3.

Distinction between high temperature carbonisation (H.T.C.) and low temperature carbonisation (L.T.C.) at a glance:

- Temperature ⇒ L.T.C. = 400–600°C
  H.T.C. = 1000–1400°C
- Economy ⇒ In L.T.C. less costly steel retorts are used whereas in the case of H.T.C. retorts made of fire bricks are used. The expenditure due to fuel is also less in the case of L.T.C. than that of H.T.C. as the working temperature is less.
- Nature of tar ⇒ The liquid volatile products are larger in quantity in the case of L.T.C., on the other hand the quantity of gaseous products is greater in the case of H.T.C. The formation of lower amount of paraffin and alicycilc compounds and higher amounts of aromatic compounds in the case of H.T.C. indicates that the process of aromatisation is greater in the case of H.T.C.
- Nature of other products ⇒ The amount of ammonia formed greatly increases with the rise of temperature showing that nitrogenous complexes are broken at higher temperature. The Tables 18.1 and 18.2 show the amount and nature of various products.
- Physical characteristics of tar ⇒ H.T.C. tars are darker in colour and more viscous than that of L.T.C. tars.
- Yield of tar ⇒ The yield of L.T.C. tar per ton of coal is much greater than that of H.T.C. tar.

There are two main types of oven for the manufacturing of coke:

(*a*) **Beehive oven:** It is a batch process and now obsolete. The firebrick chambers are of 2 m height and 3.5 m diameter and form the shape of a beehive. There are two openings, one at the top for charging the coals and the other on one side for the entry of air and also for removal of coke. Coal forms a layer of 60–90 cm depth. Carbonisation proceeds from the top to bottom and completes in 2–3 days. Heat is supplied by the burning of the volatile matter and hence no byproducts are recovered. The hot exhaust gases are utilised to run waste heat boilers to increase the heat efficiency. At the end of carbonisation, the coke is quenched by water and raked out through the side door, leaving the oven hot enough to start the next batch. The yield of coke is 80% of the coal charged (Fig. 18.3).

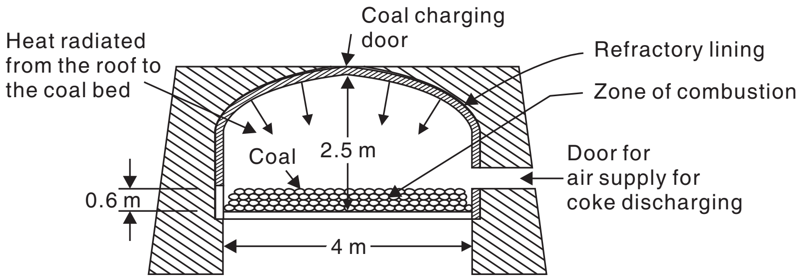


Fig. 18.3 Beehive coke oven.

The limitations of the process are (*i*) no recovery of byproducts, (*ii*) coke yield is low, (*iii*) the exhaust gases cause pollution, (*iv*) process is not flexible.

(*b*) **Byproduct coke oven:** In this process coal is heated in combustion chambers, separate from carbonisation chambers. The thermal efficiency has been increased and the valuable byproducts are recovered. The coke ovens are made of silica bricks and the temperature is about 1350°C to 1450°C. The batch process is made continuous by building ovens in a battery. The oven consists of number of narrow silica chambers (10 m × 3 m × 0.4 m) erected side by side with vertical flues in between them. There is a charging hole at the top, a gas off take and a refractory lined cast iron door at each end. It is heated externally by a portion of coal gas produced by the process itself or by producer gas or by blast furnace gas.

Highlights:

- There are two main types of coking of coal:
  (*i*) Beehive and the (*ii*) by product coking.
- Beehive coking is obsolete. It is a batch process causing a large amount of pollution. A portion of coal is burnt inside the retort to generate heat for coking.
- In byproduct coking, air is excluded so that no burning takes place within the oven, heat is supplied from the hot flue gases and 40% of the oven gas (coal gas) generated is burnt to heat the battery of ovens and the rest is used for domestic fuel locally.

Finely crushed coal is charged through the hole at the top and in a closed system it is heated to 1200°C. The flue gases produced during combustion pass their sensible heat to the checker brick-work, which is raised to 1000°C. The flow of heating gases is then reversed and the hot checker bricks heat the inlet gas. This cycle continues till the volatile matter lasts. Carbonization takes about 11 to 18 hours, after which the doors are opened and the glowing coke mass is discharged by machine driven coke-pusher into coke-quencher. The hot coke is quickly quenched by water spraying. 'Dry quenching' is also done by circulating flue gases over hot coke and the hot gases are utilised to run waste heat boilers (Fig. 18.4).

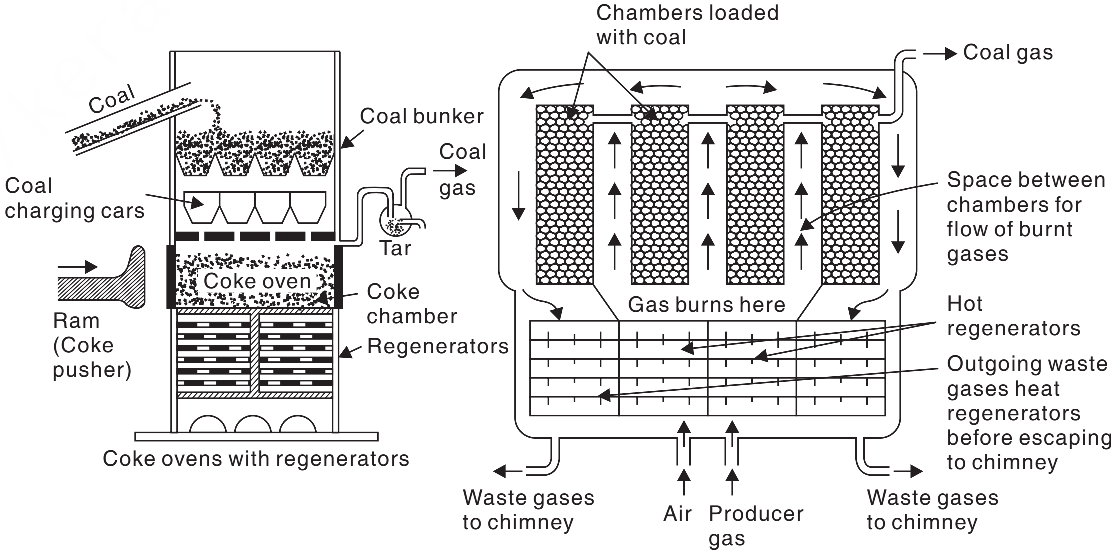


Fig. 18.4 Otto Hoffman's byproduct coke oven with regenerators.

Recovery of byproducts: The gases coming out at 600°C–700°C get a spray of flushing liquor at the goose-neck of the standpipe and the temperature is reduced to 80°C. Tar and steam get condensed. The 'Coke oven gas' is composed of NH_3, H_2O; tar contains naphthalene, benzene, moisture etc.

(*i*) Coal tar is condensed in the tank below.

(*ii*) Ammonia is recovered partly as aqueous solution and partly as sulfate.

(*iii*) Naphthalene is recovered by passing the gas through a tower where water is sprayed at very low temperature which condenses the naphthalene.

(*iv*) Benzene is recovered similarly by spraying petroleum.

(*v*) H_2S is recovered by passing the gas through moist Fe_2O_3 as:

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O$$

Fe_2S_3 is again regenerated by exposing to atmosphere

$$Fe_2S_3 + 4O_2 \longrightarrow 2FeO + 3SO_2$$

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

Beehive ovens are located in Jharia, Raniganj, Bokaro-Ramgarh in large numbers in India whereas byproduct coke ovens are on large numbers in Giridih, Durgapur, Jamshedpur, Bhilai, Rourkela, Bokaro etc.

LIQUID FUELS

Petroleum or crude oil is a deep brown oil consisting of mainly hydrocarbons, paraffins, naphthenes and aromatics in varying proportions. Sulfur, nitrogen and oxygen are present in the form of derivatives of hydrocarbons in the oil. The average ultimate analysis shows $C \Rightarrow 83–87\%$, $H \Rightarrow 11–14\%$, $S \Rightarrow 0.5–3\%$, $N \Rightarrow 0.1\%$ and $O \Rightarrow 2–3\%$. Practically all metals are found in petroleum, the most common are Si, Fe, Al, Ca, Mg, Ni.

Occurrence: The crude oil has been derived from the organic matter originally present in marine sediments. The dead organic matter settles down to the bottom of shallow seas and lagoons. The settled debris is attacked by anaerobic bacteria, whereby most of the organic compounds are destroyed and the remaining unsaturated fatty oils and fatty acids undergo polymerization.

Classification of petroleum. There are three main types petroleum according to chemical nature:

(*a*) Paraffin-base crude composed of saturated hydrocarbons upto $C_{35}H_{72}$ which are semi-solids, called waxes.

(*b*) Asphalt-base crude contains mainly naphthenes and cycloparaffins with smaller amounts of paraffins and aromatics.

(*c*) Mixed base crude contains both the above type of compounds but rich in waxes. About 90% crude produced at present fall in this last category.

Petroleum

Drilling: Oil is brought to the surface by drilling holes upto the oil bearing surface. By the hydrostatic pressure of natural gas the oil is pushed up or it is pumped up by means of a pump. Two coaxial pipes are lowered to the oil reservoir, through the outer pipe compressed air is forced, whereby the oil is forced out through the inner pipe. This crude oil is sent to the refineries for further processing and refining of the crude oils (Fig. 18.5).

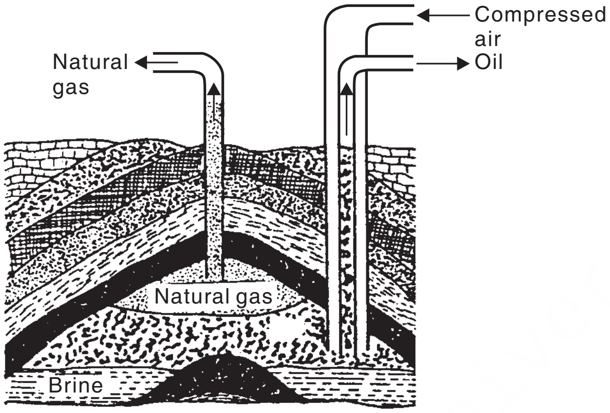


Fig. 18.5 Mining of crude oil and use of air-lift pump.

Refining: After removal of dirt, water and natural gas, the crude oil is separated into fractions by distillation and the fractions obtained are subjected to simple purification procedures or complex treatments to yield different petroleum products. All these steps are under petroleum refining which include:

1. **Coltrell's process.** Crude oil is intimately mixed with water forming an emulsion. The water is separated from the oil by passing the emulsion through Coltrell's electrostatic precipitator.

2. **Removal of objectionable compounds.** Sulfur compounds have objectionable properties of pollution so they are removed prior to distillation as copper sulfide by treatment with copper oxide.

3. **Petroleum distillation.** The crude oil is subjected to distillation to about 400°C temperature in an iron retort whereby all volatile components except the solid residue are distilled out. These are separated in a fractionating column consisting of a tall tower where the higher boiling fractions condense first. This distillation is a continuous process and the following fractions are obtained (Fig. 18.6) (Table 18.3).

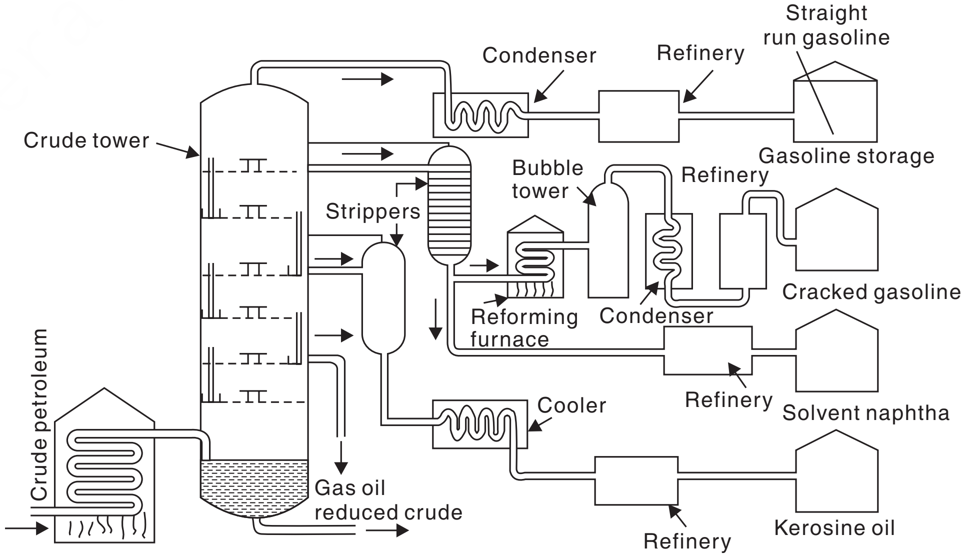


Fig. 18.6 Petroleum distillation.

(*a*) **Gasoline** is obtained upto 200°C. The naphtha is condensed and subjected to refining for the removal of sulfur, diolefins after refractionating.

(*i*) Petroleum ether boiling between 40°C–70°C and
(*ii*) Benzene boiling between 70°C–90°C and
(*iii*) Gasoline boiling between 90°C–200°C all are obtained.

Its calorific value is 14,250 kcal/kg and is used as a fuel for internal combustion engines in automobiles and aircrafts.

(*b*) **Solvent naphtha** is obtained as a side steam between 200°C–250°C. This contains some gasoline, which is passed back to the main fractionating column. Naphtha contains 6-10 carbon atoms.

(*c*) **Kerosene oil** is obtained between 250°C–300°C. The lower boiling fraction mixed with it is returned to the main column. Bottom liquid is refined and finally can be used as domestic fuel having calorific value of 1100 kcal/kg.

(*d*) **Gas oil** is obtained between 300°C–350°C. This is passed through a cooler and then extracted with liquid SO_2 to remove sulfur. It is used as a diesel engine fuel with calorific value of 11000 kcal/kg.

(*e*) The *residual liquid* coming out from the bottom on subsequent treatment yields lubricating oil, vaseline, grease, paraffin wax, asphalt-bitumen, petroleum, coke etc.

Table 18.3: Common fractions from crude

Fraction	*Boiling range*	*Composition*	*Uses*
Uncondensed gas	Within 30°C	C_1 to C_4	As domestic or industrial fuel under the name LPG (Liquefied petroleum gas)
Petroleum ether	30°C–70°C	C_5–C_7	As a solvent.
Gasoline or petrol	90°C–200°C	C_5–C_9	As a motor fuel solvent and dry washing
Naphtha	200°C–250°C	C_9–C_{10}	As a solvent
Kerosene oil	250°C–300°C	C_{10}–C_{16}	As fuel for domestic and industrial uses
Diesel oil	300°C–350°C	C_{10}–C_{18}	As a fuel for diesel engine
Heavy oil	320°C–400°C	C_{17}–C_{30}	For different fractions

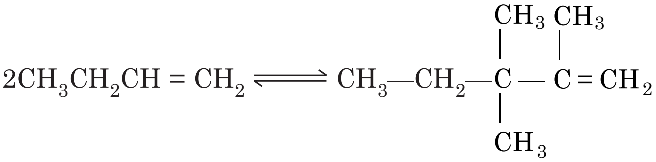
Cracking Process

Cracking is the process in an oil refinery by which heavier fraction from the fractional distillation converted into useful lighter fractions by the application of heat, with or without catalyst, *i.e.,* cracking is a process by which larger molecules break up into smaller ones. The chief application of commercial cracking in all the refineries is for the production of gasoline from gas oils. Other uses include the production of olefins from naphthas and gas oils. The surplus of heavier petroleum fractions are also cracked to get petrol. There are two methods of cracking.

1. *Thermal Cracking:* When cracking is carried out without any catalyst at high temperature from 450°C–750°C at pressures ranging from 1–70 atms, it is called *thermal cracking*. The important reactions are decomposition, dehydrogenation, isomerization and polymerization. The paraffins decompose to lower mol. wt. compounds, like paraffin and an olefin.

$$\underset{n\text{-decane}}{CH_3(CH_2)_8CH_2} \longrightarrow \underset{n\text{-hexane}}{CH_3(CH_2)_4CH_3} + \underset{\text{butene-1}}{CH_3CH_2CH = CH_2}$$

The olefins formed isomerizes and polymerizes.



$$2CH_3CH_2CH = CH_2 \rightleftharpoons CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

This cracking taking place at 475°C–530°C temperature leads to *liquid phase thermal cracking*. The products are separated by fractional distillation. When the cracking oil is vaporized and then cracked at 600°C–750°C at a low pressure, it is called *vapour phase thermal cracking*. The products have better anti-knock properties.

2. ***Catalytic Cracking.*** The use of catalyst during cracking accelerates the reactions and at the same time modifies the yield and the nature of product. Catalyst used are synthetic composition of silica and alumina, zeolites in the form of beads or pellets.

There are two main types of catalytic cracking:

(*a*) *Fixed-bed catalytic cracking:* The catalysts are fixed in towers, through which the hot oil (500°C) flows from the top and passes down. 40% of the charge is converted to gasoline and 2–4% carbon is formed. This carbon deposits on the catalyst beds. The bottom liquid is reboiled and recycled to the fractionating column and ultimately gas oil is obtained having high octane value. The gasoline is stripped off dissolved gases and purified. The carbon deposits on the catalysts are burnt by compressed air in one chamber for reactivation while the other catalyst chambers are active (Fig. 18.7).

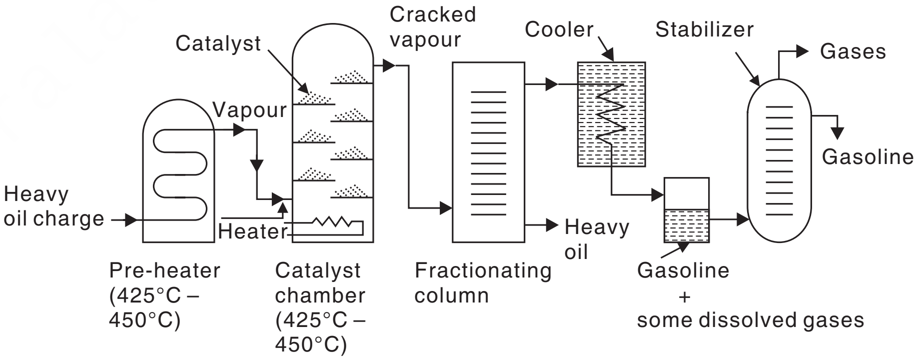


Fig. 18.7 Fixed-bed catalytic cracking.

(*b*) *Moving bed or fluidized bed catalytic cracking:* The finely powdered catalyst behaves as a fluid when suspended in gas or oil vapour. The preheated heavy oil is forced through tower along with the fluidised catalyst. At the top of the tower a cyclone separator is active to separate the cracked oil vapour and passes it to the fractionating column. The catalyst powder is retained and sent back. The catalyst becomes deactivated by a deposition, which is reactivated by burning away the deposits with compressed air in a regenerator (Fig. 18.8).

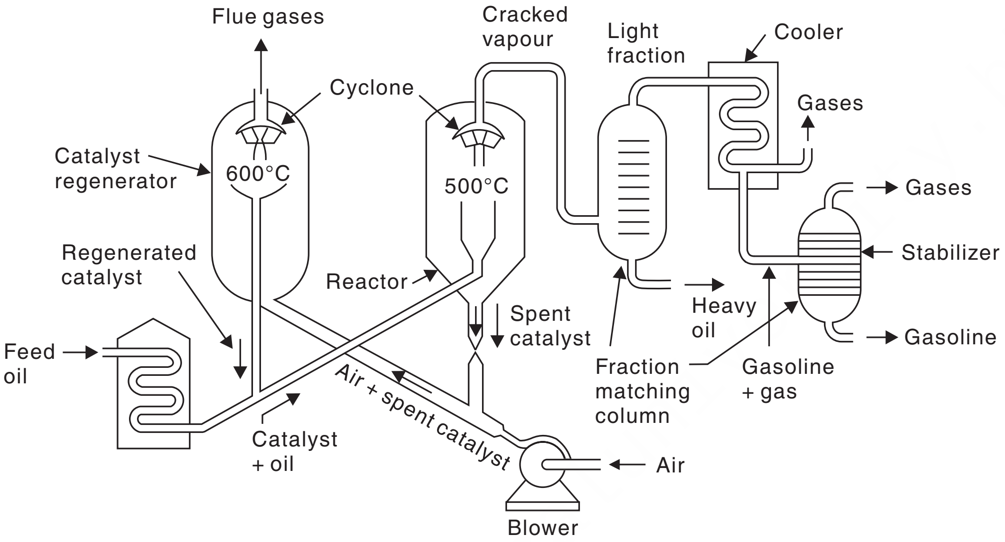


Fig. 18.8 Moving-bed type catalytic cracking.

Advantages of catalytic cracking:

(*i*) The quality and yield of petrol is better.

(*ii*) External fuel is not necessary since the coal embedded in the catalyst supplies the heat.

(*iii*) Operating pressure is lower.

(*iv*) Byproduct gas evolution being low, yield of petrol is higher.

(*v*) Due to higher aromatics content, the anti-knocking properties are higher.

(*vi*) Greater portion of S escapes as H_2S so residual S content of the oil is low.

(*vii*) Gum-forming compounds are very low.

(*viii*) In presence of specific catalysts preferentially the cracking of naphthenic materials takes place, so it becomes richer in paraffinic compounds.

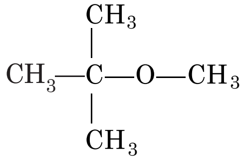
(*ix*) Only the high-boiling hydrocarbons and the side chain of the aromatics are decomposed preferentially.

Highlights:

- Gasoline is the fuel for motor engines.
- Gasoline contains alkanes C_5—C_{10} atoms.
- Enough gasoline is not produced during purified petroleum distillation.
- Oil refineries use *catalytic cracking* to make gasoline.
- For smooth running of the motors, gasoline has to burn smoothly without *knocking*.
- The octane number scale was devised by Thomas Midgley (1889-1944) and he discovered *anti-knocking* additives based on lead *i.e.*, T.E.L. (Tetra Ethyl Lead)
- Leaded fuel is now avoided and the oil companies produce high octane fuel by increasing the proportions of both branched alkanes and arenes and blending some oxygen compounds.

(*contd.*)

- The four main approaches are:
  - (*i*) *Cracking* not only makes small molecules but also forms branched chain hydrocarbons.
  - (*ii*) *Isomerisation c*onverts straight chain alkanes to branched chain by passing over Pt-catalysts.
  - (*iii*) *Reforming t*urns cyclic alkanes into arenes such as benzene and toluene.
  - (*iv*) *Addition of alcohols and ethers.* Compounds such as MTBE (Methyl Tertiary Butyl Ether) now known as 2-methoxy-2-methyl propane.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3$$

MTBE

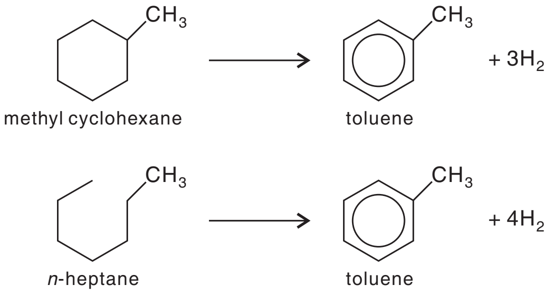
Petroleum Processing

1. *Polymerization, alkylation and isomerization.* The cracker gases in the refinery are rich in olefins. These compounds undergo polymerization either in presence of catalyst (catalytic polymerization) like phosphoric acid, H_2SO_4 or by heating at temperatures of 500°C–600°C and pressure (thermal polymerization) to yield products rich in branched-chain hydrocarbons. By this process superior quality gasolines are obtained.

$$\underset{\textit{iso}\text{-butene}}{CH_3C(CH_3) = CH_2} \longrightarrow \underset{\textit{di}\text{-isobutene}}{CH_3C(CH_3)_2CH_2C(CH_3) = CH_2}$$

Similarly, alkylation in presence of HF or H_2SO_4 gives *iso*-paraffins. Isomerization converts *n*-paraffins to *iso*-paraffins in presence of anhydrous $AlCl_3$ catalyst. All these processes supply excellent high volatile gasoline components.

2. *Reforming.* This process also helps in preparing high quality gasoline by heating with or without a catalyst, the naphtha fractions of gasoline. This upgrading is a result of reforming of molecules without disturbing their average molecular weights, like formation of aromatics from naphthene and paraffins.



The other reactions are the isomerization of *n*-paraffins to *iso*-paraffins and hydrocracking of higher paraffins to lower ones. Actually these aromatics and the *iso*-paraffins are the best gasoline components.

Similar to cracking, reforming is also thermal and catalytic. Thermal reforming has been almost completely replaced by catalytic reforming.

The catalysts used are molybdena, chromia supported on alumina, platinum on silica or alumina. The latter is more active, but gets poisoned easily by the impurities like S, As, N etc.

Reforming is a once through process. Fluid bed and moving bed processes are run at higher temperature and lower pressures and fixed bed processes are run at higher pressures (temperature 450°C–520°C, pressure 5–45 kg/cm^2) (Fig. 18.9).

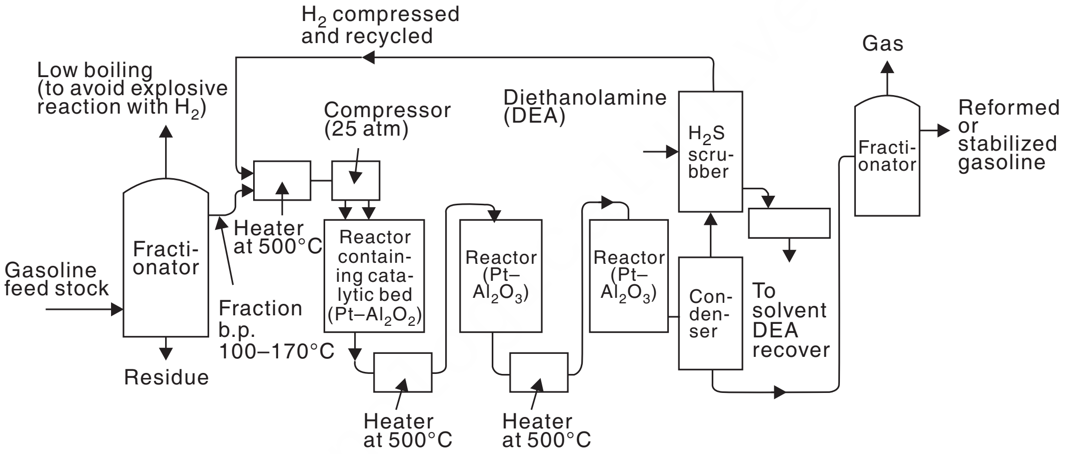


Fig. 18.9 Fixed-bed catalytic reforming process.

Refining of Gasoline

The *straight-run gasoline* obtained from the fractionation of crude petroleum contains undesirable constituents like unsaturated straight chain hydrocarbons and sulfur compounds. The former leads to gum and sludge formation and the latter leads to corrosion of engines and pollution of atmosphere. These are removed by refining processes.

(*i*) Objectionable odour forming mercaptans and H_2S make the oil sour. Oil sample treated with sodium plumbite and a little sulfur converts the sulfur compounds into disulfides (*Doctor's process*). The black PbS precipitates and the other disulfides are extracted with a suitable solvent, rendering the foul smelling stock to sweet smelling or odourless stock and the process is called *sweetening process.*

$$2RSH + Na_2PbO_2 \longrightarrow Pb(RS)_2 + 2NaOH$$

$$Pb(RS)_2 + S \longrightarrow PbS + \underset{\text{disulfide}}{RSSR}$$

(*ii*) Gasoline is percolated through "Fuller's earth" which absorbs the olefins and coloring matters present in it.

(*iii*) The storing quality of the refined gasoline is improved by adding different inhibitors of oxidations to it.

(*iv*) Refined gasoline is blended with suitable fractions of catalytically cracked gasoline to impart good combustion qualities.

Knocking

Octane Number. Maximum power is derived from gasoline when it burns silently and uniformly in an internal combustion engine. Due to presence of certain constituents in the gasoline, the rate of oxidation sometimes becomes so great that the unburnt fuel may burn rapidly with the formation of explosive violence. This is known as *knocking*. Knocking results in loss of efficiency of the engine and also leads to its short life.

The anti-knock quality of a fuel is expressed as its octane number.

Octane number is equal to the percentage by volume of iso-octane (2,2,4-trimethyl pentane) in a mixture of *n*-heptane and iso-octane having the same knocking tendency compared to the sample of gasoline being tested; iso-octane has the best antiknocking properties and assigned an octane number of 100 whereas *n*-heptane has poor antiknocking property and assigned an octane number of zero. The hydrocarbons present influence the knocking properties of gasoline which vary according to the series: straight chain paraffin > branched chain paraffin > olefin > cycloparaffin > aromatics. The fuel which has same knocking tendency with the mixture having 80% *iso*-octance has octane number 80.

The most effective antiknock agent added is tetraethyl lead (TEL) along with ethylene dibromide which prevents the deposition of lead by forming volatile lead halides. Other antiknocking agents are tetramethyl lead (TML), tertiary butyl acetate, diethyl telluride.

1.0–1.5 ml of TEL is added per litre of petrol. TEL functions by being converted to a cloud of finely divided lead oxide particles, which react with any hydrocarbon peroxide molecules formed in the engine cylinder thereby solving down the chain oxidation reaction and preventing knocking.

Cetane Number

There is a delay period between the injection of diesel fuel and its ignition. This delay period if becomes large, too much fuel accumulates in the cylinder and burn very rapidly and causes "diesel knock". This delay period is connected to the type of hydrocarbons present in the diesel. Increasing delay period occurs in the series: *n*-paraffins < olefins < naphthenes < isoparaffins < aromatics. The order is the reverse for gasoline anti-knock quality. *n*-hexadecane is given cetane number 100 and α-methyl naphthalene given cetane number zero. If a given fuel matches in quality with the blend having 40/60 blend of cetane and α-methyl naphthalene, it is assigned a cetane number 40. The cetane number of diesel can be improved by adding amyl/butyl nitrate, carbamates, ditertiary butyl peroxide and metal organic compounds.

Liquid Fuel from Coal and Coal Tar

The conversion of coal into oil is essentially raising the H:C ratio.

1. ***Bergius-Pier Process:*** Destructive hydrogenation of coal in presence of a catalyst yields oil, but it is not yet competitive with petroleum refining.

Coal is ground and made into a paste with a heavy recycle oil and a catalyst like iron, tin or molybdenum compound. The paste is preheated and treated with H_2 at 250–350 atm. pressure and 450°C–500°C temperature. The unreacted coal is filtered-off and the liquid product distilled. Hydrogen combines with coal to form saturated hydrocarbons, which decompose at high temperature yielding low-boiling hydrocarbons. The crude oil is fractionated to get (*i*) gasoline (*ii*) middle oil and (*iii*) heavy oil which is recycled. Middle oil is hydrogenated in vapour phase with catalyst to yield more gasoline. Yield of gasoline is 60% of the coal dust.

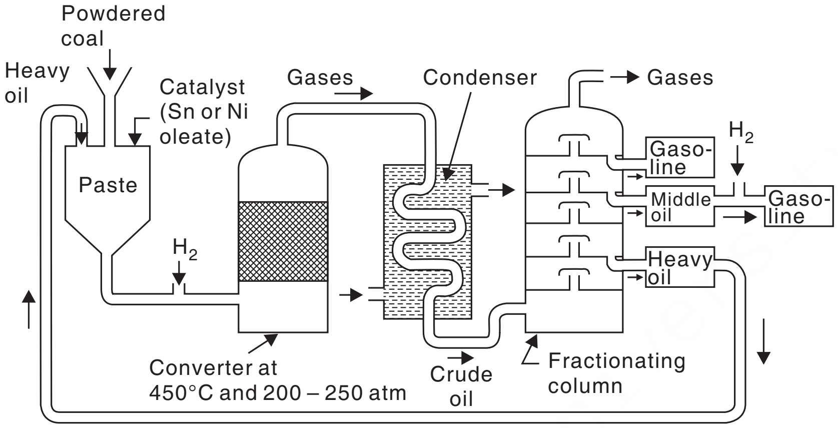


Fig. 18.10 Bergius process of hydrogenation of coal to gasoline.

2. ***Fischer-Tropsch Process.*** The process is based on the catalytic hydrogenation of carbon monoxide leading to the following reaction:

$$n\mathrm{CO} + (2n+1)\mathrm{H}_2 \longrightarrow \underset{\text{Paraffin}}{\mathrm{C}_n\mathrm{H}_{2n+2}} + \mathrm{H}_2\mathrm{O}$$

$$n\mathrm{CO} + 2n\mathrm{H}_2 \longrightarrow \underset{\text{Olefin}}{\mathrm{C}_n\mathrm{H}_{2n}} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H}_2\mathrm{O}$$

Water gas ($CO + H_2$), produced by passing steam over heated coke is mixed with hydrogen.

The gas is purified by passing over Fe_2O_3 to remove H_2S, then passing over a mixture of $Fe_2O_3.Na_2CO_3$ to remove organic sulfur compounds. The purified gas is compressed to 5 to 25 atm. at 200°C–300°C passed through a converter containing catalyst which is a mixture of 100 parts cobalt, 5 parts thorium, 8 parts magnesium and 200 parts keiselguhr.

The exothermic reaction leads to the formation of straight-chain saturated and unsaturated hydrocarbons. The crude oil on fractionation yields (*i*) gasoline and (*ii*) heavy oil, which are cracked to yield more gasoline.

The gasoline contains straight chain hydrocarbons and hence have low octane number, so needs reforming before use (Fig. 18.11).

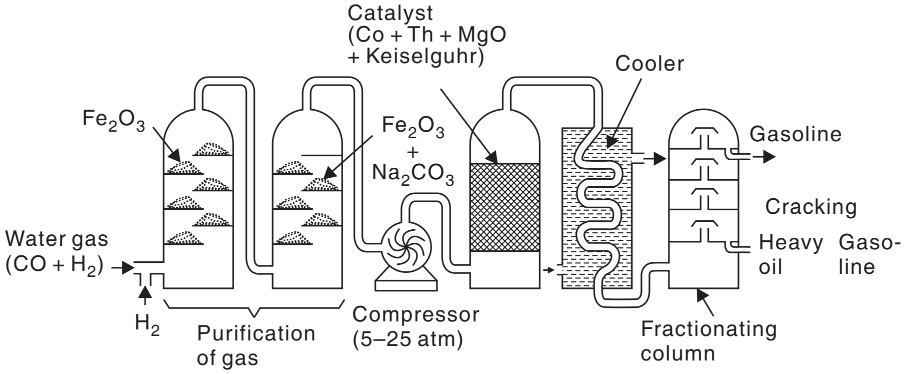


Fig. 18.11 Fisher-Tropsch method.

Important Petroleum Products

The main products of refinery are motor and aviation gasoline, kerosene, diesel fuel, fuel oils; other products include lubricating oils, wax, bitumen, coke, LPG etc.

Gasolines. It is used in reciprocating spark-ignition internal combustion engines.

Motor gasoline is a mixture of low boiling hydrocarbons (215°C) and made by blending—

(*i*) Straight run gasoline (direct distillation of crude oil), (*ii*) cracked gasoline, (*iii*) reformed naphtha and other fractions, 10% butane for easy starting of engines, TEL and other additives. Colours are added to identify different grades.

Aviation gasolines have higher volatility and higher percentages of TEL and isoparaffin.

Kerosene. Kerosene is used for domestic purpose, space heaters for jet engines. It is obtained as a straight-run distillate from crude oils. No additives are required. Purification involves removal of sulphur.

Diesel fuel. Diesel fuels are prepared from heavy distillate obtained from catalytic cracking units. It is rich in aromatics and *iso*-paraffins, the low cetane number is improved by additives. Volatility is improved by blending with light fractions. In a high-speed diesel engine, the cetane numbers should be more than 45 whereas for low speed engines it should be in the range of 25 to 35.

Fuel oils. Wide range of liquid fuels used in boilers and furnaces are covered by this term. Cycle gas oil is the light variety and needs a number of treatments for purification. The heavy fuel oil produced from the cracking units are the heavy variety.

LPG. Liquefied petroleum gas is obtained as a byproduct during the cracking of heavy oils or from natural gas. LPG contains hydrocarbons which are gaseous under atmospheric pressure but can be liquefied under pressure. They are *n*-butane, isobutane, butylene, propane etc. It is used as domestic and industrial fuels and in future it may be used as motor fuel.

Non-petroleum Fuels

1. *Benzol.* Refined benzol is essentially a mixture of 70% benzene, 18% toluene and 6% xylenes. Its octane rating ranges between 87 and 90. It is a good fuel for internal combustion engines but its initial boiling point is high (80°C), so it can be used only when blended with gasolines. The other defect is its high freezing point (55°C), so it cannot be used in cold countries.

Alcohols. Methyl and ethyl alcohols can be used in gasoline engines. Cost considerations prohibit their use. Octane number is high as 114 and 99, respectively. But their calorific values are low. Ethyl alcohol is not used as a prime fuel but used as blends with gasoline upto 25% alcohol and the mixture is called "gasohol". It serves to increase the octane rating.

The importance of ethyl alcohol as a fuel lies in the fact that it can be produced from naturally available carbohydrates by fermentation. It requires about 36 hrs. to complete whereby the fermented liquid contains 18-20% alcohol which is then fractionally distilled to recified spirit containing 90-95% alcohol, from which absolute alcohol can be obtained after treatment with lime and distillation.

GASEOUS FUELS

(*a*) Fuel gas from nature:
  (*i*) Natural gas
  (*ii*) Methane from coal mines.
(*b*) Fuel gas from solid fuels:
  (*i*) Producer gas
  (*ii*) Water gas
  (*iii*) Coal gas
  (*iv*) Blast furnace gas
(*c*) Fuel gas from petroleum:
  (*i*) Refinery gases
  (*ii*) LPG
  (*iii*) Gases from oil gasification.
(*d*) Fuel gas made by fermentation of organic wastes.

Natural Gas

Natural gas is a mixture of paraffinic hydrocarbons and methane is the principal component. Natural gas when found to occur with petroleum in oil wells is called 'wet gas' and when it is associated with crude oil the gas is called 'dry gas'. Water, dirt, H_2S, CO_2, N_2 and heavier hydrocarbons are removed from the gas and finally it contains from 50 to 95% methane, 5-10% ethane, 3% H_2 etc. The calorific value is 12,000–14000 kcal/m^3.

Natural gas is used (*i*) as a domestic fuel, (*ii*) for manufacture of various chemicals (*iii*) as raw material for the manufacture of H_2 and carbon black and (*iv*) for synthetic protein preparation from methane.

Coal Gas

Coal is produced by the high temperature carbonisation of coal in gas retorts and coke ovens. Its calorific value is around 5000 kcal/m^3. It contains 40% H_2, 32% CH_4, 7% CO, 2% C_2H_2, 3% C_2H_5, 4% N_2 and 1% CO_2. It burns with a long smoky flame.

The coke oven gas is purified in steps to obtain the coal gas finally. Tar and ammonia are first removed by cooling the gas and water scrubbing, then benzol, naphthalene are removed by creosote oil scrubbing, H_2S is finally removed by passing it over moist ferric oxide.

$$2Fe(OH)_3 + 3H_2S \longrightarrow Fe_2S_3 + 6H_2O$$

Coal gas is used (*i*) for illuminating towns and cities, (*ii*) as a fuel, (*iii*) as a raw material for NH_3 production and (*iv*) in metallurgical operations to provide reducing atmosphere.

Producer Gas

It is a mixture of combustible gases like CO and H_2 and large amount of non-combustible gases like N_2, CO_2 etc. It is prepared by passing air and steam over an incandescent bed of solid carbonaceous fuel in a reactor called "gas producer" or simply a "producer". It is a fuel of low calorific value (1300 kcal/m^3) but its advantage is its cheapness and ease of production. The carbonaceous fuel used is generally coal or coke, though wood waste, peat etc. can be used.

The gas producer consists of a steel vessel with inner lining made up of refractory bricks. The dimension of the vessel is about 4 m height and at the top there is a cone feeder and a side opening for producer gas outlet. At the base there is inlets for air and steam and an outlet for the ash.

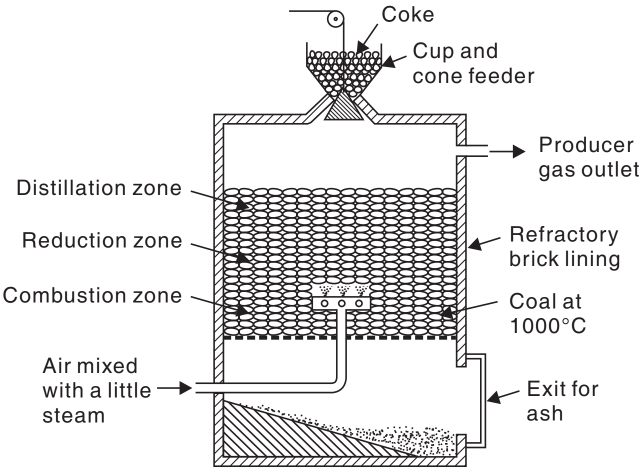


Fig. 18.12 Gas producer.

Reaction Zones in a Gas Producer

(*a*) **Ash zone.** The fuel bed in a normal producer is on metallic grate. The air-steam blast is preheated by the ash zone which also protects the grate from intense heat.

(*b*) **Oxidation zone.** This is just next to the ash zone. The oxygen is consumed within 75 to 100 mm of the bed, which constitutes the zone. CO_2 forms at the expense of O_2. Its concentration reaches a maximum at the top when CO begins to appear. The temperature at this zone is about 1100°C.

$$C + O_2 \longrightarrow CO_2 + 97 \text{ kcal}$$
$$C + \frac{1}{2} O_2 \longrightarrow CO + 29.5 \text{ kcal}$$

(*c*) **Reduction zone.**

$$CO_2 + C \longrightarrow 2CO - 36 \text{ kcal}$$
$$C + H_2O \longrightarrow CO_2 + H_2 - 29 \text{ kcal}$$
$$C + 2H_2O \longrightarrow CO_2 + 2H_2 - 19 \text{ kcal}$$

As long as O_2 is in excess, CO_2 is formed, which then undergoes reduction into CO and the reaction is endothermic and is called Bondonard reaction. Its equilibrium constant greatly increases with rise in temperature. Other reactions are also endothermic, where red hot coke, combines with steam to liberate H_2 and from oxides of C. The temperature is around 1000°C
(*d*) The uppermost layer of the bed is the *drying and carbonisation zone.* The water vapor and the volatile matter are added to the escaping gas which results in production of enriched gases. The topmost zone serves to preheat the precarbonised fuels coming in. The temperature of this zone is from 400°C-800°C. The average composition of the producer gas is CO: 22-30%, H_2: 8-12%, N_2: 52-55%, CO_2: 3%.

Producer gas is used for heating the furnaces for the production of steel and glass, muffle furnaces for coal gas production, and in metallurgical operations.

For the production of producer gas, only air can be used, steam used along with air is advantageous since (*i*) it raises the content of combustible components (CO + C_2) compared to noncombustible thereby increasing calorific value, (*ii*) the endothermic reaction of steam and C prevents localised overheating of a fuel bed and leads to diminished clinker formation.

Water Gas

Water gas is a gaseous fuel of medium calorific value (2800 kcal/m^3) generated by gasifying solid incandescent source of carbon in superheated steam. The equipment is known as water gas generator and is more or less similar to that shown in Fig. 18.12 where the following reaction takes place which is endothermic

$$C + H_2O \longrightarrow CO + H_2 - 29 \text{ kcal}$$

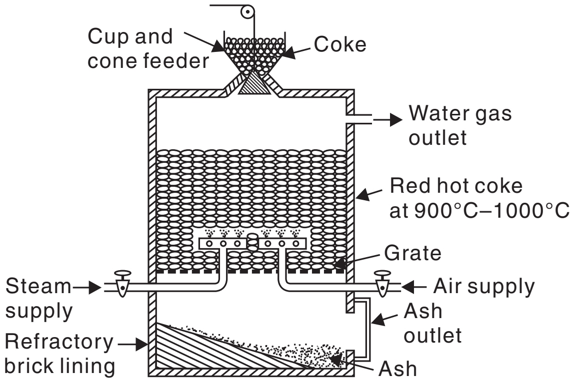


Fig. 18.13 Water gas production.

This gas burns with a blue flame owing to high carbon monoxide content and hence known as blue water gas. The bed of coke in the reactor is at 1400°C to 1000°C. As the reaction is endothermic temperature gradually falls and when it comes to 1000°C the blast of steam is stopped and air blast is passed and the following exothermic reactions occur.

$$C + O_2 \longrightarrow CO_2 + 97 \text{ kcal}$$
$$2C + O_2 \longrightarrow CO + 59 \text{ kcal}$$

The reaction again rises and these cycles alternately take place to maintain the temperature. After the production, ash is removed and the generator recharged. The water gas passing through the superheater is cooled and then purified.

The average composition is H_2: 51%, CO: 41%; N_2: 4%, CO_2: 4%

Blue water gas is used as a source of hydrogen, as a fuel gas.

The calorific value of water gas can be enhanced by adding gaseous hydrocarbons (obtained from cracking crude oils) to get *carburetted water gas* (Calorific value 4500 kcal; $CO_2 \rightarrow 3\%(m^3)$); composition of carburetted water gas is 35% H_2, 25% CO, 35% saturated and unsaturated hydrocarbons and 5% $N_2 + CO_2$.

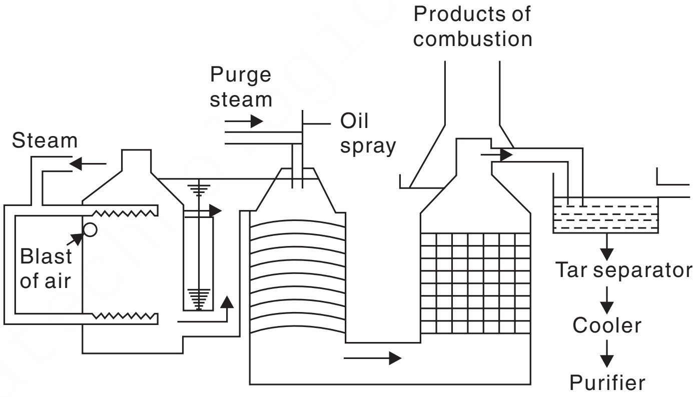


Fig. 18.14 Manufacture of carburetted water gas.

Biogas Production

Aquatic plants, organic wastes from domestic, agricultural and industrial sectors with high B.O.D. value (Feed stock) are digested anaerobically to produce *biogas*. The biogas is totally used as fuel. The chief constituent of biogas is methane, so the process is also called *biomethanation*. Composition of biogas is given below:

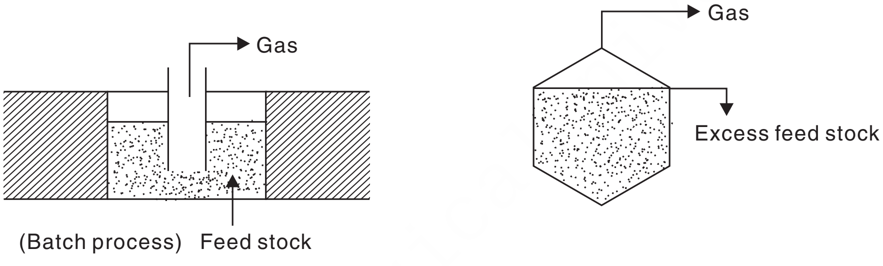
Component	*Volume%*
CH_4	52-95
CO_2	9-45
H_2S	0.001-2
H_2	0.01-2
N_2	0.1-4
O_2	0.02-6.5
CO	0.001
NH_3	Small

Conditions for Biomethanation

- Temperature = 35°
- pH = 6.8-8.2
- Anaerobic condition.
- Trace elements = Na^+, Co^{+3}, Ni^{+2} etc.

Arrangements for Biomethanation

Feed stock is mainly cowdung.



(a)

(b) Feed stock

Fig. 18.15

Better quality of coal should have low nitrogen and sulphur content. Higher percentage of oxygen is also undesirable as an increase in 1% oxygen content decreases the calorific value by about 1.7%.

Method of Analysis of Flue Gas

Analysis of flue gas will indicate the complete or incomplete combustion of a fuel; which is very essential in respect of efficient utilization of the fuel. The analysis is done in Orsat's apparatus and is based on the principle of absorption of

- CO_2 in KOH solution (500 gl^{-1}, 500 ml)
- O_2 in alkaline pyrogallic acid (25 g of pyrogallic acid in 400 gl^{-1} KOH solution, 500 ml)
- CO in ammoniacal cuprous chloride solution (100 g Cu_2Cl_2 + 125 ml liquor ammonia + Rest water to make up the volume, 500 ml).

Description of the Apparatus

It consists of a water jacketted measuring burette, connected in series with the absorption bulbs containing the above three solutions successively as depicted in the Fig. 18.16. The water jacket maintains the temperature of the gas constant. The absorption bulbs are filled with glass tubes for better absorption of the gases.

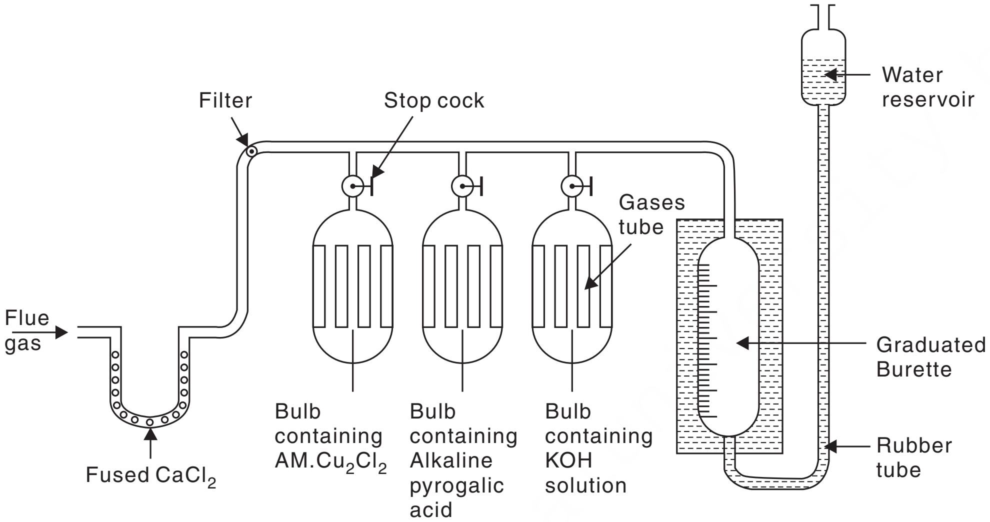


Fig. 18.16

Procedure

- The apparatus is tested for its air-lightness.
- The flue gas (100 ml) is taken in the apparatus in the measuring burette by adjusting the volume by water reservoir atmospheric pressure.
- The stopper (1) is opened for CO_2 absorption and water reservoir is raised to force the gas inside the bulb. The gas is finally taken in the burette and the volume of the gas is measured by making the levels of water inside the burette and water reservoir equal. The decrease in volume gives the percentage by volume of CO_2 in the flue gas.
- The stopper (2) is opened and provided as usual to get the percentage by volume of O_2 in the flue gas.
- The stopper (3) is opened and proceeded as usual to get the percentage by volume of CO in the gas.
- The sequence of the bulbs should be strictly followed.

Implications of the Analysis

- If the flue gas contains greater percentage of CO it is implied that considerable wastage of fuel is taking place due to incomplete combustion and the O_2 supply is insufficient.
- The greater percentage of O_2 in the flue gas indicates that O_2 supply is in excess.
- Result of the analysis will help to control the combustion process.

SOLVED EXAMPLES

Example 1. *A sample of coal contains:*

$$C = 93\%,\ H = 6\%\ \text{and ash} = 1\%$$

Calculate the gross and net calorific V value of the coal from the following data:

Weight of coal burnt (m) = 0.92 g

Weight of water taken (w) = 550 g

Water equivalent of bomb calorimeter (W) = 2,200 g.

Rise in temperature $(t_2 - t_1) = 2.42°C$*; Fuse wire correction = 10 cal.*

$L = 580$ *cal/g*$^{-1}$.

Sol.
$$\text{HCV} = \frac{(\text{W} + w)\,(t_2 - t_1) - [\text{acid} + \text{fuse}]\text{ correction}}{m}$$

$$= \frac{(2{,}200 + 530) \times 2.42 - [50 + 10]}{0.92}\ \text{cal/g}^{-1}$$

$$= \mathbf{7168.5\ cal/g}$$

Net Calorific Value (NCV)

$$= (\text{HCV} - 0.09\ \text{H} \times \text{L})\ \text{cal/g}^{-1}$$

$$= (7168.5 - 0.09 \times 6 \times 580)\ \text{cal/g}^{-1}$$

$$= \mathbf{6{,}855.3\ cal/g.}$$

Example 2. *A sample of coal was analysed as follows:*

Exactly 2.5 g was weighed in a silica crucible, after heating for 1 hr. at 110°C the residue was weighed to be 2.415 g. Next the crucible was covered with a rented lid and strongly heated for exactly 7 mins. at 1000°C. The residue was weighed to be 1.528 g. Then the crucible was heated without cover until a constant weight to 0.245 g was obtained. From the above data calculate the proximate analysis of coal.

Sol. Moisture in the sample = (2.5 – 2.915)g = 0.085 g

$$\text{So, \% moisture} = \frac{0.085}{2.5} \times 100 = 3.4$$

So, amount of volatile carbonaceous matter (VCM) in the sample = (2.415 – 1.528) g = 0.887 g.

$$\text{So, \%}\quad \text{VCM} = \frac{0.887 \times 100}{2.5} = 35.48\%$$

$$\%\ \text{Ash} = \frac{\text{Weight of ash}}{\text{Weight of coal}} \times 100$$

$$= \frac{0.245}{2.5} \times 100 = 35.48\%$$

$$\text{Fixed carbon} = (1.528 - 0.245)\text{g} = 1.283\ \text{g}$$

$$\%\ \text{Fixed carbon} = \frac{1.283 \times 100}{2.5} = 51.32\%.$$

Example 3. *On burning 0.83 g of a solid fuel in bomb calorimeter, the temperature of 3,500 g of water increased from 26.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385 g and 587 cal/g, respectively. If the fuel contains 0.77% H, calculate HCV and NCV.*

Sol.
$$\text{HCV} = \frac{(\text{W} + w)\,(t_2 - t_1)}{m}$$

$$= \frac{(385 + 3500)\,(29.2 - 26.5)}{0.83} = 12638\ \text{cal g}^{-1}$$

$$\text{NCV} = (\text{HCV} - 0.09\ \text{H} \times \text{L})\ \text{cal g}^{-1}$$

$$= (12638 - 0.09 \times 0.7 \times 587)\ \text{cal g}^{-1} = 12601\ \text{cal g}^{-1}.$$

Example 4. *An ultimate analysis of 1 g coal for nitrogen (N) estimation is the Kjelldahl method, the evolved* NH_3 *has collected in 25 ml* $\left(\frac{N}{10}\right)$ H_2SO_4 *acid solution. To neutralise the excess acid, 15 ml of 0.1 (N) NaOH was required. Calculate the % of nitrogen in the given sample.*

Sol. In the Kjelldahl method organic compounds containing nitrogen are heated with concentrated H_2SO_4 to convert to $(NH_4)_2SO_4$. This $(NH_4)_2SO_4$ during soiling with alkali liberates NH_3 that is absorbed in H_2SO_4 $\left(\frac{N}{10}\right)$. Excess acid is titrated with NaOH.

The volume of H_2SO_4 consumed by NH_3 $(25 \times .1 - 15 \times .1)$ ml (N) = 1 ml (N)

Now, 100 c.c(N) $H_2SO_4 \equiv 17$ g $NH_3 \equiv 14$ g N.

$$\therefore \quad 1 \text{ c.c(N) } H_2SO_4 = \frac{14}{1000} \text{ gN} = 0.014 \text{ gN}$$

Again 0.014 g Nitrogen is present in 1 g coal.

$$\text{So, \% of N in the coal sample} = \frac{0.014}{1} \times 100 = 1.4\%.$$

Example 5. *A gaseous fuel has the following composition of volume:*

$$H_2 = 24\%;\ CH_4 = 30\%;\ C_2H_6 = 11\%,$$
$$C_2H_4 = 4.5\%;\ C_4H_8 = 2.5\%;\ CO = 6\%;\ CO_2 = 8\%;$$
$$O_2 = 2\% \text{ and } N_2 = 12\%.$$

Calculate (i) air to fuel ratio and (ii) volume of dry products of combustion using 40% excess air.

Sol. Basis: 1 m^3 of gaseous fuel.

Volume of combustible gases (m^3)	*Reaction*	*Volume of O_2 m^3*	*Volume of products of combustion on dry basis (m^3)*
$H_2 = 0.24$	$H_2 + \frac{1}{2}O_2 = H_2O$	$0.24 \times \frac{1}{2} = 0.12$	–
$CH_4 = 0.30$	$CH_4 + 2O_2 = CO_2 + 2H_2O$	$0.3 \times 2 = 0.60$	$CO_2 = 0.3$
$C_2H_6 = 0.11$	$C_2H_6 + 3\frac{1}{2}O_2 = 2CO_2 + 3H_2O$	$0.11 \times \frac{7}{2} = 0.385$	$CO_2 = 0.11 \times 2 = 0.22$
$C_2H_4 = 0.045$	$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$	$0.045 \times 3 = 0.135$	$CO_2 = 0.045 \times 2 = 0.09$
$C_4H_8 = 0.025$	$C_4H_8 + 6O_2 = 4CO_2 + 4H_2O$	$0.025 \times 6 = 0.15$	$CO_2 = 0.025 \times 4 = 0.1$
$CO = 0.06$	$CO + \frac{1}{2}O_2 = CO_2$	$0.06 \times \frac{1}{2} = 0.03$	$CO_2 = 0.06 \times 1 = 0.06$
		Total = 1.42 m^3 Less = 0.02 m^3	Total = 0.77 m^3 CO_2 in fuel = 0.08 m^3
		Net need = 1.4 m^3 (O_2)	Net CO_2 = 0.85 m^3

Volume of air required (when 40% excess)

$$1.4 \times \frac{100}{21} \times \frac{140}{100} = 9.333 \text{ m}^3$$

$$\therefore \qquad \text{air: fuel} = 9.333{:}1 \qquad \ldots(i)$$

Total volume of dry products = CO_2 + N_2 (from fuel + air) + O_2 (excess)

$$= 0.85 + \left[0.12 + \left(\frac{79 \times 9.33}{100}\right)\right] + \left(9.33 \times \frac{21}{100} - 1.4\right) \text{m}^3 = 8.782 \text{ m}^3$$

Composition of product of combustion on dry basis.

$$CO_2 = \frac{0.82 \times 100}{8.782} = 9.337\%$$

$$N_2 = \frac{7.373 \times 100}{8.782} = 83.95\%$$

$$O_2 = \frac{.559 \times 100}{8.782} = 6.365\%.$$

Example 6. *Calculate the volume of air required for complete combustion of 1 m³ of a gaseous fuel having the composition*

$CO = 46\%$, $CH_4 = 10\%$; $H_2 = 40\%$

$C_2H_2 = 2\%$; $N_2 = 1\%$ and the remaining being CO_2.

Sol. Basis: 1 m³ of the gaseous fuel.

Combustible gases in the fuel (m³)	*Reaction*	*Volume of O_2 required (m³)*
$CO = 0.46$	$CO + \frac{1}{2} O_2 = CO_2$	$0.46 \times \frac{1}{2} = 0.23$
$CH_4 = 0.10$	$CH_4 + 2O_2 = CO_2 + 2H_2O$	$0.1 \times 2 = 0.20$
$H_2 = 0.4$	$H_2 + \frac{1}{2} O_2 = H_2O$	$0.4 \times \frac{1}{2} = 0.20$
$C_2H_2 = 0.02$	$C_2H_2 + 2\frac{1}{2} O_2 = 2CO_2 + H_2O$	$0.02 \times \frac{5}{2} = 0.05$
		Total $O_2 = 0.68$ m³ required

As air contains 21% of O_2 by volume

$$\therefore \quad \text{Volume of air required} = \left(0.68 \times \frac{100}{21}\right) \text{m}^3 = 3.238 \text{ m}^3.$$

SHORT QUESTIONS AND ANSWERS

Q. 1. What is a coke?

Ans. It is a carbonaceous residue obtained from the destructive distillation of coal, petroleum and coal tar pitch. Petroleum yields coke during cracking processes. The main source of coke is coal. Petroleum coke is used as metallurgical coke since it is pure.

Q. 2. What is a fluidised bed?

Ans. Finely divided solids suspended in a moving gas or liquid behave like a fluid. Catalyst in this form is used for catalytic cracking.

Q. 3 What is petroleum?

Ans. It is a highly complex mixture of paraffinic, cycloparaffinic (naphthenic) and aromatic compounds with traces of N, O and low percentage of S and is obtained from underground.

Q. 4. What is Naphtha?

Ans. It is a refined petroleum product 90% of which distils below 240°C and 10% distils below 175°C. It is obtained by cracking of petroleum and mainly used as thinners for paints and varnishes.

Q. 5. What is flash point?

Ans. It is the lowest temperature at which the vapour of a volatile liquid or solid gets ignited by a small flame *e.g.,* flash point of kerosene is 90°F.

Q. 6. What is an anti-knocking agent?

Ans. They are organometallic compounds that increase the octane number of gasoline when added in low percentage to it. Most common is TEL (-tetraethyl lead). They can increase the octane number over 100%.

Q. 7. What are Octane Number and Cetane Number?

Ans. See text page 396.

Q. 8. What is aviation gasoline?

Ans. It is a variety of gasoline having high octane number *i.e.,* 100 and high volatility and hence used for aircraft. The main components of aviation gasoline are isoparaffins and some TEL.

Q. 9. What is straight run gasoline?

Ans. Gasoline obtained by direct distillation of petroleum without using other conversion processes like cracking is known as straight run gasoline. Its octane number is low.

Q. 10. (a) What is LPG? (b) What is LNG?

Ans. (*a*) LPG or Liquefied petroleum gas is obtained from 'Wet Natural gas' from underground, by washing it with gas oil and fractionating the useful fraction.

(*b*) LNG is Liquefied Natural gas.

Q. 11. What is reforming?

Ans. See text page 395.

Q. 12. What is the difference between gross and net calorific values?

Ans. See text page 378.

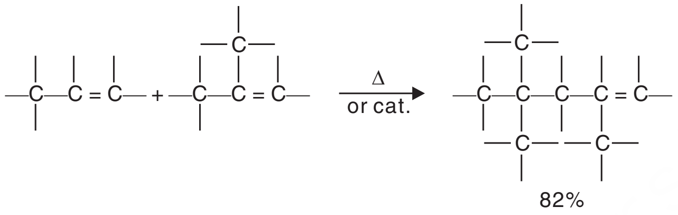
Q. 13. Mention the basic reactions or conversion processes for petrochemical industry.

Ans. Petroleum offers a fertile field both for gasoline and for petrochemicals. The following examples are a few of the more important basic reactions.

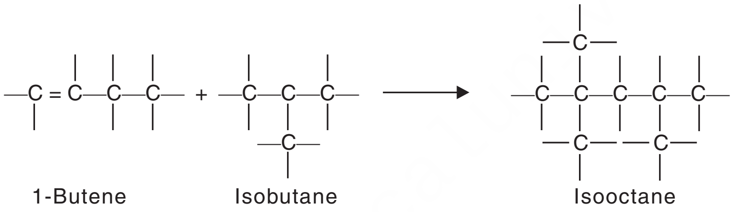
- *Cracking*

$$C_7H_{15}.C_{15}H_{30}.C_7H_{15} \xrightarrow{\Delta} \underset{\text{gasoline}}{C_7H_{16}} + \underset{\text{antiknock gasoline}}{C_6H_{12} = CH_2 + C_{14}H_{28}} = CH_2$$

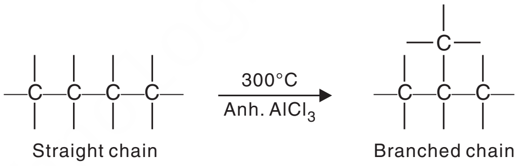
- *Polymerisation*



- *Alkylation*

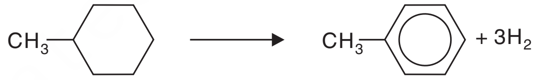


- *Isomerisation*

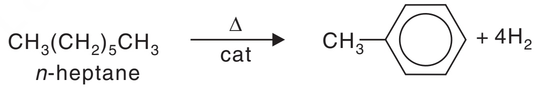


- *Hydroforming or Aromatisation*

(*i*)



(*ii*)



Q. 14. What is Benzol?

Ans. Benzol is a coal tar distillation fraction (b.p. 70-150°C) containing 70% benzene, 18% toluene and 6% xylenes. It is blended with petrol. It has octane rating 87-90. The blended petrol is a good motor fuel.

Q. 15. What is power alcohol?

Ans. Ethyl alcohol when blended with petrol to be used as a fuel for internal combustion engine, is known as power alcohol.

Q. 16. What is gasohol?

Ans. It is a mixture of gasoline and alcohol.

gasoline + alcohol = gasohol.

The use of grain alcohol as a blending agent with petrol is a controversial issue in the world. Though blending will reduce 10% petrol consumption but alochol production by fermentation will make use of food grains which is not desirable. Moreover, rectified spirit (95% alcohol) is not suitable for blending, 99.5% alcohol is to be produced which will make the cost higher. That is why now-a-days butanol is tried for the purpose.

Q. 17. What is oil gas?

Ans. Oil gas is mainly obtained by cracking of kerosene oil. But other oils like diesel and heavy oils and petrol may also be used for cracking. A device is set up where a plate is heated specially electrically and the oil is allowed to drop on the hot plate. The oil is cracked to lower gaseous hydrocarbons.

$$C_{12}H_{26} \longrightarrow CH_4 + C_2H_6 + C_2H_4 + C_2H_2 + \text{etc.} + \text{tar}$$

The resulting gases are passed generally through a hydraulic main and collected in a gas holder by displacement of water.

The composition of oil gas is

CH_4 = 25-30%, H_2 = 50-55%, CO = 10-12%, CO_2 = 3%,
Calorific value = 54000 kcal/m^3.

The gas is mainly generated for laboratory use.

Q. 18. What are the advantages of a gaseous fuel?

Ans.

- Can be distributed over a wide area by pipeline.
- Smooth combustion without smoke and ash.
- The temperature of heating can be controlled by controlling the gas flow to the burner.
- Higher calorific values.

Q. 19. Mention the disadvantages of a gaseous fuel.

Ans.

- Danger of explosion
- Larger scale fire risk.

Q. 20. What is an anti-knocking agent?

Ans. The organometallic compounds like TEL or TML, which increase octane number of a fuel.

Q. 21. What is an aviation gasoline?

Ans. The variety of gasoline specially suitable for aircraft having octane number well over 100.

Q. 22. Why is sulphur content controlled below 0.1%?

Ans. Sulphur and sulphur compounds greatly reduce effectiveness of TEL to increase the octane number of a fuel.

Q. 23. What is a natural gasoline?

Ans. A mixture of butane, pentane, and hexane obtained from natural gas.

Q. 24. What is HDA process?

Ans. Gasoline produced, for the manufacture of ethene, as a byproduct is known as pyrolysis gasoline. This gasoline is mainly used to produce benzene by Hydro-DeAlkylation (HDA) process.

$$CH_3(CH_2)_8CH_3 \xrightarrow{700\text{ K}} \underset{\text{octane}}{C_8H_{18}} + \underset{\text{ethene}}{CH_2 = CH_2}$$

$$C_8H_{18} \xrightarrow{\text{HDA}} C_6H_6$$

Q. 25. What is white gasoline?

Ans. It is unleaded gasoline used for motor boats.

Q. 26. Why is calorific value of coal gas higher than that of producer gas?

Ans. Coal gas contains all the combustible gases like CH_4, C_2H_4, C_2H_2, CO and H_2, whereas producer gas contains CO, H_2 and N_2. N_2 acts as inert diluent.

So calorific value of coal gas is higher than that of producer gas.

Q. 27. Producer gas is made by passing air and steam through a thick bed of coal. Why?

Ans. The primary purpose of steam is to use up the heat developed during exothermic reaction of coal and O_2 of air to maintain the temperature of producer.

Q. 28. Why is NCV greater than GCV?

Ans. Gross calorific value GCV includes the latent heat steam during combustion of a fuel, but Net calorific value NCV excludes the latent heat of steam.

Q. 29. Why a good solid fuel must have low ash content?

Ans. Ash is inorganic in nature. So high ash content decreases the calorific value of a fuel.

Q. 30. What is CNG?

Ans. CNG is compressed natural gas used in motor engines now-a-days instead of gasoline fuel causing less pollution.

Q. 31. What is synthesis gas or syn gas?

Ans. Modern processes produce a mixture of CO and H_2 from coal and steam more efficiently than the old water gas and producer gas plants. Two varieties of gas are obtained: (*i*) *Low heat gas* (*ii*) *Medium heat gas*. Low heat gas contains 50% N_2. These gases are known as synthesis or syn gas. The gasification is done in fixed bed: (*i*) Fluidised bed.(*ii*) Entrained bed.

Reactions:

(*i*) $C + H_2O = CO + H_2$

(*ii*) $CO + H_2O = CO_2 + H_2$

(*iii*) $C + CO_2 = 2CO$

Q. 32. What is SNG (Substitute Natural Gas)?

Ans. (*i*) During the production of syn gas, at sufficiently high pressure *i.e.*, during hydrogasification H_2 liberated converts carbon to CH_4.

$$C + 2H_2 = CH_4,\ CO + 3H_2 \xrightarrow{\text{cat}} CH_4 + H_2O$$

The gas produced was known as synthetic natural gas. But the synthetic product cannot be known as natural; so now it is called substitute natural gas (SNG). The operating pressure may be atmospheric to 7 MPA and temperature 800°C-1650°C for gasification. The higher pressure and lower temperature result in the formation of larger amount of SNG.

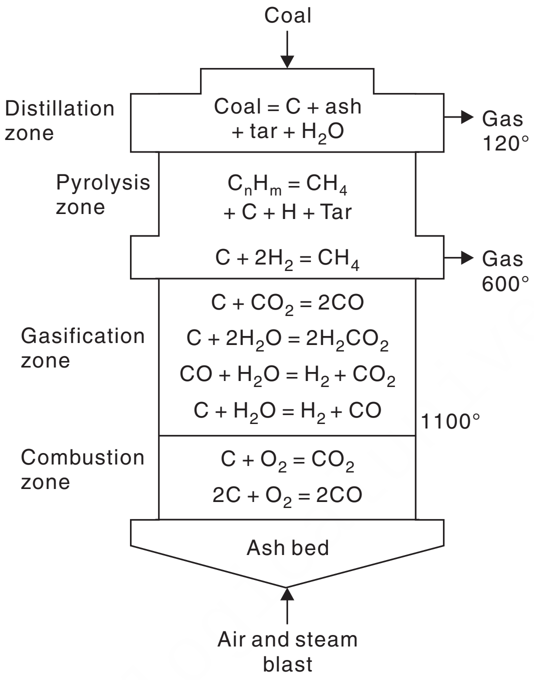


Fig. 18.17 Showing gasification reactions involved in a gasifier.

EXERCISES

1. What is sweetening of petrol?
2. What is flue gas? How is it analysed?
3. Describe the fluidized bed cracking of petroleum mentioning the catalysts used.
4. Describe the manufacture of producer gas? What are its uses?
5. What is leaded-petrol?
6. Write the difference between proximate and ultimate analyses.
7. Describe the manufacture of biogas from waste materials.
8. How is the calorific value of a fuel determined?
9. Write notes on:
   (*i*) Bomb calorimeter.
   (*ii*) Octane number
   (*iii*) Catalytic cracking
   (*iv*) Proximate analysis.
10. What is carbonization? Write the advantages of high temperature carbonization.
11. What is power alcohol?
12. Write a brief note on:
    (*i*) Synthetic petrol
    (*ii*) Blue water gas.

13. (*a*) What are fuels? How do you classify them? Describe methods employed for ultimate analysis of coal.

(*b*) Explain the terms (*i*) Knocking (*ii*) Octane number (*iii*) Cetane number.

14. (*a*) What is sweetening of petrol? Name the various fractions obtained during the fractional distillation of crude petroleum oil.

(*b*) What is the flue gas? How is it analysed?

15. What is meant by cracking of petroleum? Describe various methods used for cracking of petroleum.

16. Write a short note on biogas.

17. Describe fixed bed catalytic cracking.

18. How are gross and net calorific values of a solid fuel determined using a Bomb calorimeter?

19. Give a detailed account of petroleum refining.

20. Give at least four advantages of catalytic cracking over thermal cracking.

21. What is L.P.G.? Give its uses.

22. What do you understand by cetane number of a fuel? Distinguish between high speed diesel and low speed diesel.

23. Mention advantages and disadvantages of a gaseous fuel.

24. What is the difference between claking coals and coking coals?

25. What is power alcohol? Mention its merits and demerits?

26. Give the constituents and uses of Gobar gas.

27. Discuss giving equations, sketch, manufacture and composition of:

(*a*) Producer gas (*b*) Water gas (*c*) Oil gas.

28. Write a short note on:

Orsat's method of flue gas analysis and its significance.

29. Write short notes on:

(*i*) Catalytic converter (*ii*) Octane and cetane numbers.

30. Write a short note on: Carburetted water gas.

31. What is ultimate analysis of coal?

32. What is the difference between H.T.C. and L.T.C.?

33. Mention the byproducts of coking of coal.

OBJECTIVE TYPE QUESTIONS

1. Which of the fuel gases has highest calorific value?

(*a*) Water gas (*b*) Coal gas (*c*) Producer gas.

2. The calorific value of a coal sample is higher if its

(*a*) Moisture content is high

(*b*) Volatile matter is high

(*c*) Fixed carbon is high.

3. Calorific value of coal is decreased due to presence of

(*a*) Carbon (*b*) Sulfur (*c*) Hydrogen (*d*) Oxygen.

4. Which of the following contains highest percentage of volatile matter?

(*a*) Peat (*b*) Lignite (*c*) Bituminous coal (*d*) Anthracite.

5. Analysis of flue gases is done by:
(*a*) Bomb calorimeter (*b*) Orsat's apparatus (*c*) Boy's gas calorimeter.

6. Alcohol-blended petrol possesses
(*a*) Better calorific value
(*b*) Reduced antiknock properties
(*c*) Better antiknock properties.

7. Anthracite is a coal of
(*a*) Highest calorific value
(*b*) Lowest rank
(*c*) High volatile matter.

8. Fuel gas used as a source of hydrogen is
(*a*) Natural gas (*b*) Producer gas (*c*) Water gas.

9. Isooctane has an octane rating of
(*a*) Zero (*b*) 100 (*c*) More than 100.

10. Better diesel fuel is determined by
(*a*) Octane rating (*b*) Cetane number (*c*) C content.

11. Producer gas is a mixture of
(*a*) $CO + H_2$ (*b*) $CH_4 + H_2$ (*c*) $CO + N_2$

12. Fuel for jet plane is
(*a*) Aviation gasoline (*b*) Kerosene (*c*) Diesel.

13. Natural gas is composed of:
(*a*) *n*-butane (*b*) Methane (*c*) Isooctane.

14. Proximate analysis of fuel determines the percentage of
(*a*) C, H_2O, ash and volatile matter
(*b*) C, H, N, S (*c*) C and H.

15. Bomb calorimeter is used to measure
(*a*) Calorific value (*b*) Carbon content (*c*) Knocking properties.

19

Silicate Technology

INTRODUCTION

Glass and Pottery are the earliest products of man made chemical industry. Glass was known to the ancient Egyptians 6000 years ago. Glass is an amorphous, transparent or translucent, rigid super supercooled liquid of infinitely high viscosity comprising of *metallic silicates* one of which is usually of an alkali metal. Ceramic products are made of clay which are silicates, cement is also a mixture of silicates and other compounds. So, all these industries fall under silicate technology.

Silicates are chemical compounds of silicon and oxygen with metals. Clay and soil are different products. Clay must not be confused with soil. Soil is the thin outermost layer of the earth. *Soil is infact a mixture of clay, sand, humus (decayed vegetable matter) and various other minerals.*

Clay is a mixture of variety of minerals like bentonite, kaolinite, hauoysite etc. Basically most of these are *hydrated silicates of aluminium.* The structural pattern of silicates are important in different ceramic products which have been shown in following figures: In a silicate unit silicon atom is symmetrically surrounded by four oxygen atoms to form a tetrahedral unit. These tetrahedral units remain joined in the silicates (see Fig. 19.1).

Chain silicates. These silicates are of two types *viz., single chain silicates and double chain silicates.* Single chain silicates contain $[(SiO_3)_n]^{-2n}$ ion as the primary unit (Fig. 19.1), while double chain silicates contain $[(Si_4O_{11})_n]^{-6n}$ as the primary unit (Fig. 19.2).

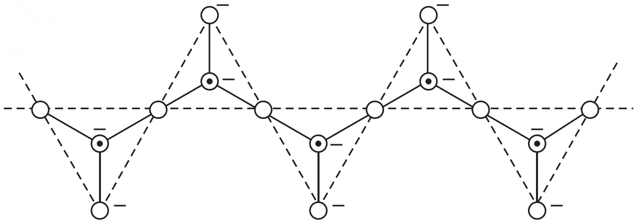


Fig. 19.1 Structure of $[(SiO_3)_n]^{-2n}$ ion (single chain). ⊙ — Silicon atom, ○ — Oxygen atom.

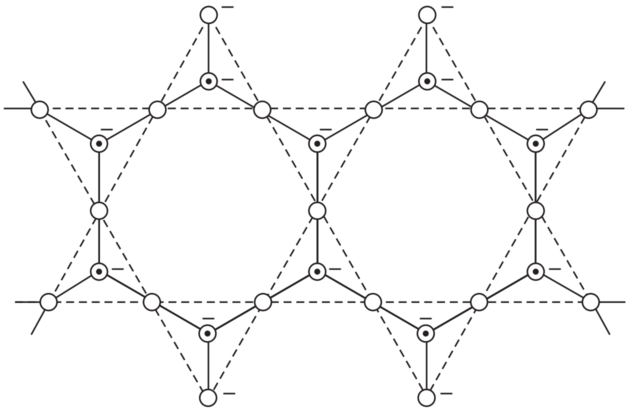
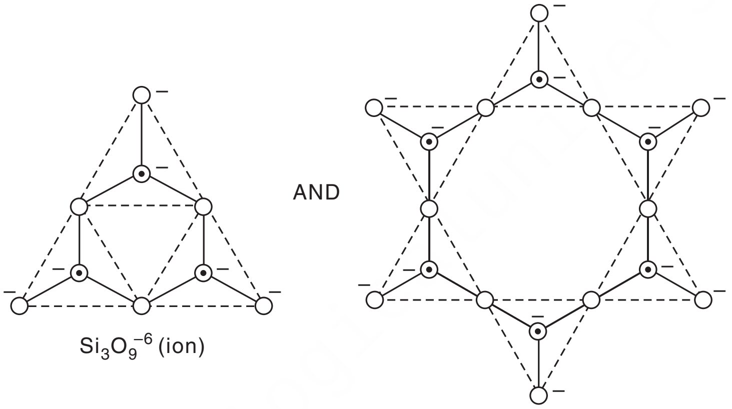


Fig. 19.2 Structure of $[(Si_4O_{11})_n]^{6n-}$ ion (double chain).

It may be noted that O-atoms, which are shared by SiO_4^{4-} tetrahedrons, do not contain any negative charge, *i.e.,* O-atoms, forming a bridge between SiO_4^{4-} tetrahedral units, do not carry any negative charge, O-atoms, forming no bridge, carry negative charge.

Cyclic or ring silicates (Fig. 19.3). These silicates have cyclic structure and contain $[(SiO_3)_n]^{-2n}$ ion as the primary unit. These silicates are formed when each SiO_4^{4-} tetrahedron shares two O-atoms (bridging O-atoms). *Bentonite* is an example: $BaTiSi_3O_9$.



$Si_3O_9^{-6}$ (ion)

$Si_6O_{18}^{-12}$ (ion)

Fig. 19.3 Structure of $Si_3O_9^{-6}$ and $Si_6O_{18}^{-12}$ ions (ring).

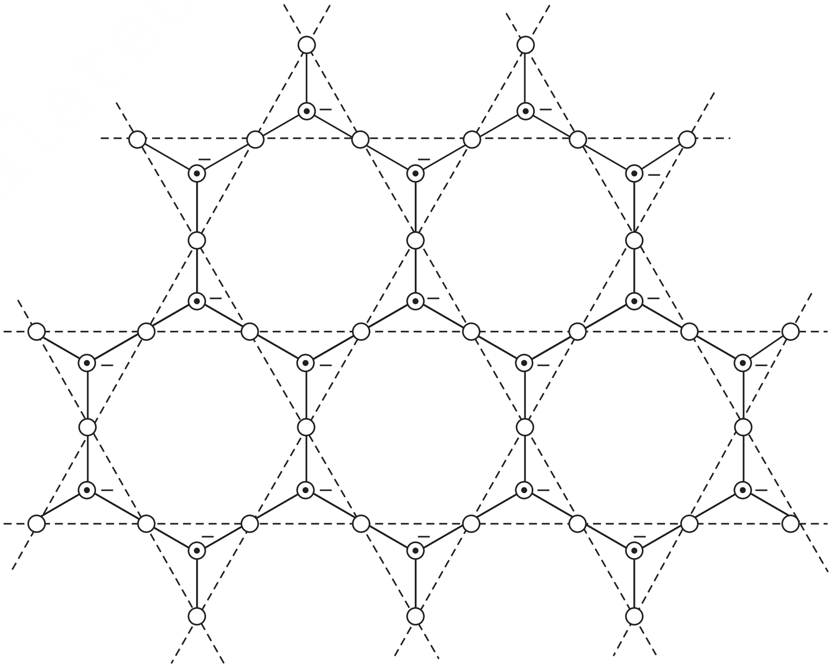


Fig. 19.4 Structure of sheet silicates (layered structure).

Clay or silicates are common raw materials for

- Ceramic industries
- Refractory industries
- Glass industries and
- Cement industries.

For that reason the technologies of these industries fall under the common name *silicate technology*. Generally silicate materials are bad conductor of heat and electricity. Now-a-days, some new types of ceramics are discovered with electrical and magnetic properties. These properties depend on their unit structure. These ceramics are called *high performance ceramics.* The individual solid metal oxides were mixed in the proper ratio, ground well and finally heated to 1000°C for 12 hrs, at this high temperature the individual oxides are converted into the mixed oxide compound. The property of super-conductivity in these compounds is dependent on a particular characteristic of arrangements of constituent atoms. For example, in $YBa_2Cu_3O_{7-y}$ (see Fig. 19.5) successive horizontal layers of copper-oxygen sheets are separated by ribbon-like chains of copper-oxygen. The square copper-oxygen sheets are the pathways of super-conducting electrons in these compounds. Even slight alteration of the arrangement of atoms destroys superconductivity. The preparation of superconducting ceramic therefore, is an exacting piece of work.

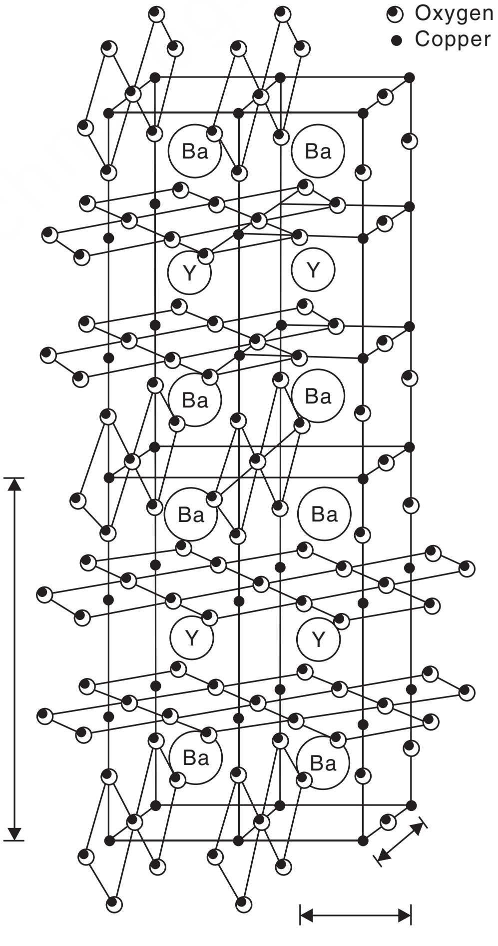


Fig. 19.5 The crystal lattice of $YBa_2Cu_3O_{7-y}$.

These types of superconductors are used in superfast magnetically leviated (maglev) train *i.e.*, superfast floating train. This is an example of application ceramic superconductor like $YBa_2Cu_3O_{7-y}$.

CEMENT

The present day civilization very much depends upon lime, mortar and cement products, *viz.* reinforced-concrete walls and girders (a chief beam), tunnels, dams and roads etc. The tremendous application of these products is due to their:

- Convenience
- Cheapness
- Adaptability
- Strength
- Durability

Man had early discovered certain natural rocks. The rocks on calcination gave a product that hardened on the addition of water. Cement was first used by the Egyptians in constructing the pyramids. The Greek and Romans used volcanic tuff for cement and a number of these structures are still standing. In 1824, an Englishman, Joseph Aspdin, patented an artificial cement made by the calcination of an argillaceous lime stone (argil-clay). He called this 'Portland' as concrete made from it resembled a famous building stone obtained from the Portland island near England. This was the start of the Portland cement industry as we know it today. The hard clinkers (Brick type) resulting from the burning of argilaceous limestone is known by the term *Portland cement* to distinguish it from natural or Pozzuolana and other cements.

The cement will set under water and therefore it is known by the name of *Hydraulic cement*. A cement is a substance, which sets to a hard mass in presence of water. Two types of cements are in use.

- Roman cement
- Portland cement.

Of these, Portland cement is now manufactured on a large scale. *Portland cement is made by mixing calcareous (lime-stone) and argilaceous materials in the proper ratios and heating to the point of incipient fusion in a kiln and grinding the resulting clinker.* The raw materials should be so proportioned as to produce a cement in which the ratio of the amount of CaO to the amount of ($2.8\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2O_3$) should not be more than 1.02 and not less than 0.66 *i.e.*,

$$0.66 \le \frac{CaO}{2.8\,SiO_2 + 1.2\,Al_2O_3 + 0.65\,Fe_2O_3} \le 1.02$$

The Portland cement is a mixture of the following compounds:

Compounds	*Formula*	*Abbreviation*
(*i*) Tricalcium aluminate	$3\ CaO\ .\ Al_2O_3$ **or** $(CaO)_3\ .\ Al_2O_3$	C_3A
(*ii*) Tricalcium silicate	$3\ CaO\ .\ SiO_2$ **or** $(CaO)_3\ .\ SiO_2$	C_3S
(*iii*) Dicalcium silicate	$(CaO_2)\ .\ SiO_2$ **or** $2CaO\ .\ SiO_2$	C_2S
(*iv*) Tetracalcium alumino ferrate	$(CaO)_4Al_2O_3\ .\ Fe_2O_3$ **or** $4CaO\ .\ Al_2O_3\ .\ Fe_2O_3$	C_4AF

Small amount of MgO derived from the raw materials is also present. Some cement contains gypsum or plaster of paris, which is added in small quantities to increase the plasticity of cement.

Varieties of Cement

- *Portland cement.* The regular Portland cement contains medium amount of CaO. *White cement contains less ferric oxide.* High early strength cement [H.E.S] is made from a raw material with a high lime to silica ratio. It contains a higher proportion of C_3S than regular Portland cement and hence hardens much more quickly. Roads constructed from H.E.S. can be put into service more quickly than if regular cement had been employed. Low heat portland cement contains high proportion of C_4AF and C_2S. A concrete of better chemical resistance contains high proportion of C_4AF.
- *Pozzuolana cement.* A pozzuolana is a material, which is not cementitious in itself but becomes so upon mixing with lime. The natural pozzuolana are volcanic tuffs, the artificial ones are burnt clays and shales.
- *High alumina cement.* It is manufactured by fusing a mixture of limestone and bauxite (contains Fe_2O_3, SiO_2, MgO etc). It is characterised by a very rapid rate of development of strength and superior resistance to sea water and sulphate carrying water.
- *Special or corrosion resisting cement.* It is mainly used for the fabrication of corrosion proof linings for chemical equipment such as storage tanks, absorption towers, acid digesters etc. Example: phenolic cement–phenol formaldehyde resins.

Raw Materials

Formerly a large proportion of cement was burned from argilaceous limestone known as cement rock. In industries for CaO of cement, chalk, cement rock and marl (mixture of $CaCO_3$) and clay are used. In addition to natural materials some plants use artificial products such as blast furnace slag and precipitated $CaCO_3$ obtained as a by-product in alkali and synthetic ammonium sulphate industry.

Sand, waste bauxite and iron ore are sometimes consumed in small amounts to adjust the composition of the mix. Gypsum (2-3%) is added to prevent rapid setting of the C_3A.

List of Raw Materials: Limestone, cement rock, clay and shale, gypsum, blast furnace slag, sand, sandstone, marl, iron material, precipitated calcium carbonate and misc.

In India, the byproduct precipitated $CaCO_3$ from Sindri Fertilizer Corporation of India was utilised by A.C.C. Bihar company to manufacture cement. Rohtas Industries Ltd., Dalmianagar, Delhi uses (1) Laterite (red clay) and (2) limestone. Limestone is partly replaced by the $CaCO_3$ mud obtained as by-product during clarification of sugarcane juice at the sugar factory of the same company.

A processing of available raw materials is necessary to correct the proportions of the mineral sources of the four oxides of Ca, Si, Al and Fe essential for cement manufacturing and discard useless constituents, *i.e.,* the purpose is to '*benificiate*' available raw materials and hence the process is named *beneficiation* process. This may involve the raising of the lime content of the raw materials or it may be for the elimination of the greater part of the silica as compared to the alumina. The complete process involves a combination of **(1) grinding, (2) classification, (3) floatation and (4) thickening operation**.

In making these differential separations, very small quantities of collecting reagents are employed. The collecting agent must selectively wet or 'film' the mineral to be removed and act with the air to cause the particles to be lifted to the surface making a froth. That is, the froth floatation process is used to remove the undesirable material in the froth and oleic acid may be employed as the *collector*. A concentration of 0.04 lb per ton of rock suspended in 4 tons of water has given good results. Frothing aids in separation of desired materials from the undesired ones.

Manufacturing Procedure

Two methods of manufacture are used:

- ***Wet process***
- ***Dry process***

The wet process was the original one. For a time it was gradually displaced by the dry process. But the wet process is now being adopted largely for new plants for more accurate control and mixing of the raw mixture.

In the wet process, the solid material after dry crushing is reduced to a fine state of division in wet tube or ball mills and passes as a slurry through the bowl classifiers or screens. The slurry is pumped to correcting tanks where rotating arms make the mixture homogeneous and allow the final adjustment in composition of raw materials to be made. This slurry is filtered in a continuous rotary filter and fed into the kiln. The moisture content of the feed is 40%.

The dry process is especially applicable to natural cement rock and to the mixtures of limestone and shale or slate. In this process, the materials are roughly crushed in jaw crushers followed by gyratory mills, then dried, sized and more finely ground in tube mills. This dry powdered material (moisture content 2%) is fed directly to the kiln. Heat is provided by burning oil, gas or pulverised coal, using preheated air from cooling the clinker. 80-160 lbs of fuel are necessary per barrel (376 lbs) of cement.

The tendency in recent years has been to lengthen the rotary kiln in order to increase its thermal efficiency. Dry process kilns may be as short as 150 ft, but in the wet process, 300-500 ft kilns are not uncommon. The internal diameter is usually 8 to 15 ft. The kilns are rotated at from 1/2 to 2 r.p.m., depending on size. The kilns are slightly inclined so that materials fed in at the upper end and travel slowly to the lower end, taking from 2-3 hrs (Fig. 19.6).

In order to obtain greater heat economy, unit operations are used for removing the part of the water from slurry by slurry filters. Waste heat boilers are used to conserve heat.

Because the lining of kiln has to withstand severe abrasion and chemical attack at the high temperatures in the clinkering zone, the choice of refractory linning is difficult. For this reason, high alumina bricks and high magnesia bricks are widely used for the lining of the kiln, although Portland cement clinker itself is satisfactory for the purpose.

Reactions at various temperatures in the kiln

Temperature	*Reactions*	*Heat change*
100°C	Evaporation of water ($H_2O\uparrow$)	Endothermic
> 500°C	$Al_2O_3 \,.\, SiO_2 \,.\, xH_2O \longrightarrow Al_2O_3.SiO_2 + xH_2O$	Endothermic
> 900°C	$CaCO_3 \longrightarrow CaO + CO_2\uparrow$	Endothermic
900°C to 1200°C	$^*5CaO + 3\,Al_2O_3 \longrightarrow 5\,CaO \,.\, 3Al_2O_3$	
	$2CaO + SiO_2 \longrightarrow 2CaO \,.\, SiO_2$	
	$3CaO + SiO_2 \longrightarrow 2CaO \,.\, SiO_2$	Exothermic
	$2CaO + Al_2O_3 \longrightarrow 2CaO \,.\, Al_2O_3$	
	$3CaO + Al_2O_3 \longrightarrow 3CaO \,.\, Al_2O_3$	

(*Contd...*)

1250°C – 1280°C > 1280°C	Commencement of liquid formation Further formation of liquid and compounds	Endothermic Endothermic
	*Main reactions between lime and clay. Lime produced combines with main constituents of clay *viz*. Al_2O_3 and SiO_2.	

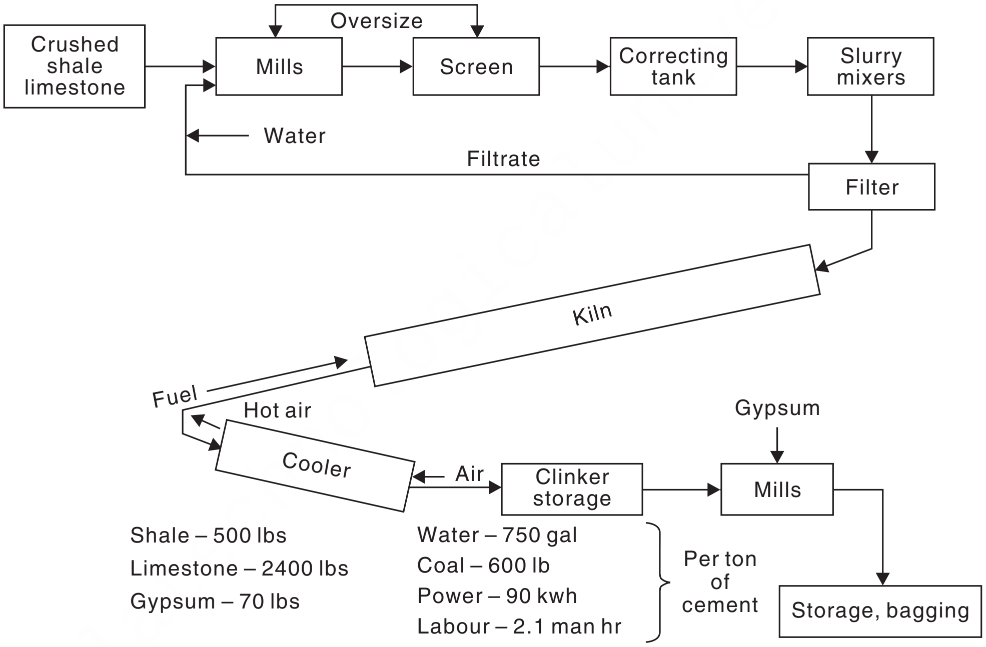


Fig. 19.6 Wet process for cement manufacture.

The analysis of typical samples of cement gives the following composition:

Lime ⇒ 55.06%; SiO_2 ⇒ 22.92%; Al_2O_3 ⇒ 8%
Fe_2O_3 ⇒ 5.46%; MgO ⇒ 0.77%; Potash ⇒ 1.13%
Soda ⇒ 1.7%; $CaSO_4$ ⇒ 1.75%; Unchanged clay and sand ⇒ 2.27%.

The final product formed consists of hard grannular masses from 1/8 to 3/4 inches in size, called **clinker**. The clinker falls through openings in the stationary firing ring of the kiln into rotating coolers, which simultaneously preheat the combustion air. Pulverising followed by the fine grinding in tube ball mills and packaging complete the steps to the finished cement. During fine grinding the following materials are added to the finished cement.

- Retarders such as gypsum
- Plaster or calcium lignosulphate
- Air entraining agents
- Dispersing agents and
- Waterproofing agents

Setting or Hardening of Cement

Setting of cement is a complicated process, and the cause of setting has been the subject of much discussion. But it is generally agreed that this takes place by hydration and hydrolysis.

On addition of water, the calcium compounds are decomposed with the formation of free $Ca(OH)_2$ and hydrated crystalline silicate and calcium aluminate, the crystals of which form an interlaced mass. Due to this interlacing of crystals the setting of cement occurs. The following equations represent these reactions:

$$C_2S + xH_2O \longrightarrow C_2S \,.\, xH_2O \text{ (amorphous)}$$
$$C_3S + xH_2O \longrightarrow C_2S \,.\, (x-1)\, H_2O \text{ (amorphous)} + Ca(OH)_2$$
$$C_3A + 6H_2O \longrightarrow C_3A \,.\, 6H_2O(c)$$

The hydration products have very low solubility in water. If this was not true, concrete would have been rapidly attacked in contact with water.

Another theory suggests that due to hydration, cement is converted into a gel of composition $C_3A.\ 6H_2O$ with absorbed water. This is followed by a slow crystallisation of the gel. The rapid increase in strength and hardness during setting of cement is mainly due to the partial hydrolysis of C_3S to form needles of $Ca(OH)_2$ in the hydrated silicate gel.

To hold up the 'flash set' caused by C_3A, some investigators assert that the gypsum added as retarder causes the temporary formation of $C_3A.3CaSO_4.3H_2O$, while others believe that the gypsum gives free $Ca(OH)_2$ by reaction with alkali and this in turn forms the more stable $C_4A(4CaO.Al_2O_3)$. The following equations represent these reactions:

$$C_3A + 6H_2O \longrightarrow C_3A \,.\, 6H_2O(c)$$
$$C_3A + 3(CaSO_4 \,.\, 2H_2O) + 25\, H_2O \longrightarrow C_3A \,.\, 3CaSO_4 \,.\, 31H_2O$$
$$C_4AF + xH_2O \longrightarrow C_3A \,.\, 6H_2O(c) + CaO \,.\, Fe_2O_3 \,.\, (x-6)\, H_2O$$
$$MgO + H_2O \longrightarrow Mg(OH)_2$$

The various compounds contribute to the heat of setting as follows:

$$C_3A > C_3S > C_4AF > C_2S$$

Lower heat of setting of cements are made low in C_3A and C_3S but high in C_2S by adding more Fe_2O_3, which takes the Al_2O_3 as C_4AF, thereby diminishing the amount of C_3A and by decreasing the CaO/SiO_2 ratio. This low heat of setting cement is used for construction of dams to avoid cracking the structure from heat stresses during setting and cooling. As an additional safeguard, the structure may be cooled during setting by circulating cold water.

The following table displays the functions of various compounds of cement.

Compounds	*Function*
C_3A	Responsible for initial set (flash set)
C_3S	Responsible for 1st strength (after 8 days)
C_2S and C_3S	Responsible for final strength (at 1 yr).
Fe_2O_3, Al_2O_3, Mg and alkalies	Lower clinkering temperature

GLASS

Glasses are *Ceramic materials* that are rigid like solids but which are not crystalline. *Glass may be considered as supercooled liquid of infinitely high viscosity.* Glass is made by melting one or more oxides in a furnace. The liquid glass is cooled until thick enough to mould and then shaped and cooled further slowly (annealing) until it sets to a solid mass.

Most glass is made from silica mixed with other oxides that melt at a lower temperature than glass made from pure silica; windows, bottles, and drinking water glasses are made of soda lime glass. Lead glass is used for decorative cut glassware. *Borosilicate glass* is used to make ovenware and laboratory glassware.

Compostion of glass

Glass is not a single compound. It is difficult to write any chemical formula for it. Generally the formula for glass may be represented thus,

$$xR_2O.\ yMO.\ 6SiO_2$$

where R = alkali metal (Na, K etc.)

M = bivalent metal (Ca, Pb etc.)

x and y = number of molecules.

Different varieties of glass

- *Vitreous Silica (quartz glass).* A glass made by fusing pure silica without a flux and is very resistant thermally and chemically. Used beyond the temperature ranges of other glasses. Transparent to U.V. radiation (ordinary glass is not transparent to U.V.).
- *Alkali silicates [Soluble glass (Soda), soluble glass (Potash), Water glass* ($Na_2O\ .\ SiO_2.\ K_2O\ .\ SiO_2$)] used in soap manufacture, for preservation of eggs, in the manufacture of artificial stones.
- *Lime glass*

(*a*) Soda lime glass, soda glass, soft glass ($Na_2O.CaO.6SiO_2$) are easily fusible, low softening temperature.

Uses. Laboratory apparatus, window and plate glass.

(*b*) Potash lime glass [Bohemian glass, Hard glass] ($K_2O.CaO.6SiO_2$). Fusion temperatures high.

Uses. Chemical apparatus withstanding high temperatures, specially combustion tubes.

- *Lead glass [Potash lead glass, Flint glass]*

($K_2O.PbO.6SiO_2$) fuses easily. sp. gr. higher; refractive index, $\mu = 1.7\text{-}1.78$ (higher than that of common glass, $\mu = 1.5$)

Uses.

(*a*) decoration and optical effects

(*b*) manufacture of lens and prism

(*c*) artificial gems

(*d*) electric bulbs.

- *Borosilicate glass.* When part of SiO_2 in glass formulation is replaced by B_2O_3 the glass formula becomes $7Na_2O.4CaO,\ 3ZnO.36(SiO_2 + B_2O_3)$; usually contains B_2O_3 = 10-13%, SiO_2 = 80-83%, low expansion coefficients, superior resistance to shock, excellent chemical stability, high electrical resistance.

Uses. Wide and ever increasing uses for these properties for laboratory glassware.

Special glasses

1. Coloured glasses

- Colour is produced by the absorption of certain light frequencies by agents in solution in the glass. The colouring agents of this group are the oxides of transitional elements, especially the first group: Ti, V, Cr, Mn, Fe, Co, Ni and Cu.

- Colour is produced by colloidal particles precipitated within an originally colourless glass by heat treatment.

Example is the precipitation of gold (colloidal) producing gold ruby glass.

- Colour is produced by microscopic or larger practicles. Selenium rods (SeO_2) used in traffic lights.

2. Opal, translucent or ground glass (ghosa kanch)

Soft glass made translucent by rubbing the surface with emery powder and turpentine, or sand and water, using HF.

3. Safety or laminated glass

Two layers of glass with an interleaf of plastic. When the glass is broken the fragments are held in place by inter layer.

4. Fibre glass

- Glass wool is impregnated with various binders and used for insulation.
- It can be spun into yarn.

5. Phosphate glass

It contains P_2O_5 as a major ingredient, wholly or partially displacing SiO_2. It can resist HF. Sight glasses for the handling of uranium hexafluoride in separation of uranium isotopes are made of phosphate glass.

6. High silica glass

96% SiO_2, 3% B_2O_3 and the rest Al_2O_3. This glass has high chemical durability and is extremely stable to all acids except HF, which attacks more slowly than others.

Properties of glass

- Physical:

(*a*) Transparent (usually) amorphous solid,

(*b*) Vitrifies easily, but devitrifies by formation of crystals under suitable conditions. On long standing or very slow cooling during annealing some of metallic silicates crystallise out. Glass is then said to devitrify.

(*c*) Hard and brittle

(*d*) No fixed melting point

(*e*) Bad conductor of heat and electricity

(*f*) Can incorporate colour maintaining transparency

- Chemical:

(*a*) Not attacked by air, water, oxidising agents, acids. Only attacked by HF readily.

$$Na_2O \,.\, SiO_2 + 6HF \longrightarrow 2NaF + SiF_4 + 3H_2O$$
$$CaO \,.\, SiO_2 + 6HF \longrightarrow CaF_2 + SiF_4 + 3H_2O$$

(*b*) Ordinary glass attacked by alkali solutions.

Functions of different constituents of glass

(*a*) K_2O: increases the softening point.

(*b*) Fe_2O_3: Inability to transmit UV is due to the presence of FeO or Fe_2O_3 in glass. Using iron free raw materials, glass capable of transmitting UV light could be manufactured.

(*c*) PbO: increases the refractive index of glass.

(*d*) B_2O_3: increases the hardness or refractory characters of glass and lowers expansion coefficient.

Raw materials

The raw materials employed in the manufacture of glass can be classified under three heads:

1. Substances of an acid character, like SiO_2, B_2O_3.
2. Substances of basic character, like soda, potash, lime, MgO, BaO, ZnO, PbO etc.
3. Various decolourising and opacifying agents like MnO_2, Pb_3O_4, nitre, Zn-compounds, SnO_2 etc.

Certain colour producing oxides are used for producing coloured glass, *e.g.,* CuO for blue colour, Cu_2O for ruby or red colour, Cr_2O_3, Fe_3O_4 for green colour, MnO_2 for violet colour etc.

- Silica is used in the form of sand. It is almost pure quartz (white sand) of which iron content should not exceed 0.045%.
- Soda, Na_2O is principally supplied by soda ash, Na_2CO_3. Other sources are salt cake and $NaNO_3$. The latter is useful in oxidising iron and accelerating the melting.
- The important sources for lime, (CaO) are limestone and burnt lime from dolomite, $CaCO_3$, $MgCO_3$. The latter introducing MgO into the batch.
- Potash is always used in the form of K_2CO_3.
- ZnO is sometimes used to replace lime.
- BaO as such or as precipitated $BaCO_3$.
- PbO in the form of Pb_3O_4.
- Boric acid as such or as B_2O_3.
- H_3PO_4 is used as an opacifying agent.
- Feldspars having the general formula $R_2O.Al_2O_3.6SiO_2$. Feldspars supply Na_2O or $K_2O.(R_2O)$ and $SiO_2.Al_2O_3$ serves to lower the melting point of the glass and to retard *devitrification.* Devitrification means slow crystallisation.
- *Cullet* is crushed glass from imperfect articles. It facilitates melting and utilises waste. It may be as low as 10% of the charge or as high as 80% of the charge.

Chemical reactions of the formation of glass in a furnace

$$Na_2CO_3 + a\,SiO_2 \longrightarrow Na_2O\,.\,a\,SiO_2 + CO_2$$

$$CaCO_3 + b\,SiO_2 \longrightarrow CaO\,.\,b\,SiO_2 + CO_2$$

$$Na_2SO_4 + c\,SiO_2 + C \longrightarrow Na_2O\,.\,c\,SiO_2 + SO_2 + CO.$$

- It should be noted that the ratios Na_2O/SiO_2 and CaO/SiO_2 need not be 1:1 molecular ratios.
- The compounds may be of the type $Na_2O.1.8SiO_2$.
- In window glass molecular ratios are approximately $2Na_2O.CaO.5SiO_2$.
- For decolourisation, MnO_2 is added to the charges which oxidises Fe^{+2} to Fe^{+3}. The green colour due to ferrous silicate being changed to yellow colour due to ferric silicate.

This yellow colour is rectified by the pale violet colour due to manganese silicate and a perfect white glass results.

Manufacturing procedure

The manufacturing procedure is divided into four major phases:

(*i*) Melting
(*ii*) Shaping
(*iii*) Annealing
(*iv*) Finishing

(*i*) **Melting.** Two types of furnaces are in use:

(*a*) *Pot furnaces* (*b*) *Tank furnaces*

Pot furnaces are employed principally in the manufacture of optical glass, art glass and plate glass and in the small scale units. The pots are really crucibles made of selected clay, high alumina fire clay such as *mulite* ($3Al_2O_3 . 2SiO_2$) or platinum. The material of the pot is attacked by prolonged action of molten glass and hence has to be changed after a number of operations except when platinum is used.

In a tank furnace, batch materials are charged into one end of a large 'tank' built of refractory blocks. The tank measures 125′ × 30′ × 5′ with a capacity of 1400 tons. The glass forms a pool in the hearth of the furnace across which the flames play alternately from one side to the other.

The 'formed' glass is worked out of the opposite end of the tank. The operation is continuous. The walls of tank furnace gradually wear away under the action hot glass.

The furnaces may be of either regenerative or recuperative design. In either of the cases the heat from the hot gases is utilised in preheating the air, for combustion of the fuel. Once the furnace has been heated, a temperature 1205°C is maintained all the time. The larger part of the heat is lost by radiation from the furnace walls.

This sort of heat loss is necessary to reduce the action of the molten glass on the furnace wall. Otherwise the furnace wall will corrode. Sometimes water cooling pipes are used to cool the furnace wall.

(*ii*) **Shaping or forming.** The glass articles are shaped either manually or by machine. In order to produce a sheet glass first a cylinder of approximate size is blown into shape. It is allowed to stand vertically on a stand. The cylinder is cut open by running a sharp knife lengthwise. At present every stage of shaping has been mechanised. The blowing is done by compressed air.

(*iii*) **Annealing.** To reduce strains, it is necessary to anneal all glass objects. Annealing involves two operations:

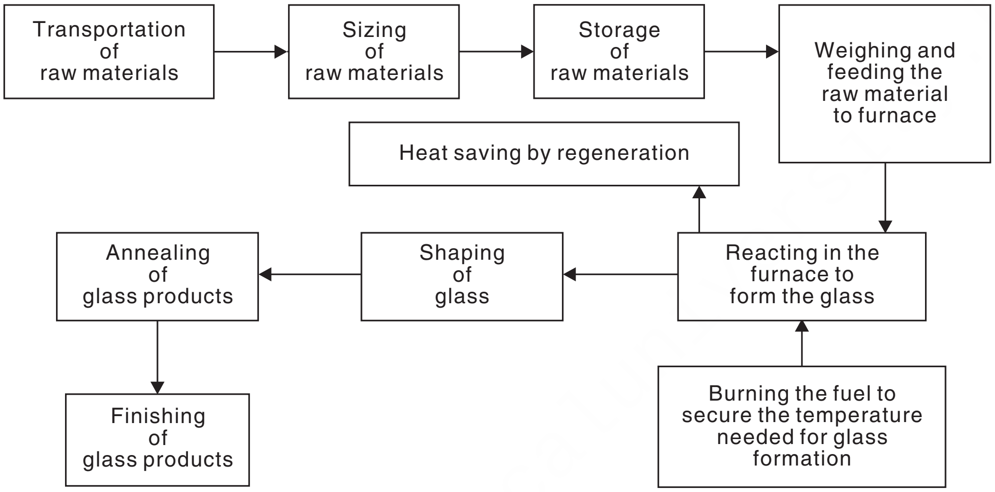
(*i*) Holding a mass of glass above a certain critical temperature, long enough to reduce internal strain by plastic flow.
(*ii*) Cooling the mass to room temperature slowly.

The annealing oven is nothing more than a carefully designed heated chamber in which the rate of cooling can be controlled.

(*iv*) **Finishing.** All types of glass articles must undergo certain finishing operations.

These include cleaning, grinding, polishing, cutting, enameling etc. Although all these are not required for every glass object, one or more is almost always necessary.

Flow diagram mentioning manufacturing sequences for glass



POTTERY AND PORCELAIN

They are generally clay fired products, sometimes enamelled or glazed.

Clay

Geologically, clays are regarded as the products of disintegration and weathering of granite rocks, in which feldspar was a original mineral but the term is also applied to most minerals which possess the property of being plastic when mixed with a suitable amount of water.

Weathering reaction:

$$\underset{\text{feldspar}}{K_2O \,.\, Al_2O_3 \,.\, 6SiO_2} + CO_2 + 2H_2O \longrightarrow K_2CO_3 + \underset{\text{kaolinite}}{Al_2O_3 \,.\, 2SiO_2 \,.\, 2H_2O} + 4SiO_2$$

Common clay

It is principally aluminium silicate mixed up with a large number of substances *viz*, compounds of Fe, Mn, Ca, Mg etc. and vegetable matters.

Kaolin or China clay

It is a pure *white burning* clay of low plasticity and is formed by weathering of feldspar.

Composition— $Al_2O_3 \,.\, 2SiO_2 \,.\, 2H_2O$

Fire clay. It contains a good deal of SiO_2 and very little Fe. When fired, it forms a material of high fusing point (1550°C and upwards). Clays are used in the manufacture of bricks, tiles, porcelain wares, pottery articles, electric insulators, drain pipes and other sanitary goods etc.

The use of clay in ceramics depends upon its following important properties:

(*i*) It is plastic enough to be moulded when it is wet,

(*ii*) It retains its shape when dried and,

(*iii*) When the moulded mass is heated to a high temperature, it sinters together forming a hard, coherent mass without losing its original colour.

Pottery: (articles made of clay)

Pottery

Non-porous
(1) China and Porcelain
(2) Earthenware
(3) Stoneware

Porous
(4) Unglazed pottery
(3) Terracotta, bricks, tiles etc.

Raw materials. The three main raw materials are: (1) clay (kaolinite), (2) feldspar, (3) sand.

Common fluxing agents. Borax, fluorspar, cryolite, boric acid, Na_2CO_3, K_2CO_3, iron oxides.

Common refractory materials. CaO, $CaCO_3$, ZnO_2, TiO_2. Both glazed and unglazed clay products are manufactured. The glazed product is obtained by applying glaze on the unglazed body. For glazing the shaped material is covered with a coating of mixture of powdered feldspar, SiO_2, borax etc., and heated at higher temperature for longer time. The thin coating melts and forms a glaze on the surface of the body. Porcelain, therefore is looked upon as partly glass and partly stoneware.

In all cases, the unglazed product is to be made. The raw materials for unglazed product are:

1. China clay
2. Ball clay
3. Flint (Pure $SiO_2 + CaCO_3$)
4. Cornish stone (Potash feldspar, $K_2O = 6\%$, $CaO = 1\%$, $Al_2O_3 = 18\%$, $SiO_2 = 75\%$)
5. Marble ($CaCO_3$)
6. Quartz (SiO_2).

Raw materials for glaze

Frit. It is a sort of glass. It is made from Borax, Feldspar, Quartz etc.

Stoneware. This is a kind of porcelain. It is not always white because the ingredients contain Fe_2O_3. It is used for sewer pipes. It is glazed with salt.

Chemical stoneware. It is used for making jars suitable for storing acids.

The reactions of porcelain formation are:

$$\begin{tikzcd}[column sep=small] \underset{\text{China clay}}{3Al_2O_3.2SiO_2.2H_2O} \arrow[r, "600°C"] & 6H_2O\uparrow + \underset{\text{(amorphous)}}{3Al_2O_3} + \underset{\text{(amorphous)}}{6SiO_2} \arrow[d, "900°C"] \\ \underset{\text{(Crystal)}}{SiO_2} \xleftarrow{1400°C} 4SiO_2 + \underset{\text{Mullite}}{3Al_2O_3.2SiO_2} & \underset{\text{Crystal line}}{\gamma\text{-}3Al_2O_3} + \underset{\text{(amorphous)}}{6SiO_2} \arrow[l, "1000°C"', "\text{Silicate formation}"] \end{tikzcd}$$

Porcelain is used for making– (*i*) dinner and tea sets, (*ii*) basin, crucibles, (*iii*) electrical insulators, floor and wall tiles, (*iv*) high class sanitary goods.

Process: It consists of the following steps:

1. *Slurry preparation:* The mixture of weighed ingredients is taken in a blunger and stirred well with water to form a creamy liquid known as clay slip.
2. *Ageing:* The slip is filter-pressed. The residual cake contains 10-30% water. The cakes are dumped for some days. This improves the plasticity of the clay mixture because of uniform hydration and gelation.
3. *Deairing:* The aged cakes are deaired in a pug mill by slicing with knives and putting under vacuum.
4. *Shaping.*
5. *Trimming and drying:* The shaped articles after airdrying are trimmed and then dried in hot air.
6. *Glazing:* The dried articles known as *blanks* are glazed. In few cases glaze is put on the blanks before firing. But in most cases, blanks are fired to produce biscuits. The firing is done in a tunnel furnace. Usual maximum temperature is 1400°C.

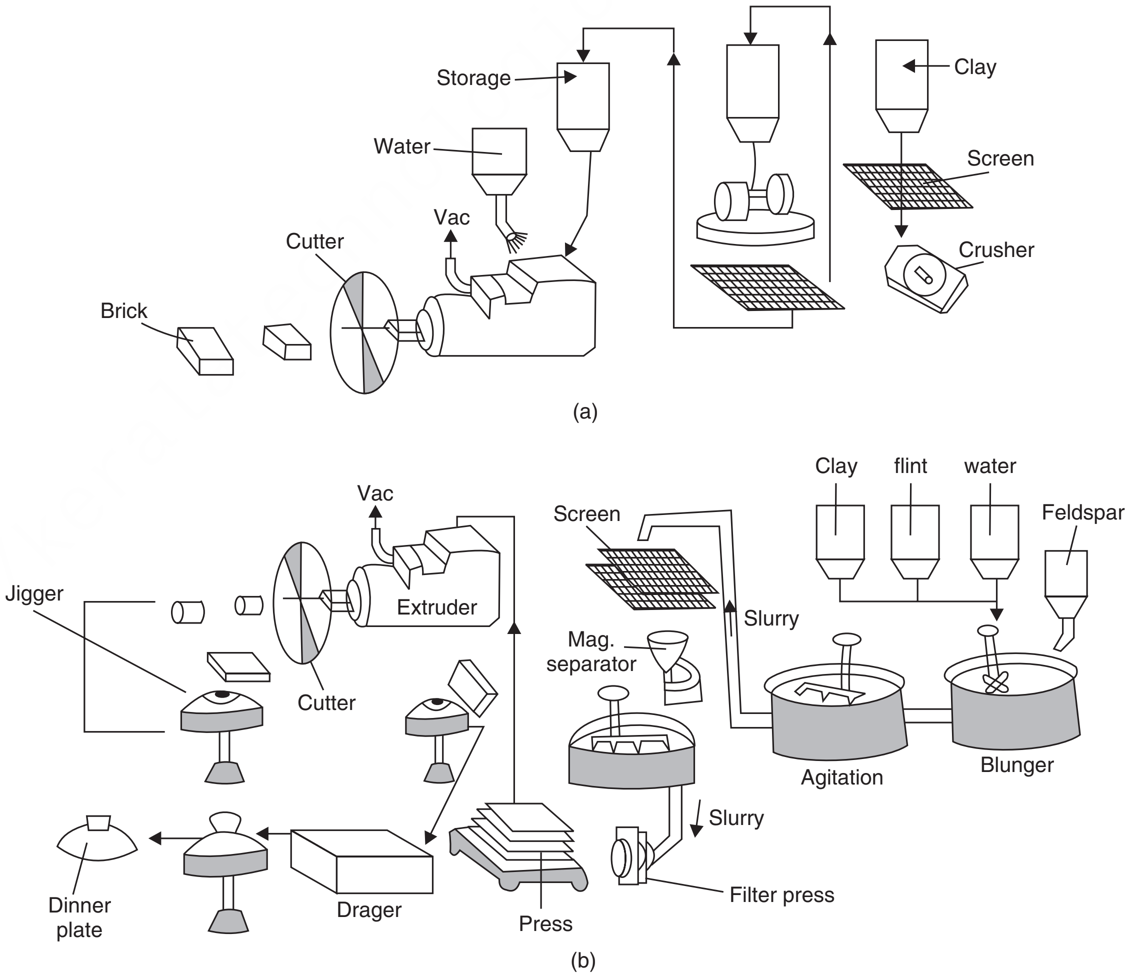


Fig. 19.7 Flow diagram: (*a*) Brick manufacture (*b*) Dinner plate manufacture.

Glazing: The glazing ingredients are finely powdered and mixed. The mixture is mixed with water to make the slip. The slip is next applied to dry blanks or more frequently to the biscuits by dipping or pouring or spraying or brushing very carefully and then heated at 1400°C. Glaze is a sort of glass, which is applied on the surface to cover the pores.

The alkali portion of feldspar and most of the fluxing agents becomes a part of the glassy or vitreous phase of the ceramic body. All ceramic bodies undergo a certain amount of vitrification or glass formation.

REFRACTORIES

The word *refractory* means resistant to melting or fusion. Broadly speaking, refractories are materials which are used to withstand high temperature, chemical and physical effects without softening or suffering a deformation in shape. Whenever very high temperatures are involved as in furnaces, kilns and electrical heating apparatus, the refractories do provide the linings or bricks, supports and other filaments. The main objective of a refractory is to confine heat (*i.e.,* to resist the heat loss) and at the same time to resist the abrasive and corrosive action of molten metals, slags and gases at high operating temperatures. *Thus refractories are those materials which are used for the construction of furnaces, kilns, ovens, crucibles, retorts, converters etc. Refractories are sold in the form of bricks, silica, magnesite, chromite bricks, silicon carbide, and zirconia refractories etc.*

Classification

Refractories are classified broadly under three heads depending on the chemical properties of their constituent substances. These are

(*i*) *Acid refractories:* They are made of clay, clay-silica mixtures and of pure silica. They are not attacked by acidic materials. Examples–silica bricks and fire clay bricks.

(*ii*) *Basic refractories:* They are made up of large proportion of lime or magnesia or a mixture of these bases or other metal oxides.

Examples–Magnesite bricks (magnesia), bauxite bricks.

(*iii*) *Neutral refractories:* They are made up of weakly acidic or basic materials like carbon, chromite (FeO, CrO_2), zirconia (ZrO_2) etc. Examples–Chromite bricks, silicon carbide and graphite.

At present some single oxide bricks have been developed. These are self bonded and have high fusion points. Examples–alumina (2050°C), magnesia (2250°C) and zirconia (2200 °C) etc.

Properties

Refractories should possess the following general properties:

(*i*) They must be able to withstand high temperature.

(*ii*) They should be infusible at the temperature to which they are liable to be exposed. The fusion temperatures of the usual refractories in use vary from 1600°C to 2700°C.

(*iii*) They should be chemically inert towards the corrosive action of gases, liquid metals and slags produced in its immediate contact in furnaces.

(*iv*) They should be able to withstand sudden change of temperature.

(*v*) They should be able to withstand spalling, *i.e.,* cracking and flaking of the bricks due to uniform expansion or contraction. Annealed bricks can better withstand spalling.

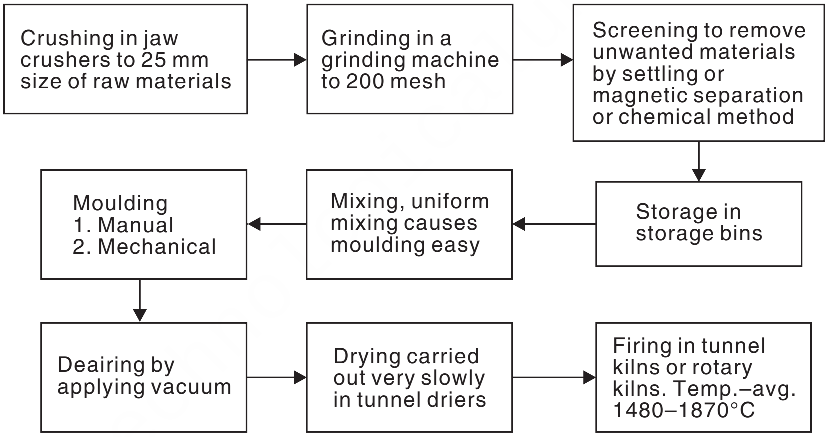
(*vi*) They must be able to withstand abrasion or erosion of the furnace charge and also the pressure of the load.

(*vii*) Porosity of a refractory is a deciding factor of the degree of penetration by molten fluxes and gases and thus the refractory material easily disintegrates, *i.e.,* the greater the porosity, the greater is the susceptibility of the refractory to chemical attack by molten fluxes and gases. Decrease in porosity increases the refractory's strength and also increases its heat capacity, thermal conductivity and chemical strength.

(*viii*) Least porous bricks have highest thermal conductivity. The reason for such incidence is due to the absence of air in the void space.

Manufacturing of refractories

The steps can be displayed schematically as follows:



Common Refractory Bricks

1. **Silica bricks:** Silica bricks contain (92-95% silica, 2% lime), the main raw materials are—quartz, quartzite, sandstone etc. During manufacture, silica bricks are heated to about 1500°C within a span of 24 hours. The cooling of the bricks takes about 1-2 weeks. During heating, the quartzite converts to crystobalite. During slow cooling, crystobalite is converted to tridymite. So silica brick contains a mixture of tridymite and crystobalite. If during heating of silica bricks, quartzite is not converted to tridymite and crystobalite the bricks will expand during use in the furnace and the refractory structure will break and fall. To attain the right composition 12 hours heating at 1500°C of the bricks is very much essential.

Uses

Main applications of silica bricks are:

- In open hearth furnaces
- In coke-oven walls
- Glass-furnaces

2. **Fire clay-bricks:** Raw material is fire clay (clay–$Al_2O_3.2SiO_2.2H_2O$)

Generally fire clay bricks contain 55% silica, 35% alumina. This is acidic fire clay brick. Basic fire clay bricks contain 55% alumina and 40% silica, rest consists of K_2O, FeO, CaO, MgO.

Properties

- Light yellow-reddish brown in colour
- Low porosity and lower refractoriness than silica bricks
- Fusion temperature 1350°C
- Crushing strength 200 kg/cm^2
- Better resistance to thermal spalling than silica bricks.
- Cheaper than silica bricks.

Uses

- In blast furnaces
- In kilns
- Charging doors etc.

3. **High alumina bricks:** Composition—50% or more alumina.

Properties

- Low coefficient of expansion
- High porosity
- Little tendency to spall
- Excellent wear resistance and stability.

Uses

- For linings for Portland cement rotary kilns
- Furnace hearths and walls
- In reverberatory furnaces
- In combustion zones of oil-fired furnaces.

4. **Magnesite bricks:** Magnesite is naturally occurring magnesium carbonate ($MgCO_3$) and is the raw material for the magnesite refractories. Calcined magnesite (at 1600°C) *i.e.,* MgO is powdered to a proper size and then mixed with caustic magnesia or iron oxide as binding material and then ground. The prepared powder is pressed into bricks in hydraulic presses. The bricks are then slowly heated to 1500°C and kept for about eight hours at this temperature and cooled then slowly.

Properties

- They are generally grey or brown in colour
- They can be used upto 1500°C under a load of 3.5 kg/cm^2
- They possess good crushing strength, good resistance to basic slags and very little shrinkage
- Their resistance to abrasion is poor.

Uses

- For the lining of basic converters and open hearth furnaces in steel industry
- They are used in hot mixer linings, copper convertors
- In reverberatory furnaces for smelting lead, copper
- In refining furnaces for gold, silver and platinum etc.

5. **Dolomite bricks:** They are made by mixing calcined dolomite (*i.e.,* mixture CaO + MgO) in equimolar proportion with silica as binding material. Other binding materials used

for the same are tar, quick lime, iron oxide, clays etc. They are then fired at 1500°C for about 24 hours.

Properties

- Dolomite bricks are less strong, more porous and have more softness and shrinkage than magnesite bricks
- They can withstand a load of 3.5 kg/cm^2 at 1650°C.
- They are not very much resistant to thermal shock
- They are more resistant to slags and spalling than magnesia bricks
- They wear out quickly.

Uses

- For repairing materials
- In Bassemer converters, open-hearth furnaces, laddle-linings etc.

6. **Chromite bricks:** Chromite is a neutral refractory. The crushed chromite ore ($FeO.Cr_2O_3$) is fired at 1500°C–1700°C after mixing with a little clay as binding material.

Properties

- They are neutral in colour
- They possess high density, resistance to acidic as well as basic slags
- They can withstand upto 1800°C under a load of 3.5 kg/cm^2.
- They possess good crushing strength
- They have moderate thermal conductivities.

7. **Carborundum or silicon carbide bricks:** They are prepared from coke and sand. **Sand (60%)** and **coke (40%)** are properly mixed and is followed by addition of some sawdust and a little salt. The mixture is then fired at 1500°C in an electric furnace. Sawdust when burned evolves gases, which by circulation increases the porosity of the charge. Salt reacts with iron and similar impurities present in the raw materials to form volatile chlorides. These volatile chlorides make the final products porous. The silicon carbides obtained from the furnace are interlocked tridiscent crystals. Bonding agents like clay, silicon nitride are mixed. The mixture is then shaped, dried and fired. The firing temperature is 2000°C. At this temperature interlaced crystals are formed.

Reaction

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Composition of silicon carbide bricks is:

- Silicon = 65%
- Carbon = 30%
- Impurities = 5%

Properties

- Colour–dark grey to black
- Hardness–high
- Fusion point – 2500°C
- Coefficient of thermal expansion is very low
- Specific gravity 3.17-3.2%
- Resistance to abrassion–high

- Resistance to spallation–high
- Oxidising action–in presence of air at 1000°C silica bricks tend to oxidise to silica.

$$2SiC + 3O_2 = 2SiO_2 + 2CO$$

- Mechanical strength–very high

Uses

- Owing to its high thermal conductivity they are used in muffle furnaces.
- Owing to their high electrical conductivity, they are used in electric arc furnaces.

8. **Zirconia bricks:** Zirconia bricks fall under pure oxide refractories. Refractory oxides of common use are **alumina** (Al_2O_3), **magnesia** (MgO), **zirconia** (ZrO_2), and **thoria** (ThO_2).

Refractory oxides do not possess plastic properties. That is why clays and bentonites are to be used to prepare the pure oxide refractory bricks. Organic plasticizers such as dextrin and resins may also be used. The use of organic plasticizers makes the brick less porous.

Zirconia brick is prepared by heating zirconite (ZrO_2). First zirconia is calcined and powdered. The powdered zirconia is kept under water for sometime and the wet zirconia is mixed with binding material, *viz.* colloidal zirconia or alumina in a mill. The materials are then moulded into bricks by hand moulding or pressing. The moulded bricks are dried and fired at about 1750°C.

Properties

- Zirconia refractories fall under neutral refractories
- They can withstand a temperature upto 2600°C.
- They are resistant to basic slags.

Uses

- Zirconia bricks are very costly
- Specially used when high temperature is used

9. **Beryllia bricks:** Beryllia minerals are used to prepare the bricks which are fired at 2000°C.

Properties

- High melting point (2550°C)
- Low electrical conductivity
- High thermal conductivity
- Good resistance to thermal shocks
- Inertness to carbon dioxide and carbon monoxide upto 2000°C.

Uses

- Beryllia is used in making crucibles to melt uranium and thorium, owing to its *low neutron absorption capacity.*
- As *radiation shields* in carbon resistant furnaces.

10. **Cermets:** Cermets are hot pressed or sintered materials comprising ceramic and metallic components.

Properties

- They are the combination of ceramics and metals
- They have high refractoriness of ceramics

- They have high thermal conductivity of metals
- They have high thermal shock resistance of metals etc.
- Refractory ceramics used in the manufacture of cermets are zirconium carbide, molybdenum carbide and tungsten carbide.
- Most cermets contain about 80% of ceramic materials and 20% of the metal. They are usually fabricated by the techniques of powder metallurgy.

Uses

- In rocket and jet engine parts.
- Spinning tools for hot metals.

11. **Enamels:** Enamelling means to impart a hard and glossy coating applied on wares for decorative and protective purposes. The enamels used to coat metallic surfaces are known as *porcelain enamels.*

Raw materials used for the manufacture of enamels are:

(*i*) Refractories
(*ii*) Fluxes
(*iii*) Opacifier
(*iv*) Colours
(*v*) Floating agents
(*vi*) Electrolytes.

For making the enamel at first *frit* is made from glass forming materials such as sand, soda ash, feldspar, borax etc; when melted, they form a glass comprising sodium, potassium, calcium borosilicate.

Application of the enamel—a thin coating of the enamel thus obtained is applied on the metal either by dipping or by brushing or by pumping, then articles are fired at 800°C.

Uses

In making:

(*i*) refrigerators
(*ii*) food processing equipments
(*iii*) motor cars
(*iv*) sanitary wares.

SHORT QUESTIONS AND ANSWERS

Q. 1. What is cement?

Ans. A cement is a substance which sets to a hard mass in presence of water.

Q. 2. What is RCC?

Ans. Concrete made with sand, stone chips and cement when reinforced with iron rod for an extra strength of the concrete is known as reinforced concrete cement (RCC).

Q. 3. What is a mortar?

Ans. The product formed after setting of lime, sand and water is known as mortar.

Q. 4. Mention the areas of application of cement.

Ans. R.C.C. walls, dams, roads etc.

Q. 5. What is a hydraulic cement?

Ans. The cement sets under water, that is why the term hydraulic came.

Q. 6. Give general composition of cement.

Ans. See text page 418.

Q. 7. What is glass?

Ans. Glass may be defined

- Physically as an amorphous, transparent or translucent, rigid supercooled liquid of infinitely high viscosity.
- Chemically as a mixture of a number of metallic silicates, one of which is an alkali metal.
- Glass has almost 100% elastic recovery.

Q. 8. What is vitrification?

Ans. The process of not forming crystals during cooling of glass is called vitrification.

Q. 9. What is devitrification of glass?

Ans. Glass-wares left unused for a long time gradually loose their transparency and become opaque due to the crystallisation of some of metallic silicates of glass. That phenomenon is known as devitrification of glass.

Q. 10. What are ceramics?

Ans. Clay materials are known as ceramics. Even at the present time ceramics remain important in many spheres of life. Building, roads, furnaces, kitchen wares, laboratory wares are made of ceramics.

The greatest uses of advanced ceramic products are in

- Aerospace industry due to their lighter weights compared to metal alloys
- Heat shields for space vehicles
- As bio materials like false teeth; bone replacement, artificial hip joints etc.

Q. 11. What are refractories?

Ans. Refractories are earthy ceramic materials of low thermal conductivity capable of withstanding extremely high temperature without any change.

Q. 12. What are primary uses of refractories?

Ans. The primary uses of refractories are for lining

(*i*) Steel furnaces

(*ii*) Coke ovens

(*iii*) Glass wares.

Q. 13. Mention some important refractories.

Ans. (*i*) Fire clay (aluminium silicates), (*ii*) Silica, (*iii*) Silicon carbide, (*iv*) High alumina (70-80% Al_2O_3), (*v*) Magnesite (MgO), (*vi*) Mullite (Clay sand), (*vii*) Zirconia (ZrO_2).

Q. 14. Mention some refractory metals.

Ans. Tungsten and tantalum (W and Ta) are refractory metals capable to withstanding high temperatures.

Q. 15. Mention some basic refractories.

Ans.

- Magnesia
- Chromite
- Forsterite.

Q. 16. Mention classification of refractories.

Ans.

(*a*) Acidic (silica, fire clay)
(*b*) Basic (magnesite, dolomite)
(*c*) Amphoteric (Al_2O_3, C, SiC).

Q. 17. What is the importance of zirconia as refractory?

Ans. Pure zirconia undergoes (*i*) a change from monoclinic crystal to tetragonal form at 980°C and (*ii*) also volume change on inversion by adding certain oxides like MgO, CaO. This type of zirconia possesses a working temperature of 2600°C.

Q. 18. Discuss the effect of heat on clay.

Ans. Clay is the common ingredient of all ceramic products, a common example is Kaolinite. At the early stages of heating, clay undergoes elimination of water of hydration at 600°C.

$$Al_2O_3.2SiO_2.2H_2O \xrightarrow{600°C} \underbrace{Al_2O_3 + 2SiO_2}_{\text{amorphous mixture}} + 2H_2O \uparrow$$

The amorphous form of alumina changes to γ-alumina, a crystalline form at 940°C. At 1000°C, Al_2O_3 and SiO_2 combine to form mullite ($3Al_2O_3 . 2SiO_2$). As the temperature increases, more SiO_2 is converted to cristobalite. So, the overall fundamental reaction of heating of clay is

$$\underset{\text{Kaolinite}}{3(Al_2O_3.2SiO_2.2H_2O)} \xrightarrow{\Delta} \underset{\text{Mullite}}{3Al_2O_3.2SiO_2} + \underset{\text{Cristobalite}}{4SiO_2} + 6H_2O$$

EXERCISES

1. What are silicates?
2. Define clay and soil.
3. Discuss the structural pattern of silicates.
4. What do you mean by silicate technology?
5. What do you mean by superconductive ceramics? Mention its uses.
6. Distinguish between (*a*) Pozzuolanic cement and (*b*) Portland cement.
7. How is portland cement prepared by wet process?
8. Explain the setting and hardening of cement.
9. Describe the rotary kiln used in cement manufacture.
10. Discuss the composition of Portland cement.
11. How are cements classified? Give the various physico-chemical reactions responsible for the setting and hardening of Portland cement.
12. Describe the setting of mortar and lime.
13. Describe various types of cement.

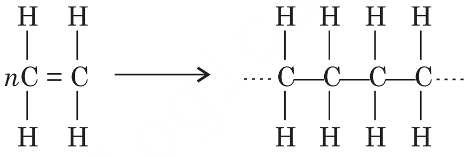
14. What are the criteria of the Portland cement raw materials?
15. What do you mean by wet and dry processes in cement manufacture?
16. How is Portland cement manufactured?
17. Describe with the help of a neat diagram of rotary kiln for the manufacture of Portland cement by wet process.
18. What is cement? Describe the composition of any cement. Briefly describe its manufacture.
19. What is glass? Discuss the physical and chemical properties of glass.
20. Classify glasses with composition and illustrations.
21. Describe the manufacture of glass by pot furnace process.
22. Write short note on soda lime glass.
23. Write notes on
  (*i*) Coloured glass
  (*ii*) Plate glass
  (*iii*) Shaping of glass
  (*iv*) Safety glass
  (*v*) Chemical action in glass making
  (*vi*) Fibre glass
  (*vii*) Annealing of glass
  (*viii*) Glass laminates
  (*ix*) Phosphate glass
24. What is glass? Write the raw materials used in the manufacture of glass.
25. Discuss the manufacture of ordinary glass with the help of flow diagram. Give reactions involved.
26. Write notes on
  (*i*) Clay and common clay
  (*ii*) China clay
  (*iii*) Fire clay
  (*iv*) Uses of clay
  (*v*) Pottery.
27. Describe the process of manufacturing of porcelain.
28. Give the reaction involved in porcelain formation.
29. What are refractories? Give an account of any four characteristics of a good refractory material.
30. Explain the theory underlying the manufacture of refractory products.
31. Describe the manufacture of:
  (*i*) Fire clay bricks
  (*ii*) Silica bricks
  (*iii*) Magnesite bricks.
32. What are basic refractories? Explain magnesite refractory in detail.
33. What are fire clay bricks? Describe the manufacture, properties and uses of fire clay bricks.
34. What are refractory materials? Write a brief note on chromite bricks.
35. Write notes on
  (*i*) Carborundum
  (*ii*) Silica refractories.
36. What are refractories? How are they classified? Give examples.
37. Explain the significance of the following properties of refractory materials
  (*i*) Porosity
  (*ii*) Dimensional stability.
38. State composition, properties and applications of the following materials:
  (*i*) Magnesite
  (*ii*) Fire clay
  (*iii*) Zirconia
  (*iv*) Silica.

20

Polymers

POLYMERIZATION

Polymers are macromolecules of high molecular weight which are formed by linkage between large numbers of small molecules called monomers, *e.g.*, polyethylene is made up of the monomers ethylene.



$$n\overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}} \longrightarrow \cdots\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}\cdots$$

ethylene polythene

There is no limit to theoretical length of the polymer, but the polymer ceases to grow for many practical reasons. The number of repeating units in a polymer is called the “degree of polymerization”.

Types of polymerization

1. Addition or chain polymerization. Monomers (M) having the general formula, CH_2=CHY (Y=X, CO_2R, CN etc.,) undergo polymerization, *i.e.,* these monomers having double or triple bonds polymerize without the liberation of small molecules. There are three ways of addition polymerization:

(*i*) Head to tail type

$$—CH_2CHY—CH_2CHY—CH_2CHY----$$

(*ii*) Head to head type

$$—CHYCH_2—CH_2CHY.CHYCH_2CH_2----$$

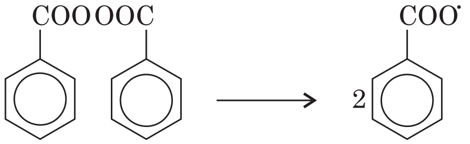
(*iii*) Random type

$$—CHYCH_2\ CHY.CH_2\ CH_2CHYCH_2\ CHY----$$

Mechanism of addition polymerization:

(*a*) Free radical polymerization is the first type which involves the following steps:

Initiation. The first step of which involves two reactions. The first is the spontaneous decomposition of an initiator into free radicals. A variety of peroxides act as initiator such as benzoyl peroxide, tertiary butyl hydroperoxide etc.



The next part of initiation involves the addition of this radical to the monomer molecule (M) to initiate the chain.

$$\underset{\substack{\text{Free}\\ \text{radical}}}{2R^\bullet} + \underset{\text{Monomer}}{M} \longrightarrow M^*$$

The M* is the initiator radical or primary radical.

Propagation. The mechanism of propagation is the reaction of the radical M* with its own monomer M.

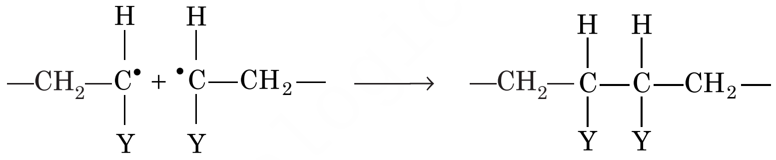
$$M^* + CH_2 = CHY \longrightarrow M\text{-}CH_2CHY^*$$

Continuous addition of new monomer in this manner will finally produce a polymer chain in which the substituents are located on alternate atoms.

Terminations. The most common terminations are the effect of

(*i*) Collision between two growing chains

i.e.,

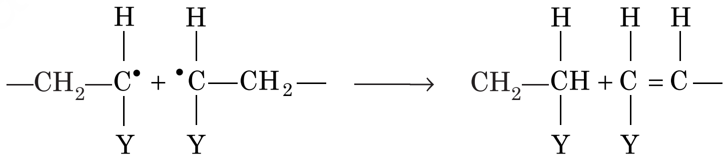


$$-CH_2-\underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{C^\bullet}} + {}^\bullet\underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{C}}-CH_2- \longrightarrow -CH_2-\underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-$$

(*ii*) Collision of a growing chain with an initiator radical when the latter is proportionately in excess.

(*iii*) Collision between a growing chain with impurities. Sometimes the chain length of the polymer is controlled by deliberately adding inhibitors.

More rarely, by disproportionation an H atom of one radical is transferred to another resulting in two polymers–one saturated and the other unsaturated.

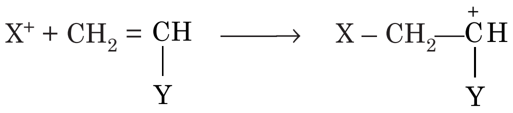


$$-CH_2-\underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{C^\bullet}} + {}^\bullet\underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{C}}-CH_2- \longrightarrow CH_2-\underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{CH}} + \underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{C}} = \overset{\overset{H}{|}}{C}-$$

(*b*) Ionic polymerization is an important class of addition polymerization which also involves the steps of initiation, propagation and termination but here, instead of free radicals, the unstable intermediates are either cations or anions.

Cationic Mechanism

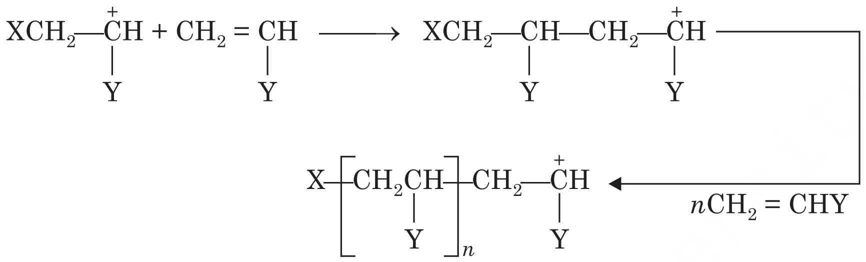
Initiation



$$X^+ + CH_2 = \underset{\underset{Y}{|}}{CH} \longrightarrow X - CH_2-\underset{\underset{Y}{|}}{\overset{+}{C}}H$$

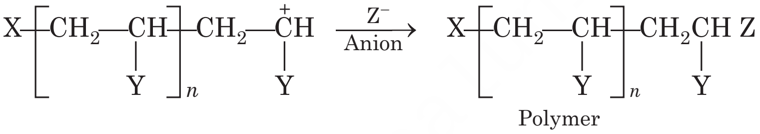
The initiators are Lewis acids like $AlCl_3$,BF_3, H_2SO_4 etc., in presence of water.

Propagation:



$$\mathrm{XCH_2-\overset{+}{\underset{Y}{CH}} + CH_2=\underset{Y}{CH} \longrightarrow XCH_2-\underset{Y}{CH}-CH_2-\overset{+}{\underset{Y}{CH}} \xrightarrow{nCH_2=CHY} X\left[CH_2\underset{Y}{CH}\right]_n CH_2-\overset{+}{\underset{Y}{CH}}}$$

Termination:

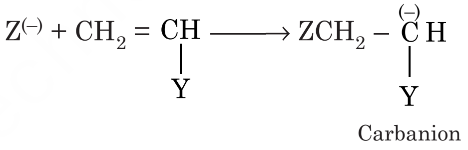


$$\mathrm{X\left[CH_2-\underset{Y}{CH}\right]_n CH_2-\overset{+}{\underset{Y}{CH}} \xrightarrow[\text{Anion}]{Z^-} \underset{\text{Polymer}}{X\left[CH_2-\underset{Y}{CH}\right]_n CH_2\underset{Y}{CH}\,Z}}$$

If the medium is of dielectric strength, the overall effect leads to an increased polymerization rate and also increased degree of polymerization, since better charge separation of ion and counter ion occurs.

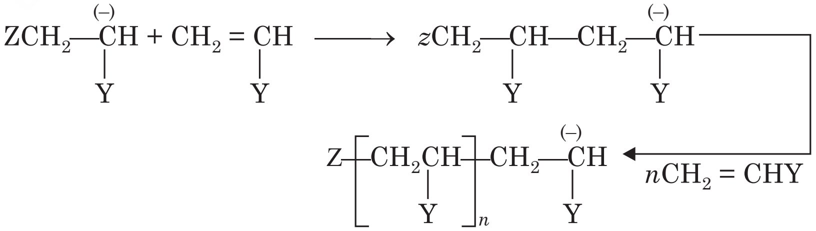
Anionic polymerization mechanism:

Initiation:



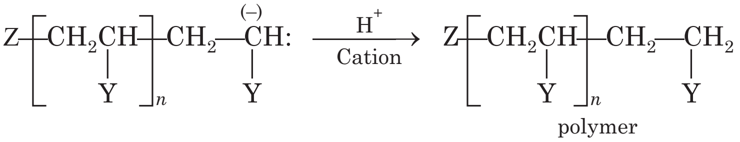
$$\mathrm{Z^{(-)} + CH_2=\underset{Y}{CH} \longrightarrow \underset{\text{Carbanion}}{ZCH_2-\overset{(-)}{\underset{Y}{C}}H}}$$

Propagation:



$$\mathrm{ZCH_2-\overset{(-)}{\underset{Y}{CH}} + CH_2=\underset{Y}{CH} \longrightarrow zCH_2-\underset{Y}{CH}-CH_2-\overset{(-)}{\underset{Y}{CH}} \xrightarrow{nCH_2=CHY} Z\left[CH_2\underset{Y}{CH}\right]_n CH_2-\overset{(-)}{\underset{Y}{CH}}}$$

Termination:



$$\mathrm{Z\left[CH_2\underset{Y}{CH}\right]_n CH_2-\overset{(-)}{\underset{Y}{CH}}: \xrightarrow[\text{Cation}]{H^+} \underset{\text{polymer}}{Z\left[CH_2\underset{Y}{CH}\right]_n CH_2-\underset{Y}{CH_2}}}$$

Polymerization of olefins with metallic sodium, sodium ethoxide takes place *via* this mechanism.

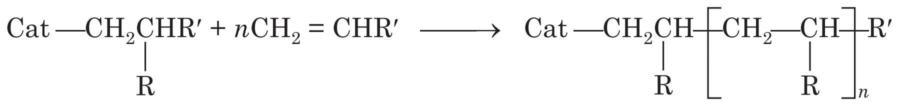
(*c*) Co-ordination polymerization or Ziegler-Natta polymerization. It was observed by Ziegler and Natta that in presence of a combination of transition metal halides ($TiCl_4$, $ZrBr_3$, and halides of V, Zr, Cr, Mo etc.) along with organometallic compounds (triethyl/trimethyl aluminium) polymerization of olefins leads to stereospecific polymerization.

Mechanism of Ziegler-Natta polymerization:

Initiation:

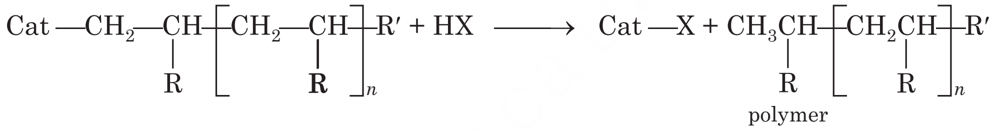
$$\text{Cat R}' + \text{CH}_2 = \text{CHR} \longrightarrow \text{Cat CH}_2\text{CH(R)R}'$$

Propagation:



$$\text{Cat}-\text{CH}_2\underset{\substack{|\\ \text{R}}}{\text{C}}\text{HR}' + n\text{CH}_2 = \text{CHR}' \longrightarrow \text{Cat}-\text{CH}_2\underset{\substack{|\\ \text{R}}}{\text{CH}}\left[\text{CH}_2-\underset{\substack{|\\ \text{R}}}{\text{CH}}\right]_n\text{R}'$$

Termination:

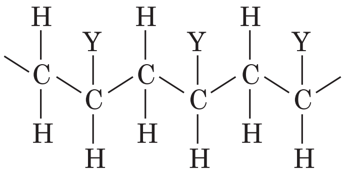


$$\text{Cat}-\text{CH}_2-\underset{\substack{|\\ \text{R}}}{\text{CH}}\left[\text{CH}_2-\underset{\substack{|\\ \textbf{R}}}{\text{CH}}\right]_n\text{R}' + \text{HX} \longrightarrow \text{Cat}-\text{X} + \text{CH}_3\underset{\substack{|\\ \text{R}\\ \text{polymer}}}{\text{CH}}\left[\text{CH}_2\underset{\substack{|\\ \text{R}}}{\text{CH}}\right]_n\text{R}'$$

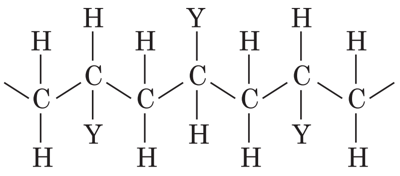
By earlier free radical polymerization of ethylene, propylene yielded polymers of low density having highly branched chain polymer of low crystallinity and mechanically weaker structure like LDPE (low density polyethylene). Ziegler-Natta polymerization yielded stereospecific structure of high mechanical strength, unbranched, high melting and highly crystalline polymer like HDPE (high density polyethylene).

Stereochemistry of polymers

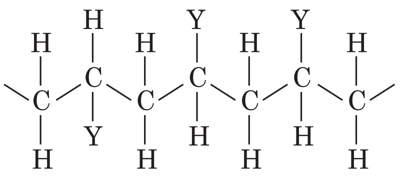
(*i*) *Isotactic polymers* have all the groups in one side of the polymeric backbone and the monomers are joined in a regular head to tail arrangement.



(*ii*) *Syndiotactic polymers* have similar head to tail arrangements but here Y groups appear on opposite sides of polymer backbone alternately.



(*iii*) *Atactic polymers* have Y groups arranged randomly along the polymeric backbone and the material is soft, elastic, rubbery.



Spatial arrangement of an atactic polymer: It is a form of *addition polymer,* such as polypropene in which the side groups along the *polymer* chain are randomly orientated. Atactic polypropene is an *amorphous,* rubbery polymer of little value unlike isotactic polypropene (Fig. 20.1).

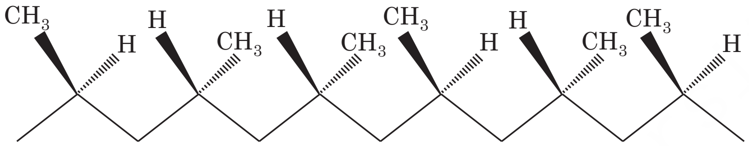
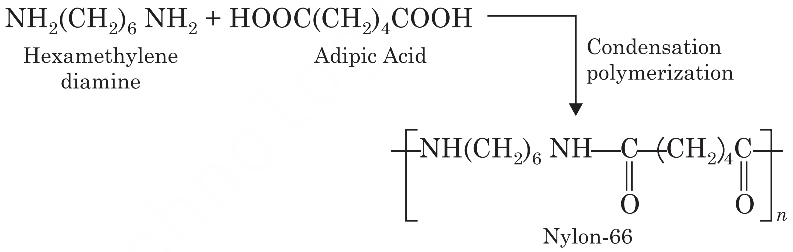


Fig. 20.1 Part of a chain of atactic polypropene.

Condensation polymerization

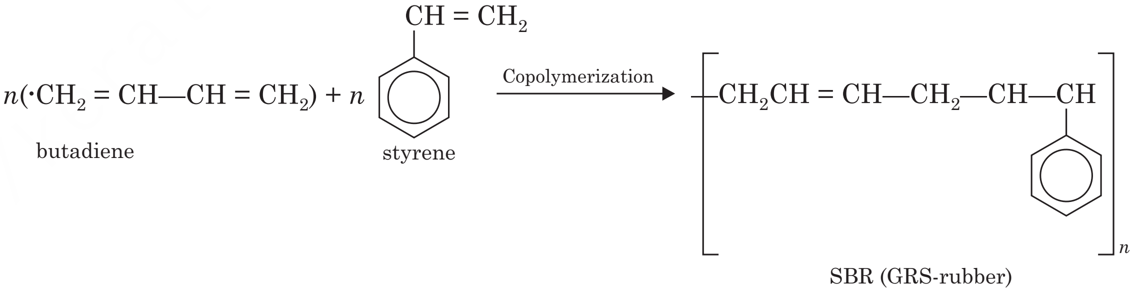
It is the type of reaction occurring between monomers containing polar groups which form polymer along with the elimination of small molecules like H_2O, HCl etc.

In this type of polymerization, as it takes place through the functional groups, when any monomer may contain two or three functional groups cross-linked polymer structure will be formed.



Co-polymerization

Two or more monomers undergoing joint polymerization is called copolymerization reaction such as the production of SBR (Styrene butadiene rubber).



Influence of structure of polymer on its properties

Strength of polymer

In cross-linked polymer, the units are linked by interchain covalent bonds forming giant, three dimensional structure and they are strong and tough as the movement of inter molecular chains are totally restricted.

Strength of straight chain polymers depends on the chain length. Polymers of low mol. wt. are soft and gummy but brittle. But higher-chain length polymers are tougher and more heat resistant. Presence of polar groups along the chain length also increases the intermolecular forces and increases the strength of polymer.

Highlights:

Types of polymerization

- Addition polymerization:

  The product polymer is exact multiple of the original monomeric molecule *e.g.*, polythene from ethene.
- Condensation polymerization:

  Combination through different functional groups of monomers with elimination of small molecules like H_2O.
- Copolymerization:

  Joint polymerization of two or more types of monomers. As for example SBR.
- Mechanisms of addition polymerization are:

(*a*) Free radical mechanism.
(*b*) Ionic mechanism.
(*c*) Co-ordination polymerization (Ziegler-Natta polymerization).

Plastic deformation

Polymers consisting of linear-chain molecules are always soluble and *thermoplastic*, even for very high molecular weight.

Three-dimensional polymer molecules are insoluble in any conventional solvent and are *thermosetting*. Hence, thermoplastic and thermosetting qualities of polymer depend on structure of the polymers. Artificially creating crosslinking converts thermoplastic material into thermosetting.

Physical state

Random arrangement of molecules in the polymer leads to amorphous state whereas regular arrangements of molecules or chains in a polymer lead to crystalline state.

The regular arrangement increases the intermolecular forces of attraction and leads to higher softening point, greater rigidity, brittleness and strength of the polymer. The amorphous nature of polymer provides flexibility.

Very long chain polymers having free rotating groups form irregularly coiled and entangled snorts, which can be stretched and again returned back to its original state giving rise to elastic character to the polymer.

Solubility and chemical resistance

Polymer containing polar groups are more soluble in polar solvents like water, alcohol but are chemically resistant to non-polar solvents like benzene, toluene, CCl_4 etc. Similarly, non-polar group containing polymers are chemically resistant to polar solvents but are soluble in non-polar solvents, particularly the greater the degree of cross-linking, less is the solubility of the polymer in a solvent.

Shapes and forms—mechanical properties

The internal arrangement of the long-chain molecules provides the forms in which the polymer may form *i.e.*, fibres, plastics and rubbers. If the internal forces between the molecules are low, molecules become bulky, form random arrangement and show rubbery character. If the internal forces are high they ultimately give rise to orderly arrangement and form fibrous nature. Intermediate forces lead to plastic nature.

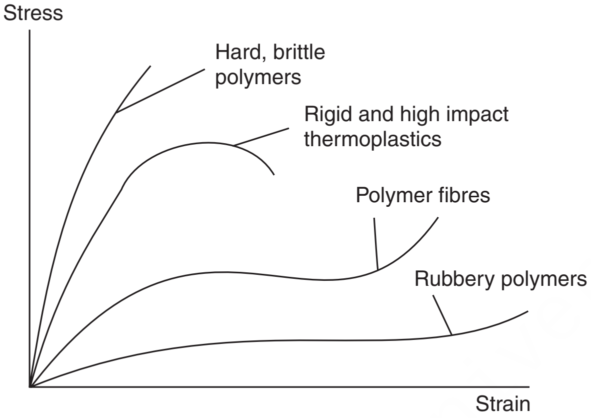


Fig. 20.2 Four types of stress-strain curves illustrating how polymers of different types behave (the lines end where the sample breaks).

The strength of the polymer is controlled by the length of the polymer chains and its cross-linking. Strength of a polymer is estimated from typical stress-strain curves for different polymers as shown in Fig. 20.2. On increasing strain continuously ultimately the polymer chains are uncoiled and fully stretched called *necking* and after this point the polymer reaches its *break point* and yields.

Effect of heat

Behaviour of polymer is controlled by the temperature. Amorphous polymers, which do not have melting point have softening points. At very low temperature both the crystalline and amorphous polymers behave like glass and on heating, the *glass transition temperature* is reached (T_g) after which they soften. Amorphous polymer becomes rubbery and then gummy and on further heating it liquefies. But the crystalline polymer on heating above T_g shows thermoplastic behaviour and finally liquefies.

PLASTICS (RESINS)

Plastics are a class of high polymers which can be moulded into any desired form by heat and pressure. Resins are actually the binders used for plastics and these two terms are used synonymously.

There are two classes of plastics or resins.

1. *Thermoplastic resins* soften on heating and harden on cooling and this change is not chemical but physical in nature, hence repeated heating and cooling also does not alter its nature.

2. *Thermosetting resins* are those which are heated during moulding and heating is continued until is set and hardened. This hardened material cannot be softened again, hence the setting is permanent and irreversible.

Compounding

Plastics for manufacturing of finished articles are always mixed with 4-10% of other materials, which impart some durable properties to the moulded material. These materials are known as additives which not only impart some properties to plastics but also make the processing easy. The process of mixing these additives to virgin plastics is called *Compounding.* Additives and their functions are discussed below:

(*i*) **Resin** is the binding constituent, which binds all the additives together. Thermosetting resins are added as linear low molecular weight polymers, which actually form crosslinking during the moulding process in presence of catalyst.

(*ii*) **Fillers.** Fillers can modify the properties of plastics to give the final plastic, better hardness, tensile strength, finish and workability.

Fibrous fillers such as wood flour, cotton fibre, chopped rags impart improved mechanical strength to the plastic; asbestos increases heat resistance; mica or slate powder improves electrical properties. Percentage of fillers may vary and can be upto 50%.

Solidified filaments of glass are bundled into strands, compressed to produce a glass mat. Plastics embedded with these mats are known as fibre reinforced plastics (FRP). FRP is very strong and can be used to make gates of dam, corrosion-resistant pipes and tanks, safety helmets, jeep bodies.

PVC laminated to steel or aluminium are called 'Composites'.

(*iii*) **Plasticizers.** Plasticizers are small molecules which penetrate into the polymer matrix and neutralize a part of the intermolecular forces of attraction between macromolecules and increase the mobility of the polymer segments so that chains can slide over each other. Thus, plasticizers act as an internal lubricant and improve the plasticity and flexibility of the polymer. Commonly used plasticizers include vegetable oils, camphor, dibutyl/dioctyl phthalate etc.

(*iv*) Waxes, oils, stearates and soaps are used to improve the finish and reduce the sticking tendency of the plastic to the moulds.

(*v*) **Colouring materials.** To improve the appeal and to impart beauty to the finished materials, colours are added to them. Soluble organic dyes are added to the transparent variety and inorganic pigments are added to the nontransparent plastics.

To give UV protection to the colours some compounds are added which preferentially absorb UV light.

(*vi*) **Other additives.** Sometimes antioxidants are added to prevent oxidative degradation of polymers. *Catalysts* like H_2O_2, benzoyl peroxide, ZnO, NH_3, Ag, Cu, Pb etc. are added to accelerate the cross-linking of the thermosetting plastics while they are in the moulds.

Stabilizers like Pb, Pb-silicate, Pb chromate etc., are added to improve the thermal stability of polymers during processing.

Antistatic agents like amines, amides etc., are added to dissipate the electric charge developed by conducting it away.

Processing of plastics

(*i*) **Calendering.** For production of continuous films or sheets this process is adopted. The compounding material is run between two highly polished metallic rollers rotating in opposite direction. While passing through the gap between the rollers the sheet is formed, whose thickness varies with the gap. Engraved rollers offer beautiful designs of embossed plastics.

(*ii*) **Die casting.** This cheap technique is used for acrylics, polyesters, phenol and urethans. Compounded material is poured into die cavities made up of metals or plaster of paris and it is heated when the crosslinking takes place and finally the finished material is cooled.

(*iii*) **Film casting.** A compounded solution in a suitable solvent is continuously dropped on a moving belt, the solvent evaporates and films are obtained. Cellophane papers and photographic films are produced by this process.

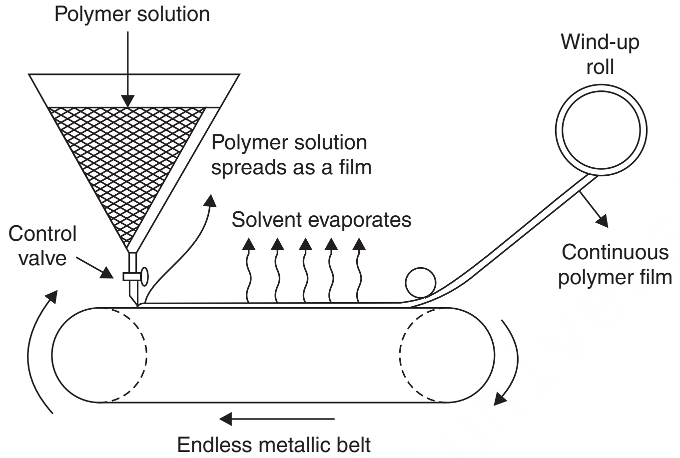


Fig. 20.3 A schematic representation of the film casting machine.

(*iv*) **Compression moulding.** This method is applicable for both thermosetting and thermoplastic materials. The mould consists of two halves. The compounding material in definite proportion fills the gap between the two pieces of mould, which are moved relative to each other. Heat and pressure applied. The cavities get filled with fluid plastic, two halves are closed slowly. Finally curing is done by heating (for thermosetting) and cooling (for thermoplastic). Furniture handles, telephone parts etc., are made by this process.

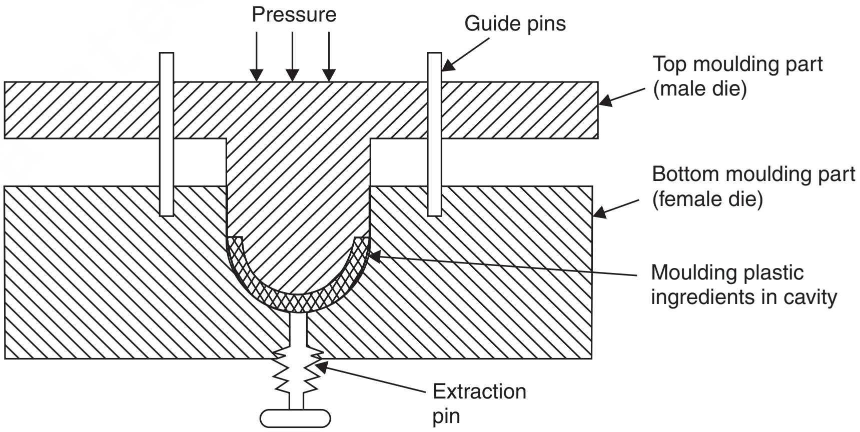


Fig. 20.4 Compressing moulding of plastics.

(*v*) **Injection moulding.** This process is applicable for thermoplastics only. Plastic powder is fed into a hot cylinder and then injected by a piston plunger into a tightly-locked mould with the help of a screw arrangement. The mould is cooled for curing and finally the half of the mould is opened for the ejection of the article. The whole process is automatic. Buckets, bowls, furniture parts are made by this process.

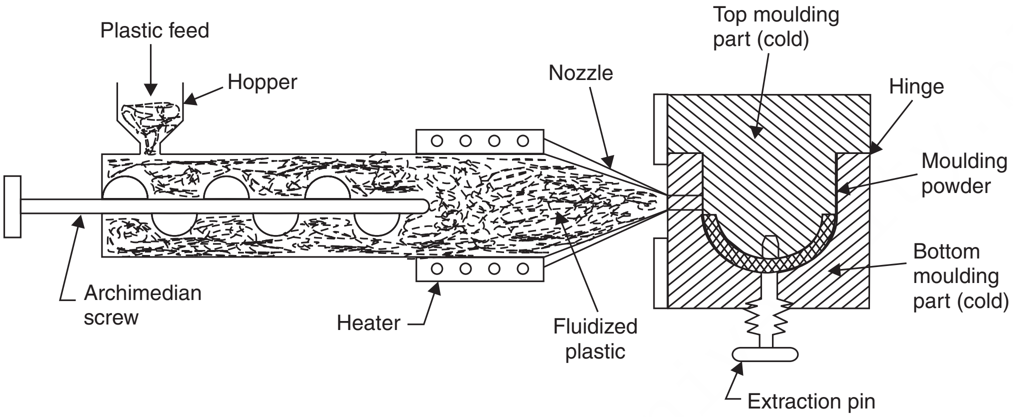


Fig. 20.5 Injection moulding of plastics.

(*vi*) **Blow moulding.** A hot softened tube of thermoplastic is placed between the two halves of mould and compressed air is blown whereby the thermoplastic takes the shape of the mould to form hollow articles like bottles, jerrycans etc. The mould is cooled and the article taken out.

(*vii*) **Extrusion moulding.** This process is used for continuous moulding of thermoplastics. The powder compounded material is introduced and electrically heated. In plastic condition, it is pushed by screw conveyer into a die whose shape is acquired by it and finally cooled.

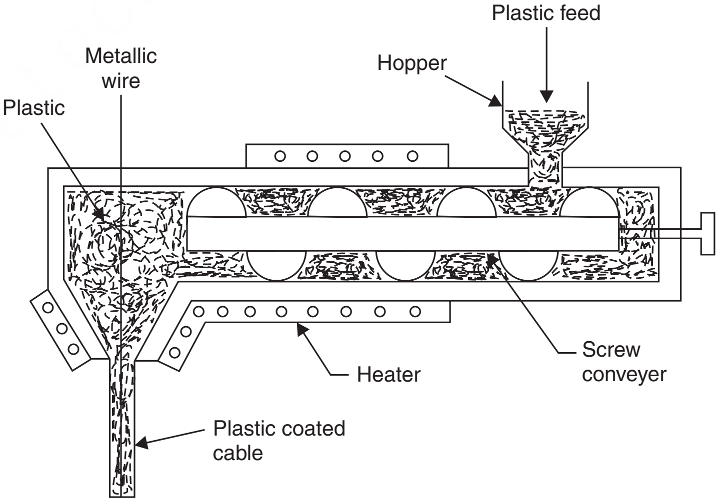


Fig. 20.6 Moulding of insulated electric cable by vertical extrusion moulding.

(*viii*) **Thermoforming.** This process is used to obtain three-dimensional articles from two-dimensional sheets. The thermoplastic sheet is heated and softened and placed between two halves of a metal die. The sheet is compressed between the die to the desired shape. Sometimes, vacuum is also applied so that the sheet sticks to the shape of the mould.

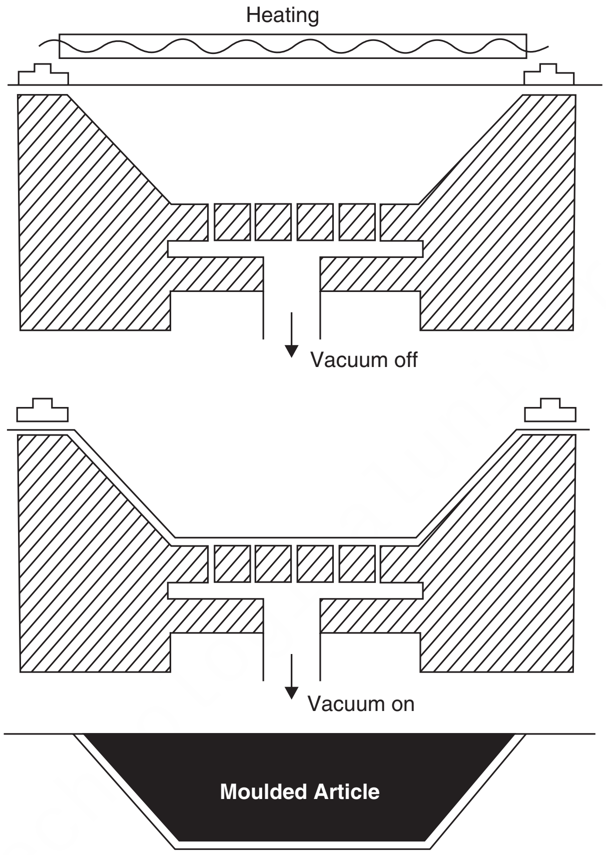


Fig. 20.7 Vacuum forming process.

Important Thermoplastics

Polyethylene

Polythene is polymerised ethylene. Ethylene is colorless gas at ordinary temperature. It is prepared in the lab by dehydration of ethyl alcohol at 160°C with concentrated H_2SO_4. Industrially dehydration of ethyl alcohol is the process for ethylene production*.

Polyethylene is manufactured by gas-phase polymerization. The ethylene gas is compressed to 1500 atmosphere and passed through a reactor maintained at 200°C in the upper and 120°C in the lower parts. O_2 (0.01%) or peroxides act as catalyst. Ethylene is polymerised into polythene, a waxy solid, which comes out from the perforated bottom of the vessel. The unreacted gas is recycled.

Two types of polyethylenes are available—LDPE (Low density polyethylene) and HDPE (high density polyethylene). HDPE is produced by using low pressure methods (31 kgf/cm^2) using ionic catalysts whereas LDPE is produced by using high pressure methods (1050-2000 kgf/cm^2) using free radical initiator.

Properties. Polyethylene is a rigid, waxy, white, translucent non-polar material. It has good chemical resistance against acids, alkalies and salt solutions, good insulating property but it is susceptible to organic solvents, particularly kerosene.

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* $C_2H_4 \xrightarrow[\text{Polymerize}]{} (C_2H_4)_n$

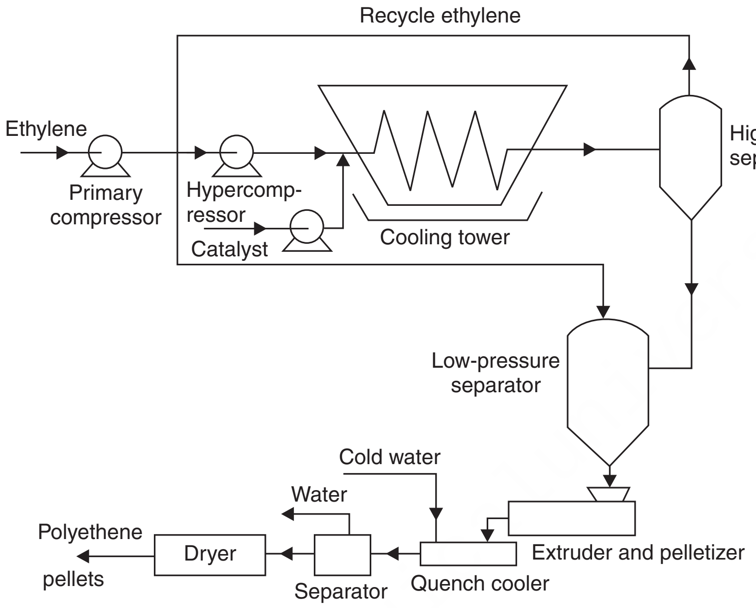


Fig. 20.8 Low-density polyethylene by high-pressure processing (LDPE).

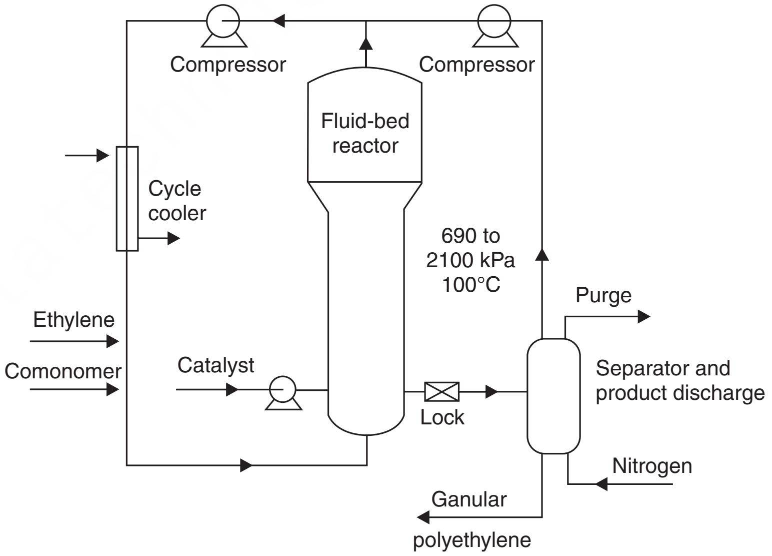


Fig. 20.9 High-density polyethylene by low-pressure resins (HDPE).

Polyethylene has highly symmetrical structure so it crystalizes easily. The degree of crystallinity varies from 40-95% depending on degree of branching. LDPE has a branched structure and hence is flexible and tough. It has low sp. gr. It has low hardness *i.e.,* about 1/10th of bakelite.

HDPE is a completely linear polymer, it has better chemical resistance, higher softening point, greater rigidity but low impact strength and it is opaque and relatively brittle.

Uses. Polythene sheets, tubes are manufactured, which are used for domestic purpose. It is also used to prepare toys, coated-wires and cables, bags for packing, bottles, caps, insulator parts.

Polypropylene

Polypropylene is obtained by polymerizing propylene in presence of Ziegler-Natta Catalyst *i.e.*, organo metallic halide with transition metal halide.

$$CH_3CH = CH_2 \xrightarrow{\text{Polymerize}} [CH_3CHCH_2]_n$$

Properties. Polypropylene is also an isotactic, highly crystalline polymer. It is superior to polyethylene w.r.t. resistance to chemicals, hardness, strength, moisture proofing quality etc. It is lightest among all high polymers.

Uses. Fibres of polypropylene are very strong and hence fibres are used for making ropes, carpets, blankets, bags, apparels etc. It is also used for packing of pharmaceutical and cosmetic products, for making sterilizable hospital equipments, washing machine parts, pipes, TV, radios, moulded luggage, colorful furniture etc.

Polyvinyl Chloride (PVC)

Vinyl chloride is the monomer for PVC and the monomer is produced by direct addition of HCl to acetylene at 60°C-80°C.

$$CH \equiv CH + HCl \xrightarrow{\text{HgCl}} CH_2 = CHCl$$

The polymerization of the gaseous monomer (b.p. 13.9°C) can be done in solution, emulsion and in suspension. The polymer is obtained in the form of fine powder and is soluble only in special solvents like dibutyl phthalate, benzyl benzoate etc. Increased solubility of the polymer is also attained by solution polymerization at high pressure and temperature.

$$nCH_2 = CHCl \xrightarrow{\text{Polymerize}} \underset{\text{PVC}}{\left(CH_2CHCl \right)_n}$$

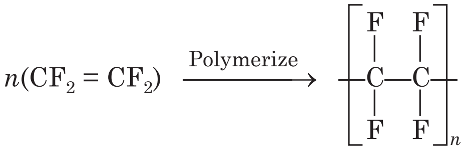
Properties: PVC is a colorless, odorless, non-flammable, chemically-inert powder. It contains 53-55% Cl_2 and softens at around 80°C.

It is resistant to water, light, O_2, inorganic acids and alkalies, oil, petrol etc., but soluble in hot chlorinated hydrocarbons.

Uses. It is the most widely used plastic. It has high rigidity and chemical resistance but brittle, so, its use is mainly in making cables, water hoses, toys, rain coats, rexin, pipes of petroleum industry, floor covering, refrigerator components, tyres, cycles and motor cycle mudguards etc.

Polytetrafluoroethylene (TEFLON)

It is obtained by polymerization of water-emulsion of tetrafluoro ethylene, under pressure and in presence of benzoyl peroxide as catalyst.

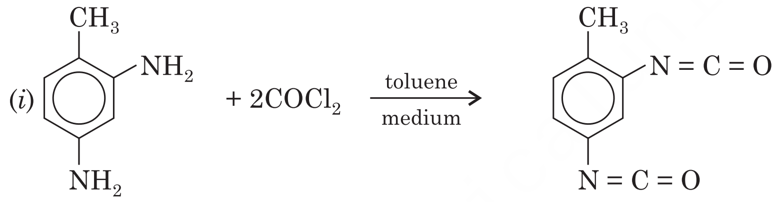


$$n(CF_2 = CF_2) \xrightarrow{\text{Polymerize}} \left[\begin{array}{cc} F & F \\ | & | \\ -C- & -C- \\ | & | \\ F & F \end{array} \right]_n$$

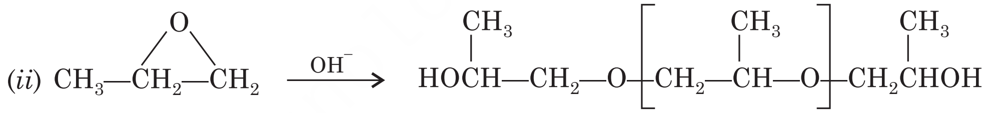
Properties. Due to the presence of highly electronegative fluorine in the regular polymer structure of TEFLON strong interchain forces are present which give the material extraordinary properties like extreme toughness, high softening point (350°C), high chemical resistance, low coefficient of friction and waxy touch, good mechanical and electrical properties. Due to all these qualities, the polymeric material can be machined. It softens at about 350°C, hence at this high temperature it can be moulded applying high pressure.

Uses. It can be used for insulating motor, transformers, cables, wires etc. Non-stick cookware coatings are made of TEFLON. It can also be used for making gaskets, pump parts, tank linings, pipes and tubes for chemical industry, non-lubricating bearings and to make non-reactive coating.

Polyurethane

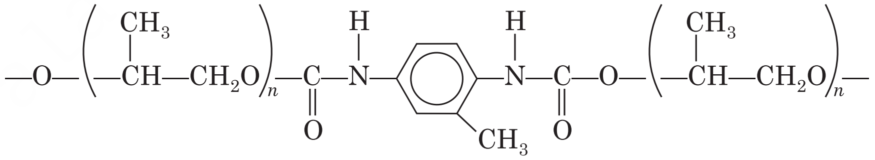


2, 4, tolulene di-isocyanate



Poly(oxypropylene) glycol

Polyurethanes are a varied range of crosslinked polymers made from two liquids—a polyol and an isocynate.



Polyurethane

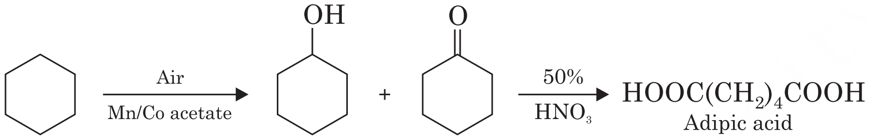
Properties. It can be foamed like polystyrene but unlike thermocoal, is soft, spongy known as 'U-foam'. It has low thermal conductivity. Its greatest advantage lies in the fact that it can be made where they are needed without any complex machinery—the two liquid ingredients can be mixed and moulded.

Uses. It is used as insulating material in refrigerators. Due to its spongy nature, it is used for making pillows and matresses. A coating of polyurethane is applied over leather, which improves the appearance and quality of the leather and hence the bags made of these look attractive and the shoes feel comfortable. It is also used to make chairs etc.

Nylon-66

Polyamides are synthetic polymers, having recurring amide groups, which have a structure similar to that of polypeptides. Nylon belonging to this class is used for making fibres.

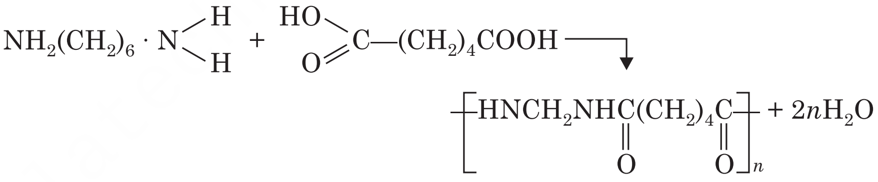
Nylon 66 is obtained by the polymerization of adipic acid with hexamethylene diamine. Adipic acid is commercially produced by oxidation of cyclohexane derived from either benzene or petroleum.



Hexamethylene is made by final hydrogenation of the adiponitrile.

$$\begin{tikzcd} & HOOC(CH_2)_4COOH + 2NH_4OH = H_4NOOC\text{—}(CH_2)_4COONH_4 \arrow[d, "\text{Distilled with } P_2O_5"] \\ \underset{\text{Hexamethylene diamine}}{H_2N(CH_2)_6NH_2} & \underset{\text{Adiponitrile}}{NC\text{—}(CH_2)_4\text{—}CN} + 4H_2O \arrow[l] \end{tikzcd}$$

Adipic acid and hexamethylene diamine mixed in equimolecular proportions in aqueous solution in an autoclave and heated at 100°C. The compounds react to form nylon salt in solution. Nylon salt is then heated at 265°C with Dow therm vapours to remove water and molten nylon results. Nylon fibre is obtained by *melt spinning process.*



$$NH_2(CH_2)_6\cdot N\begin{matrix}H\\H\end{matrix} + \begin{matrix}HO\\O\end{matrix}\!\!>\!C\text{—}(CH_2)_4COOH \longrightarrow \left[HNCH_2NH\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}\right]_n + 2nH_2O$$

Nylon can be extruded as a heavy ribbon, in an atmosphere of nitrogen which is chilled and chipped. The polymer can be remelted to spin into fibre and can be used for extrusion of molded objects.

Properties: Nylon is strong, tough, elastic and can be dyed easily. Nylon possesses high abrasion resistance and is chemically stable. It possesses high temperature stability and also high melting (160°C-264°C). It is insoluble in common organic solvents but soluble in phenol, formic acid.

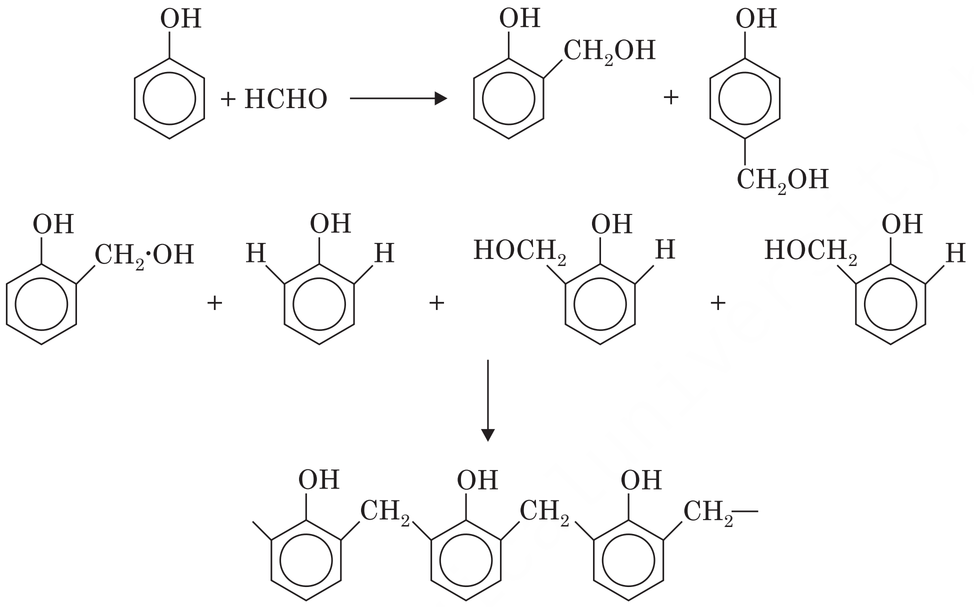
Uses: The polymer can be run directly to spinning machines to produce fibre, hence nylon 66 is primarily used for fibres, which find use in making socks, undergarments, dresses, carpets etc.

Important Thermosetting Resins

Phenolic resins

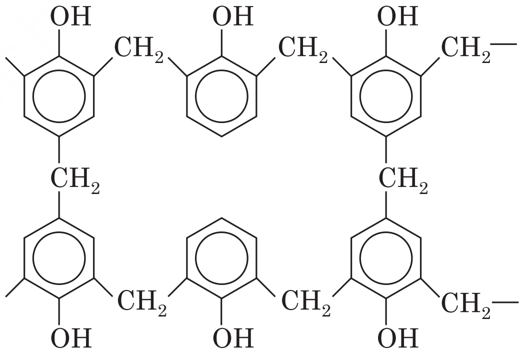
The most important of this class is *bakelite* or phenol-formaldehyde resin.

It is prepared by condensing phenol with formaldehyde in presence of acid-alkaline catalyst in an aqueous solution. In presence of acid catalyst, the first step leads to the formation of *o*-and *p*-hydroxy methyl phenol, which forms linear polymer.



Novolac

In the second step a small amount of hexamethylene tetramine added and at the steam temperature, the chain length increases and also three-dimensional resin is formed, which crosslinks the structure. Thus, the soluble novolac gets converted to insoluble *bakelite.*



bakelite

Properties. These phenolic resins are rigid, hard, water resistant. They are resistant to non-oxidising acids, organic solvents but are susceptible to alkalies. Solubilities and melting point of the resin gradually change with rise of molecular weight. These resins possess electrical insulating properties.

Uses. It can be widely used as metal substitute where high tensile strength is not necessary. As an inert material it can substitute for glass. It can be used for making insulator parts like switches, plugs, heater handles. It can be moulded to cabinets for TVs and radio and telephone parts. It is used as adhesive also used in paints and varnishes, as cation exchanger resin for water softening, in paper industry as propeller shafts.

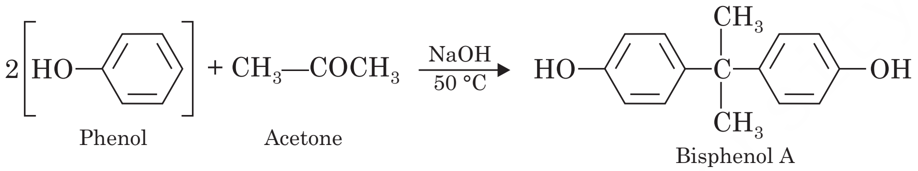
Epoxy resin

Epoxy resins are obtained from a poly condensation of epichlorohydrin with polyphenols or polyalcohols.

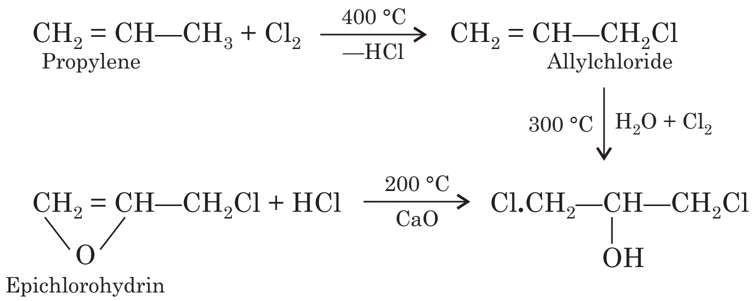
Monomers are:

(*i*) 2, 2-(*bis*)-4-hydroxy phenyl propane [*bis*-phenol]

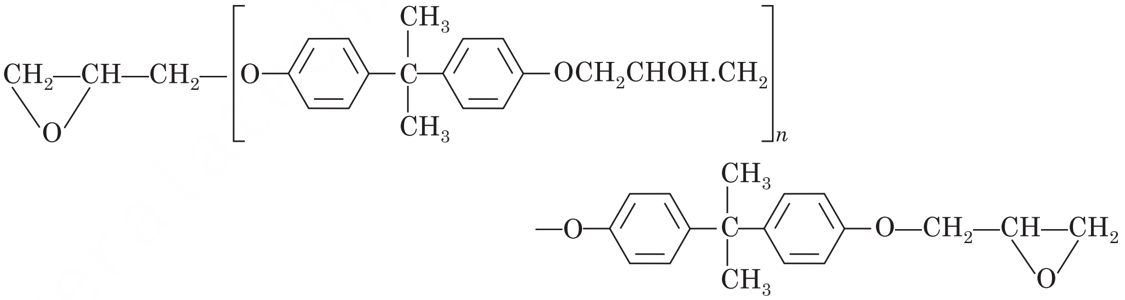
Preparation of bisphenol



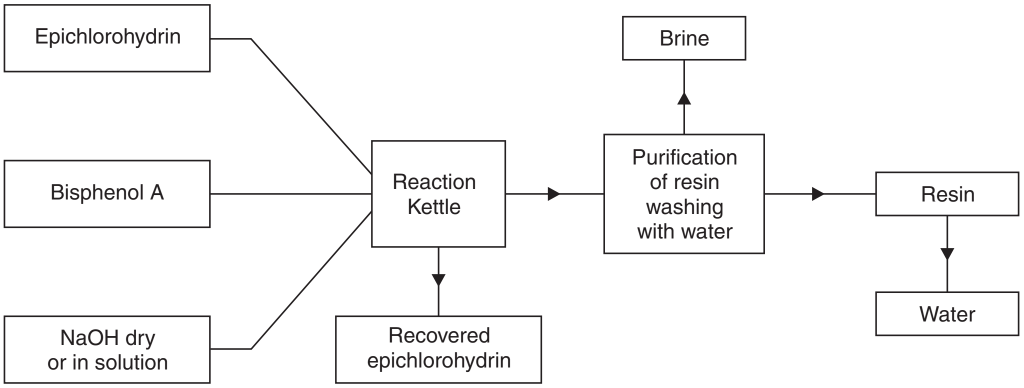
(*ii*) Epichlorohydrins



(*iii*) Structure of epoxy resin



Flow diagram for the production of epoxy resin:



Properties and Uses

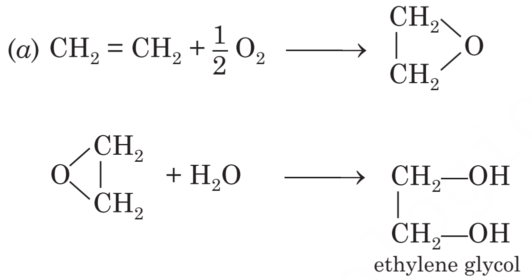
Epoxy resins possess outstanding properties of

- Adhesion to various materials
- Chemical inertness
- Stability at high temperature
- Flexibility
- Toughness
- Low shrinkage during cure.

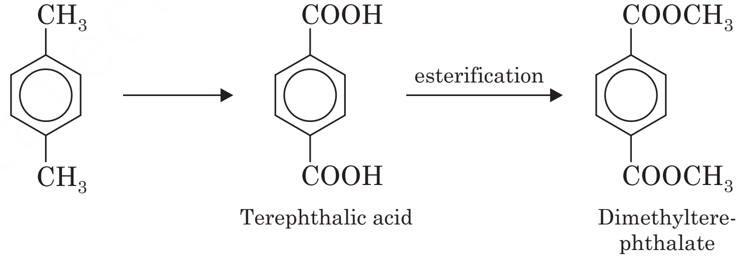
For the above properties, the epoxy resins are used as the major constituents of adhesives in paint industry and as insulator in electrical industry.

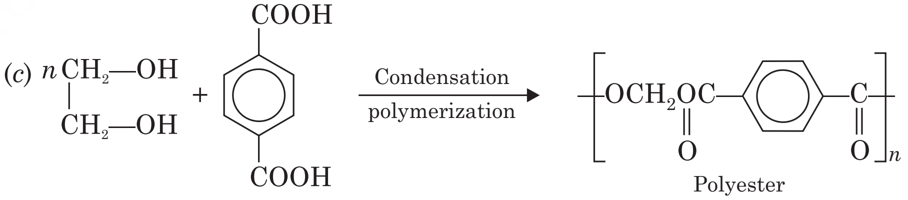
Polyester

Polyesters are the condensation products of dicarboxylic acid with dihydroxy alcohols. Terylene is the British name of Dacron, which is obtained by condensation of ethylene glycol and terephthalic acid. Ethylene is oxidised at high pressure and temperature in the presence of Ag as catalyst and the ethylene oxide is hydrolysed by dilute HCl to ethylene glycol.



(*b*) Paraxylene obtained from coal tar fraction is oxidised by neutral permanganate solution or conc. HNO_3 (50%) at about 100°C to give terephthalic acid.





The equilibrium of the reaction is not favorable for the formation of ester hence to get high yield the byproduct must be continually removed from the reaction mixture. Better yields are obtained with dimethylterephthalate.

Properties. Since the structure of the polymer is symmetrical and a number of polar groups are present it forms fibre easily. The fibre has high tensile strength and resiliency and is stable to hydrolysis. The fabric made from the fibre is crease resistant.

Uses. It is mostly used for making synthetic fibres like terylene, dacron etc., which are finally used for making garments for men, women and children.

It can be blended with wool and used for making carpets, blankets, upholsteries, quilts etc.

It can be reinforced with glass to form safety helmets, aeroplane parts, paratroop, wire insulators, fighter parachute etc.

Terylene has several advantages over cotton in respect of

(*i*) Resistance to acids

(*ii*) Strength

(*iii*) Crease resistance and

(*iv*) Gives better finish and blendable with cotton or wool.

Silicones

Silicones have alternate silicon-oxygen bonds and organic radicals attached to the silicon atoms.

The monomers are prepared as

(*i*) $$RCl + Si \xrightarrow{Cu} R_2SiCl_2$$

(*ii*) From Grignard reagent

$$SiCl_4 + RMgCl \longrightarrow RSiCl_3 + MgCl_2$$

The monomer is obtained by fractional distillation of the reaction products whereby different organo-silicon chlorides are obtained.

In the next step the chlorides are polymerized by hydrolysis involving the following steps–

$$\equiv SiCl + H_2O \longrightarrow \equiv SiOH + HCl$$

$$\equiv SiOH + HOSi \equiv \longrightarrow \equiv Si - O - Si \equiv + H_2O$$

Thus, the OH groups of Si are involved in polymerization hence when there is one or two —OH groups in Si, it leads to long chain polymers but when there are three OH groups, crosslinked polymers are formed. Reactions:

(*i*) $$2RCl + Si \xrightarrow{Cu} R_2SiCl_2$$

(*ii*) From Grignard reagent

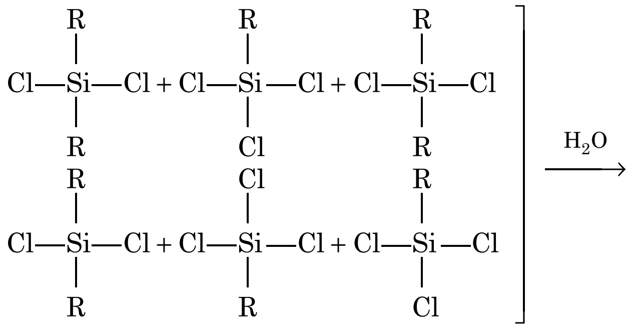
$$SiCl_4 + RMgCl \longrightarrow RSiCl_3 + MgCl_2$$

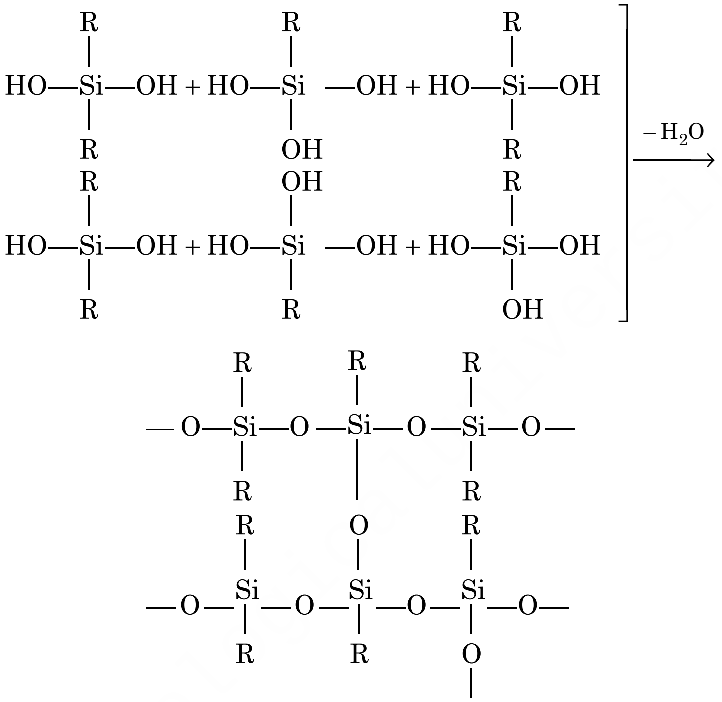
(*iii*) $$Me_2SiCl_2 \xrightarrow{H_2O} Me_2Si(OH)_2$$

Structure of Silicone Polymers

$$HO.SiMe_{2}\text{-}\underset{\text{Silicone}}{[OSiMe_2]_{n}}\text{-}OSiMe_2OH$$

Di-alkyl-di-chlorosilicane and alkyl trichloro silicone undergo hydrolysis and condensation polymerization to give a cross-linked silicone polymer.





(Cross-linked polymer)

Complete condensation of all the —OH give rise to hard, insoluble product, thus a mixture of monomers (containing one or more —OH groups) along with sufficient water for hydrolysis is heated for polymerization.

Different Types of Silicones

Depending on the proportion of various alkyl silicon halides used the final silicones may be liquids, viscous liquids, semi-solids and solids. Their properties and uses also differ accordingly.

(*i*) **Silicone fluids.** They are of relatively low molecular weight, sparkling clear fluids with an oily feel, insoluble in water but soluble in aromatic and chlorinated solvents. They have good resistance to heat and oxidation, low surface tension and show low change in viscosity with temperature.

Uses. They are used as autofoam agents, high temperature lubricants, in cosmetics, as damping and hydraulic fluids and to give water repellant finish to textiles and leathers.

(*ii*) **Silicone greases.** These are formed from the oils by adding silica, carbon black etc.

They are used as lubricants particularly for very high and low temperature applications.

(*iii*) **Silicone resins.** They are highly cross-linked polymers, possess good insulating properties, heat resistance and good dielectric properties.

Uses. Used for high voltage insulators, high temperature insulating foams, silicone-glass laminates for high temperature application, for different electrical and electronic equipment parts manufacturing.

(*iv*) **Silicone rubbers.** Silicone rubbers are formed by reaction of dimethyl silicone fluid with peroxide and appropriate inorganic fillers like TiO_2, ZnO, SiO_2 etc.

They retain rubbery properties over a much wider temperature span, good heat transfer properties, good resistance to dilute acids and alkalis. They are flexible in wide range of temperatures.

Uses. For tyre manufacturing of fighter aircrafts, as insulators of electric wires in ship, as adhesives for artificial heart valves, transfusion tubings, for special boots to be used at very low temperature, for making lubricants, paints, protective coatings etc.

Molecular weight of a polymer

Polymers are mixtures of molecules of different molecular masses, since the chain length varies. There are the following types of molecular weights for polymers.

(*i*) *Number average molecular weight*

The number average molecular weight $(\overline{M}_n)$ is defined as the total mass (w) of all the molecules of polymer divided by the total number of molecules present. Thus

$$\overline{M}_n = \frac{w}{\Sigma N} = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

where N_i is the number of molecules of mass M_i. $\overline{M}_n$ can be determined by measuring the colligative properties like lowering of vapor pressure, depression of freezing point etc.

(*ii*) *Weight-average molecular weight*

Weight average molecular weight $(\overline{M}_w)$ can be defined by the following relation:

$$\overline{M}_w = \frac{\Sigma w_i M_i}{\Sigma w_i}$$

where w_i is the weight fraction of molecules having mass M_i.

Also,

$$\overline{M}_w = \frac{\Sigma c_i M_i}{\Sigma c_i} = \frac{\Sigma c_i M_i}{c} = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

where c_i = weight concentration of M_i molecules and c = total concentration of all polymer molecules.

Now, $\overline{M}_w$ is always greater than $\overline{M}_n$.

$\overline{M}_w$ can be determined by light scattering measurements, viscosity measurements, diffusion measurements. $\overline{M}_w/\overline{M}_n$ is used as a measure of the molecular-mass distribution or "index of polydispersity" and it is 1.5 or larger for natural and synthetic polymers. $\overline{M}_w = \overline{M}_n$, in case all the polymer molecules are of identical molecular weight.

Degree of polymerization

The number of recurring units of monomers in a polymer chain is known as degree of polymerization (DP). In a polymer, actually the chain length varies, some may contain 100 to 200 monomers while others may contain 1000 or more. Hence, we use the term average degree of polymerization $(\overline{DP})$.

In a free radical polymerization, the overall rate of polymerization is proportional to the concentration of the monomer and the square root of concentration of the initiator.

$$-\frac{d(M)}{dt} = K[M][C]^{1/2} \quad M = \text{concentration of monomer}$$

C = concentration of initiator

At a certain stage of polymerization it is found that the number of active centres for polymerization is equal to the number of chain terminators. At this stage the average degree of polymerization is

$$\overline{\mathrm{D}}\mathrm{P} = \frac{\mathrm{K}.[\mathrm{M}]}{[c]^{1/2}}$$

This equation relates average degree of polymerization with monomer concentration as well as initiator concentration. The degree of polymerization influences the tensile strength of the polymer.

Highlights:

Classification of plastics

- *Thermoplastic* resins soften on heating and harden on cooling reversibly.
- Cellulose derivatives
- Polythene, Polypropylene, Polystyrene, Polyvinyl chloride, Polytetrafluoro ethylene (Teflon)
- Polyamides (nylon)
- ABS polymers.
- *Thermosetting plastics* are permanent setting resins which harden on heating during moulding and they cannot be softened again. Examples of this class include
  (*i*) *Bakelite* obtained by polymerization of phenolic derivatives with aldehydes.
  (*ii*) *Melamine* obtained by condensing melamine with formaldehyde.
  (*iii*) *Terylene* (Polyester) are condensation products of dicarboxylic acids with dihydroxy alcohols
  (*iv*) *Epoxy resins* (araldite)
  (*v*) *Silicone* resins.

RUBBER

Rubbers are high polymers, which have elastic properties and can be stretched upto about 300 percent. The unstretched rubber is amorphous and the polymer chains are in a coiled state, which on stretching gets aligned causing crystallization. In releasing the stress the chains revert back to their original coiled state.

Natural rubber. Natural rubber is polymerized isoprene, which occurs in the latex of various trees. Natural rubber came into market first in early 19th century. The molecular weight of raw rubber is about 100,000-150,000 and is made from the latex of different plants like *Havea brasillians* and gangule found in tropical and subtropical countries. The latex is collected from the mature Havea tree by making deep cuts on the bark, and by allowing the latex stream to collect in a pot attached below the cuts. Tapping is done at intervals of about 6 months.

Coagulation of the latex. Latex is diluted to contain between 15-20% of rubber, filtered to make it free from dirt. Coagulation is then effected by adding acetic acid (1 to 2% on weight basis). Rubber coagulates as soft white mass which is washed and further processed.

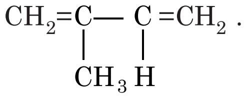
The coagulum is allowed to drain and the absorbed serum is squeezed out through steel rollers upon which water is sprayed. The coagulum is converted to a sheet with uneven rough surface resembling crepe paper and called *crepe rubber.*

Smoked rubber sheets are made from thicker sheets than crepe rubber. Coagulation is carried out in large tanks and finally allowed to settle for 16 hours. The tough slabs are passed through rollers (embossed or ribbed) to obtain ribbed pattern. The embossed sheets are then hung up in a smoking house, where on the floor, wood or coconut husk is burnt to produce heat. Smoking is done at a temperature of 45°C-50°C, whereby the sheets get dried within 4 days.

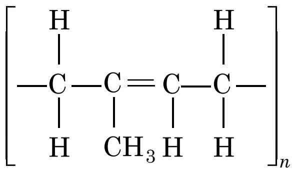
The crude rubber obtained is translucent and amber in colour and is not attacked by micro-organisms.

Properties. Natural rubber is an amorphous solid, translucent, impervious to gases, elastic in nature. It is actually polymerized *cis*-isoprene.

Rubber slowly oxidises when exposed to air. On heating it softens and liquifies. It burns to form CO_2 and H_2O. On destructive distillation rubber first softens and then decomposes producing white fumes. When the destructive distillation is carried out at higher temperature the condensate contains mostly the isoprene dimers.

Raw rubber powder catalytically reacts with H_2 gas, it decolorizes bromine water, forms ozonide with ozone, reacts with HCl. For each C_5H_8 unit in rubber molecule, one molecule each of Br_2, O_3 and HCl reacts, thus there is only one double bond. But for decomposition product of rubber *i.e.,* isoprene there is two double bonds  $CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}\underset{H}{\underset{|}{C}}{=}CH_2$.

During the process of linking, head and tail linking of isoprene molecule occurs.



Structure of natural rubber (*cis*-polyisoprene)

Rubber is attacked by strong alkalies and oxidising agents. Strong HNO_3 attacks rubber.

Limitations of natural rubber

Natural rubber softens at high temperature and becomes brittle at low temperature, it is attacked by acids, oxidising agents, non-polar solvents, it is oxidised by air. Also on excessive streteching it gets permanently deformed. To overcome these limitations rubber is vulcanized.

Vulcanization of rubber

During 1839, Charles Good Year developed the method of vulcanization of rubber by which the properties of natural rubber can be improved to a large extent. Vulcanization is a process which is essentially compounding rubber with different chemicals like, sulfur, H_2S, benzoyl chloride etc. The method is basically heating raw rubber with sulfur at 100° C-140°C, when the sulfur enters into the double bonds of rubber forming crosslinks between the chains and this gives the structure toughness. The toughness or the stiffness of vulcanization depends on the amount of sulfur included. For flexible tyre rubber, sulfur content is from 3-5% whereas for tougher variety like ebonite, content of S is 32%. Ebonite is so tough that it can be machined, it has very good electrical insulation property.

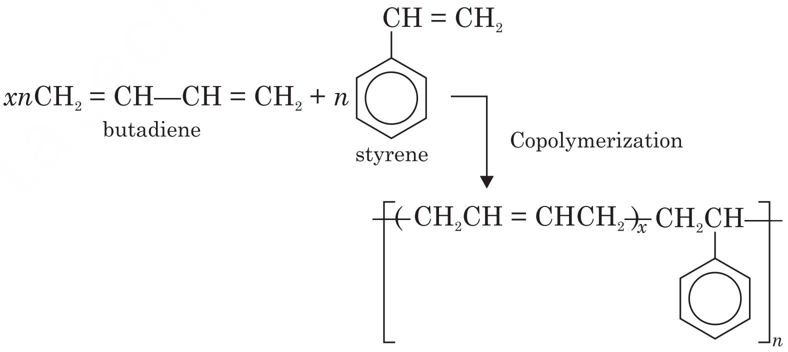
Comparative study between natural and vulcanized rubber

	Property	*Raw rubber*	*Vulcanized rubber*
1.	Elasticity	very high	low, depending on percentage of sulphur
2.	Tensile strength	200 kg/cm^2	2000 kg/cm^2
3.	Useful temperature range	10°C-60°C	40°C to 100°C
4.	Chemical resistance	very poor	higher
5.	Water absorption tendency	high	low
6.	Resilience	good	much better
7.	Insulation property	”	”
8.	Resistance to organic solvents	Low	much higher but swells
9.	Tackiness	marked	low
10.	Durability	less	better
11.	Quality	inherent	can be controlled by vulcanization

Synthetic Rubbers

Synthetic rubber is artificially produced rubber-like polymers which can be stretched to at least twice its length and on releasing the stress, it returns to its original shape and size. Some important examples are:

(*i*) *GR-S or Buna-S.* This variety is the most important synthetic rubber and it is obtained by copolymerization of butadiene and styrene.



SBR-Styrene butadiene rubber

Properties. SBR is similar to natural rubber in processing character and also as finished product. It possesses high resilience and good and tough mechanical properties. But unfortunately it is easily attacked by oxidising agents, mainly ozone. It also swells in organic solvents. It can be vulcanized as natural rubber.

Uses. It is mainly used for the manufacture of tyres. It is also used as soles and other components of shoes, for insulating wires and cables, as adhesives and lining for vessels.

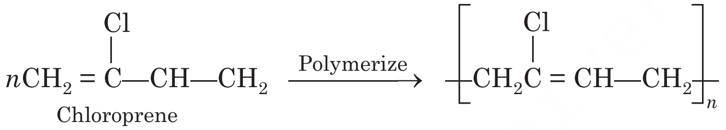
(*ii*) *GRA or Buna-N.* It is a copolymer of butadiene and acrylonitrile

$$x\mathrm{CH_2 = CH{-}CH = CH_2} + n\mathrm{CH_2 = CHCN} \xrightarrow{\text{Copolymerization}} \left[\mathrm{CH_2{-}CH = CHCH_2}\right]_x\left[\mathrm{CH_2{-}CHCN}\right]_n$$

Properties. It is highly resistant to heat, sunlight, acids, oils etc. but due to the presence of —CN group, it is much more susceptible to alkali than natural rubber. The good qualities increase as the proportion of acrylonitrile is increased and it can be vulcanized to better heat resistant variety.

Uses. Its use is versatile. It is used to manufacture parts for automobiles, aircraft. It is also used for making conveyer belts, adhesives and oil resistant foams.

(*iii*) *GR-M or Neoprene.* It is made by polymerization of chloroprene or α chlorinated butadiene.



$$n\mathrm{CH_2{=}\overset{Cl}{\overset{|}{C}}{—}CH{—}CH_2} \xrightarrow{\text{Polymerize}} \left[\mathrm{{—}CH_2\overset{Cl}{\overset{|}{C}}{=}CH{—}CH_2{—}}\right]_n$$

Chloroprene

Properties. The only difference of the structure of chloroprene and natural rubber is a single chlorine atom instead of an H atom which brings about marked resistance to temperature, atmospheric change and to oils. It can be vulcanized by heating alone. Its properties can be changed by compounding to ZnO or MgO.

Uses. It is used for making conveyer belts, adhesives, gaskets, as linings for reaction vessels and for making pipes to carry corrosive gases and oils.

Reclaimed Rubber

It is obtained from the waste rubber articles by the process of reclaimation.

Process. The waste rubber articles like tyres, tubes, footwares, gaskets etc. are cut and powdered in a cracker. The unwanted ferrous materials are separated by electromagnetic separator and then charged to an autoclave and digested with caustic soda solution at 200°C under pressure for 8-15 hours. The fibres get hydrolysed *i.e.*, devulcanization takes place. Sulphur is removed as sodium sulfide. It is washed, dried and finally reinforced with carbon black etc.

Properties: Reclaimed rubber has inferior tensile strength, elasticity etc. compared to natural rubber but has improved ageing properties. It is cheaper and easier for fabrication.

Uses. Reclaimed rubber is used for making tyres, tubes, belts, shoe soles, floor mats etc.

Compounding of rubber

Compounding is mixing of raw rubber with different chemicals to impart special properties for application.

Process. Synthetic or natural rubber is mixed with *vulcanizing agents* like sulfur, *plasticizers* like vegetable oils, waxes etc., *antioxidants* like amines and phosphites, *fillers* like C-black, *accelerators* like benzothiazole, mercaptans, and *coloring matters.* It is then repeatedly passed through hot roll mills rotating in opposite directions to soften and break down and the process is called *mastication.* Finally the material forms soft plastic mass.

Highlights:

Rubber

- Natural rubber is *cis*-polyisoprene
- Gutta percha is *trans*-polyisoprene.

Vulcanization

- The process discovered by Charles Good Year in 1839 to improve the quality of rubber by introducing sulfur at 100°C-140°C to the double bond of rubber.

(*Contd.*)

Synthetic rubber

- An elastomer produced artificially, which can be stretched to twice its length, but returns to its original shape.
  - — Styrene rubber (GR-S)
  - — Nitrile rubber (GR-A)
  - — Neoprene (GR-M)
  - — Thiocol (GR-P)
  - — Hypalon
  - — Polyurethane

Compounding of rubber

- Mixing of raw rubber with plasticizers, antioxidants, vulcanizing agents, fillers, colours etc. to impart specific properties to the finished products.

MISCELLANEOUS POLYMERS

1. **Laminate.** It is obtained by joining two or more layers of solid materials with the help of an adhesive. If the grains of the layers are parallel to each other, it is called *parallel laminate* and when they are at right angles to each other, it is called *cross laminate.*

(*a*) *Plywood.* Odd numbers of layer of wood (0.5-10 mm thick) are bonded such that grains of alternate layers are at right angles to each other (cross-laminate). By this process the plywood produced has uniform properties, length and widthwise, thus splitting of wood, shrinkage etc., are minimised and becomes more strong compared to wood of equal thickness.

Uses. Plywood is used for making railway coach, cabinets, false-ceilings and in other house building purposes.

(*b*) *Laminated Plastics*. Paper, cloth, asbestos fibre, glass, metal etc., are impregnated with thermosetting resin like phenol-formaldehyde or urea-formaldehyde solution in solvent and dried at a temperature much lower than the curing temperature of the resin, then they are cut into suitable size and then subjected to curing in a hydraulic press at about 180°C and pressure, when the resin becomes hard. The finished laminated plastics are light but strong and impermeable to water, oil etc. They are machineable and chemical resistant.

Uses. They are used for electrical and insulating materials, pump parts etc. They are also used for decorative purposes on table tops and wall panellings etc.

(*c*) *Laminated glasses.* Two glass sheets are joined by a plastic sheet in between to form laminated glass. For transparency, polyvinyl-butyl resin can be used as adhesive. Bullet proof or splinter proof laminated glass is obtained by curing the laminates in an oven under heat and pressure.

Conducting Polymers

Polymers obtained by the usual methods of polymerization are mainly insulators. Conducting polymers are made by special powders and are classified as

(*a*) *π-electrons conducting polymer.* In these polymers the backbone of the polymer is made up of molecules that contain conjugated π-electrons which extend the entire polymer and make the polymer conducting.

(*b*) *Conducting element-filled polymer*. In this type of polymer the polymer acts as binder, which binds the conducting elements like carbon black, metal oxides, metallic fibres that conduct electricity.

(*c*) *Inorganic polymer*. A metal atom with poly dentate ligand, which is a charge transfer complex is bound to the polymer to make it conducting.

(*d*) *Doped-conducting polymer*. The polymer is made conducting by exposing the surfaces to charge transfer agents in gas or in solution place.

(*e*) *Blended conducting polymer*. This type of polymer is made by blending a conventional polymer with a conducting polymer.

Industrially important conducting polymers are: Polyquinoline, polyanthrylene, polythiophene, polybutadienylene etc.

Uses. Conducting polymers are used for making (*i*) button cells, (*ii*) photovoltaic devices, (*iii*) sensors and (*iv*) biomedical devices.

SHORT QUESTIONS AND ANSWERS

Q. 1. What is functionality of a monomer?

Ans. It is the number of bonding sites of monomer.

Q. 2. What is gel point?

Ans. The monomers of alkyl resins possess functionality greater than two. During condensation polymerization it gets transformed from viscous material to a gel and the transformation is sudden. This point of transformation is the gel point. The cause of gelation is the formation of an infinite network of polymer and at this phase the resin becomes tough and less extensible.

Q. 3. What is ageing of rubber?

Ans. Ageing is the autooxidation of rubber with time due to the presence of double bond and due to this rubber becomes hard.

Q. 4. When is vulcanization done? Mention some of the uses of vulcanized rubber.

Ans. Vulcanization is done after shaping the article. The shaping is done with raw rubber along with suphur and other ingredients like accelerators, antioxidants, fillers etc.

Uses. Vulcanized rubber is used in vehicle tyres, hose, conveyer belt, electrical insulation.

Q. 5. What is the basic difference between nylon 6 and nylon 66?

Ans. Nylon 6 is an additional polymer whereas nylon 66 is a condensation polymer.

In nylon 6, the composition of the monomer is the same as that of the polymer, but nylon 66 is formed with the elimination of water molecules.

Q. 6. Differentiate between a homopolymer and copolymer?

Ans. A homopolymer consists of many identical monomer units whereas a copolymer consists of monomers of different chemical structures.

Q. 7. Differentiate between addition and condensation polymerization.

Ans. Addition polymerization is a reaction that gives a polymer, which is an exact multiple of the original monomers.

Condensation polymerization takes place through different functional groups of monomers with elimination of small molecules like H_2O etc.

Q. 8. What is copolymerization?

Ans. Copolymerization is the point polymerization of two or more monomers, *e.g.*, butadiene and styrene to yield GR-S rubber.

Q. 9. What is polydispersity index of a polymer?

Ans. Polymers are different from other small sized molecules as they are mixtures of molecules having different molecular masses. *Polydispersity index* (PDI) of a polymer is a measure of the molecular mass distribution of a polymer.

Q. 10. What is an elastomer?

Ans. Any rubber-like elastic polymer, which can be stretched to thrice its size and after removal of the stretching force it returns to its original shape is called an elastomer.

Q. 11. Why is the density of HDPE different from LDPE?

Ans. HDPE is completely a linear polymer and hence packing of the chains is efficient and hence its density is high. But for LDPE, due to its branched structure, packing efficiency is low and hence density is low.

Q. 12. Why thermosetting plastics cannot be reused?

Ans. In thermosetting plastics, the monomers are bound to each other by strong covalent bonds, which cannot be broken on heating. Thus by heating it cannot be softened to reshape and reuse.

Q. 13. What is natural rubber and what is gutta-percha?

Ans. Natural rubber is long-coiled chains of polycisisoprene and gutta-percha is horny and tough form of polytransisoprene.

Q. 14. Why is teflon highly chemical resistant?

Ans. In teflon the most electronegative element F contributes to the strong attractive force within the chains and hence is non-reactive towards other chemicals.

Q. 15. Why is PVC soft and flexible but bakelite is hard and brittle?

Ans. In PVC the molecular chains are bonded to each other by Van der Waal's forces and hence these long chains are flexible and can slip or twist on applying force but in the case of bakelite the thermosetting polymer chains are crosslinked by covalent bonds, so, it is hard and no deformation can take place on applying force. When the force becomes too large the covalent bonds are broken and it becomes brittle.

Q. 16. Why is natural rubber compounded?

Ans. Natural rubber possesses many undesirable properties and so to improve its properties it is usually compounded with different ingredients like plasticizers, antioxidants, filler, colorant etc.

Q. 17. Why is natural rubber vulcanized?

Ans. Raw rubber has high elasticity, tackiness, poor chemical resistance, poor strength, large water absorption capacity etc. Vulcanization *i.e.*, adding some sulfur at 100°C-140°C causes saturation of the double bonds by S and hence stiffening of the polymer takes place. Vulcanization, thus, improves all the above properties.

Q. 18. What changes take place with polymers near glass transition temperature?

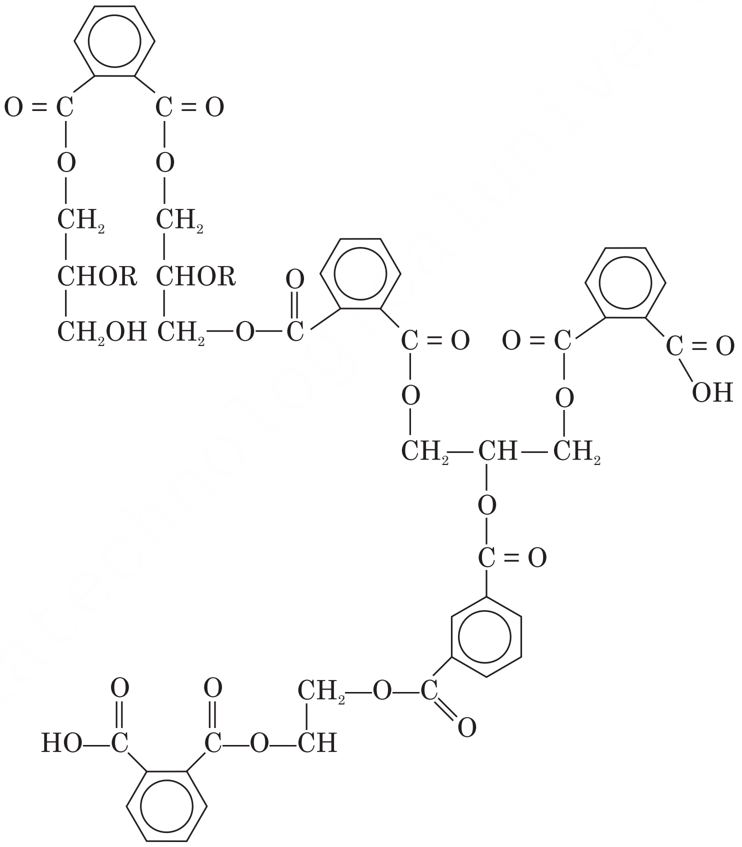
Ans. Below the glass transition temperature, the polymer is brittle and above it, they would deform but not break.

Q. 19. How can cross-linked silicone be produced?

Ans. Cross-linked silicone can be produced by adding a calculated quantity of trifunctional methyl silicon trichloride to the condensing polymer.

Q. 20. What are alkyd resins?

Ans. The basic reaction of alkyd formation is esterification. Phthalic anhydride is used instead of an acid and alcohol is polyfunctional alcohol, glycerol. The final cross-linked polymer is shown below:



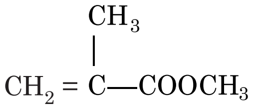
Alkyd resin (R = fatty acid chain)

Uses:

- As insulators
- As film formers in **emulsion paints**
- Automobile parts manufacture
- Switches manufacture.

Q. 21. What is polymethyl methacrylate (Trade name: Perspex)?

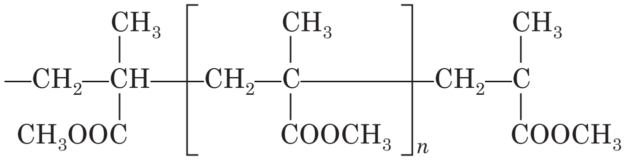
Ans. Here monomer is: Methylmethacrylate



$$CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C}—COOCH_3$$

Methylmethacrylate

Polymer is:



$$-CH_2-\underset{CH_3OOC}{\overset{CH_3}{CH}}-\left[CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-\right]_n-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}$$

Properties and uses

It is a glass-like plastic. It is used for making transparent sheets, rods etc. and also for making binoculars, camera lenses, table lamp shades. It is a component of *emulsion paint.*

Q. 22. What is polyvinyl (Trade name: Fevicol) alcohol?

Ans. Monomer is: $CH_2{=}CH—OH$ (Vinyl alcohol)

Polymer is: $-\!\!\left[CH_2—CH(OH)—CH_2CH(OH)—CH_2\right]_n\!\!-$

It is a water soluble polymer which is soft and gummy. It is used as an adhesive.

Q. 23. What do you mean by biodegradation of polymers?

Ans. Biodegradation is a process by which refuse mixes with environment by microorganisms. This biodegradation process is completely absent in the case of high polymers. Development of biodegradable polymer 'biopol' is now a challenge to scientists. Polyhydroxybutyrate is a 'biopol' which degrades within a few months in soil but it is too costly to be used very soon.

EXERCISES

1. Write short notes on (*i*) free radical polymerization (*ii*) cationic polymerization (*iii*) silicone resin.

2. Discuss various methods of plastic processing.

3. (*a*) Write short notes on

(*i*) addition polymerization (*ii*) condensation polymerization

(*iii*) thermoplastic and thermosetting plastics (*iv*) number average and molecular weight.

(*b*) Write the structures, two properties and uses of:

(*i*) PE, (*ii*) PP, (*iii*) PVC, (*iv*) PTFE, (*v*) Nylon 66.

4. Write the structures of five addition polymers and five condensation polymers, with their respective monomers.

5. Explain with example: (*i*) addition polymerization, (*ii*) co-polymerization, (*iii*) vulcanization of rubber.

6. Write short notes on:

(*i*) Rayon (*ii*) Synthetic rubber (*iii*) Types of plastics.

7. (*a*) Discuss the effect of structure of polymers on their physical properties in detail.

(*b*) Give the preparation and properties of

(*i*) Nylon 6, (*ii*) Neoprene rubber (*iii*) SBR (*iv*) Silicone rubber.

8. (*a*) What is a heterochain polymer? Give one example.

(*b*) Define the term functionality of monomers. Explain its significance with suitable examples.

(*c*) Discuss the preparation of bakelite and PVC plastic.

(*d*) What are the functions of fillers and plasticizers in plastic industry?

9. Discuss briefly the application of plastic in engineering and industry.

10. (*a*) Define the terms

(*i*) Degree of polymerization. (*ii*) Co-polymerization.

(*b*) What is the effect of polymer structure on the strength and crystalline nature of polymer?

(*c*) Give four uses of rubber.

(*d*) What are silicones? Draw the polymer obtained by hydrolysing dichlorodimethyl silicone and give its use.

11. (*a*) Explain the terms with example

(*i*) addition polymerization

(*ii*) co-polymerization

(*iii*) condensation polymerization.

(*b*) Give an account of one (*i*) Crepe rubber, (*ii*) butyl rubber.

(*c*) How are the following produced: (*i*) Buna S (*ii*) thiokols? Mention their properties and uses.

12. (*a*) What do you understand by vulcanization of rubber? What are the advantages and disadvantages? Give the structural unit of vulcanised rubber.

(*b*) Give the preparation and industrial application of PVC and neoprene.

13. (*a*) Give a brief account of vulcanization of rubber.

(*b*) Give the manufacture and uses of

(*i*) teflon (*ii*) nylon 66.

(*c*) What is an Epoxy group? Give the preparation and uses of a common Epoxy resin. Give the structure of bakelite.

14. (*a*) Outline the general method of preparation of urethanes and state their applications.

(*b*) List out the difference between HDPE and LDPE.

(*c*) Write note on glass reinforce plastic.

(*d*) What is meant by compounding of plastic?

15. Define the term crystallinity of polymer. How is it related to the chemical structure?

16. List the difference between addition and condensation polymerization.

17. Describe with a neat sketch the process of compression moulding. How does it compare with injection moulding?

18. (*a*) Discuss the mechanism of addition polymerization.

(*b*) Define monomer, homopolymer, copolymer, graft polymer.

(*c*) Write note on silicone.

19. (*a*) Discuss the preparation of natural rubber.

(*b*) Discuss the methods of preparation of urea-formaldehyde resin and polyurethane and mention their uses.

(*c*) Describe the methods of preparation of neoprene and silicone rubber. Mention their uses.

20. Write short notes on bakelite, thiokol.

21. (*a*) What is latex? How is natural rubber isolated from it?

(*b*) What is vulcanization? How does it improve the property of natural rubber?

22. Write preparation, properties and uses of

(*i*) Phenol-formaldehyde resin, (*ii*) Silicone rubber (*iii*) Polyethylene.

23. Distinguish between the following with examples:

(*i*) Natural and synthetic rubber

(*ii*) Addition and condensation polymerization

(*iii*) Thermo plastic and thermosetting plastic.

24. Write short notes on
(*i*) Teflon (*ii*) Cellulose acetate (*iii*) Silicone (*iv*) SBR.

25. (*a*) Define and give examples for
(*i*) Monomer (*ii*) Functionality (*iii*) Degree of polymerization (*iv*) Co-polymer.
(*b*) Explain how the polymers are classified on the basis of their thermal behaviour and method of polymerization. Give example of each class.

26. Distinguish between
(*i*) Thermoplastic and thermosetting plastic.
(*ii*) Addition and condensation polymerization.

27. Write note on thermoplastic and thermosetting resin.

28. What is an elastomer?
(*a*) Write short notes on preparation, properties and uses of (*i*) bakelite, (*ii*) epoxy resin.
(*b*) Name a polymer containing fluorine. Give its structure, properties and uses.

29. Distinguish between nylon 6 and nylon 66.

30. Write short notes on
(*i*) Polypropylene
(*ii*) Plexi glass.

31. Give preparation, properties and uses of (*i*) nylon 6, (*ii*) nylon 66, (*iii*) polyester or dacron, (*iv*) silicone resin.

32. (*a*) What are bakelite and PTFE? Name any four commercial thermoplastics.
(*b*) What are the materials from which an epoxy adhesive is prepared?

33. (*a*) Bring out the differences between thermoplastic and thermosetting plastic.
(*b*) Explain–Vulcanization of rubber.
(*c*) Explain–Injection moulding with a diagram.
(*d*) Explain the chemical resistant and thermal resistant polymers.

34. Give the representative formula and two important uses of each of the following:
(*i*) Plexi glass, (*ii*) Teflon, (*iii*) PVC.

35. Write a note on reclaimed rubber.

36. (*a*) What is meant by co-ordination polymerization? Explain with two examples.
(*b*) Write short notes on (*i*) Plastic deformation, (*ii*) Moulding techniques.

37. Write short notes on structure, method of preparation and uses of (*i*) HDPE, (*ii*) PVC, and (*iii*) Plexi glass.

38. Give a brief account of
(*i*) Vulcanization of rubber, (*ii*) Compounding of rubber.

39. What is the difference between-plastic, rubber, and fibre?

40. Write short notes on (*i*) rayon, (*ii*) nylon, and (*iii*) dacron.

41. (*a*) How is natural rubber obtained from latex?
(*b*) Explain compounding and vulcanization of rubber.

42. What is Zeigler-Natta polymerization?

43. Give the structures of syndiotactic, isotactic and atactic polymers.

44. How do the properties of polymer change with Zeigler-Natta polymerization?

45. (*a*) Mention the technical tests of polymers.
(*b*) Mention the influence of molecular characteristic on the properties of polymers.

46. What is biodegradation of polymers?

21

Paints

PAINTS

Paint is a uniformly dispersed mixture having viscosity ranging from a thin liquid to a semisolid paste and consisting of (*i*) a drying oil, synthetic resin or other film forming components, (*ii*) a solvent and (*iii*) an organic or inorganic pigment.

A paint is a product formulated to protect and decorate mainly metallic and wooden surfaces. A paint has three main ingredients.

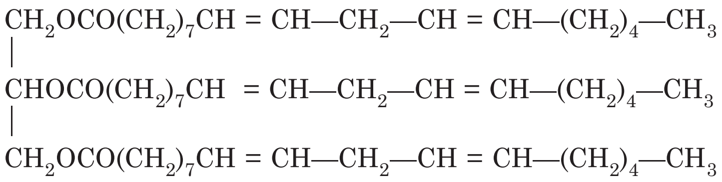
- *Pigments,* which scatter and absorb light, so that the paint covers up the surface underneath and decorates it with colour.
- *Polymers*, which hold the pigment to the surface by forming a smooth plastic film as the paint dries and sets.

In gloss paints the film forming polymers are alkyd resins; in emulsion paints they are latex polymers.

- A *vehicle,* which is a liquid in which the other ingredients are dissolved or dispersed.

In gloss paints a vehicle is traditionally a hydrocarbon solvent. In emulsion paint it is water.

In case of synthetic resins a drying oil (linseed oil, tung oil, rapeseed oil, mustard oil) may be used. Here film forming mechanism is different. The oil contains a long unsaturated fatty acid chain. Some sort of atmospheric oxidation and polymerisation occur due to the presence of unsaturation and a film is formed on the surface. The film forming substances are known as *binders*. The solvent is known as *thinner*. The binder and the solvent are collectively called a *vehicle*. Pigment extenders are generally called *fillers*. They not only reduce the cost of paint but also extends its durability.



$$\begin{array}{l} CH_2OCO(CH_2)_7CH = CH—CH_2—CH = CH—(CH_2)_4—CH_3 \\ | \\ CHOCO(CH_2)_7CH = CH—CH_2—CH = CH—(CH_2)_4—CH_3 \\ | \\ CH_2OCO(CH_2)_7CH = CH—CH_2—CH = CH—(CH_2)_4—CH_3 \end{array}$$

Drying oil (A glyceride of linolenic acid)

Characteristics of pigments

A pigment is any substance that imparts colour to another substance.

- It should be opaque.
- It should possess a good covering power.

- It should be inert.
- It should be non-toxic.

Characteristics of an ideal paint

- It should be chemically inert.
- It should be weather resistant.
- It should be non-toxic.
- It should have a suitable consistency which is generally determined by PVC.

Special types of paints

(*i*) Fire resistant paints
(*ii*) Chemical resistant paints
(*iii*) Luminous paints.
(*iv*) Marine paints.
(*v*) Emulsion paints or latex paints.
(*vi*) Metal paints.

Importance of emulsion paints (Latex paints)

(*i*) It can be employed on both interior and exterior surfaces.
(*ii*) Application of emulsion paint over a surface is an easy task.
(*iii*) It does not have any disagreeable product. And above all,
(*iv*) It is non-inflammable.

PVC (Pigment Volume Concentration)

PVC is defined as :

$$\text{PVC} = \frac{\text{Volume of pigment in paint}}{\text{Volume of pigment in the paint + volume of non-volatile vehicle in the paint}}$$

The concept of PVC is very much important in case of paints as PVC controls—*gloss, rheological properties*, *washabilities* and *durability* of a paint.

The concept of PVC is extremely useful to a paint formulator for determination of different pigment or vehicle combination *i.e.,* a range of PVC shown in the table below:

Table 21.1: Range of PVC in a given paint

Name	*%PVC*
(*i*) Flat paints	50–75
(*ii*) Semi gloss paints	35-45
(*iii*) Gloss paints	25-35
(*iv*) Exterior house paints	28-36
(*v*) Metal primers	25-40
(*vi*) Wood primers	35-40

Table 21.2: General formulations of paint are shown in the table

Constituents	*Class*	*Types and Functions*	*Example*
Vehicle	(*i*) Nonvolatile solvent based.	Oils and/or Resins (Film forming materials protect the surface from weathering), Driers (accelerate the drying of film)	Linseed oil, Tung oil, Dehydrated castor oil, Fish oils, casein, Acrylics.
		Additives in case of emulsion paints are antibacterial, stabilising surfactants and pH adjusters	Co, Mn, Zn, Pb, naphthenates.
	(*ii*) Volatile *i.e.,* low boiling solvent based (thinners)	Ketones	Methyl ethyl ketone (MEK).
		Esters	Ethyl acetate, Amyl acetate, Butyl acetate.
		Aliphatics	Naphtha and other petroleum fractions.
		Aromatics	Xylol, methylated naphthalene
Pigments	Inorganic or Organic	(*i*) Opaque	White lead, white ZnO, TiO_2.
		(*ii*) Transparent	Lithopone, chromegreen, zinc yellow.
		(*iii*) Special purpose	White extender pigments $BaCO_3 . BaSO_4$.
Extenders or Inerts		Diatomaceous earth etc.	China clay, talc, mica, etc.

Manufacturing of paints

The manufacture of paints involves only (*i*) mixing of the ingredients (*ii*) proper grinding and lastly (*iii*) packing.

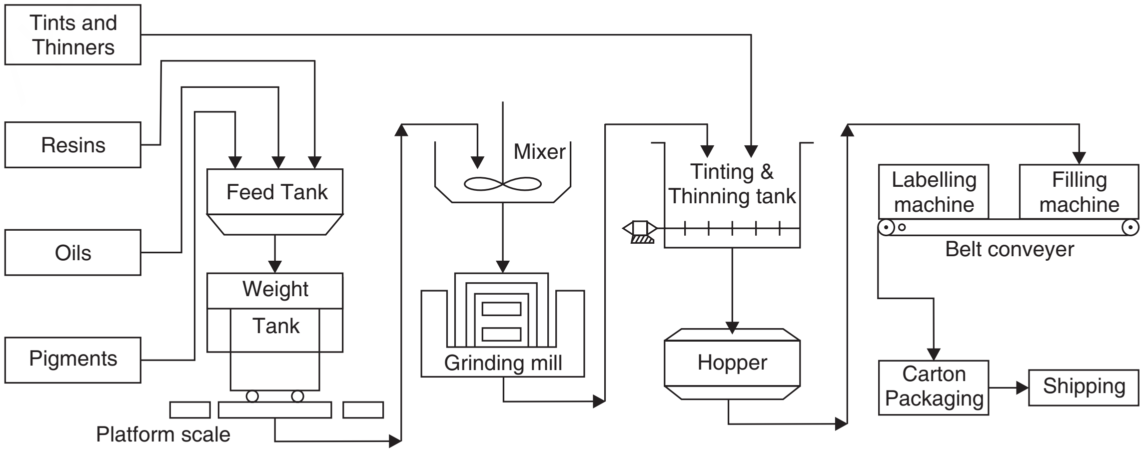


Fig. 21.1 A flow diagram of mixing of a paint.

Common pigments and their colours

White	*Red*	*Blue*	*Green*	*Yellow*	*Black*	*Orange*	*Brown*	*Metallic*
1. Titanium dioxide	1. Red lead	1. Ultra marine	1. Chrom-oxide	1. Litherge	1. Carbon black	1. Basic chromate	1. Burnt plumber	1. Copper powder
2. Zinc oxide	2. Rouge	2. Cobalt blues	2. Chrome green	2. Lead chromate	2. Lamp black	2. Cadmium orange		2. Zinc powder
3. Lithopone		3. Iron blues		3. Zine chromate	3. Furnace black			3. Aluminium powder
4. White lead								

Emulsion paints

Emulsion paints are those paints in which water is used in place of organic solvents as thinner. Emulsion paint is an emulsion of two phases viz.:

- Water and
- The vehicle of film forming material (a synthetic resin or latex).

The latex is dispersed in water by means of dispersing agent which acts as a binder. Pigments and extenders are dispersed in such an emulsion. Emulsifying agent or surface active agents, stabilisers, driers, antifoaming agents and preservatives are also added.

Advantages of an emulsion paint

- Emulsion paints can be applied on the surface of metal or wood very easily.
- Emulsion paints dry quickly.
- More durable and more impermeable to dust and dirt.
- They can be applied simply with a brush.
- The surface on which the emulsion paint is applied can be easily washed with water.
- They are free from fire risks.

Constituents of emulsion paints

Resin	*Stabiliser*	*Preservative*	*Antifoaming agent*
Polyvinyl acetate Polystyrene Alkyd	Methyl cellulose Dextrin Casein Starch alginates	Thymol Chlorothymol Mercuric chloride	Pine oil, Kerosene

Manufacture of an emulsion paint

Manufacture of emulsion paints involves following three steps:

- Protein dispersion
- Pigment dispersion
- Paint formation and addition of other ingredients.

A typical composition of an emulsion paint

Constituents	*Parts by weight*
Titanium dioxide	270
Clay	76.8
Tetrasodium pyrophosphate	1.8
Deionised water	16.5
Casein solution	764
Sodium penta chlorophenate solution	17.4
Pine oil	4.2
Tributyl phosphate	13.2
Copolymer latex	466

Distempers

Distempers are water paints comprising pigments, extenders, binders, and water as a dispersing medium. The distempers have:

(*i*) Good covering power

(*ii*) Ease of application

(*iii*) Durability

Disadvantage of distemper is that it is not moisture-proof.

Cement paints

Cement paint contains:

(*i*) White cement,

(*ii*) Colouring or pigments,

(*iii*) Hydrated limes, and

(*iv*) Fine sands as inert filler.

The dispersion medium is water or an oil. In case of brick structure the dispersion medium is water. In case of metal surface the dispersion medium is boiled linseed oil. Before applying cement paint a primer coat of a dilute solution of sodium silicate and zinc sulphate is necessary. Cement paint has marked water-proofing capacity and gives a stable and decorative film.

Varnishes

Varnishes are organic compounds used as protective coating similar to paints. But only difference is that varnishes do not contain colouring substances, *i.e.,* pigments.

Varnishes are classified under two heads:

- Oleoresinous varnishes and
- Spirit varnishes.

Oleoresinous varnishes are the solutions of one or more than one natural or synthetic resins in a drying oil and a volatile solvent. While the spirit varnishes are solutions of resins in volatile solvents only, generally methanol and ethanol. For the oleoresinous varnishes the formation of the film is due to the polymerisation of the oil and in case of spirit varnishes the film formation is due to only solvent evaporation.

Oleoresinous varnishes are also classified as:

(*i*) 'long oil' varnishes have high proportions of drying oil

(*ii*) 'short oil' type contains a lower proportion of drying oil (*iii*) 'medium oil' containing the proportion of drying oil intermediate between the two.

The classification is based on the use of drying oil in gallons per 100 lb of resin. The table below provides the type, field of application and properties of such varnishes:

Type	*Drying oil per 100 lb resins*	*Properties*	*Field of application*
(*i*) Short	6-15 gallon	Faster drying, harder and more brittle film	Floor and furniture
(*ii*) Medium	20-30 gallon	—	General purposes
(*iii*) Long	35-60 gallon	More weather resistant pliable films	Sparvarnishes

Properties of varnishes vary greatly depending on the three following factors:

- Cooking procedure
- Type of drying oil used
- Type of resin used

Manufacture

The manufacturing procedure depends on the type of oil and resin used. The sequences are as follows:

- In case of natural resin, when the resin is insoluble in oil, the resin is depolymerised first by heating it upto 350°C till foaming ceases. The preheated drying oil is then mixed and heated to obtain the desired viscosity. The mixture is cooled to 200°C and thinner and drier are added.
- In the case of synthetic resins preheating is not required and the procedure is likewise as above. In either case filtration is necessary.
- A solution of shellac in methanol or ethanol is produced by stirring followed by heating to produce spirit varnishes.

The table given below furnishes the constituents of a varnish (*i.e.,* four main ingredients of a varnish):

Film forming materials, i.e., ingredient 1	*Solvents and thinners, i.e., ingredient 2*	*Driers, i.e., ingredient 3*	*Anti-skinning agents i.e., ingredient 4*
(*i*) **Oil:** Linseed oil, tung oil, cotton seed oil, coconut oil, saya oil etc. (*ii*) **Natural resins:** Shellac, Rosin, Kauri, Copal etc. (*iii*) **Synthetic resins:** Alkyd, ester gum, coumarine-indene, chlorinated rubber, acrylates, silicones and vinyl resins.	Turpentine, kerosene, aliphatic and aromatic naphthas, xylol, alcohols.	Co, Mn, Pb, Zn resinates, octotes etc.	Guaiacol, tertiary amyl phenol.

Lacquers

Lacquers are dispersion or solution of a film forming material (like-nitrocellulose), resins and plasticizers in solvents and or diluents. The purpose of using of a lacquer is for protective and decorative aspects. The lacquer dries from the surface on which it is applied by simple evaporation of the volatile constituents, *i.e.,* solvents.

The table given below displays the constituents of lacquers:

Class	*Materials*	*Functions*
1. Film forming	(*i*) Cellulose derivative: (*i*) Nitro cellulose (*ii*) Cellulose acetate (*ii*) Resins and gums: (*i*) Ester gum (*ii*) Copal (*iii*) Synthetic resins: (*i*) Phenol aldehyde (*ii*) Alkyd	For waterproofness and durability; To improve retention of glass, adhesion and water resistance
2. Pigments (Not added in clear lacquers)	—	For pleasing colours
3. Solvents	(*i*) Esters: (*i*) Ethyl acetate (*ii*) Butyl acetate (*iii*) Amyl acetate (*ii*) Ketones: (*i*) Methyl ethyl ketone (MEK) (*ii*) Cyclohexanone (*iii*) Alcohols: (*i*) Ethyl alcohol (*ii*) Butanol (*iii*) Amyl alcohol	To dissolve film forming materials
4. Diluents	(*i*) Coal tar products: (*i*) Toluene (*ii*) Benzene (*iii*) Solvent naphtha	To reduce viscosity and cost
5. Plasticizers	(*i*) Castor oil (*ii*) Dibutyl phthalate (*iii*) Tricresyl phosphate	To reduce film brittleness and to improve adherence

Enamels and Japans

Pigmented varnishes or lacquers are known as *enamels. Japans* are closely related to enamels. Carbon black is added in deep black Japans.

Enamels are brushed or sprayed on the surface and finally hardened by baking. The deep black Japans are based on boiled linseed oil and are made by cooking linseed oil with litharge at 230°C for 5 hrs. The product is called *lead oil*. This lead oil is mixed with kerosene (thinner) and asphaltum. These Japans are applied and baked at 200°C for a few hours.

A *comparative study* of paints, varnishes, lacquers and enamels is given below:

Paint	*Varnish*	*Lacquer*	*Enamel*
1. A paint is a mixture of opaque solids dispersed in a liquid medium	A varnish is a colloidal dispersion or solution of syn-thetic or natural resins in oils or thinners	A lacquer is a colloi-dal dispersion or solution of film forming compound, *i.e.,* resin in a vol-atile solvent	Enamels are pigmented varnishes or lacquers
2. Used for protective and decorative aspect	Same	Same	Same
3. Drying is done by oxidative polymerisation	Drying by oxidative polymerisation	Drying by simple evaporation	Drying by either oxidative polymerisation or evaporation or by baking as per composition

SHORT QUESTIONS AND ANSWERS

Q. 1. What are the functions of pigments in a paint?

Ans. The functions are

(*i*) To protect the film by reflecting back the destructive UV light

(*ii*) To strengthen the film

(*iii*) To impart an aesthetic appeal

Q. 2. Name the main constituents of an oil varnish.

Ans. (*i*) Synthetic resins

(*ii*) Drying oil

(*iii*) Volatile solvents

Q. 3. What is a tonner?

Ans. Tonner is an insoluble inorganic dye used in paints.

Q. 4. How are the paint films formed?

Ans. The paint films are formed by drying an unsaturated oil.

Q. 5. What is 'drying' of an oil?

Ans. An oil is a glyceride *i.e.* ester of glycerol and fatty acids. A drying oil is generally glyceride of unsaturated fatty acids. The main function of the drying oil in a paint formulation is to form a protective film by complex chemical reactions. Otherwise, *drying* is a chemical change of an oil accompanied by oxidation and polymerisation due to the presence of unsaturation in the fatty acid portion of the formula of drying oil to form a protective film over the surface.

Q. 6. What do you mean by driers?

Ans. Driers are generally heavy metal soaps, soluble in oil and pretreated with oil (1-2% by weight) to hasten the process of *drying* by carrying oxygen to the position of unsaturation in oil.

Q. 7. What is a vehicle?

Ans. In paints, pigments and extenders are kept suspended in a vechicle. The vehicles may be film forming oil and other liquids, for example, turpentine, naphtha etc., used as diluents or a thinner during the application of paint.

Q. 8. Why are plasticisers added to a paint?

Ans. Plasticisers help to reduce cracking in paints.

Q. 9. Name some common extenders used is paints.

Ans. (*i*) China Clay
(*ii*) Gypsum
(*iii*) Mica
(*iv*) Silica
(*v*) Talc.

Q. 10. What is enamel?

Ans. Enamel is a pigmented varnish.

Q. 11. By what means is a paint applied?

Ans. (*i*) By brushing
(*ii*) By dipping
(*iii*) By spraying

Q. 12. Cite an example of a common spirit varnish.

Ans. It is a solution of shellac, which is a naturally occurring resin, in methylated spirit.

Q. 13. State the composition of an emulsion paint.

Ans. An emulsion paint consists of the following:
(*i*) Dry powders of pigments, fillers and extenders
(*ii*) A resin dispersion
(*iii*) Surface-active agents
(*iv*) Protective colloids.

Q. 14. What are the characteristics of an emulsion paint?

Ans. Emulsion paints have the following characteristics:
(*i*) Ease of application
(*ii*) Absence of disagreeable odour
(*iii*) Non-inflammbility.

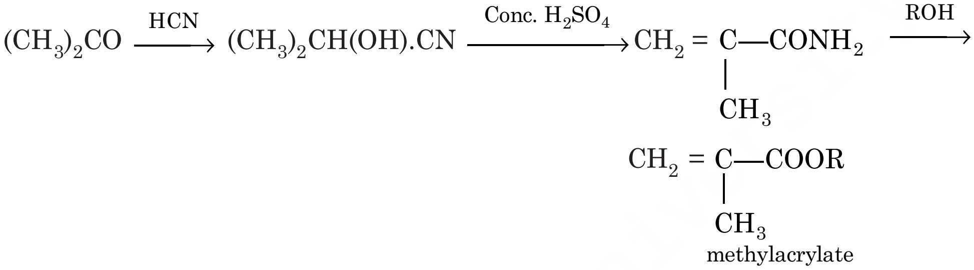
They can be employed on both interior or exterior surfaces.

Q. 15. What is an acrylic emulsion paint?

Ans. This is an emulsion paint. An acrylic acid derivative monomer is polymerised and emulsified and to it other ingredients of the paints are added. The monomer is generally ester of acrylic or methacrylic acid.

Reactions are as follows:

(*a*) $\mathrm{CH \equiv CH + CO + ROH \xrightarrow[HCl]{Ni(CO)_4} \underset{\text{acrylic ester}}{CH_2 = CHCOOR}}$

(*b*) 

$$\mathrm{(CH_3)_2CO \xrightarrow{HCN} (CH_3)_2CH(OH).CN \xrightarrow{Conc.\ H_2SO_4} CH_2 = \underset{\underset{CH_3}{|}}{C}—CONH_2 \xrightarrow{ROH} \underset{\text{methylacrylate}}{CH_2 = \underset{\underset{CH_3}{|}}{C}—COOR}}$$

Q. 16. State the specific requirements in paint application.

Ans. The requirements are as follows:

(*i*) Hiding

(*ii*) Colour

(*iii*) Weather resistance

(*iv*) Washability

(*v*) Gloss etc.

Q. 17. What do you mean by baking?

Ans. In the case of small articles, paint is applied by tumbling technique. The small articles are taken in a barrel with a required quantity of paint and the barrel is rotated while the articles get painted, the painted articles are then heated at 400 °F. This heating is known as *baking*. Baking improves adhesion, hardness, resistance to corrosion etc., to paints.

Q. 18. What is the main difference of film forming of an emulsion paint from that of an ordinary paint?

Ans. In the case of emulsion paints, the film-forming materials are various latexes whereas in ordinary paints, the film-forming materials are drying oils. In emulsion paints, forming of film takes place by coalescence of resin particles used as a base to form a strong continuous film.

EXERCISES

1. What is a paint?
2. Mention the constituents of a paint and explain their functions.
3. Give the characteristics of a good paint.
4. Write a short note on spirit varnish.
5. Distinguish between paint and varnish.
6. Write a short note on emulsion paint.
7. What are lacquers?
8. What are enamels and Japans?

22

Solid State Chemistry

Solids are mainly characterised by their definite shapes and considerable mechanical strength and rigidity. The rigidity arises due to the absence of the translatory movement of the structural units (like atoms, ions etc.) of the solid. These units remain fixed to a mean position about which they may undergo vibration. The forces of attraction between these units are large enough.

Solids are generally classified under two heads, namely **crystalline** and **amorphous**. In a crystalline solid, the constituent atoms are arranged in a definite pattern constantly repeated and in consequence giving rise to a definite geometrical configuration of crystalline solids. The crystals often have a plane fracture and they also have sharp melting points. On the other hand the amorphous solids have no definite geometrical shape. The amorphous solids melt slowly over a temperature range.

CRYSTAL

The term crystal originates from the Greek word "Krystallos" that means clear ice, and was first applied to transparent quartz stone with a wrong assumption that these stones were formed from water by extreme cold. In the 17th century the name crystal was extended to other solids possessing manifestations of solids that bore the relation to the original rock crystals of being bounded by many flat, shiny faces, arranged symmetrically.

A crystal grows from melt or a solution or from gaseous state by the deposition of atoms or ions onto its surfaces by which crystals are bounded. The surfaces are referred to as **faces** and an **edge** is formed where two surfaces intersect. The angle between the normals to the two intersecting faces is called the **interfacial angle**.

In a crystal the atoms or ions are arranged like soldiers on a parade ground in well defined columns and rows and this regularity of atomic arrangements in a crystal is the basic feature of crystals. There is a basic unit in any real crystal and when the basic unit is systematically repeated, reproduces the whole structure. Thus the first notable feature of the regularity of the crystal structure is the periodicity of their patterns and a **crystal is therefore a periodic array of atoms and molecules in space**.

The various modes of arrangement of atoms of molecules in space to satisfy the need of periodicity are governed by some specific rules and principles which lead to the development of the subject of **crystallography.**

In a more specific way a **crystal may be defined as a solid substance having a definite geometrical shape with flat faces and sharp edges**.

Fundamental laws of crystallography

Geometrical crystallography is concerned with the outward spatial arrangement of crystal planes and the geometrical shapes of the crystals and thus crystallography is dependent upon the three following fundamental laws.

- **Law of constancy of interfacial angle**
- **Law of rational indices, and**
- **Law of symmetry.**

Law of constancy of interfacial angle or Steno's law

The law states that **the angles between the corresponding faces on various crystals of the same substance are constant**. The crystals of substances are bounded by plane surfaces which are called faces. These faces always intersect at an angle, called interfacial angle. Interfacial angle has a characteristic value for a given crystalline solid.

It is often seen that the crystal faces are unequally developed, leading to various shapes of the crystals. But the angle of intersection of the two corresponding faces will be same for any crystal of the same substance. In Fig. 22.1, two crystals are represented two-dimensionally. The shapes are different but having the same interfacial angle.

For example, NaCl crystallises as cubes from aqueous solution and as octahedral from urea solution but interfacial angles of all crystals of NaCl are found to be 90°.

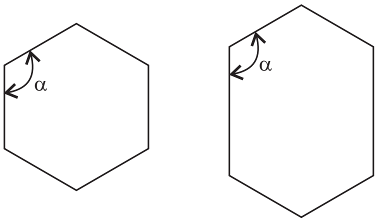


Fig. 22.1 Interfacial angle.

Law of rational indices

In 1784 Haüy proposed the **law of rational indices or rational intercepts**. This can be understood in the following way. For describing the geometry of a crystal usually three non-co-planar co-ordinate axes are selected arbitrarily. These are crystallographic axes. According to this law, the **ratio between intercepts on crystallographic axes for the different faces of a crystal can always be represented by rational numbers**.

In other words, all faces cut a given axis at distances from the origin, which bear a simple ratio to one another.

To illustrate, let us consider a plane ABC in the crystal as shown below:

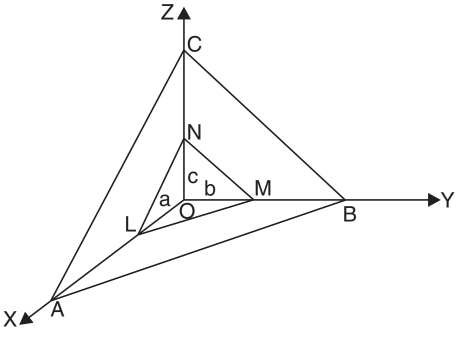


Fig. 22.2 Intercepts of crystallographic planes.

This plane has intercepts OA, OB and OC along X, Y and Z axes at distances $2a$, $3b$ and $4c$ respectively, where $OL = a$, $OM = b$ and $ON = c$ are the unit distances chosen along the three co-ordinates. These intercepts are in the ratio of $2a : 3b : 4c$, where 2, 3 and 4 are simple integral whole numbers and the standard intercepts are a, b and c. The ratio of the intercepts in terms of the standard is 2 : 3 : 4. These ratios characterise and represent any plane of the crystal. The coefficients are known as **Weiss indices** of the plane given. If any plane is parallel to one axis, then it will cut it at infinity. In such cases the use of Weiss indices are rather awkward and have consequently been replaced by **Miller indices**. The Miller indices of a plane are obtained by taking the reciprocals of the coefficients of a, b, and c *i.e.,* Weiss indices and is multiplied throughout by the least common multiple to obtain integral values. Thus, the Miller indices of the plane ($2a : b : 2c$) will be $\frac{1}{2} : 1 : \frac{1}{2}$ *i.e.,* 1 : 2 : 1 and this plane or face is indicated as (1 2 1) face of the crystal.

Now, for a plane perpendicular to one axis and parallel to the other two, having intercepts $-a : \infty b : \infty c$ will have indices, as:

Weiss indices $- 1 : \infty : \infty$

and Miller indices $- 1 : 0 : 0$ *i.e.,* (100) plane.

If a plane produces an intercept on the negative side, say $-a : -b : \infty c$, the Miller indices for the plane would be $(1\bar{1}0)$, the bar above one indicates the intersection of the plane on the negative side of the axis. The symbol $\bar{1}$ denotes minus unity.

Thus, if a face of a crystal makes intercepts OA, OB and OC on the three axes, then the lengths of the intercepts may be expressed as OA/a, OB/b and OC/c where, a, b and c are unit distances along three axes. The reciprocals of these lengths will be a/OA, b/OB and c/OC, and these reciprocal intercepts are whole number or integers *i.e.,*

$$a/\text{OA} = h;\ b/\text{OB} = k \quad \text{and} \quad c/\text{OC} = l$$

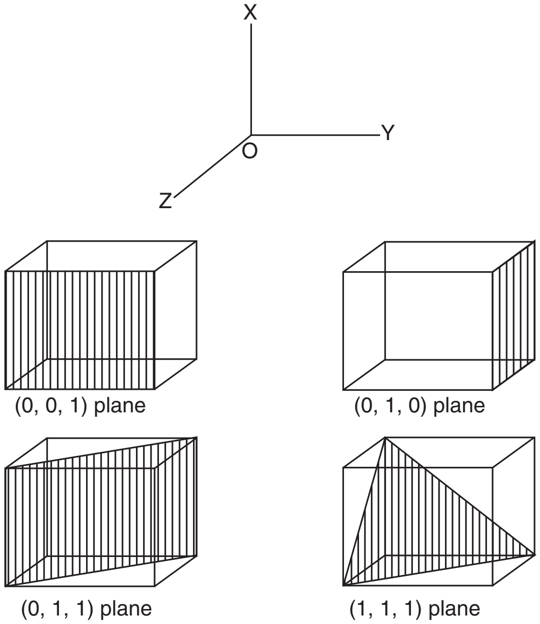
where h, k, l are Miller indices of the face or plane of the crystal and the face is defined as ($h\ k\ l$) face.

The distance between the parallel planes in a crystal is designated as d_{hkl}. For various cubic lattices, these interplanar spacings are given by the formula:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where 'a' is the length of the side of the cube and h, k, l are the Miller indices of the plane.

Some of the Miller indices in the case of cubic lattices are shown in Fig. 22.3 below.



(0, 0, 1) plane (0, 1, 0) plane

(0, 1, 1) plane (1, 1, 1) plane

Fig. 22.3 Miller indices in the case of cubic lattices.

The law of symmetry

Another important property of crystals is their symmetry. Symmetry in crystals may be with respect to : a plane, a line or a point. The law of symmetry states that: **all crystals of the same substance possess the same elements of symmetry**. There are three types of symmetry elements associated with a crystal, namely:

- plane of symmetry
- line of symmetry, and
- centre of symmetry.

Plane of symmetry

A crystal is said to have a plane of symmetry when it is divided by an imaginary plane into two halves in such a manner that one half is the mirror image of the other.

Line of symmetry

A crystal is said to possess a line of symmetry if it is possible to draw an imaginary line through the centre of the crystal and then to revolve the crystal about this line through 360° in such a way that the crystal appears unchanged more than once. The line is called the **axis of symmetry**. If similar view appears two, three, four or six times during one complete revolution of 360°, the crystal is said to possess two, three, four or six fold axes of symmetry.

Centre of symmetry

A crystal is said to possess a centre of symmetry, if every face has another identical face at an equal distance from the centre. A crystal can have only one centre of symmetry.

These planes, lines and centre of symmetry of a crystal are called its **elements of symmetry**. The cube has the greatest symmetry elements:

(*i*) Nine plane of symmetries
(*ii*) Thirteen axes of symmetries
(*iii*) One centre of symmetry *i.e.,* altogether twenty-three elements of symmetry.

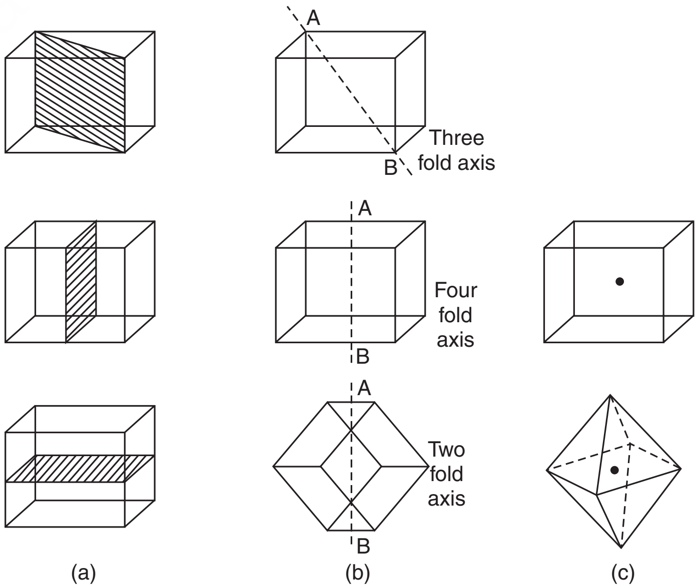
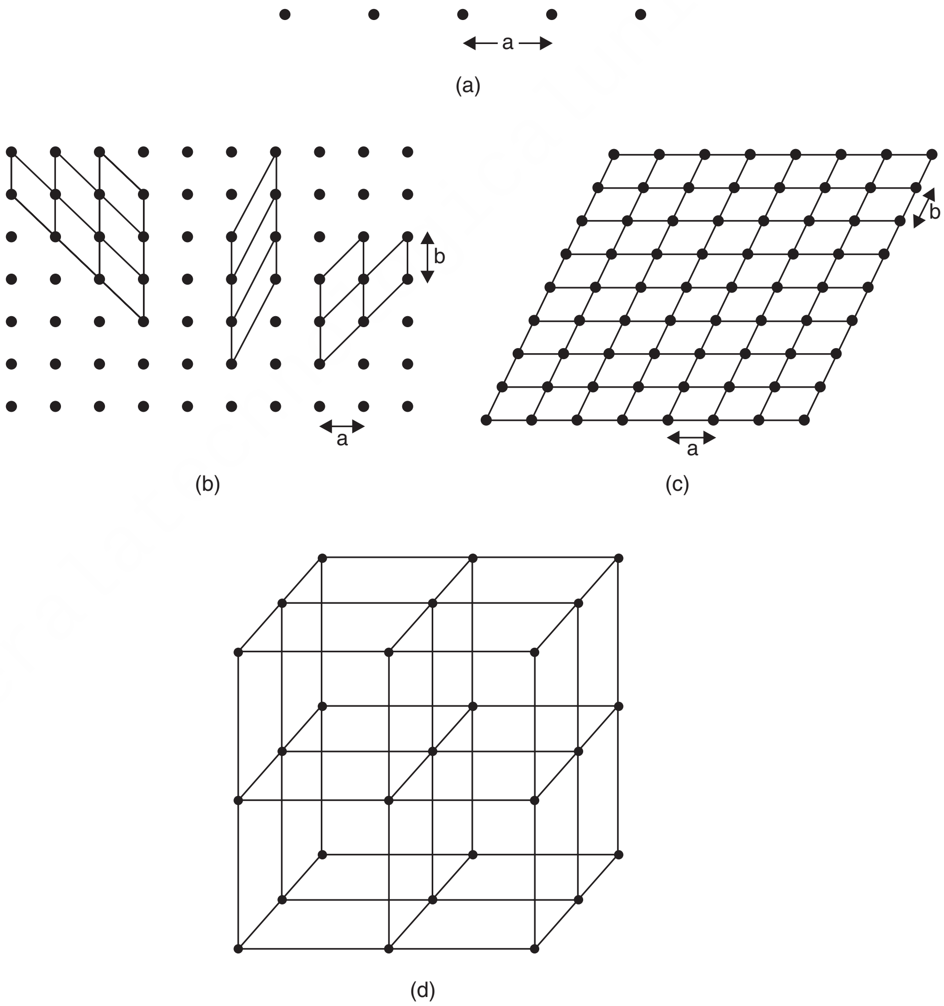


Fig. 22.4 Some elements of symmetry in crystals.
(*a*) planes of symmetry; (*b*) axes of symmetry; (*c*) centres of symmetry.

Crystal lattice

The idea of lattice developed from the internal regularity suggested from the external appearance of the crystal. A crystal lattice is a highly ordered three dimensional structure, formed by its constituent atoms or molecules or ions. Thus a lattice may be defined as **an infinite set of points repeated regularly through space**.

A set of points that are repeated at a distance '*a*' along a line form a **one-dimensional lattice**. When a set of points occur regularly in a plane, it constitutes a **two dimensional lattice**. When the set of points are repeated regularly in three dimensions, the **three dimensional lattice** or **space lattice** is obtained.



(a)

(b)

(c)

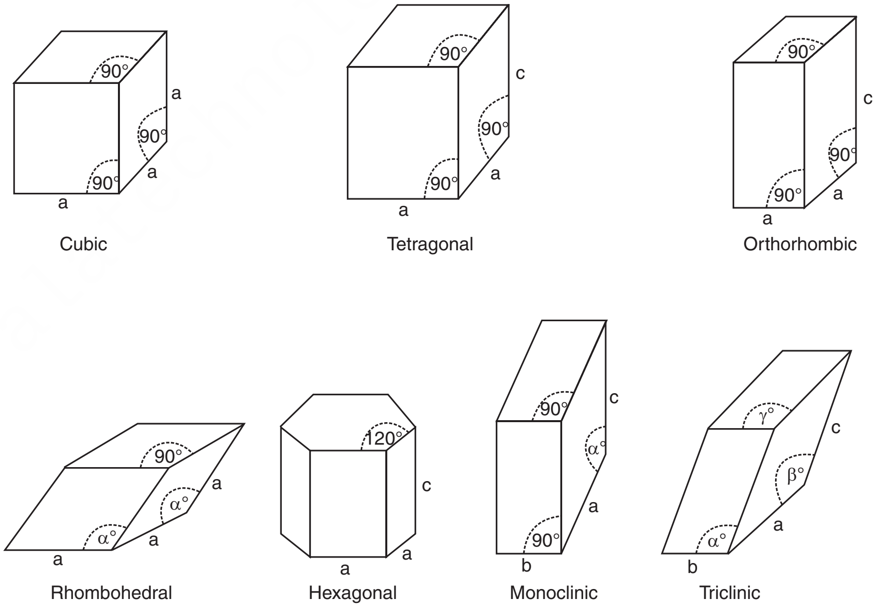
(d)

Fig. 22.5 Lattice arrangement: (*a*) one dimensional; (*b*, *c*) two dimensional; (*d*) three dimensional or space lattice.

On the basis of the arrangement of structural units in their crystal lattices, crystalline substances are classified as in Table 22.1.

Table 22.1 Crystal systems and their characteristics

System	*Axial characteristics*	*Angles*	*No. of space lattices*	*Examples*
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	3	NaCl, KCl, CsCl, ZnS
2. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	2	TiO_2, SnO_2
3. Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	4	KNO_3, K_2SO_4, $BaSO_4$, AgBr
4. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 90°$	2	$NaHCO_3$, $Na_2SO_4 . 10 H_2O$, monoclinic sulphur
5. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	1	$CuSO_4 . 5H_2O$, $K_2Cr_2O_7$, H_3PO_3
6. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	1	SiO_2, HgS, BN, PbI_2
7. Trigonal or Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	1	Al_2O_3, $CaCO_3$, graphite, Sb, $NaNO_3$



Cubic Tetragonal Orthorhombic

Rhombohedral Hexagonal Monoclinic Triclinic

Fig. 22.6 The seven crystal systems or crystalline forms.

This classification is based on the magnitude of the unit cell length and the angle of inclination between them. The **unit cell** is the smallest building unit in the space of a crystal, which when repeated over and over again in three dimensions, forms a space lattice of the crystalline substance. Thus the unit cell is the essential feature of the crystal structure. All the crystal systems are made up of 14 types of crystal lattice and these crystal lattices are known as Bravais lattices, shown in Fig. 22.7.

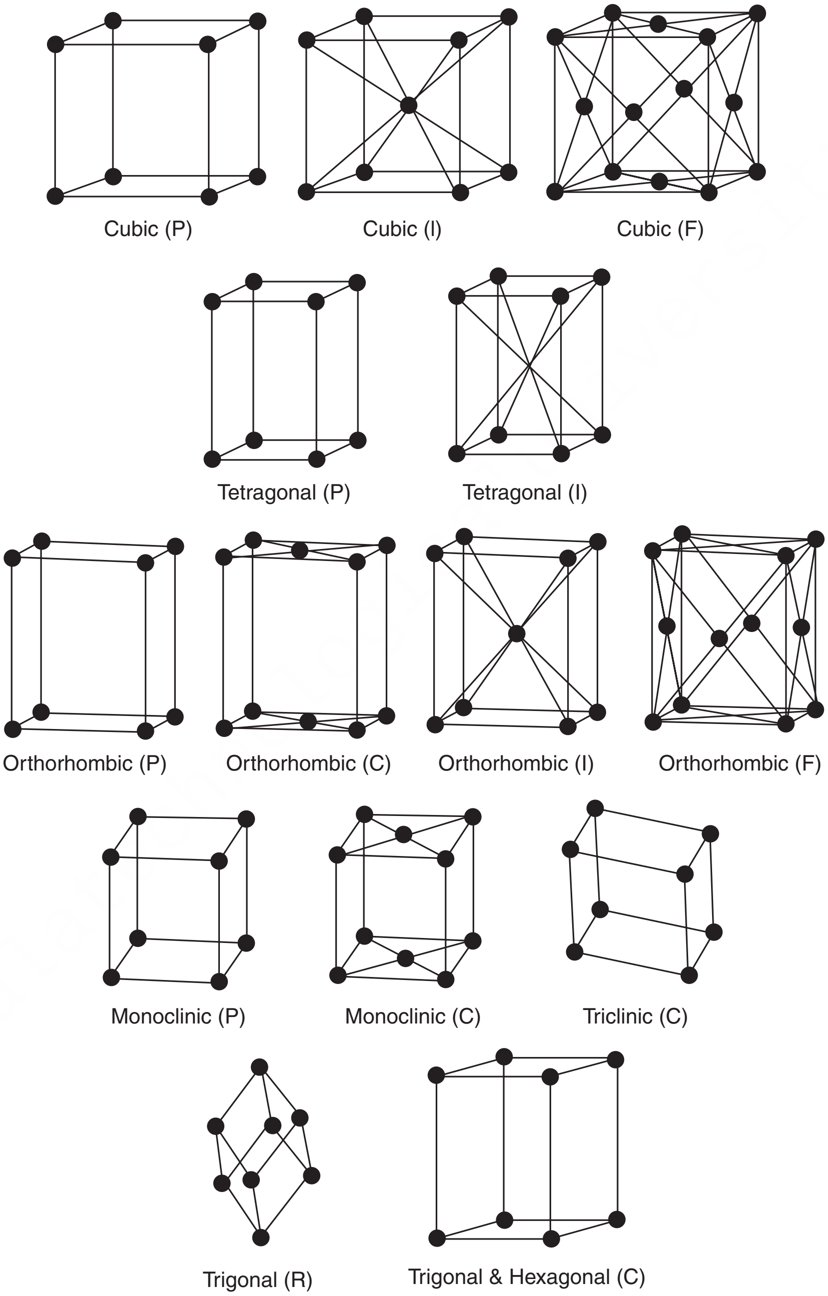


Fig. 22.7 The 14 Bravais lattices.

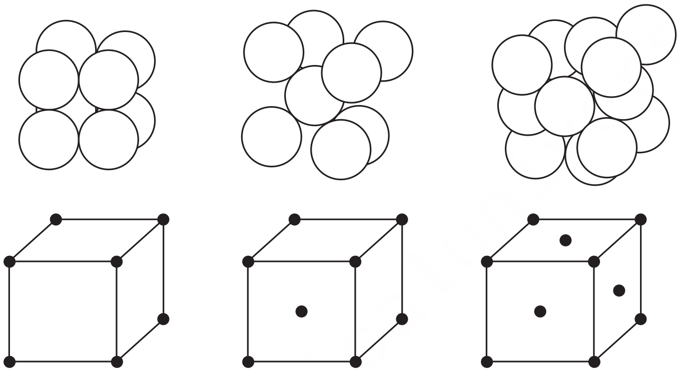
CUBIC CRYSTALS

In a cubic crystal, the intercepts on the three axes are equal and all the angles are equal to 90°. A cubic crystal can be any of the following three types:

(*i*) Simple crystal lattice (SC)
(*ii*) Body centered crystal lattice (BCC)
(*iii*) Face centered crystal lattice (FCC)

(i) Simple Crystal Lattice. In simple crystal lattice, there are lattice points at the eight corners of the unit cell. In a simple cubic structure, an atom situated at any corner of each unit, is shared by a total of eight unit cells, thus, each unit cell has 1/8 shares of every corner atom. So the total contribution of all the eight corner atoms to each cell

$$= \frac{1}{8} \times 8 = 1 \text{ atom/unit cell of SC.}$$



(a)
Simple lattice

(b)
Body centered
lattice

(c)
Face centered
lattice

Fig. 22.8 Bravais lattices of a cubic system.

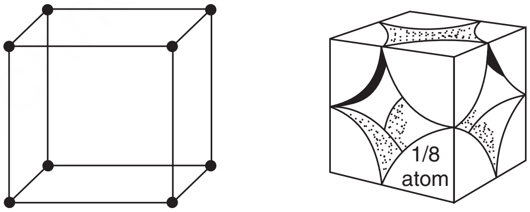


Fig. 22.9 Unit cell of simple cubic crystal.

(ii) Body Centered Crystal Lattice. In body centered crystal lattice, there are lattice points at the eight corners and at the centre of the unit cell. A BC cell has one additional atom at the centre besides having one atom each its right corners. The atom at the centre is independent of other cells, while each of the eight atoms situated at the corners is shared by a total of eight unit cells. Thus, the total number of atoms per unit cell

$$= 1 \text{ (at the centre)} + 8 \times 1/8 \text{ (at the 8 corners)}$$
$$= 1 + 1 = 2 \text{ atoms/unit cell of BCC}$$

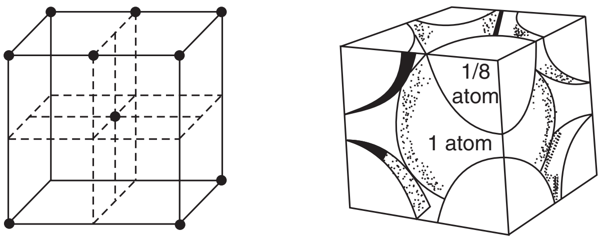


Fig. 22.10 Unit cell of body centered cubic.

(iii) Face Centered Crystal Lattice. In face-centered crystal lattice, there are lattice points at the centre of all faces, in addition to those at the eight corners of the unit cell. An FCC has one atom at the centre of the each face besides having one atom at each corner. Thus, every atom situated at the centre of a face of a unit cell is shared by two adjoining unit cells. Since there are six faces of a cube, so that total number of atoms per unit cell.

= 1/2 × 6 (at the centre of six faces) + 8 × 1/8 (at 8 corners)
= 3 + 1
= 4 atoms/ unit cell of FCC

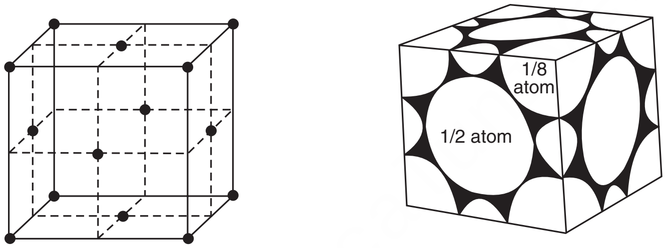


Fig. 22.11 Unit cell of face centered cubic.

The perpendicular distance between the adjacent planes is known as the **interplanar spacing** and is denoted by d_{hkl}.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a = side of the cube.

Atomic radius of a cubic lattice

Atomic radius of a unit cell may be defined as "half the distance between the centres of two immediate neighbours in a unit cell" and is denoted by 'r'.

The distance between the centres of two corner atoms of the cube is called length of the cube edge and denoted by 'a'.

Thus, for a simple cubic (SC) cell

atomic radius $r = a/2$
as we know that $a = 2r$

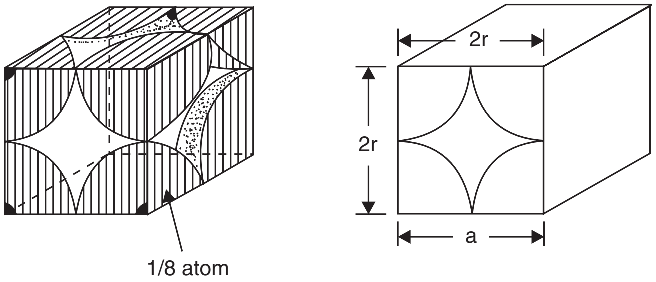


Fig.22.12 Simple cubic cell.

and for body centered cell (BCC)

$$(4r)^2 = (a^2 + a^2) + a^2 = 3a^2$$

$$\boxed{r = \sqrt{3a/4}}$$

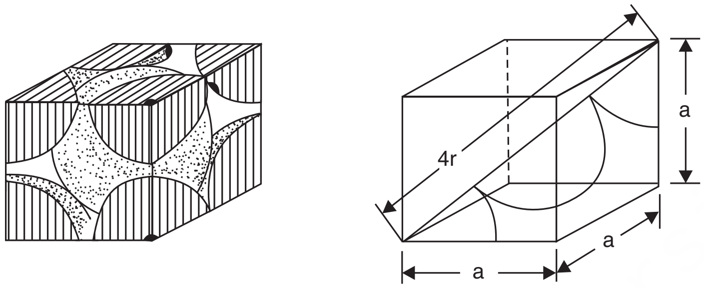


Fig. 22.13 Body centered cubic cell.

While for face centered cubic cell (FCC)

$$(4r^2) = a^2 + a^2$$

or $$16r^2 = 2a^2$$

Thus $$r = a/2\sqrt{2}$$

$$\boxed{r = a/\sqrt{8}}$$

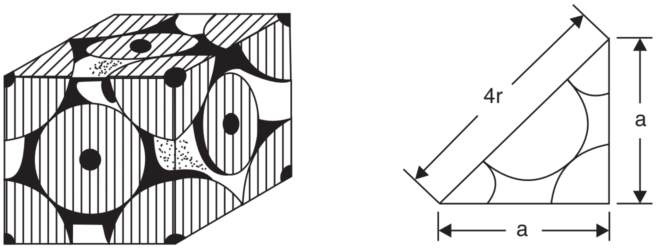


Fig. 22.14 Face centered cubic cell.

Radius ratio

Radius ratio is the ratio of the cation radius to that of the anion in an ionic solid. Thus, radius ratio

$$= \frac{\text{Radius of cation } (r_+)}{\text{Radius of anion } (r_-)}.$$

Solid defects

Crystals are formed depending on perfectly regular arrangement of structural units. But this idea of crystal is non-existent. In case of most ionic crystals, the ions are not arranged in a perfect order and these crystals are said to have **defects** or in other words this deviation may be regarded as **crystal imperfections**.

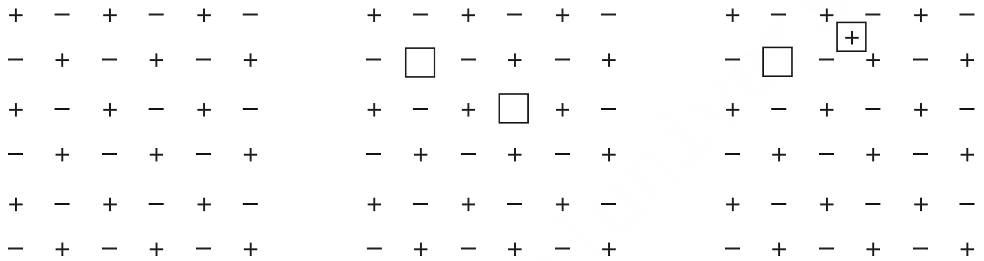
The important imperfections or defects are of the following types:

- **Stoichiometric defects:**
  (*i*) *Schottky defects* and (*ii*) *Frenkel defects.*
- **Non-stoichiometric defects or impurity defects.**

Stoichiometric defects

(*i*) **Schottky Defects.** There are certain crystals is which some of the lattice points remain unoccupied *i.e.,* the crystals have vacancies. On account of electrical neutrality, equal number of cationic and anionic vacancies would exist in the crystal lattice as shown in Fig. 22.15 below. This type of crystal defect is known as **Schottky defect**. Such defect is found in crystals of NaCl.

(*ii*) **Frenkel Defects.** Frenkel defects arise with those crystals in which an ion leaves its normal lattice site and occupies an interstitial site in the same crystal. For example, in AgBr crystal some Ag^+ ions are missing from their regular positions and are found to be squeezed between other ions.



Ideal Crystal Schottky defect Frenkel defect

Fig. 22.15 Defects in crystals.

Non-stoichiometric defects

Besides structural imperfections, crystal defects may also arise as a result of the presence of small amount of impurities. These impurities in crystalline substance drastically change their properties. For example, if a very small amount of $CaCl_2$ (less than 0.1%) is added to NaCl, the conductivity of NaCl increases by 10000 times. In the mixed crystal Ca^{2+} ions occupy the positions of Na^+ in crystal lattice and the position of Cl^- ion in the lattice remains unchanged. The insertion of Ca^{2+} ions for Na^+ ions leads to create lattice vacancies and such vacancies permit the migration of ions as a result of which the conductivity of impure crystal increases. One of the most common examples for impurity defect is semiconductors. Impurity defects are introduced under controlled conditions in germanium and silicon in the production of semiconductors.

In compounds having non-stoichiometric defects, the ratio of positive and negative ions differs from that indicated in their respective chemical formula and the balance of the positive and negative charges is maintained by extra electron or positive ions as per necessity. There is an excess of either metal or non-metal atoms in non-stoichiometric compounds. Thus two cases generate (*i*) **Metal excess** and (*ii*) **Metal deficiency**.

Metal excess may occur in the following ways:

(*a*) an anion may be missing from its lattice site and an electron be present there for maintaining charge balance. For example: when NaCl is treated with sodium vapour, such a yellow non-stoichiometric variety is obtained.

(*b*) an extra metal atom may be present in an interstitial lattice site and an electron being present in some other interstitial position balances the charge. ZnO exhibits this type of defect when its composition becomes $Zn_{1+x}O$. The free electron present is responsible for excitation to higher energy level by absorption of radiation of particular wavelengths. This phenomenon occurs when ZnO is subjected to heating and its colour changes from white to yellow.

Metal deficiency may also occur as follows:

A positive ion may be missing from its lattice position and a doubly charged cation maintains the charge balance. FeO, FeS and NiO are the examples of such defect.

Role of Silicon (Si) and Germenium (Ge) in the field of semiconductors

Semiconductors are the materials that exhibit conductivities considerably lower than those of the metals. Semiconductors are defined as *inorganic crystals* responding to electronegativity when excited by heat or electromagnetic radiation. Si and Ge in pure state are very poor conductors of electricity. However, impurity doped Si and Ge exhibit semi-conductivity. Doping of small amounts of group IV or V elements improves their electrical conductivity appreciably. Both in Si and Ge, each atom is covalently bonded to four neighbours such that all four outer electrons of each are involved in bonding.

Let us suppose an atom of group V element like P, As, Sb or Bi is introduced in place of Ge, or Si atoms, then the four electrons of this atom will be utilized in the formation of covalent bonds and the remaining one will be free to move and thus induces an enhanced conductivity. Similarly, if a group III element like B, Al etc, is introduced in place of Ge or Si, an electron vacancy in covalently bonded structure will be generated and such type of electron vacancy is known as **'hole'**. This hole instead of remaining confined to the impurity atom, migrates throughout the structure when filled by an electron. So, electrons are able to move in a crystal having such electron vacancies or hole and thus the crystal exhibits electrical conductivity.

Semiconductors that exhibit conductivity due to excess electrons are called **n-type** semiconductors where *n* stands for negative hole. In other cases, there are some semiconductors in which electrical conductivity is imposed due to presence of positive holes, they are known as **p-type** semiconductors, discussed later on.

With rise in temperature the conductivity of semiconductors increase because at high temperature the excess electrons or holes become more free to move and so the conductivity increases.

Highlight:

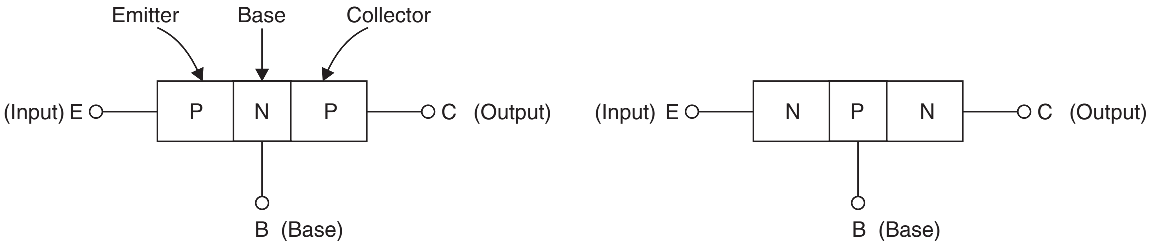
It may be noted that both type of semiconductors (*n*- and *p*-type) are electrically neutral.

Transistors (semiconductor triodes)

The word transistor is derived from two words—transfer and resistor. A triod transistor contains two P-N junction diodes placed back to back. Junction transistors are of two types:

- Grown junction type and
- Alloy junction type.

The following Fig. 22.16(*a*) and (*b*) show a grown P-N-P junction triode transistor and an N-P-N junction transistor respecttively



(a) A PNP transistor (b) An NPN transistor

Fig. 22.16 Transistors.

Function of the emitter is to inject majority charge carriers into the base, and a collector is to collect these carriers through the base.

Amplification by a transistor (current amplification or gain)

- Conduction within a PNP transistor is by hole movement from the emitter to the collector. In an NPN transistor electron moves.
- The collector current is always less than the emitter current *i.e.* $I_c = I_e - I_b$:
- The current amplification or gain (α) of a transistor is,

$$\alpha = \frac{\text{collector current}}{\text{emitter current}} = \frac{I_c'}{I_e} \ (\alpha < 1)$$

for both PNP and NPN transistors.

The alloy junction transistor is shown in the following figure (Fig. 22.17).

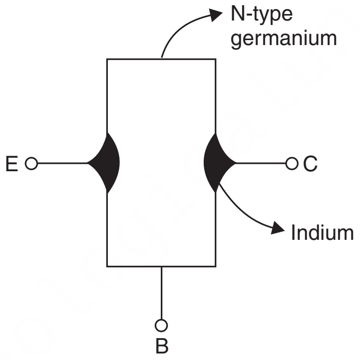


Fig. 22.17

The alloy junction transistor consists of two beads of indium metal alloyed on opposite sides of a thin slice of an N-type Ge. Collector is larger in size than the emitter.

Elements of band theory

Metals in general are characterised by certain distinct features, these are:

- High thermal and electrical conductances, the conductance decreases with increase in temperature.
- High melting and boiling points in most cases.
- Hardness and, at the same time, ductility and malleability.
- Metallic lustre
- Constancy
- Emission of electrons by some metals under the action of heat and light.

All these above properties of metal cannot be explained either by covalency or by an ionic model. Separate bonding schemes have been proposed for the metals to give an accurate explanation of the characteristics of metal. But the bond theory is the most satisfactory among all the proposed theories.

Band theory

Band theory provides the most satisfactory explanation of the characteristics of the metallic properties in a very natural manner. The theory is an extention of molecular orbital (M.O.) treatment for a large number of atoms. For homonuclear diatomic species, the combination of two atomic orbitals gives rise to two molecular orbitals and these are two new energy levels for the electrons in the two joint fields of the nuclei. If this idea is extended to an aggregate of a large number of atoms (n), each offering one orbital for the combination with others, so there will be a total of n new energy levels similar to 'n' number of molecular orbitals (M.O.s). These large number of energy levels form an energy band by spacing closely one upon another. The valence electrons from all the atoms will enter every level and a metal thus consists of energy bands formed by merging of individual atomic orbitals. Let us illustrate the following cases:

Let us consider Li as an example. The electronic configuration of a Li atom is $1s^2$, $2s^1$. So, two molecular orbitals are formed by two $2s$ atomic orbitals from two Li atoms. Similarly three or four Li atoms would give rise to formation of three or four energy levels by combination of their $2s$-atomic orbitals. Now extending this idea for 'n'-atoms, all $2s$-atomic orbitals will combine to give a $2s$-energy band with n-energy levels. Similar combination of the p-atomic orbitals will form a $2p$ energy band containing $3n$-energy levels. Each Li atom has only one valence electron and the total n-electrons from n-atoms will occupy doubly the lower $n/2$ energy levels in the $2s$-band. When the electrons gain thermal energy or are placed in an electric field. The electrons are raised to higher unfilled energy levels. This phenomenon explains the high thermal and electrical conductivities of metals.

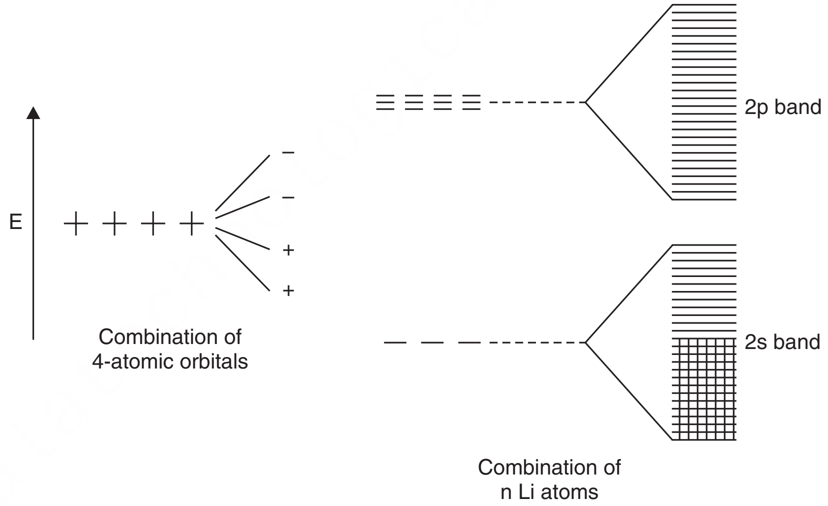


Fig. 22.18

An Mg atom has the electronic configuration $1s^2.2s^2.2p^6.3s^2$. The $3s$ band in Mg is exactly filled by the $2n$ electrons of the 'n'-Mg atoms. One finds that the $3p$ band (formed by unoccupied $3p$ atomic orbitals of the Mg atoms) overlaps the $3s$ band in Mg and there is no energy gap between the highest occupied and lowest vacant electronic energy levels and Mg is an excellent conductor.

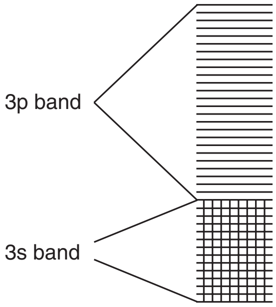


Fig. 22.19 Merger of the $3s$ and $3p$ bands in Mg.

At temperatures above the absolute zero, a few of the electrons may be promoted to energy levels higher than the actual occupied region in bands. The energy distribution of these electrons follows roughly the Maxwell–Boltzmann law. These electrons are much less in number than the valence electrons and these are responsible to the heat capacity of the metal and hence the contribution of electrons to the specific heat of metals is thus small. This conclusion is in harmony with the Dulong's and Petit's law.

Valence and conduction bands

The outermost electrons of an atom *i.e.,* electrons residing in the outermost shell of an atom are called valence electrons having the highest energy. It is these electrons which are mostly affected when a number of atoms are brought very close together as during the formation of a solid.

The band of energy occupied by the valence electrons is called the **valence band** and is the highest occupied band. It may be filled by electrons completely or partially.

The next higher permitted energy band is called the **empty band** or **conduction band**. In fact, it may be defined as the lowest unfilled energy band.

In conduction band, electrons can move freely and therefore are known as conduction electrons. The gap between these two bands, namely valence band and conduction band, is known as **forbidden energy gap**.

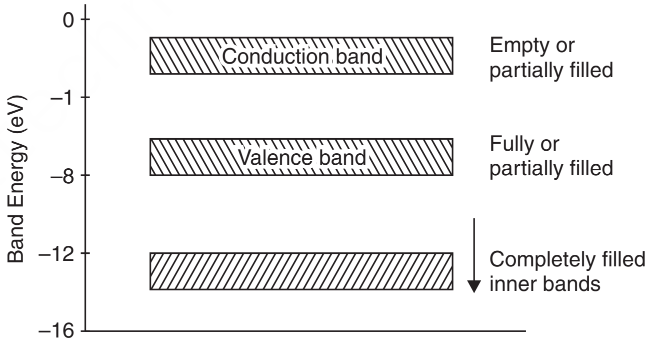


Fig. 22.20

Now if a valence electron absorbs enough energy, it jumps across the forbidden energy gap and enters the conduction band. An electron in the conduction band can jump more readily to an adjacent conduction band than it can jump back to its original position. But, however, if the conduction electron radiates too much energy, it will suddenly reappear in the valence band again. It may be noted that the covalent forces of the crystal lattice have their source in the valence band. So when an electron is raised from the valence band, a covalent bond is broken and positively charged hole is formed. This hole can travel to an adjacent atom by taking an electron from that atom, which involves the breaking an existing covalent bond and then re-establishing a covalent bond by filling up the hole. It has to be kept in mind that holes are filled by electrons which move from adjacent atoms without passing through the forbidden energy gap. This is shown in Fig. 22.21 below.

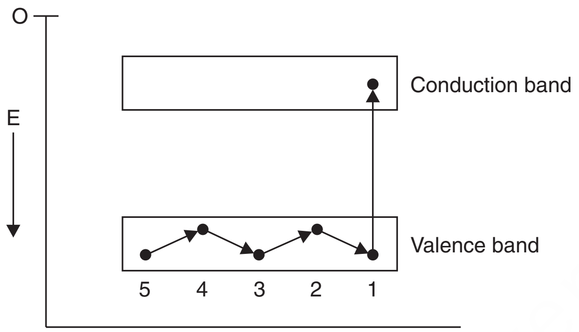


Fig. 22.21

In another way it may be concluded that the conditions in the conduction band have nothing to do with the hole flow. It denotes a very important distinction between the hole current and electron current. Although holes flow with ease, they experience more opposition than electron flow in the conduction band.

So, to summarise:

- Conduction electrons are found in conduction band and move freely in the conduction band.
- Holes exist in and move in the valence band.
- Conduction electrons move almost twice as fast as the holes.

Conductors, semiconductors and insulators

The band theory of metals may be extended to other non-metallic solids as well. The electrical conduction properties of different elements and compounds can be explained in terms of electrons having energies in the valence and conduction bands. The electrons lying in the lower energy bands, which are normally filled, play no part in the process of conduction.

Conductors

Conducting materials are those in which there is the availability of plenty of free electrons for electric conduction.

In terms of energy bands it means that electrical conductors are those which have overlapping valence and conduction bands. In fact there is no physical distinction between these two bands, hence the availability of a plenty number of conduction electrons.

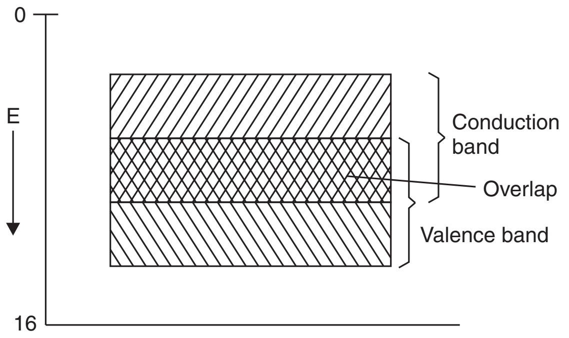


Fig. 22.22

Another point to be mentioned is that here the forbidden gap is not present for good conductors. The total current is simply a flow of electrons.

Semiconductors

A semiconductor is a material whose electrical properties lie in between those of good conductors and insulators. For example – germanium (Ge) and silicon (Si). Semiconductors are neither good conductors nor good insulators, but their electrical properties lie in between. The resistivity of the semiconductors ranges from 10^5 to 10^{-3} ohm-cm and decreases with increase in temperature according to an exponential law. This is the main difference between semiconductors and good conductors. The semiconductors which conduct even in chemically pure state are called *intrinsic semiconductors*.

In terms of energy bands, semiconductors are the materials which have almost an empty conduction band and almost filled valence band with a very narrow energy gap separating the two. The energy gap is of the order of 1 eV.

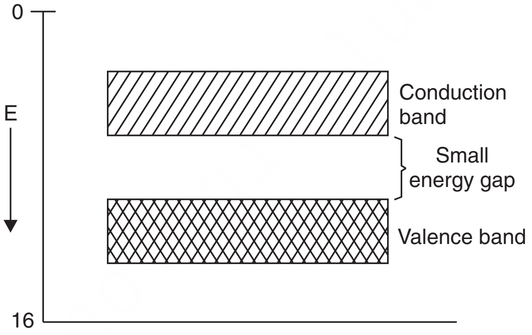


Fig. 22.23

At 0 K, there are no electrons in the condition band and the valence band is filled completely. As temperature increases, the width of the forbidden gap decreases, so that some of the electrons are liberated into the conduction band. So, the electrical conductivity of semiconductors increases with rise in temperature and in this regard they differ from the metals whose electrical conductivity decreases with rise in temperature. Semiconductors are of two types:

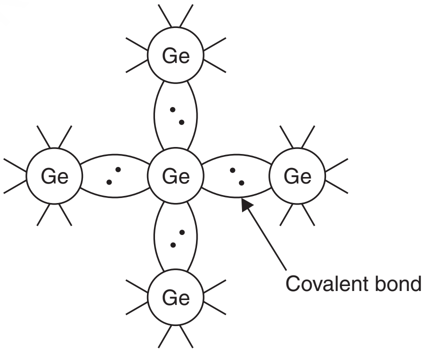


Fig. 22.23 (a) Intrinsic Ge.

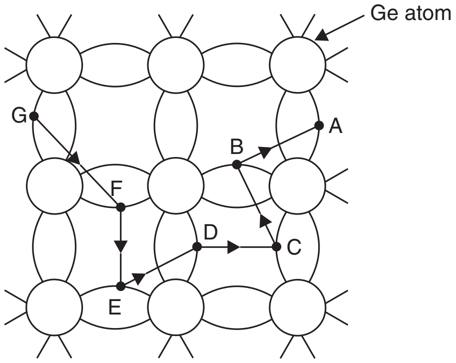


Fig. 22.23 (b) Hole formation in semiconductors (conduction of current).

(i) Pure or intrinsic semiconductors. In such semiconductors the energy gap between the valence band and conduction band is very small (Fig. 22.23). The electrons jump across the gap and hence they behave as insulators at absolute zero. But their electrical conductivity is raised with increase in temperature to break the covalent bonds (Fig. 22.23(*a*)) to get conducting electrons (Fig. 22.23(*b*)).

Let covalent bond is broken at A with increase in temperature [Fig. 22.23(*b*)] and the electron has moved leaving behind a hole at A where an electron jumps from B creating a hole there, and so on. Thus a negative charge moves from G to A. *i.e.* a positive charge from A to G alternately. An intrinsic semiconductor may be defined as one in which the number of conduction electrons is equal to the number of holes.

(ii) Impure or extrinsic semiconductors. Semiconductor behaviour may also be imposed in certain substances by the deliberate addition of impurities. Such semiconductors are called extrinsic semiconductors. Example, *n*-type and *p*-type semiconductors (discussed earlier).

Those intrinsic semiconductors to which some suitable impurity or doping agent or dopant is added in extremely small amounts (about 1 part in 10^8) are called *extrinsic* or *impurity semiconductors*.

Usually doping agents are:

- pentavalent atoms (As, Sb, P) or
- trivalent atoms (Ga, In, P, B).

Pentavalent doping atom is known as *donor atom* as it donates one electron to the conduction band of pure Ge. The trivalent atom, on the other hand, is called *acceptor* atom as it accepts one electron from Ge atom.

Depending on the type of doping agent, extrinsic semiconductors are divided into two classes:

(*i*) N-type semiconductors

(*ii*) P-type semiconductors.

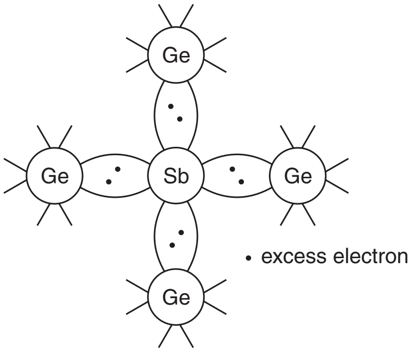


Fig. 22.23 (c) N-type semiconductor.

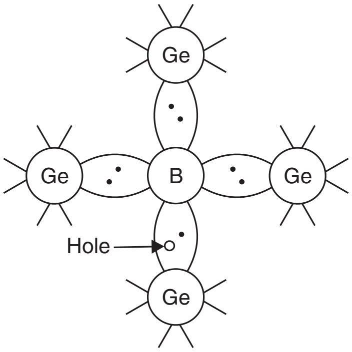


Fig. 22.23 (d) P-type semiconductor.

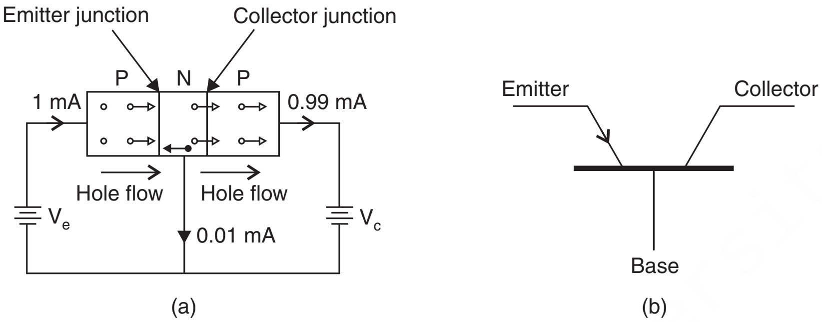


Fig. 22.23 (e) Working of a PNP transistor.

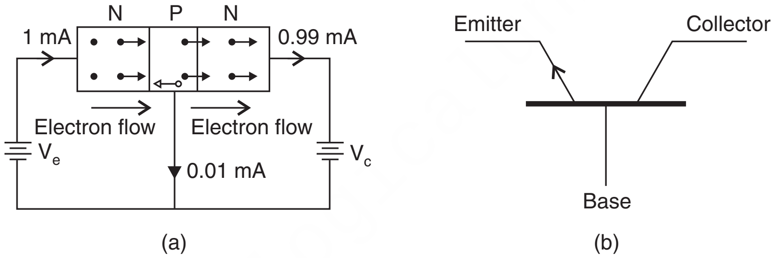


Fig. 22.23 (f) Working of an NPN transistor.

Highlight. Emitter arrow shows the direction of flow of conventional current. Obviously, electron flow will be in the opposite direction.

Insulators

Insulators are those materials in which valence electrons are bound very tightly to their parent atoms and thus require a very large electrical field to remove them from the attraction of the nuclei.

In terms of energy bands, it means that insulators are those materials which have a full valence band, have an empty conduction band and have very high energy gap between these two bands (Fig. 22.24).

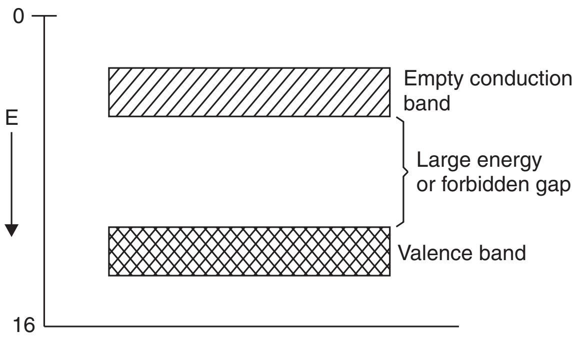


Fig. 22.24

For conduction to take place electrons must be given sufficient amount of energy to jump from the valence band to the conduction band. Increase in temperature causes some electrons to move to the conduction band, which accounts for the negative resistance temperature coefficient of insulators.

The diode as a rectifier

When a metal is heated it emits electrons. This phenomenon is known as *thermionic emission.* The electrons obtained in this process is known as *thermions*. The current obtained by flow of thermions is called thermionic current. Thermionic tubes containing two electrodes are called **diodes.** A **triode** has three elctrodes. In some types of thermionic valves, the electrons are obtained by heating a metallic wire called the *filament* or *cathode.*

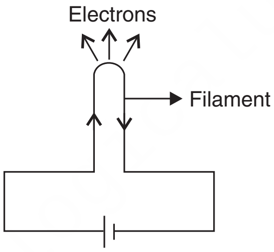


Fig. 22.25 Directly heated cathode.

By rectification, we mean the conversion of an alternating voltage to a direct voltage. A diode acts as a perfect rectifier. A simple circuit for obtaining rectification with help of a diode is shown in Fig. 22.26.

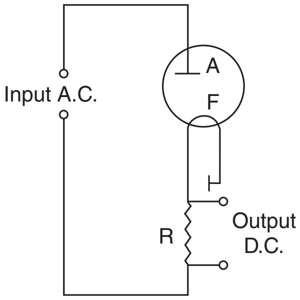


Fig. 22.26 Rectifier.

Photovoltaic cell

Photovoltaic cell is a self generating cell which utilises semiconductor contacts against metals. When light is incident on such a combination, an internal voltage is generated which causes the current to flow through internal circuit, here no external battery is needed. The e.m.f. generated is proportional to the radiant energy received in solar batteries.

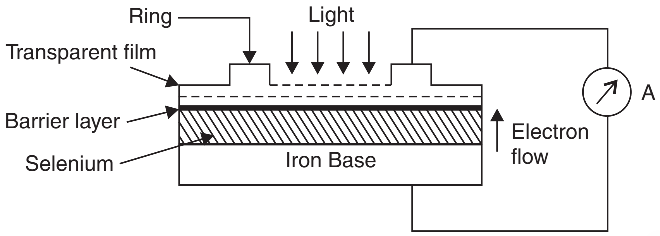


Fig. 22.27 Photovoltaic cell.

The most common photovoltaic cells are of the barrier-layer type, like iron-selenium cells. In the iron-selenium cell, selenium layer is placed on an iron disc and then extremely thin transparent film of gold or silver is formed on the selenium to act as front electrode. The barrier layer is formed by cathode sputtering the semi-transparent film on the selenium. A contact ring on the silver layer acts as one electrode and the iron base as the other.

Working

When radiant flux falls on semiconductor *i.e.* selenium, it ejects electrons which travel from selenium to the front silver electrode through the barrier layer (Fig. 22.27). The flow in the opposite direction is not permitted by the barrier layer because it acts as a rectifier. The e.m.f. generated internally between silver electrode and selenium is directly proportional to the incident flux.

Application

- The main advantage of a photovoltaic cell is that it requires no external battery for its operation, *i.e.* it is self-generating.
- The internal e.m.f. and hence current generated by it are large enough to be measured by a pointer galvanometer.
- Such cells are used
  (*a*) in devices like portable exposure meters,
  (*b*) in direct reading illumination meters and with low resistance relays for on and off operations and
  (*c*) in other monitoring operations in industries.

PROBLEMS

Problem 1. *Calculate the Miller indices of crystal planes whose Weiss indices are :*
(*a*) *a/2, 2b/3, ∞ c;* (*b*) *2a/3, 2b, c/3.*

Solution:

	(*a*)	(*b*)
Weiss indices	1/2, 2/3, ∞	2/3, 2, 1/3
Reciprocal of Weiss indices	$2, \frac{3}{2}, \frac{1}{\infty}$	$3/2, \frac{1}{2}, 3$
Clear fractions	4, 3, 0	3, 1, 6
Miller indices	(430)	(316)

Problem 2. *Determine the interplanar spacing between the (220) planes of a cubic lattice of length 450 pm.*

Solution.
$$d_{220} = \frac{a}{\sqrt{2^2 + 2^2 + 0^2}}.$$
$$= \frac{450}{\sqrt{8}} \text{ pm}$$
$$= 159 \text{ pm.}$$

Problem 3. *Classify the following unit cells into proper system:*

(*i*) $a = 10.8$ Å, $b = 9.47$ Å, $c = 5.2$ Å
$\alpha = 41°$, $\beta = 83°$, $\gamma = 93°$

(*ii*) $a = b = 10.73$ Å, $c = 14.3$ Å
$\alpha = \beta = 90°$ *and* $\gamma = 120°$

Solution. (*i*) Here $a \neq b \neq c$ *i.e.*, the three primitives are unequal. Also, no two axes are at right angles to each other. In other words, there is complete lack of symmetry, which is characteristic of triclinic structure.

(*ii*) Here $a = b \neq c$ and $\alpha = \beta = 90°$ and $\gamma = 120°$.

Therefore, this unit cell belongs to hexagonal crystal structure (see Table 22.1).

Problem 4. *Calculate the lattice constant of an NaCl crystal (fcc). Also calculate the spacing between the 110 planes of NaCl crystal. (given, density of NaCl = 2.167 g cm^{-3})*

Solution. We have, $$a^3\rho = \frac{nM}{N}$$

where, a = length of the edge, n = no. of molecules/unit cell, N = Avogadro number, M = mol. wt.

Here, M = 58.46, N = 6.023×10^{23} g mol^{-1}, $n = 4$, $\rho = 2.167$ gm cm^{-3}.

$$\therefore \quad a^3\rho = \frac{4 \times 58.46}{6.023 \times 10^{23}}$$

$$\therefore \quad a = 5.65 \times 10^{-8} \text{ cm} = 5.65 \text{ Å}$$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{5.65}{(1^2 + 1^2 + 0^2)^{1/2}} = 4 \text{ Å}.$$

Problem 5. *A transistor amplifies output current 96% of the input current. Calculate the voltage gain and comment on the voltage gain.*

Solution. Here current gain $$\alpha = \frac{\text{collector current } I_c}{\text{emitter current } I_e} = \frac{\text{current in the output circuit}}{\text{current in the input circuit}}$$
$$= 0.96.$$

If R of output circuit = 2000 ohm, then Resistance gain = $\frac{2000}{20} = 100$

[when R (input) = 20 Ω.]

According to Ohm's law, V = IR ; Hence voltage gain = current gain × resistance gain

$$= 0.96 \times 100 = 96 \text{ V}$$

Comment

Thus output voltage is 96 times the input voltage. If the output voltage is applied to a second transistor it is increased still more. By increasing the number of transistors the voltage may be increased indefinitely.

EXERCISES

1. Distinguish between (*a*) crystalline solids and amorphous solids, (*b*) semiconductors and insulators.
2. Explain: (*a*) plane of symmetry, (*b*) centre of symmetry, (*c*) axis of symmetry.
3. Explain Band Theory.
4. Explain the role of silicon and germanium in the field of semiconductors.
5. Explain the terms—amorphous and crystalline solids.
6. How can electrical conductivity to metal be explained on the basis of bond theory?
7. How many symmetry elements are there in a simple cube system?
8. What do you mean by solid defect? Describe (*a*) Frenkel defect and (*b*) Schottky defect.
9. Define the laws of crystallography.
10. Define transistors.
11. Describe conductors, semiconductors and insulators in the light of band theory.
12. What do you mean by doping agent?
13. What is the utility of doping agent in a semiconductor?
14. Explain with the neat diagram (*a*) working of a PNP and (*b*) working an NPN transistor.
15. What is a rectifier? What is its application?
16. What do you mean by a photovoltaic cell? Explain its working principle and uses.
17. If density of NaCl is 2.163 g cm^{-3}, find the spacing between the planes parallel to the cubic lattice faces of the sodium chloride crystal (2.83 Å).
18. Calculate the density of copper. Copper has FCC structure and lattice constant is 3.61 Å unit (Cu = 63.54) (8.98 g cm^{-3}).
19. Show that for BCC and FCC crystals the lattice constants are given by

$$a_{\text{BCC}} = \frac{4r}{\sqrt{3}}$$

$$a_{\text{FCC}} = \frac{4r}{\sqrt{2}}$$

where r is the atomic radius.

23

Chromatography

INTRODUCTION

Chromatography is considered as a group of techniques for the separation of the components (compounds) of mixtures by their continuous distribution between two phases, one of which is moving past the other. The systems are:

- A solid stationary phase and a liquid or gaseous mobile phase (adsorption chromatography, here the adsorption by the stationary phase is the main phenomenon for separation of the components, hence the name).
- A liquid stationary phase and a liquid or gaseous mobile phase (partition chromatography, here the partition between the stationary and mobile phases is the main cause for separation of the components, hence the name).
- A solid polymeric stationary phase containing replaceable ions, and an ionic liquid mobile phase (ion exchange chromatography, here the ion exchange is responsible for chromatographic separation, hence the name).
- An inert gel which acts as a molecular sieve, and a liquid mobile phase (gel chromatography).

The basis for the separation of the components of a mixture may be defined in terms of one of these four modes described above or by a combination.

Types of Chromatography

Type of chromatography	*Adsorbate phase*	*Adsorbent phase*
Gas-liquid	Gas	Liquid
Liquid-liquid	Liquid	Liquid
Gas-solid	Gas	Solid
Liquid-solid	Liquid	Solid

Column Chromatography

- **Adsorption chromatography**

  The technique was originally developed by the Russian botanist T.S. Wett in 1906.

Table 23.1 Adsorbents and solvents

Adsorbent (stationary phase)			*Adsorbate (mobile phase)*
Weak	Sucrose	Increasing eluting power ↓	Petroleum ether
	Starch		Carbon tetrachloride
	Insulin		Cyclohexane
	Talc.		Carbon disulphide
	Sodium carbonate		Ether
Medium	Calcium carbonate		Acetone
	Calcium phosphate		Benzene
	Magnesium carbonate		Toluene
	Magnesium oxide		Esters
	Calcium hydroxide		Acetonitrile
Strong	Activated magnesium silicate		Chloroform
	Activated alumina		Alcohols
	Activated charcoal		Water
	Activated magnesia		Pyridine
	Activated silica		etc.

Schematic representation of apparatus for column chromatography

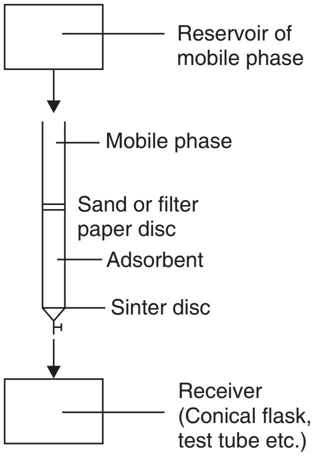


Fig. 23.1 A set-up for column chromatography.

Column Characteristics

Adsorbent/adsorbate weight ratio	*30:1*
Length/diameter ratio	*10-15:1*
Column length:	
(*i*) Multicomponent system	Long column
(*ii*) Components with similar affinities for adsorbent	Long column
(*iii*) Components with different affinities for adsorbent	Short column

Detection and Recovery of Components

- For those mixtures which are coloured, visual examination is sufficient.
- Colourless components may be detected visually if they fluoresce normally or under UV light.

It is usual practice to complete the chromatogram by eluting the various components with solvents. For colourless compounds the eluate is collected as a large number of fractions, each of small volume.

Advantages of Column Chromatography

- Separation and collection of components of a mixture in the pure form both in laboratory and industry.
- Very efficient method of separation of mixtures of components.

Example. *Separation of leaf pigments of spinach leaves viz. chlorophyll and carotenoids.*

Paper Chromatography

Paper chromatography is a type of chromatography in which the stationary phase is water in the fibres of paper and the mobile phase is another solvent. During paper chromatography the chemicals in a mixture *partition* themselves between two solvents, *viz.* water and mobile solvent. Each component in the mixture has a different equilibrium constant (partition constant), which determines whether it has a greater tendency to dissolve in the stationary phase or in the moving phase. As a result the mixture separates as the chemicals move at different speeds. The technique is, therefore, closely related to column partition chromatography.

Partition constant (partition or distribution coefficient) is defined as: the ratio of two concentrations in the two layers is a constant when a solid is shaken with two immiscible liquids as an equilibrium is set up to which the equilibrium law applies.

$$K = \frac{\text{Concentration of the solid in solvent I}}{\text{Concentration of the solid in solvent II}}$$

Paper chromatography is employed to analyse mixtures such as inks, food, colours, dyes, and amino acids.

The movement of components on the paper depends on the amount and nature of stationary phase compared with the amount of mobile phase in the same part of the paper and also on the partition coefficient.

If the conditions are kept same, each component in a mixture moves a fixed fraction of the distance moved by the solvent. The R_f value for the substance is a measure of this fraction. R_f is defined as:

$$R_f = \frac{\text{Distance travelled by centre of component}}{\text{Distance travelled by the solvent front}}$$

R_f values are of considerable importance in paper chromatography and thin layer chromatography (tlc).

There are two types of paper chromatography:

- Ascending chromatography
- Descending chromatography

The origin of the name depends on the nature of solvent movement.

Method

Ascending chromatography

- A pencil line is drawn about 3 cm from one end of the selected paper.
- 2-5 μl volumes of solutions of sample and reference compounds at about 2 cm intervals of the line.

- The paper is folded perpendicular to the line drawn.
- The edges of the paper are held with clips.
- The tank is prepared by placing the mobile phase (about 1 cm depth of the tank) and the lid is placed.
- Some time is allowed to saturate the tank with solvent vapour.
- The folded paper is placed in the tank followed by placing the lid.
- The development is allowed to take place *i.e.,* eluted until the solvent reaches a suitable height (15-20 cm).
- The paper is removed, dried and now comes the question of location of the component.

Detection of components

If the components or substances in a mixture are colourless they are invisible on the paper. If so, the analyst has to '*develop*' the paper or plate in case of tlc with a suitable '*locating agent*'. Common developing agents are (*i*) iodine vapour (*ii*) $KMnO_4$ (1%) (*iii*) bromocresol green (0.05%) (*iv*) ninhydrin for amino acid etc. Amino acids give purple spot.

Advantages

- Rapid and reliable separation and identification.
- The technique may also be used for quantitative purpose.

Disadvantages

- Large scale separation of components is not possible.
- Time consuming, it takes much time to 'elute' compared to tlc.

Thin Layer Chromatography (tlc)

Here the stationary phase is a thin layer of a solid, generally silica gel or alumina, on a glass or plastic plate while the mobile phase is a solvent. The rate at which a component moves up a **tlc** plate depends on the *equilibrium* between adsorption on the solid (stationary phase) and solution in the solvent (mobile phase). The position of equilibrium varies from one substance to another as the components of a mixture separate.

Advantages of tlc

- tlc is quick and cheap.
- Only a very small sample is required.

The technique is widely used in laboratories as well as in industries. It can be used quickly to check whether a chemical reaction is taking place as expected. During purification of a product **tlc** can indicate whether or not all the impurities have been removed from the reaction product.

Detection of the components

- Coloured compounds are easy to detect on a tlc plate.
- A quick way of detecting the position of a colourless organic compound, to allow to stand the plate in a covered chamber with iodine crystals. The iodine is absorbed by the compound giving coloured spots.
- Other methods such as spraying with certain reagents are also employed.
- Alternatively a tlc plate may be impregnated with a fluorescent chemical. When the plate is placed under a UV lamp the whole plate glows except in the areas where organic compounds absorb radiation, so that they are located as dark spots.

R_f values are used to record the distances moved by component chemicals of a mixture relative to the distance moved by the solvent.

General method

- The size of the glass plate is 20 × 20, 20 × 10, or 20 × 5 cm.
- 30 g of adsorbent (stationary phase, generally silica gel) is made to a smooth paste with requisite amount of water or solvent specified (preparation of chromatoplate).
- The slurry is quickly poured to a spreader or applicator and is spread (thickness 0.25 mm).
- The slurry is allowed to set for 3-4 min.
- The plate is transferred to a drier and allowed to dry for 1 hr.
- The plate is transferred to a desiccator over silica gel.
- Spots are given as usual.
- Eluted with mobile phase in a chromatographic chamber.
- The solvent is dried, the plate is developed and the spots are located.
- R_f is measured to identify the components, *e.g.*, R_f for L-lysine is 0.14, DL-alanine is 0.36 and L-leucine is 0.65.

High Performance Liquid Chromatography (hplc)

hplc is a sophisticated technique of liquid chromatography. The mobile phase is a solvent of very high purity. The stationary phase consists of very small particles of a solid (silica gel) packed into a long steel tube. The use of fine particles increases the surface area helping to separate the components in a mixture efficiently. A pump provides very high pressure (1-550 bar, 0.1-55 Mpa, 14.6-8000 p.s.i) to maintain a flow rate of mobile phase at the rate of 0.01-10 ml min^{-1}. The material (15-25 µl) to be chromatographed is injected through a septum into the centre of the packing material with the help of a syringe. Various types of detectors are used.

One application of **hplc** is to study the fate of drugs administered in the body.

Gas-liquid Chromatography (glc)

glc is a sensitive analytical technique for analysing *mixtures of liquids*. In a modern gas-liquid apparatus, the stationary phase is a thin film of liquid adsorbed on the inside surface of a coiled capillary tube of about 30 m long inside an oven. Sample to be analysed is injected into the hot column with the help of a syringe. The mobile phase is a gas, which carries the vapours of the sample mixture through column. The components in the mixture separate as they pass through the column. The components are detected as they come out and the signal detector is fed to a chart recorder.

The chart recorder shows how long it takes for each component of the mixture to pass through the column. This time is called retention time (t_r).

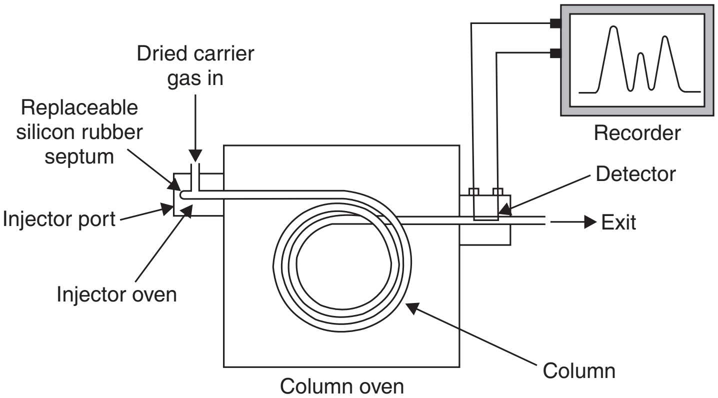


Fig. 23.2 The main features of gas-liquid chromatography.

The areas under the peaks on the print out give a measure of the proportions of the components of the mixture.

A glc machine can be calibrated by injection of known amount of compounds and recording their retention times.

Application of glc

(*i*) Source of oil pollution from the pattern of peaks which acts like a fingerprint for any batch of oil.

(*ii*) Measuring the level of alcohol in urine and blood samples.

(*iii*) Detection and measurement of pesticides in the river water.

Gas Chromatography (gc)

The separation of the components in a mixture in the gaseous state achieved by partition column chromatography using a gaseous mobile phase was first suggested by Martin and Synge in 1941.

The technique requires the vapourisation of the sample, which is carried through a prepared column, at a suitable temperature by a stream of carrier gas (mobile phase). During the passage of the vapour of the sample through the column, separation of the components of the mixture takes place by adsorption effects if the prepared column is of adsorbent only.

If the particles of adsorbent are coated with a liquid which forms a stationary phase then partition effects the separation process. It is better to use the term *support* for the liquid phase rather than *adsorbent* as adsorption effects are undesirable in partition columns.

It is essential that the sample is stable when vapourised and during its passage through prepared or *packed column* (packed with high polymer beads) in order to avoid decomposition of products and the presentation of a complex chromatogram as the carrier gas elutes the products of the column.

The basic apparatus for **gc** is shown diagrammatically.

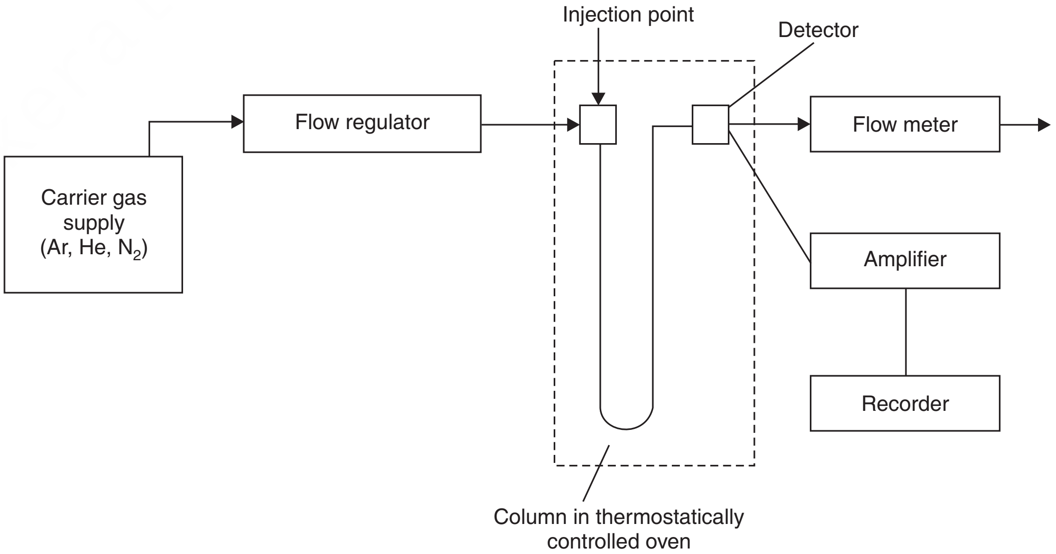


Fig. 23.3 gc apparatus.

Highlight:

- **Nernst's isotherm:**

$$K_A = \frac{C_s}{C_m}$$

where K_A = constant of distribution of component A at a given temperature.
C_s = concentration of component in stationary phase (Adsorbent)
C_m = concentration of component in mobile phase (Adsorbate)

Some parameters of gc

- **Retention time.** It refers to the time taken by the component to be extracted from the column and arrive at the detector. It is measured on the abscissa of the chromatogram from the start to the maximum peak.
- **Retention volume.** It refers to the volume of the solvent that is required to extract a component and bring it to the detector. It is measured from the start to the maximum of the peak on the abscissa of chromatogram.
- **Chromatogram.** It is a volume/speed curve which illustrates a chromatographic separation. The concentration component is found to be proportional to the signal. The signal illustrates the progress of a chromatographic separation.

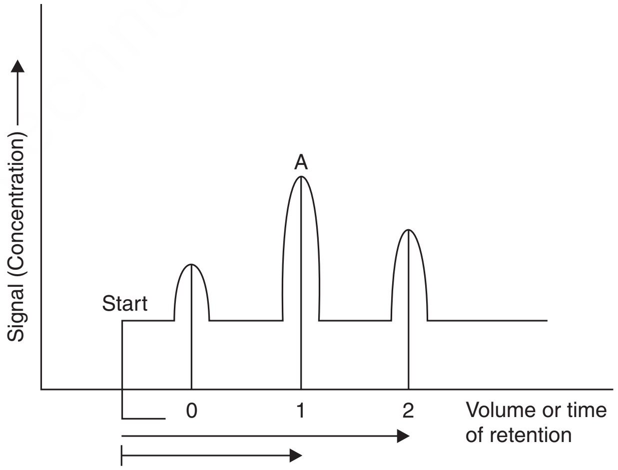


Fig. 23.4 Chromatogram.

- **Separation factor (α):**

$$\alpha = \frac{K_A}{K_B}$$

where K_A and K_B are the constants of distribution of two components A and B respectively.

- **Efficiency.** It refers to the capacity of column to separate the components.
- **Resolution.** It refers to the capacity of a column to separate two consecutive peaks of a chromatogram.

EXERCISES

1. What is chromatography?
2. Write notes on adsorption and partition chromatography.
3. What is meant by R_f in chromatography?
4. What are the advantages and disadvantages of paper chromatography?
5. What is thin layer chromatography (**tlc**)?
6. Mention the advantages of **tlc**.
7. What is column chromatography? Mention its importance.
8. What are:
   (*a*) **hplc** (*b*) **glc** (*c*) **gc?**

24

Instrumental Methods of Analysis

INTRODUCTION

The field of spectroscopy is divided into two main classes:

(i) Emission spectroscopy

(ii) Absorption spectroscopy

An emission spectrum is obtained by some light source such as a flame or an electric arc. This spectrum is due to the excitation of atoms by thermal or electrical means. In case of absorption spectroscopy energy absorbed causes electrons in a ground state to be promoted to a higher excited state. The life-time of electrons in this excited state is short and they return to either a lower excited state or to the ground state. The absorbed energy is released as light. Fluorescent lights and colours obtained by heating salts of certain elements in a flame are very common examples of *emissions spectra.* In some cases the excited states may have appreciable life-times. In these cases the excited states usually have appreciable life times and emission of light starts after excitation has ceased. Such a phenomenon is called **phosphorescence**.

An absorption spectrum is obtained by placing the substance between the spectrometer and some source of energy, usually it is an electromagnetic radiation which is applied. The spectrometer analyses the transmitted energy related to the incident energy for a given frequency of the electromagnetic radiation. The regions of electromagnetic radiation of greatest interests to the organic chemists are 200-400 mμ (ultraviolet), 400-800 mμ (visible), and 2-16 μ (infrared).

The mechanisms of absorptions of energy are different in the ultraviolet, infrared and nuclear magnetic resonance regions, but the fundamental phenomenon is the absorption of a certain amount of energy. The energy absorbed is given by

$$E = h\nu$$

where h is Planck's constant and ν is the frequency of incident light (in cycles per second, *cps*). ν is related to the wavelength λ as follows,

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

where c is the velocity of light, λ is the wavelength in cm.

The wave number is also used in the description of spectra. The wave number k is related to λ by

$$k = \frac{1}{\lambda}$$

i.e., k is the wave number in cm^{-1}.

Interpretations of molecular spectra by the organic chemists are based largely on empirical correlations with extensive compilations of data. At the present time, the various spectral methods are the more commonly used physical methods. Absorption of ultraviolet and visible light is chiefly caused by electronic excitation; the spectrum provides limited information about the structure of the molecule. Absorption in the infrared region is due to molecular vibrations of one kind or another; the spectrum is generally very complicated and contains many absorption peaks, relatively few of which can be interpreted with a high degree of assurance. On the other hand, the proton magnetic resonance (*pmr*) of a compound owing to nuclear spin transitions can usually be completely interpreted, and it provides information about the number, nature, and environment of all the protons in the molecule.

- **Ultraviolet spectroscopy**

A region of electromagnetic radiation whose interaction with a molecule gives rise to electronic transition exists at 100-8000 Å (10-800 mμ).

Visible Light and Electromagnetic Spectrum

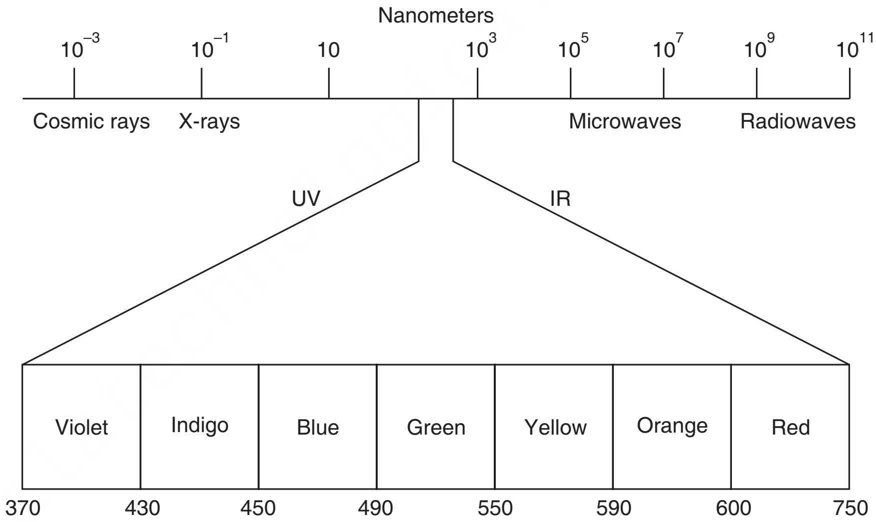


Fig. 24.1 Wavelengths of electromagnetic radiation.

The total energy (E_T) of a diatomic molecule is the sum of electronic energy (ε_e), vibrational energy (ε_v) and rotational energy (ε_r), *i.e.*,

$$E_T = \varepsilon_e + \varepsilon_r + \varepsilon_v$$

If the electromagnetic radiation in the region of 10-800 mμ interacts with a molecule, a change in the energy of the molecule from the ground state to a higher level *i.e.*, excited state occurs. The transition of energy, due to the displacement of a valence electron accompanied by the electronic excitation, is a change in ε_v and ε_r of the molecule. The energy requirements for the excitation of the latter two modes is comparatively less than that for electronic excitation.

Some terms concerning UV

Chromophore: A moiety of a molecule which is responsible for selective absorption of radiation in a given range of specially UV or visible region.

Auxochrome: A chemical group which does not give rise to an absorption band by itself, but upon being attached to a chromophore alters both the position and intensity of the absorption peak.

Bathochromic shift: It is a shift of the peak position (λ_{max}) to a higher wavelength due to the effect of a substituent group or solvent, it is also known as red shift.

Hypsochromic shift: It is a shift of λ_{max} to lower wavelength. It is also known as **blue shift.**

Hyperchromic and hypochromic effects: These terms refer to an increase and decrease in absorptivity of the molecule respectively.

Types of absorption bands: There are four types of absorption bands. They occur due to electronic transition of a molecule.

(*i*) **R-bands:** These are observed in compounds containing such groups as $>C = O$, —NO_2 etc. They involve $n - \pi^*$ transition. The ε_{max} value is less than 100. The band at 279 mμ observed in the UV spectrum of acetone is an example of an R-band.

(*ii*) **K-bands:** These arise from π–π^* transition in π–π conjugated systems and show ε_{max} greater than 10,000. 1,3,5-hexatriene is an example of such a conjugated system.

(*iii*) **B-bands:** These are due to aromatic and heterochromatic systems. The λ_{max} values are between 230-270 mμ and ε_{max} less than 2000. These bands are called **benzenoid bands**. In the presence of K-bands the position of the B-band is shifted to larger wavelengths. The UV spectrum of benzaldehyde contains K, R and B bands.

(*iv*) **E-bands:** These are also known as ethylenic bands and are characteristic of the aromatic systems as are the B-bands. Only difference is: they occur at lower wavelengths.

The presence of an auxochromic group shifts an E-band to a higher wavelength. The ε_{max} values of these bands vary from 2000-14000. The bands at 210 mμ with ε_{max} of 6200 for phenol is an example of E-band.

Instrumentation for UV spectrum

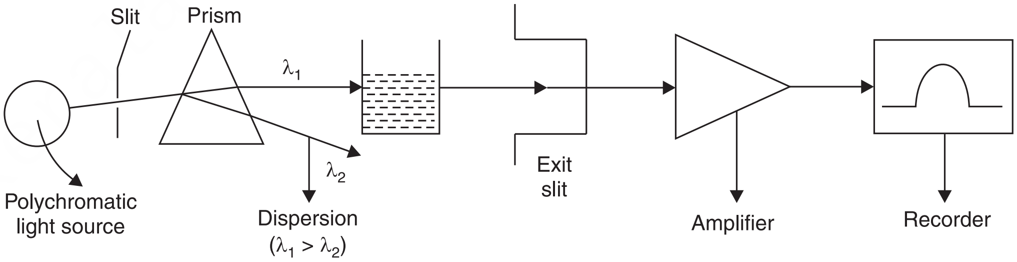


Fig. 24.2 A simplified diagram.

Radiation source. The source for the UV range is usually high pressure hydrogen or deuterium discharge lamp, which covers a range of 200-375 mμ. A xenon arc or, a mercury lamp provides a more intense radiation. The source employed for the visible range is 6 or 12V tungsten automobile head lamp bulb. UV is a plot of absorbance vs. wavelength.

Applications of UV in analytical chemistry

The working formula:

$$A = \varepsilon \, b \, c$$

is derived from Lambert-Beer's law, where A is the absorbance, E is molar extinction coefficient, *b* is the path length in cm and *c* is molar concentration (mol l^{-1}). The absorbance values of the standard solutions of known concentrations are determined from the spectrophotometer and a calibration graph is constructed. Absorbance value of the test solution is determined from the instrument and the concentration of the test solution is determined from the calibration groups.

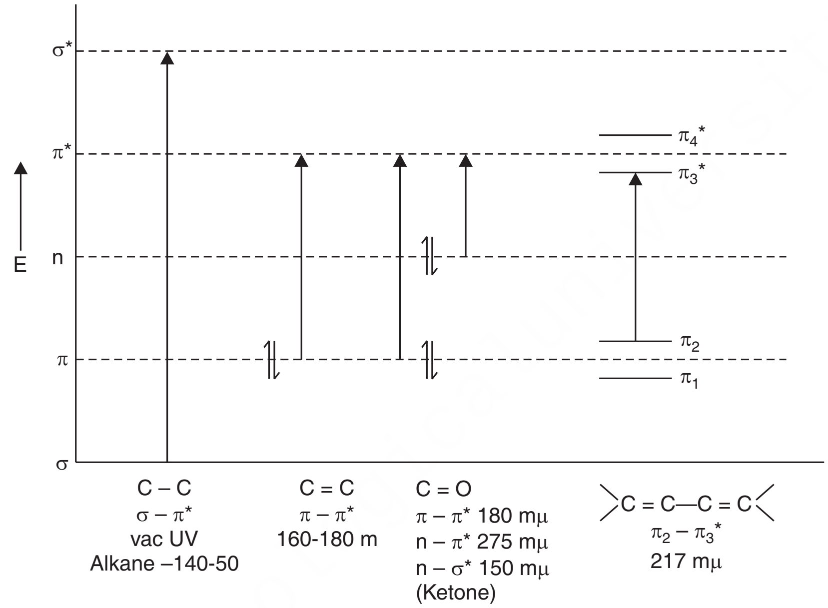


Fig. 24.3 Energy diagram for the electronic transitions.

Conjugated systems

If two or more chromophoric groups are present in a molecule and they are separated by two or more single bonds, the effect on the spectrum is additive. But there is little electronic interaction between isolated chromophoric groups. The λ_{max} values for α, β unsaturated ketones, α, β unsaturated aldehydes and conjugated dienes bear an excellent numerical correlation depending on the number of substituent groups. The rules for calculation of λ_{max} values of such compounds are relatively very simple and is exemplified below:

Calculation of λ_{max} values

- **For α, β unsaturated ketones:**

  (*i*) In order to calculate the absorption (λ_{max}) of an α, β unsaturated ketones a base value of 215 mμ is assigned.

  (*ii*) For each α-substituent 10 mμ are added to the base value.

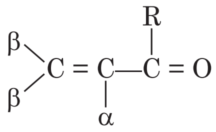
  (*iii*) For each β substituent 12 mμ are added to the base value.

  (*iv*) For each ring system (6 or 5 membered) to which the carbon-carbon double bond is exocyclic 5 mμ are added to the base value.

  (*v*) If the carbon-carbon double bond and the carboxyl group are in a five-membered ring 10 mμ subtracted from the calculated value and if only the carbon-carbon double bond is in a five membered ring 5 mμ is added.

The correlation of calculated values and experimental values is within a permissible limit.

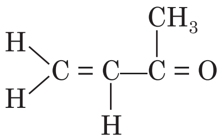
Example 1.



$$\beta\text{—}\overset{\beta}{}C=\underset{\alpha}{C}\text{—}\overset{R}{C}=O$$

α, β-unsaturated ketone

Methyl-vinyl-ketone:

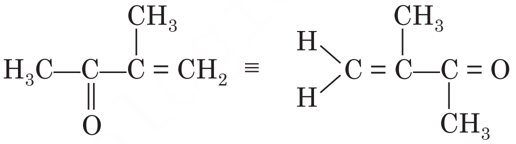


$$H_2C=\underset{H}{C}\text{—}\overset{CH_3}{C}=O$$

In this case, there is no α and β substituent. Here base value is 215 mμ and no additions are required according to rule. So, the calculated λ_{max} value is 215 mμ. The observed value is 213 mμ.

Example 2.

2-Methyl-1-butene 3 one



$$H_3C\text{—}\underset{O}{\underset{\|}{C}}\text{—}\overset{CH_3}{C}=CH_2 \equiv H_2C=\overset{CH_3}{C}\text{—}\underset{CH_3}{C}=O$$

Here, base value is 215 mμ,

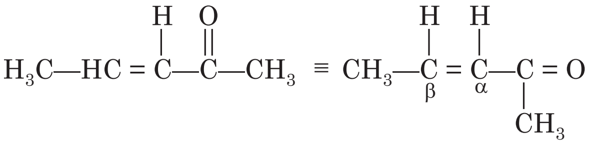
For α-substituent +10 mμ is added.

Calculated λ_{max} value = 225 mμ.

The observed value is 220 mμ.

Example 3.

3-pentene-2-one.



$$H_3C\text{—}HC=\overset{H}{C}\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3 \equiv CH_3\text{—}\underset{\beta}{\overset{H}{C}}=\underset{\alpha}{\overset{H}{C}}\text{—}\underset{CH_3}{C}=O$$

Here, base value is 215 mμ

There is no α substituent + 0 mμ

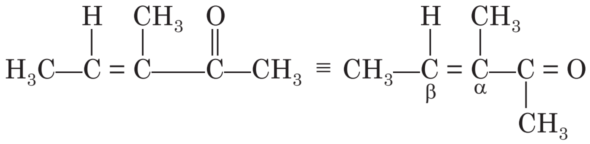
For one β substituent + 12 mμ

Calculated λ_{max} value = 227 mμ.

Observed λ_{max} value = 224 mμ.

Example 4.

3-Methyl-3 pentene-2 one.



$$H_3C\text{—}\overset{H}{C}=\overset{CH_3}{C}\text{——}\overset{O}{\overset{\|}{C}}\text{—}CH_3 \equiv CH_3\text{—}\underset{\beta}{\overset{H}{C}}=\underset{\alpha}{\overset{CH_3}{C}}\text{—}\underset{CH_3}{C}=O$$

Here base value is 215 mμ

For one α substituent + 10 mμ is added

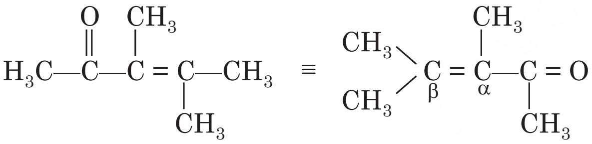
For one β substituent + 12 mμ is added.

Calculated λ_{max} value = 237 mμ.

Observed λ_{max} value = 236 mμ.

Example 5.

2,3-di methyl-2 pentene-4 one.



Here, base value is 215 mμ.

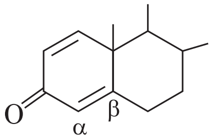
For one α substituent + 10 mμ.

For each β substituent (2 × 12) = + 24 mμ

Calculated λ_{max} value = 249 mμ.

Observed λ_{max} value = 246 mμ.

Example 6.



It is an α, β unsaturated ketone.

Here, the base value is 215 mμ

There is no α-substituent + 0 mμ

For each β-substituent + 24 mμ

For each ring to which
the double bond is exocylic + 5 mμ

Calculated λ_{max} value = 244 mμ

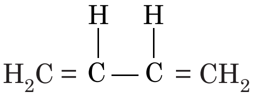
Observed λ_{max} value = 246 mμ.

Conjugated di-enes (acylic)

For acylic conjugated dienes and cyclic conjugated dienes containing non-fused six-membered ring system a base value of 217 mμ is assigned. 5 mμ are added for each acylic alkyl substituent. 5 mμ is added for each ring to which the diene system is exocylic. Absorptions of non-polar compound such as unsaturated hydrocarbon are not changed with a change in solvent.

Example 1.

Butadiene



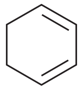
$$H_2C = \overset{H}{\overset{|}{C}} - \overset{H}{\overset{|}{C}} = CH_2$$

Here, the base value is 217 mμ

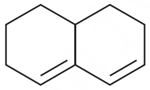
So, calculated value of λ_{max} is 217 mμ

Observed λ_{max} value is 217 mμ.

Conjugated dienes in which the double bonds are contained within rings absorb somewhat differently. If the conjugated double bonds are contained in separate, but fused, six-membered rings (a heteroannular diene), a base value of 214 mμ is used; if the conjugated double bonds are contained in the same ring (a homoannular diene), a base value of 253 mμ is used. For each alkyl substituent group on the diene system or, for each ring to which a carbon-carbon double bond is exocylic, 5 mμ are added to the calculated value.



Homoannular diene

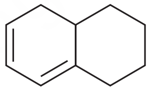


Heteroannular diene

For cyclic conjugated dienes:

Example 1.

Homoannular diene (I)



(I)

Calculated λ_{max}

Here, the base value is 253 mμ

For 3-ring residules + 5 × 3 mμ

For one ring to which

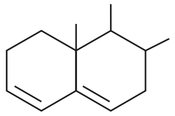
the carbon-carbon double bond is exocylic + 5 mμ

Calculated: λ_{max} value is 273 mμ.

Observed: λ_{max} value is 275 mμ.

Example 2.

Heteroannular diene (II)



(II)

Here, the base value is 214 mμ

For 3-ring residues + 15 mμ

For one ring to which the

Carbon-carbon double bond + 5 mμ is exocylic.

Calculated: λ_{max} value is 234 mμ

Observed: λ_{max} value is 235 mμ.

Quantitative application of UV spectroscopy

Absorption of light in both the ultraviolet and visible regions of the electromagnetic spectrum takes place when the energy of light matches that required to induce in the molecule and electronic transition and its associated vibrational and rotational transitions subsequently.

Beer-Lambert's law

When a beam of light is passed through a transparent cell containing a solution of an absorbing substance, then the intensity of the incident light may be reduced.

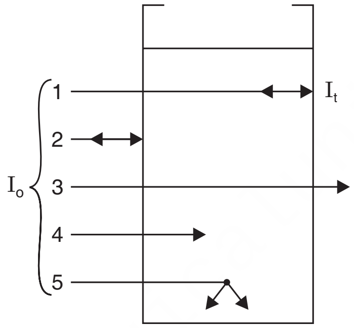


Fig. 24.4 Reduction of the intensity of light by reflection at cell faces (rays 1-2), absorption (ray 4) and scattering by particles (ray 5).

$I_{\text{absorbed}} = I_o - I_t$

$I_o \Rightarrow$ intensity of the incident light.

$I_t \Rightarrow$ intensity of the transmitted light.

Generally UV experiments are done in quartz cells as glass absorbs UV.

The transmittance (T) is:

$T = \frac{I_t}{I_o}$ and % T is given by $\% T = \frac{100\, I_t}{I_o}$

In 1760 Lambert put forward the relation between I_t and I_o for various thicknesses (b) of the substance. This relationship is given in shape of a law, which is known as Lambert's law. The law is stated as follows:

The rate of decrease in intensity of light with thickness is proportional to the intensity of the incident light.

When the law is expressed mathematically

$$-\frac{dI}{db} \propto I$$

or $$-\frac{dI}{db} = k_1 I_t \qquad [k_1 \Rightarrow \text{proportionality constant}]$$

or $$-\frac{dI}{I_t} = k_1 db$$

Integrating both sides:

$$-I_t = k_1 b + c$$

when $b = 0$, $c = -\ln I_0$

or $$-\ln I_t = k_1 b - \ln I_0 \quad \text{or} \quad \ln \frac{I_0}{I_t} = k_1 b$$

or $$\log_{10} \frac{I_0}{I_t} = \frac{k_1 b}{2.303}$$

where, $\log_{10} I_0/I_t$ is called the absorbance (A).

Absorbance is reciprocal of common logarithms of transmittance.

$$A = \log_{10} \frac{I_0}{I_t} = \log_{10} \left(\frac{1}{T}\right) = -\log_{10} T = 2 - \log (\%\, T).$$

Beer in 1852 put forward another relationship which is between absorbance and concentration which is mathematically expressed as:

$$\log_{10} \frac{I_0}{I_t} = \frac{k_2 C}{2.303}$$

Beer's law is defined as:

The intensity of a beam of parallel monochromatic radiation decreases exponentially with the number of absorbing molecules. It may be stated also as: the absorbance is proportional to the concentration.

The combination of these two laws leads to Beer–Lambert's law, which is mathematically expressed as:

$A = \log_{10}\frac{I_0}{I_t} = abc$ in which the proportionality constants $k_1/2.303$ and $k_2/2.303$ are combined to the single constant '*a*' which is known as **absorptivity**. The value of '*a*' as well as its name depend on units of concentration. When '*c*' is in moles litre^{-1}, '*a*' is called **molar absorptivity,** formerly known as **molar extinction coefficient (ε)**

then the equation takes the form:

$$A = \varepsilon . b . c.$$

When the absorbance is measured for 1% (*w*/*v*) solution in a 1 cm cell, then the equation takes the form

$$A = A_{1\text{cm}}^{1\%} . b . c.$$

$A_{1\text{cm}}^{1\%}$ is known as **specific absorbance**.

Colorimetric analysis is also based on Beer–Lambert's law. Here the light used is visible one and coloured samples are analysed.

Infrared Spectroscopy

When infrared light is passed through a sample of an organic compound, some of the frequencies are transmitted through the sample without being absorbed. If we plot the percent absorbance or percent transmittance against frequency the result is infrared (IR) spectrum.

Molecular vibration

At ordinary temperatures organic molecules are in a constant state of vibration each bond having its characteristic stretching and bending frequency and being capable of absorbing light of that frequency. The vibrations of two atoms joined together by a chemical bond can be compared to the vibrations of two balls joined by a spring, using this analogy we can justify several frequencies of infrared spectrum.

Two balls joined by a spring

For example to stretch spring requires more energy than to bend it; thus stretching energy of a bond is greater than the bending energy and stretching absorptions of a bond appear at higher frequencies in the infrared spectrum than the bending absorption of the same bond.

Calculation of vibrational frequencies

We can calculate the vibrational frequency of a bond with a reasonable accuracy, in the same way as we can calculate the vibrational frequency of a ball and spring system; the equation of calculation is Hook's law,

$$\nu = \frac{1}{2\,.\,\pi}\left(\frac{k}{m_1 m_2 / m_1 + m_2}\right)^{1/2}$$

where ν = frequency, k = a constant related to the strength of the spring (the force constant of the bond), m_1, m_2 = the masses of two balls or atoms, $m_1m_2/m_1 + m_2$ is known as reduced mass.

As an example, we can calculate the approximate frequency of C—H stretching vibration from the following data,

$$k = 500 \text{ Nm}^{-1} = 5 \times 10^5 \text{ gm s}^{-2} \times \frac{1}{m}$$

$$= 5 \times 10^5 \text{ gs}^{-2}$$

$$1 \text{ N} = 1 \text{ kg} \times \text{m/sec}^2 = 1000 \text{ gm s}^{-2}$$

$$m_C = \text{ mass of C-atom} = 20 \times 10^{-24} \text{ gm}$$

$$m_N = \text{mass of H-atom} = 1.6 \times 10^{-24} \text{ gm}$$

$$\nu = \frac{7}{2 \times 22}\left[\frac{5 \times 10^5 \text{ gs}^{-2}}{(20 \times 10^{-24}\text{ g})(1.6 \times 10^{-24}\text{ g})/(20 + 1.6)10^{-24}\text{ g}}\right]^{1/2} = 9.3 \times 10^{13} \text{ s}^{-1}$$

To express this in wave numbers ($\bar{\nu}$) we use relationship,

$$\bar{\nu} = \frac{\nu}{c} = \frac{9.3 \times 10^{13} \text{ s}^{-1}}{3 \times 10^8 \text{ ms}^{-1}} \text{ where } c = \text{velocity of light}$$

$$= 3.1 \times 10^5 \text{ m}^{-1} = 3100 \text{ cm}^{-1}$$

So, $\nu_{max.}$ for C—H (Str.) is 3100 cm^{-1}.

The vibrational frequency of a bond is expected to increase when the bond strength increases and also when the reduced mass of the system decreases. As for example,

Stretching : C = C > C—C Stretching : $>$C = O > C—O

1600 cm^{-1} 1700 cm^{-1} 1100 – 1300 cm^{-1}

Stretching : C—H > C—C Stretching : O—H > C—O

3100 cm^{-1} 3500 cm^{-1} 1100–1300 cm^{-1}

$$\frac{12 \times 1}{13} < \frac{12 \times 12}{24} \qquad \frac{16 \times 1}{17} < \frac{12 \times 16}{28}$$

Infrared spectroscopy

Infrared spectroscopy is dependent on modes of vibration of the atoms in a molecule and those have been shown in the following Fig. 24.5.

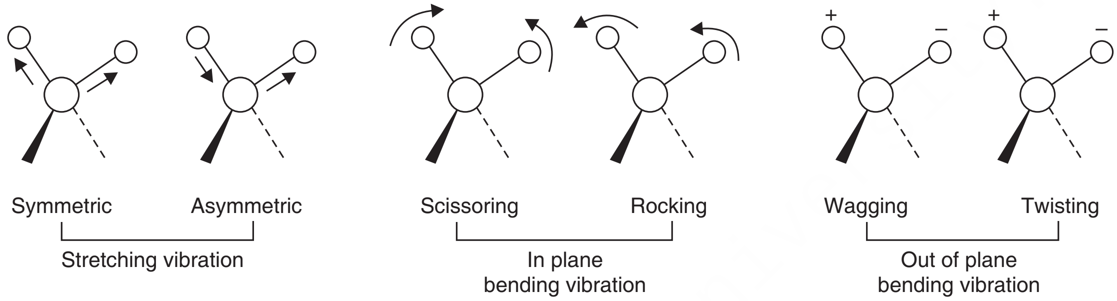


Fig. 24.5 Modes of vibration of the atoms in a molecule.

Applications of IR spectroscopy

- The IR spectrum cannot distinguish a pure sample from an impure sample.
- The progress of organic reactions can be studied with IR spectrum.
- Detection of functional groups in a molecule.
- Identity of two samples that have identical spectra, generally it occurs in Finger print region which is 1430 = 910 cm^{-1}

Examples of some stretching and bending vibrations in alkanes

			ν_{max}
C—H	stretching	—	2950 and 2820 cm^{-1}
$—CH_2—$	bending	—	1458 cm^{-1}
$C—CH_3$	bending	—	1458–1380 cm^{-1}

IR Spectrum for ether and alcohol:

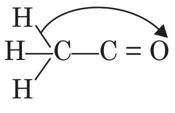
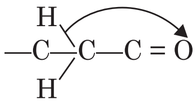
Replacement of $—CH_2—$ in alkane by 'O' results in ether. There is appearance of C—O stretching vibration at 1110 cm^{-1} in the spectrum when an H atom of a hydrocarbon is exchanged for an '–OH' group, the spectrum changes in a very predictable way, it now shows absorptions owing to 'O—H' and 'C—O' stretching vibrations in addition to the hydrocarbon chromophoric groups present *i.e.* for alcohols:

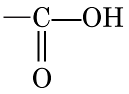
O—H stretching vibration is at 3448 cm^{-1} (polymeric association of OH groups)

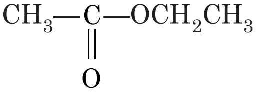
C—O stretching vibration is at 1053 cm^{-1}

In CCl_4 solution O—H stretching vibration is 3788 cm^{-1} (as the degree of association changes with dilution).

Aldehyde and ketones: IR spectra show absorption H—C = O (stretching) at 1740–20 cm^{-1} (strong); for a cyclic ketone stretching vibration is at 1725–1700 cm^{-1} (strong) (distinction from —CHO and $\rangle C = O$); C—H (stretching) in —CHO group is at 2880–2625 cm^{-1} (weak to medium)(distinction from $\rangle C = O$).

Absorption due to C—H (deformation) in  $H—\underset{H}{\overset{H}{C}}—C = O$ is at 1365–1355 cm^{-1} (shown by arrow) and in  $—C—\underset{H}{\overset{H}{C}}—C = O$ is at 1435–1405 cm (strong).

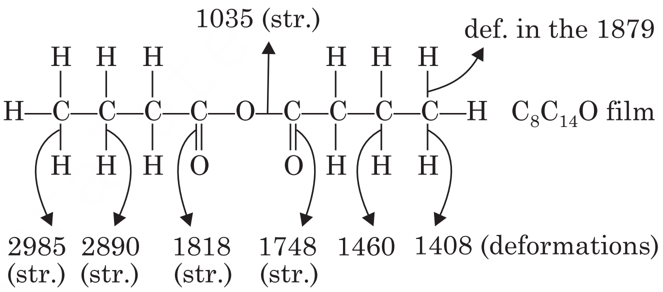
Acids: IR spectra for  $-\underset{\substack{\| \\ O}}{C}-OH$ group, —C = O (stretching) is at 1725-1700 cm^{-1} (s) (as that of acylic $>C=O$), —O—H (stretching) is at 3650-3500 cm^{-1} (s) (m) (lower than that for alcohols), stearic acid in CCl_4 solution gives ν_{max} at 2974 cm^{-1} (OH str. is hidden by C—H str), 1706 cm^{-1} for $>C=O$ str., C—H (def.) at 1460 cm^{-1}. Stearic acid in solid state gives λ_{max} at 2940, 1460 and 1370 cm^{-1} (bands for nujol) $>C=O$ stretching at 1709 and 1312, 1295, 1279, 1258, 1235, 1220 and 1188 cm^{-1}. These bands are characteristic of long chain *n*-alkyl compounds, in the solid state. The absorptions of stearic acid in CCl_4 solution and in solid state show a difference in IR spectrum of the compound.

Esters: For  $CH_3-\underset{\substack{\| \\ O}}{C}-OCH_2CH_3$

ν_{max} are:

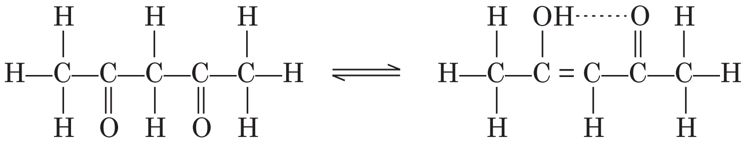
1742 cm^{-1} (C = O str. in solid aliphatic esters)
1241 cm^{-1} (C—O str. in acetate)
1370 cm^{-1} (C—H def. in CH_3)
3003 cm^{-1} (C—H str. in CH_3 or, CH_2)
1449 cm^{-1} (C—H def. in CH_3 or, CH_2)

Acid anhydrides: C = O str. in acylic anhydride are 1840-1800 (s) and 1780-1740 cm^{-1} (s). There is also a band in the region 1180-1030 cm^{-1} (s) due to C—O str in the grouping —C—O—C—. ν_{max} for various str. and def. of bonds in an anhydride are shown below with the arrows.



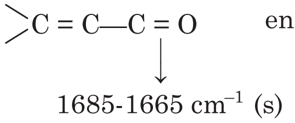
All the values are in cm^{-1}.

β-diketones:



[1725-700 cm^{-1} single stretching with greater intensity (as there are two carbonyl groups) in IR spectrum]

Absorption at 1655 cm^{-1} (s) for $>C=O$ in enols

α, β unsaturated ketones contain grouping  $>C=C-\underset{\substack{\downarrow \\ 1685\text{-}1665\ cm^{-1}\ (s)}}{C=O}$ enols contain this grouping, but the shift to 1655 cm^{-1} that occurs in these compounds is attributed to H–bonding —O—H----O = C<. True alcoholic OH absorption band near 3700 cm^{-1} in enols are absent, but there is absorption band near 2700 cm^{-1} (*s*) which is attributed to the OH group (*s*) indicates strong absorption, (*m*) indicates medium absorption.

Amines: Primary and secondary amines contain N—H bond, both types absorb in the region 3500 – 3300 cm^{-1} (*v*) but the two are distinguished by the fact that primary amines show two bands in their region, whereas secondary amines generally show only one. If there is H-bonding, then the region is 3400 – 3100 cm^{-1} (*s*) C—N – str. 1200 – 1020 cm^{-1} in aliphatic amines (*w* – *m*), C—N – str. + 200 – 1020 cm^{-1} in aromatic amines (*s*), N—H – def 1650–1590 cm^{-1} (*s* – *m*) in primary amines, N—H – def 1650 – 1550 cm^{-1} (*s*).

Because of the overlap of these regions, it is not possible to distinguish the types of amines in this way.

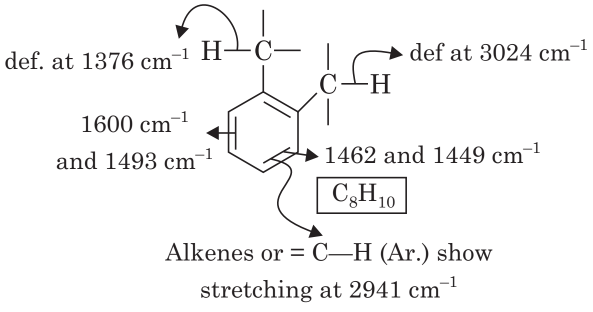
Aromatic Compounds: Aromatic compounds produce a large number of absorption bands in the IR region. The following regions are particularly useful for recognising the presence of benzene, polynuclear aromatics and benzene derivatives.

>C—H ⇒ 3080 – 3030 cm^{-1} (*w*) (str) and the bands for C = C (in plane vibration) are 1625 – 1600 cm^{-1} (*v*), 1590 – 1575 cm^{-1} (*v*) and 1525 – 1475 cm^{-1} (*v*).

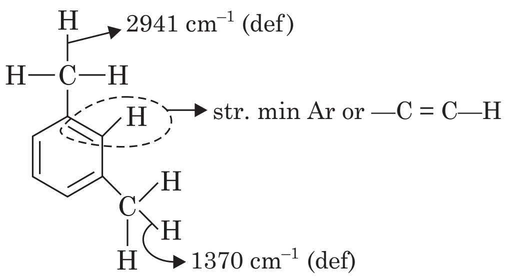
Substituent groups show very light effect on the above bands, but new bands are introduced according to orientation of the groups. However, because of a great deal of overlapping of the various bands in the region 1225–970 cm^{-1}; this region is not very useful.

On the other hand, these isomers in the aromatic system may be readily distinguished by the bands due to (C—H) (out of plane) deformation 1, 2 isomer shows ν_{max} 770 – 735 cm^{-1} (*s*) 1, 3 isomers at ν_{max} 800 – 750 cm^{-1} and 725 – 680 (m) ; 1, 4 isomer at ν_{max} 840 – 810 cm^{-1} (*s*); mono-substituted benzene ring shows ν_{max} at 770 – 730 cm^{-1} (*s*) and 710 – 690 cm^{-1} (*s*) (Two bands distinguish it from 1, 2 isomer): ν_{max} for str. and def. of the bonds are shown by the arrows.

1, 2-disubstituted benzene:



1, 3-disubstituted benzene:

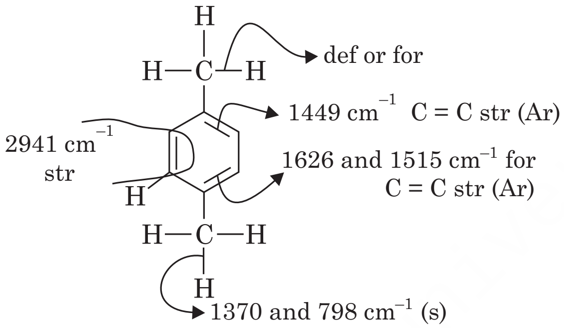


C = C (Ar) str. is at 1613, 15878 and 1490 cm^{-1}

and 1450 cm^{-1} for C—H def in CH_3

and 772 and 654 cm^{-1} (*s*) for 1, 3-disubstitution

1, 4-di-substituted benzene:



1, 4 disubstituted benzene

Abbreviations: ν_{max}–wave number cm^{-1}, *s*-strong, *w*-weak, *m*-medium, str. (stretching), def. (deformation), *v* (variable)

Some IR Spectra:

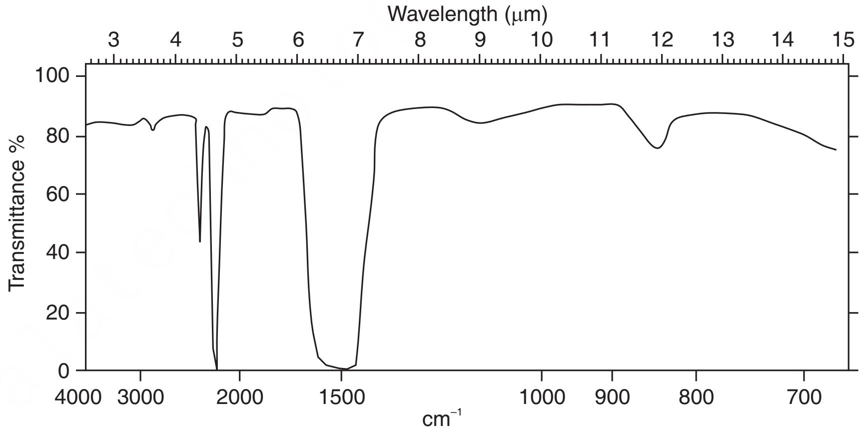


Fig. 24.6 IR spectrum of carbon disulphide (0.1 mm cell).

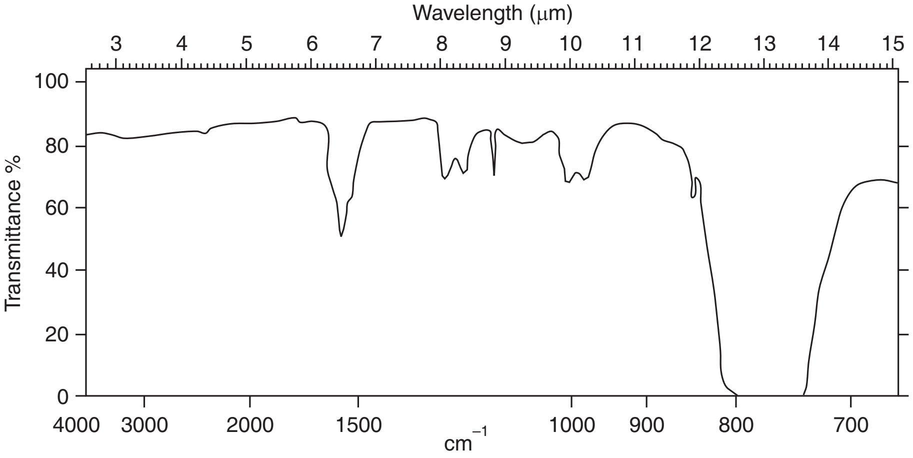


Fig. 24.7 IR spectrum of carbon tetrachloride (0.1 mm cell).

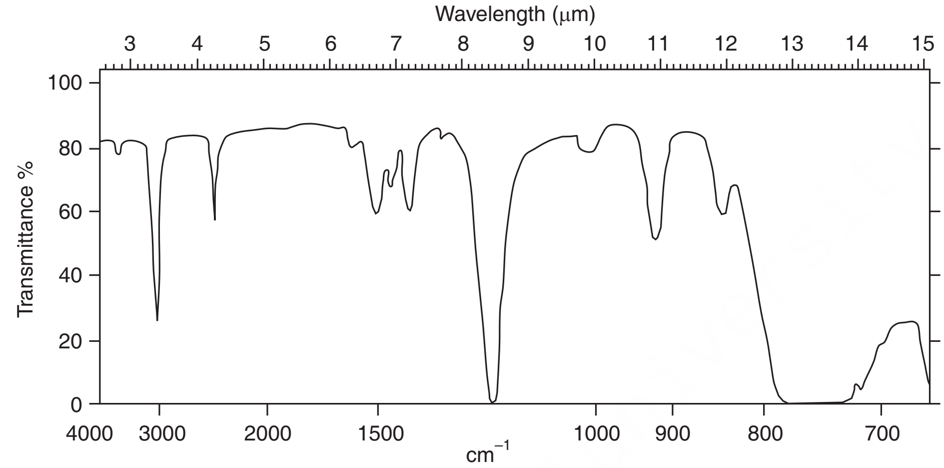


Fig. 24.8 IR spectrum of chloroform (ethanol-free) (0.1 mm cell).

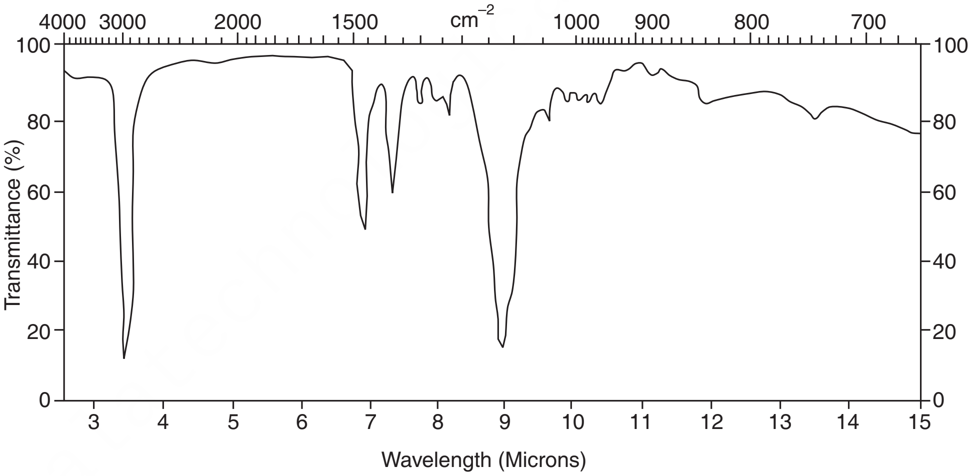


Fig. 24.9 Di-*n*-butyl ether, liquid film.

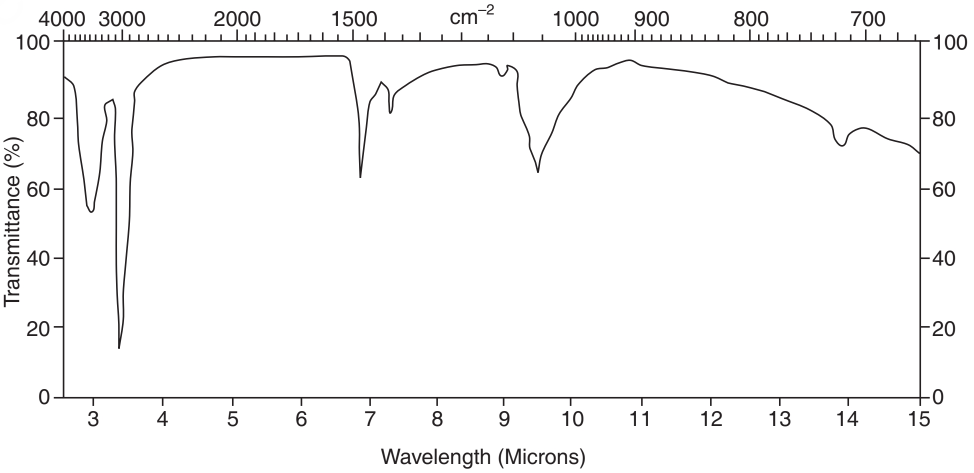


Fig. 24.10 Lauryl alcohol, liquid film.

Nuclear Magnetic Resonance (nmr) or Proton Magnetic Resonance (pmr) spectroscopy

nmr is a powerful analytical technique to evaluate the structures of carbon compounds. The technique is used (*i*) to identify unknown compounds, (*ii*) to check for impurities and (*iii*) to study the shapes of molecules. In medicine, magnetic resonance imaging uses *nmr* to detect the hydrogen nuclei in the human body, especially in water and lipids. The term 'nuclear' interprets the technique that detects nuclei of atoms such as hydrogen-1 (proton). The term 'magnetic' interprets the nuclei that act like tiny magnets that can line up either in the same direction or in the opposite direction to an external magnetic field. The term 'resonance' is the absorption of energy in the form of radio waves with the frequency corresponding to the size of energy jump as the nuclei flip from one alignment in a magnetic field to the other (Fig. 24.11).

The atomic nuclei spin about their axes. Now since a rotating charged sphere is always associated with it a magnetic moment, then all the charged particles in a nucleus will make that nucleus to behave like a tiny bar magnet, with its magnetic moment along the axis of rotation of the nucleus. The angular momentum of the spinning nucleus can be represented in terms of spin numbers (I). These numbers can attain the values 0, $\frac{1}{2}$, 1, $\frac{3}{2}$ etc. (I = 0 denotes no spin). The nuclear magnetic moment is denoted by the symbol 'μ'.

Each proton and neutron in a nucleus has its own spin and I is a resultant of these spins. If the sum of protons and neutrons is even, I is 0 or, integral (1, 2, etc.), if the sum is odd I is $\frac{1}{2}$ integral *i.e.,* $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$. If both protons and neutrons are even numbered then I is 0. That is why, both C^{12} and O^{16} have no resultant nuclear magnetic moment and give no *nmr* signal. Several nuclei H^1, F^{19}, C^{13} have a spin number I of $\frac{1}{2}$ and a uniform spherical charge distribution. Nuclei with spin number I of 1 or higher have a non-spherical charge distribution.

If a magnetic nucleus is placed in a uniform magnetic field it is seen that the magnetic dipole assumes only a discrete set of orientations. The system is said to be quantised. The magnetic nucleus can attain any one of the possible orientations indicated by (2I + 1).

Thus a proton (I = $\frac{1}{2}$) can assume only one of the two possible orientations corresponding to the energy level of $\pm \mu H_o$. One with respect to the direction of the applied magnetic field and the other is aligned against the direction of the applied field (Fig. 24.11).

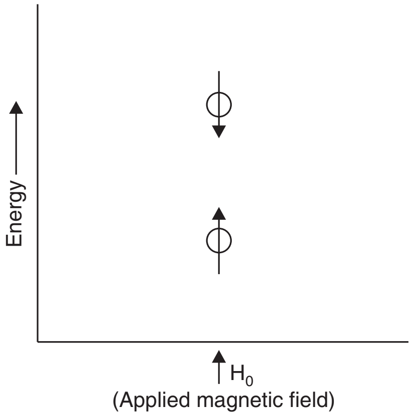


Fig. 24.11 Energy levels of a proton.

The transition of a proton from one possible orientation to another is effected by the absorption or emission of a discrete amount of energy such that,

$$E = h\nu = 2\,\mu H_o$$

where, ν = frequency of electromagnetic radion absorbed or emitted

h = Planck's constant

μ = nuclear magnetic moment

H_o = applied magnetic field.

For protons if a magnetic field 14000 Gauss is applied the frequency of such energy remains in the radio frequency region (60 megacycles per second).

Unless the axis of the nuclear magnet is oriented exactly parallel or antiparallel with the applied magnetic field (Fig. 24.11), there will be a certain force by external magnetic field to so orient the spinning nucleus. But because the nucleus is spinning, the effect is that its rotational axis draws a circle perpendicular to the applied field. Such an effect is shown in Fig. 24.12. This motion of the nucleus is called **Precession**.

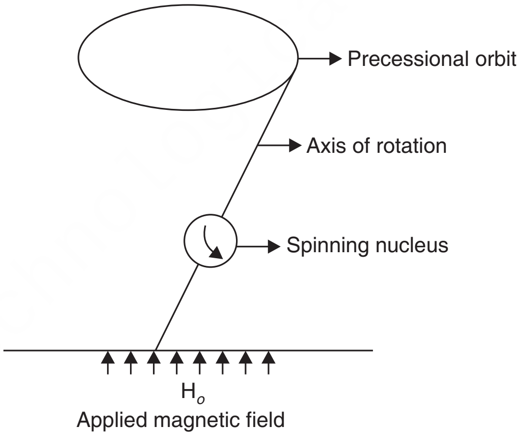


Fig. 24.12 Precession.

Theory of nuclear resonance

A proton in a static external magnetic field may assume only two possible orientations corresponding to the energies of $\pm\,\mu H_o$. The low energy orientation corresponds to that state in which the nuclear magnetic moment is aligned parallel to the external magnetic field, and the high energy orientation corresponds to that state in which the nuclear magnetic moment is aligned antiparallel (opposed) to the external magnetic field. It is possible to the induce transitions between these two orientations. The frequency ν of electromagnetic radiation necessary for such a transition is given by

$$\nu = 2\mu H_o/h$$

where H_o is the strength of the external or applied magnetic field and h is Planck's constant.

The precessional frequency of the spinning nucleus *i.e.,* nuclear magnet is exactly equal to the frequency of electromagnetic radiation necessary to induce a transition from one nuclear spin state to another. The nuclear transition corresponds to a change in the angle that the axis of the nuclear magnet makes with the applied magnetic field. This change can be brought about through the application of electromagnetic radiation whose magnetic vector component is rotating in a plane perpendicular to the main magnetic field. When the frequency of the rotating magnetic field and the frequency of the precessing nucleus become equal, they are said to be in resonance, and the absorption or emission of energy by the spinning nucleus then occurs. Thus a **nuclear resonance** will occur when a nucleus ($I > 0$) is placed in a stable magnetic field and subjected to the electromagnetic radiation of appropriate energy.

The electromagnetic radiation is supplied by an oscillator with its magnetic field at right angles to the applied field and since the position of absorption peak, that is, where resonance occurs, depends on the frequency of the oscillator or the strength of the applied magnetic field. It is possible to change from the lower to higher energy level by employing a variable frequency with a fixed applied magnetic field or vice versa. In practice it is easier to vary the magnetic field rather than the frequency, the result is the *nmr* spectra which is usually a graph of signal intensity (ordinate) against the magnetic field (abscissa) expressed in milligauss at a fixed frequency (Fig. 24.17).

Instrumentation

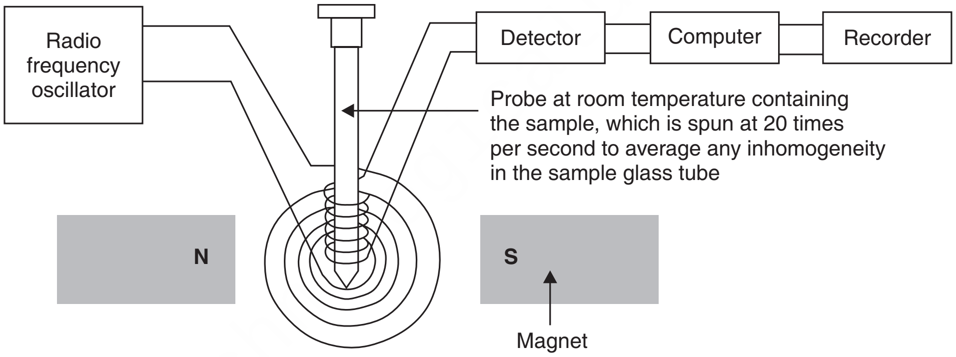


Fig. 24.13 Diagram of an *nmr* spectrometer.

Shielding, Deshielding and Chemical Shift

It might be expected that the resonance frequency for a given magnetic field depends only on the nature of atomic nucleus concerned. This, however, is not the case. The applied magnetic field causes electrons surrounding a nucleus to circulate in a plane perpendicular to the applied field, and this generates electric current to produce a magnetic field in opposition to the applied magnetic field (Fig. 24.13). Thus the effective magnetic field 'H' experienced by the nucleus is smaller than the applied magnetic field (H_o). The relationship between the two is expressed as:

$\mathbf{H = H_o(1 - \sigma)}$ σ is called the **shielding or, screening constant** (which is nondimensional) and has a positive value. But it may be negative *i.e.,* then the effective magnetic field is larger than the applied magnetic field to orient the nuclear magnetic. In that case the proton is said to be **deshielded**. Since the numerical value of σ depends on the chemical environment of a given nucleus, the shielding or deshielding varies with its electronic environment. Then at a given radiofrequency, all protons absorb at the same effective field strength, but they absorb at different applied field strengths.

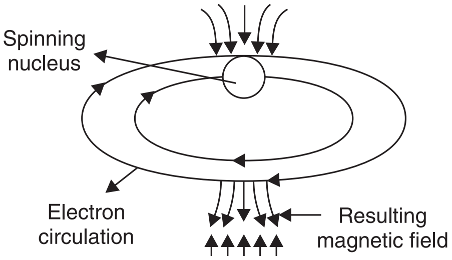
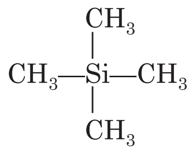


Fig. 24.14 Diamagnetic electronic circulation about a nucleus.

Each set of equivalent protons in a compound will have a slightly different electronic environment from other set of protons and hence will absorb at a slightly different applied field strength to produce the same effective field strength which can cause the 'resonance' to occur.

Shielding causes a shift of the resonance frequency to higher values of the applied field (H_o), that is , the shift is **upfield**. On the other hand, deshielding causes a shift of the resonance frequency to lower values of the applied field, that is, the shift is **downfield**. The magnitude of this shift is called **chemical shift**. Since the value of the applied field experienced by the organic compound cannot be determined accurately, chemical shifts are measured relative to some standard compound which contains the nucleus under consideration. Tetramethylsilane [TMS, $(CH_3)_4Si$] is particularly useful for proton magnetic resonance (*pmr*). TMS contains twelve equivalent protons. The *pmr* spectrum of this compound shows a single sharp line which occurs at higher field than any other protons in most of the common organic compounds. That is, most *pmr* signals occur downfield with respect to TMS.



$$(CH_3)_4Si$$

(TMS)

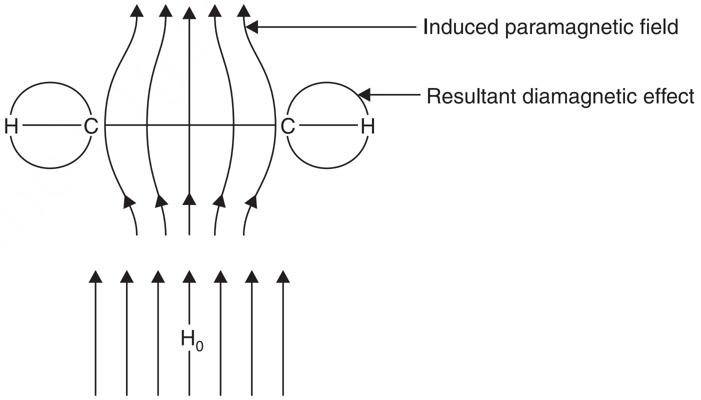


Fig. 24.15 Shielding of an acetylenic proton in terms of paramagnetic effects.

The chemical shift may be reported in various ways. The resonance frequency of the proton of the compound is dependent on the strength of the applied magnetic field. The shift may be reported as units of the magnetic field in milligauss. However, the magnetic field can also be expressed as Hertz (Hz) or cycles per second (cps). The separation in Hz is also proportional to the frequency of the oscillator, *e.g.*, if the separation between a proton signal and signal of TMS is 60 Hz at 40 MHz the separation at 60 MHz will be 90 Hz. Therefore it is desirable to repart chemical shifts in such units that are independent of the operating conditions of the spectrophotometer. This can be done very easily by defining chemical shift δ by the expression

$$\delta = \frac{\text{Separation in Hz}}{\text{Oscillator frequency}} \times 10^6$$

The factor 10^6 is introduced in order to record the chemical shift as a convenient value. This is usually in the range 1-10 and is expressed in ppm.

The dependence of the chemical shift of the oscillator frequency is shown in the following example,

$$\delta = \frac{60}{40 \times 10^6} \times 10^6 = 1.5 \text{ ppm.}$$

$$\delta = \frac{90 \times 10^6}{60 \times 10^6} = 1.5 \text{ ppm.}$$

It is now becoming common practice to express chemical shifts in τ (tau) values, defined by:

$$\tau = 10\text{-}\delta.$$

10 ppm is assigned to the line of TMS in *nmr* spectrum. Most protons have positive τ value *i.e.,* $\delta < 10$. Strong acidic protons have negative τ value *i.e.,* $\delta > 10$.

Position of signals (chemical shifts)

The greater the shielding of nucleus the larger is τ value (the smaller is δ). Since the degree of shielding depends on the electron density surrounding the proton any structural feature that decreases this electron density causes a decrease in shielding (deshielding) with consequent lowering of the τ value (the chemical shifts) movesdown field. Thus electronegativity

		τ(ppm)
CH_3I	↓ deshielding	7.83
CH_3Br		7.35
CH_3Cl		6.98
CH_3F		5.70

		τ(ppm)
CH_3—C	↓	9.12
CH_3—N		7.85
CH_3—O		6.70

of the atoms attached in the compounds in the column gradually increases as such there is gradual deshielding and τ value decreases in the column.

Si is less electronegative than carbon, so the protons of CH_3 groups in TMS are more shielded than those in C—CH_3.

Examples of Shielding and Deshielding

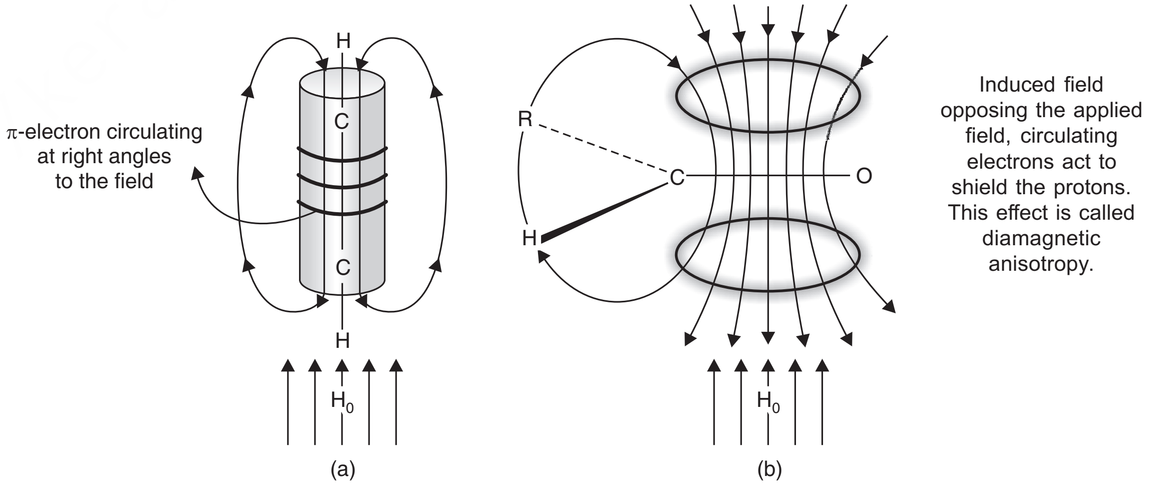


Fig. 24.16 (*a*) Shielding of an acetylenic proton and (*b*) deshielding of an aldehydic proton in terms of diamagnetic anisotropic effects.

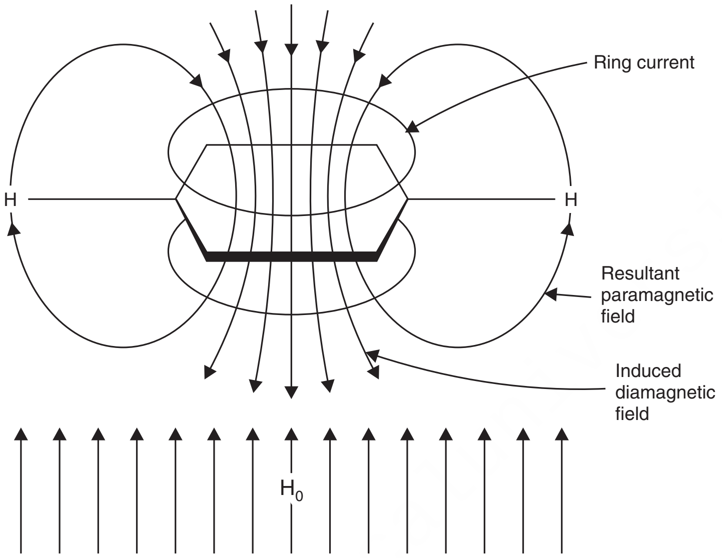


Fig. 24.17 The deshielding of aromatic protons due to a ring current effect.

The nuclear magnetic spectrum

At a given radio frequency, all the protons will absorb at a same effective field strength, but they also absorb at different applied field strengths. The applied field strength is measured and plotted against the absorption of radiation; the results are signals and the spectrum is called a nuclear magnetic resonance spectrum (Fig. 24.18(*a*) and (*b*)).

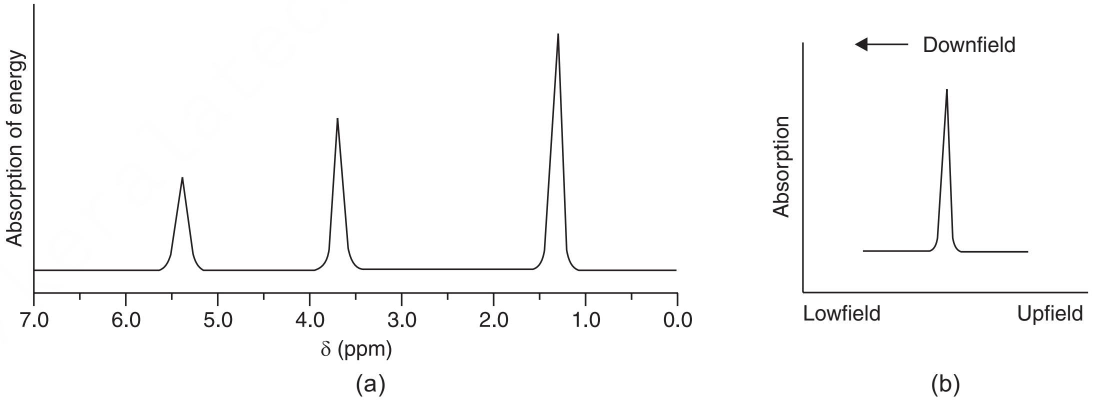


Fig. 24.18 (*a*) *NMR* spectrum for ethanol at low resolution, (*b*) a signal.

Informations predicted by the spectrum

- The number of signals indicate the different types or set of protons present in the molecule.
- The positions of signals predict something about the electronic environment of each kind of proton.
- The intensities of signals indicate how many protons of each kind is present.
- The splitting of the signals into several peaks indicates the environment of a proton with respect to other nearby protons.

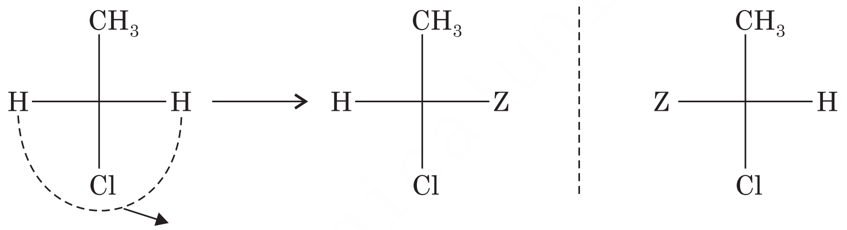
Number of signals

A set of protons with the same environment are said to be equivalent. The number of signals in the *nmr* spectrum tells us, therefore, how many sets of equivalent protons, how many kinds of protons.

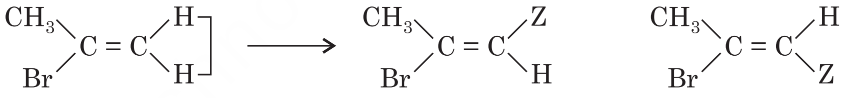
Judging the equivalent protons

Each proton in a molecule is in turn to be replaced by some other atom Z. If replacement of either of two protons by Z would yield the same product or enantiomeric products—then the two protons are chemically and magnetically equivalent.

Example. $CH_3\ CH_2$—Cl (CH_3 protons are non-equivalent to the CH_2 protons)

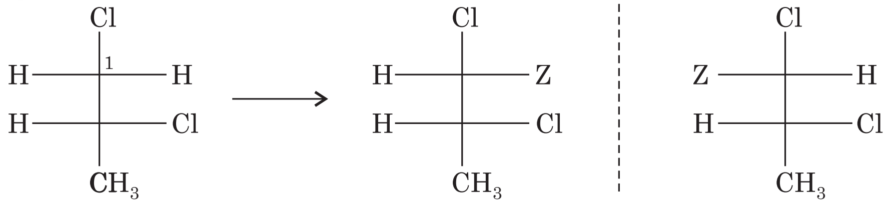


Enantiomeric protons (enantiomeric pairs)
Magnetically equivalent (one *nmr* signal) for the two protons



Diastereomeric
proton pair

The environment of these two protons are neither identical nor mirror images of each other, magnetically these protons are non-equivalent and we expect the *nmr* signal from each one.

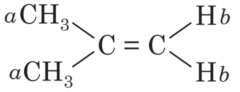


1, 2-dichloropropane (*a*) (*b*)

C–1 are diastereomeric, magnetically non-equivalent and give separate *nmr* signals

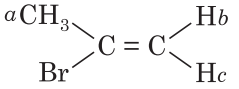
Examples: The number of signals indicate the presence of the number of sets of magnetically nonequivalent protons in the molecule of the compound.

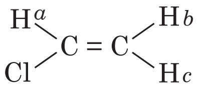
$\underset{a}{CH_3}$—$\underset{b}{C}HCl$—$\underset{a}{CH_3}$ → 2 nmr signals.



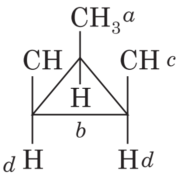
→ 2 nmr signals.

$\underset{a}{CH_3}—\underset{b}{CH_2}—\underset{c}{CH_2}—Cl$ → 3 nmr signals.

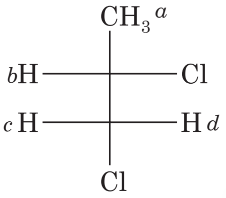

→ 3 nmr signals.


Vinyl chloride

→ 3 nmr signals.


Methyl cyclopropane

→ 4 nmr signals.


1, 2-dichloropropane

→ 4 nmr signals.

Peak area and Proton counting of a Compound

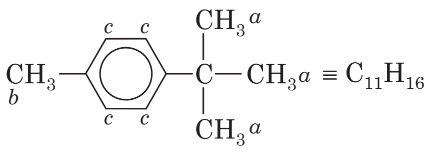
Total step heights (Fig. 24.19) for 16 protons of the compound 1, 4-methyl tertiary butylbenzene = $\underset{a}{8.8} + \underset{b}{2.9} + \underset{c}{3.8}$ = 15.5 units *i.e.,* the number of squares within an integration in an *nmr* spectra (Fig. 24.19) for the compound, $C_{11}H_{16}$ then $\frac{16H}{15.5}$ = 1.03 H is the number of protons per unit. Then number of *a* protons, *b* protons and *c* protons in the compound are:

aH = 1.03 × 8.8 = 9.1

bH = 2.9 × 1.03 = 3

cH = 1.03 × 3.8 = 3.914

i.e.,



(I)

1,4-Methyl tertiary butylbenzene

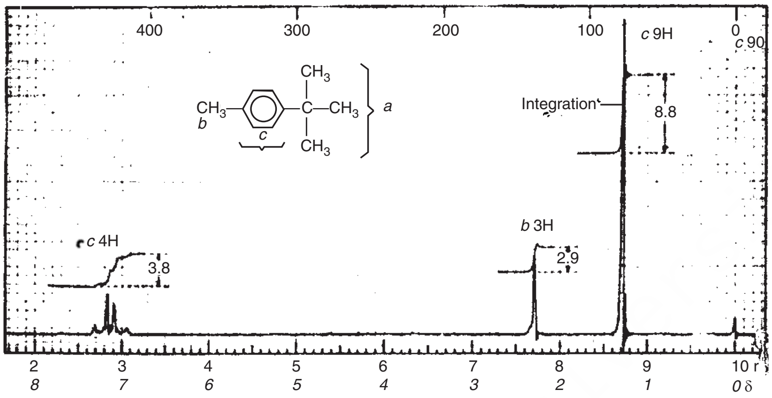
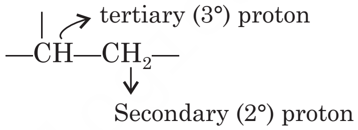


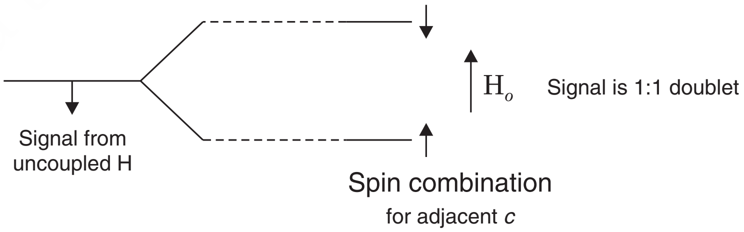
Fig. 24.19 NMR spectrum of 1, 4-methyl tertiary butylbenzene (Proton counting).

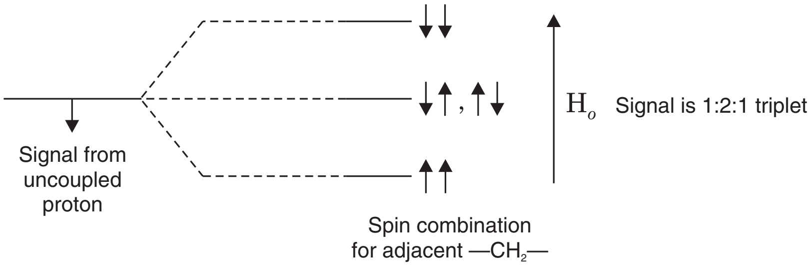
Splitting of signals; Spin–spin coupling

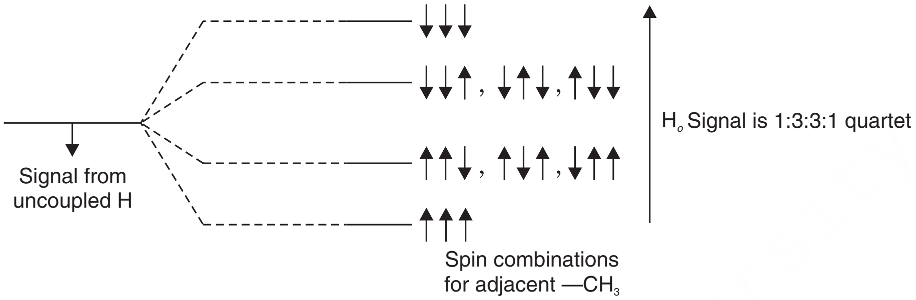


$$—CH—CH_2—$$

The magnetic field that a 2° proton (*s*H) feels at a particular instant during nmr is slightly increased tertiary or slightly decreased by the spin of neighbouring tertiary proton (*t*.H), increased if the *t*.H happens at that instant to be aligned with the applied field; or decreased if the *t*.H happens to be aligned against the applied field for half of the molecules. Then, absorption by a *s*H is shifted slightly downfield and for another half of the molecules the absorption is shifted slightly upfield. The signal is split into two peaks a doublet with equal peak intensities.







Examples:

Upfield doublet ($n + 1$)
($n = 1$) ↑
Compound (A) $CHBr_2—CH_2Br$
↓ ($n = 2$)
Downfield triplet ($n + 1$)

Upfield doublet
↑ ($n = 1$)
Compound (B) $CH_3—CHBr_2$
($n = 3$) ↓
Downfield quartet

Signal splitting is determined by the number of neighbouring protons (*n*). The number of peaks *b*(*n* + 1).

Peak area reflects the number of absorbing protons and the multiplicity of splittings reflects the number of neighbouring protons (Figs. 24.19 and 24.20).

We may expect to observe spin splitting only gives the non-equivalent neighbouring protons. By non-equivalent protons, we mean protons with different 'chemical shifts'. By neighbouring protons we mean most commonly protons on adjacent carbons.

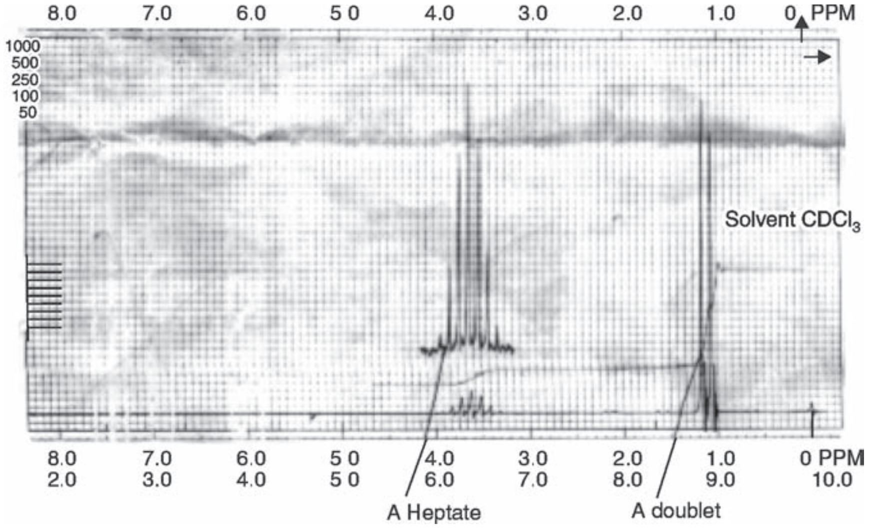


Fig. 24.20 The observed multiplicity of a given group of equivalent protons clearly depends on the number of proton on adjacent atom. The multiplicity of a given group by the expression ($n + 1$), where n is the number of protons on adjacent atoms.

Mass spectrometry

Introduction: Mass spectrometry is an accurate instrumental technique for determination of **relative atomic masses** and relative molecular masses. **Mass spectrometry can also help to determine the molecular structures and to identify unknown compounds.**

Basic principles

In the simplest mass spectrometer, an organic molecule is bombarded with electrons and is converted to highly energetic positively charged ions (molecular ions or parent ions, $M^{\overset{+}{\cdot}}$), which break up into smaller ions (daughter ions). The loss of an electron from a molecule leads to a radical cation ($M^{\overset{+}{\cdot}}$); and the whole process can be represented as follows:

$$\underset{\text{(Organic molecule)}}{M} \longrightarrow \underset{\text{(Molecule ion)}}{M^{\overset{+}{\cdot}} + 2e}$$

The molecule ion ($M^{\overset{+}{\cdot}}$) generally decomposes to a **pair of fragments**, which may be either radical plus or a small molecule plus a radical cation. Thus,

$$\underset{\text{(Molecular ion)}}{M^{\overset{+}{\cdot}}} \longrightarrow \underset{\text{(ion)}}{m_1^{+}} + \underset{\text{(radical)}}{m_2^{\cdot}} \quad \text{or} \quad \underset{\text{(radical cation)}}{m_1^{\overset{+}{\cdot}}} + \underset{\text{(small molecule)}}{m_2}$$

The molecular ions, the fragment ions and fragment radical ions are separated by deflection in a variable magnetic field according to this mass and charge, and generate a current (the ion current) at the collector in proportion to their relative abundances. **A mass spectrum is a plot of relative abundance against the ratio mass to charge (the m/z value).** For singly charged ions, the lower the mass the more easily is the ions deflected in the magnetic field. Doubly charged ions are occasionally formed, they are deflected much more than singly charged ions of the same mass; and they appear in the mass spectrum at the same value as singly charged ions of the half, since,

$$\frac{2m}{2z} = \frac{m}{z}$$

Neutral particles produced in the fragmentation, whether uncharged molecules (m_2) or radicals ($m_2^{\cdot}$) cannot be detected directly in the mass spectrometer.

Instrumentation

There is a high vacuum inside a mass spectrometer to produce and study ionised atoms and molecules including fragments of molecules.

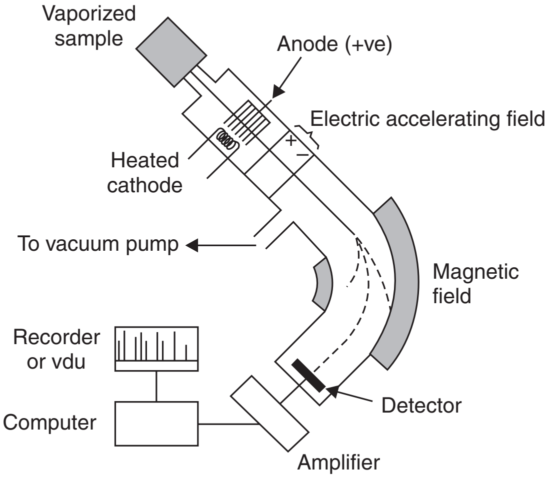
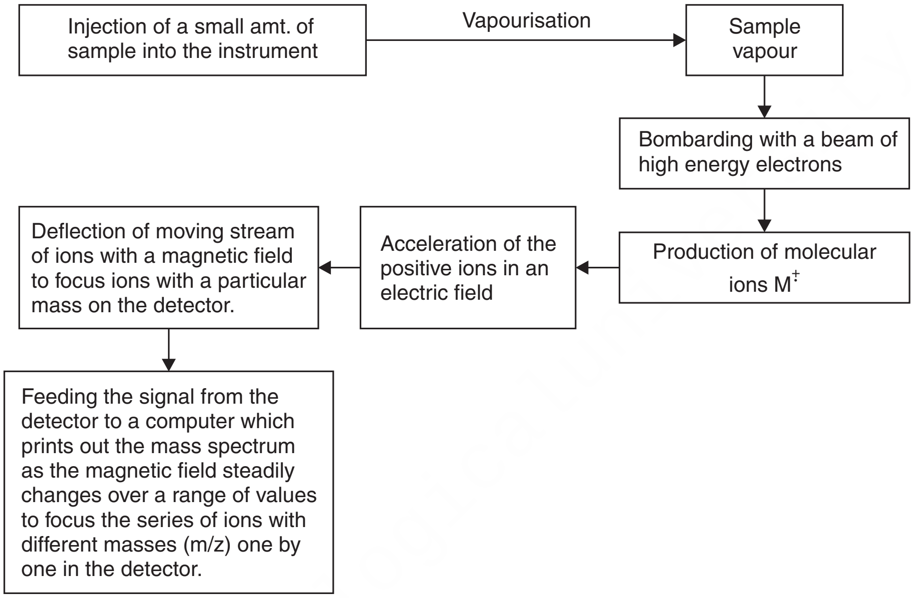


Fig. 24.21 Diagram of a mass spectrometer.

Schematic representation for production of a mass spectrum:



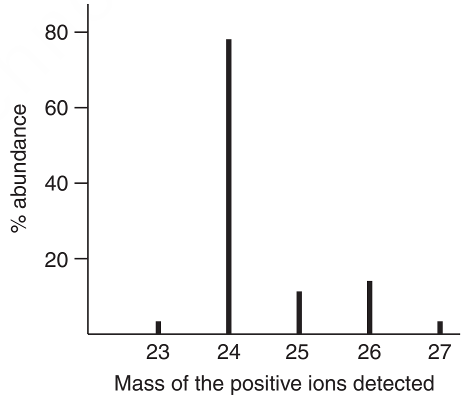


Fig. 24.22 Mass spectrum of magnesium.

The instrument needs calibration using a reference compound with a known structure and molecular mass so that the computer can print a scale on the mass spectrum.

The mass spectrum for an element displays the relative abundance of different isotopes of the element. This makes it possible to calculate the relative atomic mass for the element (see Fig. 24.22).

Applications

- **Structure elucidation**

When a molecular compound is being analysed, the peak of the ion with highest mass is usually the whole molecule ionised is known as 'molecular ion' or parent ion ($M^{+\cdot}$), which is the relative mass (molecular weight) of the compound.

Nitrogen rule. If a molecular ion has an even molecular weight, it possesses either no nitrogen or an even number of nitrogen atoms. An odd molecular weight compound requires an odd number of nitrogen atoms.

The **base peak** is the most intense line of the spectrum.

Metastable ions. Fragmentation ($m_1^+ \rightarrow m_2^+ + m_3$) in general occurs in the ion source of the mass spectrometer before the positive ions are accelerated and therefore a distinct peak results for each fragmentation.

So mass spectrum is a ‘fragmentation pattern’. The computer has a database of mass spectra so it can identify an unknown compound by matching its spectrum with one in its database.

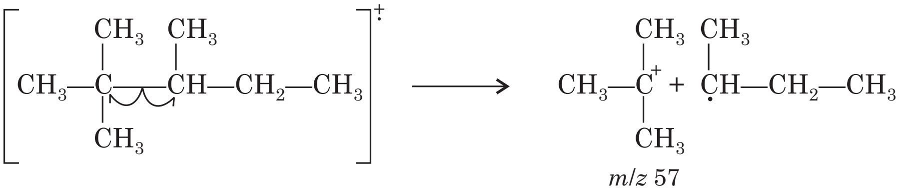
A chemist who synthesises new compounds can study their fragmentation pattern in a mass spectrometer and determine its structure with the help of other spectra like infrared spectroscopy (i.r.) and nuclear magnetic resonance (n.m.r.).

The combination of gas-liquid chromatography (glc) with mass spectrometry is of great importance in modern chemical analysis. First glc separates the components in an unknown mixture, such as a sample of polluted water, then mass spectrometry (ms) detects and identifies the components.

Highlights:

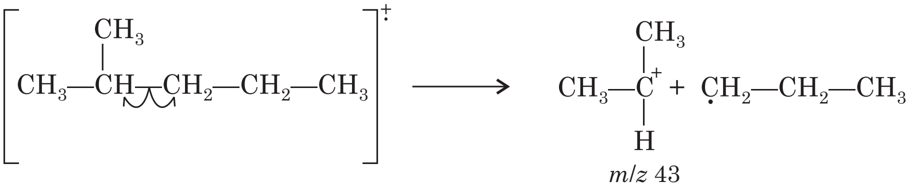
- The parent peak ($M^{+\cdot}$) is the most intense in straight-chain compounds, the intensity reduces with increased chain branching.
- In a homologous series, the intensity of M^+ decreases with increase in molecular weight.
- In branched chain hydrocarbons cleavage is preferred at the bond adjacent to the branch; thus giving rise to tertiary (3°) carbocations as 3° is more stable than 2°, which in turn is more stable than 1° carbocations.
- During representing the fragmentation, a one electron shift is represented by a ‘fish hook’ arrow ‘ ⌒ ’ and a two electron shift in the usual manner by ‘ ↷ ’ .

Examples. For Methylpentanes:



$$\left[CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_3\right]^{+\cdot} \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{+}{C}}} + \overset{\overset{CH_3}{|}}{\underset{\cdot}{C}}H-CH_2-CH_3$$

m/*z* 57

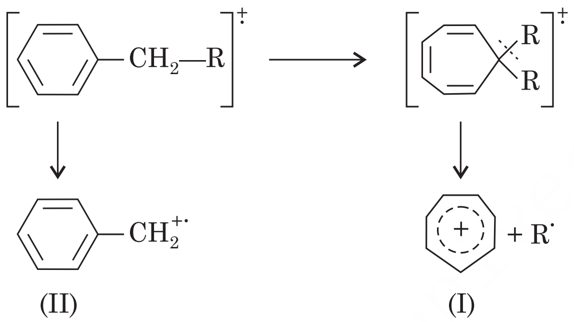


$$\left[CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-CH_3\right]^{+\cdot} \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{\overset{+}{C}}} + \underset{\cdot}{C}H_2-CH_2-CH_3$$

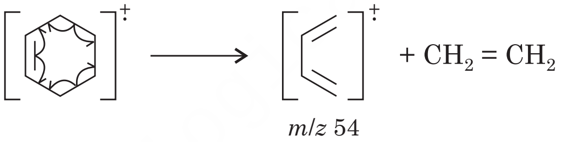
m/*z* 43

- The probability of the existence of a strong $M^{+\cdot}$ peak is high for unsaturated or cyclic systems present in the molecule. As in carbocation chemistry the carbocations formed are stabilised.

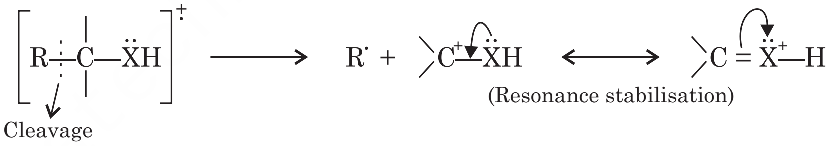
- Alkylbenzenes cleave at the C–C bond β to the aromatic ring resulting in a highly stabilised carbocation. Most alkylbenzenes give the more stable tropolium ion (I) rather than the Benzyl cation (II).



- Cyclic alkenes often undergo generally a **retro-Diels-Alder fission**.



- Compounds such as alcohols, mercaptans, amines, esters cleave at C—C— bond β to the hetero atom.



SHORT QUESTIONS AND ANSWERS

Q. 1. What is atomic spectroscopy?

Ans. Ground state of an atom means it is with normal electronic configuration. In this state the atom remains in its lowest energy state and this is the most stable state of the atom. **Excited state of an atom** refers to the electronic configuration availed by an atom after absorbing certain definite amount of energy. The valence electrons are promoted to some higher permitted energy level by absorption of energy. In the excited state, the atom is unstable and the excited electron tends to come back to the original position *i.e.,* ground state. After about 10^{-4} sec. the electron returns to the ground state by emitting the amount of energy absorbed during excitation. The energy is emitted or absorbed in the form of electromagnetic waves of definite frequency *i.e.*, of definite wavelengths. This process of excitation and return to the ground state is the basis of spectroscopic analysis of atomic absorption, emission and atomic fluorescence.

Q. 2. What is atomic absorption spectroscopy?

Ans. This is the analytical technique based on the phenomenon of light absorption (UV or visible). It is applicable both to qualitative and quantitative analyses.

Q. 3. What are the parameters for expressing the absorption?

Ans. Transmittance is the ratio of the intensity of light transmitted to the intensity of incident light.

$$\text{(Transmittance)} \quad T = \frac{I}{I_o} \qquad \text{T\% (percent transmittance)} = \frac{100 \times I}{I_o}$$

$$A = \log_{10} \frac{I_o}{I} \quad \therefore \quad A = 2 - \log T\%$$

where A = Absorbance, I_o = Intensity of incident light,

I = Intensity of transmitted light.

- Combination of Lambert–Beer's law given

$$A = A_{1\,\text{cm}}^{1\%}\, bc.$$

A = Absorbance, $A_{1\,\text{cm}}^{1\%}$ = Absorbance of 1% (w/v) solution for path length of 1 cm,

b = thickness (cm), c = concentration (g/100 ml)

$$\varepsilon \text{ (molar extinction coefficient)} = \frac{A_{1\,\text{cm}}^{1\%} \times \text{molecular wt.}}{10}.$$

Q. 4. Calculate the concentration of a substance A in an ethanolic solution of which the absorbance in a 1 cm cell at its λ_{max} 241 nm was found to be 0.890. The A (1%, 1 cm) is 540 at 241 nm.

Ans.

$$A = A_{1\,\text{cm}}^{1\%}\, bc.$$

$$0.890 = 540 \times 1 \times c$$

$$\therefore \quad C = 0.00165 \text{ g/100 ml.}$$

Q. 5. Calculate the concentration in μg ml^{-1} of a solution of substance B (mol.wt. 204.2) in 0.1 (M) HCl, showing absorbance at its λ_{max} 277 nm of 0.613 in a 4 cm cell. The molar absorptivity (ε) at 277 nm is 5432.

Ans. Here the working formula is $A = \varepsilon bc$.

$$0.613 = 5432 \times 4 \times c$$

$$\therefore \quad c = 2.82 \times 10^{-5} \text{ mol l}^{-1}$$

$$= 2.82 \times 10^{-5} \times 204.2 \text{ gl}^{-1}$$

$$= 0.00576 \text{ gl}^{-1}$$

$$= 5.76 \text{ μg ml}^{-1}.$$

Q. 6. What is molecular spectroscopy?

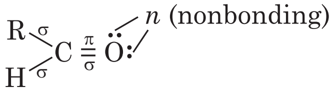
Ans. The internal energy (E) of a molecule is given by:

E = Kinetic energy + Potential energy + E_{rot} + $E_{vib.}$ + E_{trans}.

The molecular spectroscopy mainly deals with the study of interaction between radiant energy and the molecule. In general molecular spectroscopy is absorption spectroscopy.

Q. 7. What are the different electronic transitions that take place on absorption of UV light?

Ans. When a molecule, specially organic molecule, absorbs UV radiations the electrons are excited to higher energy levels. In the diagram below the electrons are represented



The following electron transitions take place:

$\sigma \rightarrow \sigma^*$ (antibonding), $n \rightarrow \sigma^*$, $n - \pi^*$ (antibonding)

$$\pi \rightarrow \pi^*$$

These electronic transitions are responsible for UV absorption of a molecule.

Q. 8. Mention the applications of UV.

Ans. (*a*) **Qualitative:**

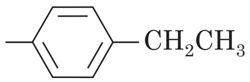
- Detection of conjugation
- Detection of functional groups
- Detection of geometrical isomers.

(*b*) **Quantitative:**

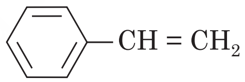
- Analysis of various samples (drugs, dyes etc.)

Q. 9. Can UV differentiate ethylbenzene from styrene?

Ans.



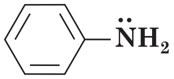
Ethylbenzene

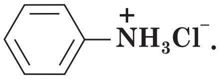


Styrene

Extended conjugation is maximum in case of styrene. So styrene will absorb at a higher wavelength.

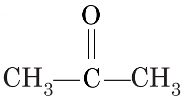
Q. 10. Which of the following compounds will have greater λ_{max}?

(*i*)


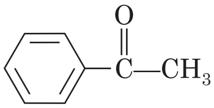
(*ii*)


Ans. Compound (*i*) shows greater λ_{max} value as the lone pair on N atom comes into resonance with the benzene ring to extend the conjugation. In (*ii*) there is no such electron pair.

Q. 11. Which of the following compounds will have greater λ_{max}?

Ans. (*i*)


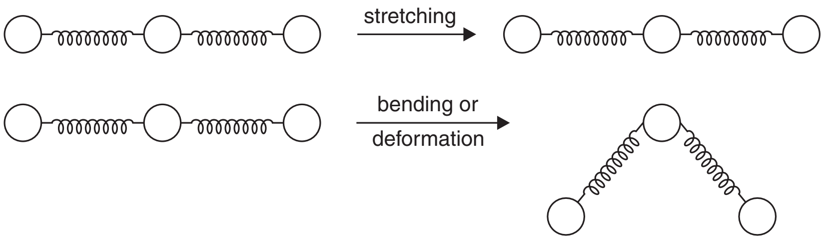
$CH_3—\overset{\overset{O}{\|}}{C}—CH_3$

(*ii*)


Compound (*ii*) will show greater λ_{max} as there is conjugation in benzene ring as well as C = O group remains in conjugation with the benzene ring.

Q. 12. What are the principles of IR?

Ans. The atoms in a molecule bond are in a state of constant vibration and rotation. They may be compared with two balls (atoms) joined by spring (bond). On absorption of IR the bond may stretch, bend etc., as shown below. So stretching and bonding of bonds are responsible for IR absorption.



Q. 13. What is the range of infrared radiations? Correlate the different units used in I.R. spectroscopy.

Ans. I.R. region lies between 0.8 to 20 μm or 800–20,000 nm of electromagnetic radiation. The region between 0.8 to 2.5 μm is called the near I.R. region and 15 to 20 μm is called far I.R. region. The region between 2.5 – 1.5 μm is the proper I.R. region.

Generally wave number ν (Nu) which is the number of vibrations of the radiation per cm.

The correlation between the different units used in I.R. is given below:

$$1\ \mu m = 10^{-6}\ m = 10^{-4}\ cm$$

So,
$$\nu = \frac{1}{\lambda\ \mu m} = \frac{10^4}{\lambda}\ cm^{-1}$$

Q. 14. What are functional group and fingerprint region in I.R.?

Ans. The **functional group region** is 2.5 to 7.4 μm (4000–1430 cm^{-1}). In this region functional groups of organic compound is detected. The **fingerprint region** is 7–11 μm (1430 – 910 cm^{-1}) gives a good deal of information about the molecule besides the functional groups of the compound. The fingerprint region can lead us to identify an organic compound.

Q. 15. How is an I.R. spectrum recorded?

Ans. (*a*) **IR source:** A Nernst glower, a rod of an allow of Zirconium, Yttrium and Erbium oxides. The rod is electrically heated to 1750 K.

(*b*) Rock salt disc or KBr disc is used as glass and quartz absorb I.R.

(*c*) **Sample preparation:** Either the sample with KBr is made to pellet or Nujol mull is used. Nujol is hydrocarbon in nature.

(*d*) **Recording of spectra:** The sample is placed in Rock salt cell in the path of I.R. The change of intensity of light transmitted draws a graph which is IR spectrum.

Q. 16. How will you distinguish CH_3COOH from CH_3COCH_3 with the help of I.R. spectra?

Ans. $>C = O$ (str.) peaks will be observed in both the spectra in the region of 1700 cm^{-1}. But an absorption bond at 2500–3000 cm^{-1} (broad) will be observed in spectrum of CH_3COOH due to dimeric association of CH_3COOH molecules through hydrogen bonding.

Q. 17. Give the structure of molecular formula C_3H_8O from the following data: I.R. (Nujol) ν_{max} – 2950 and 2820 cm^{-1}, 1110 cm^{-1}.

Ans. Three isomers for the molecular formula are:

(*i*) $CH_3CH_2\ CH_2OH$, (*ii*) $CH_3CHOH\ CH_3$ and (*iii*) $CH_3O\ CH_2CH_3$

As there is no peak near 3300 cm^{-1} the first two are ruled out. The peak at 1110 cm^{-1} is C—O (str.) for ether linkage and 2950 and 2820 cm^{-1} for C—H (str). So the compound is $CH_3OCH_2CH_3$.

Q. 18. What is nuclear magnetic resonance (n.m.r.)?

Ans. Protons and neutrons in the nucleus spin. If the particles in a nucleus don't have their spins paired, there is a net spin. Charged particles like proton when spin will generate magnetic field and magnetic moment along the axis of spin. Thus a proton or nucleus acts like a tiny bar magnet. Nuclei with even mass numbers $_8C^{12}$, $_8O^{16}$ have no resultant spin and hence the magnetic property. The magnetic property of the nucleus is responsible for nuclear magnetic resonance. The precissional frequency of the spinning nucleus when equals the frequency of the applied magnetic field (electromagnetic radiation), the nucleus changes its spin state from one to the other and the absorption or emission of energy then takes place by the nucleus and nuclear resonance then occurs. The absorption of energy is recorded in a graph and is known as n.m.r.

Q. 19. What are equivalent and non-equivalent protons in n.m.r.?

Ans. Protons present in a molecule having the same environment absorb at the same magnetic field strength. Such protons are called equivalent protons.

And protons which have different environments in a molecule absorb at different magnetic fields, such protons are called non-equivalent protons. All equivalent protons give one signal in the n.m.r. spectrum. Non-equivalent protons give different signals.

Q. 20. Give a schematic diagram of pmr spectrum.

Ans. See text.

Q. 21. Identify equivalent and non-equivalent protons in the following molecules and hence the number of signals and splitting.

(*i*) $\mathbf{CH_3—CBr_2—CH_3}$ **and** (*ii*) $\mathbf{CH_3CH_2Cl}$

Ans. (*i*) $C\overset{a}{H}_3\,CBr_2C\overset{a}{H}_3$

All are equivalent protons. So n.m.r. spectrum will show one signal *i.e.*, a 6H, *s* (six proton, singlet)

(*ii*) $\underset{2}{C}\overset{a}{H}_3\underset{1}{C}\overset{b}{H}_2Cl$

2 protons in C—1 are equivalent and 3 protons in the C—2 are equivalent; but the protons of C—1 and C—2 are non-equivalent as designated by '*a*' and '*b*'. So two signals are obtained in the n.m.r. spectrum. The upfield signal is a triplet (3H, *t*). The downfield signal is quartet (2H, quartet). 'CH_2' protons give downfield signal as the C—2 is attached to electronegative 'Cl' atom (See text).

Q. 22. What are shielding and deshielding of protons?

Ans. In the NMR spectrum of a compound, the electrons around the protons also play their role. When a compound is placed in a magnetic field, the electrons around the protons generate also a magnetic field known as induced magnetic field. This induced magnetic field may reinforce or oppose the applied field. So two cases may arise:

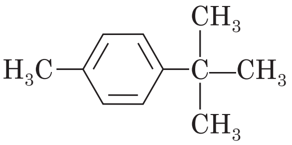
(*i*) If the induced field opposes the applied field and thus the effective magnetic field 'H' experienced by the nucleus is smaller than the applied magnetic field (H_o). H is related to H_o as $H = H_o (1 - \sigma)$ where, $\sigma \Rightarrow$ a nondimensional quantity known as shielding or screening constant and has a positive value.

The proton is said to be shielded by the electrons. A greater applied field is required for the excitation of protons.

(*ii*) If the induced field reinforces the applied field (here σ is negative), an enhanced field strength will be experienced by the proton and proton is said to be deshielded in this case.

Shielding causes a shift of the resonance frequency to higher values of the applied field (H_o) *i.e.,* the shift is upfield. On the other hand **deshielding** causes a shift of the resonance frequency to lower values of the applied field *i.e.,* the shift is downfield. The magnitude of this shift is called **chemical shift**.

Q. 23. Match the number of signals of the compounds given:

Compounds	*Signals*
(*i*) 	1
(*ii*) C_2H_5OH	3
(*iii*) $CH_3—O—CH_3$	3
(*iv*) $CH_3—O—CH_2CH_3$	3

Ans. Compound (*i*) will produce three signals because there are three types of protons *i.e.*, $—CH_3$ protons on the left side of the ring, methyl protons on the right side of the ring and ring protons. Since there is no non-equivalent protons in the molecule, all the peaks will be singlet and no splitting will take place.

Compound (*ii*) will produce three signals as there are three types of protons. It will be a triplet for $—CH_3$ protons, a quarlet for $—CH_2$ protons and a singlet for —OH proton.

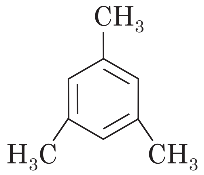
For compound (*iii*) only one signal will be obtained in case of 3rd compound as there are only one type of protons and hence it will be a singlet.

Compound (*iv*) will produce three signals. There are three types of protons. Hence a singlet for OCH_3 protons, a quartet for $—CH_2$ protons and a triplet for $—CH_3$ protons.

Q. 24. Translate the following set of NMR spectral data to a compound. Molecular formula C_9H_{12}, singlet τ 3.22, 3H; singlet τ 7.75, 9H.

Ans. (*i*) The formula C_9H_{12} corresponds to the general formula of aromatic hydrocarbon C_nH_{2n-6}. Thus the compound will contain a benzene ring with some other substitutions.

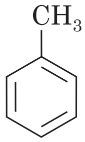
(*ii*) The compound gives two signals and thus it indicates the presence of two types of protons. These conditions are satisfied only by the structure:



1, 3, 5-trimethyl benzene

This structure explains the existence of singlet τ 3.22 due to three ring protons and singlet τ 7.75 due to nine $—CH_3$ protons.

Q. 25. Count the number of signals for the following compounds:

(1) , (2) $CHCl_2—CH_3$

Ans. (*i*) The first compound contains two types of protons, the ring protons and $—CH_3$ protons, hence two signals will be observed.

(*ii*) The second compound contains two kinds of protons as indicated by *a* and *b* (below).

$$\overset{a}{\mathrm{C}}\mathrm{H}\,\mathrm{Cl}_2—\mathrm{C}\overset{b}{\mathrm{H}}_3$$

So, two signals will be observed.

Q. 26. State the significance of peak area.

Ans. Peaks obtained in the NMR spectrum make different areas with the base line. It has been observed that area under an NMR signal is directly proportional to the number of equivalent protons that give rise to that signal. By comparing the area subtended by different signals, we can calculate the relative proportion of different types of protons. As for example, in the case of peaks obtained for benzyl alcohol, the ratios of the areas under the peaks are 1:2:5, indicating that the three types of protons are in the ratio 1:2:5. There are one —OH proton, two methylene protons and five ring protons.

Q. 27. Mention the various uses of n.m.r. spectrum.

Ans. NMR spectroscopic technique is applied in different cases.

(*i*) **For identification of functional groups.** Every functional group gives a characteristic signal in the NMR spectrum. By studying the chemical shift of compound, it becomes possible to establish what kind of functional group is present in the molecule.

(*ii*) **For structure determination of an unknown compound.** It is possible to elucidate the structure of an unknown compound from the n.m.r. studies. This is due to the protons which under different environments give different chemical shifts. By observing doublets, triplets or multiplets, it is possible to place hydrogens at appropriate place in the formula and hence a structure can be established.

(*iii*) **For comparison of two compounds.** NMR spectrum is like fingerprint of a compound. Two compounds which show same n.m.r. spectrum must be identical in structures.

Q. 28. Discuss the applications of mass spectroscopy.

Ans.

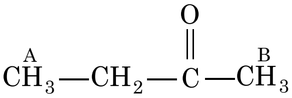
- Determination of molecular mass of a compound (known and unknown).
- Determination of molecular structure analysing the fragmentation pattern and taking the help of UV, I.R., nmr spectra.
- The combination of gas liquid chromatography (glc) with mass spectrometry (ms) is of great importance in modern chemical analysis. First glc separates the chemicals in an unknown mixture, as for example, polluted water, when the ms detects and identifies components.

Q. 29. Translate the following set of spectra to three isomeric organic compounds.

Description–Colourless liquid (b.p. – 80°C); molecular formula – C_4H_8O; I.R. $\nu_{\max}^{\text{film}}$ (cm^{-1}) – 1715 (*s*), NMR (neat liquid) – δ 1.06 (3H, *t*), δ 2.14 (3H, *s*), δ 2.43 (2H, *q*).

Ans. The IR band at 1715 cm^{-1} indicates that the compound possesses a $\rangle\mathrm{C} = \mathrm{O}$ group. This evidence, taken with the molecular formula C_4H_8O, suggests that the compound is either an aliphatic aldehyde or a ketone.

The NMR spectrum readily excludes are aldehyde as there is no resonance at about δ 9.5 and confirms the structure as butan-2-one (methyl ethyl ketone).



$$\overset{A}{C}H_3—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{B}{C}H_3$$

Methyl group (A) and the methylene group appear respectively as the expected triplet and quartet. Methyl group (B) and methylene group are both deshielded (moved to downfield) by the adjacent $>C=O$ group. The principal ions in the mass spectrum of butan-2-one are $CH_3—C \equiv O^+$ (m/z 43) and $CH_3CH_2—C \equiv O^+$ (m/z 57), and molecular weight $M^{\ddagger}$ – 72.

EXERCISES

1. (*a*) Mention the wavelengths for visible, UV and I.R. radiations.
(*b*) Name the different spectroscopic techniques which are employed for the elucidation of structures of organic compounds.

2. What do you mean by:
(*a*) absorption spectrum (*b*) emission spectrum?

3. State Beer-Lambert's law and deduce mathematical expression for the same.

4. What are the different electronic transitions that take place on the absorption of UV light?

5. Explain the terms:
(*i*) chromophore (*ii*) auxochrome (*iii*) blue shift (*iv*) red shift.

6. Mention the applications of UV spectroscopy.

7. Calculate the molar absorptivity of the solution of concentrated 1×10^{-4} mol l^{-1}, given A = 0.20 and path length = 2.5 cm. (**Ans.** 8000 $dm^3\ mol^{-1}\ cm^{-1}$)

8. Mention the principles of I.R. spectrum.

9. Indicate whether you will use I.R. or U.V. spectroscopy for distinguishing the following pairs of compounds:
(*a*) $CH_2 = CH—CH_2—O—CH_3$ and $CH_3\,CH_2\,COCH_3$
(*b*) $CH_3—O—CH_3$ and $CH_3\,CH_2\,OH$
(*c*) $CH_2 = CHCH_2OH$ and $CH_3\,CH_2\,CHO$

10. What is nuclear magnetic resonance?

11. What are equivalent and non-equivalent protons?

12. What is meant by shielding and deshielding of a proton?

13. What is chemical shift?

14. Why do we select tetramethyl silane (TMS) as a standard substance in n.m.r.?

15. What do you mean by splitting of signals?

16. What is mass spectroscopy? What is the principle of m.s.?

17. Give applications of:
(*i*) UV (*ii*) I.R. (*iii*) n.m.r. (*iv*) m.s.

25

Photochemistry

In almost all chemical reactions the molecules that take part are generally in their ground electronic states. In photochemical reactions, the reactant molecules are previously promoted by absorption of light to their electronically excited state. Light of any wave-length is associated with an energy value denoted by $E = h\nu$, where h is Planck's constant and ν is the frequency of light. Light of particular frequency corresponding to particular energy can cause the electron of a molecule to move to higher energy level. Hence an amount of light energy will be absorbed and the rest of the energy will be transmitted. Spectrophotometer is an instrument which compares the intensity of transmitted light and incident light and gives the amount of energy absorbed by the solution of a compound. The energy of electronic transitions corresponds to light in visible, UV and far UV region. Generally the colored compounds absorb in the visible range, and possess a color complementary to that of which is absorbed.

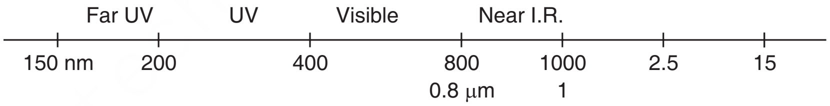


Fig. 25.1 UV, visible and I.R. portions of spectrum.

Under normal conditions, the molecules are constantly vibrating and rotating and these motions can be quantized. Thus the molecules are not only in a given electronic state but also in a vibrational and rotational state. Compared to the difference between the two electronic levels the difference between the two adjacent vibrational or rotational levels is much smaller. A sample may contain large number of molecules all in their ground electronic states, but they may be distributed among vibrational and rotational states. Thus when a particular wave-length of light is absorbed there will be many possible transitions which may give rise to a broad band, rather than giving a sharp peak. The height of the peak of absorption depends on the number of molecules making transition and is proportional to log ε where ε is the extinction coefficient.

ε may be expressed as $\varepsilon = E/cl$.

where c = concentration of molecules in moles per litre,

l = cell length in cm, and

$E = \log I_o/I$ where I_o and I are the intensities of incident and transmitted light respectively. The wavelength where the absorption is maximum is denoted by λ_{max}. UV or visible absorption peak is due to the transition of an electron from the ground state to a higher energy orbital. The functional group which causes such absorption is called a **chromophore**. Purely vibrational transitions require much less energy and are found in I.R. region whereas rotational transitions are found in far I.R. regions.

Singlet and Triplet States

In organic molecules the electrons in the ground state are paired and have opposite spin. By absorbing energy when electrons are promoted to an orbital of higher energy the electrons no longer shares an orbital and these two unpaired electrons may either have same spin which is called a '*triplet*' or the spins may be paired which is called '*singlet*'. The energy for the triplet state is lower than the corresponding singlet according to Hund's Rule. Thus a different amount of energy *i.e.,* different wavelength is required to promote an electron from ground to the excited singlet or triplet state. Any type of transitions are not permitted rather transitions between energy levels are governed by selection rules and several types of transitions are "forbidden". Two of the types of forbidden transitions are important:

(*a*) *Spin forbidden transitions*—transitions in which spin of an electron change is forbidden, *i.e.,* transitions between ideal singlet and triplet states are strictly forbidden.

(*b*) *Symmetry-forbidden transitions*—*n*–π* transition in formaldehyde is forbidden since overlaps of orbitals are forbidden.

Notation for Excited States of Organic Molecules

The excited states of molecules are different from the original ground states. Hence nomenclature of these excited states separately is important.

One common system for that is to denote the multiplicities, S for singlet and T for triplet. The ground state is denoted by so and higher excited states as S_1, S_2, S_3, T_1, T_2, T_3 etc.

M. Kasha has developed another system of expressing the electronic states in terms of initial and final orbitals involved in transition. There are four types of molecules:

(*i*) Saturated molecules with σ Molecular orbitals (MO), *e.g.* paraffinic hydrocarbons.

(*ii*) Saturated molecules with σ and non of bonding MO, *e.g.* CH_3I, H_2O.

(*iii*) Unsaturated molecules with σ and π MOs, *e.g.*, C_2H_5, aromatic hydrocarbons, CO_2 etc.

(*iv*) Unsaturated molecules with σ, π, and *n* MOs, *e.g.,* aldehydes, ketones, pyridine, other heterocyclics etc. σ MOs are formed by overlapping of *s* and p_z orbitals like sp, sp^2, sp^3 etc.

π MOs are formed by overlapping of p_x and p_y or hybridized orbitals to form double or triple bonds.

n MOs are pure nonbonding orbitals containing nonbonding electrons. Hence the types of electronic orbitals are σ, π, *n*, π* and σ*. Photochemists designate by an arrow from lower to higher energy state transitions as $n \to \pi^*$, $\pi \to \pi^*$, $n \to \sigma^*$, $a \to \sigma^*$ etc.

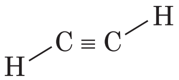
The $n \to \pi^*$ transitions have low probability and hence give weak absorption bands whereas $\pi \to \pi^*$ transitions are most important and give intense characteristic absorption (for conjungated hydrocarbons).

Properties of the Excited States

A molecule in the electronically excited state may be a completely different species from the original one. Since the charge densities are different it shows different chemistry from that of the ground state molecule, also because it has excess energy but weaker bonds. Other physical properties like dipole moment, pK values, redox potentials also differ.

A transition of electrons from the bonding to the antibonding orbital causes a triple bond to become double, a double bond to become single and a single bond to disrupt. It also leads to increase in bond distances by about 15% and also large changes in bond angles.

Formaldehyde molecule has a planar geometry in the ground state. On excitation an electron on O-atom is transferred to antibonding π MO and hence the molecule can twist along the >C—O bond. Similarly for conjugated systems like ethylene or butadiene, free rotation in the excited state leads to *cis-trans* isomerization. For *e.g.* acetylene, which is linear in ground state has a *trans* geometry with sp^2 carbons in (π, π*) state.



CO_2, CS_2, HCN are linear in their ground state but bent in excited states, whereas radicals like NH_2, HCO and NO_2 molecules are bent in their ground state but linear in excited states.

Excited phenol is more acidic and also ortho-para directing towards substitution in benzene ring. The protolytic equilibrium constant pK_a for the reaction is 10 and 5.7 in the ground and excited states. In contrast to this, aromatic carboxylic acids exhibit a decrease in acidity in excited state relative to ground state. In general, phenols, thiols and aromatic amines become stronger acids on excitation whereas carboxylic acids, aldehydes, ketones and heterocyclics become stronger bases.

The dyes like methylene blue and thionine show striking difference in redox potentials between ground and excited states.

In the excited state, the dipole moment not only has different magnitude, but different direction also. Photochemical behaviour of a molecule varies with the change in solvent for the above reason.

Highlights:

Laws of Photochemistry:

- *Grotthurs-Drapper Law (First law):*
  "Only that light which is absorbed by a system can cause chemical change".
- *Stark-Einstein Law (2nd law):*
  "One quantum of light is absorbed per molecule of absorbing and reacting substance that disappears".
- *Wigner's spin conservation rule:*
  In any allowed electronic energy transfer process, the overall spin angular momentum of the system should not change.

Photolysis

The direct dissociation of a molecule on absorption of a quantum of radiational energy becomes probable when the energy absorbed is equal to or more than the bond dissociation energy and this dissociation from an excited state is called **photolysis**. Three situations can lead to cleavage of a molecule.

(1) The promotion may bring the molecule to a very high vibrational level which lies above the right hand portion of the curve E_2 in Fig. 25.2 and hence the molecule cleaves at its first vibration.

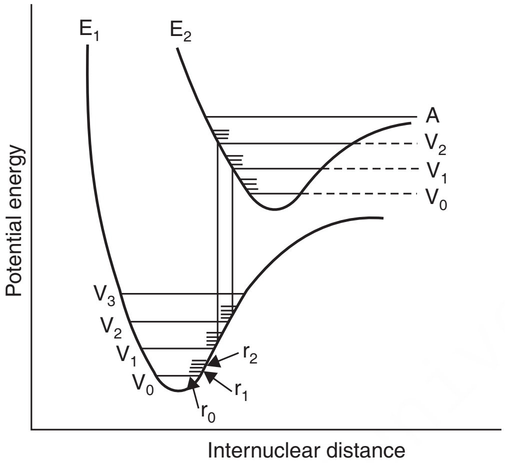


Fig. 25.2 Energy curves for a diatomic molecule. Two possible transitions are shown. When an electron has been excited to the point marked A, the molecule may cleave.

(2) When the promotion is to a lower vibrational level v_1 or v_2 which lies within the curve E_2, the molecule may cleave. From the curve in Fig. 25.2, we find that the equilibrium distance is greater for excited state than in ground state.

Franck-Condon principle states that promotion of an electron (10^{-15} sec) is much faster than the single vibration (10^{-12} sec). Hence when an electron is suddenly promoted the distance between the atoms remains unchanged and hence the bond behaves like a compressed-spring, the condition is suddenly relieved by breaking the bond.

(3) In some cases as in Fig. 25.3, the excited state entirely leads to dissociation. *E.g.,* is the $\sigma - \sigma^*$ promotion in hydrogen molecule leading to cleavage. The photolytic cleavage may break the molecule into two smaller molecules or into free radicals. Free radicals behave in a similar way like free radicals produced in other processes, except that the former are in excited state. Rarely the molecule breaks into two ions.

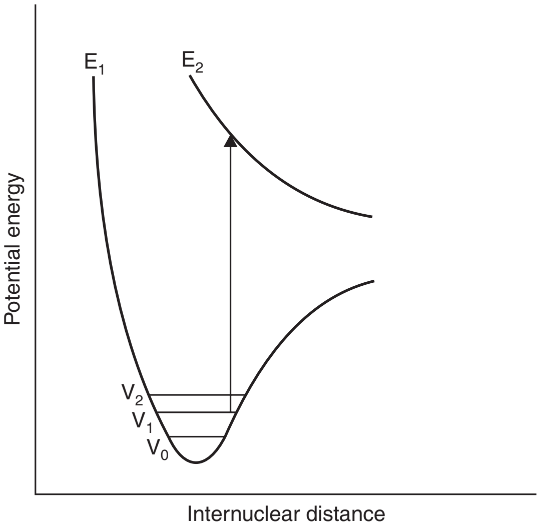


Fig. 25.3 Promotion to a dissociative state results in bond cleavage.

Types of Photophysical Pathways

A molecule excited to a higher energy state must return to the ground state. Promotions are from S_0 to S_1 states, as promotion from S to triplet states is 'forbidden'. Promotion to other higher singlet states like S_2 takes place, but in liquids and solids these higher energy states are short lived (10^{-13} to 10^{-11} sec.) and usually drop back to S_1 state. The energy lost by these drops from S_2, S_3 to S_1 states is given up to the environment by collision with other neighbouring molcules and the process is called **energy cascade**. The decay from the higher energy states initially populates many vibrational levels of S_1, but finally comes down to the lowest vibrational levels of S_1, which is therefore the only important excited singlet state. This state can undergo different physical and chemical processes. The pathways are shown and listed in modified Jablonski diagram (Fig. 25.4) and in Table 25.1.

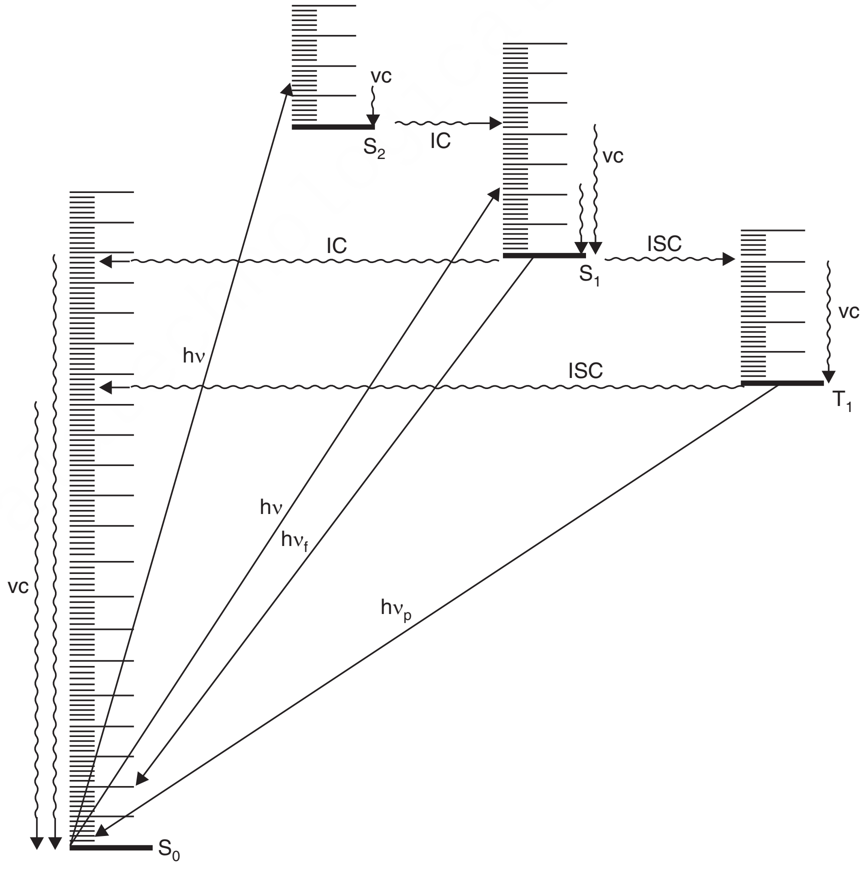


Fig. 25.4 Modified Jablonski diagram.

Table 25.1 Physical processes undergone by excited molecules

The superscript v indicates vibrationally excited state: excited states higher than S_1 or T_1 are omitted.

$S_0 + h\nu \rightarrow S_1{}^{v}$	Excitation
$S_1{}^{v} \rightsquigarrow S_1 + \text{heat}$	Vibrational relaxation
$S_1 \rightarrow S_0 + h\nu$	Fluorescence
$S_1 \rightsquigarrow S_0 + \text{heat}$	Internal conversion
$S_1 \rightsquigarrow T_1{}^{v}$	Intersystem crossing
$T_1{}^{v} \rightsquigarrow T_1 + \text{heat}$	Vibrational relaxation
$T_1 \rightarrow S_0 + h^{v}$	Phosphorescence
$T_1 \rightsquigarrow S_0 + \text{heat}$	Intersystem crossing
$S_1 + A_{(S_0)} \rightarrow S_0 + A_{(S_1)}$	Singlet-singlet transfer (photosensitization)
$T_1 + A_{(S_0)} \rightarrow S_0 + A_{(T_1)}$	Triplet–triplet transfer (photosensitization)

(1) Energy absorption may promote molecule to a higher energy state like S_2, S_3, etc. or to higher vibrational levels of S_1 within 10^{-5} sec. obeying Franck-Condon principle. The electronic energy of the higher states or excess vibrational energy of S_1 state is quickly lost to the surroundings by a mechanism called internal conversion (IC).

(2) The molecule in the S_1 state can drop to some low vibrational level of S_0 at once giving off the energy in the form of light within 10^{-9} sec. called **fluorescence**. This process is slow and not very common except for aromatics and diatomic molecules.

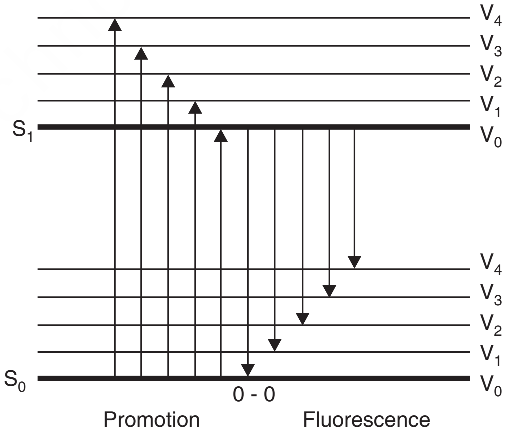


Fig. 25.5 Promotion and fluorescence between S_1 and S_0 states.

(3) **Intersystem crossing (ISC)**, involves non-radiative transition from singlet to triplet states ($S_1 \rightarrow T_1$) which is a 'forbidden' pathway. Since a singlet state usually has a higher energy than the corresponding triplet and hence energy must be given up. The molecule thus might cross from S_1 to T_1 states at a high vibrational level and then cascade down to its lowest vibrational level of T_1. This cascade is very rapid (10^{-12} sec).

(4) Molecule from the T_1 state may return to S state by giving up heat (reverse intersystem crossing) or light (radiative phosphorescence emission). But due to spin restriction (forbidden) both the processes are slow (10^{-3} to 10^{1} sec). Thus T_1 state has much longer lifetime.

(5) The last option is that a molecule in an excited state (S_1, T_1) may transfer its total energy to another molecule of the environment. The process is called **photo-sensitization**, the donor molecule D is called **photosensitizer**, and the acceptor reaches its excited state.

$$D^* + A \rightarrow A^* + D$$

This energy transfer takes place according to *Wigner-spin conservation rule*, which states that the total electron spin does not change after the energy transfer.

According to Wigner-rule two important types of photosensitization are:

$$D_{T_1} + A_{S_0} \longrightarrow A_{T_1} + D_{S_0} \qquad \text{(Triplet-triplet transfer)}$$

$$D_{S_1} + A_{S_0} \longrightarrow A_{S_1} + D_{S_0} \qquad \text{(Singlet-singlet transfer)}$$

Singlet-singlet transfer can take place over long distances (40 Å) whereas triplet-triplet transfer requires collision between the molecules. Since triplet states are usually difficult to prepare by direct irradiation hence triplet-triplet transfer is an important process of transferring energy by photosensitization.

For a reaction photosensitizer should be chosen such that it does not absorb light in the same region as the acceptor since two might then compete.

Highlights:

(*i*) Differences in charge distribution in various energy states of a molecule create differences in the chemical and physical properties of excited and ground state molecules.

(*ii*) Electronic transitions between energy states are governed by Franck-Condon principle.

(*iii*) Geometry of the molecules may change on excitation which has an important effect on the photochemistry of the molecule.

(*iv*) A transition may be forbidden due to

- Conservation of spin moments
- Symmetry restrictions.

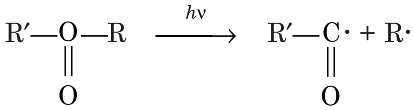
(*v*) After absorbing a photon, an atom or a molecule, if does not participate in photochemical reaction, can return to ground state by any of the many photophysical pathways, some of which are radiative and some are nonradiative.

Photochemical Processes for Excited Molecules

Excited singlet species have very short lifetime (>10^{-10} sec) and hence generally undergo one of the many physical processes already discussed. The triplet states have much longer lifetime and hence they react chemically. Thus photochemistry is the chemistry of **triplet states.**

There are several types of chemical reactions which can occur with excited molecules. The primary reactions are being discussed which may be followed by secondary reactions since the products of the primary reactions are frequently radicals or carbenes.

(1) **Simple cleavage into radicals.** Aldehydes and ketones absorb in 230 to 330 nm region, whereby n–π^* singlet-singlet transition occurs and the carbonyl compounds cleave. In case of ketones, this reaction is called **Norrish type I reaction** which involves α-cleavage giving rise to an acyl and an alkyl radical. The acyl radical is essentially decarbonylated at high temperature.

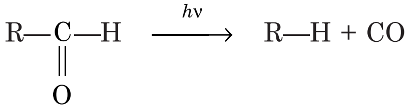


$$R'\text{—}\underset{\underset{O}{\|}}{O}\text{—}R \xrightarrow{h\nu} R'\text{—}\underset{\underset{O}{\|}}{C}\cdot + R\cdot$$

This dissociation is favoured if a relatively stable alkyl radical is formed and usually favoured in vapor phase rather than in solvent.

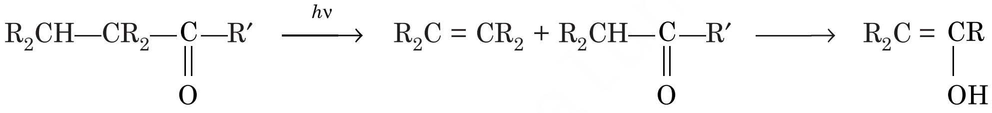
The other examples are cleavage of Cl_2 to Cl atoms, cleavage of O—O bonds in peroxy compounds, and C—N bonds in aliphatic azo compounds (since stable N_2 is the product).

(2) **Decomposition into molecules.** Aldehydes can also cleave to form CO and alkane.



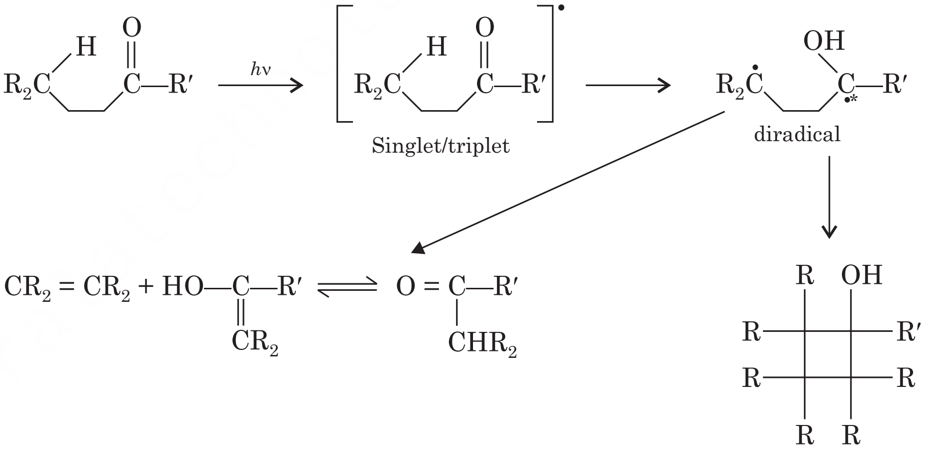
$$R-\underset{\underset{O}{\|}}{C}-H \xrightarrow{h\nu} R-H + CO$$

Carbonyl compounds possessing γ-hydrogen atoms proceed by a shift of γ–H to oxygen with subsequent cleavage to an olefine and an enol. This is **Norrish type II reaction.**

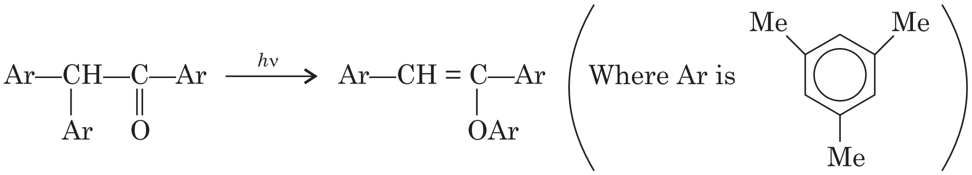


$$R_2CH-CR_2-\underset{\underset{O}{\|}}{C}-R' \xrightarrow{h\nu} R_2C=CR_2 + R_2CH-\underset{\underset{O}{\|}}{C}-R' \longrightarrow R_2C=\underset{\underset{OH}{|}}{C}R$$

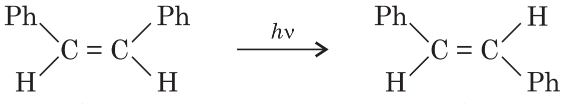
The reaction can occur from both the excited singlet and the triplet states. Sometimes the intermediate can also cyclize to a cyclobutanol as side product. Carboxylic esters, anhydrides can also give this type of reaction.



3. **Intramolecular rearrangement.** Trimesityl compound to enol ether



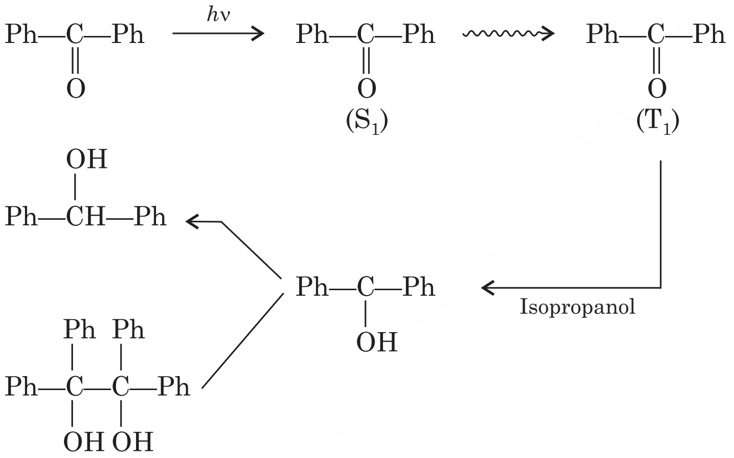
4. **Photoisomerization.** The common example is the *cis-trans* isomerization of stilbene.



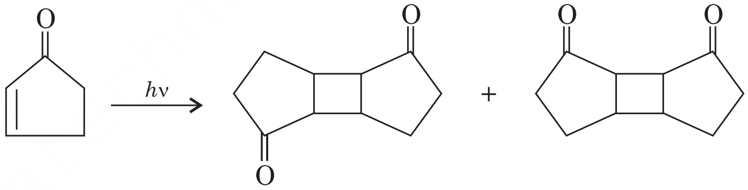
cis-isomer *trans*-isomer

In this case in the excited state, both in S_1 and T_1 of olefins the geometry is perpendicular rather than planar and so no *cis-trans* isomers for excited states. When the excited molecule returns to the ground state (S_o) either of the isomer can be formed.

5. **Hydrogen atom abstraction.** Benzophenone when irradiated goes to S_1 state and then to T_1 state whereby it abstracts one H atom from the solvent isopropyl alcohol and then subsequently another H to form benzhydrol or it may dimerize to form benzpinacol.



6. **Photodimerization**



Dimerization of cyclopentenone

Photosynthesis

Photosynthesis involves a series of complex reactions in the chloroplast of plants with the overall conversion of water and carbon dioxide to carbohydrates and dioxygen.

$$nCO_2 + nH_2O \xrightarrow[\text{680 nm}]{h\nu} (CH_2O)_n + nO_2$$

Chlorophyll

All the oxygen comes from H_2O. The reaction is initiated by visible solar radiation (600–700 nm) and it is endothermic. The photosystem consists of two parts—an antenna complex consisting of chlorophyll molecules which absorb the solar energy and the second part is photochemical reaction centre, which is a transmembrane protein-pigment-cofactors complex. The antenna *i.e.,* the light-harvesting pigment complex (LHC) absorbs light quanta and within picosecond transfers the energy to the reaction centre. The overall photosynthetic conversion involves light absorption at two different wavelengths—Photosystem I (PS-I) and Photosystem—II (PS-II)—light reactions. PS-I and PS II are identified as P700 and P 680 pigments respectively.

(a) Photosystem I (P 700). P700 is excited and it transfers an electron to bound ferredoxin (Fe-S protein). The bound ferredoxin in turn transfers the electron to soluble-ferredoxin, which again transfers it to NADP$^+$ forming NADPH (Fig. 25.6).

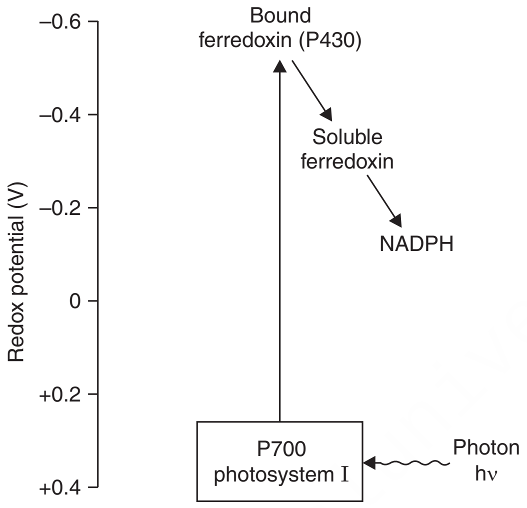


Fig. 25.6 Formation of NADPH by photosystem I.

Non-oxygen evolving photosynthetic bacterium contains PS-I only.

(b) Photosystem II. In oxygen-evolving systems PS-I and PS-II are serially linked to produce NADPH and ATP by a two-step process.

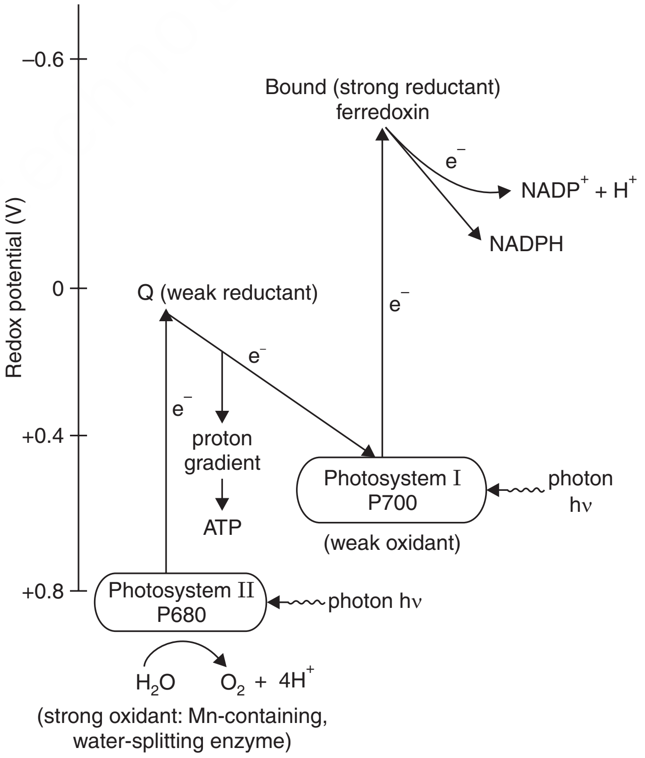
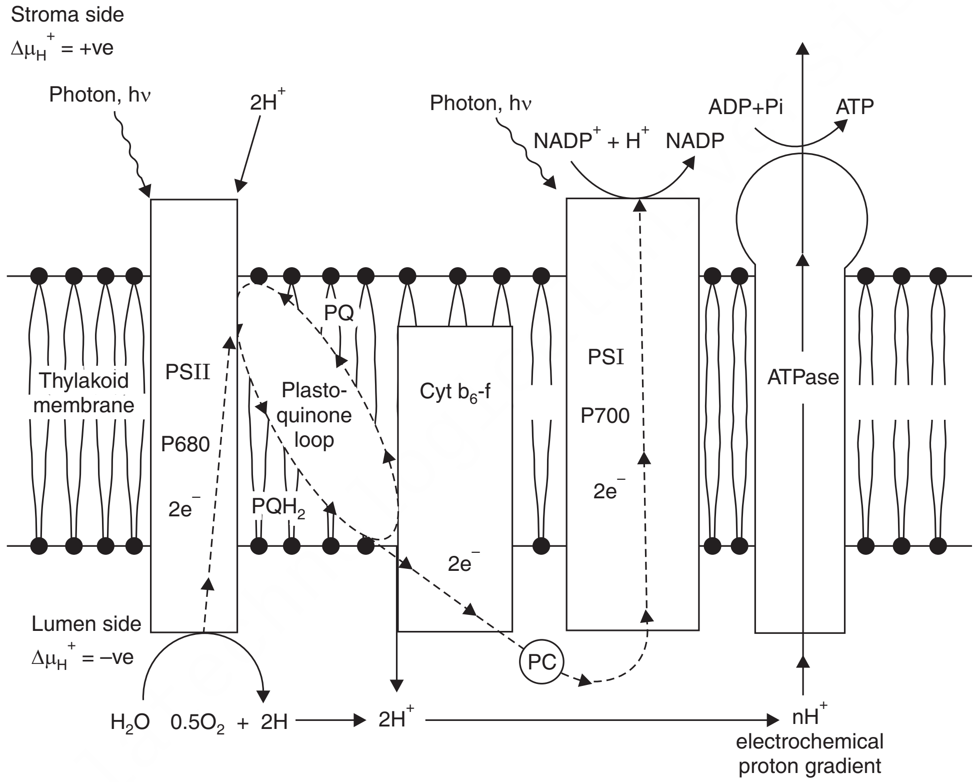


Fig. 25.7 Electron transport and oxidation of H_2O in noncyclic photo-phosphorylation (Z-scheme).

By absorbing light PS-II is raised to excited state and an electron is transferred to plasto quinone (or) which in turn transfers it to cytochrome *b* 559. The final electron-carrier from

PS-II to PS-I is a plastocyanin (Cu containing protein). PS-I accepts electrons from PS-II. By means of two-step electron-energising processes, catalysed by each photosystem, electrons are finally transferred from H_2O to the final acceptor bound-ferredoxin P430 (Fig. 25.7). Light energy causes electrons to flow from H_2O to NADPH.

The processes of photosynthetic system of P680 and P700 are summarized in Fig. 25.8.



PO = Plastoquinone; PC = Plastocyanin;
⟶ electron transport by electron carriers PQ and PC

Fig. 25.8 Schematic representation of energy transduction by reaction centres PS-II and PS-I in the noncyclic photosynthetic reaction process (According to Tanz and Zieger, "Plant Physiology" Benjamin/ Cummings, Redwood City, CA. (1991).

The electron transport process creating electro-chemical proton gradient across the thylakoid membrane drives the synthesis of ATP from ADP and P_i by ATP synthase.

$$2H_2O + 2NADP^+ + 3ADP^{3-} + 3HPO^{2-} \xrightarrow{4\,h\nu} 2H^+ + O_2 + 2NADPH + 3ATP^{4-}$$

Chloroplasts can also synthesize only ATP without producing NADPH involving cyclic photophosphorylation.

Dark reactions. The NADPH and ATP formed by the 'light reactions' are utilized for synthesizing carbohydrates from CO_2 in stroma for which sunlight is not required. These CO_2 fixing reactions are called **Hill reactions**, which can take place in dark.

Plants generate glyceraldehyde-3-phosphate (GAP) as the starting material for higher carbohydrates from three molecules of CO_2 by utilising 9 ATP and 6 NADPH. This metabolic pathway for carbohydrate synthesis is called **Calvin-Benson** cycle.

$$3CO_2 + 9ATP + 6NADPH + H_2O \longrightarrow GAP + 6NADP^+ + 8\,P_i + 9\,ADP.$$

Chemistry of vision

Photoreceptor cell in vertebrate eye consists of:

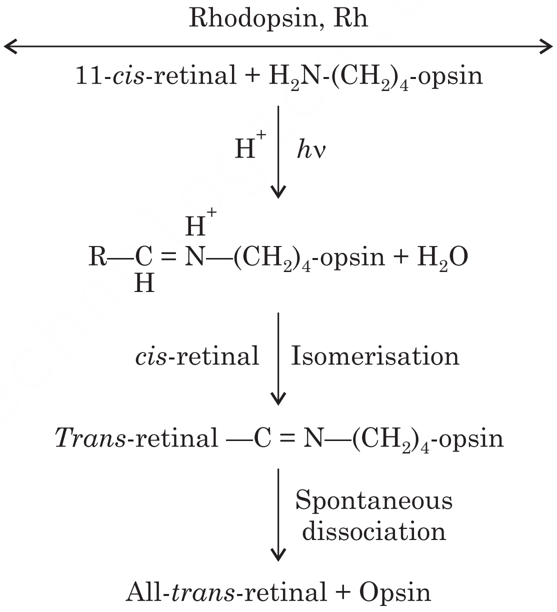
(*i*) Outer segment consisting of stack of membrane discs in rods and cones, which acts as antennae for receiving photons (containing lipoprotein complex, which is specialised for photon reception).

(*ii*) Inner segment of metabolic and nuclear sources.

(*iii*) Synaptic region for contacting with nerve cells of retina.

The outer segment of the rod cell contains a transmembrane chromoprotein called **rhodopsin** composed of a glycoprotein **opsin** and a chromophore **retinal**.

Absorption of light leads to the photo-isomerisation of *cis*-retinal to *trans* isomer, which dissociates spontaneously to all-*trans*-retinal and opsin. The scheme is:



$$\begin{tikzcd}[row sep=large]
\overset{\text{Rhodopsin, Rh}}{\longleftrightarrow} \\
\text{11-}cis\text{-retinal} + H_2N\text{-}(CH_2)_4\text{-opsin} \arrow[d, "h\nu", "H^+"'] \\
R\text{—}\underset{H}{C} = \overset{H^+}{N}\text{—}(CH_2)_4\text{-opsin} + H_2O \arrow[d, "\text{Isomerisation}", "cis\text{-retinal}"'] \\
Trans\text{-retinal —}C = N\text{—}(CH_2)_4\text{-opsin} \arrow[d, "\text{Spontaneous dissociation}"] \\
\text{All-}trans\text{-retinal} + \text{Opsin}
\end{tikzcd}$$

Signal transduction. A general scheme of photoreaction is:

(*i*) Absorption of a photon of light causing 11-*cis*-retinal to all-*trans*-retinal form and conformational change of opsin.

(*ii*) Cleavage of all-*trans*-retinal from opsin. Rhodopsin Rh is activated to Rh^*.

(*iii*) The photoreceptor potential in the rod cell maintained by closure of Na^+ ion channels. Photoabsorption alters the membrane potential and conductance of Na^+, resulting in transient opening of Na^+ channel and Na^+ ion influx.

(*iv*) Change in membrane permeability to Ca^{2+} causes closure of the channel and restoration to resting state.

Absorption of a single photon blocks the influx of million of Na^+ ions by closing hundreds of Na^+ channels in the membrane. This signal amplification is achieved by enzyme cascade involving cyclic GMP.

Perception of color is by (*a*) *additive* and (*b*) *subtractive processes*.

In additive process perception of color is by mixing of primary colors, red, blue and green. Combination of primary colors (two) gives secondary colors which again can be mixed to give the full range of colors.

In subtractive process, pigments absorb certain colors and reflect back other colors. In this process, the primary colors are magenta, yellow and blue-green. Each pigment absorbs one primary color and reflects back the other two. Perception of color is quantitative and subjective, it differs among individuals.

Highlights:

- The initial photon absorption gives rise to a short lived singlet state which subsequently passes to long-lived triplet state, which actually participates in redox chain.
- Photosynthesis involves a series of complex reactions with the overall conversion of water and carbon dioxide to carbohydrates and dioxygen in the chloroplast.

EXERCISES

1. State: (*a*) Grotthurs-Drapper law (*b*) Stark-Einstein law.
2. Explain: (*a*) Franck-Condon principle.
3. Mention physical processes undergone by excited molecules.
4. What is energy cascade?
5. What are ISC and Photosensitizer?
6. Give examples of some photochemical reactions.
7. What is Norrish type I reaction? Give example.
8. Explain the chemistry of vision.
9. What are the Dark and Hill reactions?
10. Give a schematic representation of energy transduction in the noncyclic photosynthetic reaction process.
11. Explain photosynthesis in the light of photochemical reactions.

26

Role of Metals in Biology

Metal ions are required for many critical functions in biological systems. The normal concentration range for each metal in biological system is narrow, with both deficiencies and excesses causing pathological changes. The elements required in human nutrition can be grouped into **bulk** and **trace** groups. The bulk elements are required in excess of 100 mg/day, whereas the trace elements are required in amounts not greater than a few mg/day. The transition metals for which biological storage and transport are significant are in order of decreasing abundance: iron, zinc, copper, molybdenum, cobalt, chromium, vanadium and nickel. The form of the metals is always ionic, but the oxidation states can vary on biological needs. The metals are generally found either bound directly to proteins or in cofactors such as porphyrins or cobalamins. Proteins with which transition metals and zinc are most commonly associated catalyze the intra and intermolecular rearrangement of electrons. In this respect, the redox properties of the metals are important, in others metals appear to contribute to the structure of the active state. An essential metal ion may function as a potent electron-withdrawing agent at some point in the catalytic function of enzymes which require metal ions for their activities and are called metalloenzymes (Table 26.1).

Elements required in Human nutrition

Bulk elements
- Calcium
- Magnesium
- Sodium
- Potassium

Trace elements
- Copper
- Iron
- Manganese
- Molybdenum
- Selenium
- Zinc

Table 26.1: Some Enzymes Containing or Requiring Essential Inorganic Elements as Cofactors

Fe^{2+} or Fe^{3+}	Cytochrome oxidase Catalase Peroxidase
Cu^{2+}	Cytochrome oxidase
Zn^{2+}	DNA polymerase Carbonic anhydrase Alcohol dehydrogenase
Mg^{2+}	Hexokinase Glucose 6-phosphatase
Mn^{2+}	Arginase
K^+	Pyruvate kinase (also requires Mg^{2+})
Ni^{2+}	Urease
Mo	Nitrate reductase
Se	Glutathione peroxidase

Iron

Iron is the most abundant transition element in the Earth's crust and in general in all forms of life. The total amount of iron in humans is quite large, averaging 3 to 5 gm for a healthy adult. Iron is absorbed in its ferrous form (Fe^{2+}). Absorption and excretion of iron are relatively slow and controlled by different factors. Iron present in different food varies in their absorption characteristics, such as iron is best absorbed from meat, less absorbed from cereal grains.

Most of the iron is present in **haemoglobin**, the plasma oxygen-transport protein, where iron functions to deliver oxygen for respiration. A much smaller amount is present in **myoglobin**—which is a muscle oxygen-transport protein. It is present in **cytochromes** and **cytochrome oxidase**. Iron transport from the storage sites to locations where cells synthesize iron containing proteins is done by an iron-containing protein called **transferrin**. In the tissues it is stored in the form of **ferritin**, an iron-protein containing ferric hydroxide and ferric phosphate. The liver, spleen and bone marrow contain much ferritin. Iron is excreted from the body *via* bile and faeces and menstrual blood. Since during menstruation, iron loss becomes double or triple, hence large amount of iron is required for women compared to men.

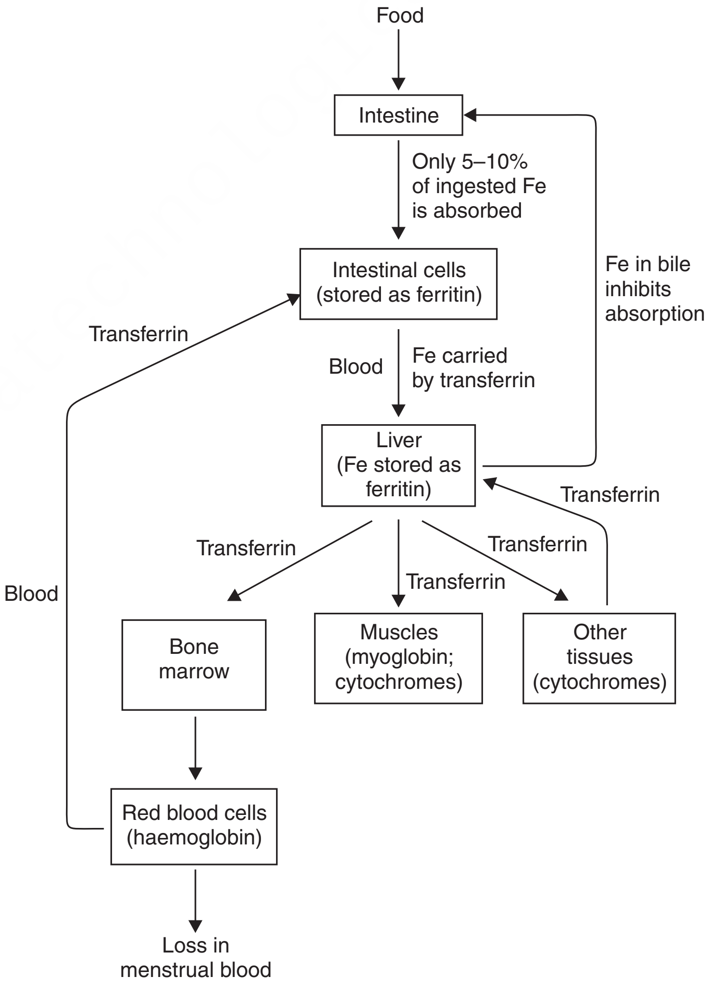


Fig. 26.1 Iron absorption and transport.

The processes and reaction in which iron participates are crucial for the survival of organisms and they include DNA synthesis, respiration, photosynthesis, nitrogen reduction, oxygen transport and oxygenations.

Deficiency of iron leads to **iron-deficiency anemia**, in which the number of red blood cells are normal but the amount of hemoglobin in the cells is low.

Copper

Copper is essential in the diet because it is involved in the proper utilization of iron especially for the synthesis of cytochrome oxidase, which contains both iron and copper. It is required to the extent of 2.5 to 5 mg/day and is found in meat, seafood, nuts, and vegetables.

Copper and iron proteins participate in many of the biological reactions:

- for cytochrome oxidase synthesis which catalyzes the transfer of electrons from water to dioxygen during respiration.
- reversible binding of dioxygen, *e.g.* hemoglobin, hemocyanin etc.
- activation of dioxygen.
- dismutation of superoxide by Cu or Fe as the active metal.

Use of stored iron is reduced by copper deficiency, which suggests that iron metabolism may depend on copper proteins.

Copper is also present in the active group of **lysyl oxidase**, an enzyme responsible for cross-linking in collagen and elastin. Hence animals that are copper deficient develop defective collagen molecules (due to absence of cross-linking) leading to rupture of arteries.

In the photosynthetic electron transport, the actual carrier of electrons is the blue copper protein—plastocyanin. Here the copper atom carries the electron undergoing Cu(I)–Cu(II) cycles.

Zinc

Zinc is an essential component of nearly about 80 to 100 different enzymes as part of their prosthetic groups. The enzymes include alcohol dehydrogenase, carbonic anhydrase, DNA and RNA polymerases, carboxy peptidase. It is also present in many NAD and NADP linked dehydrogenases which promote the transfer of hydride ions from substrates to NAD^+/$NADP^+$.

As a part of the carbonic anhydrase, it catalyzes the hydration of CO_2 to H_2CO_3, whereas in carboxypeptidases, it participates in proteolytic activity. Zinc is found in high concentration in sperm cells, prostate gland and eyes. The hormone insulin is stored complexed with zinc. Zinc also has a role in the functioning of taste and smell receptors respectively of tongue and nose.

Mechanism

Zinc has such an important role as the prosthetic group of large number of enzymes since it can co-ordinate with four, five or six ligands without any preference. The ligands can be easily exchanged with one water molecule. Zinc acts as a Lewis acid, it does not change its protein ligand nor does it change its oxidation state but only changes the co-ordination sphere on the side exposed to water/solvent. Zinc has a high affinity for nitrogen, oxygen and sulfur. It is therefore found to be bound to histidines, glutamates or aspartates. It does not always participate in the catalytic steps but its presence increases catalytic rate. Thus from above it can be said that zinc plays both structural and regulating roles for the enzymes.

Daily requirement of zinc for an adult is 15 mg. It is present in abundance in meat, egg, sea foods, milk and liver but in low amount in fruit and green vegetables.

Manganese

Manganese plays a critical role in oxygen evolution catalysed by the proteins of the photosynthetic reaction center. How the multiple manganese atoms participate in the removal of four electrons and protons from water is yet to be investigated. The **superoxide dismutase** of bacteria and mitochondria and **pyruvate carboxylase** in mammals also contain manganese. Manganese is also present in **arginase** which hydrolyzes arginine to urea, which is the end product of human amino group metabolism. Mn^{2+} also serves as a cofactor for phosphate-transferring enzymes.

Cobalt

Cobalt is a vital part of vitamin B_{12} molecule and hence is required by the micro-organisms for its synthesis. In different animals also Co is required for the synthesis of B_{12} by the microorganisms of the G.I. tract.

The most common type of reaction in which cobalamine enzymes participate results in reciprocal exchange of H atoms if they are on adjacent C atoms.

Unlike most animals, ruminants have a high nutritional requirement for cobalt.

Deficiency of cobalt may lead to lower production of B_{12} which may lead to anaemia.

Nickel

Nickel is a component of urease, hydrogenase, CO dehydrogenase, S-methyl CoM reductase, which catalyzes the terminal step in methane production by methanogenic bacteria. All Ni-proteins are obtained from plants and bacteria. Nickel is a component of **urease** which was the first enyme crystallized in 1926. Nickel may also be found in the nucleic acid binding proteins.

Vanadium and **chromium** have several features in common. Biological roles of each remain largely unknown and they are both present in only small amounts in organisms. In proteins, vanadium is a cofactor in an algal bromoperoxidase and in certain prokaryotic nitrogenases. It is also found in blood cells of a primitive vertebrate but its role is unclear. It is found to function in the active sites of certain flavin dehydrogenases. It is also needed for proper growth of bone and connective tissues of human.

Chromium is involved in the glucose uptake by animal tissues, but little is known about the complexes or factors of chromium from plants, animals and bacteria.

Molybdenum proteins catalyze the reduction of nitrogen and nitrates as well as oxidation of aldehydes, purines and sulfite. Mo proteins are also Fe-proteins with iron centres. Some Mo-proteins contain additional cofactors such as flavins, *e.g.* in xanthine oxidase and aldehyde oxidase. Xanthine oxidase catalyzes the oxidation of purine to yield the excretory product uric acid. The number of redox centres in Mo-proteins exceeds the number of electrons transferred.

Selenium combined in an amino acid is an essential component of the prosthetic groups of several enzymes including glutathione peroxidase, which functions with glutathione to protect cells against the destructive action of hydrogen peroxide. The ferrous (Fe II) of the haemoglobin is readily oxidised by H_2O_2 to methemoglobin (inactive oxygen carrier). This is protected by glutathione peroxidase which contains selenocysteine in which the S of cysteine is replaced by Se.

Little is known about the biological storage of any metal except iron which is stored in ferritin. However, zinc and copper are bound to metallothionein in a form which may be stored.

Zinc, copper, vanadium, chromium, manganese and molybdenum are transported as simple salts or loosely bound protein complexes. But for iron, high-affinity chelators or proteins are required for transport.

Copper, cobalt, zinc, manganese and nickel, although essential in the diet, are also toxic in excess and cause health hazards. Chromium in the form of chromate is mutagenic in bacterial and mammalian systems.

Lastly **silicon**, ubiquitous as silica (SiO_2) and as calcium aluminium silicate, is the major component of clay and is required by rat, chick and other animals fed with synthetic diet. The function of silicon is not known, but it occurs in greatest concentration in bone and connective tissues of animals in an organic form.

Calcium and Magnesium

The adult human body contains more than a kilogram of calcium, nearly all of which is concentrated in bones and teeth along with phosphate and as insoluble crystalline calcium hydroxyapatite. Calcium also plays a very important role in all cells as an intracellular regulator and messenger, mediating a wide range of biological processes like muscle contraction, secretion, glycolysis and gluconeogenesis, iron transport, cell division; and growth.

Ca^{2+} and the cytoplasmic Ca^{2+}-binding proteins (*e.g*. Calmodulin) function as intracellular messengers for different hormones. Free Ca^{2+} present in the cytosol is very low about 10^{-6} M. Transitory increase in the Ca^{2+} concentration which results from hormonal action on a membrane receptor leads to the conformational changes of the Ca^{2+} binding proteins. These proteins in turn stimulate different protein kinases which are involved in different cellular activities.

After these responses another important class of transport proteins (Ca^{2+} ATPases) transport the excess intracellular Ca^{2+} (released from different sources) across the membrane and maintain the original low concentration of Ca^{2+}.

Ca^{2+} ions are also known to play various roles outside cells. In the plants Ca^{2+} forms link between individual cells and is required for maintaining the rigidity of whole plants.

Calcium is abundant in foods like milk, cheese, cereal grains, legumes, nuts and vegetables. Absorption of Ca from intestine is controlled by complex factors like pH, Ca:P ratio in diet, presence of fatty acids and vitamin D in diet.

Pregnant and lactating women and children require more calcium (1200 mg/day) compared to normal human (800 mg/day). The calcium present in the cereal grains is not readily absorbed.

The body contains about 25 g of **magnesium** mostly present in bones. Concentration of magnesium is rather high in all the cells, *i.e.,* 5-10 mM, since it plays a vital role on the action of a large number of enzymes involved in the glycolysis and ATP transport mechanisms. Mg^{2+} forms complexes with the phosphate groups of the glycolytic intermediates and ADP/ATP and the substrate binding sites of many of these enzymes are specific for Mg^{2+} complexes of phosphorylated intermediates. Magnesium is abundant in chlorophyll of green leafy vegetables. The recommended magnesium intake is 350 mg/day for adults. Alcoholics and elderly people are found to be magnesium deficient.

Electron Transfer

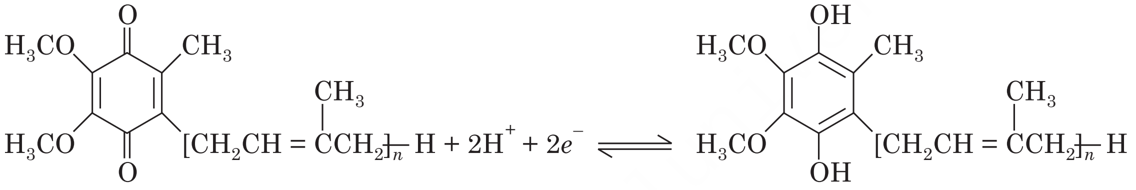
Reactions in which electrons are transferred from one molecule to another are redox reactions. Reducing and oxidising agents function as conjugate pairs (redox pairs).

$$\text{electron donor} \rightleftharpoons e^- + \text{electron acceptor}$$

Three types of redox centres are found in biology—protein, small molecules and redox cofactors. Mainly in the class of small molecules for electron transfers nicotinamide and quinone coenzymes are found in biosphere.

Nicotinamide adenine dinucleotide (NAD) and NADP participate with the 4-position of the pyridine ring being active.

Coenzyme A, also called ubiquinone, found in all cells both in free and in protein bound forms functions as follows:



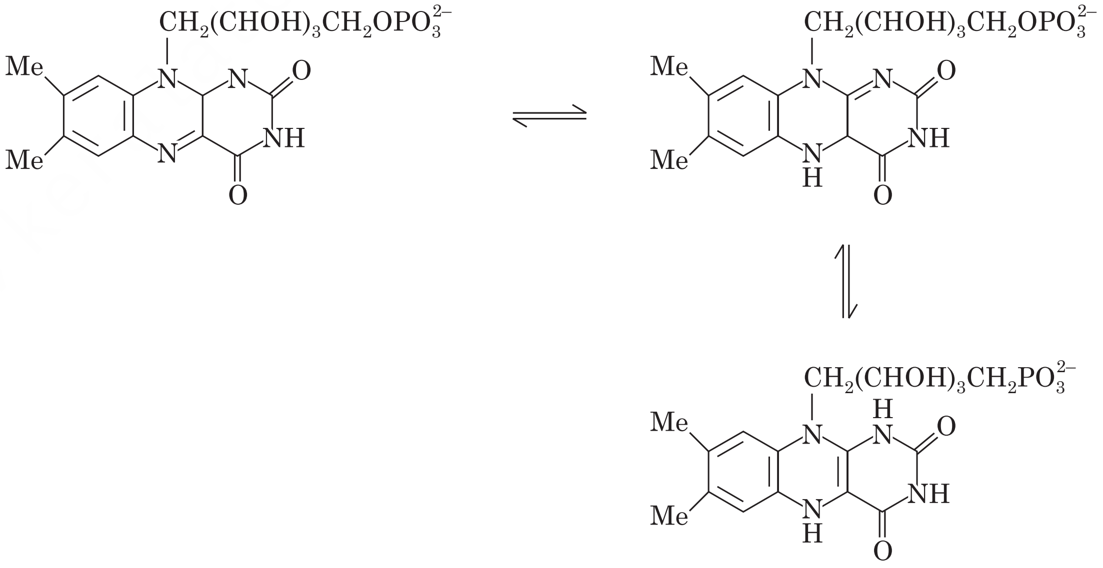
Metalloproteins act as electron-transfer proteins, also called ‘electron transferases’, possess some characteristics like:

(*a*) Possess a suitable cofactor which acts as electron sink.

(*b*) Possess one hydrophobic shell close to cofactor which forms hydrogen bonds with the hydrophobic environment to stabilize the oxidised and the reduced forms.

(*c*) Small structural changes accompanying electron transfer. These transferases are of four classes—flavodoxins, blue copper proteins, iron-sulfur proteins, cytochromes.

The flavodoxins contain organic redox cofactor flavin mononucleotide (FMN). They are found mainly in bacteria and algae. FMN can act as 1 or 2 elctron redox center and functions as



The blue copper proteins function in bacteria and plants. The geometry of the copper site is trigonal planar and three ligands bind to copper and have a relatively high reduction potential.

The iron-sulfur proteins play important role as electron carriers in all living organisms and participate in the important functions like plant photosynthesis, nitrogen fixation, steroid metabolism, oxidative phosphorylation etc. The simplest is rubredoxin found in anaerobic bacteria. The ferredoxins (2Fe-2S) are found in plant chloroplasts and mammalian tissues. The other types of ferredoxin (4Fe-4S) are found in many strains of bacteria. In these the Fe is co-ordinated to the S of cysteins.

Lastly, the cytochromes are the most thoroughly characterized electron transferases. Cytochrome contains heme cofactors and according to the type of heme *i.e.,* heme *a*, heme *b* and heme *c*, cytochromes are also classified. Class I cytochrome *c* have a distinctive role in the mitochondrial electron transfer in mammalian system. Class II cytochrome *c* are found in photosynthetic bacteria. Class III cytochrome *c* contain four hemes which are associated with the cytoplasmic membrane of sulfate-reducing bacteria.

Electron transfer reactions play key roles in biological processes like collagen synthesis, steroid metabolism, immune response, drug activation, neurotransmission, nitrogen fixation, respiration and photosynthesis. From the point of global bioenergetics, aerobic respiration and photosynthesis are complementary processes (Fig. 26.2).

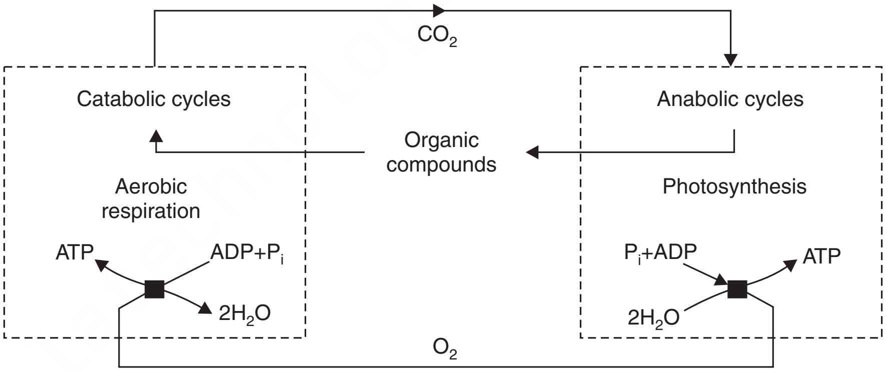


Fig. 26.2 Aerobic respiration and photosynthesis—Complementary processes.

The oxygen evolved by photosynthesis is consumed by aerobic bacteria and animals. Similarly, the end products of aerobic respiration (CO_2 and H_2O) are the major nutritional requirements of photosynthetic organisms.

The energy extracted from the organic compounds by several catabolic pathways (*e.g.* citric acid cycle) involves oxidation of these compounds to CO_2 and H_2O with concomitant production of water soluble reductants like NADH and succinate. These reductants donate electrons to the components of mitochondrial electron transfer chain leading to reduction of O_2 to H_2O.

In aerobic system the terminal oxidant is O_2 and in anaerobic system it is the inorganic sulfates and nitrates. These reactions are coupled to ATP synthesis (called oxidative phosphorylation).

Electron Transport and Oxidative Phosphorylation

Electron transport from NADH—Electrons are transported from NADH to oxygen along the electron transport chain (respiratory chain). NADH passes electrons to NADH-dehydrogenase, a large protein complex containing FMN and two types of FeS proteins. FMN accepts the electrons and is converted to $FMNH_2$ and then passed to FeS. Then electron from NADH dehydrogenase passes to coenzyme *a* converting it to $CoQH_2$ and then to the cytochrome bc_1 complex. Cytochrome bc_1 in turn passes the electrons to cytochrome *c* which again in turn passes them to cytochrome oxidase. Finally cytochrome oxidases pass four electrons to molecular oxygen to form two molecules of water.

All the electron carriers in the electron transport chain interact according to their redox potentials and it is obvious that the next electron acceptor has a higher affinity for electron than the donor. Thus there is a unidirectional flow of electrons from NADH to O_2. The three main protein complexes—the NADH dehydrogenase, cytochrome bc_1 and cytochrome oxidase act as H^+ pump driven by electron transport and create an H^+ gradient across the inner mitochondrial membrane to intermembrane space. Detail of the electron transport is depicted in Fig. 26.3.

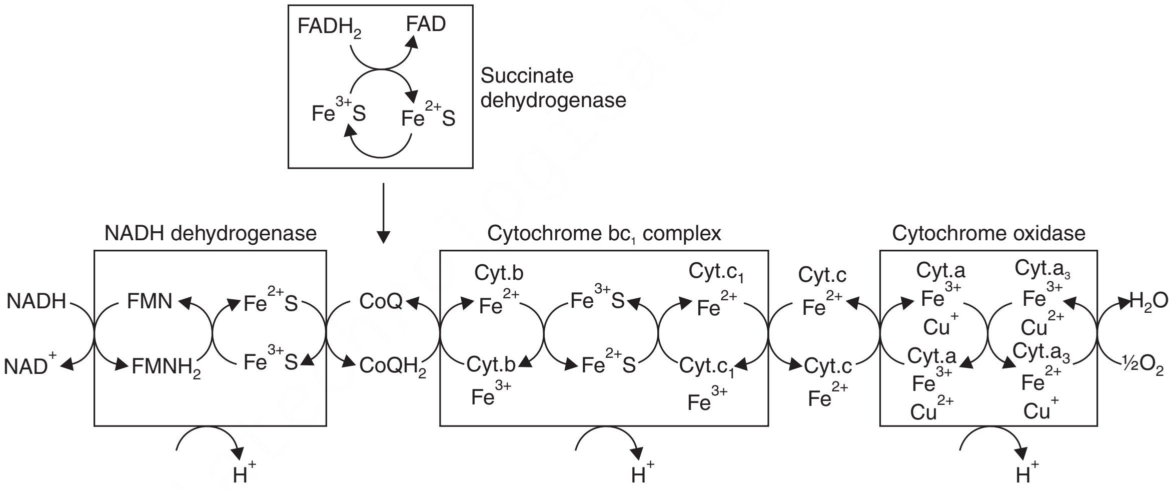


Fig. 26.3 Details of electron transport.

Electron transport from $FADH_2$: $FADH_2$ while getting reoxidised to FAD donates two electrons to succinate-CoQ-reductase, which in turn passes the electrons to ubiqninone (CoQ). These electrons enter the main electron transport chain similar to that from the oxidation of NADH.

Electron transport inhibitors

- **Rotenone** and **amytal** inhibit electron transport of NADH dehydrogenase.
- **Antimycin A** inhibits the cytochrome bc_1.
- **Cyanide** (CN^-), **azide** (N_3^-) and **carbon monoxide** (CO) all inhibit cytochrome oxidase.

Oxidative phosphorylation: Oxidative phosphorylation is ATP synthesis linked to the oxidation of NADH and $FADH_2$ via the electron transport chain. The mechanism was originally proposed as chemiosmotic hypothesis. Energy liberated by electron transport is used to pump H^+ ions out of the mitochondrion and create an electrochemical proton gradient. The protons flow back into the mitochondrion through the ATP synthase which synthesizes ATP. About 3 molecules of ATP are synthesized per NADH oxidised and two ATP molecules per $FADH_2$ oxidised. Electron transport is tightly coupled to ATP synthesis so that respiratory control ensures electron flow only when ATP synthesis is required.

Highlights:

- **Calcium** is mainly concentrated in bones and teeth along with phosphate. Calcium also plays an important role in all animal cells as intracellular regulator or messenger.

  It helps to regulate the activity of skeletal muscle, heart and many other tissues.
- **Magnesium** plays an important role in the action of the enzymes of glycolytic pathway and also in ATP-dependent reactions.
- **Copper** is essential in the diet since it is involved in the proper utilization of iron, development of connective tissues and blood vessels.
- **Iron** is required for the synthesis of haemoglobin, cytochromes etc.
- **Zinc** is essential for every adult in his diet and acts as the prosthetic group of about 80 enzymes.
- **Nickel**, **vanadium, chromium** and **silicon** are needed for the proper growth of bone and connective tissue.
- **Selenium** is an essential component of glutathione peroxidase.
- **Molybdenum** is the part of the prosthetic group of xanthine oxidase.
- Some plants have shown requirements for **boron** and **aluminium**.

SHORT QUESTIONS AND ANSWERS

Q. 1. What are metalloproteins?

Ans. Proteins which contain metal ions like Fe, Co, Zn, Cu, Mg etc., *e.g.,* ceruloplasmin (Cu).

Q. 2. What is the difference between metal-activated enzymes and metalloenzymes?

Ans. In metal-activated enzymes the metal is not tightly held by the enzyme and can be easily exchanged with other cations, *e.g.*, ATPase (Mg^{2+} and Ca^{2+}).

In metalloenzymes the metal is held tightly by the enzyme and cannot be readily exchanged, *e.g.*, xanthine oxidase (Mo).

Q. 3. Which are the principal elements of the body?

Ans. The seven principal elements constitute 60-80% of the body's inorganic material. They are Ca^{2+}, Mg^{2+}, P, Na^+, K^+, Cl^-, S.

Q. 4. What are the factors promoting Ca absorption?

Ans. Vitamin D (calcitrol), parathyroid hormone, low pH (acidic), lactose and amino acids like lysine and arginine promote Ca absorption.

Q. 5. What is the significance of Ca:P ratio?

Ans. The Ca:P ratio is important for calcification of bones. The product of Ca × P (in mg/dl) should be around 50 for adults.

Q. 6. What are the biochemical functions of Mg?

Ans. Mg is required for the formation of teeth, it serves as the cofactor for different enzymes like different kinases and adenylate cyclase. Mg is also required for neuromuscular functions.

Q. 7. In what form is sulfur present in our body?

Ans. Sulfur in our body is mostly present in the organic form. It is present in the proteins in amino acids namely cystine, cysteine, methionine.

Q. 8. Why is iron called the one-way substance?

Ans. Iron metabolism occurs in a closed system. It is not inactivated or excreted during metabolic processes like other vitamins or organic and inorganic substances rather it is lost from the body only through bile, sweat, blood loss and hairloss. Hence only the entry of iron in the body by absorption is controlled and hence it is called the one-way substance.

Q. 9. What is hemocyanin?

Ans. Hemocyanin is a copper-protein complex which functions like haemoglobin in invertebrates.

Q. 10. What is fluorosis?

Ans. Fluorosis is caused by excessive intake of fluorine. Manifestations are – discoloration of teeth, hypercalcification of limb bones, ligaments and spine leading ultimately to crippling of an individual.

EXERCISES

1. What are the functions of minerals in our body?
2. How are minerals classified according to their requirements?
3. What are the principal functions of Ca in our body?
4. Name the diseases related to Ca in our body.
5. What are the different proteins associated with iron in our system?
6. What are the biochemical functions of Cu?
7. Name the enzymes whose functions are dependent on zinc and molybdenum.
8. Why are Mn and Co required in our body?
9. What is lysyl oxidase?
10. Explain the role of Zn in the body.
11. Zn has much important role as the prosthetic group—explain.
12. What do you mean by bulk and trace groups?
13. What are cofactors? Give examples.
14. What is the role of iron in the body?
15. What do you mean by iron deficiency anemia?
16. Explain the role of following elements in the body:
    (*a*) Ni (*b*) V (*c*) Cr (*d*) Mo (*e*) Se (*f*) Si
17. What is electron transfer?
18. Electron transfer reactions play key roles in biological processes–explain.
19. What are electron transport and oxidative phosphorylation?
20. What are metalloenzymes?

27

Pollution Prevention and Waste Minimisation

Pollution may be defined as "the excessive discharge or addition of undesirable substances or unwanted foreign matters into the environment, thereby adversely altering the natural quality of the environment, and causing damage to human, plant or animal life". Using the term environment we mean air, water and soil.

Our environment is a complex and dynamic system involving all forms of life which are virtually inter-dependent. Human being, the best form of life on earth, is ruling the earth and for his comfort, power and thirst for knowledge has been constantly changing the natural characteristics by adding toxic components to the environment and as a consequence every living organism is facing environmental hazards. The principal causes of these hazards are (*i*) population explosion, (*ii*) deforestation and depletion of forest cover, (*iii*) rapid urbanisation, (*iv*) depleting surface and ground water rapidly, (*v*) emission of heat, particles and toxic gases from industries, (*vi*) no recycling of waste products. Apart from all these man-made problems natural factors like volcanic erruptions, radioactivity and natural disasters also contribute to pollution.

AIR POLLUTION

Air is a mixture of gases that form the atmosphere. The clean air is composed of the gases having concentration

$$\begin{array}{lll} O_2 \rightarrow 20.92\%, & N_2 \rightarrow 78.1\%, & Ar \rightarrow 0.9325\% \\ CO_2 \rightarrow 0.03\%, & H_2 \rightarrow 0.01\%, & Ne \rightarrow 0.0018\% \\ He \rightarrow 0.0005\%, & Kr \rightarrow 0.0001\% & \end{array}$$

Air pollution has become an important factor of environmental degradation. The increasing industrialisation, urbanisation, excessive burning of fuel etc. produce a large amount of polluting substances, that have damaging effect to human, plants and animal lives. Diseases like bronchial asthma, lung cancer, heart and brain damages etc. have become prevalent due polluted air.

Air Pollutants

Air pollutants are either in solid, liquid or gaseous forms. According to mode of formation, pollutants which enter the air directly are called **primary pollutants**, and those which are created in the air from pollutants under electromagnetic radiation from the sun are called **secondary pollutants**.

(*i*) Carbon monoxide (CO)

Carbon monoxide is a colourless, odourless, highly toxic gas released by the partial combustion of fuels from automobile, industries, oil refineries, coals, woods etc. About 290 million tonnes of CO is discharged into the atmosphere annually, 90% of which originates from oxidation of methane produced by decaying organic matter. Out of man-made CO emission, 90% of it arises from transport sector. CO is also produced in large quantities in thermal power plants by burning coal.

CO causes toxic effects like headache, visual disturbances, paralysis and even death. It combines with haemoglobin in human blood to form carboxyhaemoglobin, which impairs oxygen transport. Presence of 2-5% of carboxyhaemoglobin affects the normal functioning of the nervous system. CO also affects the cardiovascular system, causing heart diseases.

(*ii*) Sulfur dioxide (SO_2)

SO_2 is a colourless gas with a suffocating and strong pungent odour. On a global scale, half of the ambient SO_2 originates from the oxidation of H_2S given off by decaying organic matter. Annually 90 million tonnes of SO_2 is poisoning the air of earth. Main contributors are burning of sulphur-containing coal and diesel in thermal power plants. Other sources are petroleum industry, oil refineries, sulfuric acid plants, sulfide ore roasting plants.

Long term or chronic exposure to SO_2 causes respiratory diseases like bronchitis, particularly in young children. It causes irritation to throat and eyes, chest constriction, headache, vomiting and death. It causes corrosion of metals. SO_2 causes membrane damage, chlorophyll destruction, metabolism inhibition, growth yield reduction in plants.

(*iii*) Sulfur trioxide (SO_3)

It is formed by the oxidation of SO_2 under the effect of sunlight. SO_3, even at the concentration of 1 ppm, causes breathing problem and respiratory problems.

Both the oxides of sulfur are converted to sulfurous and sulfuric acids in the atmosphere with water vapours which is the cause of **acid rain** and is harmful for all living and non-living forms on the earth.

(*iv*) Nitrogen oxides (NO, NO_2 etc)

All the oxides of nitrogen, *e.g.,* NO, NO_2, are represented by NO_x. On a global basis, 60% of NO_x is produced from biomass burning, fixation by lightning, inflow from the stratosphere, chemical conversion from NH_3 in the troposphere and loss of NO_2 from the soil. The other sources include combustion of fuels like coal, diesel, petrol, motor vehicle exhausts, acid manufacturing etc.

NO_x have various direct and indirect effects on human. They inhibit ciliary action so that soot and dust penetrate the lungs to cause bronchitis and respiratory diseases. NO_x readily combines with water forming HNO_3 which forms acid rain. It also causes eye irritation. In presence of sunlight NO_x and hydrocarbons (combustion products of petroleum) form **smog** and this smog again causes eye irritation, breathing difficulties and limits visibility of roads. Annually about 10 million tonnes of NO_x are entering the atmosphere.

Acid Rain

Over the last few decades, simple rainfall has taken on a threatening complexity in some parts of the world. The rain and snow falling down is getting polluted with atmospheric oxides of sulfur and nitrogen forming sulfuric acid and nitric acid and water. This is known as acid precipitation or acid rain.

$$SO_2 + H_2O \rightarrow H_2SO_3,\ 2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$$

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3.$$

The longer the SO_x and NO_x remain in the atmosphere the greater is the chance of their being converted to H_2SO_4 or HNO_3 by various catalytic and photochemical reactions.

Rains tend to be acidic naturally due to the dissolution of atmospheric CO_2 to yield H_2CO_3. Other atmospheric substances from volcanic eruptions, forest fires etc. also contribute to the acidity. But still then the amount of acidity is sufficient to dissolve minerals in the earth's crust and make them available to animals and plants but not damaging to lives. However the contributions of SO_x and NO_x polluting the atmosphere contributes to disturb the balance in the acidity, causing damage to the environment.

Harmful effects of this acid rain include (*i*) damage to freshwater life, (*ii*) causes irritation to eyes and mucous membranes, (*iii*) accelerates corrosion of rocks, minerals and metals, (*iv*) damage to buildings, bridges etc. causing faster weathering, (*v*) dissolves out metals and salts that increase the content of these in natural water resources to even toxic levels, (*vi*) in mist form damages the plants.

The practical approaches to counter the problem of acid rain are–

(*i*) Energy conservation leading to reduced fuel consumption and hence lesser elimination of SO_x and NO_x.

(*ii*) Desulfurisation and denitrification of fuels leading to lower emissions of SO_x and NO_x.

(*iii*) Substitution of fossil fuels with other alternative sources of energy.

SO_x emission is reduced by coal cleaning, bio-desulfurisation of liquid fuel and other methods of desulfurisation.

NO_x emission is reduced by modifying the designs of furnace and burner and using catalysts for different processes etc.

Acid rains are likely to occur more in cities and industrialised areas and also in the sectors where large amounts of these oxides are emitted by the automobiles.

(*v*) Carbon dioxide (CO_2)

CO_2 is not a pollutant itself. It comes mainly from the burning of fossil fuels, oxidation of carbon stored in the trees and soil humus, and released when forests are fired for shifting cultivation. Increasing population on earth is causing faster increase in the concentration of CO_2 in the atmosphere. Thus CO_2 is used as main feed stock for the photosynthesis of green vegetation. Deforestation is leading to the loss of balance of this CO_2 cycle. The excess of CO_2 in the atmosphere causes respiratory disorders and suffocation. CO_2 also has many indirect effects like climatic changes, increase in global temperature. This increase in global temperature further brings about the change in rainfall pattern, melting of ice in the polar region resulting in rise of sea level, changes in fish production, forest and water supply.

At present, the concentration of CO_2 in the atmosphere is approx. 350 ppm and the annual increase rate is about 1.5 ppm. Hence by the middle of the next century, CO_2 concentration in the global atmosphere will be approximately double the present concentration.

Green House Effects

The earth is heated by sunlight and some of the heat is absorbed while the rest is radiated back into the space. The gases like CO_2, water vapour, CH_4 and man-made chlorofluorocarbons act as glass in a green-house and allow the sunlight coming in but strongly absorb the infrared radiation given out by the earth's surface. The net result is the heating of the earth's surface called the "green-house effect".

Actually, the green-house gases are responsible for keeping our planet warm and sustaining life, otherwise the temperature of the earth would have gone down to sub-zero level. But, however, if the concentration of these green-house gases is too much, they trap too much of heat that may ultimately threaten the life on earth, *e.g.,* CO_2 in the atmosphere of

Venus is 60,000 times that of earth and average temperature of Venus is 425°C making existence of life impossible.

It is estimated that atmospheric CO_2 content has increased by 25% during last two centuries, which has raised the global temperature already. It is estimated that within 50–100 years the temperature may increase by 4 to 5°C which will increase the surface water evaporation and change the climate which may finally influence the growing of crops.

Global warming may also trigger melting of glaciers resulting in rising of sea level. It also causes floods, hurricanes, tornadoes, and increased breeding of pests.

To minimise the green-house effect it is required to reduce the use of fossil fuels, use of alternative source of energy. Conservation of forests, reduction in use of automobiles, ban on CFC's and nuclear explosions, encouraging and developing green technologies and checking population growth and awaring people are the other alternatives to check the green-house effect or global warming.

Depletion of Ozone Layer (O_3)

Ozone is an important chemical species present in the stratosphere, *i.e.*, above 20 km from the earth's surface and its concentration is around 10 ppm. It is formed in the stratosphere by photochemical reaction:

$$O_2 + h\nu \text{ (242 nm)} \longrightarrow O + O$$

$$O + O_2 + M \text{ (such as } N_2 \text{ or } O_2) \longrightarrow O_3 + M$$

The species M absorbs the excess energy liberated in the reaction and the molecule of ozone is stabilized. It is constantly formed. It is destructive to fabrics, rubber goods, crops etc. At the same time it acts as a protective shield for the life on earth, by strongly absorbing UV-radiations coming from the sun (220-230 nm) which is harmful for life on earth.

Ozone is destroyed by Cl_2, released due to volcanic activity and also by reactions with (*i*) NO, (*ii*) atomic oxygen, (*iii*) reactive —OH radical present in the atmosphere.

Chlorofluorocarbons (CFCs) come out from jumbo jets and supersonic aircraft, nuclear explosions, CFCs are also used as coolants in refrigerators, air conditioners, aerosols, plastic foams. CFC's escape and accumulate at high altitude, undergo decomposition, under UV light, the decomposition product being Cl_2. Each atom of Cl reacts with more than 0.5 molecules of oxygen in chain reaction converting ozone to oxygen and thereby leads to depletion of ozone layer.

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

The environmental hazards due to the CFCs were recognized in 1970 and the detection of ozone hole over Antarctica in 1985. The use of CFCs were limited since then.

The SO_x and NO_x also react with ozone

$$SO_2 + O_2 \longrightarrow SO_3 + O_2$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

Hence emissions of all these pollutants are also needed to be minimised.

The depletion of ozone layer allows the harmful UV radiations to reach earth which finally causes skin cancer, sunburns, breast cancer, cataract, leukemia, lung cancer, visual impairment, premature aging, DNA damage and even may lead to death.

(*vi*) Hydrogen fluoride (HF)

It is given out from phosphate fertiliser industries, aluminium industries, metallurgical processes, brick kiln and coal burnings. This causes "fluorosis" in cattle breeding on affected plants and also causes bone, tooth and skeleton disorders and respiratory diseases in human.

(*vii*) Hydrocarbons

Different types of hydrocarbons in high concentrations present in the atmosphere cause many serious problems like irritation to mucous membranes, respiratory problems, lung cancer, nervous system disorders and even may cause death if in toxic level. Additionally, different mutagenic organic compounds affect DNA replication and act as potential carcinogens.

(*viii*) Lead oxide (PbO)

Lead exists in a variety of chemical compounds with different characteristics. The atmospheric lead contamination comes from the automobiles. 2 to 4 μg of lead is present per litre of fuel. Lead is ingested and inhaled and about half of it is absorbed, some enters the blood, some enters the bones. Adverse effects of lead are found in population with blood levels of 10 mg/dl of Pb. Lead poisoning leads to anaemia, brain damage and loss of kidney function. Lead also enters the atmosphere from sources other than the automobiles, *i.e.,* from mining of lead bearing ores, lead plumbing and soldering, use of paints and ceramic glass and lead-zinc battery disposal.

Particulates as pollutants

(*i*) **Dust.** There are large number of sources of dust in the atmosphere, some of these include mines, furnaces, vehicles, ceramic factories, forest fires, household dusts, rubber tyre abrasion, natural winds etc. Dust causes respiratory and allergic problems. Silica containing dusts cause silicosis.

(*ii*) **Smoke.** Smoke is produced due to incomplete combustion of fuel, and the sources are locomotives, power plants, incinerators, diesel and gasoline engines, open fires, furnaces etc.

Smoke leads to loss of fuel, spoilage of exteriors of buildings and even it can cause cancer.

(*iii*) **Smog.** It is a combination of smoke and fog in droplets. It is of two types:

(*a*) *London smog.* It is coal smoke and fog. The latter consists of a mixture of SO_2 and SO_3. In presence of sunlight the oxidation of SO_2 to SO_3 is facilitated which followed by reaction with water droplets forms sulfuric acid aerosol. This type of smog causes respiratory problems, eye irritation etc., and it also reduces the visibility.

(*b*) *Los Angeles smog (photochemical smog).* Photochemical smog is initiated by the photochemical dissociation of NO_2 and the secondary reactions of these with unsaturated hydrocarbons, free radicals lead to the formation of peroxides and ozone. This is facilitated in sunny days. Photochemical smog also causes eye irritation and reduces visibility and it also damages plants and rubber goods.

(*iv*) **Asbestos.** This fibrous silicate material is used mainly for its mechanical strength and insulating properties. The tiny asbestos fibres penetrate the lung tissues and mucous membranes and stay there for a long period. Sometimes it gives rise to cancer.

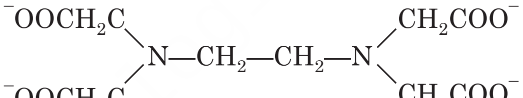
(*v*) **Heavy metals.** Lead, Mercury and Cadmium are the generally found heavy metals in the atmosphere that cause toxicity.

Lead is mainly emitted from the automobiles as it is added to gasoline to improve antiknock properties particularly in the form of tetraethyl lead. Presence of hydrocarbon group helps it to pass through the membranes in our body; it mainly concentrates in blood, bones etc. It reacts with the active —SH groups of enzymes producing haemoglobin and hence leads to anaemia.

Similarly, mercury also reacts with —SH group of different essential proteins and inhibits enzymatic activities. Toxicity of mercury depends on its state. Pure mercury, insoluble inorganic mercury compounds have lower toxicities whereas soluble salts of mercury, mercury vapour and organic mercury compounds like dimethyl mercury etc. cause mercury poisoning. Its harmful effects include sore gums, loose teeth, brain damage, irritability and emotional disturbances.

Mercury in natural water reservoirs are metabolised by certain micro-organisms forming dimethyl mercury which may be eaten up by small fishes and thereby it may enter the food chain called **biomagnification** and ultimately reach higher animals.

The best remedy for these heavy metals is treating with chelating agents like ethylene diamine tetraacetate which removes heavy metals from the blood by forming complexes.



EDTA

Pollution from internal combustion engines

One of the major pollution of the atmosphere is due to the internal combustion engines of the automobiles. Fuels used such as diesel, petrol etc., contain largely the hydrocarbons with other S and N containing impurities. Burning or incomplete burning of these fuels causes release of CO_2, CO, SO_2, NO_2, hydrocarbons etc. All these pollute the atmosphere, form smog and cause damage to lives.

This type of pollution can be minimised by using (*i*) better and pollution-free fuels, (*ii*) using engines with better performances, (*iii*) using catalysts for the conversion of pollutants to less harmful substances by joining a device in the exhaust system of an automobile. The device is known as **catalytic converter** (Fig. 27.1), (*iv*) by mixing exhaust gases with more air for better combustion.

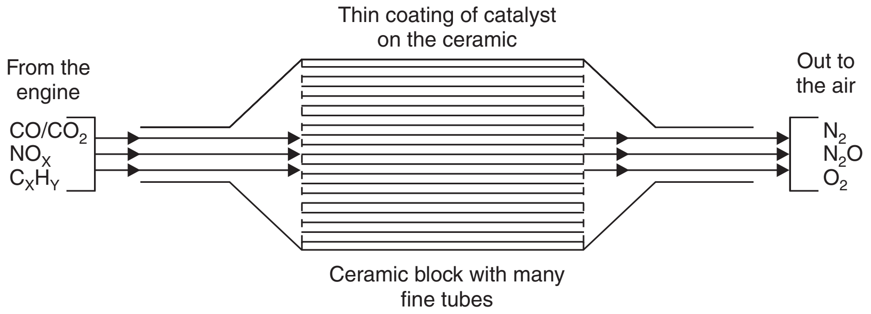


Fig. 27.1 Catalytic converter.

Highlights:

Pollution:

(*i*) "The excessive discharge or addition of undesirable substances or unwanted foreign matter into the environment, thereby adversely altering the natural quality of the environment, and causing damage to human, plants or animal life".

(*ii*) **Major Air Pollutants:**

- Gases like SO_2, SO_3, H_2S, NO, NO_2, CO, CO_2, hydrocarbons.
- Particulates like dust, smoke, smog, lead, mercury, cadmium.

(*iii*) **Control of Air Pollution:**

- Using chimneys
- Using cyclone separator, electrostatic precipitator
- By cleaning the fuels like coal, petroleum
- By treating the exhaust gases
- By plantation of trees

(*iv*) **Important effects of Air Pollution:**

1. Acid rain
2. Green-house effect
3. Depletion of ozone layer
4. Photochemical smog formation
5. Heavy metal poisoning

Air pollution control

Air pollution can be controlled by preventing the formation of the pollutants at the source. Some of the following remedies can be helpful:

1. (*a*) Pollution due to **emissions from automobiles** can be minimised by using catalysts to aid the effective combustion.

   (*b*) By purifying the fuel, removing sulfur by bio and normal methods of desulfurization and also by reducing the emission of SO_2 in flue gases by treating with liq. NH_3, alk. $KMnO_4$ etc.

2. (*a*) The industrial process can be improved by **modifying the old machineries** so that pollution due to imperfect conversions can be corrected.

   (*b*) **Installation of air treatment** plants for the purification of vent gases containing objectionable pollutants.

3. The use of "**tall stacks or chimneys**" reduces the concentration of air pollutants in the ground level. The gases discharged through these get diluted and are dispersed to a height that reduces pollution in ground level.

4. **Alternative source of energy** is to be tried instead of conventional fuels causing pollution.

5. **Installation of devices**

   (*a*) **Cyclone collector.** It is used for precleaning of air for removal of dry particulates of size ranging from 5–20 μm. The air/gas is passed through a tight circular spiral-fitted chamber. The centrifugal forces throw the particulates towards the wall from where they settle down due to gravity. The collected particles are periodically removed. The action of cyclone separator is as shown in Fig. 27.2.

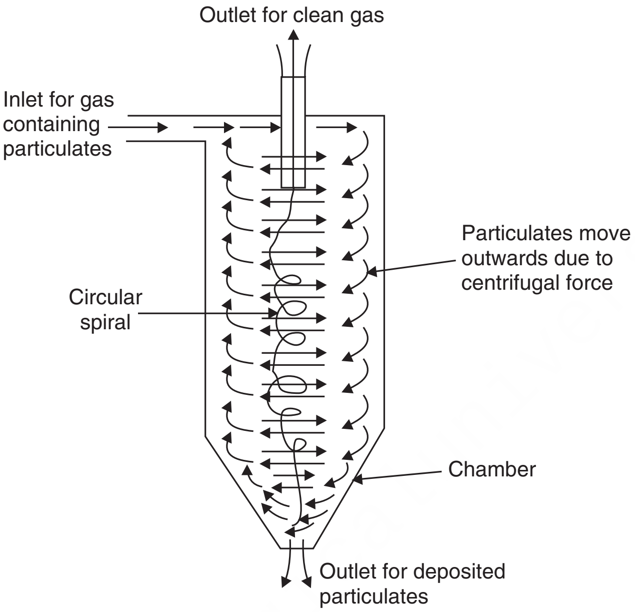


Fig. 27.2 A cyclone collector.

(*b*) **Cottrell electrostatic precipitator.** Smoke as well as the particulates can be removed by this device. Smoke is a colloidal suspension of negatively charged carbon particles in air. Smoke/air is passed through a chamber maintained to a very high potential of 30,000 volts. Under the influence of strong electrical field the particles (charged) get attracted towards opposite charge and the hot gas passes away.

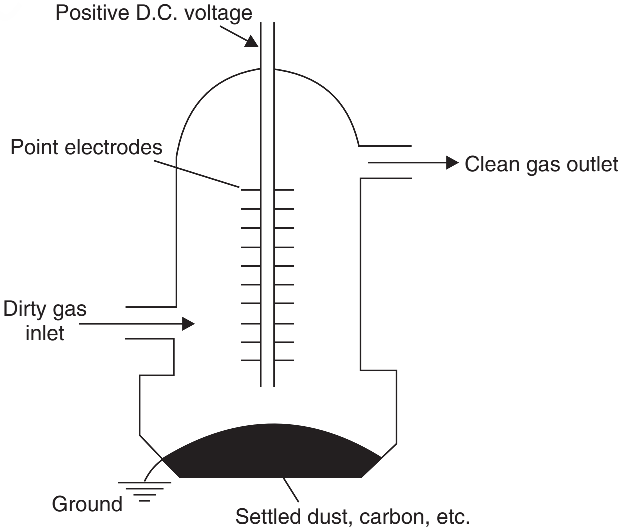


Fig. 27.3 Cottrell electrostatic precipitator.

(*c*) Dust is eliminated by "**extraction ventilation**". The air containing dust is passed at very high speed and the rate is suddenly reduced whereby the dust particles settle out.

(*d*) **Filters.** Cloth bags acting as filters are used to separate the particulates from the stack gases in electric power plants.

(*e*) **Scrubbers.** These are used to remove particle as well as acids and chemical fumes. The polluted air is passed through a tower filled with coke and fine mist of water sprinkled which removes about 99% particles and 80-95% SO_x.

6. **Plantation of trees.** Trees especially broad leaved plants help to reduce excess CO_2 of the environment and also help to deposit the suspended particles from the air and make air less polluted.
7. **Zoning.** To avoid air pollution problems, there should be "buffer zones" between the proper "industrial zones" and domestic areas. Thus dilution of the polluted air takes place before reaching common people.
8. **Enforcement of Air (Prevention and Control) Pollution Act**, **1981.** Air quality standards as recommended by the Central Pollution Control Board must be strictly implemented.

WATER POLLUTION

Water from nature is used by man for drinking, domestic, agricultural, transport and industrial purposes. **Pollution of water** is defined as the presence of foreign organic, inorganic, biological, radiological and physical substances that tend to degrade its quality and constitute health hazards or decrease its quality.

Water may be contaminated by the following:

1. Dissolved gases like H_2S, CO_2, NH_3, N_2 etc.
2. Dissolved minerals like sodium, calcium, magnesium salts.
3. Suspended impurities like clay, sand, mud, organic matter.
4. Micro-organisms like bacteria, viruses, protozoa.
5. Contaminated with radiological substances.

Sources of Water Pollution Include

1. **Domestic sewage.** The domestic and municipal wastes consisting of human excretions, kitchen wastes and other organic wastes drain out into the canal and through it to the rivers and other natural water reservoirs deteriorating its quality and also act as a source of food for micro-organisms. This finally leads to various diseases of stomach and skin for human.
2. **Industrial waters.** Acids, alkalies, metals, salts and numerous other chemicals pollute the water. Particularly, the waste water from paper, sugar, soap, textiles, leather tanneries, pharmaceuticals, oil refineries etc., contributes a lot of pollutants to the water.
3. **Fertilizer plants.** These plants add nitrates, phosphates, ammonia etc., to water.
4. **Agricultural discharges.** Pesticides, insecticides, plant debris, fertilizer manures etc., are the pollutants.
5. **Natural pollutants from other sources.** Clay, fines of soil, oil, detergents, bacteria, viruses, protozoa, dead bodies of animals and human etc., cause water pollution which finally causes outbreak of infectious diseases.
6. Processing of **radioactive materials** causes water pollution.

Control of Water Pollution

The problem of water pollution can be controlled by adopting the following procedures:

1. By reducing the waste at source.
2. Diluting the waste water from different sources before discharging since the dissolved oxygen of diluting water helps in biodegradation of different toxic chemicals by micro-organisms to inocuous chemicals before mixing with natural water.
3. By chemical treatment the polluted water can be made safe.
4. By physical methods like reverse osmosis, electrodialysis, ion-exchange etc., polluted water can be purified.
5. By recycling of waste water before discharging involves treatments like use of activated sludge, trickling filter etc.
6. Reclamation of waste water: sewage water can be made useable for irrigation, fish-farm raising, as it contains essential nutrients.

Sewage and its Treatment

Sewage is the liquid waste from domestic and municipal waste water, industrial waste water, ground wastes etc. **Domestic-sewage** has objectionable odour due to S and N containing compounds and a grey to green color due to the presence of discharges from kitchens, bath and lavatories.

Industrial wastes have different color or odour depending on types of industries present and the chemical constituents also vary accordingly. The treatments consist of **aerobic and anaerobic** oxidations, which are brought about by the aerobic or anaerobic bacteria present in the sewage.

The aerobic bacteria oxidize the organic compounds present in the sewage by the dissolved oxygen leading to the formation of nitrates, sulfates and phosphates which is called aerobic oxidation.

$$\begin{array}{c}\text{Sewage}\\ +\\ \text{Air (to}\\ \text{supply dissolved}\\ \text{oxygen)}\end{array} \xrightarrow[\text{Aerobic bacteria}]{\text{Oxidation by}} \begin{array}{c}\text{Nitrates, sulfates,}\\ \text{phosphates etc.}\end{array}$$

Aerobic oxidation

In the absence of the supply of free oxygen, the anaerobic bacteria convert the organic compounds in the sewage to methane, H_2S, ammonium sulfide etc. (offensive odour).

In this type of anaerobic oxidation process the required oxygen is supplied by the nitrates, sulfates and organic compounds.

$$\text{Sewage} \xrightarrow[\text{Anaerobic bacteria}]{\text{Oxidation by}} \begin{array}{c}\text{Oxidation to}\\ \text{produce } H_2S,\\ PH_3,\ CH_4 \text{ etc.}\end{array}$$

Anaerobic oxidation

Biological Oxygen Demand (BOD)

BOD of a sewage is defined as the amount of free oxygen required to oxidize the organic matter present in the sewage by the aerobic bacteria present in it at 27°C for a period of 3 days. The unit of BOD is ppm or mg/litre. BOD, therefore, gives an idea of the level of pollution of the sewage as it is an index of the amount of decomposable organic matter. Higher the BOD, greater is the degree of pollution. An average sewage has a BOD level 100–150 ppm.

Determination of BOD

The BOD test is based on mainly bio-assay procedures which measures the dissolved oxygen consumed by micro-organism while assimilating and oxidising the organic matter under aerobic condition.

A known volume of sample is diluted with dilution water (which is aerated to a known dissolved oxygen concentration). It is incubated at 27°C for 3 days in dark. After this the dissolved oxygen concentration is determined, the principle of which is given below. The difference between the initial and final dissolved oxygen gives the BOD.

Principle for DO

It is the modified Winkler method. By this method a ppt of manganous hydroxide is formed first which rapidly absorbs oxygen dissolved in water forming a higher oxide.

$$MnSO_4 + 2KOH \longrightarrow Mn(OH)_2 + K_2SO_4$$

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2$$

On acidification in presence of iodide, I_2 is liberated in a quantity equivalent to the dissolved oxygen present.

$$MnO(OH)_2 + 2KI + H_2O \longrightarrow Mn(OH)_2 + I_2 + 2KOH$$

The liberated I_2 is titrated with standard sodium thiosulfate solution using starch solution as indicator.

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^{1-}.$$

Chemical Oxygen Demand (COD)

It is a measure of the oxidizable impurities present in the sewage. It represents both the biologically oxidizable as well as biologically non-oxidizable impurities present and hence the value is higher than the corresponding BOD of the sewage. It is advantageous to measure COD to assess the level of impurities since COD determination takes only 3 hrs.

Determination of COD

250 ml of the sample of water is refluxed for $1\frac{1}{2}$ hrs. with a known excess of 1N $K_2Cr_2O_7$ and dil H_2SO_4 and a little Ag_2SO_4 as catalyst. After the oxidation is over the excess $K_2Cr_2O_7$ is titrated back with standard Mohr's salt solution. The oxygen equivalent of $K_2Cr_2O_7$ consumed for the oxidation reaction is the measure of COD.

$$1 \text{ ml of } 1N\ K_2Cr_2O_7 \equiv 0.008 \text{ gm of oxygen.}$$

Municipal Sewage Treatment

Disposal of sewage has become of prime importance as it causes undesirable and harmful effects on living beings and the environment. The main objectives of sewage treatment are (*i*) removal of compounds causing bad odour, (*ii*) removal of impurities causing public health problem, (*iii*) rendering the sewage finally safe to be discharged to natural water reservoirs such that aquatic life is not disturbed.

Municipal sewage treatment processes are called sewarage and it involves the following steps:

(*i*) **Primary treatment.** First the sewage is subjected to mechanical processes like flowing, dilution and sedimentation to remove the coarse solid materials. It is passed through a series of filters of graded openings and then flows to a sedimentation tank. Coarse materials collect at the sedimentation tank called sludge. The liquid effluent then undergoes secondary treatment.

(*ii*) **Secondary treatment.** This is a purely biological treatment having two phases– aerobic and anaerobic. The aerobic process involves aerobic digestion of sludge by processes like trickling filters, oxidation ponds and activated sludge process.

In the **trickling filter process** the effluent from the primary treatment is allowed to flow through 6–10 ft deep bed of crushed stone, gravel, coal etc. It is sprayed over the bed when it gets saturated with aerial oxygen and the micro-organisms present start aerobic digestion while the water passes through the filter bed, degrading the organic compounds and finally rendering the effluent harmless which collects at the bottom and enters the tertiary treatment (Fig. 27.4).

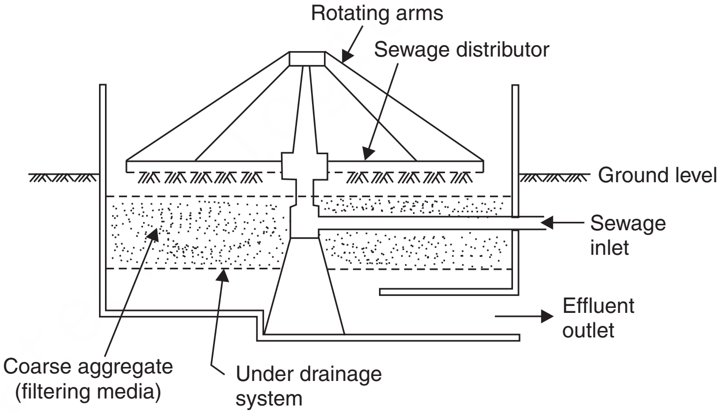


Fig. 27.4 Trickling filter.

In the **oxidation ponds** which are shallow ponds the water is exposed to atmosphere whereby the algae *Chlorella pyrenoidosa* grow and their growth helps in maintaining the aerobic condition in the sewage and the microorganisms present digest the organic matters present and render the water harmless.

In the activated sludge process the sewage is vigorously aerated and due to the presence of microorganisms colloidal aggregates of “floccules’ are formed which finally settle down after a long-time. This settled sludge is the ‘activated sludge’ which consists of a large number of very actively metabolizing bacteria, yeasts, molds and protozoa. When this activated sludge is added to the fresh batch of aerated sewage, flocculation takes place in very short period and hence the whole process takes very short time. This method is also known as **activated sludge process.** But disposal of this activated sludge is a problem.

Anaerobic Digestion

The sludge collected after primary treatment is added to the anaerobic digestion tank which is a closed tank and the micro-organisms digest the organic compounds in the absence of oxygen for about 30 days. The gaseous products consist of 60-70% CH_4, 20-30% CO_2, small amount of H_2S, H_2, N_2. This gas can be used as a fuel for power generation or for city supply. 400 to 600 litres of gas is produced per kg. of solid sludge.

(*iii*) **Tertiary treatment.** The effluent from secondary treatment contains nitrate, phosphate etc. This is subjected to chemical treatment. After the chemical treatment the water is chlorinated to free it from micro-organisms. After this tertiary treatment the water is safe for human use (Fig. 27.5).

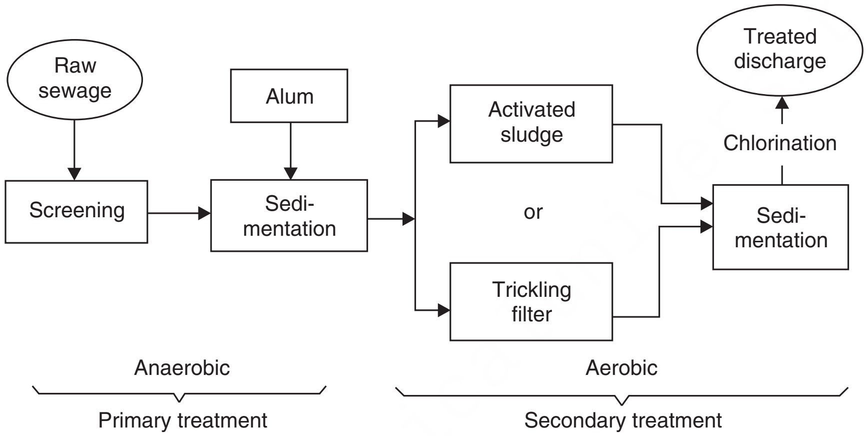


Fig. 27.5 Flow diagram for sewage treatment.

Water pollution can be prevented by:

(*a*) Preventing the use of chemical fertilizers

(*b*) Using bio-degradable detergents.

(*c*) Proper treatment of sewage before draining to natural reservoirs.

(*d*) **Phyto-plankton,** a layer of the tiny animals and plants that live on the surface of sea water. They are capable of absorbing floated minute particles, dirt and help to check water pollution. The pollution in water hampers the growth of plankton and affects marine life.

SOIL POLLUTION

The contamination of soil or land with rain, excess of fertilisers, wrong fertilisers, insecticides and herbicides is called soil pollution.

Sources of Soil Pollution

1. Repeated and excess use of fertilizers and pesticides cause soil pollution. By excess use of $(NH_4)_2 SO_4$, the SO_4^{2-} ion accumulates into the soil and makes it infertile due to acidity. Similarly, repeated use of fertilizers containing KNO_3, $NaNO_3$ etc., causes accumulation of Na^+, K^+ and leads to alkalinity of the soil.
2. Soil is polluted by the cysts of entamoeba, ascaris, pigworm etc., which enter the food chain and infect human being.
3. The sewage containing human and animal excreta, solid and liquid wastes pollutes soil.
4. Spraying of insecticides and herbicides for fruits and vegetables also causes soil pollution. These also enter the food chain and thereby entering human and animal bodies. This can be taken care of by properly washing the vegetables, fruits, seeds with sufficient water before their intake.
5. Acid rain is also a source of soil pollution.
6. Soil erosion takes place due to deforestation, unplanned irrigation and defective methods of cultivation.

7. Soil is erroded due to removal of upper fertile layer.
8. Dumping of wastes from mines, power generation plants and metal smelting cause land pollution.
9. Radioactive wastes discharged from industrial and research centres cause pollution.
10. All sorts of chemicals in the atmosphere, plastic bodies ultimately lead to soil pollution.

Control of Soil Pollution

1. Control use of fertilizers and pesticides.
2. Before dumping the sewage the harmful chemicals should be removed.
3. Deforestation is to be minimised and plantation carried out.
4. Avoiding the spillage of garbage, ash, sludge, bottles, plastics etc.
5. Industrial waste to be treated properly before disposal.
6. Precaution to be taken to neutralise acid rain.
7. The waste gases releasing from automobiles and industries should be purified before reaching the ground.
8. The digging of larger pits or grooves in view of granite mines, aquaculture, addition of various chemicals to grow water bodies etc., are to be avoided to protect the soil pollution.

RADIOACTIVE POLLUTION

This is mainly due to (*i*) nuclear explosions, (*ii*) discharges from nuclear reactors.

They emit radiations which are harmful for living beings because they bring about changes in chromosomal DNAs and lead to genetic disorders, and diseases. These radio-nuclides are sometimes very short lived and sometimes persist for thousands of years and hence create both short time and long time hazards. These hazards are not confined to the explosion sites only because they are carried by air, water etc., by different routes to different parts of the earth and through the food chain they enter the biological processes.

Damages due to radioactive radiations include:

(*a*) Pathological damage—producing diseases leading to death also.

(*b*) Genetic damage—radiations lead to chromosomal damage to any living system causing permanent changes for generations.

(*c*) Radiations also cause loss of immunity, less enzymic activities and hence cause health problems.

Radioactive wastes can be:

(*a*) **High level wastes.** These wastes are predominantly used as fuel. They are intensely radioactive and some of them have long half-lives *e.g.,* Plutonium-239, half-life 24,000 years. Extreme precautions are to be taken to avoid such high level contamination in air, water etc.

(*b*) **Low level wastes.** These are related to nuclear energy production, wastes from uranium refineries.

Disposal of radioactive wastes

Accidents from radioactive rays have increased public concern worldwide to lead to safe disposal of these wastes. On-site storage of these wastes over short term and then final disposal for long term involve land, air and water.

1. **Ground** disposal is both cheap and easier. The wastes are either burried deep in the ground away from dwelling areas, in vacated coal-mines, in salt-heaps (salts absorb radioactive rays) inside mines. The areas for disposal should have low rainfall.

2. **Air.** Generally radioactive gases are stored in tanks, buried in the ground and finally vented to air so that there is low level of activity in the air, otherwise it may be inhaled and may enter the living system.
3. **Water.** For long term disposal ultimately the wastes are encased in non-corrosive lead, titanium or copper containers and burried deep into the ocean. It must be secured or it may affect the aquatic life, fishes and enter the food chain or enter the ground water.

Radionuclides

Radionuclides are the products of the natural decay of uranium. Uranium tailings contain a variety of radioactive atoms or radionuclides like, Ra-226, Th-230, Pb-210 etc.. Some of these have long half lives, *e.g.,* Th-230 has a half life of 80,000 years. Depending on the pH of the tailings, these nuclides become soluble and available.

The main exposure pathways for radioactivity from tailings are γ radiation, inhalation of radioactive particulates, radionuclides entering the food chain. There are more than 1000 radionuclides in the atmosphere. Both the long life and short life types of nuclides are of concern for public health problems. The table below indicates the active sites for and the half-life of different radionuclides.

Table 27.1. Some Important radionuclides and their half -lives

Radionuclide	*Target tissue*	*Half-life*
Calcium-45	Bone	165 days
Carbon-14	Whole body	5760 years
Caesium-137	Soft tissue, genital organs	27 years
Iodine-129	Thyroid	17 million years
Iodine-131	Thyroid	8 days
Plutonium-239	Bone, liver, spleen	24,400 years
Radium-226	Bone	1620 years
Strontium-90	Bone	28 years
Tritium (^{3}H)	Whole body	12.3 years

NOISE POLLUTION

Discomfort caused by hearing unpleasant, undesirable sound at wrong places and at wrong times is called "noise pollution". Noise pollution is expressed in Decibel units (dB). The smallest sound unit audible and undisturbing to a healthy person having good hearing capacity is "one decibel".

Crowded cities, mechanised transport, heavy industries, modes of entertainment cause noise pollution.

Sources of Sound Pollution

Heavy automobiles, scooters, trains, aeroplanes, horns, sirens, factories, loud speakers, radio, TV, air conditioners, generators, different functions and meetings are the different sources of noise pollution.

WHO has recommended that a person can sleep upto 35 dB noise, 75 dB is the explosive limit, 80 dB is harmful, damaging the hearing system.

Effects of Noise Pollution on Man

1. Noise pollution causes discomfort and loss of efficiency.
2. Prolonged exposure is harmful for central nervous system and affects memory.
3. Noise pollution causes increase in heart rate, damage to brain, kidney, liver.
4. Creates emotional disturbances.
5. Partial or permanent hearing loss.
6. Dilatation of pupil of eyes.
7. Creates headache.
8. Decreases working efficiency.
9. Disturbs sleep.
10. Leads to violence, tiredness, decreased colour perception, depression etc.
11. High pitched noise leads to road accidents.
12. Leads to hyper and hypoglycaemia, hypokalaemia, eosinophilia due to change in blood and body fluids.

Control of Noise Pollution

1. Noise pollution due to automobiles can be minimised by fitting silencers.
2. Setting industries away from residential areas.
3. Restricting the use of loud speakers.
4. Imposing laws to control noise.
5. Planting Ashok, Neem, Eucalyptus trees on both sides of highways, beside school, college, industrial buildings.
6. The walls of living houses, office buildings, cinema halls should be covered with sound absorbers.
7. Noise creating machinery should either be lubricated regularly or covered with insulating materials.
8. Wearing of earplugs, ear muffs for workers and others to minimise noise effects.

THERMAL POLLUTION

The release of hot vapours from nuclear power plants, industrial effluents, nuclear reactors, coal fired power plants, hydroelectric plants raises the atmospheric temperature and causes thermal pollution. Hence due to thermal pollution the average temperature of cities are about 10°C higher than the villages. The dissolved oxygen concentration of water bodies becomes low due to rise in temperature. This in turn causes harm to fishes, aquatic plants and to aerobic aquatic microorganisms.

By the combustion of coal and petroleum products CO_2 concentration in atmosphere increases which results increased temperature of the earth and green-house effect.

Highlights:

(*i*) **Sources of water pollution**

- Domestic sewage
- Industrial effluents
- Agricultural discharges containing pesticides etc.
- Oils, greases from automobiles, machines.
- Radioactive wastes.

(*ii*) **Municipal sewage treatment**

1. Preliminary mechanical filtration
2. Settling in sedimentation tanks
3. Biological treatment
   (*a*) Aerobic process involving (*i*) Trickling filters, (*ii*) Oxidation ponds, and (*iii*) Activated sludge process
   (*b*) Anaerobic process.

(*iii*) **Other types of pollution**

- Soil or Land Pollution
- Radioactive Pollution
- Noise Pollution
- Thermal Pollution

(*iv*) **BOD**

- Biological oxygen demand is the amount of free O_2 in mg required for the biological oxidation of the organic matter present in 1 litre of sewage.

(*v*) **COD**

- Chemical oxygen demand is a measure of oxidisable impurities present in sewage.

SHORT QUESTIONS AND ANSWERS

Q. 1. What is Pollution?

Ans. See text page no. 571.

Q. 2. What are the principal causes of pollution?

Ans. (*i*) Population explosion.

(*ii*) Rapid urbanization.

(*iii*) Rapid industrialization.

(*iv*) Deforestation.

(*v*) Natural disasters.

Q. 3. What are the undesirable effects of excess of oxides of sulfur in the atmosphere?

Ans. See text page no. 572.

Q. 4. What is acid rain?

Ans. The oxides of sulfur and nitrogen formed due to air pollution dissolve in the moisture present in the atmosphere to form the corresponding acids, which fall with the rain slowly on earth and lowers the pH of the rain water below pH = 5.

Q. 5. What is green-house effect?

Ans. Gases such as CO_2, CH_4, NO etc., do not allow the radiating infrared rays from the earth's surface to pass through thereby increasing the atmospheric temperature of the earth which is called green-house effect. This leads to about 0.05°C rise of temperature per year.

Q. 6. What is the importance of ozone layer?

Ans. Ozone at an elevation of 30 km from the earth's surface absorbs the most harmful UV radiation coming from the sun and thereby protects the living beings on earth.

Q. 7. What are the causes of 'ozone hole'?

Ans. Chlorofluorocarbons coming out from the exhaust of the supersonic jets and from the refrigerators, aerosols etc., lead to the breakdown of ozone into oxygen by a chain reaction and cause the depletion and thereby formation of ozone hole over Antarctica.

Q. 8. What is photochemical smog? Mention its effects.

Ans. See text page no. 575.

Q. 9. What are effects of particulate matter on human?

Ans. Presence of excessive particulate matter in air leads to allergy and respiratory diseases in human. The two most common diseases taking place are bronchial asthma and lung cancer.

Q. 10. What is sewage?

Ans. The liquid waste, which includes human and household waters, industrial wastes, street washing ground wastes containing mainly water and other organic and inorganic matters is called sewage.

Q. 11. What is BOD?

Ans. The amount of free oxygen in mg required for the biological oxidation of the organic matter present in 1 litre of sewage is called its biological oxygen demand (BOD).

Q. 12. What is COD?

Ans. Chemical oxygen demand (COD) is a measure of oxidisable impurities present in sewage.

Q. 13. What is the importance of BOD or COD measurement?

Ans. BOD or COD is very important in sewage treatment since it indicates the amount of oxidisable organic matter present in the sewage. Hence greater the value of BOD, higher is the pollution level of the sewage.

Q. 14. What is 'water table' and how does it fall?

Ans. The depth in the soil below which soil is filled with bed of water only.

The water table falls when the rate of pumping out of water is greater than the rate of rainwater percolation.

Q. 15. How is reforestation important in controlling atmospheric pollution?

Ans. Plants utilize the CO_2 of air for their photosynthesis and give out O_2 in the air, thereby reducing the load of CO_2 in air and enriching it with O_2.

Moreover, air flowing through the trees in the forests slows down leading to deposition of particulate matters carried by the air.

Q. 16. How can we decrease the lead pollution due to automobiles?

Ans. Lead pollution due to the automobiles can be decreased by using unleaded petrol as fuel.

Q. 17. What is eutrophication?

Ans. Algae in rivers, lakes multiply rapidly by fertilizers from farmland or by nutrients from sewage. Thus formed thick layers of algae block out the light to plants growing below the surface so that they can no more produce oxygen, and aquatic life becomes endangered. The phenomenon is known as eutrophication.

EXERCISES

1. Mention the harmful effects of the air pollutants: SO_2 and CO.

2. What is green-house effect? Name a few green-house gases.

3. What is the difference between aerobic and anaerobic oxidations of sewage?

4. Describe the activated sludge process for treatment of sewage.

5. What are BOD and COD? Indicate their significance in sewage treatment.

6. Write down the principles involved in the determination of BOD and COD.

7. Explain the cause of depletion of ozone layer. Why is the ozone layer important for us?

8. Write the sources of radioactive pollution. How can it be controlled?

9. Write notes on:

(*i*) Trickling filter method.
(*ii*) Electrostatic precipitator and its use.
(*iii*) Activated sludge process.
(*iv*) Acid rain.
(*v*) Photochemical smog.
(*vi*) Cyclone separator.

10. What is noise pollution? How can it be minimised?

11. What are the sources of water and soil pollution?

12. Explain (*a*) Pollution control can be effected by reforestation (*b*) BOD is the measure of pollution of water.

13. State the measures to be taken to control:

(*a*) Air pollution (*b*) Water pollution (*c*) Noise pollution
(*d*) Soil pollution (*e*) Radioactive pollution.

14. Discuss the methods of municipal sewage treatment.

15. How can pollution from internal combustion engines be controlled?