Unit

1

The Solid State

Objectives

After studying this Unit, you will be able to

- describe general characteristics of solid state;
- distinguish between amorphous and crystalline solids;
- classify crystalline solids on the basis of the nature of binding forces;
- define crystal lattice and unit cell;
- explain close packing of particles;
- describe different types of voids and close packed structures;
- calculate the packing efficiency of different types of cubic unit cells;
- correlate the density of a substance with its unit cell properties;
- describe the imperfections in solids and their effect on properties;
- correlate the electrical and magnetic properties of solids and their structure.

The vast majority of solid substances like high temperature superconductors, biocompatible plastics, silicon chips, etc. are destined to play an ever expanding role in future development of science.

We are mostly surrounded by solids and we use them more often than liquids and gases. For different applications we need solids with widely different properties. These properties depend upon the nature of constituent particles and the binding forces operating between them. Therefore, study of the structure of solids is important. The correlation between structure and properties helps in discovering new solid materials with desired properties like high temperature superconductors, magnetic materials, biodegradable polymers for packaging, biocompliant solids for surgical implants, etc.

From our earlier studies, we know that liquids and gases are called *fluids* because of their ability to flow. The fluidity in both of these states is due to the fact that the molecules are free to move about. On the contrary, the constituent particles in solids have fixed positions and can only oscillate about their mean positions. This explains the rigidity in solids. In crystalline solids, the constituent particles are arranged in regular patterns.

In this Unit, we shall discuss different possible arrangements of particles resulting in several types of structures. The correlation between the nature of interactions within the constituent particles and several properties of solids will also be explored. How these properties get modified due to the structural imperfections or by the presence of impurities in minute amounts would also be discussed.

1.1 General Characteristics of Solid State

In Class XI you have learnt that matter can exist in three states namely, solid, liquid and gas. Under a given set of conditions of temperature and pressure, which of these would be the most stable state of a given substance depends upon the net effect of two opposing factors. Intermolecular forces tend to keep the molecules (or atoms or ions) closer, whereas thermal energy tends to keep them apart by making them move faster. At sufficiently low temperature, the thermal energy is low and intermolecular forces bring them so close that they cling to one another and occupy fixed positions. These can still oscillate about their mean positions and the substance exists in solid state. The following are the characteristic properties of the solid state:

(i) They have definite mass, volume and shape.
(ii) Intermolecular distances are short.
(iii) Intermolecular forces are strong.
(iv) Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.
(v) They are incompressible and rigid.

1.2 Amorphous and Crystalline Solids

Solids can be classified as *crystalline* or *amorphous* on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids. An amorphous solid (Greek *amorphos* = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only *short range order*. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only. Such portions are scattered and in between the arrangement is disordered. The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig. 1.1 (a) and (b) respectively. While the two structures are almost identical, yet in the case of amorphous quartz glass there is no *long range order*. The structure of amorphous solids is similar to that of liquids. Glass, rubber and plastics are typical examples of amorphous solids. Due to the differences in the arrangement of the constituent particles, the two types of solids differ in their properties.

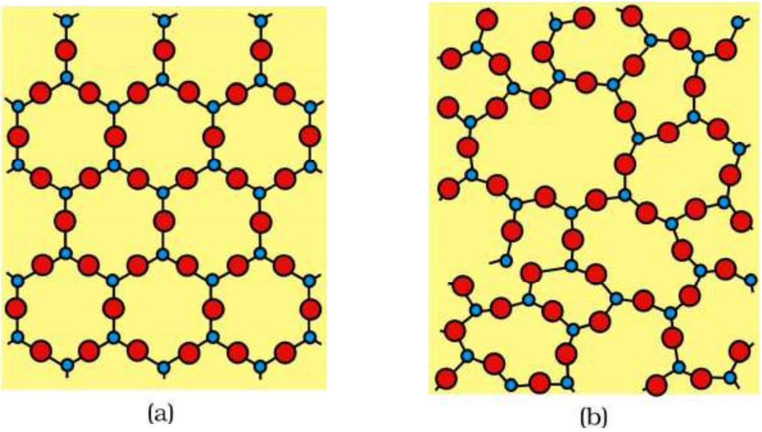

(a) (b)

***Fig. 1.1:** Two dimensional structure of (a) quartz and (b) quartz glass*

Crystalline solids have a sharp melting point. On the other hand, amorphous solids soften over a range of temperature and can be moulded and blown into various shapes. On heating they become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called *pseudo solids* or *super cooled liquids*. Glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

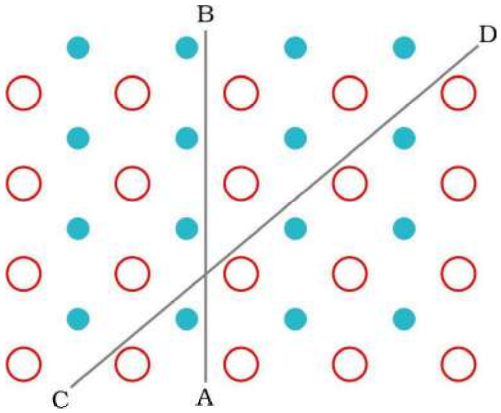


Fig. 1.2: *Anisotropy in crystals is due to different arrangement of particles along different directions.*

Crystalline solids are *anisotropic* in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions. This is illustrated in Fig. 1.2. Since the arrangement of particles is different along different directions, the value of same physical property is found to be different along each direction.

Amorphous solids on the other hand are *isotropic* in nature. It is because there is no *long range* order in them and arrangement is irregular along all the directions. Therefore, value of any physical property would be same along any direction. These differences are summarised in Table 1.1.

Table 1.1: Distinction between Crystalline and Amorphous Solids

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order.

Amorphous solids are useful materials. Glass, rubber and plastics find many applications in our daily lives. Amorphous silicon is one of the best photovoltaic material available for conversion of sunlight into electricity.

Intext Questions

1.1 Why are solids rigid?

1.2 Why do solids have a definite volume?

1.3 Classify the following as amorphous or crystalline solids: Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper.

1.4 Why is glass considered a super cooled liquid?

1.5 Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property?

1.3 Classification of Crystalline Solids

In Section 1.2, we have learnt about amorphous substances and that they have only short range order. However, most of the solid substances are crystalline in nature. For example, all the metallic elements like iron, copper and silver; non – metallic elements like sulphur, phosphorus and iodine and compounds like sodium chloride, zinc sulphide and naphthalene form crystalline solids.

Crystalline solids can be classified on the basis of nature of intermolecular forces operating in them into four categories viz., molecular, ionic, metallic and covalent solids. Let us now learn about these categories.

1.3.1 Molecular Solids

Molecules are the constituent particles of molecular solids. These are further sub divided into the following categories:

(i) *Non polar Molecular Solids*: They comprise of either atoms, for example, argon and helium or the molecules formed by non polar covalent bonds for example H_2, Cl_2 and I_2. In these solids, the atoms or molecules are held by weak dispersion forces or London forces about which you have learnt in Class XI. These solids are soft and non-conductors of electricity. They have low melting points and are usually in liquid or gaseous state at room temperature and pressure.

(ii) *Polar Molecular Solids*: The molecules of substances like HCl, SO_2, *etc.* are formed by polar covalent bonds. The molecules in such solids are held together by relatively stronger dipole-dipole interactions. These solids are soft and non-conductors of electricity. Their melting points are higher than those of non polar molecular solids yet most of these are gases or liquids under room temperature and pressure. Solid SO_2 and solid NH_3 are some examples of such solids.

(iii) *Hydrogen Bonded Molecular Solids*: The molecules of such solids contain polar covalent bonds between H and F, O or N atoms. Strong hydrogen bonding binds molecules of such solids like H_2O (ice). They are non-conductors of electricity. Generally they are volatile liquids or soft solids under room temperature and pressure.

1.3.2 Ionic Solids

Ions are the constituent particles of ionic solids. Such solids are formed by the three dimensional arrangements of cations and anions bound by strong coulombic (electrostatic) forces. These solids are hard and brittle in nature. They have high melting and boiling points. Since the ions are not free to move about, they are electrical insulators in the solid state. However, in the molten state or when dissolved in water, the ions become free to move about and they conduct electricity.

1.3.3 Metallic Solids

Metals are orderly collection of positive ions surrounded by and held together by a sea of free electrons. These electrons are mobile and are evenly spread out throughout the crystal. Each metal atom contributes one or more electrons towards this sea of mobile electrons. These free and mobile electrons are responsible for high electrical and thermal conductivity of metals. When an electric field is applied, these electrons flow through the network of positive ions. Similarly, when heat is supplied to one portion of a metal, the thermal energy is uniformly spread throughout by free electrons. Another important characteristic of metals is their lustre and colour in certain cases. This is also due to the presence of free electrons in them. Metals are highly malleable and ductile.

1.3.4 Covalent or Network Solids

A wide variety of crystalline solids of non-metals result from the formation of covalent bonds between adjacent atoms throughout the crystal. They are also called **giant molecules**. Covalent bonds are strong and directional in nature, therefore atoms are held very strongly at their positions. Such solids are very hard and brittle. They have extremely high melting points and may even decompose before melting. They are insulators and do not conduct electricity. Diamond (Fig. 1.3) and silicon carbide are typical examples of such solids. Graphite is soft and a conductor of electricity. Its exceptional properties are due to its typical structure (Fig. 1.4). Carbon atoms are arranged in different layers and each atom is covalently bonded to three of its neighbouring atoms in the same layer. The fourth valence electron of each atom is present between different layers and is free to move about. These free electrons make graphite a good conductor of electricity. Different layers can slide one over the other. This makes graphite a soft solid and a good solid lubricant.

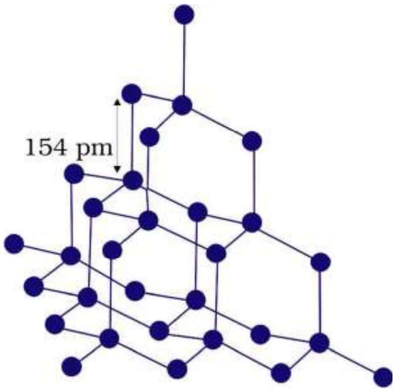


Fig. 1.3: *Network structure of diamond*

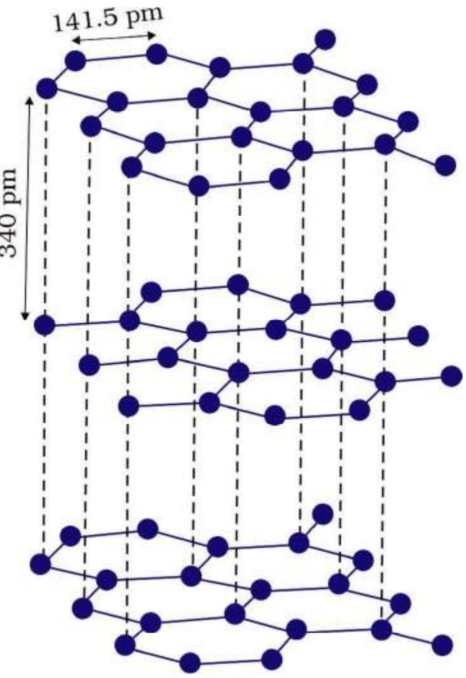


Fig. 1.4: *Structure of graphite*

The different properties of the four types of solids are listed in Table 1.2.

Table 1.2: Different Types of Solids

Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
(1) Molecular solids						
(i) Non polar	Molecules	Dispersion or London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very low
(ii) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
(2) Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
(4) Covalent or network solids	Atoms	Covalent bonding	SiO_2 (quartz), SiC, C (diamond), AlN,	Hard	Insulators	Very high
			$C_{(graphite)}$	Soft	Conductor (exception)	

Intext Questions

1.6 Classify the following solids in different categories based on the nature of intermolecular forces operating in them:

Potassium sulphate, tin, benzene, urea, ammonia, water, zinc sulphide, graphite, rubidium, argon, silicon carbide.

1.7 Solid A is a very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it?

1.8 Ionic solids conduct electricity in molten state but not in solid state. Explain.

1.9 What type of solids are electrical conductors, malleable and ductile?

1.4 Crystal Lattices and Unit Cells

The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called *crystal lattice*. Thus, a regular three dimensional arrangement of points in space is called a **crystal lattice**. A portion of a crystal lattice is shown in Fig. 1.5.

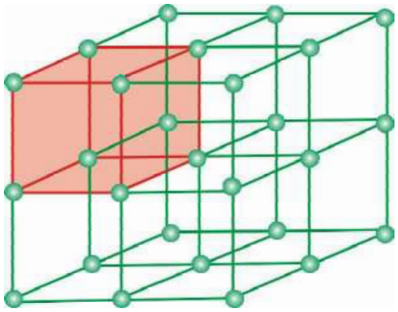


Fig. 1.5: *A portion of a three dimensional cubic lattice and its unit cell.*

There are only 14 possible three dimensional lattices. These are called **Bravais Lattices** (after the French mathematician who first described them). The following are the characteristics of a crystal lattice:

(a) Each point in a lattice is called lattice point or lattice site.

(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

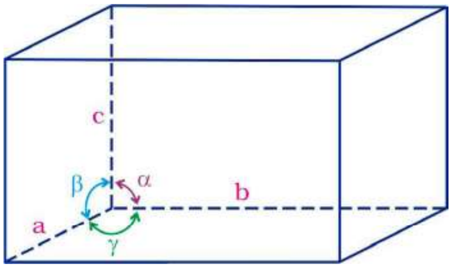


Fig. 1.6: *Illustration of parameters of a unit cell*

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterised by:

(i) its dimensions along the three edges, *a*, *b* and *c*. These edges may or may not be mutually perpendicular.

(ii) angles between the edges, α (between *b* and *c*) β (between *a* and *c*) and γ (between *a* and *b*). Thus, a unit cell is characterised by six parameters, *a*, *b*, *c*, α, β and γ.

These parameters of a typical unit cell are shown in Fig. 1.6.

1.4.1 Primitive and Centred Unit Cells

Unit cells can be broadly divided into two categories, primitive and centred unit cells.

(a) Primitive Unit Cells

When constituent particles are present only on the corner positions of a unit cell, it is called as **primitive unit cell**.

(b) Centred Unit Cells

When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a **centred unit cell**. Centred unit cells are of three types:

(i) *Body-Centred Unit Cells:* Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.

(ii) *Face-Centred Unit Cells:* Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.

(iii) *End-Centred Unit Cells:* In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

In all, there are seven types of primitive unit cells (Fig. 1.7).

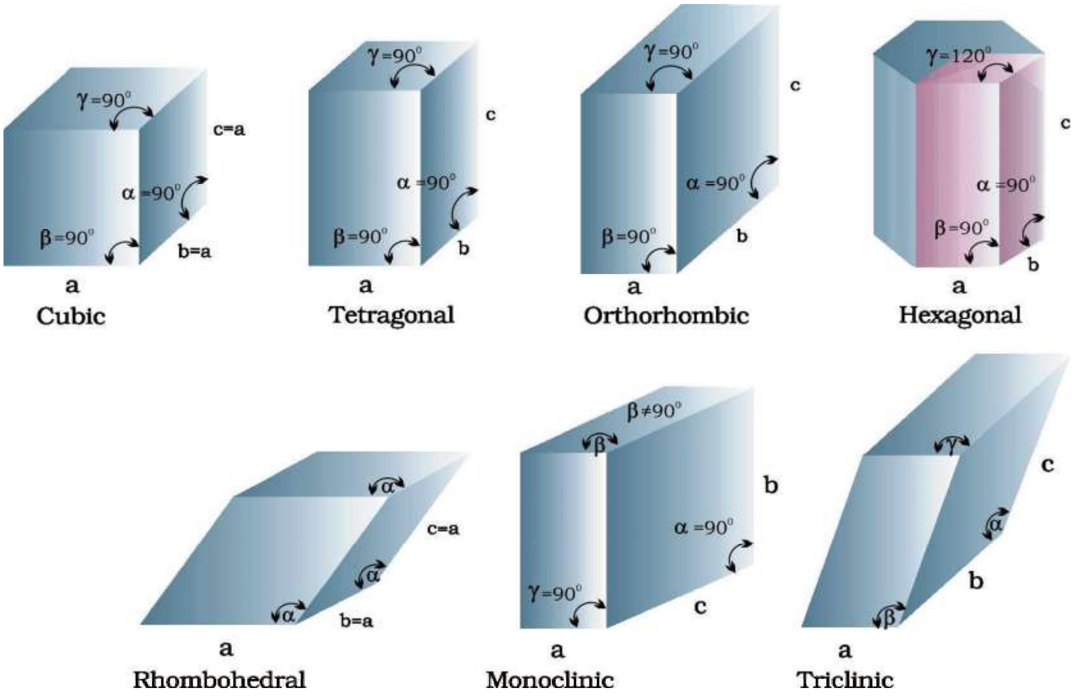


Fig. 1.7: *Seven primitive unit cells in crystals*

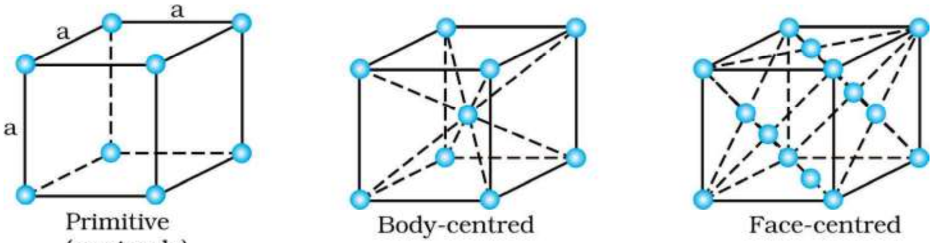
Their characteristics along with the centred unit cells they can form have been listed in Table 1.3.

Table 1.3: Seven Primitive Unit Cells and their Possible Variations as Centred Unit Cells

Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2, $CaSO_4$
Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	Graphite, ZnO,CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), HgS (cinnabar)

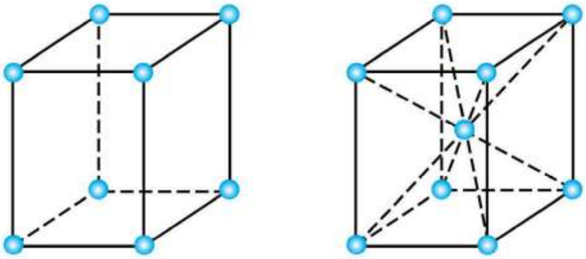
Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 90°$	Monoclinic sulphur, $Na_2SO_4.10H_2O$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4$. $5H_2O$, H_3BO_3

Unit Cells of 14 Types of Bravais Lattices



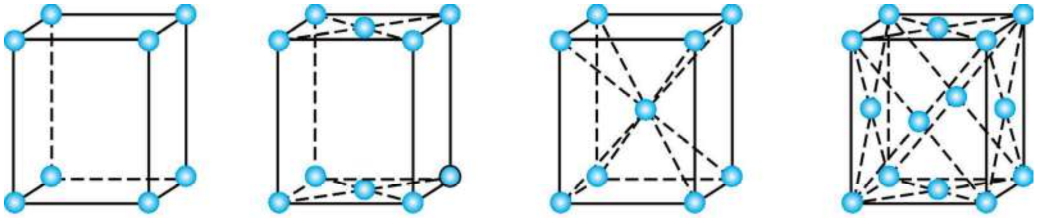
Primitive (or simple) Body-centred Face-centred

The three cubic lattices: all sides of same length, angles between faces all 90°



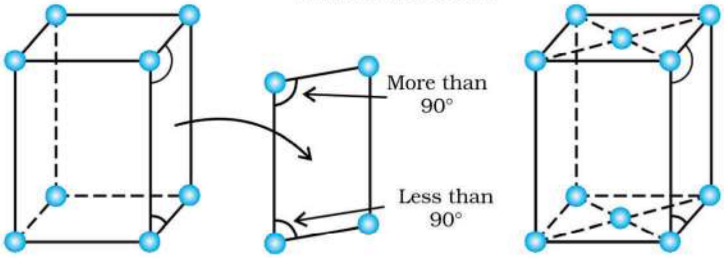
Primitive Body-centred

The two tetragonal: one side different in length to the other, two angles between faces all 90°



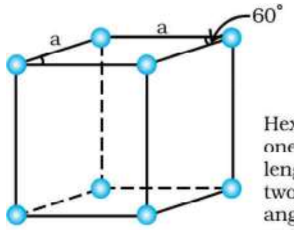
Primitive End-centred Body-centred Face-centred

The four orthorhombic lattices: unequal sides, angles between faces all 90°

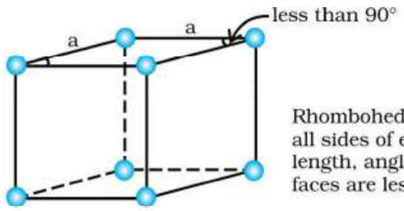


Primitive End-centred

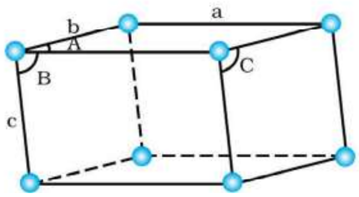
The two monoclinic lattices: unequal sides, two faces have angles different from 90°



Hexagonal lattice–
one side different in
length to the other
two, the marked
angles on two faces
are 60°



Rhombohedral lattice–
all sides of equal
length, angles on two
faces are less than 90°



Triclinic lattice–
unequal sides a, b, c,
A, B, C are unequal
angles with none equal to 90°

1.5 Number of Atoms in a Unit Cell

We know that any crystal lattice is made up of a very large number of unit cells and every lattice point is occupied by one constituent particle (atom, molecule or ion). Let us now work out what portion of each particle belongs to a particular unit cell.

We shall consider three types of cubic unit cells and for simplicity assume that the constituent particle is an atom.

1.5.1 Primitive Cubic Unit Cell

Primitive cubic unit cell has atoms only at its corner. Each atom at a corner is shared between eight adjacent unit cells as shown in Fig. 1.8, four unit cells in the same layer and four unit cells of the upper (or lower) layer. Therefore, only $\frac{1}{8}$ th of an atom (or molecule or ion) actually belongs to a particular unit cell. In Fig. 1.9, a primitive cubic unit cell has been depicted in three different ways. Each small sphere in Fig. 1.9 (a) represents only the centre of the particle occupying that position and not its actual size. Such structures are called *open structures*. The arrangement of particles is easier to follow in open structures. Fig. 1.9 (b) depicts space-filling representation of the unit cell with actual particle size and Fig. 1.9 (c) shows the actual portions of different atoms present in a cubic unit cell.

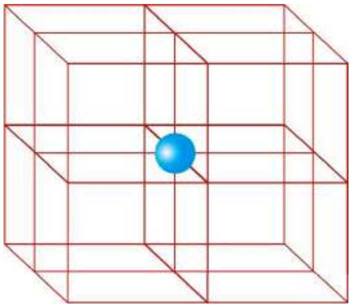


Fig. 1.8: *In a simple cubic unit cell, each corner atom is shared between 8 unit cells.*

In all, since each cubic unit cell has 8 atoms on its corners, the total number of atoms in one unit cell is $8 \times \frac{1}{8} = 1$ atom.

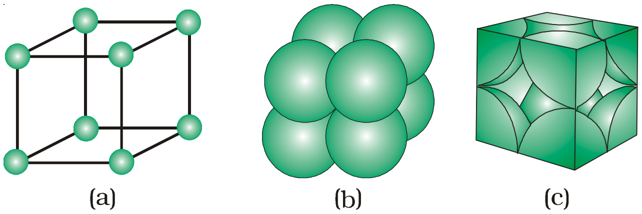

(a) (b) (c)

Fig. 1.9: *A primitive cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.*

1.5.2 Body-Centred Cubic Unit Cell

A body-centred cubic (*bcc*) unit cell has an atom at each of its corners and also one atom at its body centre. Fig. 1.10 depicts (a) open structure (b) space filling model and (c) the unit cell with portions of atoms actually belonging to it. It can be seen that the atom at the body centre wholly belongs to the unit cell in which it is present. Thus in a body-centered cubic (bcc) unit cell:

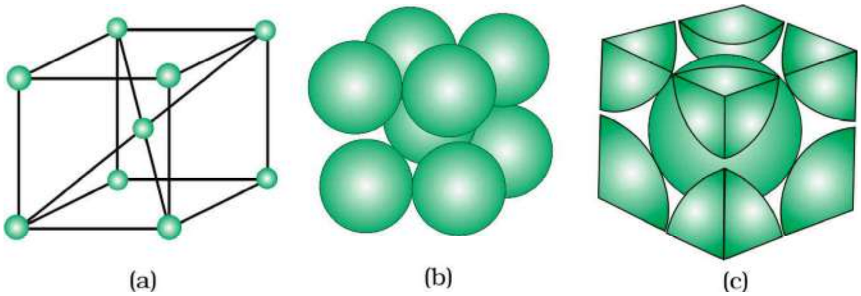


Fig. 1.10: *A body-centred cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.*

(i) 8 corners × $\frac{1}{8}$ per corner atom $= 8 \times \frac{1}{8}$ = 1 atom

(ii) 1 body centre atom = 1 × 1 = 1 atom

$\therefore$ Total number of atoms per unit cell = 2 atoms

1.5.3 Face-Centred Cubic Unit Cell

A face-centred cubic (*fcc*) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. It can be seen in Fig. 1.11 that each atom located at the face-centre is shared between two adjacent unit cells and only $\frac{1}{2}$ of each atom belongs to a unit cell. Fig. 1.12 depicts (a) open structure (b) space-filling model and (c) the unit cell with portions of atoms actually belonging to it. Thus, in a face-centred cubic (*fcc*) unit cell:

(i) 8 corners atoms × $\frac{1}{8}$ atom per unit cell $= 8 \times \frac{1}{8}$ = 1 atom

(ii) 6 face-centred atoms × $\frac{1}{2}$ atom per unit cell = 6 × $\frac{1}{2}$ = 3 atoms

$\therefore$ Total number of atoms per unit cell = 4 atoms

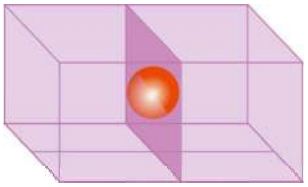


Fig. 1.11: *An atom at face centre of unit cell is shared between 2 unit cells*

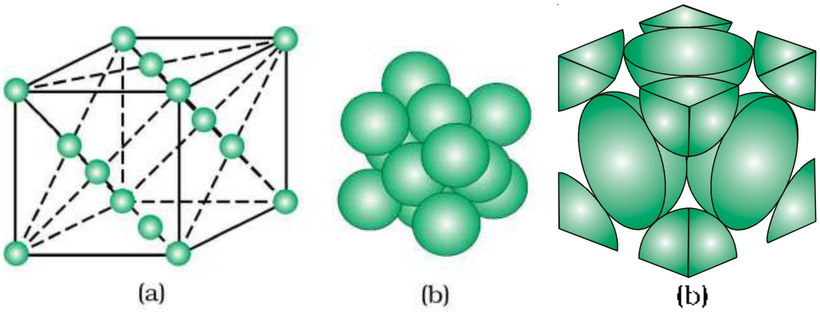


Fig 1.12: *A face-centred cubic unit cell (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell.*

Intext Questions

1.10 Give the significance of a 'lattice point'.

1.11 Name the parameters that characterise a unit cell.

1.12 Distinguish between

(i) Hexagonal and monoclinic unit cells

(ii) Face-centred and end-centred unit cells.

1.13 Explain how much portion of an atom located at (i) corner and (ii) body-centre of a cubic unit cell is part of its neighbouring unit cell.

1.6 Close Packed Structures

In solids, the constituent particles are close-packed, leaving the minimum vacant space. Let us consider the constituent particles as identical hard spheres and build up the three dimensional structure in three steps.

(a) Close Packing in One Dimension

There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange them in a row and touching each other (Fig. 1.13).

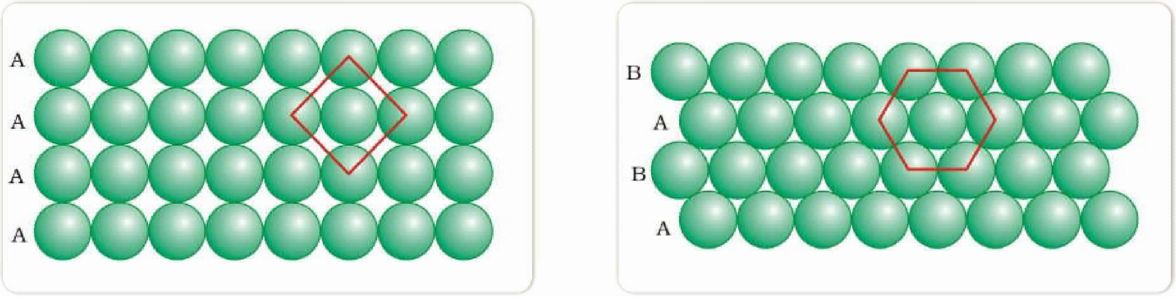
Fig. 1.13: *Close packing of spheres in one dimension*

In this arrangement, each sphere is in contact with two of its neighbours. The number of nearest neighbours of a particle is called its **coordination number**. Thus, in one dimensional close packed arrangement, the coordination number is 2.

(b) Close Packing in Two Dimensions

Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. This can be done in two different ways.

(i) The second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row. The spheres of the two rows are aligned horizontally as well as vertically. If we call the first row as 'A' type row, the second row being exactly the same as the first one, is also of 'A' type. Similarly, we may place more rows to obtain AAA type of arrangement as shown in Fig. 1.14 (a).



(a) (b)

Fig. 1.14: *(a) Square close packing (b) hexagonal close packing of spheres in two dimensions*

In this arrangement, each sphere is in contact with four of its neighbours. Thus, the two dimensional coordination number is 4. Also, if the centres of these 4 immediate neighbouring spheres are joined, a square is formed. Hence this packing is called **square close packing in two dimensions**.

(ii) The second row may be placed above the first one in a staggered manner such that its spheres fit in the depressions of the first row. If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type. When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also of 'A' type. The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type). Hence this arrangement is of ABAB type. In this arrangement there is less free space and this packing is more efficient than the square close packing. Each sphere is in contact with six of its neighbours and the two dimensional coordination number is 6. The centres of these six spheres are at the corners of a regular hexagon (Fig. 1.14b) hence this packing is called **two dimensional hexagonal close-packing.** It can be seen in Figure 1.14 (b) that in this layer there are some voids (empty spaces). These are triangular in shape. The triangular voids are of two different types. In one row, the apex of the triangles are pointing upwards and in the next layer downwards.

(c) Close Packing in Three Dimensions

All real structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other. In the last Section, we discussed close packing in two dimensions which can be of two types; square close-packed and hexagonal close-packed. Let us see what types of three dimensional close packing can be obtained from these.

(i) *Three dimensional close packing from two dimensional square close-packed layers:* While placing the second square close-packed layer above the first we follow the same rule that was followed when one row was placed adjacent to the other. The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically as shown in Fig. 1.15. Similarly, we may place more layers one above the other. If the arrangement of spheres in the first layer is called 'A' type, all the layers have the same arrangement. Thus this lattice has AAA.... type pattern. The lattice thus generated is the simple cubic lattice, and its unit cell is the primitive cubic unit cell (See Fig. 1.9).

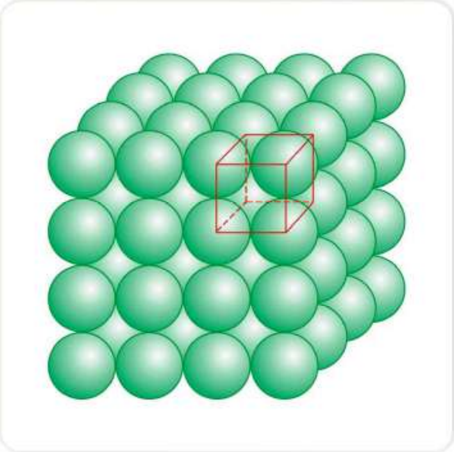


Fig. 1.15: *Simple cubic lattice formed by A A A .... arrangement*

(ii) *Three dimensional close packing from two dimensional hexagonal close packed layers:* Three dimensional close packed structure can be generated by placing layers one over the other.

(a) Placing second layer over the first layer

Let us take a two dimensional hexagonal close packed layer 'A' and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer. Since the spheres of the two layers are aligned differently, let us call the second layer as B. It can be observed from Fig. 1.16 that not all the triangular voids of the first layer are covered by the spheres of the second layer. This gives rise to different arrangements. Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed. These voids are called **tetrahedral voids** because a *tetrahedron* is formed when the centres of these four spheres are joined. They have been marked as 'T' in Fig. 1.16. One such void has been shown separately in Fig. 1.17.

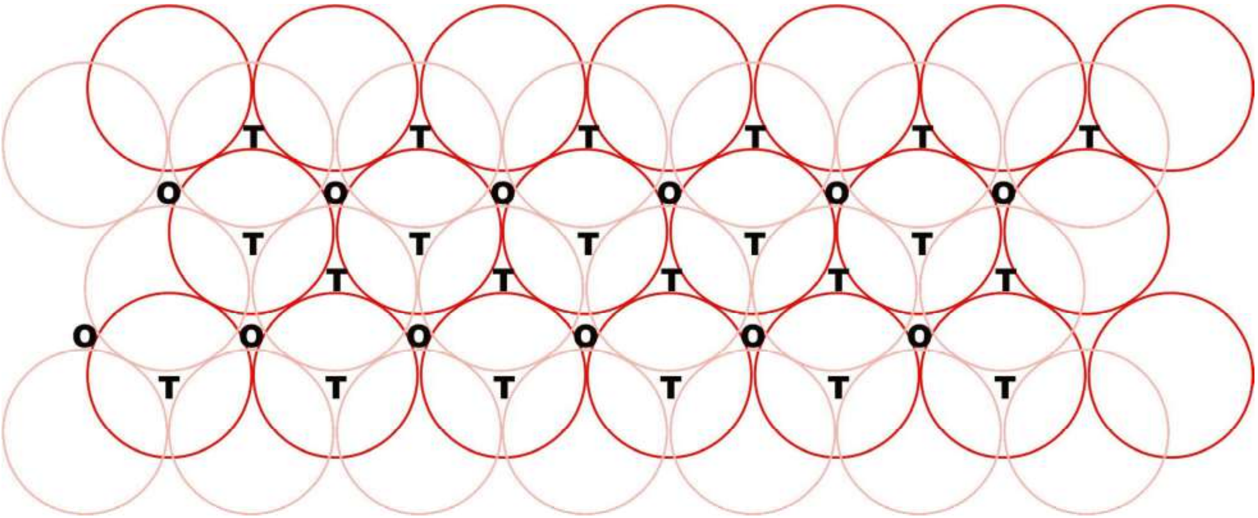
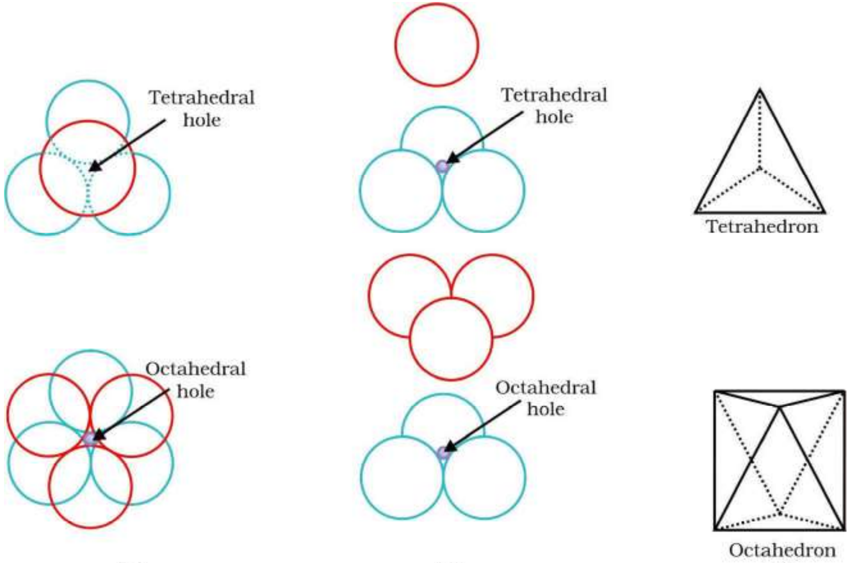


Fig. 1.16: *A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void*



(a) (b) (c)

Fig 1.17
Tetrahedral and octahedral voids
(a) top view
(b) exploded side view and
(c) geometrical shape of the void.

At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as 'O' in Fig. 1.16. Such voids are surrounded by six spheres and are called **octahedral voids.** One such void has been shown separately in Fig. 1.17. The number of these two types of voids depend upon the number of close packed spheres.

Let the number of close packed spheres be N, then:

The number of octahedral voids generated = N

The number of tetrahedral voids generated = $2N$

(b) Placing third layer over the second layer

When third layer is placed over the second, there are two possibilities.

(i) *Covering Tetrahedral Voids*: Tetrahedral voids of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB .... pattern. This structure is called hexagonal close packed (*hcp*) structure (Fig. 1.18). This sort of arrangement of atoms is found in many metals like magnesium and zinc.

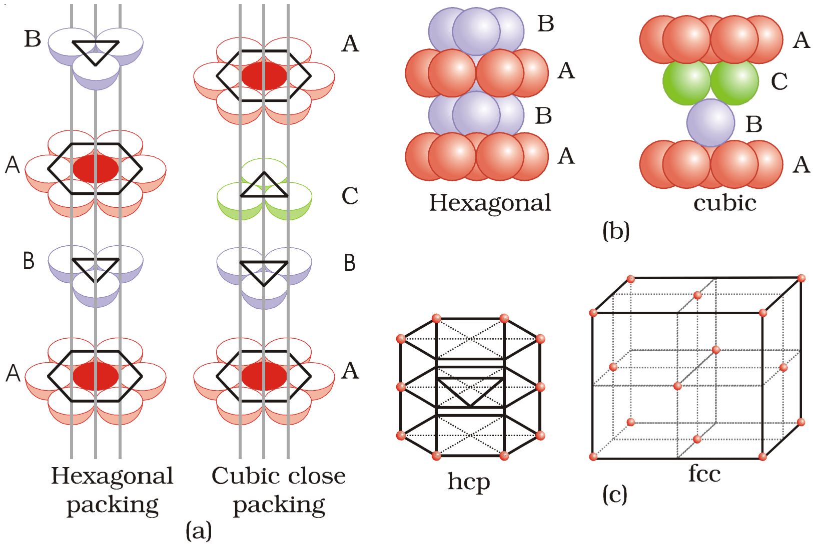


Fig. 1.18
(a) Hexagonal cubic close-packing exploded view showing stacking of layers of spheres (b) four layers stacked in each case and (c) geometry of packing.

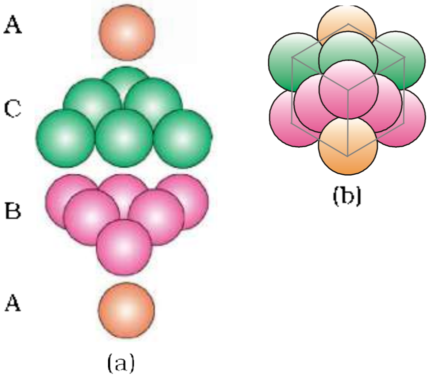


Fig. 1.19
(a) ABCABC... arrangement of layers when octahedral void is covered (b) fragment of structure formed by this arrangement resulting in cubic closed packed (ccp) or face centred cubic (fcc) structure.

(ii) *Covering Octahedral Voids*: The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called 'C' type. Only when fourth layer is placed, its spheres are aligned with those of the first layer as shown in Figs. 1.18 and 1.19. This pattern of layers is often written as ABCABC .... This structure is called cubic close packed (*ccp*) or face-centred cubic (*fcc*) structure. Metals such as copper and silver crystallise in this structure.

Both these types of close packing are highly efficient and 74% space in the crystal is filled. In either of them, each sphere is in contact with twelve spheres. Thus, the coordination number is 12 in either of these two structures.

1.6.1 Formula of a Compound and Number of Voids Filled

Earlier in the section, we have learnt that when particles are close-packed resulting in either *ccp* or *hcp* structure, two types of voids are generated. While the number of octahedral voids present in a lattice is equal to the number of close packed particles, the number of tetrahedral voids generated is twice this number. In ionic solids, the bigger ions (usually anions) form the close packed structure and the smaller ions (usually cations) occupy the voids. If the latter ion is small enough then tetrahedral voids are occupied, if bigger, then octahedral voids. Not all octahedral or tetrahedral voids are occupied. In a given compound, the fraction of octahedral or tetrahedral voids that are occupied, depends upon the chemical formula of the compound, as can be seen from the following examples.

Example

A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make *ccp* and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Solution

The *ccp* lattice is formed by the element Y. The number of octahedral voids generated would be equal to the number of atoms of Y present in it. Since all the octahedral voids are occupied by the atoms of X, their number would also be equal to that of the element Y. Thus, the atoms of elements X and Y are present in equal numbers or 1:1 ratio. Therefore, the formula of the compound is XY.

Example

Atoms of element B form *hcp* lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the elements A and B?

Solution

The number of tetrahedral voids formed is equal to twice the number of atoms of element B and only 2/3rd of these are occupied by the atoms of element A. Hence the ratio of the number of atoms of A and B is 2 × (2/3):1 or 4:3 and the formula of the compound is A_4B_3.

Locating Tetrahedral and Octahedral Voids

We know that close packed structures have both tetrahedral and octahedral voids. Let us take *ccp* (or *fcc*) structure and locate these voids in it.

(a) Locating Tetrahedral Voids

Let us consider a unit cell of *ccp* or *fcc* lattice [Fig. 1(a)]. The unit cell is divided into eight small cubes.

Each small cube has atoms at alternate corners [Fig. 1(a)]. In all, each small cube has 4 atoms. When joined to each other, they make a regular tetrahedron. Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total. Each of the eight small cubes have one void in one unit cell of *ccp* structure. We know that *ccp* structure has 4 atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms.

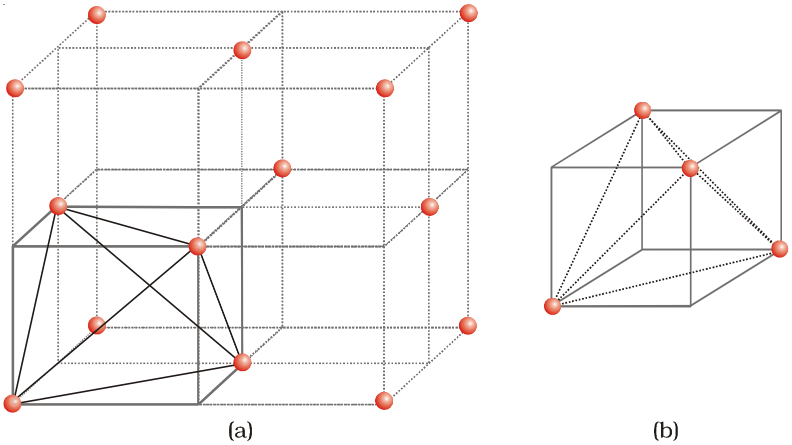


Fig. 1: *(a) Eight tetrahedral voids per unit cell of ccp structure (b) one tetrahedral void showing the geometry.*

(b) Locating Octahedral Voids

Let us again consider a unit cell of *ccp* or *fcc* lattice [Fig. 2(a)]. The body centre of the cube, C is not occupied but it is surrounded by six atoms on face centres. If these face centres are joined, an octahedron is generated. Thus, this unit cell has one octahedral void at the body centre of the cube.

Besides the body centre, there is one octahedral void at the centre of each of the 12 edges. [Fig. 2(b)]. It is surrounded by six atoms, four belonging to the same unit cell (2 on the corners and 2 on face centre) and two belonging to two adjacent unit cells. Since each edge of the cube is shared between four adjacent unit cells, so is the octahedral void located on it. Only $\frac{1}{4}^{\text{th}}$ of each void belongs to a particular unit cell.

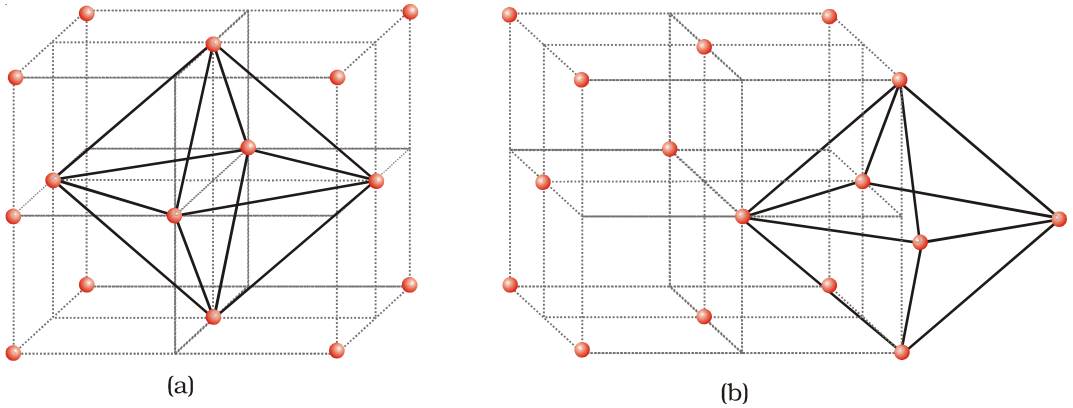


Fig. 2: *Location of octahedral voids per unit cell of ccp or fcc lattice (a) at the body centre of the cube and (b) at the centre of each edge (only one such void is shown).*

Thus in *cubic close packed structure*:

Octahedral void at the body-centre of the cube = 1

12 octahedral voids located at each edge and shared between four unit cells

$$= 12 \times \frac{1}{4} = 3$$

∴ Total number of octahedral voids = 4

We know that in ccp structure, each unit cell has 4 atoms. Thus, the number of octahedral voids is equal to this number.

1.7 Packing Efficiency

In whatever way the constituent particles (atoms, molecules or ions) are packed, there is always some free space in the form of voids. **Packing efficiency** is the percentage of total space filled by the particles. Let us calculate the packing efficiency in different types of structures.

1.7.1 Packing Efficiency in *hcp* and *ccp* Structures

Both types of close packing (*hcp* and *ccp*) are equally efficient. Let us calculate the efficiency of packing in ccp structure. In Fig. 1.20 let the unit cell edge length be 'a' and face diagonal AC = b.

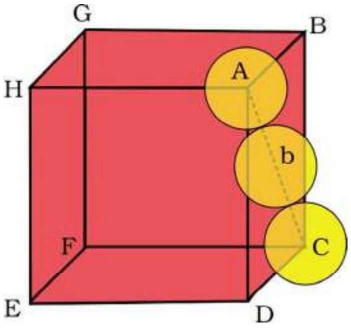


Fig. 1.20: *Cubic close packing other sides are not provided with spheres for sake of clarity.*

In Δ ABC

$AC^2 = b^2 = BC^2 + AB^2$

$= a^2 + a^2 = 2a^2$ or

$b = \sqrt{2}a$

If r is the radius of the sphere, we find

$b = 4r = \sqrt{2}a$

or $a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$

(we can also write, $r = \frac{a}{2\sqrt{2}}$)

We know, that each unit cell in ccp structure, has effectively 4 spheres. Total volume of four spheres is equal to $4 \times (4/3)\pi r^3$ and volume of the cube is a^3 or $(2\sqrt{2}r)^3$.

Therefore,

$$\text{Packing efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\%$$

$$= \frac{4 \times (4/3)\pi r^3 \times 100}{(2\sqrt{2}r)^3}\%$$

$$= \frac{(16/3)\pi r^3 \times 100}{16\sqrt{2}r^3}\% = 74\%$$

1.7.2 Efficiency of Packing in Body-Centred Cubic Structures

From Fig. 1.21, it is clear that the atom at the centre will be in touch with the other two atoms diagonally arranged.

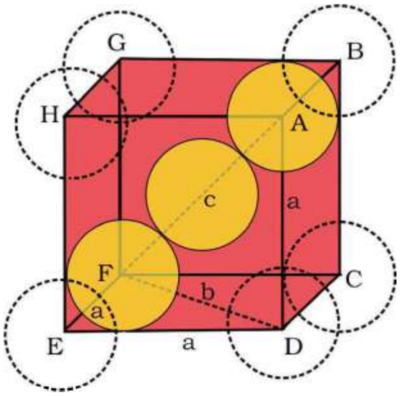


Fig. 1.21: Body-centred cubic unit cell (sphere along the body diagonal are shown with solid boundaries).

In Δ EFD,

$$b^2 = a^2 + a^2 = 2a^2$$

$$b = \sqrt{2}a$$

Now in Δ AFD

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

$$c = \sqrt{3}a$$

The length of the body diagonal c is equal to 4r, where r is the radius of the sphere (atom), as all the three spheres along the diagonal touch each other.

Therefore, $\sqrt{3}a = 4r$

$$a = \frac{4r}{\sqrt{3}}$$

Also we can write, $r = \frac{\sqrt{3}}{4}a$

In this type of structure, total number of atoms is 2 and their volume is $2 \times \left(\frac{4}{3}\right)\pi r^3$.

Volume of the cube, a^3 will be equal to $\left(\frac{4}{\sqrt{3}}r\right)^3$ or $a^3 = \left(\frac{4}{\sqrt{3}}r\right)^3$.

Therefore,

$$\text{Packing efficiency} = \frac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\%$$

$$= \frac{2 \times (4/3)\pi r^3 \times 100}{\left[\left(4/\sqrt{3}\right)r\right]^3}\%$$

$$= \frac{(8/3)\pi r^3 \times 100}{64/\left(3\sqrt{3}\right)r^3}\% = 68\%$$

1.7.3 Packing Efficiency in Simple Cubic Lattice

In a simple cubic lattice the atoms are located only on the corners of the cube. The particles touch each other along the edge (Fig. 1.22). Thus, the edge length or side of the cube 'a', and the radius of each particle, r are related as

$$a = 2r$$

The volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$

Since a simple cubic unit cell contains only 1 atom

The volume of the occupied space = $\frac{4}{3}\pi r^3$

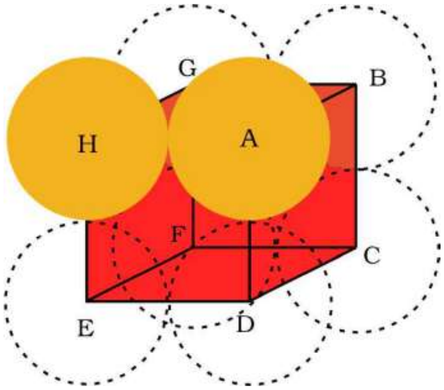


Fig. 1.22 *Simple cubic unit cell. The spheres are in contact with each other along the edge of the cube.*

∴ Packing efficiency

$$= \frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100\%$$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100$$

$$= 52.36\% = 52.4\ \%$$

Thus, we may conclude that *ccp* and *hcp* structures have maximum packing efficiency.

Calculations Involving Unit Cell Dimensions

From the unit cell dimensions, it is possible to calculate the volume of the unit cell. Knowing the density of the metal, we can calculate the mass of the atoms in the unit cell. The determination of the mass of a single atom gives an accurate method of determination of Avogadro constant. Suppose, edge length of a unit cell of a cubic crystal determined by X-ray diffraction is a, d the density of the solid substance and M the molar mass. In case of cubic crystal:

Volume of a unit cell = a^3

Mass of the unit cell

= number of atoms in unit cell × mass of each atom = $z \times m$

(Here z is the number of atoms present in one unit cell and m is the mass of a single atom)

Mass of an atom present in the unit cell:

$$m = \frac{M}{N_A} \ (M \text{ is molar mass})$$

Therefore, density of the unit cell

$$= \frac{\textit{mass of unit cell}}{\textit{volume of unit cell}}$$

$$= \frac{z.m}{a^3} = \frac{z.M}{a^3.N_A} \quad or \quad d = \frac{zM}{a^3 N_A}$$

Remember, the density of the unit cell is the same as the density of the substance. The density of the solid can always be determined by other methods. Out of the five parameters (d, z M, a and N_A), if any four are known, we can determine the fifth.

Example An element has a body-centred cubic *(bcc)* structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm^3. How many atoms are present in 208 g of the element?

Solution Volume of the unit cell = (288 pm)^3

$= (288\times10^{-12}\ \text{m})^3 = (288\times10^{-10}\ \text{cm})^3$

$= 2.39\times10^{-23}\ \text{cm}^3$

Volume of 208 g of the element

$$= \frac{mass}{density} = \frac{208g}{7.2\,g\,cm^{-3}} = 28.88\,cm^3$$

Number of unit cells in this volume

$$= \frac{28.88cm^3}{2.39\times10^{-23}\,cm^3\,/\,unit\ cell} = 12.08\times10^{23}\ \text{unit cells}$$

Since each *bcc* cubic unit cell contains 2 atoms, therefore, the total number of atoms in 208 g = 2 (atoms/unit cell) × 12.08 × 10^{23} unit cells

$= 24.16\times10^{23}$ atoms

Example

X-ray diffraction studies show that copper crystallises in an *fcc* unit cell with cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm^3, calculate the atomic mass of copper.

Solution

In case of *fcc* lattice, number of atoms per unit cell, z = 4 atoms

Therefore, $M = \dfrac{dN_Aa^3}{z}$

$$= \frac{8.92\,g\ cm^{-3}\times6.022\times10^{23}\ atoms\,mol^{-1}\times(3.608\times10^{-8}\,cm)^3}{4\,atoms}$$

= 63.1 g/mol

Atomic mass of copper = 63.1u

Example

Silver forms *ccp* lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic mass = 107.9 u).

Solution

Since the lattice is *ccp*, the number of silver atoms per unit cell = z = 4

Molar mass of silver = 107.9 g mol^{-1} = 107.9×10^{-3} kg mol^{-1}

Edge length of unit cell = a = 408.6 pm = 408.6×10^{-12} m

Density, $d = \dfrac{z.M}{a^3.N_A}$

$$= \frac{4\times\left(107.9\times10^{-3}\,kg\,mol^{-1}\right)}{\left(408.6\times10^{-12}\,m\right)^3\left(6.022\times10^{23}\,mol^{-1}\right)} = 10.5\times10^3\ kg\ m^{-3}$$

$= 10.5\ g\ cm^{-3}$

Intext Questions

1.14 What is the two dimensional coordination number of a molecule in *square close*-packed layer?

1.15 A compound forms *hexagonal close-packed* structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

1.16 A compound is formed by two elements M and N. The element N forms *ccp* and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

1.17 Which of the following lattices has the highest packing efficiency (i) simple cubic (ii) body-centred cubic and (iii) hexagonal close-packed lattice?

1.18 An element with molar mass 2.7×10^{-2} kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^{3} kg m^{-3}, what is the nature of the cubic unit cell?

1.9 Imperfections in Solids

Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. Usually a solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rate. Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of defects. The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, *point defects* and *line defects*. **Point defects** are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the *line defects* are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called *crystal defects*. We shall confine our discussion to point defects only.

1.9.1 Types of Point Defects

Point defects can be classified into three types : (i) stoichiometric defects (ii) impurity defects and (iii) non-stoichiometric defects.

(a) Stoichiometric Defects

These are the point defects that do not disturb the stoichiometry of the solid. They are also called *intrinsic* or **thermodynamic defects.** Basically these are of two types, vacancy defects and interstitial defects.

(i) *Vacancy Defect*: When some of the lattice sites are vacant, the crystal is said to have **vacancy defect** (Fig. 1.23). This results in decrease in density of the substance. This defect can also develop when a substance is heated.

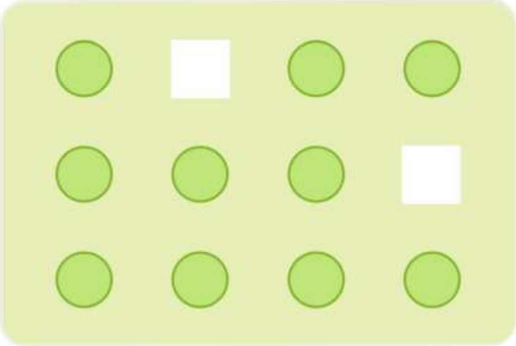


Fig. 1.23: *Vacancy defects*

(ii) *Interstitial Defect*: When some constituent particles (atoms or molecules) occupy an **interstitial** site, the crystal is said to have **interstitial defect** (Fig. 1.24). This defect increases the density of the substance.

Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as **Frenkel and Schottky defects.**

(iii) *Frenkel Defect*: This defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site (Fig. 1.25). It creates a *vacancy defect* at its original site and an **interstitial defect** at its new location.

Frenkel defect is also called **dislocation defect**. It does not change the density of the solid. Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^+ ions.

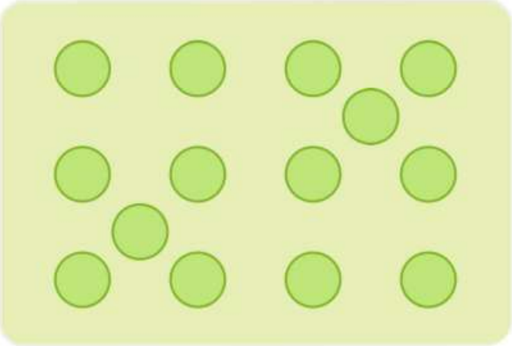


Fig. 1.24: *Interstitial defects*

(iv) *Schottky Defect*: It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (Fig. 1.26).

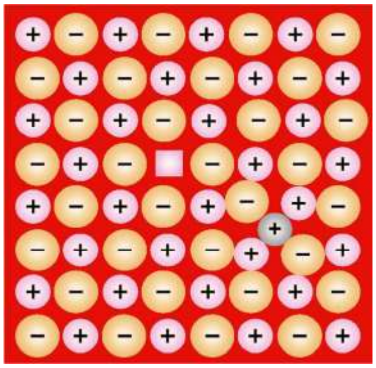


Fig. 1.25: *Frenkel defects*

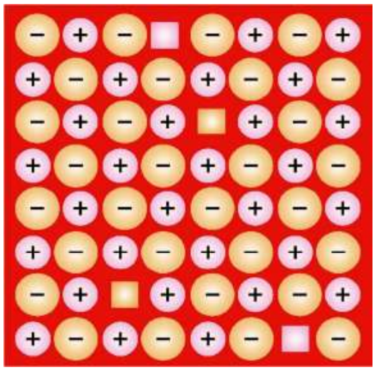


Fig. 1.26: *Schottky defects*

Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

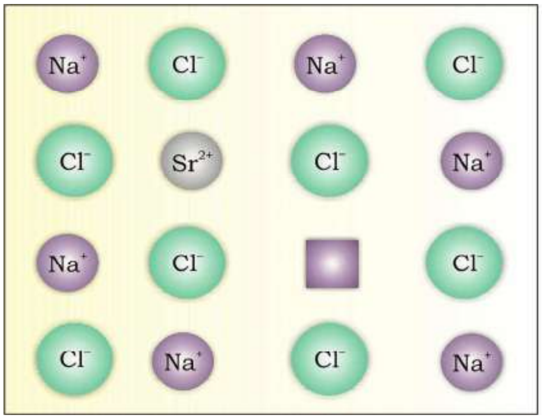


Fig. 1.27: *Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}*

(b) Impurity Defects

If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} (Fig. 1.27). Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions. Another similar example is the solid solution of $CdCl_2$ and AgCl.

(c) Non-Stoichiometric Defects

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) *Metal Excess Defect*

- *Metal excess defect due to anionic vacancies*: Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites (Fig. 1.28). As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called *F-centres* (from the German word *Farbenzenter* for colour centre). They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

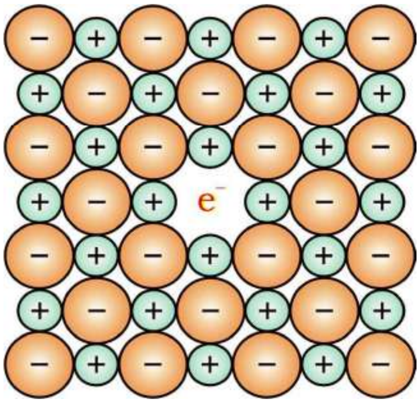


Fig. 1.28: *An F-centre in a crystal*

- *Metal excess defect due to the presence of extra cations at interstitial sites*: Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(ii) *Metal Deficiency Defect*

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of $Fe_{0.95}O$. It may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

Electrical Properties

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from 10^{-20} to 10^{7} ohm^{-1} m^{-1}. Solids can be classified into three types on the basis of their conductivities.

(i) *Conductors*: The solids with conductivities ranging between 10^4 to 10^7 ohm^{-1}m^{-1} are called conductors. Metals have conductivities in the order of 10^7 ohm^{-1}m^{-1} are good conductors.

(ii) *Insulators* : These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} ohm^{-1}m^{-1}.

(iii) *Semiconductors* : These are the solids with conductivities in the intermediate range from 10^{-6} to 10^{4} ohm^{-1}m^{-1}.

1.10.1 Conduction of Electricity in Metals

A conductor may conduct electricity through movement of electrons or ions. Metallic conductors belong to the former category and electrolytes to the latter.

Metals conduct electricity in solid as well as molten state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other as to form a **band.** If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity (Fig. 1.29 a).

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electrons cannot jump to it and such a substance has very small conductivity and it behaves as an insulator (Fig. 1.29 b).

1.10.2 Conduction of Electricity in Semi-conductors

In case of semiconductors, the gap between the valence band and conduction band is small (Fig. 1.29c). Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band. Substances like silicon and germanium show this type of behaviour and are called *intrinsic semiconductors*.

The conductivity of these intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called

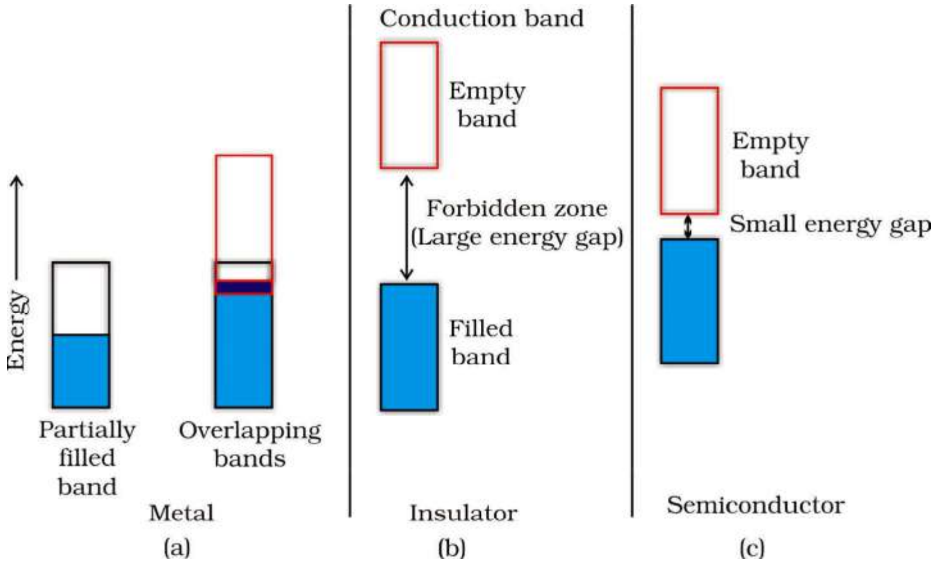


Fig. 1.29 Distinction among (a) metals (b) insulators and (c) semiconductors. In each case, an unshaded area represents a conduction band.

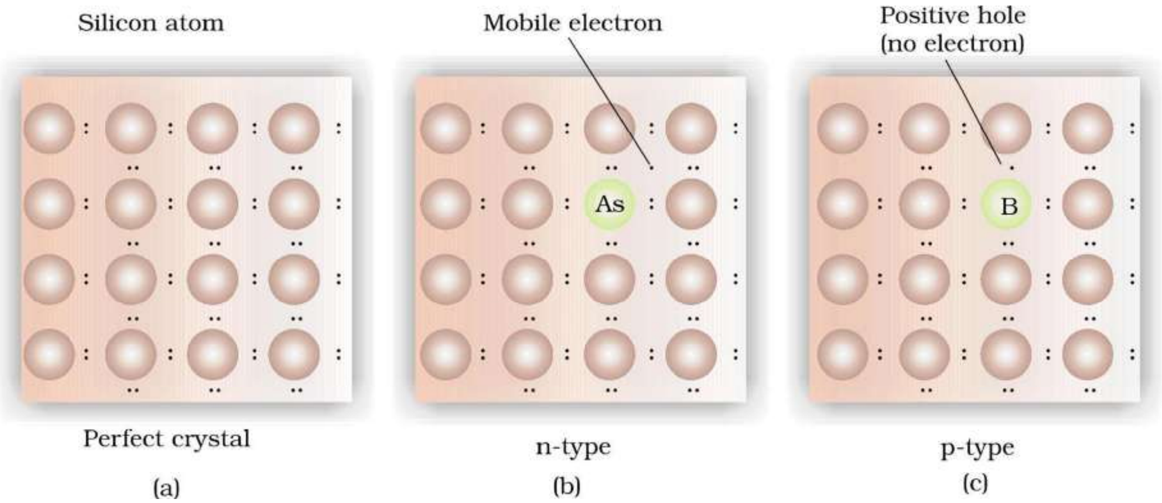
doping. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce *electronic defects* in them.

(a) Electron – rich impurities

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours (Fig. 1.30 a). When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal (Fig. 1.30 b). Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the *negatively* charged electron, hence silicon doped with electron-rich impurity is called *n*-type semiconductor.

(b) Electron – deficit impurities

Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called *electron hole* or *electron vacancy* (Fig. 1.30 c). An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semi conductors are called *p-type* semiconductors.



(a) (b) (c)

Fig. 1.30: *Creation of n-type and p-type semiconductors by doping groups 13 and 15 elements.*

Applications of n-type and p-type semiconductors

Various combinations of *n*-type and *p*-type semiconductors are used for making electronic components. *Diode* is a combination of *n*-type and *p*-type semiconductors and is used as a rectifier. Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. *npn* and *pnp* type of transistors are used to detect or amplify radio or audio signals. The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

Germanium and silicon are group 14 elements and therefore, have a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of groups 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13 – 15 are InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of groups 12 – 16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO_2 and ReO_3 behave like metals. Rhenium oxide, ReO_3 is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO_2, VO_3 and TiO_3 show metallic or insulating properties depending on temperature.

Magnetic Properties

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis (Fig. 1.31). Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called *Bohr magneton*, μ_B. It is equal to 9.27×10^{-24} A m^2.

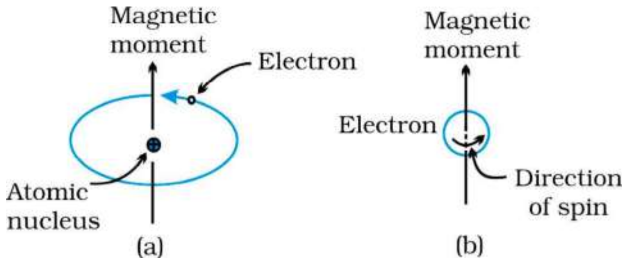


Fig.1.31: *Demonstration of the magnetic moment associated with (a) an orbiting electron and (b) a spinning electron.*

On the basis of their magnetic properties, substances can be classified into five categories: (i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic.

(i) *Paramagnetism*: Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} are some examples of such substances.

(ii) *Diamagnetism*: Diamagnetic substances are weakly repelled by a magnetic field. H_2O, NaCl and C_6H_6 are some examples of such substances. They are weakly magnetised in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

(iii) *Ferromagnetism*: A few substances like iron, cobalt, nickel, gadolinium and CrO_2 are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called *domains*. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field (Fig. 1.32 a) and a strong magnetic effect is produced. This ordering of domains persist even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

(iv) *Antiferromagnetism*: Substances like MnO showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment (Fig. 1.32 b).

(v) *Ferrimagnetism*: Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers (Fig. 1.32 c). They are weakly attracted by magnetic field as compared to ferromagnetic substances. Fe_3O_4 (magnetite) and ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$ are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.

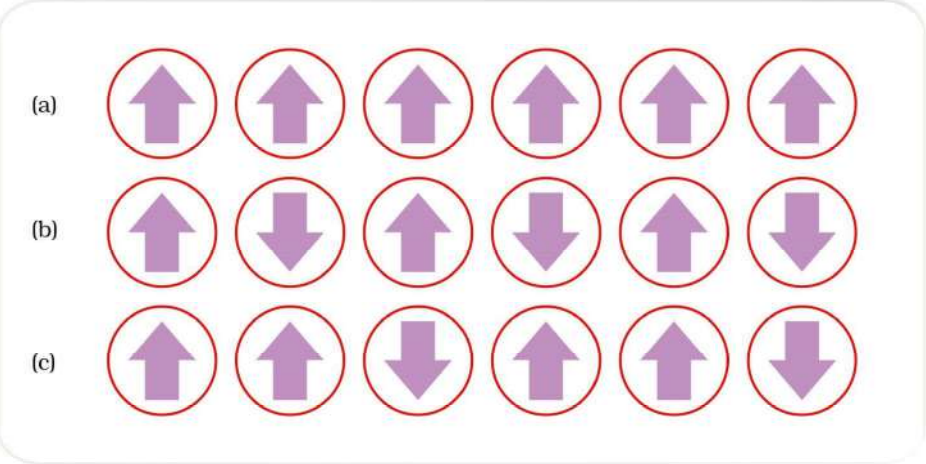


Fig 1.32: *Schematic alignment of magnetic moments in (a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic.*

Intext Questions

1.19 What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?

1.20 What type of stoichiometric defect is shown by:
(i) ZnS (ii) AgBr

1.21 Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.

1.22 Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.

1.23 A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?

1.24 What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic. Justify your answer.

Summary

Solids have definite mass, volume and shape. This is due to the fixed position of their constituent particles, short distances and strong interactions between them. In **amorphous** solids, the arrangement of constituent particles has only **short range order** and consequently they behave like **super cooled liquids**, do not have sharp melting points and are isotropic in nature. In crystalline solids there is long range order in the arrangement of their constituent particles. They have sharp melting points, are anisotropic in nature and their particles have characteristic shapes. Properties of **crystalline** solids depend upon the nature of interactions between their constituent particles. On this basis, they can be divided into four categories, namely: **molecular**, **ionic**, **metallic** and **covalent** solids. They differ widely in their properties.

The constituent particles in crystalline solids are arranged in a regular pattern which extends throughout the crystal. This arrangement is often depicted in the form of a three dimensional array of points which is called crystal lattice. Each **lattice point** gives the location of one particle in space. In all, fourteen different types of lattices are possible which are called **Bravais lattices**. Each lattice can be generated by repeating its small characteristic portion called **unit cell**. A unit cell is characterised by its edge lengths and three angles between these edges. Unit cells can be either **primitive** which have particles only at their corner positions or **centred**. The centred unit cells have additional particles at their body centre (**body-centred**), at the centre of each face (**face-centred**) or at the centre of two opposite faces (**end-centred**). There are seven types of **primitive unit** cells. Taking centred unit cells also into account, there are fourteen types of unit cells in all, which result in fourteen **Bravais lattices**.

Close-packing of particles result in two highly efficient lattices, **hexagonal close-packed** (**hcp**) and **cubic close-packed** (**ccp**). The latter is also called face-centred cubic (**fcc**) lattice. In both of these packings 74% space is filled. The remaining space is present in the form of two types of voids-octahedral voids and tetrahedral voids. Other types of packing are not close-packings and have less efficient packing of particles. While in **body-centred cubic lattice (bcc)** 68% space is filled, in simple cubic lattice only 52.4 % space is filled.

Solids are not perfect in structure. There are different types of **imperfections** or **defects** in them. Point defects and line defects are common types of defects. Point defects are of three types - **stoichiometric defects**, **impurity defects** and **non-stoichiometric defects**. **Vacancy defects** and **interstitial defects** are the two basic types of stoichiometric point defects. In ionic solids, these defects are present as **Frenkel** and **Schottky defects**. Impurity defects are caused by the presence of an impurity in the crystal. In ionic solids, when the ionic impurity has a different valence than the main compound, some vacancies are created. Non-stoichiometric defects are of **metal excess type** and **metal deficient type.** Sometimes calculated amounts of impurities are introduced by **doping in semiconductors** that change their electrical properties. Such materials are widely used in electronics industry. Solids show many types of magnetic properties like **paramagnetism**, **diamagnetism**, **ferromagnetism**, **antiferromagnetism** and **ferrimagnetism**. These properties are used in audio, video and other recording devices. All these properties can be correlated with their electronic configurations or structures.

Exercises

1.1 Define the term 'amorphous'. Give a few examples of amorphous solids.

1.2 What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?

1.3 Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.

- (i) Tetra phosphorus decoxide (P_4O_{10})
- (ii) Ammonium phosphate $(NH_4)_3PO_4$
- (iii) SiC
- (iv) I_2
- (v) P_4
- (vi) Plastic
- (vii) Graphite
- (viii) Brass
- (ix) Rb
- (x) LiBr
- (xi) Si

1.4 (i) What is meant by the term 'coordination number'?

(ii) What is the coordination number of atoms:

(a) in a cubic close-packed structure?

(b) in a body-centred cubic structure?

1.5 How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell? Explain.

1.6 'Stability of a crystal is reflected in the magnitude of its melting points'. Comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the intermolecular forces between these molecules?

1.7 How will you distinguish between the following pairs of terms:

(i) Hexagonal close-packing and cubic close-packing?

(ii) Crystal lattice and unit cell?

(iii) Tetrahedral void and octahedral void?

1.8 How many lattice points are there in one unit cell of each of the following lattice?

(i) Face-centred cubic

(ii) Face-centred tetragonal

(iii) Body-centred

1.9 Explain

(i) The basis of similarities and differences between metallic and ionic crystals.

(ii) Ionic solids are hard and brittle.

1.10 Calculate the efficiency of packing in case of a metal crystal for

(i) simple cubic

(ii) body-centred cubic

(iii) face-centred cubic (with the assumptions that atoms are touching each other).

1.11 Silver crystallises in fcc lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3}, calculate the atomic mass of silver.

1.12 A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body-centre. What is the formula of the compound? What are the coordination numbers of P and Q?

1.13 Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass 93 u.

1.14 If the radius of the octahedral void is r and radius of the atoms in close-packing is R, derive relation between r and R.

1.15 Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}.

1.16 Analysis shows that nickel oxide has the formula $Ni_{0.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?

1.17 What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanism.

1.18 Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a p-type semiconductor?

1.19 Ferric oxide crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

1.20 Classify each of the following as being either a p-type or a n-type semiconductor:

(i) Ge doped with In (ii) Si doped with B.

1.21 Gold (atomic radius = 0.144 nm) crystallises in a face-centred unit cell. What is the length of a side of the cell?

1.22 In terms of band theory, what is the difference

(i) between a conductor and an insulator

(ii) between a conductor and a semiconductor?

1.23 Explain the following terms with suitable examples:

(i) Schottky defect (ii) Frenkel defect (iii) Interstitials and (iv) F-centres.

1.24 Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.

(i) What is the length of the side of the unit cell?

(ii) How many unit cells are there in 1.00 cm^3 of aluminium?

1.25 If NaCl is doped with 10^{-3} mol % of $SrCl_2$, what is the concentration of cation vacancies?

1.26 Explain the following with suitable examples:

(i) Ferromagnetism

(ii) Paramagnetism

(iii) Ferrimagnetism

(iv) Antiferromagnetism

(v) 12-16 and 13-15 group compounds.

Answers to Some Intext Questions

1.14 4

1.15 Total number of voids = 9.033×10^{23}

Number of tetrahedral voids = 6.022×10^{23}

1.16 M_2N_3

1.18 ccp

Unit

2

Solutions

Objectives

After studying this Unit, you will be able to

- describe the formation of different types of solutions;
- express concentration of solution in different units;
- state and explain Henry's law and Raoult's law;
- distinguish between ideal and non-ideal solutions;
- explain deviations of real solutions from Raoult's law;
- describe colligative properties of solutions and correlate these with molar masses of the solutes;
- explain abnormal colligative properties exhibited by some solutes in solutions.

Almost all processes in body occur in some kind of liquid solutions.

In normal life we rarely come across pure substances. Most of these are mixtures containing two or more pure substances. Their utility or importance in life depends on their composition. For example, the properties of brass (mixture of copper and zinc) are quite different from those of German silver (mixture of copper, zinc and nickel) or bronze (mixture of copper and tin); 1 part per million (ppm) of fluoride ions in water prevents tooth decay, while 1.5 ppm causes the tooth to become mottled and high concentrations of fluoride ions can be poisonous (for example, sodium fluoride is used in rat poison); intravenous injections are always dissolved in water containing salts at particular ionic concentrations that match with blood plasma concentrations and so on.

In this Unit, we will consider mostly liquid solutions and their formation. This will be followed by studying the properties of the solutions, like vapour pressure and colligative properties. We will begin with types of solutions and then various alternatives in which concentrations of a solute can be expressed in **liquid solution**.

21 Types of Solutions

Solutions are **homogeneous** mixtures of two or more than two components. By homogenous mixture we mean that its composition and properties are uniform throughout the mixture. Generally, the component that is present in the largest quantity is known as **solvent**. Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called **solutes.** In this Unit we shall consider only **binary solutions** (i.e., consisting of two components). Here each component may be solid, liquid or in gaseous state and are summarised in Table 2.1.

Table 2.1: Types of Solutions

Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

2.2 Expressing Concentration of Solutions

Composition of a solution can be described by expressing its concentration. The latter can be expressed either qualitatively or quantitatively. For example, qualitatively we can say that the solution is dilute (i.e., relatively very small quantity of solute) or it is concentrated (i.e., relatively very large quantity of solute). But in real life these kinds of description can add to lot of confusion and thus the need for a quantitative description of the solution.

There are several ways by which we can describe the concentration of the solution quantitatively.

(i) *Mass percentage* (w/w): The mass percentage of a component of a solution is defined as:

Mass % of a component

$$= \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100 \qquad (2.1)$$

For example, if a solution is described by 10% glucose in water by mass, it means that 10 g of glucose is dissolved in 90 g of water resulting in a 100 g solution. Concentration described by mass percentage is commonly used in industrial chemical applications. For example, commercial bleaching solution contains 3.62 mass percentage of sodium hypochlorite in water.

(ii) *Volume percentage* (*V/V*): The volume percentage is defined as:

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100 \qquad (2.2)$$

For example, 10% ethanol solution in water means that 10 mL of ethanol is dissolved in water such that the total volume of the solution is 100 mL. Solutions coxntaining liquids are commonly expressed in this unit. For example, a 35% (*v*/*v*) solution of ethylene glycol, an antifreeze, is used in cars for cooling the engine. At this concentration the antifreeze lowers the freezing point of water to 255.4K (–17.6°C).

(iii) *Mass by volume percentage* (w/V): Another unit which is commonly used in medicine and pharmacy is mass by volume percentage. It is the mass of solute dissolved in 100 mL of the solution.

(iv) *Parts per million*: When a solute is present in **trace** quantities, it is convenient to express concentration in **parts per million (ppm)** and is defined as:

Parts per million =

$$= \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6 \quad (2.3)$$

As in the case of percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume. A litre of sea water (which weighs 1030 g) contains about 6×10^{-3} g of dissolved oxygen (O_2). Such a small concentration is also expressed as 5.8 g per 10^6 g (5.8 ppm) of sea water. The concentration of pollutants in water or atmosphere is often expressed in terms of $\mu g\ mL^{-1}$ or ppm.

(v) *Mole fraction*: Commonly used symbol for mole fraction is x and subscript used on the right hand side of x denotes the component. It is defined as:

Mole fraction of a component =

$$\frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}} \quad (2.4)$$

For example, in a binary mixture, if the number of moles of A and B are n_A and n_B respectively, the mole fraction of A will be

$$x_A = \frac{n_A}{n_A + n_B} \quad (2.5)$$

For a solution containing i number of components, we have:

$$x_i = \frac{n_i}{n_1 + n_2 + \ldots\ldots + n_i} = \frac{n_i}{\sum n_i} \quad (2.6)$$

It can be shown that in a given solution sum of all the mole fractions is unity, i.e.

$$x_1 + x_2 + \ldots\ldots\ldots\ldots\ldots\ldots + x_i = 1 \quad (2.7)$$

Mole fraction unit is very useful in relating some physical properties of solutions, say vapour pressure with the concentration of the solution and quite useful in describing the calculations involving gas mixtures.

Example 2.1 Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

Solution Assume that we have 100 g of solution (one can start with any amount of solution because the results obtained will be the same). Solution will contain 20 g of ethylene glycol and 80 g of water.

Molar mass of $C_2H_6O_2 = 12 \times 2 + 1 \times 6 + 16 \times 2 = 62 \text{ g mol}^{-1}$.

$$\text{Moles of } C_2H_6O_2 = \frac{20 \text{ g}}{62 \text{ g mol}^{-1}} = 0.322 \text{ mol}$$

$$\text{Moles of water} = \frac{80 \text{ g}}{18 \text{ g mol}^{-1}} = 4.444 \text{ mol}$$

$$x_{\text{glycol}} = \frac{\text{moles of } C_2H_6O_2}{\text{moles of } C_2H_6O_2 + \text{moles of } H_2O}$$

$$= \frac{0.322 \text{ mol}}{0.322 \text{ mol} + 4.444 \text{ mol}} = 0.068$$

$$\text{Similarly, } x_{\text{water}} = \frac{4.444 \text{ mol}}{0.322 \text{ mol} + 4.444 \text{ mol}} = 0.932$$

Mole fraction of water can also be calculated as: 1 – 0.068 = 0.932

(vi) *Molarity*: Molarity (*M*) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution,

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}} \quad (2.8)$$

For example, 0.25 mol L^{-1} (or 0.25 M) solution of NaOH means that 0.25 mol of NaOH has been dissolved in one litre (or one cubic decimetre).

Example 2.2 Calculate the molarity of a solution containing 5 g of NaOH in 450 mL solution.

Solution $$\text{Moles of NaOH} = \frac{5 \text{ g}}{40 \text{ g mol}^{-1}} = 0.125 \text{ mol}$$

Volume of the solution in litres = 450 mL / 1000 mL L^{-1}

Using equation (2.8),

$$\text{Molarity} = \frac{0.125 \text{ mol} \times 1000 \text{ mL L}^{-1}}{450 \text{ mL}} = 0.278 \text{ M}$$

$$= 0.278 \text{ mol L}^{-1}$$

$$= 0.278 \text{ mol dm}^{-3}$$

(vii) *Molality*: Molality (*m*) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as:

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \qquad (2.9)$$

For example, 1.00 mol kg^{-1} (or 1.00 m) solution of KCl means that 1 mol (74.5 g) of KCl is dissolved in 1 kg of water.

Each method of expressing concentration of the solutions has its own merits and demerits. Mass %, ppm, mole fraction and molality **are independent of temperature, whereas molarity is a function of temperature. This is because volume depends on temperature and the mass does not.**

Example 2.

Calculate molality of 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene.

Solution

Molar mass of $C_2H_4O_2$: $12 \times 2 + 1 \times 4 + 16 \times 2 = 60\ g\ mol^{-1}$

$$\text{Moles of } C_2H_4O_2 = \frac{2.5\ g}{60\ g\ mol^{-1}} = 0.0417\ mol$$

Mass of benzene in kg = $75\ g/1000\ g\ kg^{-1} = 75 \times 10^{-3}\ kg$

$$\text{Molality of } C_2H_4O_2 = \frac{\text{Moles of } C_2H_4O_2}{\text{kg of benzene}} = \frac{0.0417\ mol \times 1000\ g\ kg^{-1}}{75\ g}$$

$$= 0.556\ mol\ kg^{-1}$$

Intext Questions

2.1 Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

2.2 Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

2.3 Calculate the molarity of each of the following solutions: (a) 30 g of $Co(NO_3)_2 . 6H_2O$ in 4.3 L of solution (b) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL.

2.4 Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution.

2.5 Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1}.

2. Solubility

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature. It depends upon the nature of solute and solvent as well as temperature and pressure. Let us consider the effect of these factors in solution of a solid or a gas in a liquid.

2.3.1 Solubility of a Solid in a Liquid

Every solid does not dissolve in a given liquid. While sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not. It is observed that polar solutes dissolve in polar solvents and non polar solutes in non-polar solvents. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say **like dissolves like**.

When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution. Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallisation. A stage is reached when the two processes occur at the same rate. Under such conditions, number of solute particles going into solution will be equal to the solute particles separating out and a state of dynamic equilibrium is reached.

$$\text{Solute} + \text{Solvent} \qquad \text{Solution} \tag{2.10}$$

At this stage the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure. Similar process is followed when gases are dissolved in liquid solvents. Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution**. An *unsaturated solution* is one in which more solute can be dissolved at the same temperature. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent. Thus, the concentration of solute in such a solution is its solubility.

Earlier we have observed that solubility of one substance into another depends on the nature of the substances. In addition to these variables, two other parameters, i.e., temperature and pressure also control this phenomenon.

Effect of temperature

The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the equilibrium represented by equation 2.10. This, being dynamic equilibrium, must follow **Le Chateliers Principle.** In general, if in a *nearly saturated solution*, the dissolution process is endothermic ($\Delta_{sol} H > 0$), the solubility should increase with rise in temperature and if it is exothermic ($\Delta_{sol} H < 0$) the solubility should decrease. These trends are also observed experimentally.

Effect of pressure

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

2.3.2 Solubility of a Gas in a Liquid

Many gases dissolve in water. Oxygen dissolves only to a small extent in water. It is this dissolved oxygen which sustains all aquatic life. On the other hand, hydrogen chloride gas (HCl) is highly soluble in water. Solubility of gases in liquids is greatly affected by pressure and temperature. The solubility of gases increase with increase of pressure. For solution of gases in a solvent, consider a system as shown in Fig. 2.1 (a). The lower part is solution and the upper part is gaseous system at pressure p and temperature T. Assume this system to be in a state of dynamic equilibrium, i.e., under these conditions rate of gaseous particles entering and leaving the solution phase is the same. Now increase the pressure over the solution phase by compressing the gas to a smaller volume [Fig. 2.1 (b)]. This will increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of solution to enter it. The solubility of the gas will increase until a new equilibrium is reached resulting in an increase in the pressure of a gas above the solution and thus its solubility increases.

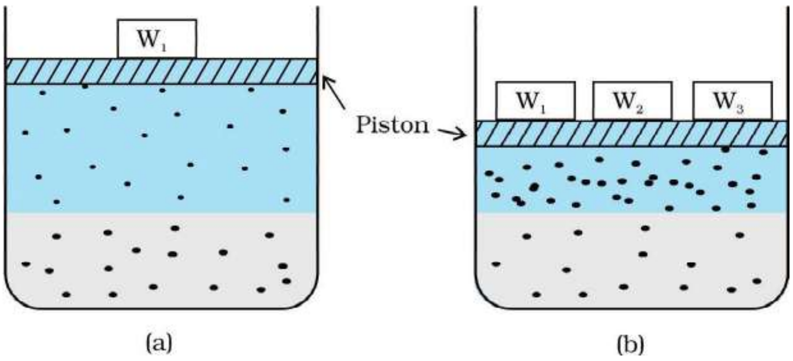


Fig. 2.1: *Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.*

Henry was the first to give a quantitative relation between pressure and solubility of a gas in a solvent which is known as **Henry's law**. The law states that at a constant temperature, **the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.** Dalton, a contemporary of Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of partial pressure of the gas. If we use the mole fraction of a gas in the solution as a measure of its solubility, then it can be said that the **mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.** The most commonly used form of Henry's law states that "**the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution**" and is expressed as:

$$p = K_H \, x \tag{2.11}$$

Here K_H is the Henry's law constant. If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in Fig. 2.2.

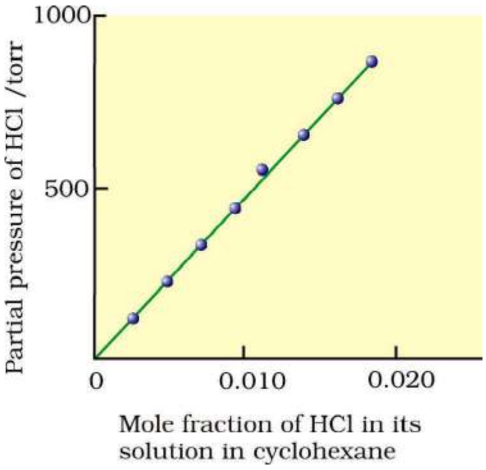


Fig. 2.2: *Experimental results for the solubility of HCl gas in cyclohexane at 293* K. *The slope of the line is the Henry's Law constant,* K_H.

Different gases have different K_H values at the same temperature (Table 2.2). This suggests that K_H is a function of the nature of the gas.

It is obvious from equation (2.11) that higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid. It can be seen from Table 2.2 that K_H values for both N_2 and O_2 increase with increase of temperature indicating that the solubility of gases

Table 2.2: Values of Henry's Law Constant for Some Selected Gases in Water

Gas	Temperature/K	K_H /kbar	Gas	Temperature/K	K_H/kbar
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	Formaldehyde	298	1.83×10^{-5}
N_2	303	88.84			
O_2	293	34.86	Methane	298	0.413
O_2	303	46.82	Vinyl chloride	298	0.611

increases with decrease of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

Example 2.

If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 *k*bar.

Solution

The solubility of gas is related to the mole fraction in aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus:

$$x\,(\text{Nitrogen}) = \frac{p\,(\text{nitrogen})}{K_H} = \frac{0.987\text{bar}}{76{,}480\text{ bar}} = 1.29 \times 10^{-5}$$

As 1 litre of water contains 55.5 mol of it, therefore if n represents number of moles of N_2 in solution,

$$x\,(\text{Nitrogen}) = \frac{n\text{ mol}}{n\text{ mol} + 55.5\text{ mol}} = \frac{n}{55.5} = 1.29 \times 10^{-5}$$

(n in denominator is neglected as it is $<<$ 55.5)

Thus $n = 1.29 \times 10^{-5} \times 55.5\text{ mol} = 7.16 \times 10^{-4}\text{ mol}$

$$= \frac{7.16\times10^{-4}\text{ mol} \times 1000\text{ mmol}}{1\text{ mol}} = 0.716\text{ mmol}$$

Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
- Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as *bends*, which are painful and dangerous to life.

To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

- At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as *anoxia*.

Effect of Temperature

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. We have learnt in the last Section that dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's Principle. As dissolution is an exothermic process, the solubility should decrease with increase of temperature.

Intext Questions

2.6 H_2S, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

2.7 Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

2.4 Vapour Pressure of Liquid Solutions

Liquid solutions are formed when solvent is a liquid. The solute can be a gas, a liquid or a solid. Solutions of gases in liquids have already been discussed in Section 2.3.2. In this Section, we shall discuss the solutions of liquids and solids in a liquid. Such solutions may contain one or more volatile components. Generally, the liquid solvent is volatile. The solute may or may not be volatile. We shall discuss the properties of only binary solutions, that is, the solutions containing two components, namely, the solutions of (i) liquids in liquids and (ii) solids in liquids.

2.4.1 Vapour Pressure of Liquid-Liquid Solutions

Let us consider a binary solution of two volatile liquids and denote the two components as 1 and 2. When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapour phase and the liquid phase. Let the total vapour pressure at this stage be p_{total} and p_1 and p_2 be the partial vapour pressures of the two components 1 and 2 respectively. These partial pressures are related to the mole fractions x_1 and x_2 of the two components 1 and 2 respectively.

The French chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them. The relationship is known as the **Raoult's law** which states that **for a solution of volatile liquids,**

the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

Thus, for component 1

$$p_1 \propto x_1$$

and $$p_1 = p_1^0 \, x_1 \qquad (2.12)$$

where p_1^0 is the vapour pressure of pure component 1 at the same temperature.

Similarly, for component 2

$$p_2 = p_2^0 \, x_2 \qquad (2.13)$$

where p_2^0 represents the vapour pressure of the pure component 2.

According to **Dalton's law of partial pressures**, the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as:

$$p_{total} = p_1 + p_2 \qquad (2.14)$$

Substituting the values of p_1 and p_2, we get

$$p_{total} = x_1 \, p_1^0 + x_2 \, p_2^0$$

$$= (1 - x_2) \, p_1^0 + x_2 \, p_2^0 \qquad (2.15)$$

$$= p_1^0 + (p_2^0 - p_1^0) \, x_2 \qquad (2.16)$$

Following conclusions can be drawn from equation (2.16).

(i) Total vapour pressure over the solution can be related to the mole fraction of any one component.

(ii) Total vapour pressure over the solution varies linearly with the mole fraction of component 2.

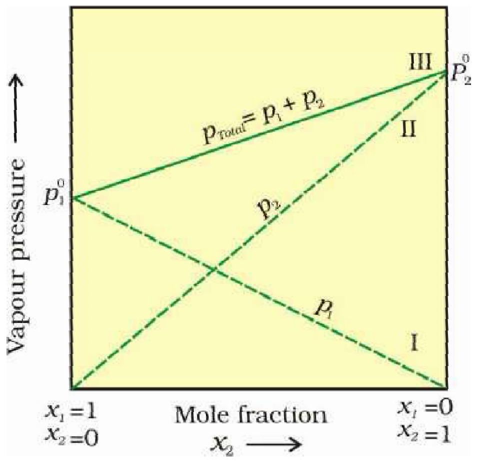


Fig. 2.3: *The plot of vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that p_1 and p_2 are directly proportional to x_1 and x_2, respectively). The total vapour pressure is given by line marked III in the figure.*

(iii) Depending on the vapour pressures of the pure components 1 and 2, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 1.

A plot of p_1 or p_2 versus the mole fractions x_1 and x_2 for a solution gives a linear plot as shown in Fig. 2.3. These lines (I and II) pass through the points for which x_1 and x_2 are equal to unity. Similarly the plot (line III) of p_{total} versus x_2 is also linear (Fig. 2.3). The minimum value of p_{total} is p_1^0 and the maximum value is p_2^0, assuming that component 1 is less volatile than component 2, i.e., $p_1^0 < p_2^0$.

The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If y_1 and y_2 are the mole fractions of the components 1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressures:

$$p_1 = y_1\ p_{total} \tag{2.17}$$

$$p_2 = y_2\ p_{total} \tag{2.18}$$

In general

$$p_i = y_i\ p_{total} \tag{2.19}$$

Example 2.

Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively. (i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at 298 K and, (ii) mole fractions of each component in vapour phase.

Solution

(i) Molar mass of CH_2Cl_2 = $12 \times 1 + 1 \times 2 + 35.5 \times 2 = 85\ \text{g mol}^{-1}$

Molar mass of $CHCl_3$ = $12 \times 1 + 1 \times 1 + 35.5 \times 3 = 119.5\ \text{g mol}^{-1}$

Moles of CH_2Cl_2 $= \dfrac{40\ \text{g}}{85\ \text{g mol}^{-1}} = 0.47\ \text{mol}$

Moles of $CHCl_3$ $= \dfrac{25.5\ \text{g}}{119.5\ \text{g mol}^{-1}} = 0.213\ \text{mol}$

Total number of moles = 0.47 + 0.213 = 0.683 mol

$$x_{CH_2Cl_2} = \frac{0.47\ \text{mol}}{0.683\ \text{mol}} = 0.688$$

$$x_{CHCl_3} = 1.00 - 0.688 = 0.312$$

Using equation (2.16),

$$p_{total} = p_1^0 + (p_2^0 - p_1^0)\ x_2 = 200 + (415 - 200) \times 0.688$$

$$= 200 + 147.9 = 347.9\ \text{mm Hg}$$

(ii) Using the relation (2.19), $y_i = p_i/p_{total}$, we can calculate the mole fraction of the components in gas phase (y_i).

$$p_{CH_2Cl_2} = 0.688 \times 415\ \text{mm Hg} = 285.5\ \text{mm Hg}$$

$$p_{CHCl_3} = 0.312 \times 200\ \text{mm Hg} = 62.4\ \text{mm Hg}$$

$$y_{CH_2Cl_2} = 285.5\ \text{mm Hg}/347.9\ \text{mm Hg} = 0.82$$

$$y_{CHCl_3} = 62.4\ \text{mm Hg}/347.9\ \text{mm Hg} = 0.18$$

Note: Since, CH_2Cl_2 is a more volatile component than $CHCl_3$, [$p^0_{CH_2Cl_2}$ = 415 mm Hg and $p^0_{CHCl_3}$ = 200 mm Hg] and the vapour phase is also richer in CH_2Cl_2 [$y_{CH_2Cl_2}$ = 0.82 and y_{CHCl_3} = 0.18], it may thus be concluded that **at equilibrium, vapour phase will be always rich in the component which is more volatile.**

2.4.2 Raoult's Law as a special case of Henry's Law

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $p_i = x_i\, p_i^0$. In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and we have already seen that its solubility is given by Henry's law which states that

$$p = K_H\, x.$$

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. Only the proportionality constant K_H differs from p_1^0. Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_1^0.

2.4.3 Vapour Pressure of Solutions of Solids in Liquids

Another important class of solutions consists of solids dissolved in liquid, for example, sodium chloride, glucose, urea and cane sugar in water and iodine and sulphur dissolved in carbon disulphide. Some physical properties of these solutions are quite different from those of pure solvents. For example, vapour pressure. We have learnt in Unit 5, Class XI, that liquids at a given temperature vapourise and under equilibrium conditions the pressure exerted by the vapours of the liquid over the liquid phase is called vapour pressure [Fig. 2.4 (a)]. In a pure liquid the entire surface is occupied by the molecules of the liquid. If a non-volatile solute is added to a solvent to give a solution [Fig. 2.4.(b)], the vapour pressure of the solution is solely from the solvent alone. This vapour pressure of the solution at a given temperature is found to be lower than the vapour pressure of the pure solvent at the same temperature. In the solution, the surface has both solute and solvent molecules; thereby the fraction of the surface covered by the solvent molecules gets reduced. Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced, thus, the vapour pressure is also reduced.

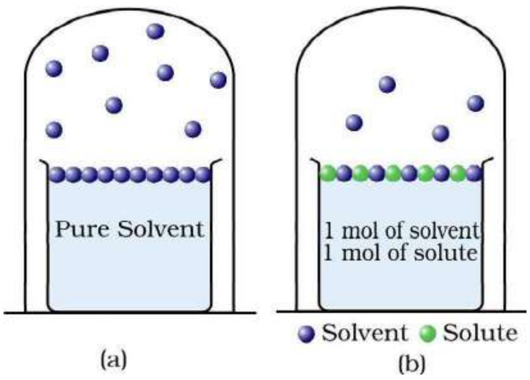


Fig. 2.4: *Decrease in the vapour pressure of the solvent on account of the presence of solute in the solvent (a) evaporation of the molecules of the solvent from its surface is denoted by ●, (b) in a solution, solute particles have been denoted by ● and they also occupy part of the surface area.*

The decrease in the vapour pressure of solvent depends on the quantity of non-volatile solute present in the solution, irrespective of its nature. For example, decrease in the vapour pressure of water by adding 1.0 mol of sucrose to one kg of water is nearly similar to that produced by adding 1.0 mol of urea to the same quantity of water at the same temperature.

Raoult's law in its general form can be stated as, **for any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.**

In a binary solution, let us denote the solvent by 1 and solute by 2. When the solute is non-volatile, only the solvent molecules are present in vapour phase and contribute to vapour pressure. Let p_1 be

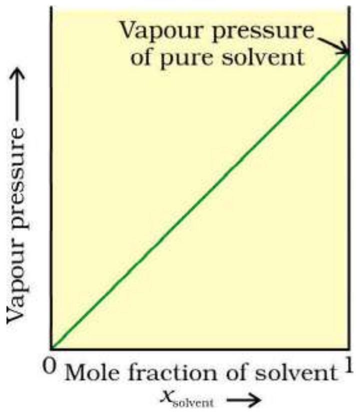


Fig. 2.5
If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent.

the vapour pressure of the solvent, x_1 be its mole fraction, p_1^0 be its vapour pressure in the pure state. Then according to Raoult's law

$$p_1 \propto x_1$$

and $$p_1 = x_1 \, p_1^0 \qquad (2.20)$$

The proportionality constant is equal to the vapour pressure of pure solvent, p_1^0. A plot between the vapour pressure and the mole fraction of the solvent is linear (Fig. 2.5).

2.5 Ideal and Non-ideal Solutions

Liquid-liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.

2.5.1 Ideal Solutions

The solutions which obey Raoult's law over the entire range of concentration are known as *ideal solutions*. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

$$\Delta_{mix}H = 0, \qquad \Delta_{mix}V = 0 \qquad (2.21)$$

It means that no heat is absorbed or evolved when the components are mixed. Also, the volume of solution would be equal to the sum of volumes of the two components. At molecular level, ideal behaviour of the solutions can be explained by considering two components A and B. In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of ideal solution. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Solution of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

2.5.2 Non-ideal Solutions

When a solution does not obey Raoult's law over the entire range of concentration, then it is called *non-ideal solution*. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law (equation 2.16). If it is higher, the solution exhibits **positive deviation** and if it is lower, it exhibits **negative deviation** from Raoult's law. The plots of vapour pressure as a function of mole fractions for such solutions are shown in Fig. 2.6.

The cause for these deviations lie in the nature of interactions at the molecular level. In case of positive deviation from Raoult's law, A-B interactions are weaker than those between A-A or B-B, i.e., in this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. This will increase the vapour

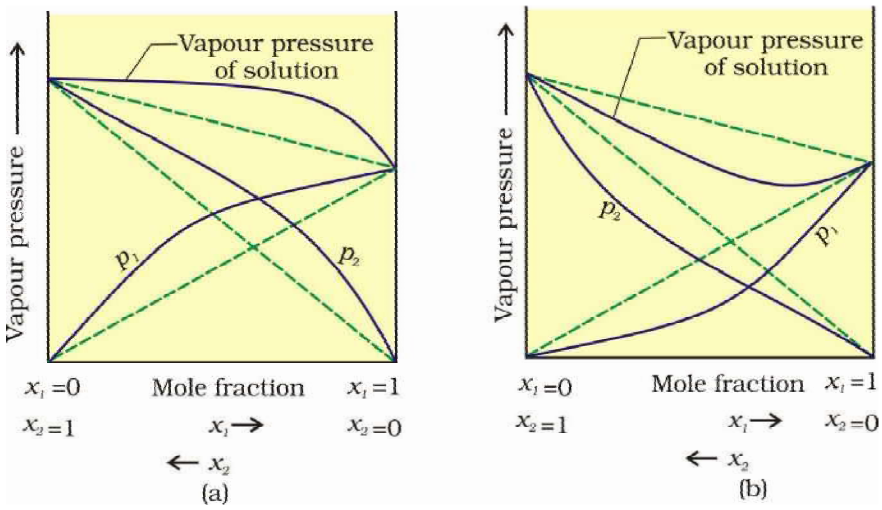
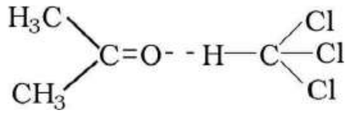


Fig.2.6 *The vapour pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law.*

pressure and result in positive deviation. Mixtures of ethanol and acetone behave in this manner. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law [Fig. 2.6 (a)]. In a solution formed by adding carbon disulphide to acetone, the dipolar interactions between solute-solvent molecules are weaker than the respective interactions among the solute-solute and solvent-solvent molecules. This solution also shows positive deviation.

In case of negative deviations from Raoult's law, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and leads to decrease in vapour pressure resulting in negative deviations. An example of this type is a mixture of phenol and aniline. In this case the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules. Similarly, a mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown.



This decreases the escaping tendency of molecules for each component and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law [Fig. 2.6. (b)].

Some liquids on mixing, form **azeotropes** which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called **minimum boiling azeotrope and maximum boiling azeotrope**. The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.

For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, known as azeotrope composition, has been achieved, the liquid and vapour have the same composition, and no further separation occurs.

The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

Intext Question

2.8 The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K . Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

2.6 Colligative Properties and Determination of Molar Mass

We have learnt in Section 2.4.3 that the vapour pressure of solution decreases when a non-volatile solute is added to a volatile solvent. There are many properties of solutions which are connected with this decrease of vapour pressure. These are: (1) relative lowering of vapour pressure of the solvent (2) depression of freezing point of the solvent (3) elevation of boiling point of the solvent and (4) osmotic pressure of the solution. **All these properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Such properties are called *colligative properties*** (colligative: from Latin: co means together, ligare means to bind). In the following Sections we will discuss these properties one by one.

2.6.1 Relative Lowering of Vapour Pressure

We have learnt in Section 2.4.3 that the vapour pressure of a solvent in solution is less than that of the pure solvent. Raoult established that the lowering of vapour pressure depends only on the concentration of the solute particles and it is independent of their identity. The equation (2.20) given in Section 2.4.3 establishes a relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent, i.e.,

$$p_1 = x_1\, p_1^0 \tag{2.22}$$

The reduction in the vapour pressure of solvent (Δp_1) is given as:

$$\Delta p_1 = p_1^0 - p_1 = p_1^0 - p_1^0\, x_1$$

$$= p_1^0\,(1 - x_1) \tag{2.23}$$

Knowing that $x_2 = 1 - x_1$, equation (2.23) reduces to

$$\Delta p_1 = x_2\, p_1^0 \tag{2.24}$$

In a solution containing several non-volatile solutes, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes.

Equation (2.24) can be written as

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2 \tag{2.25}$$

The expression on the left hand side of the equation as mentioned earlier is called **relative lowering of vapour pressure and is equal to the mole fraction of the solute**. The above equation can be written as:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2} \quad \left(\text{since } x_2 = \frac{n_2}{n_1 + n_2}\right) \tag{2.26}$$

Here n_1 and n_2 are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_2 << n_1$, hence neglecting n_2 in the denominator we have

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1} \tag{2.27}$$

or $$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \tag{2.28}$$

Here w_1 and w_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute respectively.

From this equation (2.28), knowing all other quantities, the molar mass of solute (M_2) can be calculated.

Example 2. The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g mol^{-1}). Vapour pressure of the solution, then, is 0.845 bar. What is the molar mass of the solid substance?

Solution The various quantities known to us are as follows:

$p_1^0 = 0.850$ bar; $p = 0.845$ bar; $M_1 = 78$ g mol^{-1}; $w_2 = 0.5$ g; $w_1 = 39$ g

Substituting these values in equation (2.28), we get

$$\frac{0.850 \text{ bar} - 0.845 \text{ bar}}{0.850 \text{ bar}} = \frac{0.5 \text{ g} \times 78 \text{ g mol}^{-1}}{M_2 \times 39 \text{ g}}$$

Therefore, $M_2 = 170$ g mol^{-1}

2.6.2 Elevation of Boiling Point

We have learnt in Unit 5, Class XI, that the vapour pressure of a liquid increases with increase of temperature. It boils at the temperature at which its vapour pressure is equal to the atmospheric pressure. For example, water boils at 373.15 K (100° C) because at this temperature the vapour pressure of water is 1.013 bar (1 atmosphere). We have also learnt in the last section that vapour pressure of the solvent decreases in the presence of non-volatile solute. Fig. 2.7 depicts the variation of vapour pressure of the pure solvent and solution as a function of temperature. For example, the vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K. In order to make this solution boil, its vapour pressure must be increased to 1.013 bar by raising the temperature above the boiling temperature of the pure solvent (water). Thus, the boiling

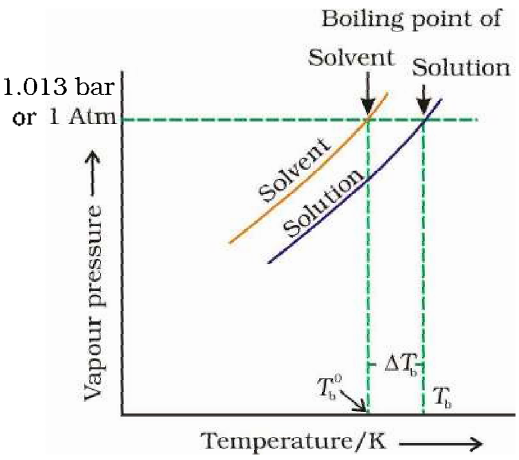


Fig. 2.7: *The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.*

point of a solution is always higher than that of the boiling point of the pure solvent in which the solution is prepared as shown in Fig. 2.7. Similar to lowering of vapour pressure, the elevation of boiling point also depends on the number of solute molecules rather than their nature. A solution of 1 mol of sucrose in 1000 g of water boils at 373.52 K at one atmospheric pressure.

Let T_b^0 be the boiling point of pure solvent and T_b be the boiling point of solution. The increase in the boiling point $\Delta T_b = T_b - T_b^0$ is known as **elevation of boiling point**.

Experiments have shown that for **dilute solutions** the elevation of boiling point (ΔT_b) is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m \qquad (2.29)$$

or $$\Delta T_b = K_b\, m \qquad (2.30)$$

Here *m* (molality) is the number of moles of solute dissolved in 1 kg of solvent and the constant of proportionality, K_b is called **Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant)**. The unit of K_b is K kg mol^{-1}. Values of K_b for some common solvents are given in Table 2.3. If w_2 gram of solute of molar mass M_2 is dissolved in w_1 gram of solvent, then molality, m of the solution is given by the expression:

$$m = \frac{w_2/M_2}{w_1/1000} = \frac{1000 \times w_2}{M_2 \times w_1} \qquad (2.31)$$

Substituting the value of molality in equation (2.30) we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1} \qquad (2.32)$$

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1} \qquad (2.33)$$

Thus, in order to determine M_2, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined experimentally for a known solvent whose K_b value is known.

□□□ple 2.□

18 g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a saucepan. At what temperature will water boil at 1.013 bar? K_b for water is 0.52 K kg mol^{-1}.

Solution

Moles of glucose = 18 g/ 180 g mol^{-1} = 0.1 mol
Number of kilograms of solvent = 1 kg
Thus molality of glucose solution = 0.1 mol kg^{-1}
For water, change in boiling point

$\Delta T_b = K_b \times m = 0.52 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1} = 0.052 \text{ K}$

Since water boils at 373.15 K at 1.013 bar pressure, therefore, the boiling point of solution will be 373.15 + 0.052 = 373.202 K.

□□□ple 2.□ The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. K_b for benzene is 2.53 K kg mol^{-1}

Solution The elevation (ΔT_b) in the boiling point = 354.11 K – 353. 23 K = 0.88 K

Substituting these values in expression (2.33) we get

$$M_2 = \frac{2.53 \text{ K kg mol}^{-1} \times 1.8 \text{ g} \times 1000 \text{ g kg}^{-1}}{0.88 \text{ K} \times 90 \text{ g}} = 58 \text{ g mol}^{-1}$$

Therefore, molar mass of the solute, $M_2 = 58 \text{ g mol}^{-1}$

2.6.3 Depression of Freezing Point

The lowering of vapour pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent (Fig. 2 8). We know that at the freezing point of a substance, the solid phase is in dynamic equilibrium with the liquid phase. Thus, the freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase. A solution will freeze when its vapour pressure equals the vapour pressure of the pure solid solvent as is clear from Fig. 2.8. According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.

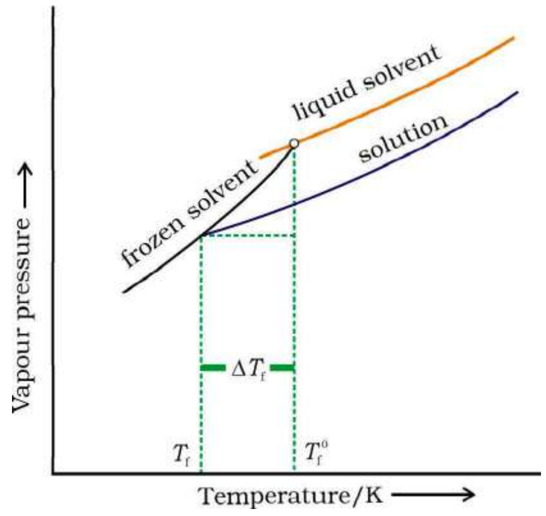


Fig. 2.8: *Diagram showing ΔT_f, depression of the freezing point of a solvent in a solution.*

Let T_f^0 be the freezing point of pure solvent and T_f be its freezing point when non-volatile solute is dissolved in it. The decrease in freezing point.

$\Delta T_f = T_f^0 - T_f$ is known as depression in freezing point.

Similar to elevation of boiling point, depression of freezing point (ΔT_f) for **dilute solution** (ideal solution) is directly proportional to molality, m of the solution. Thus,

$$\Delta T_f \propto \mathbf{m}$$

or $$\Delta T_f = K_f \text{ m} \qquad (2.34)$$

The proportionality constant, K_f, which depends on the nature of the solvent is known as **Freezing Point Depression Constant or Molal**

Depression Constant or Cryoscopic Constant. The unit of K_f is K kg mol^{-1}. Values of K_f for some common solvents are listed in Table 2.3.

If w_2 gram of the solute having molar mass as M_2, present in w_1 gram of solvent, produces the depression in freezing point ΔT_f of the solvent then molality of the solute is given by the equation (2.31).

$$m = \frac{w_2 \,/\, M_2}{w_1/1000} \tag{2.31}$$

Substituting this value of molality in equation (2.34) we get:

$$\Delta T_f = \frac{K_f \times w_2 \,/\, M_2}{w_1 \,/1000}$$

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1} \tag{2.35}$$

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1} \tag{2.36}$$

Thus for determining the molar mass of the solute we should know the quantities w_1, w_2, ΔT_f, along with the molal freezing point depression constant.

The values of K_f and K_b, which depend upon the nature of the solvent, can be ascertained from the following relations.

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus}H} \tag{2.37}$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap}H} \tag{2.38}$$

Here the symbols R and M_1 stand for the gas constant and molar mass of the solvent, respectively and T_f and T_b denote the freezing point and the boiling point of the pure solvent respectively in kelvin. Further, $\Delta_{fus}H$ and $\Delta_{vap}H$ represent the enthalpies for the fusion and vapourisation of the solvent, respectively.

Table 2.3: Molal Boiling Point Elevation and Freezing Point Depression Constants for Some Solvents

Solvent	b. p./K	K_b/K kg mol^{-1}	f. p./K	K_f/K kg mol^{-1}
Water	373.15	0.52	273.0	1.86
Ethanol	351.5	1.20	155.7	1.99
Cyclohexane	353.74	2.79	279.55	20.00
Benzene	353.3	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.79
Carbon tetrachloride	350.0	5.03	250.5	31.8
Carbon disulphide	319.4	2.34	164.2	3.83
Diethyl ether	307.8	2.02	156.9	1.79
Acetic acid	391.1	2.93	290.0	3.90

Example 2.

45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution.

Solution

Depression in freezing point is related to the molality, therefore, the molality of the solution with respect to ethylene glycol $= \dfrac{\text{moles of ethylene glycol}}{\text{mass of water in kilogram}}$

$$\text{Moles of ethylene glycol} = \frac{45\ \text{g}}{62\ \text{g mol}^{-1}} = 0.73\ \text{mol}$$

$$\text{Mass of water in kg} = \frac{600\text{g}}{1000\text{g kg}^{-1}} = 0.6\ \text{kg}$$

$$\text{Hence molality of ethylene glycol} = \frac{0.73\ \text{mol}}{0.60\ \text{kg}} = 1.2\ \text{mol kg}^{-1}$$

Therefore freezing point depression,

$$\Delta T_f = 1.86\ \text{K kg mol}^{-1} \times 1.2\ \text{mol kg}^{-1} = 2.2\ \text{K}$$

Freezing point of the aqueous solution = 273.15 K – 2.2 K = 270.95 K

Example 2.1

1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 K kg mol^{-1}. Find the molar mass of the solute.

Solution

Substituting the values of various terms involved in equation (2.36) we get,

$$M_2 = \frac{5.12\ \text{K kg mol}^{-1} \times 1.00\ \text{g} \times 1000\ \text{g kg}^{-1}}{0.40 \times 50\ \text{g}} = 256\ \text{g mol}^{-1}$$

Thus, molar mass of the solute = 256 g mol^{-1}

2.6.4 Osmosis and Osmotic Pressure

There are many phenomena which we observe in nature or at home. For example, raw mangoes shrivel when pickled in brine (salt water); wilted flowers revive when placed in fresh water, blood cells collapse when suspended in saline water, etc. If we look into these processes we find one thing common in all, that is, all these substances are bound by membranes. These membranes can be of animal or vegetable origin and these occur naturally such as pig's bladder or parchment or can be synthetic such as cellophane. These membranes appear to be continuous sheets or films, yet they contain a network of submicroscopic holes or pores. Small solvent

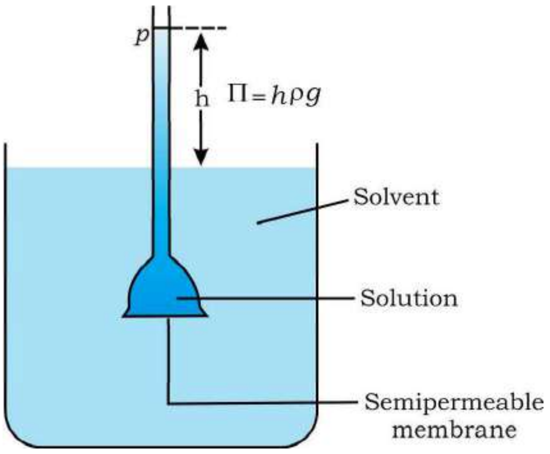


Fig. 2.9 Level of solution rises in the thistle funnel due to osmosis of solvent.

molecules, like water, can pass through these holes but the passage of bigger molecules like solute is hindered. Membranes having this kind of properties are known as *semipermeable membranes* (SPM).

Assume that only solvent molecules can pass through these semipermeable membranes. If this membrane is placed between the solvent and solution as shown in Fig. 2.9, the solvent molecules will flow through the membrane from pure solvent to the solution. **This process of flow of the solvent is called *osmosis*.**

The flow will continue till the equilibrium is attained. The flow of the solvent from its side to solution side across a semipermeable membrane can be stopped if some extra pressure is applied on the solution. **This pressure that just stops the flow of solvent is called *osmotic pressure* of the solution.** The flow of solvent from dilute solution to the concentrated solution across a semipermeable membrane is due to osmosis. The important point to be kept in mind is that solvent molecules always flow from lower concentration to higher concentration of solution. The osmotic pressure has been found to depend on the concentration of the solution.

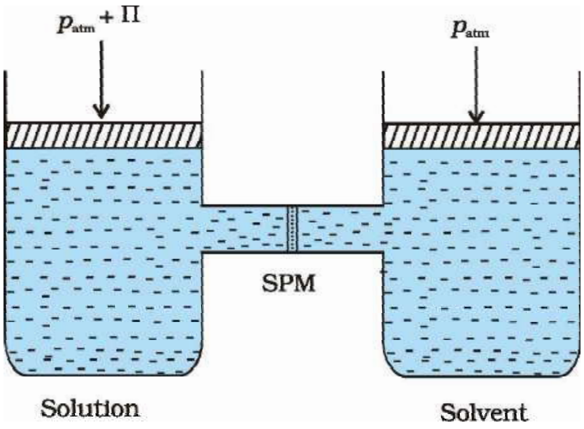


Fig. 2.10: *The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis.*

The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e., to stop the passage of solvent molecules through a semipermeable membrane into the solution. This is illustrated in Fig. 2.10. Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity. For dilute solutions, it has been found experimentally that **osmotic pressure is proportional to the molarity, *C* of the solution at a given temperature *T*.** Thus:

$$\Pi = C R T \quad (2.39)$$

Here Π is the osmotic pressure and R is the gas constant.

$$\Pi = (n_2 / V) R T \quad (2.40)$$

Here V is volume of a solution in litres containing n_2 moles of solute. If w_2 grams of solute, of molar mass, M_2 is present in the solution, then $n_2 = w_2 / M_2$ and we can write,

$$\Pi V = \frac{w_2 R T}{M_2} \quad (2.41)$$

or
$$M_2 = \frac{w_2 R T}{\Pi V} \quad (2.42)$$

Thus, knowing the quantities w_2, T, Π and V we can calculate the molar mass of the solute.

Measurement of osmotic pressure provides another method of determining molar masses of solutes. This method is widely used to determine molar masses of proteins, polymers and other macromolecules. The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and the molarity of the solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilute solutions. The technique of osmotic pressure for determination of molar mass of solutes is particularly useful for biomolecules as they are generally not stable at higher temperatures and polymers have poor solubility.

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by semipermeable membrane no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called **hypertonic**. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be **hypotonic**. In this case, water will flow into the cells if placed in this solution and they would swell.

Example 2.11 200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the protein.

Solution The various quantities known to us are as follows: $\Pi = 2.57 \times 10^{-3}$ bar,

$V = 200\ cm^3 = 0.200$ litre

$T = 300$ K

$R = 0.083$ L bar mol^{-1} K^{-1}

Substituting these values in equation (2.42) we get

$$M_2 = \frac{1.26\ g \times 0.083\ L\ bar\ K^{-1}\ mol^{-1} \times 300\ K}{2.57 \times 10^{-3} bar \times 0.200\ L} = 61{,}022\ g\ mol^{-1}$$

The phenomena mentioned in the beginning of this section can be explained on the basis of osmosis. A raw mango placed in concentrated salt solution loses water via osmosis and shrivel into pickle. Wilted flowers revive when placed in fresh water. A carrot that has become limp because of water loss into the atmosphere can be placed into the water making it firm once again. Water will move into them through osmosis. When placed in water containing less than 0.9% (mass/volume) salt, blood cells swell due to flow of water in them by osmosis. People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting puffiness or swelling is called **edema**. Water movement from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis. The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.

2.6.5 Reverse Osmosis and Water Purification

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called **reverse osmosis** and is of great practical utility. Reverse osmosis is used in desalination of sea water. A schematic set up for the process is shown in Fig. 2.11. When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. A variety of polymer membranes are available for this purpose.

The pressure required for the reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water. These days many countries use desalination plants to meet their potable water requirements.

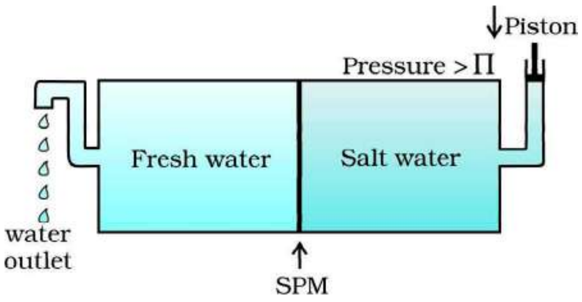


Fig. 2.11: *Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.*

Intext Questions

2.9 Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea (NH_2CONH_2) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

2.10 Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C.

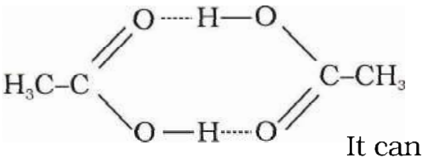
2.11 Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. K_f = 3.9 K kg mol^{-1}.

2.12 Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

2.7 Abnormal Molar Masses

We know that ionic compounds when dissolved in water dissociate into cations and anions. For example, if we dissolve one mole of KCl (74.5 g) in water, we expect one mole each of K^+ and Cl^- ions to be released in the solution. If this happens, there would be two moles of particles in the solution. If we ignore interionic attractions, one mole of KCl in one kg of water would be expected to increase the boiling point by 2 × 0.52 K = 1.04 K. Now if we did not know about the degree of dissociation, we could be led to conclude that the mass of 2 mol particles is 74.5 g and the mass of one mole of KCl would be 37.25 g. This brings into light the rule that, when there is dissociation of solute into ions, the experimentally determined molar mass is always lower than the true value.

2 CH_3COOH $(CH_3COOH)_2$



Molecules of ethanoic acid (acetic acid) dimerise in benzene due to hydrogen bonding. This normally happens in solvents of low dielectric constant. In this case the number of particles is reduced due to dimerisation. Association of molecules is depicted as follows:

It can be undoubtedly stated here that if all the molecules of ethanoic acid associate in benzene, then ΔT_b or ΔT_f for ethanoic acid will be half of the normal value. The molar mass calculated on the basis of this ΔT_b or ΔT_f will, therefore, be twice the expected value. Such a molar mass that is either lower or higher than the expected or normal value is called as **abnormal molar mass.**

In 1880 van't Hoff introduced a factor *i*, known as the van't Hoff factor, to account for the extent of dissociation or association. This factor *i* is defined as:

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

Here abnormal molar mass is the experimentally determined molar mass and calculated colligative properties are obtained by assuming that the non-volatile solute is neither associated nor dissociated. In case of association, value of *i* is less than unity while for dissociation it is greater than unity. For example, the value of *i* for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.

Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent,

$$\frac{p_1^o - p_1}{p_1^o} = i.\frac{n_2}{n_1}$$

Elevation of Boiling point, $\Delta T_b = i\, K_b\, m$

Depression of Freezing point, $\Delta T_f = i\, K_f\, m$

Osmotic pressure of solution, $\Pi = i\, n_2\, R\, T\, /\, V$

Table 2.4 depicts values of the factor, *i* for several strong electrolytes. For KCl, NaCl and $MgSO_4$, *i* approach 2 as the solution becomes very dilute. As expected, the value of *i* gets close to 3 for K_2SO_4.

Table 2.4: Values of van't Hoff factor, *i*, at Various Concentrations for NaCl, KCl, $MgSO_4$ and K_2SO_4.

Salt	*Values of *i*			van't Hoff Factor *i* for complete dissociation of solute
	0.1 m	0.01 m	0.001 m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
$MgSO_4$	1.21	1.53	1.82	2.00
K_2SO_4	2.32	2.70	2.84	3.00

* *represent i values for incomplete dissociation.*

Example 2.12

2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms dimer in solution?

Solution

The given quantities are: w_2 = 2 g; K_f = 4.9 K kg mol^{-1}; w_1 = 25 g, ΔT_f = 1.62 K

Substituting these values in equation (2.36) we get:

$$M_2 = \frac{4.9\text{ K kg mol}^{-1} \times 2\text{ g} \times 1000\text{ g kg}^{-1}}{25\text{ g} \times 1.62\text{ K}} = 241.98\text{ g mol}^{-1}$$

Thus, experimental molar mass of benzoic acid in benzene is = 241.98 g mol^{-1}

Now consider the following equilibrium for the acid:

$$2\,C_6H_5COOH \qquad (C_6H_5COOH)_2$$

If *x* represents the degree of association of the solute then we would have (1 – *x*) mol of benzoic acid left in unassociated form and correspondingly $\frac{x}{2}$ as associated moles of benzoic acid at equilibrium. Therefore, total number of moles of particles at equilibrium is:

$$1 - x + \frac{x}{2} = 1 - \frac{x}{2}$$

Thus, total number of moles of particles at equilibrium equals van't Hoff factor *i*.

$$\text{But } i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{122 \text{ g mol}^{-1}}{241.98 \text{ g mol}^{-1}}$$

or $\frac{x}{2} = 1 - \frac{122}{241.98} = 1 - 0.504 = 0.496$

or $x = 2 \times 0.496 = 0.992$

Therefore, degree of association of benzoic acid in benzene is 99.2 %.

Example 2.1

0.6 mL of acetic acid (CH_3COOH), having density 1.06 g mL^{-1}, is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C. Calculate the van't Hoff factor and the dissociation constant of acid.

Solution

Number of moles of acetic acid $= \frac{0.6 \text{ mL} \times 1.06 \text{ g mL}^{-1}}{60 \text{ g mol}^{-1}}$

$= 0.0106 \text{ mol} = n$

$$\text{Molality} = \frac{0.0106 \text{ mol}}{1000 \text{ mL} \times 1 \text{ g mL}^{-1}} = 0.0106 \text{ mol kg}^{-1}$$

Using equation (2.35)

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 0.0106 \text{ mol kg}^{-1} = 0.0197 \text{ K}$$

$$\text{van't Hoff Factor } (i) = \frac{\text{Observed freezing point}}{\text{Calculated freezing point}} = \frac{0.0205 \text{ K}}{0.0197 \text{ K}} = 1.041$$

Acetic acid is a weak electrolyte and will dissociate into two ions: acetate and hydrogen ions per molecule of acetic acid. If x is the degree of dissociation of acetic acid, then we would have $n(1 - x)$ moles of undissociated acetic acid, nx moles of CH_3COO^- and nx moles of H^+ ions,

$$\begin{array}{ccc} CH_3COOH & \rightleftharpoons & H^+ + CH_3COO^- \\ n \text{ mol} & & 0 \qquad 0 \\ n(1-x) & & nx \text{ mol} \qquad nx \text{ mol} \end{array}$$

Thus total moles of particles are: $n(1 - x + x + x) = n(1 + x)$

$$i = \frac{n(1+x)}{n} = 1 + x = 1.041$$

Thus degree of dissociation of acetic acid $= x = 1.041 - 1.000 = 0.041$

Then $[CH_3COOH] = n(1 - x) = 0.0106\,(1 - 0.041)$,

$[CH_3COO^-] = nx = 0.0106 \times 0.041$, $[H^+] = nx = 0.0106 \times 0.041$.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{0.0106 \times 0.041 \times 0.0106 \times 0.041}{0.0106\,(1.00 - 0.041)}$$

$$= 1.86 \times 10^{-5}$$

Summary

A solution is a homogeneous mixture of two or more substances. Solutions are classified as solid, liquid and gaseous solutions. The concentration of a solution is expressed in terms of mole fraction, molarity, molality and in percentages. The dissolution of a gas in a liquid is governed by **Henry's law**, according to which, at a given temperature, the **solubility of a gas in a liquid is directly proportional to the partial pressure of the gas**. The vapour pressure of the solvent is lowered by the presence of a non-volatile solute in the solution and this lowering of vapour pressure of the solvent is governed by Raoult's law, according to which the **relative lowering of vapour pressure of the solvent over a solution is equal to the mole fraction of a non-volatile solute present in the solution**. However, in a binary liquid solution, if both the components of the solution are volatile then another form of Raoult's law is used. Mathematically, this form of the Raoult's law is stated as: $p_{\text{total}} = p_1^0 x_1 + p_2^0 x_2$. **Solutions which obey Raoult's law over the entire range of concentration are called ideal solutions**. Two types of deviations from Raoult's law, called positive and negative deviations are observed. Azeotropes arise due to very large deviations from Raoult's law.

The properties of solutions which depend on the number of solute particles and are independent of their chemical identity are called colligative properties. These are lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. The process of osmosis can be reversed if a pressure higher than the osmotic pressure is applied to the solution. Colligative properties have been used to determine the molar mass of solutes. Solutes which dissociate in solution exhibit molar mass lower than the actual molar mass and those which associate show higher molar mass than their actual values.

Quantitatively, the extent to which a solute is dissociated or associated can be expressed by van't Hoff factor *i*. This factor has been defined as ratio of normal molar mass to experimentally determined molar mass or as the ratio of observed colligative property to the calculated colligative property.

Exercises

2.1 Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.

2.2 Give an example of a solid solution in which the solute is a gas.

2.3 Define the following terms:

(i) Mole fraction (ii) Molality (iii) Molarity (iv) Mass percentage.

2.4 Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL^{-1}?

2.5 A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of solution is 1.2 g mL^{-1}, then what shall be the molarity of the solution?

2.6 How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of both?

2.7 A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

2.8 An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1}, then what shall be the molarity of the solution?

2.9 A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass):

(i) express this in percent by mass

(ii) determine the molality of chloroform in the water sample.

2.10 What role does the molecular interaction play in a solution of alcohol and water?

2.11 Why do gases always tend to be less soluble in liquids as the temperature is raised?

2.12 State Henry's law and mention some important applications?

2.13 The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas?

2.14 What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{mix}H$ related to positive and negative deviations from Raoult's law?

2.15 An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?

2.16 Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?

2.17 The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

2.18 Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

2.19 A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate:

(i) molar mass of the solute (ii) vapour pressure of water at 298 K.

2.20 A 5% solution (by mass) of cane sugar in water has freezing point of 271K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K.

2.21 Two elements A and B form compounds having formula AB_2 and AB_4. When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K kg mol^{-1}. Calculate atomic masses of A and B.

2.22 At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bars at the same temperature, what would be its concentration?

2.23 Suggest the most important type of intermolecular attractive interaction in the following pairs.

(i) n-hexane and n-octane
(ii) I_2 and CCl_4
(iii) $NaClO_4$ and water
(iv) methanol and acetone
(v) acetonitrile (CH_3CN) and acetone (C_3H_6O).

2.24 Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCl, CH_3OH, CH_3CN.

2.25 Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?

(i) phenol
(ii) toluene
(iii) formic acid
(iv) ethylene glycol
(v) chloroform
(vi) pentanol.

2.26 If the density of some lake water is 1.25g mL^{-1} and contains 92 g of Na^+ ions per kg of water, calculate the molality of Na^+ ions in the lake.

2.27 If the solubility product of CuS is 6×10^{-16}, calculate the maximum molarity of CuS in aqueous solution.

2.28 Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN.

2.29 Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of $1.5 - 10^{-3}$ m aqueous solution required for the above dose.

2.30 Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol.

2.31 The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

2.32 Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86$ K kg mol^{-1}.

2.33 19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0^0 C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

2.34 Vapour pressure of water at 293 *K* is 17.535 mm Hg. Calculate the vapour pressure of water at 293 *K* when 25 g of glucose is dissolved in 450 g of water.

2.35 Henry's law constant for the molality of methane in benzene at 298 *K* is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 *K* under 760 mm Hg.

2.36 100 g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 Torr.

2.37 Vapour pressures of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total}, $p_{chloroform}$, and $p_{acetone}$ as a function of $x_{acetone}$. The experimental data observed for different compositions of mixture is:

100 x $x_{acetone}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{acetone}$ /mm Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{chloroform}$ /mm Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

2.38 Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of toluene.

2.39 The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K if the Henry's law constants for oxygen and nitrogen at 298 K are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.

2.40 Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27° C.

2.41 Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25° C, assuming that it is completely dissociated.

Answers to Some Intext Questions

2.1 C_6H_6 = 15.28%, CCl_4 = 84.72%

2.2 0.459, 0.541

2.3 0.024 M, 0.03 M

2.4 36.946 g

2.5 1.5 mol kg^{-1} , 1.45 mol L^{-1} 0.0263

2.9 23.4 mm Hg

2.10 121.67 g

2.11 5.077 g

2.12 30.96 Pa

Unit

3

Electrochemistry

Chemical reactions can be used to produce electrical energy, conversely, electrical energy can be used to carry out chemical reactions that do not proceed spontaneously.

Objectives

After studying this Unit, you will be able to

- describe an electrochemical cell and differentiate between galvanic and electrolytic cells;
- apply Nernst equation for calculating the emf of galvanic cell and define standard potential of the cell;
- derive relation between standard potential of the cell, Gibbs energy of cell reaction and its equilibrium constant;
- define resistivity (ρ), conductivity (κ) and molar conductivity (Λ_m) of ionic solutions;
- differentiate between ionic (electrolytic) and electronic conductivity;
- describe the method for measurement of conductivity of electrolytic solutions and calculation of their molar conductivity;
- justify the variation of conductivity and molar conductivity of solutions with change in their concentration and define Λ_m° (molar conductivity at zero concentration or infinite dilution);
- enunciate Kohlrausch law and learn its applications;
- understand quantitative aspects of electrolysis;
- describe the construction of some primary and secondary batteries and fuel cells;
- explain corrosion as an electrochemical process.

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations. The subject is of importance both for theoretical and practical considerations. A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods. Batteries and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices. The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, study of electrochemistry is important for creating new technologies that are ecofriendly. The transmission of sensory signals through cells to brain and vice versa and communication between the cells are known to have electrochemical origin. Electrochemistry, is therefore, a very vast and interdisciplinary subject. In this Unit, we will cover only some of its important elementary aspects.

Electrochemical Cells

In Class XI, Unit 8, we had studied the construction and functioning of **Daniell cell** (Fig. 3.1). This cell converts the chemical energy liberated during the redox reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad (3.1)$$

to electrical energy and has an electrical potential equal to 1.1 V when concentration of Zn^{2+} and Cu^{2+} ions is unity (1 mol dm^{-3})*. Such a device is called a **galvanic** or a **voltaic** cell.

If an external opposite potential is applied in the galvanic cell [Fig. 3.2(a)] and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V [Fig. 3.2(b)] when, the reaction stops altogether and no current flows through the cell. Any further increase in the external potential again starts the reaction but in the opposite direction [Fig. 3.2(c)]. It now functions as an **electrolytic cell**, a device for using electrical energy to carry non-spontaneous chemical reactions. Both types of cells are quite important and we shall study some of their salient features in the following pages.

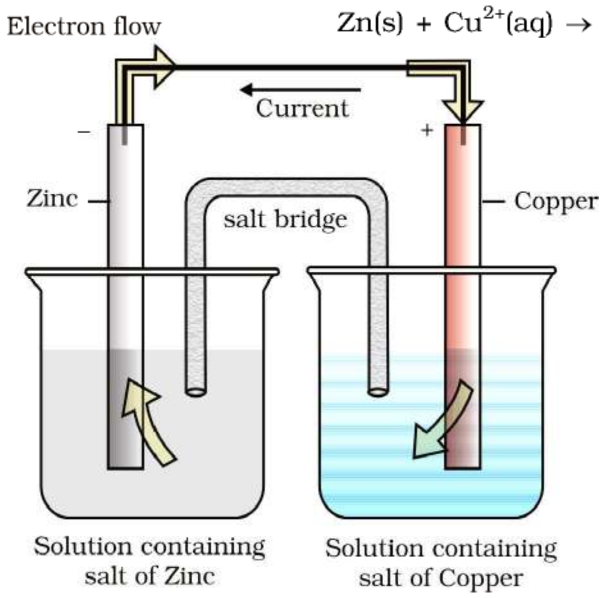
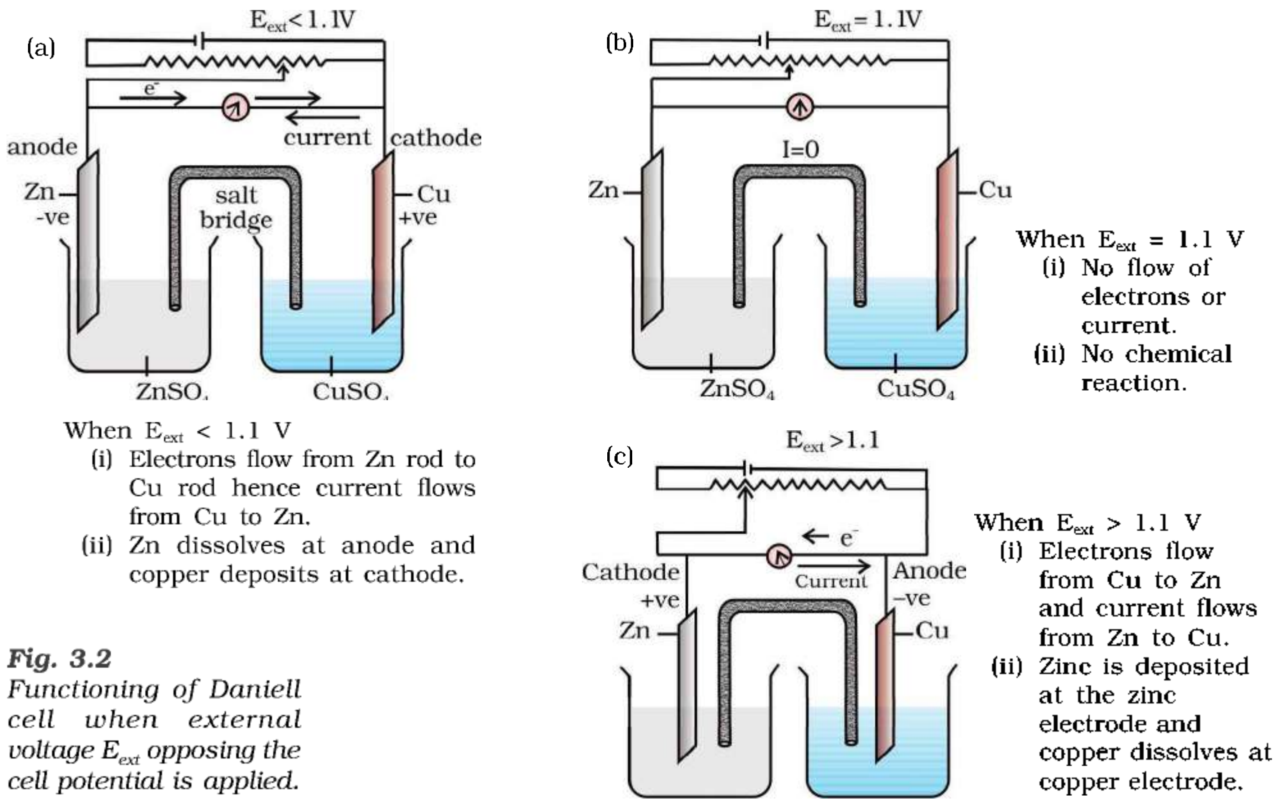


Fig. 3.1: *Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.*



When E_{ext} < 1.1 V
(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
(ii) Zn dissolves at anode and copper deposits at cathode.

When E_{ext} = 1.1 V
(i) No flow of electrons or current.
(ii) No chemical reaction.

When E_{ext} > 1.1 V
(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.
(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

Fig. 3.2
Functioning of Daniell cell when external voltage E_{ext} opposing the cell potential is applied.

Strictly speaking activity should be used instead of concentration. It is directly proportional to concentration. In dilute solutions, it is equal to concentration. You will study more about it in higher classes.

3.2 Galvanic Cells

As mentioned earlier (Class XI, Unit 8) a galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadgets like heater, fan, geyser, etc.

Daniell cell discussed earlier is one such cell in which the following redox reaction occurs.

$$\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}\ (aq) + Cu(s)}$$

This reaction is a combination of two half reactions whose addition gives the overall cell reaction:

(i) $\mathrm{Cu^{2+} + 2e^- \rightarrow Cu(s)}$ (reduction half reaction) (3.2)

(ii) $\mathrm{Zn(s) \rightarrow Zn^{2+} + 2e^-}$ (oxidation half reaction) (3.3)

These reactions occur in two different portions of the Daniell cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples**. The copper electrode may be called the reduction half cell and the zinc electrode, the oxidation half-cell.

We can construct innumerable number of galvanic cells on the pattern of Daniell cell by taking combinations of different half-cells. Each half-cell consists of a metallic electrode dipped into an electrolyte. The two half-cells are connected by a metallic wire through a voltmeter and a switch externally. The electrolytes of the two half-cells are connected internally through a salt bridge as shown in Fig. 3.1. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt bridge.

At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution. A potential difference develops between the electrode and the electrolyte which is called **electrode potential**. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials. In a galvanic cell, the half-cell in which oxidation takes place is called **anode** and it has a negative potential with respect to the solution. The other half-cell in which reduction takes place is called **cathode** and it has a positive potential with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of electron flow.

The potential difference between the two electrodes of a galvanic cell is called the *cell potential* and is measured in volts. The *cell potential* is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the *cell electromotive force* (emf) of the cell when no current is drawn through the cell. It is now an accepted convention that we keep the anode on the left and the cathode on the right while representing the galvanic cell. A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge. Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side i.e.,

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

This is illustrated by the following example:

Cell reaction:

$$\text{Cu(s)} + 2\text{Ag}^{+}\text{(aq)} \longrightarrow \text{Cu}^{2+}\text{(aq)} + 2\ \text{Ag(s)} \qquad (3.4)$$

Half-cell reactions:

$$\text{Cathode } (\textit{reduction}): \quad 2\text{Ag}^{+}\text{(aq)} + 2\text{e}^{-} \rightarrow 2\text{Ag(s)} \qquad (3.5)$$

$$\text{Anode } (\textit{oxidation}): \quad \text{Cu(s)} \rightarrow \text{Cu}^{2+}\text{(aq)} + 2\text{e}^{-} \qquad (3.6)$$

It can be seen that the sum of (3.5) and (3.6) leads to overall reaction (3.4) in the cell and that silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as:

$$\text{Cu(s)}\,|\,\text{Cu}^{2+}\text{(aq)}\,||\,\text{Ag}^{+}\text{(aq)}\,|\,\text{Ag(s)}$$

$$\text{and we have } E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{Ag}^{+}|\text{Ag}} - E_{\text{Cu}^{2+}|\text{Cu}} \qquad (3.7)$$

3.2.1 Measurement of Electrode Potential

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. If we arbitrarily choose the potential of one electrode (half-cell) then that of the other can be determined with respect to this. According to convention, a half-cell called standard hydrogen electrode (Fig.3.3) represented by $\text{Pt(s)}\,|\,\text{H}_2\text{(g)}\,|\,\text{H}^{+}\text{(aq)}$, is assigned a zero potential at all temperatures corresponding to the reaction

$$\text{H}^{+}\text{(aq)} + \text{e}^{-} \rightarrow \frac{1}{2}\text{H}_2\text{(g)}$$

The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity (Fig. 3.3). This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.

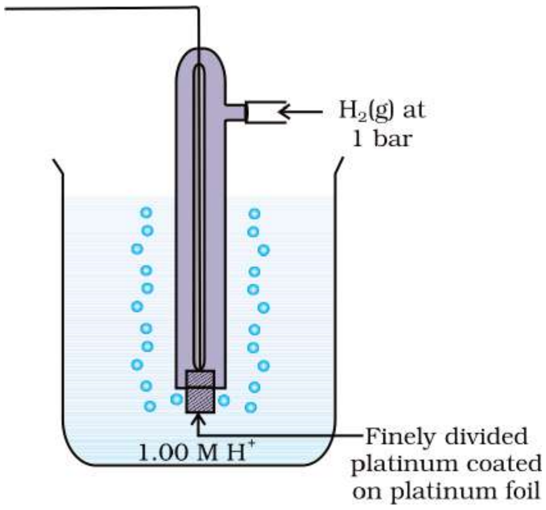


Fig. 3.3: *Standard Hydrogen Electrode (SHE).*

At 298 K the emf of the cell, standard hydrogen electrode || second half-cell constructed by taking standard hydrogen electrode as anode (reference half-cell) and the other half-cell as cathode, gives the reduction potential of the other half-cell. If the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential, $E^\ominus_R$ of the given half-cell.

$$E^\ominus = E^\ominus_R - E^\ominus_L$$

As $E^\ominus_L$ for standard hydrogen electrode is zero.

$$E^\ominus = E^\ominus_R - 0 = E^\ominus_R$$

The measured emf of the cell:

$$\text{Pt(s)} \mid \text{H}_2\text{(g, 1 bar)} \mid \text{H}^+ \text{(aq, 1 M)} \parallel \text{Cu}^{2+} \text{(aq, 1 M)} \mid \text{Cu}$$

is 0.34 V and it is also the value for the standard electrode potential of the half-cell corresponding to the reaction:

$$\text{Cu}^{2+} \text{(aq, 1M)} + 2\,\text{e}^- \rightarrow \text{Cu(s)}$$

Similarly, the measured emf of the cell:

$$\text{Pt(s)} \mid \text{H}_2\text{(g, 1 bar)} \mid \text{H}^+ \text{(aq, 1 M)} \parallel \text{Zn}^{2+} \text{(aq, 1M)} \mid \text{Zn}$$

is -0.76 V corresponding to the standard electrode potential of the half-cell reaction:

$$\text{Zn}^{2+} \text{(aq, 1 M)} + 2\text{e}^- \rightarrow \text{Zn(s)}$$

The positive value of the standard electrode potential in the first case indicates that Cu^{2+} ions get reduced more easily than H^+ ions. The reverse process cannot occur, that is, hydrogen ions cannot oxidise Cu (or alternatively we can say that hydrogen gas can reduce copper ion) under the standard conditions described above. Thus, Cu does not dissolve in HCl. In nitric acid it is oxidised by nitrate ion and not by hydrogen ion. The negative value of the standard electrode potential in the second case indicates that hydrogen ions can oxidise zinc (or zinc can reduce hydrogen ions).

In view of this convention, the half reaction for the Daniell cell in Fig. 3.1 can be written as:

Left electrode: $\text{Zn(s)} \rightarrow \text{Zn}^{2+} \text{(aq, 1 M)} + 2\,\text{e}^-$

Right electrode: $\text{Cu}^{2+} \text{(aq, 1 M)} + 2\,\text{e}^- \rightarrow \text{Cu(s)}$

The overall reaction of the cell is the sum of above two reactions and we obtain the equation:

$$\text{Zn(s)} + \text{Cu}^{2+} \text{(aq)} \rightarrow \text{Zn}^{2+} \text{(aq)} + \text{Cu(s)}$$

$$\text{emf of the cell} = E^0_{\text{cell}} = E^0_R - E^0_L$$

$$= 0.34\text{V} - (-0.76)\text{V} = 1.10\text{ V}$$

Sometimes metals like platinum or gold are used as inert electrodes. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for the conduction of electrons. For example, Pt is used in the following half-cells:

Hydrogen electrode: $\text{Pt(s)} \mid \text{H}_2\text{(g)} \mid \text{H}^+\text{(aq)}$

With half-cell reaction: $\text{H}^+ \text{(aq)} + \text{e}^- \rightarrow \tfrac{1}{2}\,\text{H}_2\text{(g)}$

Bromine electrode: $\text{Pt(s)} \mid \text{Br}_2\text{(aq)} \mid \text{Br}^-\text{(aq)}$

With half-cell reaction: ½ $Br_2(aq) + e^- \rightarrow Br^-(aq)$

The standard electrode potentials are very important and we can extract a lot of useful information from them. The values of standard electrode potentials for some selected half-cell reduction reactions are given in Table 3.1. If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species. It can be seen that the standard electrode potential for fluorine is the highest in the Table indicating that fluorine gas (F_2) has the maximum tendency to get reduced to fluoride ions (F^-) and therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent. Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution. It may be seen that as we go from top to bottom in Table 3.1 the standard electrode potential decreases and with this, decreases the oxidising power of the species on the left and increases the reducing power of the species on the right hand side of the reaction. Electrochemical cells are extensively used for determining the pH of solutions, solubility product, equilibrium constant and other thermodynamic properties and for potentiometric titrations.

Intext Questions

3.1 How would you determine the standard electrode potential of the system $Mg^{2+} | Mg$?

3.2 Can you store copper sulphate solutions in a zinc pot?

3.3 Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

Nernst Equation

We have assumed in the previous section that the concentration of all the species involved in the electrode reaction is unity. This need not be always true. Nernst showed that for the electrode reaction:

$M^{n+}(aq) + ne^- \rightarrow M(s)$

the electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{(M^{n+}/M)} = E^{V}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

but concentration of solid M is taken as unity and we have

$$E_{(M^{n+}/M)} = E^{V}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \qquad (3.8)$$

$E^{V}_{(M^{n+}/M)}$ has already been defined, R is gas constant (8.314 $JK^{-1}\,mol^{-1}$), F is Faraday constant (96487 C mol^{-1}), T is temperature in kelvin and $[M^{n+}]$ is the concentration of the species, M^{n+}.

Table 3.1: Standard Electrode Potentials at 298 K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s.

Reaction (Oxidised form + ne^-	→ Reduced form)	$E^{\ominus}$/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**	**0.00**
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	–0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	–0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	–0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	–0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	–0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	–0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	–1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	–2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	–2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	–2.87
$K^+ + e^-$	$\rightarrow K(s)$	–2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	–3.05

Increasing strength of oxidising agent ↑

Increasing strength of reducing agent ↓

1. A negative $E^{\ominus}$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive $E^{\ominus}$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

In Daniell cell, the electrode potential for any given concentration of Cu^{2+} and Zn^{2+} ions, we write

For Cathode:

$$E_{(Cu^{2+}/Cu)} = E^{\ominus}_{(Cu^{2+}/Cu)} - \frac{RT}{2F}\ln\frac{1}{[Cu^{2+}(aq)]} \tag{3.9}$$

For Anode:

$$E_{(Zn^{2+}/Zn)} = E^{\ominus}_{(Zn^{2+}/Zn)} - \frac{RT}{2F}\ln\frac{1}{[Zn^{2+}(aq)]} \tag{3.10}$$

The cell potential, $E_{(cell)} = E_{(Cu^{2+}/Cu)} - E_{(Zn^{2+}/Zn)}$

$$= E^{\ominus}_{(Cu^{2+}/Cu)} - \frac{RT}{2F}\ln\frac{1}{[Cu^{2+}(aq)]} - E^{\ominus}_{(Zn^{2+}/Zn)} + \frac{RT}{2F}\ln\frac{1}{[Zn^{2+}(aq)]}$$

$$= E^{\ominus}_{(Cu^{2+}/Cu)} - E^{\ominus}_{(Zn^{2+}/Zn)} - \frac{RT}{2F}\left[\ln\frac{1}{[Cu^{2+}(aq)]} - \ln\frac{1}{[Zn^{2+}(aq)]}\right]$$

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{3.11}$$

It can be seen that $E_{(cell)}$ depends on the concentration of both Cu^{2+} and Zn^{2+} ions. It increases with increase in the concentration of Cu^{2+} ions and decrease in the concentration of Zn^{2+} ions.

By converting the natural logarithm in Eq. (3.11) to the base 10 and substituting the values of R, F and T = 298 K, it reduces to

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{3.12}$$

We should use the same number of electrons (n) for both the electrodes and thus for the following cell

$$Ni(s) | Ni^{2+}(aq) || Ag^{+}(aq) | Ag$$

The cell reaction is $Ni(s) + 2Ag^{+}(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$

The Nernst equation can be written as

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F}\ln\frac{[Ni^{2+}]}{[Ag^{+}]^2}$$

and for a general electrochemical reaction of the type:

$$a\,A + bB \xrightarrow{ne^-} cC + dD$$

Nernst equation can be written as:

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{nF}\ln Q$$

$$= E^{\ominus}_{(cell)} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{3.13}$$

Example

Represent the cell in which the following reaction takes place
$Mg(s) + 2Ag^{+}(0.0001M) \rightarrow Mg^{2+}(0.130M) + 2Ag(s)$

Calculate its $E_{(cell)}$ if $E^{V}_{(cell)} = 3.17$ V.

Solution

The cell can be written as $Mg|Mg^{2+}(0.130M)||Ag^{+}(0.0001M)|Ag$

$$E_{(cell)} = E^{V}_{(cell)} - \frac{RT}{2F}\ln\frac{[Mg^{2+}]}{[Ag^{+}]^2}$$

$$= 3.17\text{ V} - \frac{0.059V}{2}\log\frac{0.130}{(0.0001)^2} = 3.17\text{ V} - 0.21\text{V} = 2.96\text{ V}.$$

3.3.1 Equilibrium Constant from Nernst Equation

If the circuit in Daniell cell (Fig. 3.1) is closed then we note that the reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad (3.1)$$

takes place and as time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing. At the same time voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained. In this situation the Nernst equation may be written as:

$$E_{(cell)} = 0 = E^{V}_{(cell)} - \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\text{or } E^{V}_{(cell)} = \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium,

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c \text{ for the reaction 3.1}$$

and at T = 298K the above equation can be written as

$$E^{V}_{(cell)} = \frac{0.059\text{ V}}{2}\log K_C = 1.1\text{ V} \qquad (E^{V}_{(cell)} = 1.1\text{V})$$

$$\log K_C = \frac{(1.1\text{V} \times 2)}{0.059\text{ V}} = 37.288$$

$$K_C = 2 \times 10^{37} \text{ at 298K.}$$

In general,

$$E^{V}_{(cell)} = \frac{2.303RT}{nF}\log K_C \qquad (3.14)$$

Thus, Eq. (3.14) gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place. Thus, equilibrium constants of the reaction, difficult to measure otherwise, can be calculated from the corresponding $E^{\square}$ value of the cell.

Example Calculate the equilibrium constant of the reaction:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

$$E^{V}_{(cell)} = 0.46\ V$$

Solution

$$E^{V}_{(cell)} = \frac{0.059\ V}{2} \log K_C = 0.46\ V \text{ or}$$

$$\log K_C = \frac{0.46\ V \times 2}{0.059\ V} = 15.6$$

$$K_C = 3.92 \times 10^{15}$$

3.3.2 Electrochemical Cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf of the cell is E and nF is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction, then

$$\Delta_r G = -\ nFE_{(cell)} \qquad (3.15)$$

It may be remembered that $E_{(cell)}$ is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on n. Thus, if we write the reaction

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad (3.1)$$

$$\Delta_r G = -\ 2FE_{(cell)}$$

but when we write the reaction

$$2\ Zn\ (s) + 2\ Cu^{2+}(aq) \longrightarrow 2\ Zn^{2+}(aq) + 2Cu(s)$$

$$\Delta_r G = -\ 4FE_{(cell)}$$

If the concentration of all the reacting species is unity, then $E_{(cell)} = E^{V}_{(cell)}$ and we have

$$\Delta_r G^{\ominus} = -\ nFE^{V}_{(cell)} \qquad (3.16)$$

Thus, from the measurement of $E^{V}_{(cell)}$ we can obtain an important thermodynamic quantity, $\Delta_r G^{\ominus}$, standard Gibbs energy of the reaction. From the latter we can calculate equilibrium constant by the equation:

$$\Delta_r G^{\ominus} = -RT \ln K.$$

Example The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Solution $\Delta_r G^{\ominus} = -\ nFE^{V}_{(cell)}$

n in the above equation is 2, F = 96487 C mol^{-1} and $E^{V}_{(cell)} = 1.1$ V

Therefore, $\Delta_r G^{\ominus} = -\ 2 \times 1.1V \times 96487\ C\ mol^{-1}$

$= -\ 21227\ J\ mol^{-1}$

$= -\ 212.27\ kJ\ mol^{-1}$

Intext Questions

3.4 Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

3.5 Calculate the emf of the cell in which the following reaction takes place:
$Ni(s) + 2Ag^{+}\ (0.002\ M) \rightarrow Ni^{2+}\ (0.160\ M) + 2Ag(s)$

Given that $E^{V}_{(cell)} = 1.05\ V$

3.6 The cell in which the following reaction occurs:

$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$ has $E^{0}_{cell} = 0.236\ V$ at 298 K.
Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Conductance of Electrolytic Solutions

It is necessary to define a few terms before we consider the subject of conductance of electricity through electrolytic solutions. The electrical resistance is represented by the symbol '*R*' and it is measured in ohm (Ω) which in terms of SI base units is equal to (kg m^2)/(S^3 *A*^{2}). It can be measured with the help of a Wheatstone bridge with which you are familiar from your study of physics. The electrical resistance of any object is directly proportional to its length, *l*, and inversely proportional to its area of cross section, *A*. That is,

$$R \propto \frac{l}{A} \text{ or } R = \rho\,\frac{l}{A} \qquad (3.17)$$

The constant of proportionality, ρ (Greek, rho), is called **resistivity** (specific resistance). Its SI units are ohm metre (Ω m) and quite often its submultiple, ohm centimetre (Ω cm) is also used. IUPAC recommends the use of the term resistivity over specific resistance and hence in the rest of the book we shall use the term resistivity. Physically, the resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m^2. It can be seen that:

$$1\ \Omega\ m = 100\ \Omega\ cm \text{ or } 1\ \Omega\ cm = 0.01\ \Omega\ m$$

The inverse of resistance, *R*, is called **conductance**, *G*, and we have the relation:

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa\frac{A}{l} \qquad (3.18)$$

The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to ohm^{-1} (also known as mho) or Ω^{-1}. The inverse of resistivity, called **conductivity** (specific conductance) is represented by the symbol, κ (Greek, kappa). IUPAC has recommended the use of term conductivity over specific conductance and hence we shall use the term conductivity in the rest of the book. The SI units of conductivity are S m^{-1} but quite often, κ is expressed in S cm^{-1}. Conductivity of a material in S m^{-1} is its conductance when it is 1 m long and its area of cross section is 1 m^2. It may be noted that 1 S cm^{-1} = 100 S m^{-1}.

Table 3.2: The values of Conductivity of some Selected Materials at 298.15 K

Material	Conductivity/ S m^{-1}	Material	Conductivity/ S m^{-1}
Conductors		***Aqueous Solutions***	
Sodium	2.1×10^{3}	Pure water	3.5×10^{-5}
Copper	5.9×10^{3}	0.1 M HCl	3.91
Silver	6.2×10^{3}	0.01M KCl	0.14
Gold	4.5×10^{3}	0.01M NaCl	0.12
Iron	1.0×10^{3}	0.1 M HAc	0.047
Graphite	1.2×10	0.01M HAc	0.016
Insulators		***Semiconductors***	
Glass	1.0×10^{-16}	CuO	1×10^{-7}
Teflon	1.0×10^{-18}	Si	1.5×10^{-2}
		Ge	2.0

It can be seen from Table 3.2 that the magnitude of conductivity varies a great deal and depends on the nature of the material. It also depends on the temperature and pressure at which the measurements are made. Materials are classified into conductors, insulators and semiconductors depending on the magnitude of their conductivity. Metals and their alloys have very large conductivity and are known as conductors. Certain non-metals like carbon-black, graphite and some organic polymers* are also electronically conducting. Substances like glass, ceramics, etc., having very low conductivity are known as insulators. Substances like silicon, doped silicon and gallium arsenide having conductivity between conductors and insulators are called semiconductors and are important electronic materials. Certain materials called superconductors by definition have zero resistivity or infinite conductivity. Earlier, only metals and their alloys at very low temperatures (0 to 15 K) were known to behave as superconductors, but nowadays a number of ceramic materials and mixed oxides are also known to show superconductivity at temperatures as high as 150 K.

Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on

(i) the nature and structure of the metal

(ii) the number of valence electrons per atom

(iii) temperature (it decreases with increase of temperature).

---

* *Electronically conducting polymers – In 1977 MacDiarmid, Heeger and Shirakawa discovered that acetylene gas can be polymerised to produce a polymer, polyacetylene when exposed to vapours of iodine acquires metallic lustre and conductivity. Since then several organic conducting polymers have been made such as polyaniline, polypyrrole and polythiophene. These organic metals, being composed wholly of elements like carbon, hydrogen and occasionally nitrogen, oxygen or sulphur, are much lighter than normal metals and can be used for making light-weight batteries. Besides, they have the mechanical properties of polymers such as flexibility so that one can make electronic devices such as transistors that can bend like a sheet of plastic. For the discovery of conducting polymers, MacDiarmid, Heeger and Shirakawa were awarded the Nobel Prize in Chemistry for the year 2000.*

As the electrons enter at one end and go out through the other end, the composition of the metallic conductor remains unchanged. The mechanism of conductance through semiconductors is more complex.

We already know (Class XI, Unit 7) that even very pure water has small amounts of hydrogen and hydroxyl ions ($\sim10^{-7}$M) which lend it very low conductivity (3.5×10^{-5} S m^{-1}). When electrolytes are dissolved in water, they furnish their own ions in the solution hence its conductivity also increases. The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on:

(i) the nature of the electrolyte added
(ii) size of the ions produced and their solvation
(iii) the nature of the solvent and its viscosity
(iv) concentration of the electrolyte
(v) temperature (it increases with the increase of temperature).

Passage of direct current through ionic solution over a prolonged period can lead to change in its composition due to electrochemical reactions (Section 3.4.1).

3.4.1 Measurement of the Conductivity of Ionic Solutions

We know that accurate measurement of an unknown resistance can be performed on a Wheatstone bridge. However, for measuring the resistance of an ionic solution we face two problems. Firstly, passing direct current (DC) changes the composition of the solution. Secondly, a solution cannot be connected to the bridge like a metallic wire or other solid conductor. The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called **conductivity cell.** It is available in several designs and two simple ones are shown in Fig. 3.4.

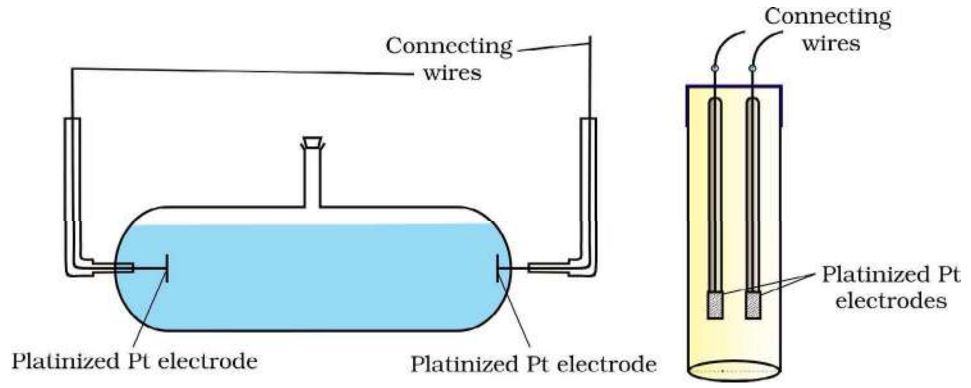


Fig. 3.4
Two different types of conductivity cells.

Basically it consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically). These have area of cross section equal to ‘A’ and are separated by distance ‘l’. Therefore, solution confined between these electrodes is a column of length l and area of cross section A. The resistance of such a column of solution is then given by the equation:

$$R = \rho \frac{l}{A} = \frac{l}{\kappa A} \tag{3.17}$$

The quantity l/A is called cell constant denoted by the symbol, G^*. It depends on the distance between the electrodes and their area of cross-section and has the dimension of length^{-1} and can be calculated if we know l and A. Measurement of l and A is not only inconvenient but also unreliable. The cell constant is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known. For this purpose, we generally use KCl solutions whose conductivity is known accurately at various concentrations (Table 3.3) and at different temperatures. The cell constant, G^*, is then given by the equation:

$$G^* = \frac{l}{A} = \mathrm{R}\,\kappa \qquad (3.18)$$

Table 3.3: Conductivity and Molar conductivity of KCl solutions at 298.15K

Concentration/Molarity		Conductivity		Molar Conductivity	
mol L^{-1}	mol m^{-3}	S cm^{-1}	S m^{-1}	S cm^{2}mol^{-1}	S m^2 mol^{-1}
1.000	1000	0.1113	11.13	111.3	111.3×10^{-4}
0.100	100.0	0.0129	1.29	129.0	129.0×10^{-4}
0.010	10.00	0.00141	0.141	141.0	141.0×10^{-4}

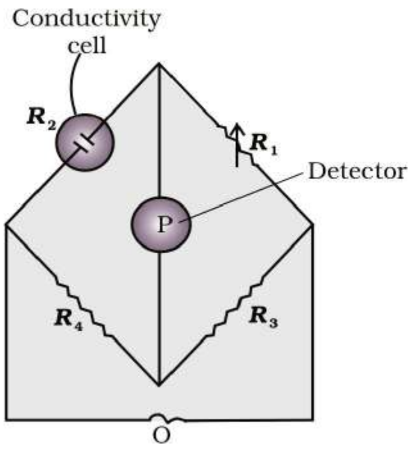


Fig. 3.5: *Arrangement for measurement of resistance of a solution of an electrolyte.*

Once the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution. The set up for the measurement of the resistance is shown in Fig. 3.5.

It consists of two resistances R_3 and R_4, a variable resistance R_1 and the conductivity cell having the unknown resistance R_2. The Wheatstone bridge is fed by an oscillator O (a source of a.c. power in the audio frequency range 550 to 5000 cycles per second). P is a suitable detector (a headphone or other electronic device) and the bridge is balanced when no current passes through the detector. Under these conditions:

$$\text{Unknown resistance } R_2 = \frac{\mathrm{R_1\,R_4}}{\mathrm{R_3}} \qquad (3.19)$$

These days, inexpensive conductivity meters are available which can directly read the conductance or resistance of the solution in the conductivity cell. Once the cell constant and the resistance of the solution in the cell is determined, the conductivity of the solution is given by the equation:

$$\kappa = \frac{\text{cell constant}}{\mathrm{R}} = \frac{\mathrm{G^*}}{\mathrm{R}} \qquad (3.20)$$

The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to charge and size of the ions in which they dissociate, the concentration of ions or ease with which the ions move under a potential gradient. It, therefore, becomes necessary to define a physically more meaningful quantity called **molar conductivity** denoted by the symbol Λ_m (Greek, lambda). It is related to the conductivity of the solution by the equation:

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c} \qquad (3.21)$$

In the above equation, if κ is expressed in S m^{-1} and the concentration, c in mol m^{-3} then the units of Λ_m are in S m^2 mol^{-1}. It may be noted that:

1 mol m^{-3} = 1000(L/m^3) × molarity (mol/L), and hence

$$\Lambda_m(\text{S cm}^2\ \text{mol}^{-1}) = \frac{\kappa\ (\text{S cm}^{-1})}{1000\ \text{L m}^{-3} \times \text{molarity (mol L}^{-1})}$$

If we use S cm^{-1} as the units for κ and mol cm^{-3}, the units of concentration, then the units for Λ_m are S cm^2 mol^{-1}. It can be calculated by using the equation:

$$\Lambda_m(\text{S cm}^2\ \text{mol}^{-1}) = \frac{\kappa\ (\text{S cm}^{-1}) \times 1000\ (\text{cm}^3/\text{L})}{\text{molarity (mol/L)}}$$

Both type of units are used in literature and are related to each other by the equations:

$$1\ \text{S m}^2\text{mol}^{-1} = 10^4\ \text{S cm}^2\text{mol}^{-1} \quad \text{or}$$
$$1\ \text{S cm}^2\text{mol}^{-1} = 10^{-4}\ \text{S m}^2\text{mol}^{-1}.$$

Example

Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 S/m.

Solution

The cell constant is given by the equation:

Cell constant = G^* = conductivity × resistance

= 1.29 S/m × 100 Ω = 129 m^{-1} = 1.29 cm^{-1}

Conductivity of 0.02 mol L^{-1} KCl solution = cell constant / resistance

$$= \frac{G^*}{R} = \frac{129\ \text{m}^{-1}}{520\ \Omega} = 0.248\ \text{S m}^{-1}$$

Concentration $= 0.02\ \text{mol L}^{-1}$

$= 1000 \times 0.02\ \text{mol m}^{-3} = 20\ \text{mol m}^{-3}$

Molar conductivity $= \Lambda_m = \dfrac{\kappa}{c}$

$$= \frac{248 \times 10^{-3}\ \text{S m}^{-1}}{20\ \text{mol m}^{-3}} = 124 \times 10^{-4}\ \text{S m}^2\text{mol}^{-1}$$

Alternatively, $\kappa = \dfrac{1.29\ \text{cm}^{-1}}{520\ \Omega} = 0.248 \times 10^{-2}\ \text{S cm}^{-1}$

and $$\Lambda_m = \kappa \times 1000\ \text{cm}^3\ \text{L}^{-1}\ \text{molarity}^{-1}$$

$$= \frac{0.248 \times 10^{-2}\ \text{S cm}^{-1} \times 1000\ \text{cm}^3\ \text{L}^{-1}}{0.02\ \text{mol L}^{-1}}$$

$$= 124\ \text{S cm}^2\ \text{mol}^{-1}$$

Example The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Solution $A = \pi r^2 = 3.14 \times 0.5^2\ \text{cm}^2 = 0.785\ \text{cm}^2 = 0.785 \times 10^{-4}\ \text{m}^2$

$l = 50\ \text{cm} = 0.5\ \text{m}$

$$R = \frac{\rho\, l}{A} \quad \text{or} \quad \rho = \frac{RA}{l} = \frac{5.55 \times 10^3\,\Omega \times 0.785\,\text{cm}^2}{50\,\text{cm}} = 87.135\ \Omega\ \text{cm}$$

$$\text{Conductivity} = \kappa = \frac{1}{\rho} = \left(\frac{1}{87.135}\right)\ \text{S cm}^{-1}$$

$$= 0.01148\ \text{S cm}^{-1}$$

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{c}\ \text{cm}^3\ \text{L}^{-1}$$

$$= \frac{0.01148\ \text{S cm}^{-1} \times 1000\ \text{cm}^3\ \text{L}^{-1}}{0.05\ \text{mol L}^{-1}}$$

$$= 229.6\ \text{S cm}^2\ \text{mol}^{-1}$$

If we want to calculate the values of different quantities in terms of ‘m’ instead of ‘cm’,

$$\rho = \frac{RA}{l}$$

$$= \frac{5.55 \times 10^3\ \Omega \times 0.785 \times 10^{-4}\ \text{m}^2}{0.5\ \text{m}} = 87.135 \times 10^{-2}\ \Omega\ \text{m}$$

$$\kappa = \frac{1}{\rho} = \frac{100}{87.135}\ \Omega\ \text{m} = 1.148\ \text{S m}^{-1}$$

and $$\Lambda_m = \frac{\kappa}{c} = \frac{1.148\ \text{S m}^{-1}}{50\ \text{mol m}^{-3}} = 229.6 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}.$$

3.4.2 Variation of Conductivity and Molar Conductivity with Concentration

Both conductivity and molar conductivity change with the concentration of the electrolyte. Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length. This is clear from the equation:

$G = \frac{\kappa A}{l} = \kappa$ (both A and l are unity in their appropriate units in m or cm)

Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length. Therefore,

$$\Lambda_m = \frac{\kappa A}{l} = \kappa$$

Since $l = 1$ and $A = V$ (volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa\ V \qquad (3.22)$$

Molar conductivity increases with decrease in concentration. This is because the total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume. Physically, it means that at a given concentration, Λ_m can be defined as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity** and is represented by the symbol Λ°_m. The variation in Λ_m with concentration is different (Fig. 3.6) for strong and weak electrolytes.

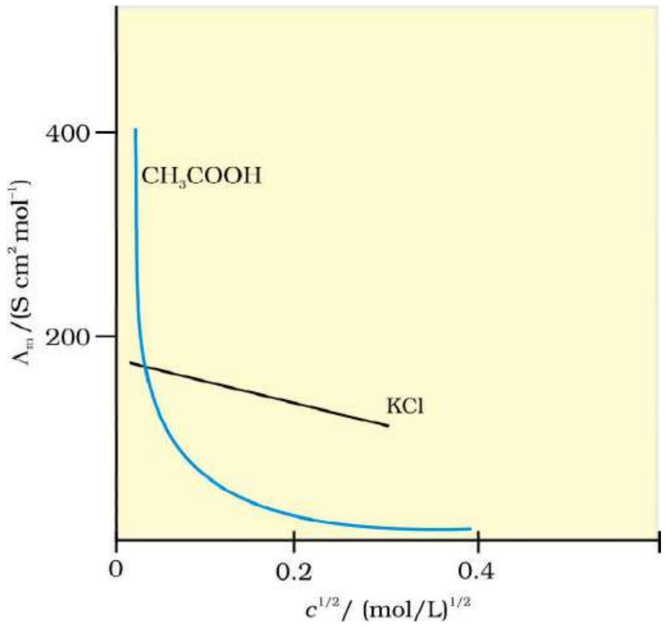


Fig. 3.6: *Molar conductivity versus c½ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.*

Strong Electrolytes

For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation:

$$\Lambda_m = \Lambda^\circ_m - A\ c^{1/2} \qquad (3.23)$$

It can be seen that if we plot (Fig. 3.12) Λ_m against $c^{1/2}$, we obtain a straight line with intercept equal to Λ°_m and slope equal to '–A'. The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for 'A'.

Example The molar conductivity of KCl solutions at different concentrations at 298 K are given below:

c/mol L^{-1}	Λ_m/S cm^2 mol^{-1}
0.000198	148.61
0.000309	148.29
0.000521	147.81
0.000989	147.09

Show that a plot between Λ_m and $c^{1/2}$ is a straight line. Determine the values of Λ_m° and A for KCl.

Solution Taking the square root of concentration we obtain:

$c^{1/2}$/(mol L^{-1})$^{1/2}$	Λ_m/S cm^{2}mol^{-1}
0.01407	148.61
0.01758	148.29
0.02283	147.81
0.03145	147.09

A plot of Λ_m(y-axis) and $c^{1/2}$ (x-axis) is shown in (Fig. 3.7). It can be seen that it is nearly a straight line. From the intercept ($c^{1/2}$ = 0), we find that

Λ_m°= 150.0 S cm^2 mol^{-1} and

A = – slope = 87.46 S cm^2 mol^{-1}/(mol/L^{-1})$^{1/2}$.

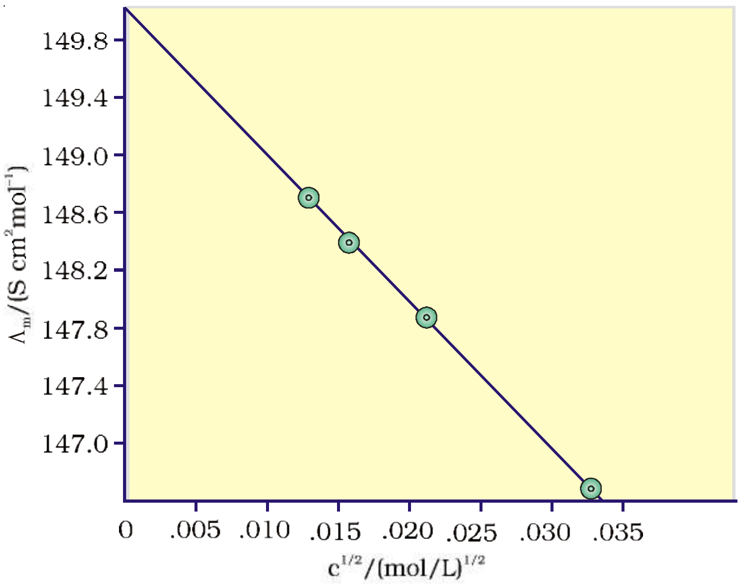


Fig. 3.7: *Variation of Λ_m against c½.*

Kohlrausch examined Λ°_m values for a number of strong electrolytes and observed certain regularities. He noted that the difference in Λ°_m of the electrolytes NaX and KX for any X is nearly constant. For example at 298 K:

$$\Lambda^\circ_{m\,(KCl)} - \Lambda^\circ_{m\,(NaCl)} = \Lambda^\circ_{m\,(KBr)} - \Lambda^\circ_{m\,(NaBr)}$$

$= \Lambda^\circ_{m\,(KI)} - \Lambda^\circ_{m\,(NaI)}$ □ 23.4 S cm^2 mol^{-1}

and similarly it was found that

$\Lambda^\circ_{m\,(NaBr)} - \Lambda^\circ_{m\,(NaCl)} = \Lambda^\circ_{m\,(KBr)} - \Lambda^\circ_{m\,(KCl)}$ □ 1.8 S cm^2 mol^{-1}

On the basis of the above observations he enunciated **Kohlrausch law of independent migration of ions**. The law states that *limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. Thus, if $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are limiting molar conductivity* of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$$\Lambda^\circ_{m\,(NaCl)} = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \qquad (3.24)$$

In general, if an electrolyte on dissociation gives ν_+ cations and ν_- anions then its limiting molar conductivity is given by:

$$\Lambda^\circ_m = \nu_+ \lambda^0_+ + \nu_- \lambda^0_- \qquad (3.25)$$

Here, λ^0_+ and λ^0_- are the limiting molar conductivities of the cation and anion respectively. The values of λ^0 for some cations and anions at 298 K are given in Table 3.4.

Table 3.4: Limiting Molar Conductivity for some Ions in Water at 298 K

Ion	λ^0/(S cm^{2}mol^{-1})	Ion	λ^0/(S cm^2 mol^{-1})
H^+	349.6	OH^-	199.1
Na^+	50.1	Cl^-	76.3
K^+	73.5	Br^-	78.1
Ca^{2+}	119.0	CH_3COO^-	40.9
Mg^{2+}	106.0	SO_4^{2-}	160.0

Weak Electrolytes

Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte. In such cases Λ_m increases steeply (Fig. 3.12) on dilution, especially near lower concentrations. Therefore, Λ°_m cannot be obtained by extrapolation of Λ_m to zero concentration. At infinite dilution (i.e., concentration $c \rightarrow$ zero) electrolyte dissociates completely (α□=1), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately. Therefore, Λ°_m for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions (Example 3.8). At any concentration c, if α is the degree of dissociation then it can be approximated to the ratio of molar conductivity Λ_m at the concentration c to limiting molar conductivity, Λ_m°. Thus we have:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} \qquad (3.26)$$

But we know that for a weak electrolyte like acetic acid (Class XI, Unit 7),

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m^2}{\Lambda_m^{\circ 2}\left(1-\frac{\Lambda_m}{\Lambda_m^\circ}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^\circ\left(\Lambda_m^\circ - \Lambda_m\right)} \qquad (3.27)$$

Applications of Kohlrausch law

Using Kohlrausch law of independent migration of ions, it is possible to calculate Λ_m° for any electrolyte from the λ° of individual ions. Moreover, for weak electrolytes like acetic acid it is possible to determine the value of its dissociation constant once we know the Λ_m° and Λ_m at a given concentration c.

Example

Calculate Λ_m° for $CaCl_2$ and $MgSO_4$ from the data given in Table 3.4.

Solution

We know from Kohlrausch law that

$$\Lambda^\circ_{m(CaCl_2)} = \lambda^\circ_{Ca^{2+}} + 2\lambda^\circ_{Cl^-} = 119.0 \text{ S cm}^2 \text{ mol}^{-1} + 2(76.3) \text{ S cm}^2 \text{ mol}^{-1}$$
$$= (119.0 + 152.6) \text{ S cm}^2 \text{ mol}^{-1}$$
$$= 271.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ_{m(MgSO_4)} = \lambda^\circ_{Mg^{2+}} + \lambda^\circ_{SO_4^{2-}} = 106.0 \text{ S cm}^2 \text{ mol}^{-1} + 160.0 \text{ S cm}^2 \text{ mol}^{-1}$$
$$= 266 \text{ S cm}^2 \text{ mol}^{-1} .$$

Example

Λ_m° for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ° for HAc.

Solution

$$\Lambda^\circ_{m(HAc)} = \lambda^\circ_{H^+} + \lambda^\circ_{Ac^-} = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} + \lambda^\circ_{Ac^-} + \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-} - \lambda^\circ_{Na^+}$$
$$= \Lambda^\circ_{m(HCl)} + \Lambda^\circ_{m(NaAc)} - \Lambda^\circ_{m(NaCl)}$$
$$= (425.9 + 91.0 - 126.4\ ) \text{ S cm}^2 \text{ mol}^{-1}$$
$$= 390.5 \text{ S cm}^2 \text{ mol}^{-1} .$$

Example

The conductivity of 0.001028 mol L^{-1} acetic acid is 4.95 × 10^{-5} S cm^{-1}. Calculate its dissociation constant if Λ_m° for acetic acid is 390.5 S cm^2 mol^{-1}.

Solution

$$\Lambda_m = \frac{\kappa}{c} = \frac{4.95\times10^{-5}\,\text{S cm}^{-1}}{0.001028\,\text{mol L}^{-1}} \times \frac{1000\,\text{cm}^3}{\text{L}} = 48.15 \text{ S cm}^3 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{48.15 \text{ S cm}^2 \text{mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.1233$$

$$k = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028\,\text{mol L}^{-1}\times(0.1233)^2}{1-0.1233} = 1.78 \times 10^{-5} \text{ mol L}^{-1}$$

Intext Questions

3.7 Why does the conductivity of a solution decrease with dilution?

3.8 Suggest a way to determine the Λ_m° value of water.

3.9 The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given $\lambda^0(H^+)$ = 349.6 S cm^2 mol^{-1} and $\lambda^0(HCOO^-)$ = 54.6 S cm^2 mol^{-1}.

Electrolytic Cells and Electrolysis

In an **electrolytic cell** external source of voltage is used to bring about a chemical reaction. The electrochemical processes are of great importance in the laboratory and the chemical industry. One of the simplest electrolytic cell consists of two copper strips dipping in an aqueous solution of copper sulphate. If a DC voltage is applied to the two electrodes, then Cu^{2+} ions discharge at the cathode (negatively charged) and the following reaction takes place:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s) \qquad (3.28)$$

Copper metal is deposited on the cathode. At the anode, copper is converted into Cu^{2+} ions by the reaction:

$$Cu(s) \rightarrow Cu^{2+}(s) + 2e^- \qquad (3.29)$$

Thus copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This is the basis for an industrial process in which impure copper is converted into copper of high purity. The impure copper is made an anode that dissolves on passing current and pure copper is deposited at the cathode. Many metals like Na, Mg, Al, etc. are produced on large scale by electrochemical reduction of their respective cations where no suitable chemical reducing agents are available for this purpose.

Sodium and magnesium metals are produced by the electrolysis of their fused chlorides and aluminium is produced (Class XII, Unit 6) by electrolysis of aluminium oxide in presence of cryolite.

Quantitative Aspects of Electrolysis

Michael Faraday was the first scientist who described the quantitative aspects of electrolysis. Now Faraday's laws also flow from what has been discussed earlier.

Faraday's Laws of Electrolysis

After his extensive investigations on electrolysis of solutions and melts of electrolytes, Faraday published his results during 1833-34 in the form of the following well known Faraday's two laws of electrolysis:

(i) *First Law*: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

(ii) *Second Law*: The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

There were no constant current sources available during Faraday's times. The general practice was to put a coulometer (a standard electrolytic cell) for determining the quantity of electricity passed from the amount of metal (generally silver or copper) deposited or consumed. However, coulometers are now obsolete and we now have constant current (I) sources available and the quantity of electricity Q, passed is given by

$$Q = It$$

Q is in coloumbs when I is in ampere and t is in second.

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. For example, in the reaction:

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad (3.30)$$

One mole of the electron is required for the reduction of one mole of silver ions.

We know that charge on one electron is equal to 1.6021×10^{-19}C.

Therefore, the charge on one mole of electrons is equal to:

$$N_A \times 1.6021 \times 10^{-19} \text{ C} = 6.02 \times 10^{23} \text{mol}^{-1} \times 1.6021 \times 10^{-19}$$
$$\text{C} = 96487 \text{ C mol}^{-1}$$

This quantity of electricity is called **Faraday** and is represented by the symbol **F**.

For approximate calculations we use $1F \approx 96500 \text{ C mol}^{-1}$.

For the electrode reactions:

$$Mg^{2+}(l) + 2e^- \longrightarrow Mg(s) \qquad (3.31)$$

$$Al^{3+}(l) + 3e^- \longrightarrow Al(s) \qquad (3.32)$$

It is obvious that one mole of Mg^{2+} and Al^{3+} require 2 mol of electrons (2F) and 3 mol of electrons (3F) respectively. The charge passed through the electrolytic cell during electrolysis is equal to the product of current in amperes and time in seconds. In commercial production of metals, current as high as 50,000 amperes are used that amounts to about 0.518 F per second.

Example

A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

Solution

t = 600 s charge = current × time = 1.5 A × 600 s = 900 C

According to the reaction:

$$Cu^{2+}(aq) + 2e^- = Cu(s)$$

We require 2F or 2 × 96487 C to deposit 1 mol or 63 g of Cu.

For 900 C, the mass of Cu deposited

$$= (63 \text{ g mol}^{-1} \times 900 \text{ C})/(2 \times 96487 \text{ C mol}^{-1}) = 0.2938 \text{ g}.$$

3.5.1 Products of Electrolysis

Products of electrolysis depend on the nature of material being electrolysed and the type of electrodes being used. If the electrode is inert (e.g., platinum or gold), it does not participate in the chemical reaction and acts only as source or sink for electrons. On the other hand, if the electrode is reactive, it participates in the electrode reaction. Thus, the products of electrolysis may be different for reactive and inert electrodes.The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to take place and extra potential (called *overpotential*) has to be applied, which makes such process more difficult to occur.

For example, if we use molten NaCl, the products of electrolysis are sodium metal and Cl_2 gas. Here we have only one cation (Na^+) which is reduced at the cathode ($Na^+ + e^- \rightarrow Na$) and one anion ($Cl^-$) which is oxidised at the anode ($Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$). During the electrolysis of aqueous sodium chloride solution, the products are NaOH, Cl_2 and H_2. In this case besides Na^+ and Cl^- ions we also have H^+ and OH^- ions along with the solvent molecules, H_2O.

At the cathode there is competition between the following reduction reactions:

$$Na^+ (aq) + e^- \rightarrow Na (s) \qquad E^{V}_{(\text{cell})} = -2.71 \text{ V}$$

$$H^+ (aq) + e^- \rightarrow \tfrac{1}{2} H_2 (g) \qquad E^{V}_{(\text{cell})} = 0.00 \text{ V}$$

The reaction with higher value of $E^{\square}$ is preferred and therefore, the reaction at the cathode during electrolysis is:

$$H^+ (aq) + e^- \rightarrow \tfrac{1}{2} H_2 (g) \qquad (3.33)$$

but H^+ (aq) is produced by the dissociation of H_2O, i.e.,

$$H_2O (l) \rightarrow H^+ (aq) + OH^- (aq) \qquad (3.34)$$

Therefore, the net reaction at the cathode may be written as the sum of (3.33) and (3.34) and we have

$$H_2O (l) + e^- \rightarrow \tfrac{1}{2}H_2(g) + OH^- \qquad (3.35)$$

At the anode the following oxidation reactions are possible:

$$Cl^- (aq) \rightarrow \tfrac{1}{2} Cl_2 (g) + e^- \qquad E^{V}_{(\text{cell})} = 1.36 \text{ V} \qquad (3.36)$$

$$2H_2O (l) \rightarrow O_2 (g) + 4H^+(aq) + 4e^- \qquad E^{V}_{(\text{cell})} = 1.23 \text{ V} \qquad (3.37)$$

The reaction at anode with lower value of $E^{\square}$ is preferred and therefore, water should get oxidised in preference to Cl^- (aq). However, on account of overpotential of oxygen, reaction (3.36) is preferred. Thus, the net reactions may be summarised as:

$$NaCl (aq) \xrightarrow{H_2O} Na^+ (aq) + Cl^- (aq)$$

Cathode: $H_2O(l) + e^- \rightarrow \frac{1}{2} H_2(g) + OH^- (aq)$

Anode: $Cl^- (aq) \rightarrow \frac{1}{2} Cl_2(g) + e^-$

Net reaction:

$$NaCl(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g)$$

The standard electrode potentials are replaced by electrode potentials given by Nernst equation (Eq. 3.8) to take into account the concentration effects. During the electrolysis of sulphuric acid, the following processes are possible at the anode:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E^{V}_{(\text{cell})} = +1.23 \text{ V} \qquad (3.38)$$

$$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^- \qquad E^{V}_{(cell)} = 1.96\ V \qquad (3.39)$$

For dilute sulphuric acid, reaction (3.38) is preferred but at higher concentrations of H_2SO_4, reaction (3.39) is preferred.

Intext Questions

3.10 If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

3.11 Suggest a list of metals that are extracted electrolytically.

3.12 Consider the reaction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?

3.6 Batteries

Any battery (actually it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries.

3.6.1 Primary Batteries

In the primary batteries, the reaction occurs only once and after use over a period of time battery becomes dead and cannot be reused again. The most familiar example of this type is the dry cell (known as Leclanche cell after its discoverer) which is used commonly in our transistors and clocks. The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon (Fig.3.8). The space between the electrodes is filled by a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$). The electrode reactions are complex, but they can be written approximately as follows :

Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Cathode: $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state. Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.

Mercury cell, (Fig. 3.9) suitable for low current devices like hearing aids, watches, etc. consists of zinc – mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are given below:

Anode: $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

Cathode: $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

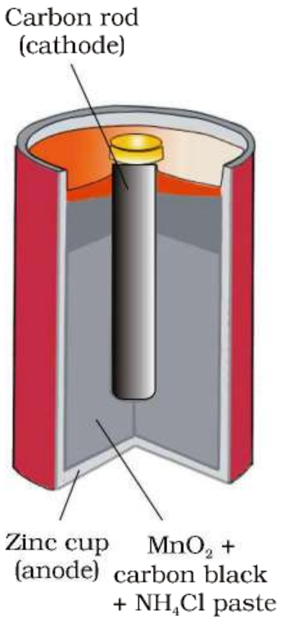
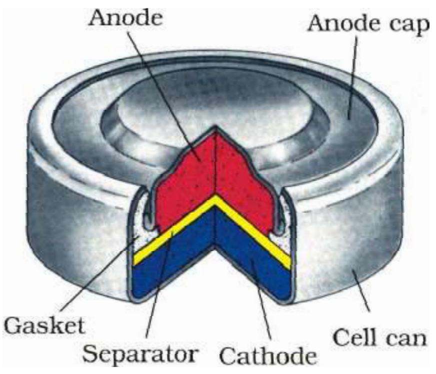


Fig. 3.8: *A commercial dry cell consists of a graphite (carbon) cathode in a zinc container; the latter acts as the anode.*

Fig. 3.9 *Commonly used mercury cell. The reducing agent is zinc and the oxidising agent is mercury (II) oxide.*



The overall reaction is represented by

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

3.6.2 Secondary Batteries

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles. The most important secondary cell is the lead storage battery (Fig. 3.10) commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

The cell reactions when the battery is in use are given below:

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

i.e., overall cell reaction consisting of cathode and anode reactions is:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.

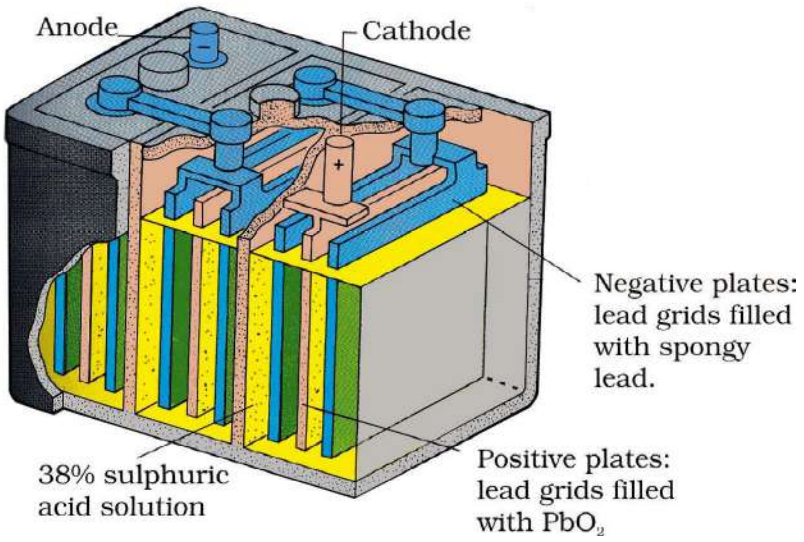


Fig. 3.10: The Lead storage battery.

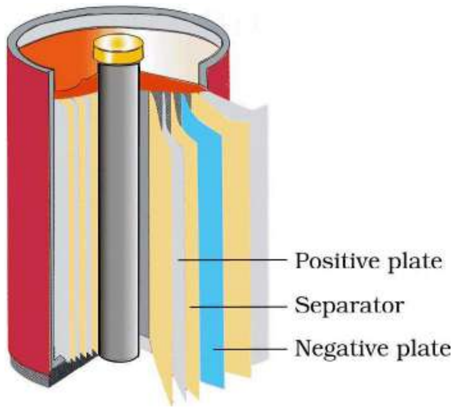


Fig. 3.11
A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

Another important secondary cell is the nickel-cadmium cell (Fig. 3.11) which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:

$$Cd\ (s) + 2Ni(OH)_3\ (s) \rightarrow CdO\ (s) + 2Ni(OH)_2\ (s) + H_2O\ (l)$$

Fuel Cells

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells**.

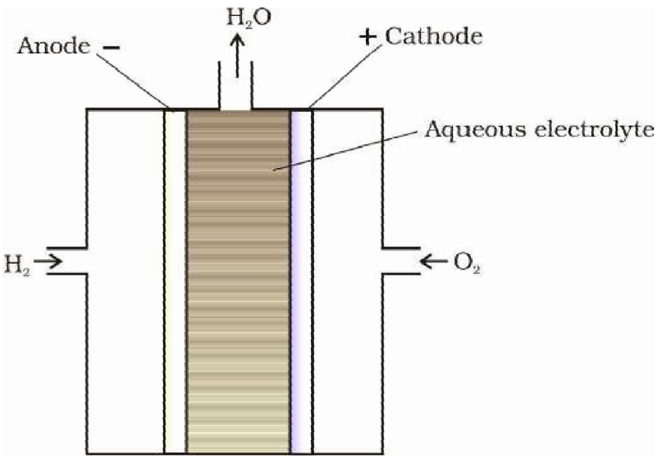


Fig. 3.12: *Fuel cell using H_2 and O_2 produces electricity.*

One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water (Fig. 3.12). The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
Anode: $2H_2\ (g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

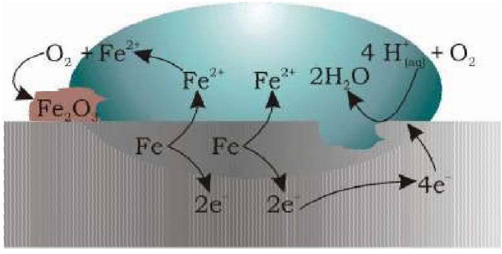
Overall reaction being:

$$2H_2(g) + O_2(g) \longrightarrow 2\ H_2O(l)$$

The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried.

Corrosion

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion.



Oxidation: Fe (s)$\rightarrow$ Fe^{2+} (aq) $+2e^-$

Reduction: O_2 (g) + $4H^+$(aq) $+4e^- \rightarrow 2H_2O$(l)

Atomospheric
oxidation: $2Fe^{2+}$(aq) + $2H_2O$(l) + ½O_2(g) $\rightarrow$ **Fe_2O_3(s) + $4H^+$(aq)**

Fig. 3.13: *Corrosion of iron in atmosphere*

In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot (Fig. 3.13) of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction

$$\text{Anode: } 2\ Fe\ (s) \longrightarrow 2\ Fe^{2+} + 4\ e^- \qquad E^{V}_{(Fe^{2+}/Fe)} = -\ 0.44\ V$$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction

$$\text{Cathode: } O_2(g) + 4\ H^+(aq) + 4\ e^- \longrightarrow 2\ H_2O\ (l) \quad E^{V}_{H^+|O_2\ |\ H_2O} = 1.23\ V$$

The overall reaction being:

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2\ H_2O\ (l) \qquad E^{V}_{(cell)} = 1.67\ V$$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide (Fe_2O_3. $x\ H_2O$) and with further production of hydrogen ions.

Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

Intext Questions

3.13 Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

3.14 Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

3.15 Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

The Hydrogen Economy

At present the main source of energy that is driving our economy is fossil fuels such as coal, oil and gas. As more people on the planet aspire to improve their standard of living, their energy requirement will increase. In fact, the per capita consumption of energy used is a measure of development. Of course, it is assumed that energy is used for productive purpose and not merely wasted. We are already aware that carbon dioxide produced by the combustion of fossil fuels is resulting in the 'Greenhouse Effect'. This is leading to a rise in the temperature of the Earth's surface, causing polar ice to melt and ocean levels to rise. This will flood low-lying areas along the coast and some island nations such as Maldives face total submergence. In order to avoid such a catastrope, we need to limit our use of carbonaceous fuels. Hydrogen provides an ideal alternative as its combustion results in water only. Hydrogen production must come from splitting water using solar energy. Therefore, hydrogen can be used as a renewable and non polluting source of energy. This is the vision of the Hydrogen Economy. Both the production of hydrogen by electrolysis of water and hydrogen combustion in a fuel cell will be important in the future. And both these technologies are based on electrochemical principles.

Summary

An **electrochemical cell** consists of two metallic electrodes dipping in electrolytic solution(s). Thus an important component of the electrochemical cell is the ionic conductor or electrolyte. Electrochemical cells are of two types. In **galvanic cell**, the **chemical energy** of a **spontaneous redox reaction** is converted into electrical work, whereas in an electrolytic cell, electrical energy is used to carry out a **non-spontaneous redox reaction**. The **standard electrode potential** for any electrode dipping in an appropriate solution is defined with respect to standard electrode potential of **hydrogen electrode** taken as zero. The standard potential of the cell can be obtained by taking the difference of the standard potentials of cathode and anode ($E^V_{(cell)}$ = $E^{\ominus}$cathode – $E^{\ominus}$anode). The standard potential of the cells are related to standard Gibbs energy ($\Delta_r G^{\ominus} = -nFE^V_{(cell)}$) and **equilibrium constant** ($\Delta_r G^{\ominus} = -RT \ln K$) of the reaction taking place in the cell. Concentration dependence of the potentials of the electrodes and the cells are given by Nernst equation.

The **conductivity**, κ, of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature. **Molar conductivity**, Λ_m, is defined by = κ/c where c is the concentration. Conductivity decreases but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolytes while the increase is very steep for weak electrolytes in very dilute solutions. Kohlrausch found that molar conductivity at infinite dilution, for an electrolyte is sum of the contribution of the molar conductivity of the ions in which it dissociates. It is known as **law of independent migration of ions** and has many applications. Ions conduct electricity through the solution but oxidation and reduction of the ions take place at the electrodes in an electrochemical cell. **Batteries** and **fuel cells** are very useful forms of galvanic cell. **Corrosion** of metals is essentially an **electrochemical phenomenon**. Electrochemical principles are relevant to the **Hydrogen Economy**.

Exercises

3.1 Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn.

3.2 Given the standard electrode potentials,

$K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$,

$Hg^{2+}/Hg = 0.79V$

$Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74V$

Arrange these metals in their increasing order of reducing power.

3.3 Depict the galvanic cell in which the reaction

$Zn(s)+2Ag^+(aq) \rightarrow Zn^{2+}(aq)+2Ag(s)$ takes place. Further show:

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode.

3.4 Calculate the standard cell potentials of galvanic cell in which the following reactions take place:

(i) $2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$

(ii) $Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$

Calculate the $\Delta_r G^\ominus$ and equilibrium constant of the reactions.

3.5 Write the Nernst equation and emf of the following cells at 298 K:

(i) $Mg(s)|Mg^{2+}(0.001M)||Cu^{2+}(0.0001\ M)|Cu(s)$

(ii) $Fe(s)|Fe^{2+}(0.001M)||H^+(1M)|H_2(g)(1bar)|\ Pt(s)$

(iii) $Sn(s)|Sn^{2+}(0.050\ M)||H^+(0.020\ M)|H_2(g)\ (1\ bar)|Pt(s)$

(iv) $Pt(s)|Br^-(0.010\ M)|Br_2(l)||H^+(0.030\ M)|\ H_2(g)\ (1\ bar)|Pt(s)$.

3.6 In the button cells widely used in watches and other devices the following reaction takes place:

$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Determine $\Delta_r G^\ominus$ and $E^\ominus$ for the reaction.

3.7 Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

3.8 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

3.9 The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}.

3.10 The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa/\mathrm{S\ m^{-1}}$	1.237	11.85	23.15	55.53	106.74

Calculate δ_m for all concentrations and draw a plot between δ_m and $c^{1/2}$. Find the value of Λ_m^0.

3.11 Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ_m^0 for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

3.12 How much charge is required for the following reductions:
(i) 1 mol of Al^{3+} to Al?
(ii) 1 mol of Cu^{2+} to Cu?
(iii) 1 mol of MnO_4^- to Mn^{2+}?

3.13 How much electricity in terms of Faraday is required to produce
(i) 20.0 g of Ca from molten $CaCl_2$?
(ii) 40.0 g of Al from molten Al_2O_3?

3.14 How much electricity is required in coulomb for the oxidation of
(i) 1 mol of H_2O to O_2?
(ii) 1 mol of FeO to Fe_2O_3?

3.15 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

3.16 Three electrolytic cells A,B,C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

3.17 Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:
(i) Fe^{3+}(aq) and I^-(aq)
(ii) Ag^+ (aq) and Cu(s)
(iii) Fe^{3+} (aq) and Br^- (aq)
(iv) Ag(s) and Fe^{3+} (aq)
(v) Br_2 (aq) and Fe^{2+} (aq).

3.18 Predict the products of electrolysis in each of the following:
(i) An aqueous solution of $AgNO_3$ with silver electrodes.
(ii) An aqueous solution of $AgNO_3$ with platinum electrodes.
(iii) A dilute solution of H_2SO_4 with platinum electrodes.
(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

Answers to Some Intext Questions

3.5 $E_{(cell)} = 0.91$ V

3.6 $\Delta_r G^V = -45.54\ \mathrm{kJ\ mol^{-1}}$, $K_c = 9.62 \times 10^7$

3.9 0.114, 3.67×10^{-4} mol L^{-1}

Unit 4

Chemical Kinetics

Chemical Kinetics helps us to understand how chemical reactions occur.

Objectives

After studying this Unit, you will be able to

- define the average and instantaneous rate of a reaction;
- express the rate of a reaction in terms of change in concentration of either of the reactants or products with time;
- distinguish between elementary and complex reactions;
- differentiate between the molecularity and order of a reaction;
- define rate constant;
- discuss the dependence of rate of reactions on concentration, temperature and catalyst;
- derive integrated rate equations for the zero and first order reactions;
- determine the rate constants for zeroth and first order reactions;
- describe collision theory.

Chemistry, by its very nature, is concerned with change. Substances with well defined properties are converted by chemical reactions into other substances with different properties. For any chemical reaction, chemists try to find out

(a) the feasibility of a chemical reaction which can be predicted by thermodynamics (as you know that a reaction with $\Delta G < 0$, at constant temperature and pressure is feasible);

(b) extent to which a reaction will proceed can be determined from chemical equilibrium;

(c) speed of a reaction i.e. time taken by a reaction to reach equilibrium.

Along with feasibility and extent, it is equally important to know the rate and the factors controlling the rate of a chemical reaction for its complete understanding. For example, which parameters determine as to how rapidly food gets spoiled? How to design a rapidly setting material for dental filling? Or what controls the rate at which fuel burns in an auto engine? All these questions can be answered by the branch of chemistry, which deals with the study of reaction rates and their mechanisms, called **chemical kinetics**. The word kinetics is derived from the Greek word 'kinesis' meaning movement. Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction. For example, thermodynamic data indicate that diamond shall convert to graphite but in reality the conversion rate is so slow that the change is not perceptible at all. Therefore, most people think that diamond is forever. Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates can be altered. The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction. At the macroscopic level, we are interested in amounts reacted or formed and the rates of their consumption or formation. At the molecular level, the reaction mechanisms involving orientation and energy of molecules undergoing collisions, are discussed.

In this Unit, we shall be dealing with average and instantaneous rate of reaction and the factors affecting these. Some elementary ideas about the collision theory of reaction rates are also given. However, in order to understand all these, let us first learn about the reaction rate.

4.1 Rate of a Chemical Reaction

Some reactions such as ionic reactions occur very fast, for example, precipitation of silver chloride occurs instantaneously by mixing of aqueous solutions of silver nitrate and sodium chloride. On the other hand, some reactions are very slow, for example, rusting of iron in the presence of air and moisture. Also there are reactions like inversion of cane sugar and hydrolysis of starch, which proceed with a moderate speed. Can you think of more examples from each category?

You must be knowing that speed of an automobile is expressed in terms of change in the position or distance covered by it in a certain period of time. Similarly, the speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in terms of:

(i) the rate of decrease in concentration of any one of the reactants, or

(ii) the rate of increase in concentration of any one of the products.

Consider a hypothetical reaction, assuming that the volume of the system remains constant.

$$R \rightarrow P$$

One mole of the reactant R produces one mole of the product P. If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then,

$$\Delta t = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1$$

$$\Delta [P] = [P]_2 - [P]_1$$

The square brackets in the above expressions are used to express molar concentration.

Rate of disappearance of R

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \qquad (4.1)$$

Rate of appearance of P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = +\frac{\Delta[\text{P}]}{\Delta t} \qquad (4.2)$$

Since, Δ[R] is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –1 to make the rate of the reaction a positive quantity.

Equations (4.1) and (4.2) given above represent the average rate of a reaction, r_{av}.

Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur (Fig. 4.1).

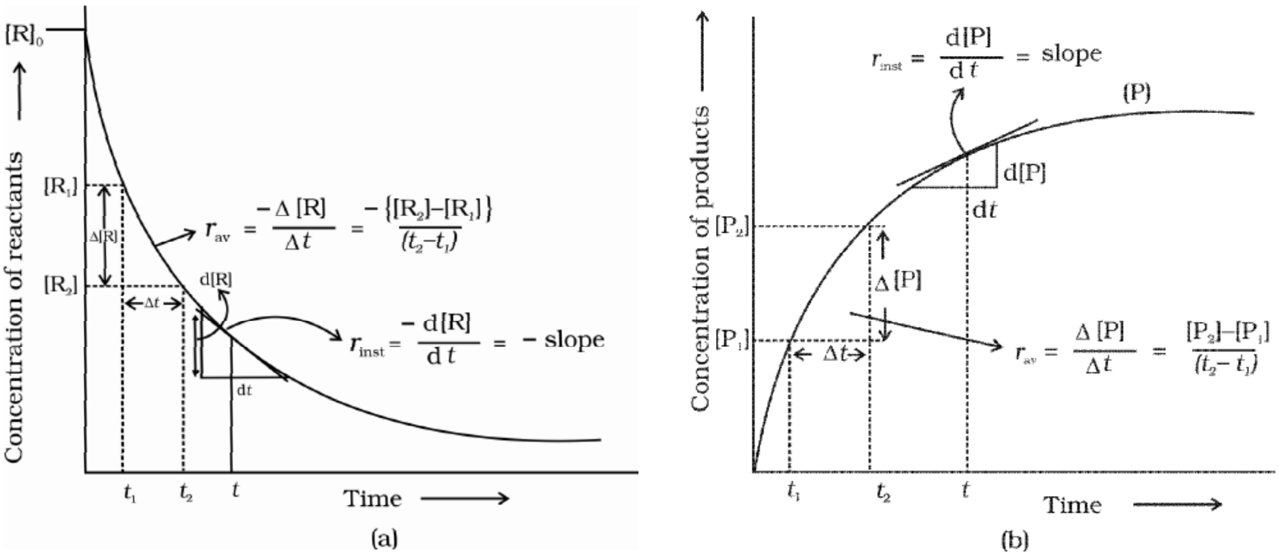


Fig. 4.1: *Instantaneous and average rate of a reaction*

Units of rate of a reaction

From equations (4.1) and (4.2), it is clear that units of rate are concentration time^{-1}. For example, if concentration is in mol L^{-1} and time is in seconds then the units will be mol L^{-1}s^{-1}. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s^{-1}.

Example

From the concentrations of C_4H_9Cl (butyl chloride) at different times given below, calculate the average rate of the reaction:

$$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$$

during different intervals of time.

t/s	0	50	100	150	200	300	400	700	800
[C_4H_9Cl]/mol L^{-1}	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210	0.017

Solution

We can determine the difference in concentration over different intervals of time and thus determine the average rate by dividing Δ[R] by Δt (Table 4.1).

Table 4.1: Average rates of hydrolysis of butyl chloride

$[C_4H_9Cl]_{t_1}$ / mol L^{-1}	$[C_4H_9Cl]_{t_2}$ / mol L^{-1}	t_1/s	t_2/s	$r_{av} \times 10^4$/mol L^{-1}s^{-1} $= -\left\{[C_4H_9Cl]_{t_2} - [C_4H_9Cl]_{t_1}/(t_2 - t_1)\right\} \times 10^4$
0.100	0.0905	0	50	1.90
0.0905	0.0820	50	100	1.70
0.0820	0.0741	100	150	1.58
0.0741	0.0671	150	200	1.40
0.0671	0.0549	200	300	1.22
0.0549	0.0439	300	400	1.10
0.0439	0.0335	400	500	1.04
0.0210	0.017	700	800	0.4

It can be seen (Table 4.1) that the average rate falls from 1.90 × 0^{-4} mol L^{-1}s^{-1} to 0.4 × 10^{-4} mol L^{-1}s^{-1}. However, average rate cannot be used to predict the rate of a reaction at a particular instant as it would be constant for the time interval for which it is calculated. So, to express the rate at a particular moment of time we determine the **instantaneous rate**. It is obtained when we consider the average rate at the smallest time interval say dt (i.e. when Δt approaches zero). Hence, mathematically for an infinitesimally small dt instantaneous rate is given by

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \qquad (4.3)$$

$$\text{As} \quad \Delta t \to 0 \qquad \text{or} \qquad r_{inst} = \frac{-d[R]}{dt} = \frac{d[P]}{dt}$$

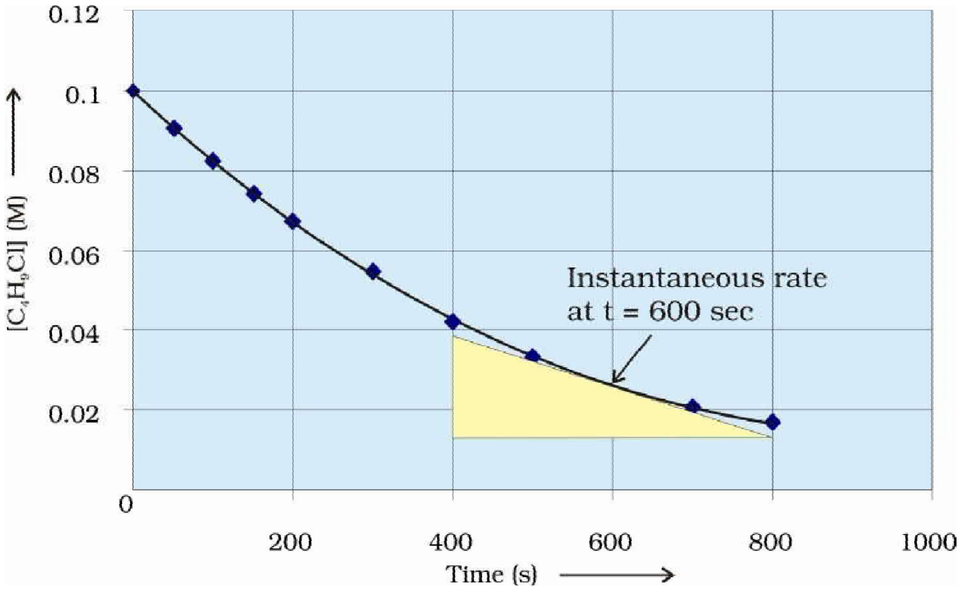


Fig 4.2
Instantaneous rate of hydrolysis of butyl chloride(C_4H_9Cl)

It can be determined graphically by drawing a tangent at time t on either of the curves for concentration of R and P vs time t and calculating its slope (Fig. 4.1). So in problem 4.1, r_{inst} at 600s for example, can be calculated by plotting concentration of butyl chloride as a function of time. A tangent is drawn that touches the curve at $t = 600$ s (Fig. 4.2).

The slope of this tangent gives the instantaneous rate.

$$\text{So, } r_{\text{inst}} \text{ at } 600 \text{ s} = -\left(\frac{0.0165 - 0.037}{(800 - 400)\,\text{s}}\right) \text{mol L}^{-1} = 5.12 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

At $t = 250$ s $r_{\text{inst}} = 1.22 \times 10^{-4}$ mol $L^{-1}s^{-1}$

$t = 350$ s $r_{\text{inst}} = 1.0 \times 10^{-4}$ mol $L^{-1}s^{-1}$

$t = 450$ s $r_{\text{inst}} = 6.4 \times 10^{-5}$ mol $L^{-1}s^{-1}$

Now consider a reaction

$$\text{Hg(l)} + \text{Cl}_2\text{(g)} \rightarrow \text{HgCl}_2\text{(s)}$$

Where stoichiometric coefficients of the reactants and products are same, then rate of the reaction is given as

$$\text{Rate of reaction} = -\frac{\Delta[\text{Hg}]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = \frac{\Delta[\text{HgCl}_2]}{\Delta t}$$

i.e., rate of disappearance of any of the reactants is same as the rate of appearance of the products. But in the following reaction, two moles of HI decompose to produce one mole each of H_2 and I_2.

$$2\text{HI(g)} \rightarrow \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$$

For expressing the rate of such a reaction where stoichiometric coefficients of reactants or products are not equal to one, rate of disappearance of any of the reactants or the rate of appearance of products is divided by their respective stoichiometric coefficients. Since rate of consumption of HI is twice the rate of formation of H_2 or I_2, to make them equal, the term Δ[HI] is divided by 2. The rate of this reaction is given by

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$

Similarly, for the reaction

$$5\,\text{Br}^-\text{(aq)} + \text{BrO}_3^-\text{(aq)} + 6\,\text{H}^+\text{(aq)} \rightarrow 3\,\text{Br}_2\text{(aq)} + 3\,\text{H}_2\text{O (l)}$$

$$\text{Rate} = -\frac{1}{5}\frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species and hence, rate can also be expressed as rate of change in partial pressure of the reactant or the product.

Example

The decomposition of N_2O_5 in CCl_4 at 318K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.33 mol L^{-1} and after 184 minutes, it is reduced to 2.08 mol L^{-1}. The reaction takes place according to the equation

$$2\,N_2O_5\,(g) \rightarrow 4\,NO_2\,(g) + O_2\,(g)$$

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO_2 during this period?

Solution

$$\text{Average Rate} = \frac{1}{2}\left\{-\frac{\Delta[N_2O_5]}{\Delta t}\right\} = -\frac{1}{2}\left[\frac{(2.08-2.33)\,\text{mol L}^{-1}}{184\,\text{min}}\right]$$

$= 6.79 \times 10^{-4}$ mol L^{-1}/min $= (6.79 \times 10^{-4}$ mol L^{-1} $min^{-1}) \times (60$ min/1h)

$= 4.07 \times 10^{-2}$ mol L^{-1}/h

$= 6.79 \times 10^{-4}$ mol $L^{-1} \times$ 1min/60s

$= 1.13 \times 10^{-5}$ mol $L^{-1}s^{-1}$

It may be remembered that

$$\text{Rate} = \frac{1}{4}\left\{\frac{\Delta[NO_2]}{\Delta t}\right\}$$

$$\frac{\Delta[NO_2]}{\Delta t} = 6.79 \times 10^{-4} \times 4 \text{ mol L}^{-1}\text{min}^{-1} = 2.72 \times 10^{-3} \text{ mol L}^{-1}\text{min}^{-1}$$

Intext Questions

4.1 For the reaction R → P, the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

4.2 In a reaction, 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?

Factors Influencing Rate of a Reaction

Rate of reaction depends upon the experimental conditions such as concentration of reactants (pressure in case of gases), temperature and catalyst.

4.2.1 Dependence of Rate on Concentration

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products. The representation of rate of reaction in terms of concentration of the reactants is known as **rate law**. It is also called as rate equation or rate expression.

4.2.2 Rate Expression and Rate Constant

The results in Table 4.1 clearly show that rate of a reaction decreases with the passage of time as the concentration of reactants decrease. Conversely, rates generally increase when reactant concentrations increase. So, rate of a reaction depends upon the concentration of reactants.

Consider a general reaction

$$aA + bB \rightarrow cC + dD$$

where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is

$$\text{Rate} \propto [A]^x \ [B]^y \qquad (4.4)$$

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants. Above equation can also be written as

$$\text{Rate} = k \ [A]^x \ [B]^y \qquad (4.4a)$$

$$-\frac{d[R]}{dt} = k[A]^x [B]^y \qquad (4.4b)$$

This form of equation (4.4 b) is known as differential rate equation, where k is a proportionality constant called **rate constant**. The equation like (4.4), which relates the rate of a reaction to concentration of reactants is called rate law or rate expression. Thus, **rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation**. For example:

$$2NO(g) + O_2(g) \rightarrow 2NO_2 \ (g)$$

We can measure the rate of this reaction as a function of initial concentrations either by keeping the concentration of one of the reactants constant and changing the concentration of the other reactant or by changing the concentration of both the reactants. The following results are obtained (Table 4.2).

Table 4.2: Initial rate of formation of NO_2

Experiment	Initial [NO]/ mol L^{-1}	Initial $[O_2]$/ mol L^{-1}	Initial rate of formation of NO_2/ mol $L^{-1}s^{-1}$
1.	0.30	0.30	0.096
2.	0.60	0.30	0.384
3.	0.30	0.60	0.192
4.	0.60	0.60	0.768

It is obvious, after looking at the results, that when the concentration of NO is doubled and that of O_2 is kept constant then the initial rate increases by a factor of four from 0.096 to 0.384 mol $L^{-1}s^{-1}$. This indicates that the rate depends upon the square of the concentration of NO. When concentration of NO is kept constant and concentration of O_2 is doubled the rate also gets doubled indicating that rate depends on concentration of O_2 to the first power. Hence, the rate equation for this reaction will be

$$\text{Rate} = k[NO]^2[O_2]$$

The differential form of this rate expression is given as

$$-\frac{d[R]}{dt} = k[NO]^2[O_2]$$

Now, we observe that for this reaction in the rate equation derived from the experimental data, the exponents of the concentration terms are the same as their stoichiometric coefficients in the balanced chemical equation.

Some other examples are given below:

Reaction	Experimental rate expression
1. $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$	Rate = $k\,[CHCl_3]\;[Cl_2]^{1/2}$
2. $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$	Rate = $k\,[CH_3COOC_2H_5]^1\;[H_2O]^0$

In these reactions, the exponents of the concentration terms are not the same as their stoichiometric coefficients. Thus, we can say that:

Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.

4.2.3 Order of a Reaction

In the rate equation (4.4)

Rate = $k\,[A]^x\;[B]^y$

x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., x + y in (4.4) gives the overall order of a reaction whereas x and y represent the order with respect to the reactants A and B respectively.

Hence, **the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction**.

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

Example

Calculate the overall order of a reaction which has the rate expression

(a) Rate = $k\,[A]^{1/2}\;[B]^{3/2}$

(b) Rate = $k\,[A]^{3/2}\;[B]^{-1}$

Solution

(a) Rate = $k\,[A]^x\;[B]^y$

order = x + y

So order = 1/2 + 3/2 = 2, i.e., second order

(b) order = 3/2 + (–1) = 1/2, i.e., half order.

A balanced chemical equation never gives us a true picture of how a reaction takes place since rarely a reaction gets completed in one step. The reactions taking place in one step are called **elementary reactions**. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called **complex reactions**.

These may be consecutive reactions (e.g., oxidation of ethane to CO_2 and H_2O passes through a series of intermediate steps in which alcohol, aldehyde and acid are formed), reverse reactions and side reactions (e.g., nitration of phenol yields *o*-nitrophenol and *p*-nitrophenol).

Units of rate constant

For a general reaction

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate} = k\,[A]^x\,[B]^y$$

Where x + y = n = order of the reaction

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

$$= \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n} \qquad (\text{where } [A]=[B])$$

Taking SI units of concentration, mol L^{-1} and time, s, the units of k for different reaction order are listed in Table 4.3

Table 4.3: Units of rate constant

Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1}\text{s}^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1}\text{L s}^{-1}$

Example

Identify the reaction order from each of the following rate constants.

(i) $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}

(ii) $k = 3 \times 10^{-4}$ s^{-1}

Solution

(i) The unit of second order rate constant is L mol^{-1} s^{-1}, therefore $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1} represents a second order reaction.

(ii) The unit of a first order rate constant is s^{-1} therefore $k = 3 \times 10^{-4}$ s^{-1} represents a first order reaction.

4.2.4 Molecularity of a Reaction

Another property of a reaction called molecularity helps in understanding its mechanism. **The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.** The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

$NH_4NO_2 \rightarrow N_2 + 2H_2O$

Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

$2HI \rightarrow H_2 + I_2$

Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,

$2NO + O_2 \rightarrow 2NO_2$

The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed.

It is, therefore, evident that complex reactions involving more than three molecules in the stoichiometric equation must take place in more than one step.

$KClO_3 + 6FeSO_4 + 3H_2SO_4 \rightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O$

This reaction which apparently seems to be of tenth order is actually a second order reaction. This shows that this reaction takes place in several steps. Which step controls the rate of the overall reaction? The question can be answered if we go through the mechanism of reaction, for example, chances to win the relay race competition by a team depend upon the slowest person in the team. Similarly, the overall rate of the reaction is controlled by the slowest step in a reaction called the **rate determining step**. Consider the decomposition of hydrogen peroxide which is catalysed by iodide ion in an alkaline medium.

$$2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$$

The rate equation for this reaction is found to be

$$\text{Rate} = \frac{-d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

This reaction is first order with respect to both H_2O_2 and I^-. Evidences suggest that this reaction takes place in two steps

(1) $H_2O_2 + I^- \rightarrow H_2O + IO^-$

(2) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

Both the steps are bimolecular elementary reactions. Species IO^- is called as an intermediate since it is formed during the course of the reaction but not in the overall balanced equation. The first step, being slow, is the rate determining step. Thus, the rate of formation of intermediate will determine the rate of this reaction.

Thus, from the discussion, till now, we conclude the following:

(i) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.

(ii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.

(iii) For complex reaction, order is given by the slowest step and molecularity of the slowest step is same as the order of the overall reaction.

Intext Questions

4.3 For a reaction, A + B → Product; the rate law is given by, $r = k[\text{A}]^{1/2}[\text{B}]^2$. What is the order of the reaction?

4.4 The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y ?

4.3 Integrated Rate Equations

We have already noted that the concentration dependence of rate is called differential rate equation. It is not always convenient to determine the instantaneous rate, as it is measured by determination of slope of the tangent at point '*t*' in concentration vs time plot (Fig. 4.1). This makes it difficult to determine the rate law and hence the order of the reaction. In order to avoid this difficulty, we can integrate the differential rate equation to give a relation between directly measured experimental data, i.e., concentrations at different times and rate constant.

The integrated rate equations are different for the reactions of different reaction orders. We shall determine these equations only for zero and first order chemical reactions.

4.3.1 Zero Order Reactions

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$\text{R} \rightarrow \text{P}$$

$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k[\text{R}]^0$$

As any quantity raised to power zero is unity

$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k \times 1$$

$$d[\text{R}] = -k\,dt$$

Integrating both sides

$$[\text{R}] = -k\,t + \text{I} \qquad (4.5)$$

where, I is the constant of integration.

At $t = 0$, the concentration of the reactant $\text{R} = [\text{R}]_0$, where $[\text{R}]_0$ is initial concentration of the reactant.

Substituting in equation (4.5)

$$[\text{R}]_0 = -k \times 0 + \text{I}$$

$$[\text{R}]_0 = \text{I}$$

Substituting the value of I in the equation (4.5)

$$[\text{R}] = -kt + [\text{R}]_0 \qquad (4.6)$$

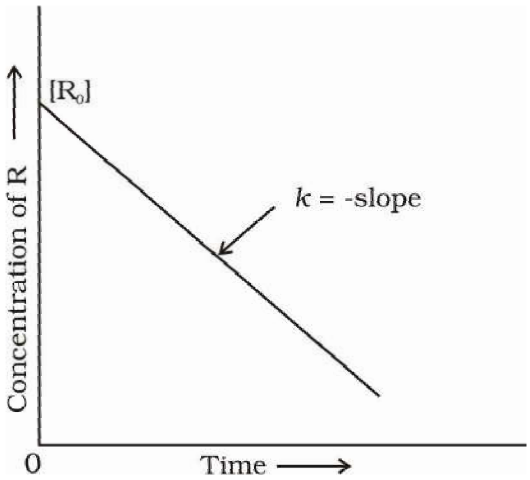


Fig. 4.3: *Variation in the concentration vs time plot for a zero order reaction*

Comparing (4.6) with equation of a straight line, y = mx + c, if we plot [R] against t, we get a straight line (Fig. 4.3) with slope = $-k$ and intercept equal to $[R]_0$.

Further simplifying equation (4.6), we get the rate constant, k as

$$k = \frac{[R]_0 - [R]}{t} \qquad (4.7)$$

Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions. The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

$$2NH_3(g) \xrightarrow[\text{Pt catalyst}]{1130K} N_2(g) + 3H_2(g)$$

$$\text{Rate} = k\,[NH_3]^0 = k$$

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. The thermal decomposition of HI on gold surface is another example of zero order reaction.

4.3.2 First Order Reactions

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant R. For example,

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\text{or} \quad \frac{d[R]}{[R]} = -k\,dt$$

Integrating this equation, we get

$$\ln[R] = -kt + I \qquad (4.8)$$

Again, I is the constant of integration and its value can be determined easily.

When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation (4.8) can be written as

$$\ln[R]_0 = -k \times 0 + I$$

$$\ln[R]_0 = I$$

Substituting the value of I in equation (4.8)

$$\ln[R] = -kt + \ln[R]_0 \qquad (4.9)$$

Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = -kt$$

$$\text{or } k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \qquad (4.10)$$

At time t_1 from equation (4.8)

$$^*\ln[R]_1 = -kt_1 + {}^*\ln[R]_0 \qquad (4.11)$$

At time t_2

$$\ln[R]_2 = -kt_2 + \ln[R]_0 \qquad (4.12)$$

where, $[R]_1$ and $[R]_2$ are the concentrations of the reactants at time t_1 and t_2 respectively.

Subtracting (4.12) from (4.11)

$$\ln[R]_1 - \ln[R]_2 = -kt_1 - (-kt_2)$$

$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2} \qquad (4.13)$$

Equation (4.9) can also be written as

$$\ln \frac{[R]}{[R]_0} = -kt$$

Taking antilog of both sides

$$[R] = [R]_0\, e^{-kt} \qquad (4.14)$$

Comparing equation (4.9) with $y = mx + c$, if we plot ln [R] against t (Fig. 4.4) we get a straight line with slope = $-k$ and intercept equal to $\ln [R]_0$

The first order rate equation (4.10) can also be written in the form

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \qquad (4.15)$$

$$^*\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between log $[R]_0/[R]$ vs t, (Fig. 4.5), the slope = $k/2.303$

Hydrogenation of ethene is an example of first order reaction.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Rate = $k\,[C_2H_4]$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

---

* *Refer to Appendix-IV for ln and log (logarithms).*

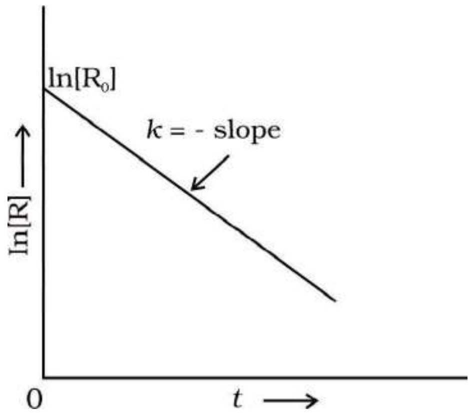


Fig. 4.4: *A plot between ln[R] and t for a first order reaction*

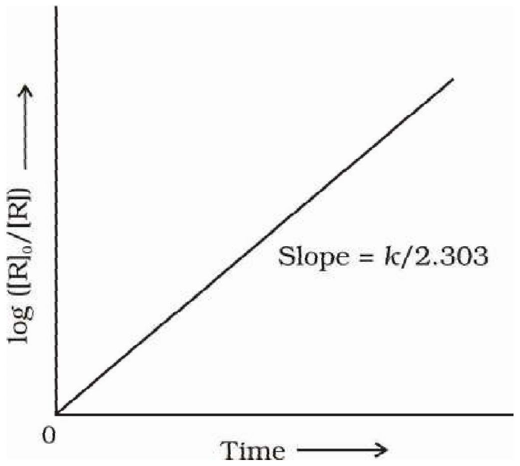


Fig. 4.5: *Plot of log [R]$_0$/[R] vs time for a first order reaction*

$$^{226}_{88}\text{Ra} \rightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}$$

Rate = k [Ra]

Decomposition of N_2O_5 and N_2O are some more examples of first order reactions.

Example The initial concentration of N_2O_5 in the following first order reaction $N_2O_5(g) \rightarrow 2\ NO_2(g) + 1/2O_2\ (g)$ was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.

Solution For a first order reaction

$$\log\frac{[R]_1}{[R]_2} = \frac{k(t_2 - t_1)}{2.303}$$

$$k = \frac{2.303}{(t_2 - t_1)}\log\frac{[R]_1}{[R]_2}$$

$$= \frac{2.303}{(60\,\text{min} - 0\,\text{min})}\log\frac{1.24\times10^{-2}\,\text{mol}\,L^{-1}}{0.20\times10^{-2}\,\text{mol}\,L^{-1}}$$

$$= \frac{2.303}{60}\log 6.2\,\text{min}^{-1}$$

$$k = 0.0304\ \text{min}^{-1}$$

Let us consider a typical first order gas phase reaction

$$A(g) \rightarrow B(g) + C(g)$$

Let p_i be the initial pressure of A and p_t the total pressure at time 't'. Integrated rate equation for such a reaction can be derived as

Total pressure $p_t = p_A + p_B + p_C$ (pressure units)

p_A, p_B and p_C are the partial pressures of A, B and C, respectively.

If x atm be the decrease in pressure of A at time *t* and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

	A(g)	→	B(g)	+	C(g)
At $t = 0$	p_i atm		0 atm		0 atm
At time t	$(p_i - x)$ atm		x atm		x atm

where, p_i is the initial pressure at time $t = 0$.

$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

where, $p_A = p_i - x = p_i - (p_t - p_i)$

$$= 2p_i - p_t$$

$$k = \left(\frac{2.303}{t}\right)\left(\log\frac{p_i}{p_A}\right) \qquad (4.16)$$

$$= \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

Example

The following data were obtained during the first order thermal decomposition of N_2O_5 (g) at constant volume:

$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

S.No.	Time/s	Total Pressure/(atm)
1.	0	0.5
2.	100	0.512

Calculate the rate constant.

Solution

Let the pressure of N_2O_5(g) decrease by 2x atm. As two moles of N_2O_5 decompose to give two moles of N_2O_4(g) and one mole of O_2 (g), the pressure of N_2O_4 (g) increases by 2x atm and that of O_2 (g) increases by x atm.

	$2N_2O_5(g)$	→	$2N_2O_4(g)$	+	$O_2(g)$
Start $t = 0$	0.5 atm		0 atm		0 atm
At time t	(0.5 – 2x) atm		2x atm		x atm

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$

$$= (0.5 - 2x) + 2x + x = 0.5 + x$$

$$x = p_t - 0.5$$

$$p_{N_2O_5} = 0.5 - 2x$$

$$= 0.5 - 2\,(p_t - 0.5) = 1.5 - 2p_t$$

At $t = 100$ s; $p_t = 0.512$ atm

$$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476 \text{ atm}$$

Using equation (4.16)

$$k = \frac{2.303}{t}\log\frac{p_i}{p_A} = \frac{2.303}{100\,\text{s}}\log\frac{0.5\,\text{atm}}{0.476\,\text{atm}}$$

$$= \frac{2.303}{100\,\text{s}} \times 0.0216 = 4.98 \times 10^{-4}\,\text{s}^{-1}$$

4.3.3 Half-Life of a Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

For a zero order reaction, rate constant is given by equation 4.7.

$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, \quad [R] = \frac{1}{2}[R]_0$$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For the first order reaction,

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} \qquad (4.15)$$

$$\text{at } t_{1/2} \quad [R] = \frac{[R]_0}{2} \qquad (4.16)$$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]/2}$$

$$\text{or} \quad t_{1/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k} \qquad (4.17)$$

It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.

For zero order reaction $t_{1/2} \propto [R]_0$. For first order reaction $t_{1/2}$ is independent of $[R]_0$.

Example

A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half-life of the reaction.

Solution

Half-life for a first order reaction is

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

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14} s^{-1}} = 1.26 \times 10^{13} s$$

Example

Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction.

Solution

When reaction is completed 99.9%, $[R]_n = [R]_0 - 0.999[R]_0$

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{t} \log \frac{[R]_0}{[R]_0 - 0.999[R]_0} = \frac{2.303}{t} \log 10^3$$

$$t = 6.909/k$$

For half-life of the reaction

$$t_{1/2} = 0.693/k$$

$$\frac{t}{t_{1/2}} = \frac{6.909}{k} \times \frac{k}{0.693} = 10$$

Table 4.4 summarises the mathematical features of integrated laws of zero and first order reactions.

Table 4.4: Integrated Rate Laws for the Reactions of Zero and First Order

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	R→P	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	[R] vs t	$[R]_0/2k$	conc $time^{-1}$ or $mol\ L^{-1}s^{-1}$
1	R→P	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln\{[R]_0/[R]\}$	ln[R] vs t	$\ln 2/k$	$time^{-1}$ or s^{-1}

Pseudo First Order Reaction

The order of a reaction is sometimes altered by conditions. Consider a chemical reaction between two substances when one reactant is present in large excess. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning (t = 0) and completion (t) of the reaction are given as under.

	$CH_3COOC_2H_5$	$+ H_2O$	$\xrightarrow{H^+}$	CH_3COOH	$+ C_2H_5OH$
$t = 0$	0.01 mol	10 mol		0 mol	0 mol
t	0 mol	9.9 mol		0.01 mol	0.01 mol

The concentration of water does not get altered much during the course of the reaction. So, in the rate equation

$$\text{Rate} = k'[CH_3COOC_2H_5]\,[H_2O]$$

the term $[H_2O]$ can be taken as constant. The equation, thus, becomes

$$\text{Rate} = k\,[CH_3COOC_2H_5]$$

where $k = k'[H_2O]$

and the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions.

Inversion of cane sugar is another pseudo first order reaction.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\text{Rate} = k\;[C_{12}H_{22}O_{11}]$$

Example

Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below.

t/min	0	30	60	90
C/mol L^{-1}	0.8500	0.8004	0.7538	0.7096

Show that it follows a pseudo first order reaction, as the concentration of water remains nearly constant (55 mol L^{-1}), during the course of the reaction. What is the value of k' in this equation?

$$\text{Rate} = k'[CH_3COOCH_3][H_2O]$$

Solution For pseudo first order reaction, the reaction should be first order with respect to ester when $[H_2O]$ is constant. The rate constant k for pseudo first order reaction is

$$k = \frac{2.303}{t}\log\frac{C_0}{C} \qquad \text{where} \quad k = k'[H_2O]$$

From the above data we note

t/min	C/ mol L^{-1}	k'/min^{-1}
0	0.8500	–
30	0.8004	2.004×10^{-3}
60	0.7538	2.002×10^{-3}
90	0.7096	2.005×10^{-3}

It can be seen that k' $[H_2O]$ is constant and equal to 2.004×10^{-3} min^{-1} and hence, it is pseudo first order reaction. We can now determine k from

$$k' [H_2O] = 2.004 \times 10^{-3} \text{ min}^{-1}$$

$$k' [55 \text{ mol L}^{-1}] = 2.004 \times 10^{-3} \text{ min}^{-1}$$

$$k' = 3.64 \times 10^{-5} \text{ mol}^{-1} \text{ L min}^{-1}$$

Intext Questions

4.5 A first order reaction has a rate constant 1.15×10^{-3} s^{-1}. How long will 5 g of this reactant take to reduce to 3 g?

4.6 Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Temperature Dependence of the Rate of a Reaction

Most of the chemical reactions are accelerated by increase in temperature. For example, in decomposition of N_2O_5, the time taken for half of the original amount of material to decompose is 12 min at 50°C, 5 h at 25°C and 10 days at 0°C. You also know that in a mixture of potassium permanganate ($KMnO_4$) and oxalic acid ($H_2C_2O_4$), potassium permanganate gets decolourised faster at a higher temperature than that at a lower temperature.

It has been found that **for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.**

The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation (4.18). It was first proposed by Dutch chemist, J.H. van't Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation.

$$k = A\, e^{-Ea/RT} \qquad (4.18)$$

where A is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and E_a is activation energy measured in joules/mole ($J\ mol^{-1}$).

It can be understood clearly using the following simple reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate (Fig. 4.6). It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

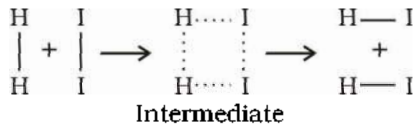


Fig. 4.6: *Formation of HI through the intermediate*

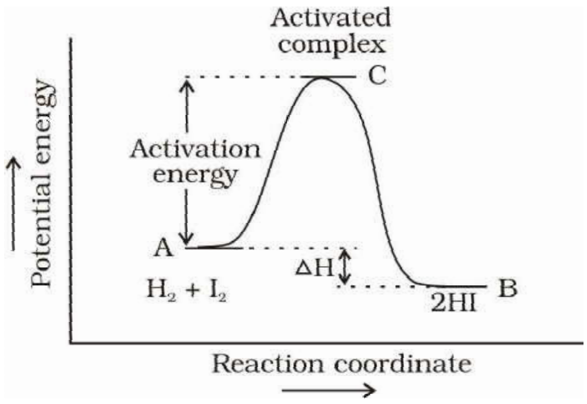


Fig. 4.7: *Diagram showing plot of potential energy vs reaction coordinate.*

The energy required to form this intermediate, called **activated complex** (C), is known as **activation energy (E_a)**. Fig. 4.7 is obtained by plotting potential energy vs reaction coordinate. Reaction coordinate represents the profile of energy change when reactants change into products.

Some energy is released when the complex decomposes to form products. So, the final enthalpy of the reaction depends upon the nature of reactants and products.

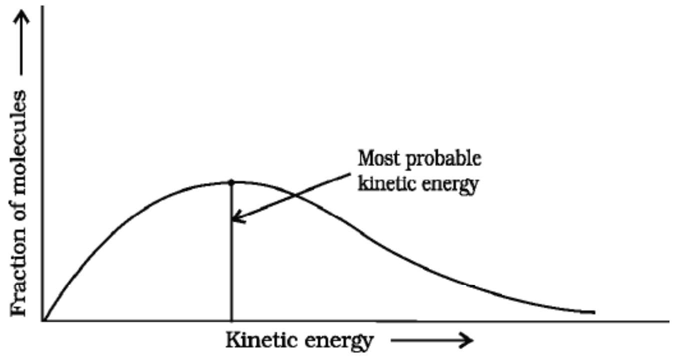


Fig. 4.8: *Distribution curve showing energies among gaseous molecules*

All the molecules in the reacting species do not have the same kinetic energy. Since it is difficult to predict the behaviour of any one molecule with precision, Ludwig Boltzmann and James Clark Maxwell used statistics to predict the behaviour of large number of molecules. According to them, the distribution of kinetic energy may be described by plotting the fraction of molecules (N_E/N_T) with a given kinetic energy (E) vs kinetic energy (Fig. 4.8). Here, N_E is the number of molecules with energy E and N_T is total number of molecules.

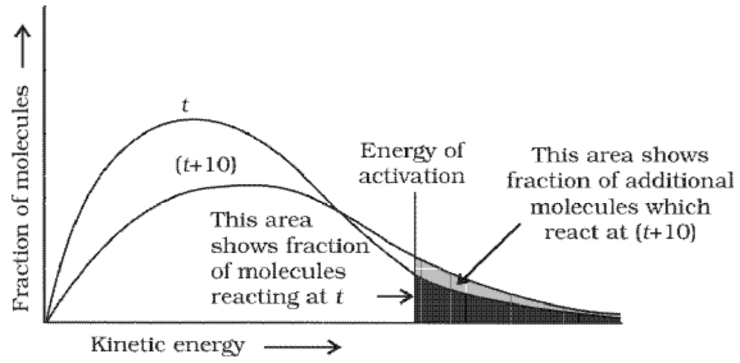


Fig. 4.9: *Distribution curve showing temperature dependence of rate of a reaction*

The peak of the curve corresponds to the **most probable kinetic energy**, i.e., kinetic energy of maximum fraction of molecules. There are decreasing number of molecules with energies higher or lower than this value. When the temperature is raised, the maximum of the curve moves to the higher energy value (Fig. 4.9) and the curve broadens out, i.e., spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times. We can mark the position of E_a on Maxwell Boltzmann distribution curve (Fig. 4.9).

Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than E_a. It is clear from the diagram that in the curve at $(t + 10)$, the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

In the Arrhenius equation (4.18) the factor $e^{-Ea/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a. Taking natural logarithm of both sides of equation (4.18)

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad (4.19)$$

The plot of ln k vs 1/T gives a straight line according to the equation (4.19) as shown in Fig. 4.10.

Thus, it has been found from Arrhenius equation (4.18) that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

In Fig. 4.10, slope $= -\frac{E_a}{R}$ and intercept = ln A. So we can calculate E_a and A using these values.

At temperature T_1, equation (4.19) is

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \qquad (4.20)$$

At temperature T_2, equation (4.19) is

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \qquad (4.21)$$

(since A is constant for a given reaction)

k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively.

Subtracting equation (4.20) from (4.21), we obtain

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (4.22)$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\text{R}}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

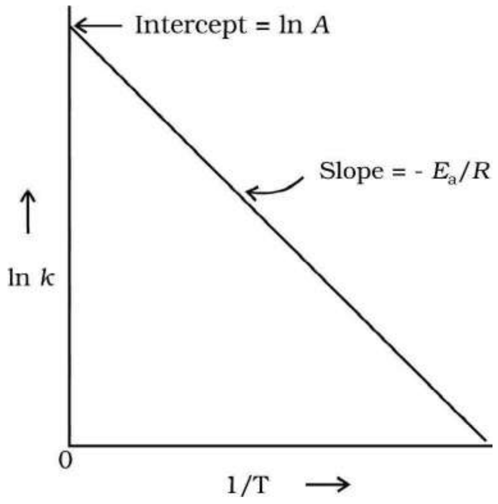


Fig. 4.10: *A plot between ln k and 1/T*

Example The rate constants of a reaction at 500K and 700K are $0.02s^{-1}$ and $0.07s^{-1}$ respectively. Calculate the values of E_a and A.

Solution

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{0.07}{0.02} = \left(\frac{E_a}{2.303 \times 8.314\ JK^{-1}mol^{-1}}\right)\left[\frac{700 - 500}{700 \times 500}\right]$$

$$0.544 = E_a \times 5.714 \times 10^{-4}/19.15$$

$$E_a = 0.544 \times 19.15/5.714 \times 10^{-4} = 18230.8\ J$$

Since $k = Ae^{-Ea/RT}$

$$0.02 = Ae^{-18230.8/8.314 \times 500}$$

$$A = 0.02/0.012 = 1.61$$

Example The first order rate constant for the decomposition of ethyl iodide by the reaction

$$C_2H_5I(g) \rightarrow C_2H_4\ (g) + HI(g)$$

at 600K is $1.60 \times 10^{-5}\ s^{-1}$. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700K.

Solution We know that

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log k_2 = \log k_1 + \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \log(1.60 \times 10^{-5}) + \frac{209000\ J\ mol\ L^{-1}}{2.303 \times 8.314\ J\ mol\ L^{-1}K^{-1}}\left[\frac{1}{600\ K} - \frac{1}{700\ K}\right]$$

$$\log k_2 = -\ 4.796 + 2.599 = -\ 2.197$$

$$k_2 = 6.36 \times 10^{-3}\ s^{-1}$$

4.5.1 Effect of Catalyst

A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change. For example, MnO_2 catalyses the following reaction so as to increase its rate considerably.

$$2KClO_3 \xrightarrow{MnO_2} 2\ KCl + 3O_2$$

The word catalyst should not be used when the added substance reduces the rate of raction. The substance is then called inhibitor. The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

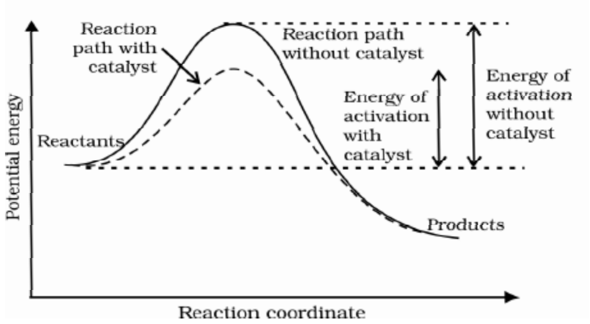


Fig. 4.11: *Effect of catalyst on activation energy*

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier as shown in Fig. 4.11.

It is clear from Arrhenius equation (4.18) that lower the value of activation energy faster will be the rate of a reaction.

A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter Gibbs energy, ΔG of a reaction. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions. It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

Collision Theory of Chemical Reactions

Though Arrhenius equation is applicable under a wide range of circumstances, collision theory, which was developed by Max Trautz and William Lewis in 1916 -18, provides a greater insight into the energetic and mechanistic aspects of reactions. It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. **The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).** Another factor which affects the rate of chemical reactions is activation energy (as we have already studied). For a bimolecular elementary reaction

$$A + B \rightarrow \text{Products}$$

rate of reaction can be expressed as

$$\text{Rate} = Z_{AB}\,e^{-E_a/RT} \qquad (4.23)$$

where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a. Comparing (4.23) with Arrhenius equation, we can say that A is related to collision frequency.

Equation (4.23) predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy (called threshold energy*) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as **effective collisions.**

---

* *Threshold energy = Activation Energy + energy possessed by reacting species.*

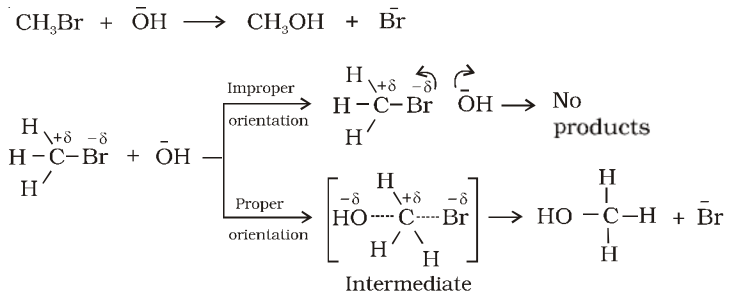


Fig. 4.12: Diagram showing molecules having proper and improper orientation

For example, formation of methanol from bromoethane depends upon the orientation of reactant molecules as shown in Fig. 4.12. *The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.*

To account for effective collisions, another factor *P*, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$\text{Rate} = PZ_{AB}e^{-E_a/RT}$$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

Collision theory also has certain drawbacks as it considers atoms/molecules to be hard spheres and ignores their structural aspect. You will study details about this theory and more on other theories in your higher classes.

Intext Questions

4.7 What will be the effect of temperature on rate constant ?

4.8 The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate E_a.

4.9 The activation energy for the reaction

$$2\,HI(g) \rightarrow H_2 + I_2\,(g)$$

is 209.5 kJ mol^{-1} at 581K.Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Summary

Chemical kinetics is the study of chemical reactions with respect to reaction rates, effect of various variables, rearrangement of atoms and formation of intermediates. The rate of a reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst, affect the rate of a reaction. Mathematical representation of rate of a reaction is given by **rate law**. It has to be determined experimentally and cannot be predicted. **Order of a reaction** with respect to a reactant is the power of its concentration which appears in the rate law equation. The order of a reaction is the sum of all such powers of concentration of terms for different reactants. **Rate constant** is the proportionality factor in the rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation. **Molecularity** is defined only for an elementary reaction. Its values are limited from 1 to 3 whereas order can be 0, 1, 2, 3 or even a fraction. Molecularity and order of an elementary reaction are same.

Temperature dependence of rate constants is described by Arrhenius equation ($k = Ae^{-Ea/RT}$). E_a corresponds to the **activation energy** and is given by the energy difference between activated complex and the reactant molecules, and *A* (Arrhenius factor or pre-exponential factor) corresponds to the collision frequency. The equation clearly shows that increase of temperature or lowering of E_a will lead to an increase in the rate of reaction and presence of a catalyst lowers the activation energy by providing an alternate path for the reaction. According to collision theory, another factor *P* called steric factor which refers to the orientation of molecules which collide, is important and contributes to effective collisions, thus, modifying the Arrhenius equation to $k = PZ_{AB}e^{-E_a/RT}$.

Exercises

4.1 From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

(i) $3NO(g) \rightarrow N_2O\ (g)$ Rate = $k[NO]^2$

(ii) $H_2O_2\ (aq) + 3I^-\ (aq) + 2H^+ \rightarrow 2H_2O\ (l) + I_3^-$ Rate = $k[H_2O_2][I^-]$

(iii) $CH_3CHO\ (g) \rightarrow CH_4\ (g) + CO(g)$ Rate = $k[CH_3CHO]^{3/2}$

(iv) $C_2H_5Cl\ (g) \rightarrow C_2H_4\ (g) + HCl\ (g)$ Rate = $k[C_2H_5Cl]$

4.2 For the reaction:

$$2A + B \rightarrow A_2B$$

the rate = $k[A][B]^2$ with k = 2.0×10^{-6} mol^{-2} L^2 s^{-1}. Calculate the initial rate of the reaction when [A] = 0.1 mol L^{-1}, [B] = 0.2 mol L^{-1}. Calculate the rate of reaction after [A] is reduced to 0.06 mol L^{-1}.

4.3 The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}$ mol^{-1} L s^{-1}?

4.4 The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by

$$\text{Rate} = k\ [CH_3OCH_3]^{3/2}$$

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,

$$\text{Rate} = k\left(p_{CH_3OCH_3}\right)^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

4.5 Mention the factors that affect the rate of a chemical reaction.

4.6 A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled (ii) reduced to half ?

4.7 What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively?

4.8 In a pseudo first order hydrolysis of ester in water, the following results were obtained:

t/s	0	30	60	90
[Ester]/mol L^{-1}	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

4.9 A reaction is first order in A and second order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of B three times?

(iii) How is the rate affected when the concentrations of both A and B are doubled?

4.10 In a reaction between A and B, the initial rate of reaction (r_0) was measured for different initial concentrations of A and B as given below:

A/ mol L^{-1}	0.20	0.20	0.40
B/ mol L^{-1}	0.30	0.10	0.05
r_0/mol $L^{-1}s^{-1}$	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction with respect to A and B?

4.11 The following results have been obtained during the kinetic studies of the reaction:

$$2A + B \rightarrow C + D$$

Experiment	[A]/mol L^{-1}	[B]/mol L^{-1}	Initial rate of formation of D/mol L^{-1} min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

4.12 The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	[A]/ mol L^{-1}	[B]/ mol L^{-1}	Initial rate/ mol L^{-1} min^{-1}
I	0.1	0.1	2.0×10^{-2}
II	–	0.2	4.0×10^{-2}
III	0.4	0.4	–
IV	–	0.2	2.0×10^{-2}

4.13 Calculate the half-life of a first order reaction from their rate constants given below:

(i) 200 s^{-1} (ii) 2 min^{-1} (iii) 4 $years^{-1}$

4.14 The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

4.15 The experimental data for decomposition of N_2O_5

$[2N_2O_5 \rightarrow 4NO_2 + O_2]$

in gas phase at 318K are given below:

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5]$/ mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot $[N_2O_5]$ against *t*.
(ii) Find the half-life period for the reaction.
(iii) Draw a graph between $\log[N_2O_5]$ and *t*.
(iv) What is the rate law ?
(v) Calculate the rate constant.
(vi) Calculate the half-life period from *k* and compare it with (ii).

4.16 The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

4.17 During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

4.18 For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

4.19 A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

4.20 For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

4.21 The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.

$$SO_2Cl_2\,(g) \rightarrow SO_2\,(g) + Cl_2\,(g)$$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

4.22 The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

$T/°C$	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between ln k and $1/T$ and calculate the values of A and E_a. Predict the rate constant at 30° and 50°C.

4.23 The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5} s^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

4.24 Consider a certain reaction A → Products with $k = 2.0 \times 10^{-2} s^{-1}$. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L^{-1}.

4.25 Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2}$ = 3.00 hours. What fraction of sample of sucrose remains after 8 hours ?

4.26 The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10^{11} s^{-1})\ e^{-28000K/T}$$

Calculate E_a.

4.27 The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.34 - 1.25 \times 10^4 K/T$$

Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes?

4.28 The decomposition of A into product has value of k as $4.5 \times 10^3\ s^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1}. At what temperature would k be $1.5 \times 10^4 s^{-1}$?

4.29 The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the value of A is $4 \times 10^{10} s^{-1}$. Calculate k at 318K and E_a.

4.30 The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Answers to Some Intext Questions

4.1 $r_{av} = 6.66 \times 10^{-6}\ Ms^{-1}$

4.2 Rate of reaction = rate of diappearance of A
= 0.005 mol litre^{-1}min^{-1}

4.3 Order of the reaction is 2.5

4.4 $X \rightarrow Y$
Rate = $k[X]^2$
The rate will increase 9 times

4.5 t = 444 s

4.6 $1.925 \times 10^{-4}\ s^{-1}$

4.8 Ea = 52.897 kJ mol^{-1}

4.9 1.471×10^{-19}

Unit 5

Surface Chemistry

Some of the most important chemicals are produced industrially by means of reactions that occur on the surfaces of solid catalysts.

Objectives

After studying this Unit, you will be able to

- describe interfacial phenomenon and its significance;
- define adsorption and classify it into physical and chemical adsorption;
- explain mechanism of adsorption;
- explain the factors controlling adsorption from gases and solutions on solids;
- explain adsorption results on the basis of Freundlich adsorption isotherms;
- appreciate the role of catalysts in industry;
- enumerate the nature of colloidal state;
- describe preparation, properties and purification of colloids;
- classify emulsions and describe their preparation and properties;
- describe the phenomenon of gel formation;
- list the uses of colloids.

Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface or surface is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas. Due to complete miscibility, there is no interface between the gases. The bulk phases that we come across in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends on the size of the particles of bulk phases. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

To accomplish surface studies meticulously, it becomes imperative to have a really clean surface. Under very high vacuum of the order of 10^{-8} to 10^{-9} pascal, it is now possible to obtain ultra clean surface of the metals. Solid materials with such clean surfaces need to be stored in vacuum otherwise these will be covered by molecules of the major components of air namely dioxygen and dinitrogen.

In this Unit, you will be studying some important features of surface chemistry such as adsorption, catalysis and colloids including emulsions and gels.

5.1 Adsorption

There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. **The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption**. The molecular species or substance, which concentrates or accumulates at the surface is termed **adsorbate** and the material on the surface of which the adsorption takes place is called **adsorbent**.

Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents.

Adsorption in action

(i) If a gas like O_2, H_2, CO, Cl_2, NH_3 or SO_2 is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.

(ii) In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.

(iii) Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.

(iv) The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by virtue of adsorption. The process of removing an adsorbed substance from a surface on which it is adsorbed is called **desorption**.

5.1.1 Distinction between Adsorption and Absorption

In adsorption, the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent, while in absorption, the substance is uniformly distributed throughout the bulk of the solid. For example, when a chalk stick is dipped in ink, the surface retains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption. On breaking the chalk stick, it is found to be white from inside. A distinction can be made between absorption and adsorption by taking an example of water vapour. Water vapours are absorbed by anhydrous calcium chloride but adsorbed by silica gel. In other words, in adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.

Both adsorption and absorption can take place simultaneously also. The term sorption is used to describe both the processes.

5.1.2 Mechanism of Adsorption

Adsorption arises due to the fact that the surface particles of the adsorbent are not in the same environment as the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides, and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface.The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to decrease in the entropy of the gas after adsorption, i.e., ΔS is negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative, i.e., there is a decrease in Gibbs energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $- T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state equilibrium is attained.

5.1.3 Types of Adsorption

There are mainly two types of adsorption of gases on solids. If accumulation of gas on the surface of a solid occurs on account of weak van der Waals' forces, the adsorption is termed as **physical adsorption or physisorption**. When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed **chemical adsorption or chemisorption**. The chemical bonds may be covalent or ionic in nature. Chemisorption involves a high energy of activation and is, therefore, often referred to as activated adsorption. Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, dihydrogen is first adsorbed on nickel by van der Waals' forces. Molecules of hydrogen then dissociate to form hydrogen atoms which are held on the surface by chemisorption.

Some of the important characteristics of both types of adsorption are described below:

Characteristics of physisorption

(i) *Lack of specificity:* A given surface of an adsorbent does not show any preference for a particular gas as the van der Waals' forces are universal.

(ii) *Nature of adsorbate:* The amount of gas adsorbed by a solid depends on the nature of gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed as van der Waals' forces are stronger near the critical temperatures. Thus, 1g of activated charcoal adsorbs more sulphur dioxide (critical temperature 630K), than methane (critical temperature 190K) which is still more than 4.5 mL of dihydrogen (critical temperature 33K).

(iii) *Reversible nature:* Physical adsorption of a gas by a solid is generally reversible. Thus,

$$\text{Solid} + \text{Gas} \rightleftharpoons \text{Gas/Solid} + \text{Heat}$$

More of gas is adsorbed when pressure is increased as the volume of the gas decreases (Le–Chateliers's principle) and the gas can be removed by decreasing pressure. Since the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increasing temperature (Le-Chatelier's principle).

(iv) *Surface area of adsorbent:* The extent of adsorption increases with the increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.

(v) *Enthalpy of adsorption:* No doubt, physical adsorption is an exothermic process but its enthalpy of adsorption is quite low (20–40 kJ mol^{-1}). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals' forces.

Characteristics of chemisorption

(i) *High specificity:* Chemisorption is highly specific and it will only occur if there is some possibility of chemical bonding between adsorbent and adsorbate. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.

(ii) *Irreversibility:* As chemisorption involves compound formation, it is usually irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, adsorption often increases with rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually high pressure is also favourable for chemisorption.

(iii) *Surface area:* Like physical adsorption, chemisorption also increases with increase of surface area of the adsorbent.

(iv) *Enthalpy of adsorption:* Enthalpy of chemisorption is high (80-240 kJ mol^{-1}) as it involves chemical bond formation.

Table 5.1: Comparison of Physisorption and Chemisorption

Physisorption	Chemisorption
1. It arises because of van der Waals' forces.	**1.** It is caused by chemical bond formation.
2. It is not specific in nature.	**2.** It is highly specific in nature.
3. It is reversible in nature.	**3.** It is irreversible.
4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	**4.** It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
5. Enthalpy of adsorption is low (20-40 kJ mol^{-1})in this case.	**5.** Enthalpy of adsorption is high (80-240 kJ mol^{-1}) in this case.

6. Low temperature is favourable for adsorption. It decreases with increase of temperature.	**6.** High temperature is favourable for adsorption. It increases with the increase of temperature.
7. No appreciable activation energy is needed.	**7.** High activation energy is sometimes needed.
8. It depends on the surface area. It increases with an increase of surface area.	**8.** It also depends on the surface area. It too increases with an increase of surface area.
9. It results into multimolecular layers on adsorbent surface under high pressure.	**9.** It results into unimolecular layer.

5.1.4 Adsorption Isotherms

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as **adsorption isotherm**.

Freundlich adsorption isotherm: Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation:

$$\frac{x}{m} = k.p^{1/n} \; (n > 1) \qquad \text{... (5.1)}$$

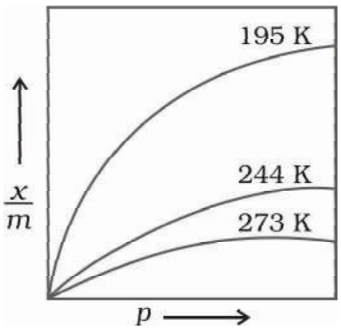


Fig. 5.1: Adsorption isotherm

where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure P, k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature. The relationship is generally represented in the form of a curve where mass of the gas adsorbed per gram of the adsorbent is plotted against pressure (Fig. 5.1). These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.

Taking logarithm of eq. (5.1)

$$\log\frac{x}{m} = \log k + \frac{1}{n} \log p \qquad \text{... (5.2)}$$

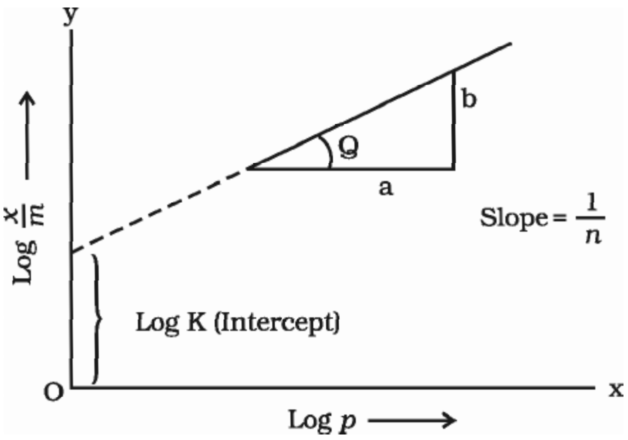


Fig. 5.2: Freundlich isotherm

The validity of Freundlich isotherm can be verified by plotting log $\frac{x}{m}$ on y-axis (ordinate) and log p on x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid, otherwise not (Fig. 5.2). The slope of the straight line gives the value of $\frac{1}{n}$. The intercept on the y-axis gives the value of log k.

Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor $\frac{1}{n}$ can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation (5.2) holds good over a limited range of pressure.

When $\frac{1}{n} = 0, \frac{x}{m}$ = constant, the adsorption is independent of pressure.

When $\frac{1}{n} = 1, \frac{x}{m} = k\,p$, i.e. $\frac{x}{m} \propto p$, the adsorption varies directly with pressure.

Both the conditions are supported by experimental results. The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.

5.1.5 Adsorption from Solution Phase

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution. Similarly, the litmus solution when shaken with charcoal becomes colourless. The precipitate of $Mg(OH)_2$ attains blue colour when precipitated in presence of magneson reagent. The colour is due to adsorption of magneson. The following observations have been made in the case of adsorption from solution phase:

(i) The extent of adsorption decreases with an increase in temperature.

(ii) The extent of adsorption increases with an increase of surface area of the adsorbent.

(iii) The extent of adsorption depends on the concentration of the solute in solution.

(iv) The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

The precise mechanism of adsorption from solution is not known. Freundlich's equation approximately describes the behaviour of adsorption from solution with a difference that instead of pressure, concentration of the solution is taken into account, i.e.,

$$\frac{x}{m} = kC^{1/n} \qquad \text{...(5.3)}$$

(C is the equilibrium concentration, i.e., when adsorption is complete). On taking logarithm of the above equation, we have

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C \qquad \text{...(5.4)}$$

Plotting $\log \frac{x}{m}$ against $\log C$ a straight line is obtained which shows the validity of Freundlich isotherm. This can be tested experimentally by taking solutions of different concentrations of acetic acid. Equal volumes of solutions are added to equal amounts of charcoal in different flasks. The final concentration is determined in each flask after adsorption. The difference in the initial and final concentrations give the value of x. Using the above equation, validity of Freundlich isotherm can be established.

5.1.6 Applications of Adsorption

The phenomenon of adsorption finds a number of applications. Important ones are listed here:

(i) *Production of high vacuum*: The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.

(ii) *Gas masks*: Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

(iii) *Control of humidity*: Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

(iv) *Removal of colouring matter from solutions*: Animal charcoal removes colours of solutions by adsorbing coloured impurities.

(v) *Heterogeneous catalysis*: Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H_2SO_4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

(vi) *Separation of inert gases*: Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.

(vii) *In curing diseases*: A number of drugs are used to kill germs by getting adsorbed on them.

(viii) *Froth floatation process*: A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent (see Unit 6).

(ix) *Adsorption indicators*: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.

(x) *Chromatographic analysis*: Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

Intext Questions

5.1 Write any two characteristics of Chemisorption.

5.2 Why does physisorption decrease with the increase of temperature?

5.3 Why are powdered substances more effective adsorbents than their crystalline forms?

Catalysis

Potassium chlorate, when heated strongly decomposes slowly giving dioxygen. The decomposition occurs in the temperature range of 653-873K.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

However, when a little of manganese dioxide is added, the decomposition takes place at a considerably lower temperature range, i.e., 473-633K and also at a much accelerated rate. The added manganese dioxide remains unchanged with respect to its mass and composition. In a similar manner, the rates of a number of chemical reactions can be altered by the mere presence of a foreign substance.

The systematic study of the effect of various foreign substances on the rates of chemical reactions was first made by Berzelius, in 1835. He suggested the term **catalyst** for such substances.

Substances, which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as catalysts, and the phenomenon is known as catalysis. You have already studied about catalysts and its functioning in Section 4.5.

Promoters and poisons

Promoters are substances that enhance the activity of a catalyst while poisons decrease the activity of a catalyst. For example, in Haber's process for manufacture of ammonia, molybdenum acts as a promoter for iron which is used as a catalyst.

$$N_2(g) + 3H_2(g) \xrightarrow[Mo(s)]{Fe(s)} 2NH_3(g)$$

5.2.1
Homogeneous and Heterogeneous Catalysis

Catalysis can be broadly divided into two groups:

(a) ***Homogeneous catalysis***

When the reactants and the catalyst are in the same phase (i.e., liquid or gas), the process is said to be homogeneous catalysis. The following are some of the examples of homogeneous catalysis:

(i) Oxidation of sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

The reactants, sulphur dioxide and oxygen, and the catalyst, nitric oxide, are all in the same phase.

(ii) Hydrolysis of methyl acetate is catalysed by H^+ ions furnished by hydrochloric acid.

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq) + CH_3OH(aq)$$

Both the reactants and the catalyst are in the same phase.

(iii) Hydrolysis of sugar is catalysed by H^+ ions furnished by sulphuric acid.

$$\underset{\text{Solution}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{H_2SO_4(l)} \underbrace{\underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}}_{\text{Solution}}$$

Both the reactants and the catalyst are in the same phase.

(b) ***Heterogeneous catalysis***

The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis. Some of the examples of heterogeneous catalysis are given below:

(i) Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt.

$$2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

The reactant is in gaseous state while the catalyst is in the solid state.

(ii) Combination between dinitrogen and dihydrogen to form ammonia in the presence of finely divided iron in Haber's process.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

The reactants are in gaseous state while the catalyst is in the solid state.

(iii) Oxidation of ammonia into nitric oxide in the presence of platinum gauze in Ostwald's process.

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

The reactants are in gaseous state while the catalyst is in the solid state.

(iv) Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst.

$$\text{Vegetable oils(l)} + H_2(g) \xrightarrow{Ni(s)} \text{Vegetable ghee(s)}$$

One of the reactants is in liquid state and the other in gaseous state while the catalyst is in the solid state.

5.2.2 Adsorption Theory of Heterogeneous Catalysis

This theory explains the mechanism of heterogeneous catalysis. The old theory, known as adsorption theory of catalysis, was that the reactants in gaseous state or in solutions, are adsorbed on the surface of the solid catalyst. The increase in concentration of the reactants on the surface increases the rate of reaction. Adsorption being an exothermic process, the heat of adsorption is utilised in enhancing the rate of the reaction.

The catalytic action can be explained in terms of the intermediate compound formation, the theory of which you have already studied in Section 4.5.1

The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localised on the surface of the catalyst. The mechanism involves five steps:

(i) Diffusion of reactants to the surface of the catalyst.

(ii) Adsorption of reactant molecules on the surface of the catalyst.

(iii) Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate (Fig. 5.3).

(iv) Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur.

(v) Diffusion of reaction products away from the catalyst's surface. The surface of the catalyst unlike the inner part of the bulk, has free valencies which provide the seat for chemical forces of attraction. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. If different molecules are adsorbed side by side, they may react with each other resulting in the formation of new molecules. Thus, formed molecules may evaporate leaving the surface for the fresh reactant molecules.

This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective

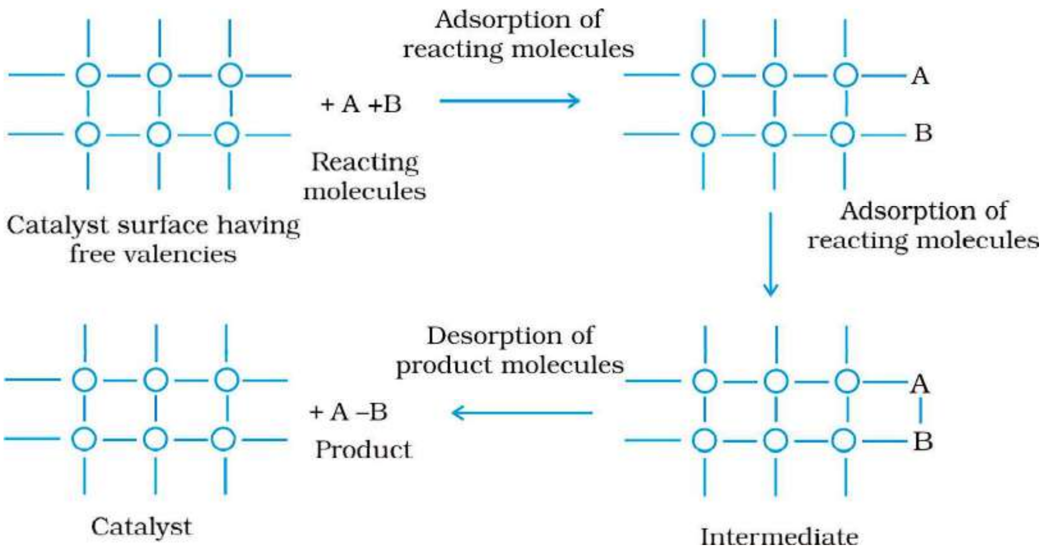


Fig. 5.3 Adsorption of reacting molecules, formation of intermediate and desorption of products

even in small quantities. It however, does not explain the action of catalytic promoters and catalytic poisons.

Important features of solid catalysts

(a) Activity

The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactants must get adsorbed reasonably strongly on to the catalyst to become active. However, they must not get adsorbed so strongly that they are immobilised and other reactants are left with no space on the catalyst's surface for adsorption. It has been found that for hydrogenation reaction, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity being shown by groups 7-9 elements of the periodic table (Class XI, Unit 3).

$$2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$$

(b) Selectivity

The selectivity of a catalyst is its ability to direct a reaction to yield a particular product selectively, when under the same reaction conditions many products are possible. Selectivity of different catalysts for same reactants is different. For example, starting with H_2 and CO, and using different catalysts, we get different products.

(i) $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

(ii) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO\text{-}Cr_2O_3} CH_3OH(g)$

(iii) $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

Thus, it can be inferred that the action of a catalyst is highly selective in nature. As a result a substance which acts as a catalyst in one reaction may fail to catalyse another reaction.

5.2.3 Shape-Selective Catalysis by Zeolites

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called **shape-selective catalysis.** Zeolites are good shape-selective catalysts because of their honeycomb-like structures. They are microporous aluminosilicates with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al–O–Si framework. The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites. They are found in nature as well as synthesised for catalytic selectivity.

Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

5.2.4 Enzyme Catalysis

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass and form colloidal solutions in water. They are very effective catalysts; catalyse numerous reactions, especially those connected with natural processes. Numerous reactions that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes. The enzymes are, thus, termed as **biochemical catalysts** and the phenomenon is known as **biochemical catalysis**.

Many enzymes have been obtained in pure crystalline state from living cells. However, the first enzyme was synthesised in the laboratory in 1969. The following are some of the examples of enzyme-catalysed reactions:

(i) *Inversion of cane sugar*: The invertase enzyme converts cane sugar into glucose and fructose.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$$

(ii) *Conversion of glucose into ethyl alcohol*: The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$\underset{\text{Glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

(iii) *Conversion of starch into maltose*: The diastase enzyme converts starch into maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n(aq)} + nH_2O(l) \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}(aq)}$$

(iv) *Conversion of maltose into glucose*: The maltase enzyme converts maltose into glucose.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6(aq)}$$

(v) *Decomposition of urea into ammonia and carbon dioxide*: The enzyme urease catalyses this decomposition.

$$NH_2CONH_2(aq) + H_2O(l) \xrightarrow{\text{Urease}} 2NH_3(g) + CO_2(g)$$

(vi) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.

(vii) *Conversion of milk into curd*: It is an enzymatic reaction brought about by lacto bacilli enzyme present in curd.

Table 5.2 gives the summary of some important enzymatic reactions.

Table 5.2: Some Enzymatic Reactions

Enzyme	Source	Enzymatic reaction
Invertase	Yeast	Sucrose → Glucose and fructose
Zymase	Yeast	Glucose → Ethyl alcohol and carbon dioxide
Diastase	Malt	Starch → Maltose
Maltase	Yeast	Maltose → Glucose
Urease	Soyabean	Urea → Ammonia and carbon dioxide
Pepsin	Stomach	Proteins → Amino acids

Characteristics of enzyme catalysis

Enzyme catalysis is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

(i) *Most highly efficient*: One molecule of an enzyme may transform one million molecules of the reactant per minute.

(ii) *Highly specific nature*: Each enzyme is specific for a given reaction, i.e., one catalyst cannot catalyse more than one reaction. For example, the enzyme urease catalyses the hydrolysis of urea only. It does not catalyse hydrolysis of any other amide.

(iii) *Highly active under optimum temperature*: The rate of an enzyme reaction becomes maximum at a definite temperature, called the optimum temperature. On either side of the optimum temperature, the enzyme activity decreases. The optimum temperature range for enzymatic activity is 298-310K. Human body temperature being 310 K is suited for enzyme-catalysed reactions.

(iv) *Highly active under optimum pH*: The rate of an enzyme-catalysed reaction is maximum at a particular pH called optimum pH, which is between pH values 5-7.

(v) *Increasing activity in presence of activators and co-enzymes*: The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein (vitamin) is present along with an enzyme, the catalytic activity is enhanced considerably.

Activators are generally metal ions such as Na^+, Mn^{2+}, Co^{2+}, Cu^{2+}, etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride i.e., Na^+ ions are catalytically very active.

(vi) *Influence of inhibitors and poisons*: Like ordinary catalysts, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes. The use of many drugs is related to their action as enzyme inhibitors in the body.

Mechanism of enzyme catalysis

There are a number of cavities present on the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as $-NH_2$, -COOH, -SH, -OH, etc. These are actually the active

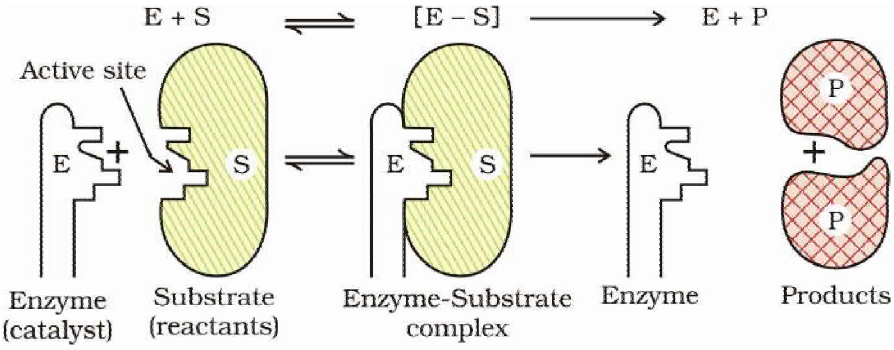


Fig. 5.4: *Mechanism of enzyme catalysed reaction*

centres on the surface of enzyme particles. The molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products.

Thus, the enzyme-catalysed reactions may be considered to proceed in two steps.

Step 1: Binding of enzyme to substrate to form an activated complex.

$$E + S \rightarrow ES^{\neq}$$

Step 2: Decomposition of the activated complex to form product.

$$ES^{\neq} \rightarrow E + P$$

5.2.5 Catalysts in Industry

Some of the important technical catalytic processes are listed in Table 5.3 to give an idea about the utility of catalysts in industries.

Table 5.3: Some Industrial Catalytic Processes

Process	Catalyst
1. Haber's process for the manufacture of ammonia $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	Finely divided iron, molybdenum as promoter; conditions: 200 bar pressure and 723-773K temperature. Now-a-days, a mixture of iron oxide, potassium oxide and alumina is used.
2. Ostwald's process for the manufacture of nitric acid. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$	Platinised asbestos; temperature 573K.
3. Contact process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $SO_3(g) + H_2SO_4(aq) \rightarrow \underset{\text{oleum}}{H_2S_2O_7(l)}$ $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$	Platinised asbestos or vanadium pentoxide (V_2O_5); temperature 673-723K.

Intext Questions

5.4 In Haber's process, hydrogen is obtained by reacting methane with steam in presence of NiO as catalyst. The process is known as steam reforming. Why is it necessary to remove CO when ammonia is obtained by Haber's process?

5.5 Why is the ester hydrolysis slow in the beginning and becomes faster after sometime?

5.6 What is the role of desorption in the process of catalysis.

5.3 Colloids

We have learnt in Unit 2 that solutions are homogeneous systems. We also know that sand in water when stirred gives a suspension, which slowly settles down with time. Between the two extremes of suspensions and solutions we come across a large group of systems called colloidal dispersions or simply colloids.

A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

The essential difference between a solution and a colloid is that of particle size. While in a solution, the constituent particles are ions or small molecules, in a colloid, the dispersed phase may consist of particles of a single macromolecule (such as protein or synthetic polymer) or an aggregate of many atoms, ions or molecules. Colloidal particles are larger than simple molecules but small enough to remain suspended. Their range of diameters is between 1 and 1000 nm (10^{-9} to 10^{-6} m).

Colloidal particles have an enormous surface area per unit mass as a result of their small size. Consider a cube with 1 cm side. It has a total surface area of 6 cm^2. If it were divided equally into 10^{12} cubes, the cubes would be the size of large colloidal particles and have a total surface area of 60,000 cm^2 or 6 m^2. This enormous surface area leads to some special properties of colloids to be discussed later in this Unit.

5.4 Classification of Colloids

Colloids are classified on the basis of the following criteria:

(i) Physical state of dispersed phase and dispersion medium
(ii) Nature of interaction between dispersed phase and dispersion medium
(iii) Type of particles of the dispersed phase.

5.4.1 Classification Based on Physical State of Dispersed Phase and Dispersion Medium

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The examples of the various types of colloids along with their typical names are listed in Table 5.4.

Table 5.4: Types of Colloidal Systems

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

Many familiar commercial products and natural objects are colloids. For example, whipped cream is a foam, which is a gas dispersed in a liquid. Firefighting foams, used at emergency airplane landings are also colloidal systems. Most biological fluids are aqueous sols (solids dispersed in water). Within a typical cell, proteins and nucleic acids are colloidal-sized particles dispersed in an aqueous solution of ions and small molecules.

Out of the various types of colloids given in Table 5.4, the most common are **sols** (solids in liquids), **gels** (liquids in solids) and **emulsions** (liquids in liquids). However, in the present Unit, we shall take up discussion of the 'sols' and 'emulsions' only. Further, it may be mentioned that if the dispersion medium is water, the sol is called aquasol or hydrosol and if the dispersion medium is alcohol, it is called alcosol and so on.

5.4.2 Classification Based on Nature of Interaction between Dispersed Phase and Dispersion Medium

Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, **lyophilic** (solvent attracting) and **lyophobic** (solvent repelling). If water is the dispersion medium, the terms used are hydrophilic and hydrophobic.

(i) *Lyophilic colloids*: The word 'lyophilic' means liquid-loving. Colloidal sols directly formed by mixing substances like gum, gelatine, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called lyophilic sols. An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called **reversible sols**. Furthermore, these sols are quite stable and cannot be easily coagulated as discussed later.

(ii) *Lyophobic colloids*: The word 'lyophobic' means liquid-hating. Substances like metals, their sulphides, etc., when simply mixed with the dispersion medium do not form the colloidal sol. Their colloidal sols can be prepared only by special methods (as discussed later). Such sols are called lyophobic sols. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and hence, are not stable. Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, these sols are also called **irreversible sols**. Lyophobic sols need stabilising agents for their preservation.

5.4.3 Classification Based on Type of Particles of the Dispersed Phase, Multimolecular, Macromolecular and Associated Colloids

Depending upon the type of the particles of the dispersed phase, colloids are classified as: multimolecular, macromolecular and associated colloids.

(i) *Multimolecular colloids*: On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in the colloidal range (1–1000 nm). The species thus formed are called multimolecular colloids. For example, a gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of S_8 sulphur molecules.

(ii) *Macromolecular colloids*: Macromolecules (Unit 15) in suitable solvents form solutions in which the size of the macromolecules may be in the colloidal range. Such systems are called macromolecular colloids. These colloids are quite stable and resemble true solutions in many respects. Examples of naturally occurring macromolecules are starch, cellulose, proteins and enzymes; and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.

(iii) *Associated colloids (Micelles)*: There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called **micelles**. These are also known as **associated colloids**. The formation of micelles takes place only above a particular temperature called **Kraft temperature** (**T_k**) and above a particular concentration called **critical micelle concentration (CMC)**. On dilution, these colloids revert back to individual ions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is 10^{-4} to 10^{-3} mol L^{-1}. These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

Mechanism of micelle formation

Let us take the example of soap solutions. Soap is sodium or potassium salt of a higher fatty acid and may be represented as $RCOO^-Na^+$ (e.g., sodium stearate $CH_3(CH_2)_{16}COO^-Na^+$, which is a major component of many bar soaps). When dissolved in water, it dissociates into $RCOO^-$ and Na^+ ions. The $RCOO^-$ ions, however, consist of two parts — a long hydrocarbon chain R (also called non-polar 'tail') which is hydrophobic (water repelling), and a polar group COO^- (also called polar-ionic 'head'), which is hydrophilic (water loving).

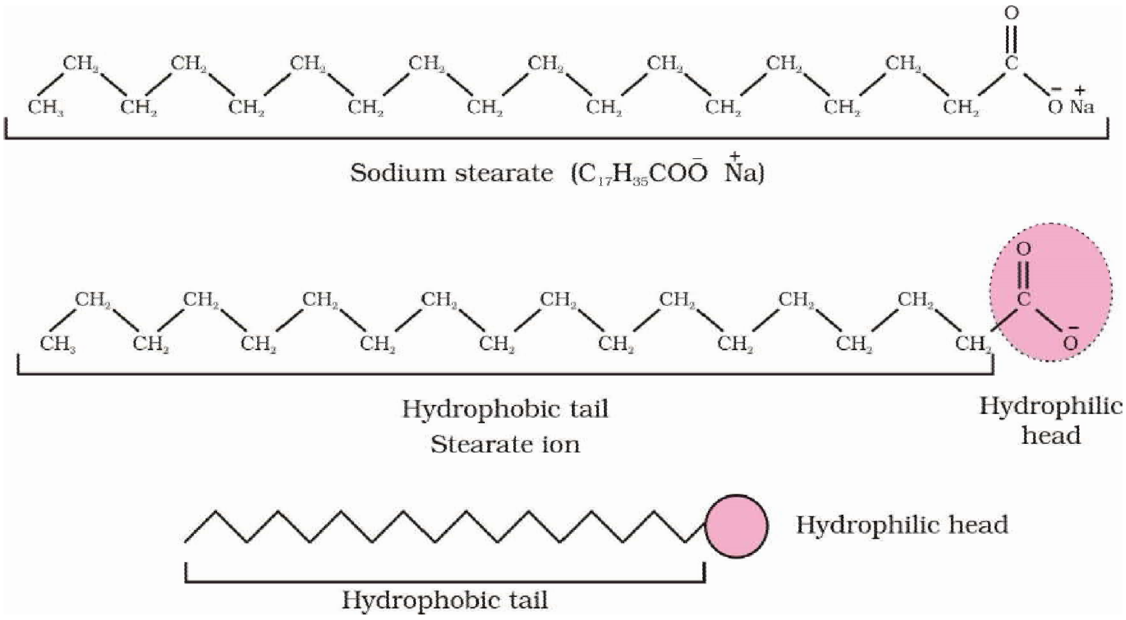


Fig. 5.5: *Hydrophobic and hydrophilic parts of stearate ion*

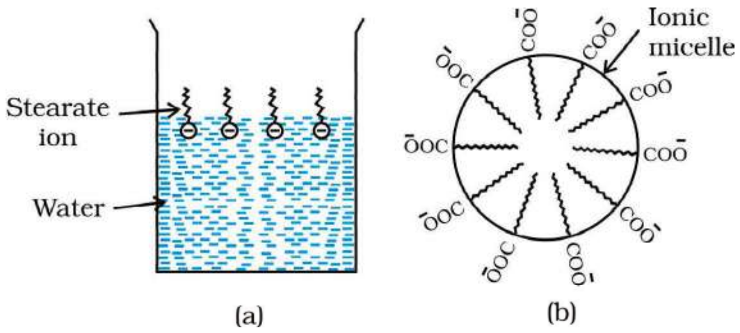


Fig. 5.6: *(a) Arrangement of stearate ions on the surface of water at low concentrations of soap*
(b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap

The $RCOO^-$ ions are, therefore, present on the surface with their COO^- groups in water and the hydrocarbon chains R staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with COO^- part remaining outward on the surface of the sphere. An aggregate thus formed is known as '**ionic micelle**'. These micelles may contain as many as 100 such ions.

Similarly, in case of detergents, e.g., sodium laurylsulphate, $CH_3(CH_2)_{11}SO_4^-Na^+$, the polar group is $-SO_4^-$ along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is same as that of soaps.

Cleansing action of soaps

It has been mentioned earlier that a micelle consists of a hydrophobic hydrocarbon – like central core. The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles (Fig. 5.7). Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

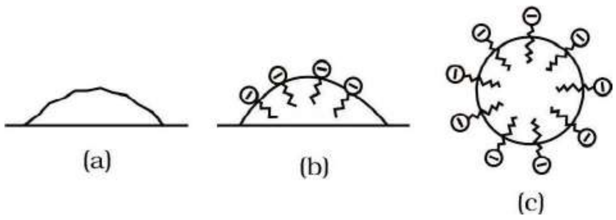


Fig. 5.7: *(a) Grease on cloth (b) Stearate ions arranging around the grease droplet and (c) Grease droplet surrounded by stearate ions (micelle formed)*

5.4.4 Preparation of Colloids

A few important methods for the preparation of colloids are as follows:

(a) Chemical methods

Colloidal dispersions can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction or hydrolysis. These molecules then aggregate leading to formation of sols.

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decompostion}} As_2S_3(\text{sol}) + 3H_2O$$

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(\text{sol}) + 2H_2O$$

$$2\,AuCl_3 + 3\,HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au(\text{sol}) + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\ (\text{sol}) + 3HCl$$

(b) Electrical disintegration or Bredig's Arc method

This process involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared by this method. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium (Fig. 5.8). The intense heat produced vapourises the metal, which then condenses to form particles of colloidal size.

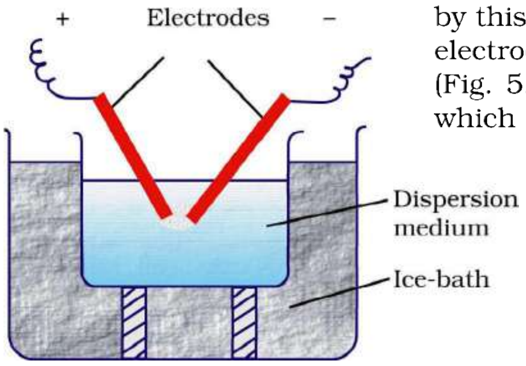


Fig. 5.8: *Bredig's Arc method*

(c) Peptization

Peptization may be defined as the **process of converting a precipitate into colloidal sol** by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called **peptizing agent**. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol.

During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates, which ultimately break up into smaller particles of the size of a colloid.

5.4.5 Purification of Colloidal Solutions

Colloidal solutions when prepared, generally contain excessive amount of electrolytes and some other soluble impurities. While the presence of traces of electrolyte is essential for the stability of the colloidal solution, larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. **The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution**. The purification of colloidal solution is carried out by the following mehods:

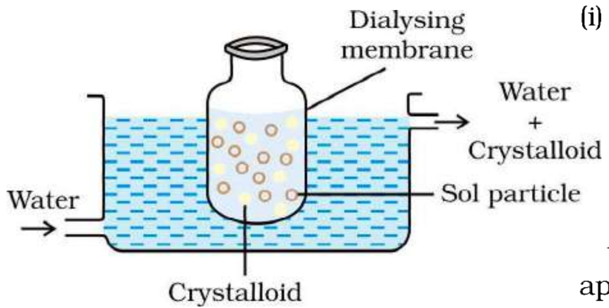


Fig. 5.9: *Dialysis*

(i) *Dialysis*: **It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane.** Since particles (ions or smaller molecules) in a true solution can pass through animal membrane (bladder) or parchment paper or cellophane sheet but not the colloidal particles, the membrane can be used for dialysis. The apparatus used for this purpose is called **dialyser**. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing (Fig. 5.9). The molecules and ions diffuse through membrane into the outer water and pure colloidal solution is left behind.

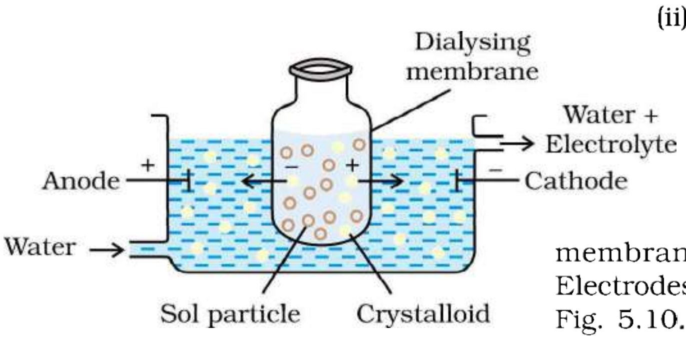


Fig. 5.10: *Electro-dialysis*

(ii) *Electro-dialysis*: Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte. The process is then named electrodialysis. The colloidal solution is placed in a bag of suitable membrane while pure water is taken outside. Electrodes are fitted in the compartment as shown in Fig. 5.10. The ions present in the colloidal solution migrate out to the oppositely charged electrodes.

(iii) *Ultrafiltration*: Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles. Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with **collodion** solution to stop the flow of colloidal particles. The usual collodion is a 4% solution of nitrocellulose in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the filter paper in a collodion solution, hardening by formaldehyde and then finally drying it. Thus, by using ultra-filter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied. The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

5.4.6 Properties of Colloidal Solutions

Various properties exhibited by the colloidal solutions are described below:

(i) *Colligative properties*: Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a true solution. Hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentrations.

(ii) *Tyndall effect*: If a homogeneous solution placed in dark is observed in the direction of light, it appears clear and, if it is observed from a direction at right angles to the direction of light beam, it appears perfectly dark. Colloidal solutions viewed in the same way may also appear reasonably clear or translucent by the transmitted light but they show a mild to strong opalescence, when viewed at right angles to the passage of light, i.e., the path of the beam is illuminated by a bluish light. This effect was first observed by Faraday and later studied in detail by Tyndall and is termed as **Tyndall effect**. The bright cone of the light is called **Tyndall cone** (Fig. 5.11). The Tyndall effect is due to the fact that colloidal particles scatter light in all directions in space. This scattering of light illuminates the path of beam in the colloidal dispersion.

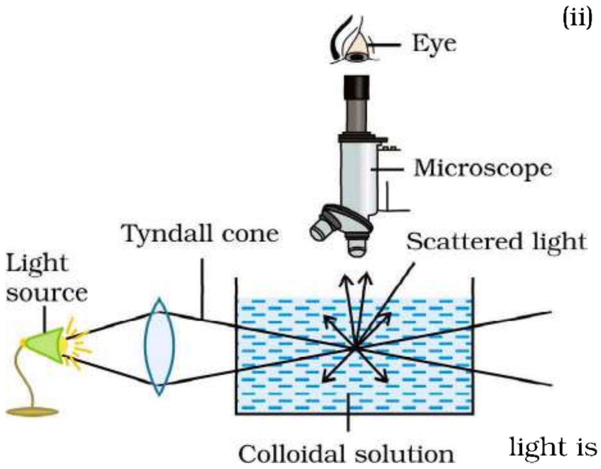


Fig. 5.11: *Tyndall effect*

Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. Tyndall effect is observed only when the following two conditions are satisfied.

(i) The diameter of the dispersed particles is not much smaller than the wavelength of the light used; and

(ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.