PREFACE

In the curricular structure introduced by this University for students of Post-Graduate degree programme, the opportunity to pursue Post-Graduate course in Subject introduced by this University is equally available to all learners. Instead of being guided by any presumption about ability level, it would perhaps stand to reason if receptivity of a learner is judged in the course of the learning process. That would be entirely in keeping with the objectives of open education which does not believe in artificial differentiation.

Keeping this in view, study materials of the Post-Graduate level in different subjects are being prepared on the basis of a well laid-out syllabus. The course structure combines the best elements in the approved syllabi of Central and State Universities in respective subjects. It has been so designed as to be upgradable with the addition of new information as well as results of fresh thinking and analyses.

The accepted methodology of distance education has been followed in the preparation of these study materials. Co-operation in every form of experienced scholars is indispensable for a work of this kind. We, therefore, owe an enormous debt of gratitude to everyone whose tireless efforts went into the writing, editing and devising of a proper lay-out of the materials. Practically speaking, their role amounts to an involvement in invisible teaching. For, whoever makes use of these study materials would virtually derive the benefit of learning under their collective care without each being seen by the other.

The more a learner would seriously pursue these study materials the easier it will be for him or her to reach out to larger horizons of a subject. Care has also been taken to make the language lucid and presentation attractive so that they may be rated as quality self-learning materials. If anything remains still obscure or difficult to follow, arrangements are there to come to terms with them through the counselling sessions regularly available at the network of study centres set up by the University.

Needless to add, a great deal of these efforts is still experimental—in fact, pioneering in certain areas. Naturally, there is every possibility of some lapse or deficiency here and there. However, these do admit of rectification and further improvement in due course. On the whole, therefore, these study materials are expected to evoke wider appreciation the more they receive serious attention of all concerned.

Professor (Dr.) Manimala Das
Vice-Chancellor

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POST GRADUATE ZOOLOGY
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	Writer	Editor
Unit-1	Prof. Manotosh Dasgupta Dr. Bibhas Guha	Prof. Manotosh Dasgupta Dr. Bibhas Guha
Units-2–5	Prof. Kanailal Mukherjee	Prof. Manotosh Dasgupta

NETAJI SUBHAS
OPEN UNIVERSITY

PGZO – 4
Basic Physical and
Chemical Principles

Group
A

UNIT 1 ❑ Energetics

Structure

1.1 Free energy functions

One of the problems of entropy calculation is that one has to work out the entropy change in the system and that in the surroundings, and then consider the sign of their sum. Towards the end of the 19th century foundation of chemical thermo dynamics was laid and the same led to a means to combine the two calculations into one.

Two thermodynamic functions are thus used, which are as follows :

[1] Gibbs free energy or Gibb's energy, G and

[2] Helmhotz free energy, A

They are defined as : [1] $G = H - TS$ .... (1)

[2] $A = U - TS$ .... (2)

Now, $q = T\Delta S = T(S_2 - S_1)$; so TS is an energy quantity and can be algebraically added to energy quantities V or H.

Again, V, H, T and S are state properties and so A and G will also be state functions, i.e. they will be defined by states of the system. In other words dA and dG will be exact differetials.

Since, $H = U + Pv$ .... (3)

$G = H - TS = U + PV - TS = A + PV$ .... (4)

1.1.1 Gibbs free energy, G

$G = H - TS = U + PV - TS$

or, $\Delta G = \Delta U + P\Delta V + V\Delta P - T\Delta S - S\Delta T$ .... (5)

If a system undergoes an isothermal change at constant presence, then

$\Delta G_{P,T} = \Delta U + P\Delta V - T\Delta S = \Delta U + P\Delta V - q$

$= P\Delta V - \omega$

or, $\leftarrow\ -\Delta G_{PT} = \omega - P\Delta V$ .... (6)

Here PΔV is the mechanical or expansional work involved in the system during the transfromation and ω denotes the maximum total work output. So Gibbs free energy signifies that **the value of ΔG for a process gives the maximum amount of non-expansion work that can be extracted from the process at constant temperature and pressure.** By non-expansion work (W') is meant any work other than that arising from the expansion of the system. It may include any kind of work received for any external use (exclusive of the mechanical work in the change of the system itself) : thus it may include electrical work (if the process takes place inside an electrochemical or biological cell), other kinds of external work such as winding of a spring or contraction of a muscle.

Gibbs free energy (G) is thus a property of the system whose decrease is the measure of the external work available during the system itself.

Referring to (S)

$dG = dU + PdV + VdP - TdS - SdT$

In a reversible mechanical process, $dU + PdV = TdS$

$\therefore\ dG = VdP - SdT$

For an isobaric process $\left(\frac{\partial G}{\partial T}\right)_P = -S$ .... (7)

For an isothermal process $\left(\frac{\partial G}{\partial P}\right)_T = V$ .... (8)

1.1.2 Maximum non-expansion work

At constant temperature and pressure

$dG = dU + PdV - TdS = dw + dq + PdV - TdS \quad (\because\ dU = dw + dq)$

The work done on the system comprises both expansion work $-P_{ex}dV$, and non-expansion work dw'.

So,

$dG = -P_{ex}dV + dw' + dq + pdV - TdS$ (at constant pressure and temperature) .... (9)

If the change is considered reversible, pexdV = pdV.

Again since heat transfer is reversible dq = TdS.

Thus, $dG = dw'_{rev}$ .... (10)

Alternatively we can write, $dG = dw'_{max}$ .... (11)

For overall change to we can write $\Delta G = W'_{max}$ .... (12)

Thus the importance of Gibbs energy in chemistry is apprant. Non-expansional work obtainable form an electrochemical cell, that in biological cells available from the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) can be calculated from knowledge of ΔG.

In section 1.3 one can see that for any reversible process in equilibrium at constant presence and temperature $(\partial G)_{P,T} = o$, for spontaneity $(\partial G)_{P,T} < o$

1.1.3 Standard state

Gibbs free energy G is a state function. So to calculate numerical values to Gibbs free energy change of a system, a standard state is to be assigned with a value thereof. Generally this standard state refers to 25°C and 1 atmosphere pressure for a pure substance.

Now, at constant temperature,

$\left(\frac{\partial G}{\partial P}\right)_T = V$ (equ. 8)

or, $\int_I^P dG = \int_I^P VdP$ [I ≡ initial i.e. at one atmosphere pressure ; P ≡ that at pressure P]

or, $G - G^O = \int_I^P VdP$ .... (13)

This G^O is the standard free energy i.e., free energy at the standard state.

Let the system is one of 'n' moles of a perfect gas at a temperature T K, then,

$$G = G^O + \int_I^P n\frac{RT}{P}dP = G^O + nRT\ln\frac{P}{1}$$

or, $G = G^O + nRT\ln P$ or, $\frac{G}{n} = \frac{G^o}{n} + RT\ln P$ .... (14)

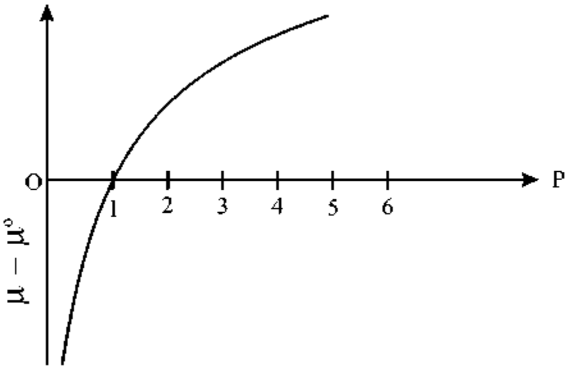
i.e. $\overline{G} = \overline{G^O} + RT\ln P$ (for 1 mole of gas) .... (15)

Free energy per g-mole of a gas is customarily referred to as μ (chemical potential)

$\therefore \mu = \mu^\circ + RT\ln P$ .... (16)

or, $\mu - \mu^\circ = RT\ln P$ .... (17)

Plot of $\mu - \mu^\circ$ against P is shown in figure



1.2 Helmholtz free energy

By definition, A = U − TS

For an isothermal ireversible change,

$\Delta A_T = \Delta U - T\Delta S \ (\Delta T = o)$

$= \Delta U - q = -W_{max}$ .... (18)

or, $-\Delta A_T = w_{max}$ .... (19)

W_{max} refers to maximum work involved.

Thus it can be inferred that Helmholtz free energy A is such a thermodynamic function. the decrease of which for a system denotes the maximum amount of work available during an isothermal transformation of the system. This is the total work viz. purely mechanical (or otherwise) or partly mechanical and partly external.

In thermodynamics we are concerned with reversible processes. If, however, the transformation be irreversible then also there would be a drop in A-value, but it would exceed the output of work, i.e. $-\Delta A > \omega$.

In case, the change is not isothermal, the change in A will not be equivalent to maximum work.

Recalling $A = U - TS$

or, $dA = dU - TdS - SdT$

or, $dA = dU - dq - SdT \ [\because TdS = dq]$

or, $dA = dU - dU - PdV - SdT$

or, $dA = -PdV - SdT$ .... (20)

Now, (i) If volume be kept constant i.e the process in isochoric,

$$\left(\frac{\partial A}{\partial T}\right)_v = -S \quad \text{.. (21)}$$

(ii) If temperature be kept constant, i.e. the process is isothermal,

$$\left(\frac{\partial A}{\partial T}\right)_T = -P \quad \text{.. (22)}$$

A change in a system at constant temperature and volume would be spontaneous if $(\partial A)_{T,V} = 0$ and the condition for spontaneity will be $(\partial A)T,V < 0$. A system moves spontaneously towords states of lower A if a path is available. Equilibrium would mean if that neither the forward nor the reverse process has a tendency to occur.

Significant of A lies in the fact that it points at a criterion of spontaneity (equilibrium); but besides and rather above that ; the change in the Helmholtz free energy is equal to the maximum work accompanying a process.

Thus $dW_{max} = dA$ .... (23)

That is why A is called the 'maximum work function' or the 'Work function' and G is often called simply 'free energy'.

For a microscopic is otherhand change (23) is written as $W_{max} = \Delta A$.

1.3 Gibbs-Helmholtz equation

Gibbs-Helmholtz equations aim at expressing the variation of free energies (Gibbs and Helmholtz) with temperature.

We have known,

$$\left(\frac{\partial A}{\partial T}\right)_V = -S, \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

And, $A = V - TS$, $G = H - TS$

From there we can easily have,

$$A = U + T\left(\frac{\partial A}{\partial T}\right)_V \quad \text{... (23)}$$

$$\text{and } G = H + T\left(\frac{\partial G}{\partial T}\right)_P \quad \text{.. (24)}$$

These couple of equations are known as Gibbs-Helmholtz equations.

Reavtraging these we get,

$\left(\frac{\partial A}{\partial T}\right)_V = \frac{A-U}{T}$ and $\left(\frac{\partial G}{\partial T}\right)_P = \frac{G-T}{T}$ .... (25, 26)

These are also useful forms of Gibbs-Helmholtz equations.

Gibbs-Helmholtz equations may be represented in other forms too. These are shown below—

As sometimes it becomes important to know the dependence of the function G/T on temperature.

We have known $\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{1}{T^2}G$ .... (27)

Using the equation $\left(\frac{\partial G}{\partial T}\right)_P = -S$, (27) becomes

$\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{G+TS}{T^2}$ .... (28)

or, $\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2}$ .... (29)

Very similarly we can have, $\left(\frac{\partial(A/T)}{\partial T}\right)_V = -\frac{U}{T^2}$ .... (30)

Since d(1/T) = $\frac{1}{T^2}$ dT or, (29) can be written as

$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P = H$ .... (31)

and very similarly $\left(\frac{\partial(A/T)}{\partial(\perp/T)}\right)_V = U$ .... (32)

There are still another set of Gibbs-Helmholtz equation

Let us now have a further set

In an isothermal change, $G_1 = H_1 - TS_1$

$G_2 = H_2 - TS_2$

(Subtracting) $\Delta G = \Delta H - T\Delta S$ .... (33)

But, $\Delta S = S_\perp - S_2 = \left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right] = -\left[\frac{\partial \Delta G}{\partial T}\right]_P$ .... (34)

From (33) and (34), $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$ .... (35)

or, $\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = \frac{\Delta G - \Delta H}{T}$ .... (36)

Very similarly, $\left(\frac{\partial(\Delta A)}{\partial T}\right)_P = \frac{\Delta A - \Delta U}{T}$ .... (37)

1.4 Application of energetics in the field of biology

Energy is an essential part in biological system as well as in environment. The behaviour of energy in ecosystem can be termed as energy flow due to unidirectional flow of energy. From energitics point of view it is essential to understand for an ecosystem—

(i) efficiency of absorption and conversion of solar energy by the producers, i.e. the Green plants.
(ii) use of the converted chemical from of energy by the consumers.
(iii) total input of energy in the form of food and its efficiency of assimilation.
(iv) loss of energy via respiration, excretion and heat.
(v) the gross net production.

In ecological energetics, we study—

(a) quantity of solar energy reaching an ecosystem :

A fraction, i.e., about 1/50 millionth of the total solar radiation reaches the earth's atmosphere. About 34% of the sunlight is reflected back in the atmosphere, 10% is held by ozone layer, water vapour and other atmospheric gases. The rest 56% reaches the earth's surface.

(b) Quantity of energy used by green plants : 1 to 5% of this energy, i.e. 56% of the total energy is used by green plants for photosynthesis and the rest is absorbed as heat by ground vegetation or water. However, only about 0.02% of the sunlight is used in photosynthesis.

(c) Quantity of energy flow from producers to consumers : There is a successive reduction in energy flow at successive trophic levels, i.e. from producers to consumers. As for example, in a freshwater ecosystem the total solar radiation was 118, 872 g cal/cm^2/yr became 3.0 g cal/cm^2/yr in carnivore level through producer (111·0 g cal/cm^2/yr) and herbivores (15.0 g cal/cm^2/yr) level (Lindeman, 1942).

1.5 Standard state as applied to biochemistry

In biochemistry the hydrogen ion concentration [H$^+$] at the standard state is taken to be ~10^{7}M (pH=7) because of the physiological condition to be like this.

So for a process $A+B \rightarrow C+xH^+$, ... (37)

$$\Delta G = \Delta G^{o} + RT\ln \frac{[C]_{IM}\ [H^{+}]_{10^{-7}M}}{[A]_{IM}\,[B]_{IM}} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (38)$$

and for $C + xH^{+} \rightarrow A+B$ ………………………………………………… (39)

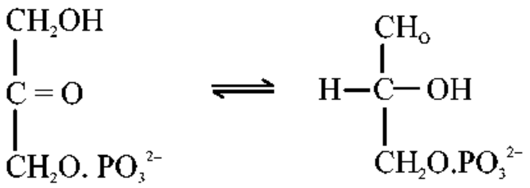
$$\Delta G = \Delta G^{o} + RT\ln \frac{[A]_{IM}\ [B]_{IM}}{[C]_{IM}\ [M^{+}]_{10^{-7}M}} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (40)$$

For (38) $\Delta G = \Delta G^{o} + 40.0$ kJ

and for (40) $\Delta G\ \ \Delta G^{o} - 40.0$kJ

Thus reaction (37) will be more spontaneous at pH 7 that at pH O and reverse will be in case of (39). For reactions not involving H^{+}, $\Delta G = \Delta G^{o}$.

Let us consider the particular reaction :



$$\begin{array}{c} CH_2OH \\ | \\ C=O \\ | \\ CH_2O.\ PO_3^{2-} \end{array} \rightleftharpoons \begin{array}{c} CH_O \\ | \\ H-C-OH \\ | \\ CH_2O.PO_3^{2-} \end{array} \ \ldots\ldots\ldots\ldots\ldots\ldots (X)$$

dihydroxyacetone phosphate (DHAP)   glyceraldehyde 3-phosphate (G-3-P)

At equilibrium at 298K and $[H^{+}] = 10^{-7}$ M, it is find that

$$\frac{[G-3-P]}{[DHAP]} = 0.0475$$

$K'_{eq} = 0.0475$

As $\Delta G = \Delta G^{o} + RT\ln K'eqn$, and system involves x_oH^{+},

$\Delta G^{o} = -RT\ln K'eqn = -2.303 \times 1.98 \times 10^{-3} \times 298 \times \log 0.0475$

$= +1.8$ kCal $mole^{-1}$.

If now, $[DHAP] = 2\times10^{-4}$ M and $[G\text{-}3\text{-}P] = 3\times10^{-6}$ M

$$\text{then } \Delta G = \Delta G^{o} + RT\ln \frac{3\times10^{-6}}{2\times10^{-4}}$$

$$= 1{\cdot}8 + 2{\cdot}303 \times 1{\cdot}98 \times 298 \log (1.5\times10^{-2})$$

$$= -0.7 \text{kCal mol}^{-1} = -2.93 \text{KJmol}^{-1}$$

Implication of negative ΔG is that the reaction (X) can take place spontaneously at the condition specified. Depending on conditions it may be positive also.

It has been found that hydrolysis of esters ($\Delta G^{o} = -13{\cdot}807$ KJmol^{-1}), hydrolysis of amides ($\Delta G^{o} = -14.225$ kJ mol^{-1}), hydrolysis of glycerides ($\Delta G^{o}{-}9{\cdot}205$ kJmol^{-1})

takes place with lent small standard free energy change. On the other hand hydrolysis of anhydrides occure with relatively large standard free energy.

1.6 Questions

1. For a reaction at 127°C, $\Delta G = -12$KCal and $\Delta H = 17{\cdot}5$ KCal Find ΔS.
2. Explain clearly the difference between mechanical and non-mechanical work.
3. Suppose 3.0 mol of $N_2(g)$ expands for 36 Cm^3 to 60 Cm^3 at 300k. What would be the ΔG for the process.
4. At constant pressure $\Delta G/J = -85{\cdot}40 + 36{\cdot}5\ (T/K)$. Calculate ΔS.
5. Prove :

$$\left(\frac{\partial H}{\partial V}\right)_T = -V^2\left(\frac{\partial \delta}{\partial T}\right)\left(\frac{\partial (T/V)}{\partial V}\right)_P$$

1.7 Answers

2. $\Delta S = 73.75$ eu
3. 3.8J
4. $-36.5 JK^{-1}$

UNIT 2 ❑ Chemical Thermodynamics

Structure

2.1 Thermodynamics

Thermodynamics is a branch of science that deals with the changes due to various physical and chemical transformations and it establishes the relationship between heat, work and temperature by some laws.

The word thermodynamics is derived from Greek word "Thermos" means "heat" and "dynamics" means "motion or flow".

There are many forms of energy, i.e. mechanical energy, electrical energy, chemical energy, kinetic energy, potential energy etc. Heat is a form of energy. The various forms of energy are interconvertible and these interconversions are governed by the thermodynamics laws. We can make some predictions about the transformation and energy changes by studying the thermodynamics.

2.2 Thermodynamic Terminology

Before describing the thermodynamics laws we are going to define some terms used in thermodynamics.

(i) System **:** Any part of universe separated by a real or imaginary boundary from universe is known as system in thermodynamics, for example, gas contained in a closed cylinder or vessel, a reaction vessel, a heat engine, electrical cell, cells of plant and animal etc.

The partition, which seperates a system from its surroundings and permits energy to pass through it, is known as diathermic partition and which does not permit energy to pass through is known as adiabatic partition.

(ii) Surroundings **:** The rest of universe outside the system separated by bounderies is known as surroundings usually, we measure various aspects of systems from its surroundings. These boundaries may be real, imaginary or movable.

(iii) Types of System **:** There are different types of system, for example,

(a) Homogeneous system : A system having identical physical, chemical properties and composition is known as homogeneous system. A gas in a closed vessel is a homogeneous system. A homogeneous system is a single phase system.

(b) Heterogeneous system : A system having two or more phases separated by mechanical boundaries is known as heterogeneous system, for example, a system containing solid, liquid; liquid, gas or solid, liquid and gas.

(c) Open system : A system which can exchange both matter and energy through its boundaries to the surroundings is known as open system. An open vessel containing water can exchange both matter and energy to its surroundings. All living matters are the examples of an open system because they can exchange both matter and energy to their surroundings.

(d) Closed system : A closed system can exchange only energy in the form of heat or work and not the matter to its surroundings. There is no change in the mass of a closed system, but there may be a rise or fall of temperature in the system due to exchange of energy. A heat permeable sealed system is an example of closed system.

(e) Isolated system : An isolated system cannot exchange matter or energy to its surroundings The total quantities of matter and energy remain same in an isolated system.

(iv) Intensive property : A property that does not depend upon the amount of matters of a system is known as intensive property, for example, temperature, pressure, density, refractive index, concentration, viscosity, surface tension, specific heat etc.

(v) Extensive property : A property that depends on the amount of matter(s) of a system is known as extensive property of system, for example, volume, energy, internal energy, enthalpy, entropy etc.

(vi) State functions of a system : A thermodynamic system is sufficiently large so that we can measure its various properties like volume, pressure, temperature and amount of material, composition and density etc. These properties are known as thermodynamic functions or variables which depend on the initial and final states of a system and do not depend on their past history. The change of any state variable does not depend also on the path in which this change takes place. Heat and work are not state variables since their changes depend on path.

A state variable which depends on other variables is known as a dependent variable and other variables are known as independent variables. The state of a system is defined when state variables have definite values. But this does not mean that values of all the variable should be known. Since they are interdependent, for example, we can write the ideal gas equation $P = \frac{nRT}{V}$, where P is dependent variable, but n, T and V are independent variables, since R is a constant.

(vii) Thermodynamic processes : The processes which are used to change the state of a system are known as thermodynamic processes, for example,

(a) Isothermal process : The temperature of a system remains constant in an isothermal process by exchanging the energy (heat) with its surroundings which in this case is a thermostat. So the temperature difference of initial and final states of system will be zero ($dT = 0$). The melting and boiling of a substance are the examples of isothermal processes.

(b) Adiabatic process : No heat is allowed to enter or leave the system during an adiabatic process. In an adiabatic process a system is thermally insulated from its surroundings. Energy involved or absorbed during an adiabatic process will remain within the system, thereby increasing or decreasing the temperature of system. But the change of heat ($dq = 0$) will be zero.

(c) Isochoric process : In an isochoric process the volume of a system remains constant ($dV = 0$). So a chemical process in a sealed container of constant volume is an example of isochoric process.

(d) Isobaric process : In an isobaric process the pressure of a system remains constant ($dP = 0$). Boiling of a substance in an open vessel is an example of isobaric process, since it occurs always at atmospheric pressure which is supposed to be unchanged during the process.

(e) Cyclic process : The process in which a system after performing a number of intermediate changes returns to its initial or original state, then that process is known as cyclic process. In a cyclic process the change in internal energy of the system is zero i.e. $dU = 0$ and also $dH = 0$, where dH = change in enthalpy.

(f) Reversible process : Reversible process is an ideal thermodynamic process in which the direction of the process can be reversed by the infinitesimal change of the external conditions like temperature and pressure of the system.

Let us consider that a gas at a pressure P is kept in a cylinder fitted with a airtight piston. When the pressure (P) of the gas is equal to the external pressure, the piston remains stationary. But on minute increasing in the external pressure (dP) the volume of gas can be decreased minutely. Similarly on decreasing the external pressure by dP the volume of the gas can be increased minutely.

So the direction of reversible process can be changed with minute change in the magnitude of the driving force.

(g) Irreversible process : Any process which is not reversible is known as irreversible process. All natural processes are irreversible. Irreversible process is also known as spontaneous process. Water flows from higher altitude to lower attitude and it is a natural process. Hence it is an irreversible or spontaneous process.

Therefore, a spontaneity refers to the tendency of a change or a chemical change to take place on its own way. A spontaneous process may be very fast or slow. Therefore it has no rrelation with the rate of change. A common salt dissolves in water spontaneously. Metallic zinc reacts spontaneously with the dilute HCl. An acid reacts spontaneously with alkali to produce salt. The reverse of any spontaneous process is never spontaneous and it is always non-spontaneous, for example, water cannot flow spontaneously from lower altitude to higher altitude, or an acid and alkali cannot be obtained spontaneously from the aqueous salt solution. A non-spontaneous process may be brought about by some external agency or by application of thermal or electrical energy, for example, water can be lifted from lower altitude to higher altitude with the help of a pump. Aqueous solution of a salt can be separated by heating the solution. Metallic sodium reacts spontaneously with chlorine gas to give NaCl. Metallic sodium and Cl_2 gas can be obtained by the electrolysis of a molten NaCl and it is a non-spontaneous process. The rate of a spontaneous process may be increased by application of heat or a catalyst. Oxidation of glucose into CO_2 and H_2O is a extremely slow spontaneous process unless it is heated to a suitable temperature or it is oxidized in presence of biological catalyst.

(h) Thermodynamic Equilibrium : A system is in thermodynamic equilibrium when its all state variables remain same throughout the system. A gas is said to be in thermodynamic equalibrium when it is kept in a cylinder fitted with a weightless and frictionless piston to make its state variables, such as the volume, pressure and temperature remain to the same.

(i) Thermodynamic non-equilibrium : A system which is not in thermodynamic equilibrium is known as thermodynamic non-equilibrium, i.e. its state variables are not same throughout the system.

Work, Energy and Heat : Work (W) is a fundamental physical property in thermodynamics and is defined as the product of force (F) applied on a body and the displacement (l) of that body along the direction of force.

$$W = F \times l \qquad \dots (1.1)$$

Work can be done in various ways due to the different physical origin of the force. Work is not a state function because if depends on path. If work is done on the system then its value is positive and if work is done by the system then its value is negative.

(i) Pressure volume work : The expansion or compression of a gas against an external pressure is an example of pressure volume work because it can push up or down the piston.

$$W = P \times A \times dl \qquad \dots (1.2)$$

$$= P \times dV \qquad \dots (1.3)$$

where P = pressure of gas

A = area of piston

dl = Difference in length

Because $A \times dl = dV$ (Difference in volume)

This type of mechanical work is performed when a system changes its volume against an opposing pressure (external pressure).

2.2.1 Energy :

The energy of a system is the capacity of doing work. When work is done on a system its capacity of doing work is increased and when work is done by a system then its capacity of doing work is decreased. Thus compressing a gas against a pressure increases its energy and expansion of a gas decreases its energy. There are various forms of energy, for example, heat energy, kinetic energy, potential energy, electrical energy, light energy, sound energy etc. One form of energy can be converted into other form and a material body is required for this transformation. The unit of energy in SI system is joule (J).

2.2.2 Heat :

Heat is a form of energy. The energy of a system can be changed by means of many methods other than work itself. The energy of a system can be transferred due to difference of temperature between a system and its surroundings in the form of heat. When a hot body is immersed into in a vessel containing water at normal temperature (system) the temperature of water is increased due to transfer of heat from the hot body to water. Therefore capacity of doing work of the system is increased. All boundaries between system and its surroundings may or may not allow the energy to transfer. A boundary which allows the energy to transfer is known as diathermic, for example, metal or glass. A boundary that does not allow the energy to transfer is known as adiabatic.

A process in which energy is released is known exothermic process and a process in which energy is absorbed is known as endothermic process. All combustion reaction are exothermic. The evaporation of any liquid is an example of endothermic process. In an exothermic process heat is allowed to pass through the diathermic boundary to its surrounding and thereby increase the temperature of the surroundings. Similarly in an endothermic process heat is allowed to transfer from the surroundings to the system through the diathermic boundary. The heat evolved (or absorbed) within a system having a adiabatic container will increase (or decrease) the temperature of the system.

2.2.3 Internal energy :

The internal energy of a system is the total energy of its constituent atoms or molecules including all forms of kinetic energy and also energy due to every type of interactions between molecules and their subparticles. Internal energy is a state variable and its absolute value cannot be determined. But the difference of internal energy (ΔU) of a system can be determined. The difference of internal energy depends only on the initial and final states of system and is independent of the path to which this change takes place.

2.3 The first law of thermodynamics

Law of conservation of energy is the first law of thermodynamics. It can be stated in a number of ways.

(i) Energy cannot be created or destroyed, although one form of energy can be changed into other form.

(ii) The energy of an isolated system remains constant.

(iii) It is impossible to construct a perpetual motion machine which can work endlessly without the expenditure of energy. (Such a motion machine which requires no energy for its functions is known as perpetual motion machine)

The first law of thermodynamics can be expressed mathematically by the following equations—

$$q = \Delta U + W \qquad \ldots (1.4)$$

or, $\Delta U = q - W$

or, $W = q - \Delta U$

where ΔU = change in the internal energy,

q = amount of energy

W = work done.

That is if q quantity of heat is supplied to a system than a part of this heat is used to increase the internal energy of the system and remaining part of the heat is used to perform work by the system on the surroundings.

The total work done by the system when the volume of gas V_i to V_f is calculated by integrating the above equation (1.4)

$$W = -\int_{V_i}^{V_f} P_{\text{Ext}} dV$$

But this is a general expression for calculating pressure, volume and work both in isothermal and adiabatic process. The value of work is negative if the gas expands and positive if the gas contracts, therefore in expansion dV is positive and in contration dV is negative.

2.3.1 Work done in Isothermal Irreversible Process

Let us suppose that the external pressure is constant through out the expansion at constant temperature isothermally and irreversibly. Let the initial and final volumes of gas be V_i and V_f respectively. Then the total work done on the system is obtained by integrating the equation—

$$W = -\int_{V_i}^{V_f} P_{\text{Ext}} dV$$

$$= -P_{\text{Ext}} \times (V_f - V_i)$$

$$= -P_{\text{Ext}} \times \Delta V$$

where ΔV = Volume change during the process.

and P_{Ext} = External pressurs

2.3.2 Work done in Isothermal Reversible Process :

In thermodynamics, a process that can be reversed by either direction by infinitesimal change of a variable is known as reversible process.

Suppose a gas is enclosed in a cylinder fitted with a frictionless piston. The pressure of the gas is P and the external pressure on piston is P_{Ext}. In reversible expansion P_{Ext} is equal to P at each step of expansion. So the equation

$dW = -P_{\text{Ext}} dV$ can be written as

$$dW = -PdV \qquad \dots (1.5)$$

So the total work done is by expansion of gas isothermally and reversibly from V_1 to V_2

$$W = -\int_{V_1}^{V_2} PdV$$

If the gas behaves ideally, them we can write

$$P = \frac{nRT}{V}$$

$$W = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$= -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= -nRT \ln \frac{V_2}{V_1} = -2.303\ nRT \log \frac{V_2}{V_1}$$

$$= 2.303\ nRT \log \frac{V_1}{V_2} \qquad \dots (1.6)$$

If $V_2 < V_1$, then the gas is compressed and W is positive, i.e. work is done on the system.

If $V_2 > V_1$, the gas undergoes expansion and W is negative, i.e. work is done by the system.

Again in isothermal condition

$$P_1V_1 = P_2V_2$$

or $$\frac{V_1}{V_2} = \frac{P_2}{P_1}$$

Putting the value of $\frac{V_1}{V_2}$ in the equation (1.6) we can write

$$W = 2.303\ nRT \log\frac{P_2}{P_1} = -\ 2.303\ nRT \log\frac{P_1}{P_2}$$

2.3.3 Some special cases of the first law of thermodynamics

(i) Free expansion of a gas : Expansion of a gas against zero pressure or expansion of a gas in vacuum is known as free expansion. The work done (dW) in free expansion is zero, because $P = 0$

$\therefore\ dW = PdV = 0.$

and total work (W) is also zero.

(ii) For a process in which there is no volume change of the system, i.e. in a isochoric process no work is done. So $W = 0$.

$\therefore\ \Delta U = q_v$

So in isochoric process heat supplied to a system will solely increase its internal energy.

(iii) For isothermal reversible process the change in internal energy is zero, i.e. $dU = 0$.

$$\therefore\ q = -\ W = -\ 2.303\ nRT \log\frac{V_2}{V_1}$$

(iv) For adiabatic process $q = 0$, i.e. the system is well insulated and the system does not gain or lose energy.

So $\quad \Delta U = -W_q$

Therefore work done by the system is exactly equal to the loss of its internal energy.

2.3.4 Enthalpy

Enthalpy H is a very useful thermodynamic function which can be expressed by the following equation,

$$H = U + PV \qquad \text{... (1.7)}$$

where U, P, V are the internal energy, pressure and volume respectively. Since U, P and V are the state variables, therefore H is also a state variable. So the change in enthalpy (ΔH) depends on initial and final states of system and does not depend on path to which this change takes place. So the ΔH can be given by,

$$\Delta H = H_2 - H_1 \qquad \dots (1.8)$$

where H_1 = Initial enthalpy, H_2 = final enthalpy of the system.

$$= (U_2 + P_2V_2) - (U_1 + P_1V_1) \qquad \dots (1.9)$$

$$= (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$= \Delta U + P(V_2 - V_1) \qquad \text{At constant pressure } P_1 = P_2 = P.$$

$$(\Delta H)_p = \Delta U + P\Delta V \qquad \dots (1.10)$$

$$q_p = \Delta U + P\Delta V \qquad \dots (1.11)$$

$$\therefore\ \Delta H_p = q_p$$

Therefore heat supplied to a system at constant pressure q_p is equal to the change in the internal energy plus pressure-volume work done by the system to the surroundings.

2.3.5 Limitations of the first law of Thermodynamics

(i) From the first law of thermodynamics we know that during a process one form of energy can be converted into other form, although the total energy remains unchanged. Or we can say that during a process if there is an increase in energy of a system then same amount of energy will disappear from the surroundings and vice versa. But the first law neither tells us about the direction of flow of energy nor the spontaneity of the process, i.e. feasibility of the process.

(ii) By first law of thermodynamics, it is not impossible to transfer heat from colder body to a hotter body without the help of a machine, i.e. it is not impossible to boil water by abstracting heat from ice. But it is our common experience that heat always flows from hotter body to a colder body spontaneously. Similarly water flows from higher level to lower level spontaneously and electricity flows from higher potential region to lower potential region.

The direction of change in any process that does not require any work is spontaneous. All spontaneous processes are irreversible and unidirectional. But we can compressed a certain volume of gas into smaller volume. Water or any body can be cooled into a refrigerator or we can force a reaction into opposite direction, for example, electrolysis of water or any electrolyte. In all changes mentioned above require work to bring about the changes. So these are the examples of non-spontaneous processes.

2.4 The second law of thermodynamics

In order to remove the limitations of first law of thermodynamics, the second law was proposed. The second law can be stated in a number of ways.

(i) "All spontaneous process in nature are thermodynamically irreversible."
(ii) It is impossible to convert heat into equivalent amount of work without producing some change elsewhere.
(iii) Heat can not be transferred to a hotter body from a colder body without the help of a machine.
(iv) The heat which is evolved by cooling a system or its parts from the surroundings with the help of an engine cannot be converted into work.
(v) It is impossible to take heat from a hot reserve and convert it completely into work by a cyclic process without transforming a part of heat into sink at lower temperature.
(vi) Entropy of universe continuously increases by every spontaneous process.

2.4.1 Characteristics of a spontaneous process

(i) All spontaneous processes are unidirectional and work must be done to reverse the direction of a spontaneous process.
(ii) A spontaneous process may be slow or fast.
(iii) A spontaneous change is inevitable if the system is not in an equilibrium state and this change takes place until it comes to in equilibrium.
(iv) Once a system attains equilibrium no further spontaneous change will take place.
(v) Entropy of a system will increase by a spontaneous process and more the entropy of a system more is the disorder of the system.

2.5 Entropy

From Cannot cycle we know that the efficiency of any engine cannot be 100%. So a thermodynamic function is required to describe the amount of energy obtained for performing the permissible work. This function is known as entropy (S). Entropy is also a state variable (function) like internal energy and enthalpy. The more the amount of entropy of a system, the less is the amount of work obtained from it. Entropy is also a measure of disorder of a system and the more the disorder of a system the more is the entropy of the system. So that an ordered system has less entropy. *During a spontaneous change the entropy of an isolated system increases.* This is also a statement of second law of thermodynamics.

The change of entropy of a system depends only on the initial and final states of the system and does not depend on the path. So the change of entropy can be expressed as—

$$\Delta S = S_{\text{final}} - S_{\text{initial}} \qquad \dots (1.12)$$

Again an infinitesimal change of entropy can be described as,

$$dS = \frac{dq_r}{T} \qquad \dots (1.13)$$

where dq_r is the infinitesimal quantity of energy absorbed under reversible manner at the temperature T (Absolute) by any process. Equation (1.13) is the mathematical definition of the entropy. For a measurable change of entropy between initial (1) and final (2) state can be calculated by integrating the expression—

$$\Delta S = \int_1^2 \frac{dq_r}{T} \qquad \dots (1.14)$$

In equation (1.14) dq_r and T are expressed as joule and kelvin respectively. So the SI unit of entropy is expressed as joule per kelvin (JK^{-1}). For molar entropy, the entropy is divided by molar amount. i.e. joule per kelvin per mole ($JK^{-1}mol^{-1}$).

In cgs sustem the unit of entropy is calories (or ergs) per kelvin per mole [cal(or egr) $K^{-1}mol^{-1}$].

2.5.1 Characteristics of entropy

(i) Entropy is an extensive property, i.e. it depends on the amount of substance.

(ii) Entropy is a state function.

(iii) Change of entropy is independent of path.

(iv) Change of entropy in a cyclic process is zero.

(v) ΔS should be positive, (i.e. $\Delta S > 0$) in a spontaneous process in an isolated system.

(vi) Total change of entropy ΔS of a non-isolated system is given by

$$\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

(vii) In any reversible process change of entropy is zero, i.e. $\Delta S = 0$.

$$\therefore \ \Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

(viii) In any spontaneous process, the entropy of universe increases.

$$\Delta S_{\text{univ}} > 0.$$

Now there is no easy way to determine the entropy change of surroundings or universe. So nothing can be predicted about the driving force of a process or a reaction. To remove this difficulty Gibbs introduced a new thermodynamic function which is known as Gibbs free energy (G).

2.6 The third law of thermodynamics

At absolute zero there is no thermal motion of a substance and if in a crystal the atoms or ions are in a highly regular arrangement, so that there is no disorder, then such crystalline substance have zero entropy. This is known as third law of thermodynamics which can be stated that the entropy of all pure crystalline substances may be zero at absolute zero. Or in other words during a physical or chemical transformation the change of entropy tends to zero as the temperature tends to absolute zero. This is also known as **Nernst heat theorem.**

2.7 Gibbs free energy

The spontaneity of any reaction or process cannot be predicted by enthalpy (H) or entropy (S) of a system. For this reason Gibbs free energy was introduced.

The maximum amount of energy available for doing useful work for a process (even reversibly) of a system is known as Gibbs free energy. Gibbs free energy determines the ability of a system for doing useful work. A part of the total work done by a system may be used to perform the pressure volume work of the system. So the amount of energy necessary for the pressure volume is not available for doing the useful work.

$\therefore$ Net useful work = Work done – Pressure volume work.

$\therefore$ At constant pressure and temperature network

$$= W_{\max} - P(V_2 - V_1) = W_{\max} - P\Delta V$$

where change in volume $\Delta V = V_2 - V_1$.

This can be precisely expressed by the following equation,

$$G = H - TS \qquad ...(1.15)$$

where G = Gibbs free energy, H = enthalpy of the system, T = absolute temperature and S = entropy of the system.

The change in Gibbs free energy ΔG is more important than G itself in a chemical reaction or a process. So the change in free energy between two states of a system can be expressed by

$$G_2 - G_1 = (H_2 - T_2S_2) - (H_1 - T_1S_1)$$

or $$\Delta G = (H_2 - H_1) - (T_2S_2 - T_1S_1)$$

At constant temperature

$\Delta G = \Delta H - T(S_2 - S_1) = \Delta H - T\Delta S$ ...(1.16)

This equation is known as Gibbs Helmholtz equation.

(i) The process is spontaneous if ΔG is negative.

(ii) The process is in equilibrium if $\Delta G = 0$.
At equilibrium the concentration of each spacies of both reactants and products will remain constant. There is no net reaction on either direction.

(iii) If ΔG is positive, the process is non-spontaneous. So the process cannot take place in the forward direction. It may take place in the reverse direction.

(iv) If ΔH is negative and ΔS is positive then ΔG is negative. So the reaction is spontaneous at any temperature.

(vi) If ΔH is positve and ΔS is negative, the ΔG is positive at any temperature than the reaction is non-spontaneous at any temperature.

(vii) If ΔH is negative and ΔS is negative then the reaction is spontaneous only at low temperature i.e ΔG is negative. But ΔG is positive at high temperature in this case . So in that case reaction is non-spontaneous.

(viii) If ΔH is positive and ΔS is positive then ΔG is negative at high temperature. So the reactions is spontaneous at high temperature. But in this case ΔG is positive at low temperature. So in that case the reaction is non-spontaneous.

2.7.1 Gibbs free energy change and the spontaneity of a process

We know that,

$G = H - TS$ and $H = U + PV$

$\therefore\ G = U + PV - TS.$

or, $dG = dU + PdV + VdP - TdS - SdT.$

or $dG = dq + dW + PdV + VdP - TdS - SdT$ (since $dU = dq + dW$) for very small change

This equation is true for both reversible and irreversible processes.

Now for reversible process $dq_{rev} = TdS$ and any process occurring in an isolated system the $dq \leq TdS$.

$\therefore\ dG - dW - PdV - VdP + TdS + SdT \leq dq$

or, $dG - dW - PdV - VdP + TdS + SdT \leq TdS$

or, $dG - dW - PdV - VdP + SdT \leq 0$

If only pressure volume work is done by the system, then $-dW = PdV$

$\therefore\ dG + PdV - PdV - VdP + SdT \leq 0$

or, $dG - VdP + SdT \leq 0$

Now at constant pressure and temperature

$(dG)_{P,T} \leq 0$ or, $(\partial G)_{P,T} \leq 0$.

For any reversible process in equilibrium at constant pressure and temperature $(\partial G)_{P,T} = 0$. But for any irreversible process at constant pressure and temperature $(\partial G)_{P,T} < 0$. So for spontaneous process the value of $(\partial G)_{P,T}$ should be negative.

2.7.2 Standard free energy change in a chemical reaction

In order to establish a relation between free energy change in a chemical reaction and the equilibrium constant of a reaction, let us take the following reaction—

$$\underset{\text{Rectants}}{aA + bB} \rightleftharpoons \underset{\text{Products}}{cC + dD}$$

In this reaction a moles of A reacts with b moles of B to give c moles of C and d moles of D reversibly. Then the free energy change of this reaction at constant temperature is given by,

$$\Delta G = \Delta G^\circ + RT \text{ In } \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \qquad ...(1.17)$$

where ΔG = free energy change of the reaction,

ΔG° = standard free energy change and

R = gas constant and T = temperature in kelvin

The standard free energy of a reaction is a constant term at a given temperature. But ΔG varies with concentrations of both reactants and products at constant temperature. So we can calculate the free energy change of a reaction at a given temperature provided we know the value of ΔG°. At equilibrium $\Delta G = 0$ at a given temperature.

$$\therefore\ O = \Delta G^\circ + RT \text{ In } \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

$$\Delta G^\circ = -RT \text{ In} \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} = -2.303\ RT \log K_{eq} \qquad ...(1.18)$$

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \qquad \text{where } K_{eq} = \text{equilibrium constant}$$

where $[A]$, $[B]$, $[C]$ and $[D]$ represent the molar concentration of A, B, C and D respectively.

But when the concentration of each reactant and product is one mole per litre then in the equation (1.17) the second term is equal to zero ($\log 1 = 0$)

$$\therefore \Delta G = \Delta G^\circ \qquad \text{...(1.19)}$$

At equilibrium the value of ΔG°_{298K} (at 298K or 25°C) is given by

$$\Delta G^\circ_{298K} = -2.303 \times 8.314 \text{J.K}^{-1}\text{mol}^{-1} \times 298 \text{ K} \log K_{eq}$$

$$= -5705.85 \log K_{eq} \text{ J mol}^{-1} \ (\text{R} = 8.314 \text{JK}^{-1}\text{mol}^{-1})$$

$$= -5.706 \log K_{eq} \text{ kJmol}^{-1}$$

$$= -5.706 \times 4.18 \log K_{eq} \text{ kcal mol}^{-1} \ (1 \text{ Joule} = 4.18 \text{ calorie})$$

So at a given temperature ΔG° can be calculated provided we know the value of K_{eq}, when the value of $K_{eq} < 1$, then the value of $\Delta G^\circ > 0$, (i.e positive) and reaction have positive value of ΔG° is known as endergonic, when $K_{eq} > 1$ negative value of ΔG° is known as exergonic.

Now when the reaction is in equilibrium and the value of K_{eq} is equal to 1 [which means that the concentration of each reactant and product is 1(M)], then ΔG° is also equal to zero.

The biochemical reactions in cells are generally occurred at pH 7.0 rather than at pH zero [i.e 1(M) H^+ ion concentration]. So necessary correction is done for the standard free energy change at pH 7. The standard free energy change at pH other than zero is expressed as $\Delta G^{\circ\prime}$. When a reaction in a cell does not depend on the H^+ ion concentration (i.e. on pH), $\Delta G^\circ = \Delta G^{\circ\prime}$ and in such reactions H^+ or OH^- ion is neither formed or utilized. If H^+ or OH^- ions at all form then those H^+ (or OH^-) ions must react with some other substance so that the concentration of H^+ (or OH^-) ions remains unaltered.

Relation between equilibrium constant (K'_{eq}) and standard free energy change at 293K (25°C), where K'_{eq} = equilibrium constant at pH other than zero

K'_{eq}	$\Delta G^{\circ\prime} = -2.303 \text{ RT} \log K'_{eq}$ In J mol^{-1}	In calorie mol^{-1}
0.01	115411.7	2730.0
0.1	5705.8	1365.0
1.0	0	0
10	– 5705.8	– 1365.0
100	– 11411.7	– 2730.0

Let us now calculate the standard free energy change of the following reversible reaction in presence of an enzyme phosphoglucose mutase at 25°C.

Glucose 1-phosphate $\rightleftharpoons$ Glucose 6-phosphate

If the initial concentration of glucose 1-phosphate is 0.02 (M) and at equilibrium the concentration of glucose 1-phosphate deceases to 0.001 (M) then concentrations of glucose 6-phosphate is therefore 0.019.

$$\therefore K'_{eq} = \frac{\text{Conc}^{n}\text{of glucose 6} - \text{phosphate}}{\text{Conc}^{n}\text{of glucose 1} - \text{phosphate}} = \frac{0.019}{0.001} = 19$$

$$\begin{aligned}\therefore \Delta G^{\circ\prime} &= -2.303 \text{ RT} \log K'_{eq} \\ &= -2.303 \times 8.314 \times 298 \times \log 19 \\ &= -7296.4 \text{ J mol}^{-1} = -7.296 \text{ kJ mol}^{-1} \\ &= -1.745 \text{ kcal mol}^{-1}\end{aligned}$$

In this relation H^+ ion is not formed or utilized. So this reaction is independent of pH hence $\Delta G^\circ = \Delta G^{\circ\prime}$. The value of ΔG° in this reaction is negative, so the convertion of glucose 1-phosphate with glucose 6-phosphate is an exergonic reaction and this reaction is spontaneous.

The standard free energy change (ΔG°) of any chemical reaction is given by the following equation—

$$\Delta G^\circ = \Sigma G^\circ_{\text{Products}} - \Sigma G^\circ_{\text{Reactants}}$$

where $\Sigma G^\circ_{\text{Products}}$ = sum of the free energies of all the products and $\Sigma G^\circ_{\text{Reactants}}$ = sum of the free energies of all the reactants.

This equation can be used to calculate the standard free energy change of the oxidation of dilute aqueous αD-glucose solution at 25°C and 7 pH.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

$$\begin{aligned}\Delta G^{\circ\prime} &= [6 \times \Delta G^{\circ\prime}_{CO_2} + 6\Delta G^{\circ\prime}_{H_2O}] - [\Delta G^{\circ\prime}_{C_6H_{12}O_6} + 6 \times \Delta G^{\circ\prime}_{O_2}] \\ &= [6 \times (-94.45) + 6 \times (-56.69)] - [-219.22 + 6 \times 0] \\ &= -906.84 + 219.22 \\ &= -687.62 \text{ kcal mol}^{-1}\end{aligned}$$

where value of $\Delta G^{\circ\prime}_{C_6H_{12}O_6} = -219.22$ kcal mol^{-1}

$\Delta G^{\circ\prime}_{O_2} = 0$ (because it is in the elemental form)

$\Delta G^{\circ\prime}_{CO_2} = -94.45$ kcal mol^{-1}

$\Delta G^{\circ\prime}_{H_2O} = -56.69$ kcal mol^{-1}

The oxidation of αD-glucose into CO_2 and H_2O is highly exergonic for very large negative value of $\Delta G^{\circ\prime}$. A very high negative value of $\Delta G^{\circ\prime}$ does not mean that the reaction will proceed very fast. That is it does not reflect any light on the rate of a reaction. The rate of oxidation reaction of glucose (or any other reaction) depends on temperature and also on catalyst present.

The rate of any chemical reaction depends on the number of molecules those possess energy of activation. These activated molecules form the intermediate activated complex (A*) in converting A into B by a chemical reaction. The average difference of energy between A* and A is known as activation energy and energy of A* is always greater than that of A.

Lower the activation energy greater is the rate of reaction. Now if the activation energy is very high the reaction will proceed very slowly or the reaction does not take place at all. The use of a catalyst or an enzyme in a reaction lowers down the activation energy, so that the reaction can proceed easily.

In a case of consecutive chemical reactions the total standard free energy change of all the reactions is equal to sum of the standard free energy change in each reaction, i.e. it is additive in nature. Let us take the following consecutive chemical reactions—

$$A \xrightarrow{\text{1st Step}} B \xrightarrow{\text{2nd Step}} C \xrightarrow{\text{3rd Step}} D$$

$$\therefore \Delta G^{\circ}_{\text{sum}} = \Delta G^{\circ}_{1} + \Delta G^{\circ}_{2} + \Delta G^{\circ}_{3}.$$

where $\Delta G^{\circ}_{\text{sum}}$ = Total standard free energy change for the above consecutive reactions from A to D and ΔG°_{1}, ΔG°_{2} and ΔG°_{3} are standard free energy changes of 1 step, 2nd step and 3rd step respectively.

The ATP on hydrolysis gives ADP and inorganic phosphate (p_i). In this hydrolysis reaction a large amount of free energy is released because ATP is a energy rich compound. ADP on further hydrolysis gives AMP and inorganic phosphate (p_i)

$$\text{ATP} + H_2O \rightleftharpoons \text{ADP} + p_i$$

In this hydrolysis reaction the equilibrium constant K'_{eq} at 7.0 pH can be calculated by the following equation provided we know the concentration

$$\Delta G^{\circ\prime} = -\,2.303 \text{ RT} \log K'_{eq}$$

of ATP and ADP and phosphate at the equilibrium. But at the practical point of view it is difficult to know when the equilibrium has been reached and what are the concentrations of reactants and products at the equilibrium.

The standard free energy charge ($\Delta G^{\circ\prime}_{\text{ATP}}$) of hydrolysis of ATP to ADP and p_i can be calculated by consecutive reactions very easily, where ATP reacts with glucose in presence of enzyme hexokinase to give ADP and glucose 6-phosphate.

$$\text{ATP} + \text{glucose} \rightleftharpoons \text{ADP} + \text{glucose 6-phosphate}$$

The K'_{eq_1} of this reaction can be determined by the concentration of ATP and ADP and glucose 6-phosphate at the equilibrium very easily and knowing the value of K'_{eq_1} of this reaction the value of $\Delta G^{\circ\prime}_{1}$ is found to be

$-16.72 kJmol^{-1}$ (-4 kcal mol^{-1}). The glucose 6-phosphate obtained by the previous reaction on further hydrolysis in presence of enzyme glucose 6-phosphatase gives glucose and phosphate (p_i).

Glucose 6-phosphate + $H_2O \rightleftharpoons$ glucose + phosphate

The standard free energy $\Delta G_2^{\circ\prime}$ of this reaction can be also calculated from the equilibrium constant K'_{eq_2} of this reaction and value of $\Delta G_2^{\circ\prime} = -13.8$ kJ mol^{-1} (-3.3 kcal mol^{-1}).

Therefore, the total standard free energy changes of these two consecutive reactions will give the actual standard free energy change of hydrolysis of ATP into ADP and phosphate.

$$\therefore \Delta G^{\circ\prime}_{ATP} = \Delta G_1^{\circ\prime} + \Delta G_2^{\circ\prime}$$

$$= -16.72 - 13.94 = -30.514 \text{ kJmol}^{-1}$$

$$(-7.3 \text{ kcal mol}^{-1})$$

This value of $\Delta G^{\circ\prime}_{ATP}$ can also be verified by other consecutive reactions.

2.8 Questions

1. State and explain the first law of thermodynamics. Express the first law mathematically.
2. Define the following terms—(i) system (ii) surroundings, (iii) homogeneous system (iv) heterogeneous system, (v) open system, (vi) closed system, (vii) isolated system, (viii) intensive property, (ix) extensive property, (x) thermodynamic property, (xi) isothermal process, (xii) adiabatic process, (xiii) isochoric process, (xiv) isobaric process, (xv) cyclic process, (xvi) reversible process, (xvii) irreversible process, (xviii) work, (xix) energy, (xx) heat, (xxi) internal energy, (xxii) thermodynamic equilibrium.
3. Deduce an expression for pressure volume work.
4. Express work done in isothermal reversible process mathematically.
5. What is the amount of work done due to the expansion of gas against zero pressure?
6. What is the amount of work done in an isochoric process?
7. What are the limitations of first law of thermodynamics.
8. What do mean by spontaneous process? Give some examples of spontaneous processes. What are the chracteristics of a spontaneous process?
9. State the second law of thermodynamics.
10. Define entropy. What are the characteristics of entropy?
11. State the third law of thermodynamics.
12. What is Gibbs free energy? Express it mathematically.
13. Deduce Gibbs Helmholtz equation.

14. Define the standard free energy of a chemical reaction.

15. Deduce the standard free energy change of the following chemical reaction
$aA + bB \rightleftharpoons cC + dD$

16. In a reversible isothermal process, the change in internal energy is—
(a) zero (b) positive (c) negative (d) none of the above.

17. From adiabatic process, which of the following is correct?
(a) $PdV = 0$ (b) $q = -W$ (c) $\Delta U = q$ (d) $q = 0$

18. What is the difference between ΔG° and $\Delta G^{\circ\prime}$. When $\Delta G^\circ = \Delta G^{\circ\prime}$? Calculate the value of $\Delta G^{\circ\prime}$ if the $K'_{eq} = 18$ at a temperature of 25°C.

UNIT 3 ❑ Chemical Bonds

Structure

3.1 Chemical bonds

3.1.1 Defintion :

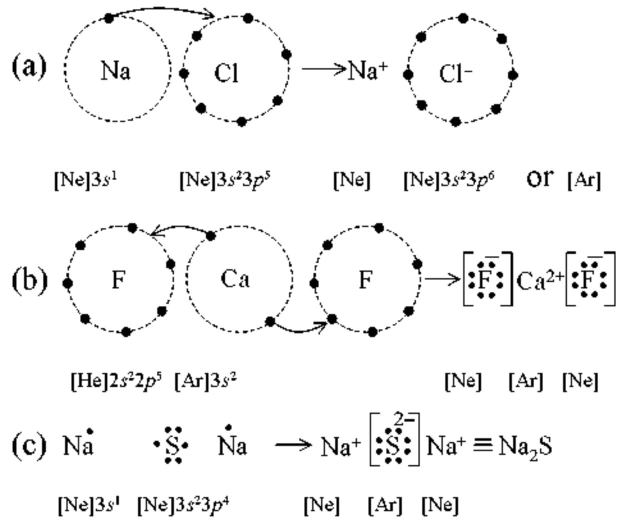
A chemical bond is a force which holds two atoms of element(s) together forming a linkage between the two atoms. The combining capacity of an atom is known as valency which is measured by number of hydrogen atoms combine with one atom of any element directly or indirectly.

3.1.2 Types of chemical bonds :

The formation of a chemical bond by combining two or more atoms (same or different) depends on many factors like number of electrons and protons present in the atom, atomic volume, electronegativity etc. Since atoms of different elements differ from one another in these respect, so different types of chemical bonds are formed during the combination of the atoms. Following are the types of chemical bonds—(i) Electorvalent bonds (ii) Covalent bond (iii) Co-ordinate covalent bond. During the formation of a bond each atom forming a bond tries to attend the stable electronic configuration by gaining, losing or sharing electrons from other atom.

3.1.3 Electrovalent bond or ionic bond :

Electrovalent bonds are formed by transfer of one or more electrons from the valence shell of one atom of an element to the valence shell of an atom of other element. During the transfer of electron(s), atom of each element attains the stable inert gas electronic configuration. The atom which loses electron(s) forms a cation and the atom which gains electron(s) forms an anion. The charge gained by cation or anion is equal to the number of electrons that an atom loses or gains respectively. Energy is released due to the electrostatic attraction force (coulombic force) between cation and anion. The compound thus formed has less energy than the individual atoms, so the stability of compound increases. This coulombic force is known as electrovalent bond or ionic bond.



(a) The position of sodium in the periodic table is in the IA (alkali metals) group. The atomic number of sodium is 11. So the electronic configuration of sodium is $1s^2 2s^2 2p^6 3s^1$ or $[Ne]3s^1$ and neon is the nearest inert gas to sodium. Again the atomic number of chlorine is 17 and the electronic configuration of chlorine is $1s^2 2s^2 2p^6 3s^2 3p^5$. Argon is the nearest inert gas to chlorine.

Sodium has only one electron in its valence shell and sodium can lose this valence electron very easily forming stable sodium cation (Na^+). The electronic configuration of Na^+ is $1s^2 2s^2 2p^6$ which is the electronic configuration of inert gas neon, on the other hand chlorine (which is a highly electonegative element) has 7 electrons in its valence shell. So chlorine atom by gaining one electron can attain the electronic configuration of argon with a negative charge on it (Cl^-). Thus Na^+ (cation) and Cl^- (anion) are held together by electrostatic force of attraction forming NaCl ionic compound.

3.1.3.1 Factors favouring electrovalent or ionic bond

(i) One of the element must be generally a metal having low ionization potential, so that it can lose electron easily. Greater the radius of the metal lower is the ionization potential.

(ii) Other element (non metal) must have high electron affinity, so that it can hold the extra electron(s). The size of the non-metal should be small in size.

(iii) The lattice energy which is the electrostatic attraction force between the oppositely charged ions should be high.

(iv) The electronic configurations of the cation and anion should be inert gas electronic configuration.

3.1.3.2 Characteristics of electrovalent or ionic compounds

(i) All ionic compounds are solid at room temperature.

(ii) Ionic compounds are formed by the cation and the anion, so no true molecule is formed and ionic bonds are non-directional.

(iii) Ionic compounds have high melting and boiling points, density and low volatility.

(iv) In solution or in molten condition ionic compound can conduct electricity.

(v) Ionic compounds are soluble in polar solvent or a solvent having high dielectric constant like H_2O and are insoluble in non-polar solvents like benzene, toluene, ether etc.

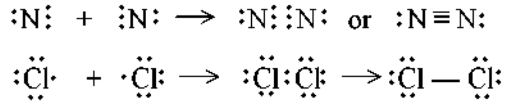
3.1.4 Covalent bond

There are many substances where molecular structures cannot be explained on the basis of electrovalent or ionic bond, for example, Cl_2, O_2, N_2, CH_4, etc. The molecular structures of these substances are explained on the basis of covalent bond.

The covalent bond is formed between two atoms (same or differant) having comparable electronegativity. In the formation of covalent bond between two atoms, each atom contributes same number of electron(s) and pair(s) of electrons thus formed is (are) shared equally between the two atoms to complete octet (or duet in the case H_2) in their outermost shells. The two atoms are held together by these shared pair(s) of electrons localized between them and a bond thus formed is known as covalent bond. A compound having covalent bond(s) is known as covalent compound. When each atom contributes one electron and pair thus formed is shared by both the atoms then a single covalent bond is formed. When 2 or 3 pairs are shared equally by the two atoms then double bond and triple bond are formed, for example,

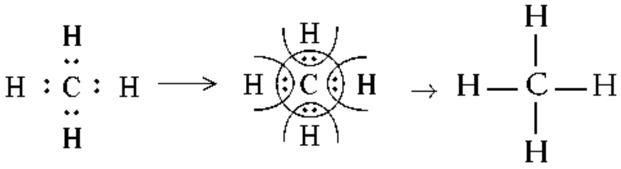
$$H\cdot\ \cdot H \rightarrow H : H \quad \text{or} \quad H — H$$

$$:\ddot{O}: + :\ddot{O}: \longrightarrow :\ddot{O}::\ddot{O}: \quad \text{or} \quad \underset{\cdot\cdot}{\ddot{O}}=\underset{\cdot\cdot}{\ddot{O}}$$



$$:\dot{\underset{\cdot}{N}}\!: + :\dot{\underset{\cdot}{N}}\!: \rightarrow :N\vdots\vdots N: \text{ or } :N\equiv N:$$

$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \rightarrow :\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}: \rightarrow :\ddot{\underset{\cdot\cdot}{Cl}}-\ddot{\underset{\cdot\cdot}{Cl}}:$$



In some cases, all the electrons present in the valency shell of an atom may not be used up completely in the formation of covalent bond and number of unused electron pair left on atom is known as lone pair electrons.

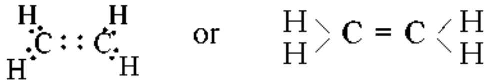
There is one covalent bond between two hydrogen atoms forming hydrogen molecule (H_2) and their is no lone pair left on either of H-atoms present in H_2 molecule. In H_2 molecule duet (having two electron like He atom configuration) is formed.

Oxygen oxygen double bond is present in O_2 molecule and each oxygen atom in O_2 molecule has two lone pairs.

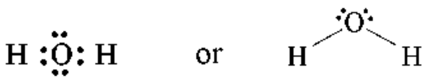
A triple bond is present in N_2 and each nitrogen atom carries one lone pair.

In case of methane, carbon atom completes its octet, while each H-atom completes its duet.

Other examples of covalent molecules—



$H\!:\!C\vdots\vdots C\!:\!H$ or $H—C\equiv C—H$



3.1.4.1 Characteristics of covalent compounds

(i) Covalent compounds are molecular in nature.

(ii) Hence covalent compounds have low melting and boiling points and are less dense.

(iii) Covalent bond is weaker than ionic bond.

(iv) Covalent compounds are soluble in non-polar solvent and are generally insoluble in polar solvent. Some covalent compounds which can form hydrogen bonding are soluble in H_2O (Polar solvent).

(v) Covalent bond has definite direction and hence covalent compounds are rigid in nature.

(vi) Covalent compounds are non-conductor of electricity.

3.1.5 Coordinate covalency or coordinate bond

Coordinate bond is special type of covalent bond in which the shared paired of electrons between two atoms are donated by either of the atoms and then it is shared by both the atoms in order to complete their octet in their outermost shells. The compounds formed by coordinate bond are known as coordinate compounds.

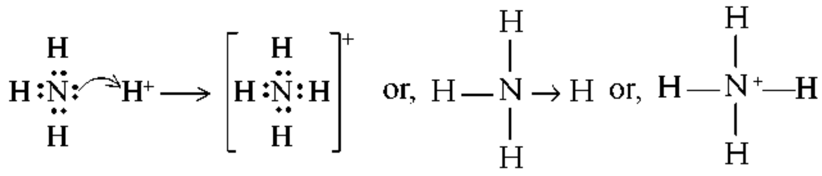
In a coordinate compound the atom which donates the electron pair is known as donor atom and the atom which accepts the electron pair is known as acceptor.

The coordinate bond is shown by arrow mark (→) and the tip of the arrow is pointed towards the acceptor atom from donor atom.

The donor atom must have one or more lone pairs and acceptor atom or ion must have an empty orbital to accommodate the lone pair.

3.1.5.1 Examples of coordinate compounds

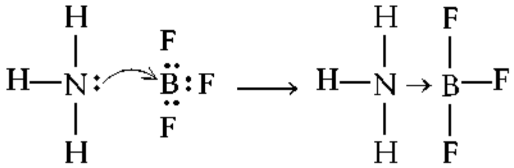
(a)



$$\mathrm{H_3N{:}} + \mathrm{H^+} \longrightarrow \left[\mathrm{H_3N{:}H}\right]^+ \text{ or, } \mathrm{H_3N \rightarrow H} \text{ or, } \mathrm{H_3N^+{-}H}$$

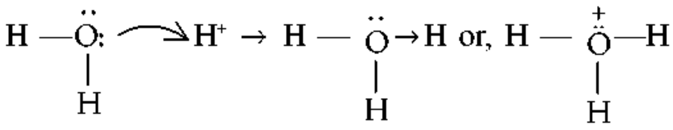
Ammonium ion

(b)



$$\mathrm{H_3N{:}} + \mathrm{BF_3} \longrightarrow \mathrm{H_3N \rightarrow BF_3}$$

(c)



$$\mathrm{H_2\ddot{O}{:}} + \mathrm{H^+} \rightarrow \mathrm{H_2\ddot{O} \rightarrow H} \text{ or, } \mathrm{H_2\overset{+}{\ddot{O}}{-}H}$$

Hydronium ion

3.1.6 Hydrogen bond

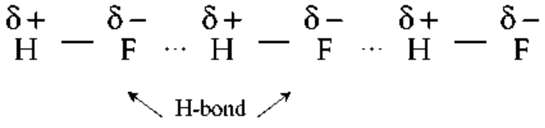
When hydrogen atom is covalently bonded with the strong electronegative element like fluorine, oxygen or nitrogen atoms, the electron pair forming the covalent bond between hydrogen atom and electronegative element is displaced slightly towards the electronegative element. As a result of this displacement of electron pair a slight negative charge develops on electronegative atom and slight positive change develops on the hydrogen atom. A pole is formed which acts like a bar magnet.

$$\overset{\delta+}{\mathrm{H}} \rightarrowtail \overset{\delta-}{\mathrm{F}}$$

This type of molecules comes closure to one another due to the dipole dipole attraction for which slightly positively charged H-atom forms a bridge or a partial bond with negatively charged atom. This partial bond is known as hydrogen bond which is weaker than covalent bond. The strength of H-bond is about 3-5 kcal mol^{-1} (where a covalent bond is 50-100 kcal mol^{-1}). Hence, formation of H-bond is due to a weak interaction. A H-bond is shown by a dotted line.

H-bond can be formed between the molecules of same compound or between different compounds.

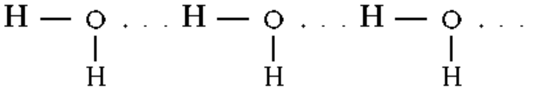
(i)



$$\overset{\delta+}{\mathrm{H}} - \overset{\delta-}{\mathrm{F}} \cdots \overset{\delta+}{\mathrm{H}} - \overset{\delta-}{\mathrm{F}} \cdots \overset{\delta+}{\mathrm{H}} - \overset{\delta-}{\mathrm{F}}$$

hydrofluoric acid

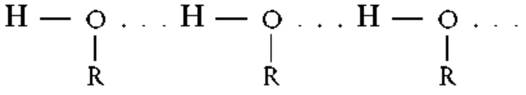
(ii)



$$\mathrm{H} - \underset{\mathrm{H}}{\underset{|}{\mathrm{O}}} \ldots \mathrm{H} - \underset{\mathrm{H}}{\underset{|}{\mathrm{O}}} \ldots \mathrm{H} - \underset{\mathrm{H}}{\underset{|}{\mathrm{O}}} \ldots$$

water

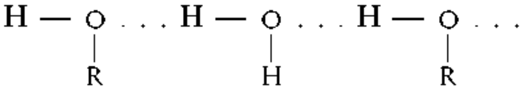
(iii)



$$\mathrm{H} - \underset{\mathrm{R}}{\underset{|}{\mathrm{O}}} \ldots \mathrm{H} - \underset{\mathrm{R}}{\underset{|}{\mathrm{O}}} \ldots \mathrm{H} - \underset{\mathrm{R}}{\underset{|}{\mathrm{O}}} \ldots$$

Alcohol

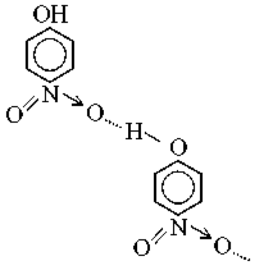
(iv)



$$\mathrm{H} - \underset{\mathrm{R}}{\underset{|}{\mathrm{O}}} \ldots \mathrm{H} - \underset{\mathrm{H}}{\underset{|}{\mathrm{O}}} \ldots \mathrm{H} - \underset{\mathrm{R}}{\underset{|}{\mathrm{O}}} \ldots$$

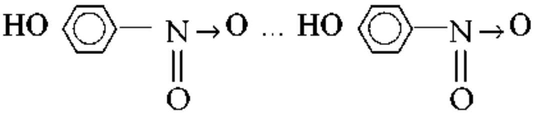
Alcohol and H_2O

(v)



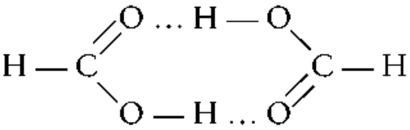
para nitrophenol

or



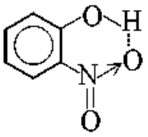
para nitrophenol

(vi)



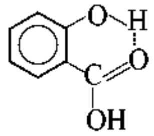
Formic acid (dimer)

(vii)



ortho-nitrophenol

(viii)



Salicylic acid

There are two types of hydrogen bonding— (i) intermolecular hydrogen bonds and (ii) intramolecular hydrogen bonds.

(i) Intermolecular hydrogen bonds : Hydrogen bonds formed between two or more molecules of same or different compounds are known as intermolecular hydrogen bonds. (i) to (vi) are examples of intermolecular hydrogen bonds. The helical structure of DNA allows the formation of interchain hydrogen bonds. An α-helic structure of keratin also allows the formation of interchain hydrogen bonds.

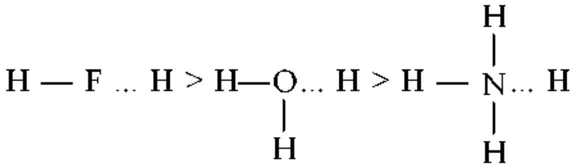
(ii) Intramolecular hydrogen bonds : The hydrogen bond formed between the two atoms of same molecule is known intramolecular hydrogen bond. (vii) and (viii) are the examples of intermolecular hydrogen bonds.

3.1.6.1 Nature of hydrogen bonds

(i) Hydrogen bond is formed due the attraction between oppositely charged atoms present in a same molecule or different molecules.

(ii) Hydrogen bond is confined between hydrogen atom and strong electronegative element like F, O, N.

(iii) Greater the electronegativity and smaller the size of atom, stronger is the hydrogen bond. The decreasing order of hydrogen bonds is shown below—



$$H-F\ldots H > \underset{\displaystyle H}{\underset{|}{H-O}}\ldots H > H-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{N}}}}\ldots H$$

3.1.6.2 Effects of hydrogen bonds

(i) The molecular weight of water (18) is less than that of H_2S (Molecular weight 34), still water is liquid at normal temperature while H_2S is a gas. Because water molecules associate through hydrogen bonds which require more energy to get separated for vaporization, on the other hand H_2S forms a very weak hydrogen bond because electronegativity of sulphur is less than that of oxygen and size of sulphur is greater than that of oxygen. So H_2S is gas at ordinary temperature.

(ii) The molecular weight of propane and ethanol are 44 and 46 respectively, but ethanol is liquid at ordinary temperature while propane is a gas. Because ethanol can form hydrogen bond white propane cannot.

	C_2H_5OH Ethanol	$CH_3CH_2CH_3$ Propane
Molecular at	46	44
Boiling point	78.3°C	– 45°C

(iii) o-nitrophenol can be steam distilled while *p*-nitrophenol can not be steam distilled. Because o-nitrophenol forms intramolecular hydrogen bond, so its molecules cannot associate through hydrogen bond. It remains as a discrete molecule. So it can be steam volatile. Where as *p*-nitrophenol molecules associate through hydrogen bonds and forms intermolecular hydrogen bonds. So it cannot be steam volatile.

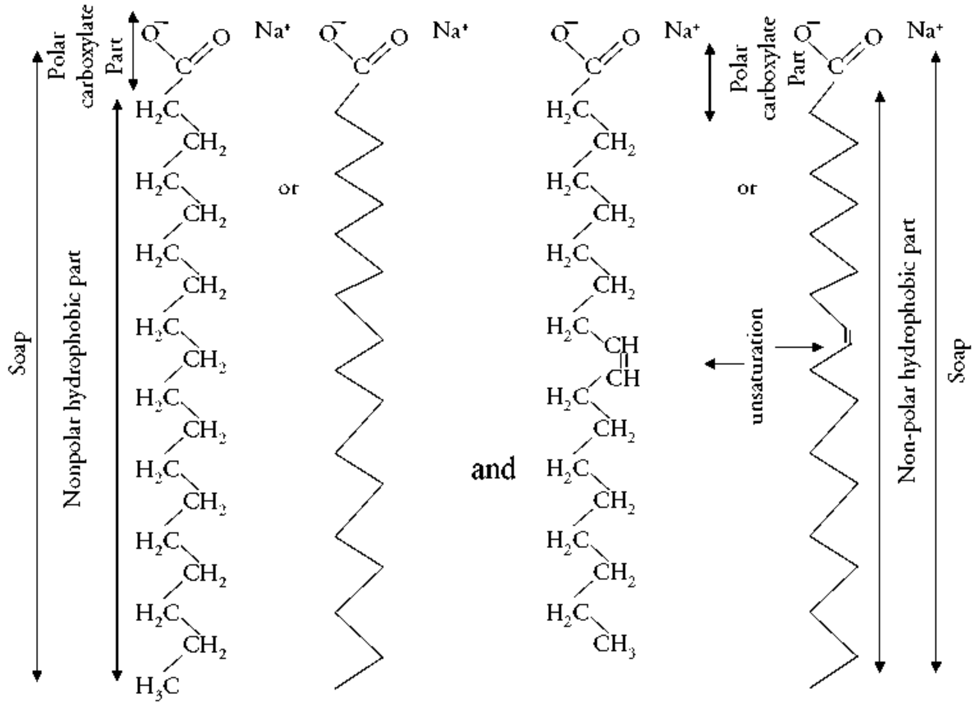
(iv) o-nitrophenol cannot form hydrogen bond with water, but *p*-nitrophenol can form hydrogen bonds with H_2O molecules. So o-nitrophenol is insoluble in water whereas *p*-nitrophenol is soluble in H_2O. Covalent compound which can form hydrogen bonds with H_2O are soluble in H_2O though water is polar solvent, for example, glucose, a covalent compound is soluble in water because glucose has many hydroxyl groups which can form hydrogen bonds with H_2O molecules.

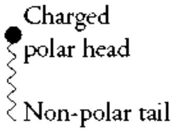
(v) Water molecules can form tetrahedral open cage like structure due to H-bonds in ice (solid) having much empty space in the cage. For this reason the density of ice is less than that of liquid water.

(vi) The molecules of a covalent compound can associate due to the intermolecular hydrogen bonds in a zigzag way. Such associated substance has less power for free movement. Hence the viscosity of such substance will increase, for example, glycerol.

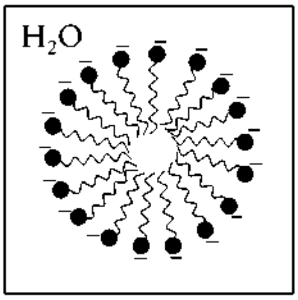
(vii) **Hydrogen bonds in biological system :** Hydrogen bonds are very important for biological systems. A major part of water present in the living systems (both plants and animals) is associated with the proteins by hydrogen bonds. Hydrogen bonds play a very important role in the structures of proteins and nucleic acids (RNA and DNA). Proteins molecules consist of large number of amino acids joined together by peptide linkage (—NH—CO—), $> C = O$ group of a peptide linkage forms a hydrogen bond with hydrogen atom present in the nitrogen atom of another peptide linkage in the same helical chain or with the different chains. Keratin is a protein forming wool, hair, horns, hoofs and silk. Hydrogen bonds are present in the parallel and antiparallel polypeptide chains of keratin. Hydrogen bonds are also present in double helical structures of nucleic acids. Hydrogen bonds stabilize the structures of proteins and nucleic acid.

3.1.6.3 Hydrophobic bond : Sodium or potassium salts of higher fatty acids (saturated or unsaturated) are generally known as soaps e.g. sodium stearate ($C_{18}H_{35}COONa$) or Na-oleate ($C_{17}H_{33}COONa$). In an aqueous medium these salts are completely ionized in carboxylate ions and cation (Na^+or K^+). This carboxylate ion has two parts, one the strong polar head and another the non-polar long chain hydrocarbon part. The polar carboxylate part forms hydrogen bonds with water molecules very easily. But the non-polar hydrocarbon parts donot like water and are insoluble in water. Hence any soap does not form a true solution with water, but disperses into water to form micelles, which may contain soap molecules. In micelles the negatively charged carboxylate parts are exposed to water to form hydrogen bonds while the non-polar hydrocarbon parts are hidden inside and away from water molecules. The negatively charged carboxylate ions repel each other forming


Soap
Polar carboxylate Part
Nonpolar hydrophobic part
Na⁺
or
and
unsaturation
Non-polar hydrophobic part

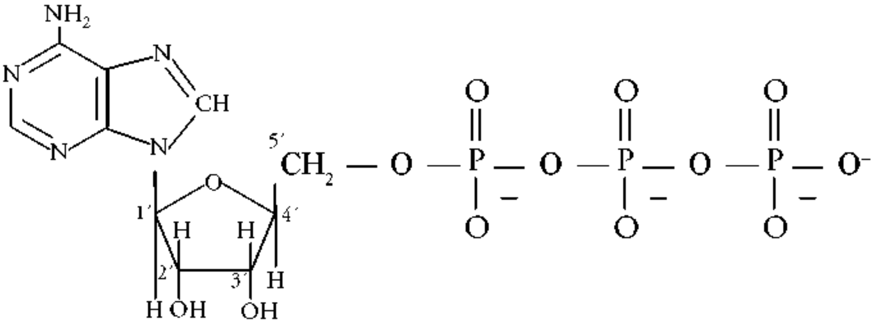

Charged polar head
Non-polar tail

a spherical shape substance known as micelle inside which the non-polar parts are hidden. But a weak Vander Waals' force of attraction acts among the non-polar parts with in the micelle. This weak force of attraction is known as hydrophobic bond or interaction. Due to the mutual force of repulsion among the negatively charged ions the micelles are remained suspended into aqueous medium. Molecules having non-polar and strong polar parts are known as amphipathic. Many amino acids are amphipathic like soaps. Hydrophobic interactions are also shown by proteins, polar lipids and nucleic acids molecules.

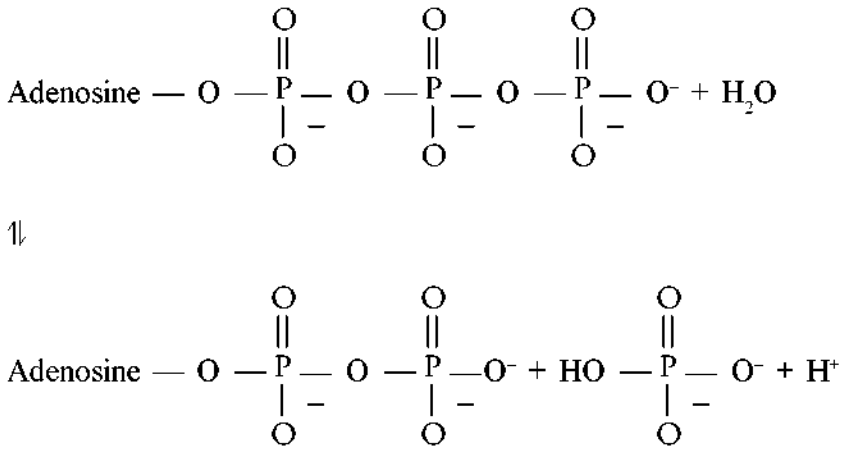


3.1.7 Energy rich bonds

Formation of bond requires energy while dissociation of bond releases energy. If high energy is obtained by the dissociation of any bond of a compound, then that bond is known as high energy bond and the said compound is known as high energy compound. Adenosine triphosphate compound (ATP) is an example of high energy compound because there is a large decrease in standard free energy change during the hydrolytic cleavage of this compound. The energy thus released is then utilized for the biosyntheses in the living cells.



Adenosine triphosphates $[ATP]^{4-}$ (adenine ribose triphosphate)



$$\text{Adenosine}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{}^{-}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{}^{-}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{}^{-}-O^{-}+H_2O$$

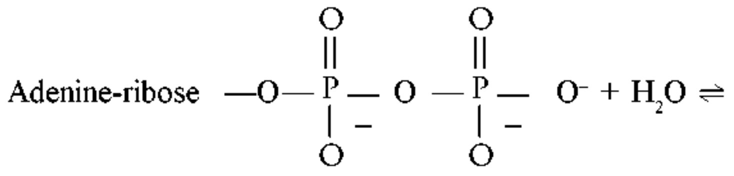
$$\rightleftharpoons$$

$$\text{Adenosine}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{}^{-}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{}^{-}-O^{-}+HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{}^{-}-O^{-}+H^{+}$$

ADP^{3-}

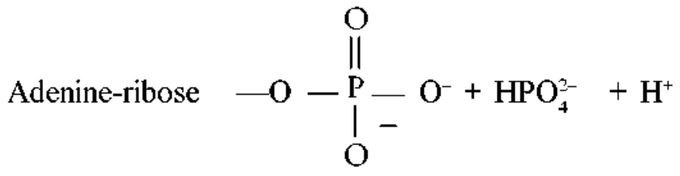
ATP on hydrolylic cleavage forms ADP, orthophosphoric acid and proton. The standard free energy change ($\Delta G^{\circ\prime}$) at 7 pH of this reaction is – 30.5kJ.

Similarly ADP on hydrolysis give adenosine monophosphate (AMP), phosphoric acid and proton and $\Delta G^{\circ\prime}$ at 7 pH of this reaction is also –30.5 kJ.



$$\text{Adenine-ribose}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{}^{-}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{}^{-}-O^{-}+H_2O\rightleftharpoons$$

ADP (Adenosine diphosphate)



$$\text{Adenine-ribose}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{}^{-}-O^{-}+HPO_4^{2-}+H^{+}$$

AMP (Adenosine monophosphate)

Energy rich bonds are present in many compounds of biological interest at pH 7. The standard free energy changes of hydrolysis of some compounds are given below.

	Compounds	$\Delta G^{\circ\prime}$	$\Delta G^{\circ\prime}$
(kcal mol^{-1})		(kJ mol^{-1})	
1.	Phosphonyl pyruvate	– 14.8	– 61.92
2.	Acetyle AMP	– 13.3	– 55.65
3.	1,3-diphosphoglycerate	– 11.8	– 49.37
4.	Phosphocreatine	– 10.3	– 43.1
5.	Acetyl phosphate	– 10.3	– 43.1
6.	Pyrophosphate	– 7.9	– 33.0
7.	ATP ($\rightarrow$ AMP + pp_i)	– 7.5	– 31.38
	ATP ($\rightarrow$ ADP + p_i)	– 7.3	– 30.5
8.	ADP (AMP + p_i)	– 7.3	– 30.5
9.	AMP	– 3.4	– 14.23
10.	Glucose 6-phosphate	– 3.3	– 13.8

3.1.8. Vander Waals forces

Vander Waals forces are intermolecular forces acting among the molecules and due to these interactions practically molecules remain chemically same. Vander Waals forces are also weak in nature. These forces arise due to three factors—(i) orientation, (ii) induction and (iii) dispersion.

(i) Orientation of molecules : Orientation arises due to permanent depoles of the molecules because the negatively charged atom of the molecule will attract the positively charged atom of another molecule due the electrostatic force and the molecules will come closer to one another.

(ii) Induction : Molecules having permanent dipole moment will polarised the neighboring molecules causing induced dipoles in the molecules. Hence there is a force of attraction between the permanent and induced dipoles.

(iii) Dispersion : The dispersion effect arises due to the vibrations of electrons clouds with respect to nuclei of atoms present in a molecule. For this effect a very small amount of dipole moments will develop within the molecule in a specific direction. This will attract the other molecules having permanent dipoles. This type of force is known as dispersion force.

Beside these three types of attractive forces between molecules, their is also repulsive force acting between molecules on close approach.

So actual Vander Waals force is the sum of the three interactions viz. orientation, induction and dispersion minus the force of repulsion.

Vander Waals force is a weak force in comparison to strong bond like ionic and covalent bond. Even it is weaker than hydrogen bond. Higher the molecular weight higher is the Vander Waals force. Amino acids having non-polar side chain are hydrophobic in nature and there non-polar side chains are held together between different parts of the peptide bonds by the Vander Waals forces. Similarly nonpolar hydrocarbon chains of soap molecules are held together by Vander Waals forces and these forces help in the formation of micelles.

3.2 Questions

1. What do you mean by a chemical bond? How many different types of chemical bonds are there? Give examples in each type.
2. Define ionic or electrovalent bond and compound. What are factors favouring the ionic bond? What are the characteristics of ionic bond?
3. Define covalent bond and compound.What are the characteristics of covalent bond?
4. Define coordinate covalency with example.
5. What do you mean by hydrogen bond? How many different types of hydrogen bonds are there? Give example in each case. Discuss the different effects of hydrogen bonds.
6. What do you mean by hydrophobic bond? How micelles are formed?
7. What are Vander Waals forces?
8. What do you mean by energy rich bond?

UNIT 4 ❑ Nuclear Hazards

Structure

4.1 Nuclear hazards

In 1895 Henry Becquerel first noticed that invisible rays were emitted by the uranium salt, potassium zinc uranyl sulphate spontaneously and continuously. These rays affect photographic plate in dark causing fogging on the plate. These rays can ionize the atmospheric air and produce scintillations on zinc sulphide screen. Many elements or their compounds can emit these rays. This emission of rays cannot be controlled by the pressure, temperature or light. This property of emission of invisible rays (radiations) from some substances (elements or compounds) is known as radioactivity and substances which possess this property are known as radioactive substances. The elements which are responsible for radioactivity are known as radioactive elements or radioelement.

Atoms having same atomic number but different mass numbers are known as isotopes.

e.g. ${}_1^1H$, ${}_1^2H$, ${}_1^3H$ and ${}^{12}C$, ${}^{13}C$ and ${}^{14}C$

The spontaneous emission of radiations by some unstable isotopes of elements like radium, uranium polonium, thorium etc. is known as radioactivity and the elements which posses this property are known as radioactive elements or radioelement. There are certain elements whose one or more isotopes may non-radioactive while others are radioactive, for example, hydrogen isotopes of mass numbers 1 and 2 are non-radioactive while mass number 3 is a radiactive isotope. Similarly ${}^{12}C$ and ${}^{13}C$ are stable isotopes while ${}^{14}C$ is a radioactive isotope. All the isotopes of any element whose atomic number greater than bismuth (At No. 83) are radioactive. A radioelement breaks down into other elements by the emission of radiations. This is known as radioactive disintegration. Three types of radiations known as α (alpha), β (beta) and γ (gama) radiations are emitted from a radioelement.

(i) α-rays : α-rays are the stream of doubly charged (positive) helium ions (${}_2^4H^{2+}$) having a mass number 4 and charge twice that of a proton. These rays can be deflected by the magnetic and electric fields and can ionize the medium. It can penetrate thin sheet of aluminium. α-rays convert into helium gas (atoms) by loosing charge. From the direction of deflection by magnetic or electrical field it can be proved that α-rays are positively charged particles. α-rays affect the photographic film. The velocity of α-rays is about 1/10th of the speed of light. The slow movement of α-particle is due to its size and mass. α-particles frequently collide with atoms or molecules in their path, causing intense ionization and excitation. For this reason their energy is dissipated very rapidely and so they are not very penetrating.

(ii) β-rays : β-rays are the stream of negatively charged minute particles. β-rays are similar to cathode rays consisting of electrons moving with very high velocities ranging from 1/3 to 9/10 of the velocity of light. β-rays can be deflected more than α-rays by the magnetic or electric field and from the nature of defection it can be proved that β-rays are negatively charged particles like electrons. They can ionize the medium, but their ionizing power is less than that of α-rays. Due to negligible mass and high velocities of β--rays their penetrating power are more than α-particles. They can penetrate 0.1 cm thick aluminium sheet. β-rays affect photographic film. They have a very bad effect on the living bodies.

(iii) γ-rays : γ-rays are stream of high energy photons. Hence γ-rays donot consist of any particle and are electrically neutral. They are actually electromagnetic wave of very short wave lenghts, even shorter than x-ray. The velocity of γ-rays is almost same with that of light. γ-rays can not be deflected by magnetic or electrical fields as they are electrically neutral. These rays can ionize medium very slightly, almost nil and can affect photographic film. The penetrating power of γ-rays is very high. These rays can penetrate 8cm thick lead sheet. These rays are very harmful to living objects. Mutation of genes takes place when living cells are exposed to γ-rays. These rays can produce cancer when the man or animals are exposed to these rays for a long time. Still these rays can be used in controlled doses to destroy the malignant cells.

4.1.1 Theory of radioactive disintegration

In 1903, Rutherford and Soddy put forward the theory of radioactive disintegration in the following manner—*radioactive elements disintegrate spontaneously forming new elements by the emission of radiations.*

If a radioactive element emits α particles then the α-particles must emit from the nuclei of the element. The nuclei of radioactive elements are unstable and disintegrate spontaneously liberating α and β-particles, whether nuclei of radioactive element are present in atoms or in compounds. Because radioactivity is a nuclear phenomena. Due to this radioactive disintegration new element is formed having different physical and chemical properties from those of the parent element and new-born element is known as daughter element and if this new element is also radioactive element then it will also disintegrate into another element.

This process continues until a non-radioactive element is formed at the end. This non-radioactive element is known as end product. The formation of new elements by the emission of α and β-particles from a radioactive element is known as radioactive disintegration. After the emission of α and β particles from a radioactive element the excess energy which is stored in the atomic nuclei is radiated in the form of γ-radiation. In any radioactive disintegration γ-radiation will not come first. γ-radiation takes place only after the α and β-radiations. α and β radiations donot take place simultaneously in any radioactive disintegration process.

4.1.2 Rate of radioactive decay

The rate of disintregration or decay of a radioactive element at any instant is directly proportional to the number of radioactive atoms (or nuclei) present at that instant. The rate of radioactive decay cannot be changed or influenced by the chemical or physical processes. The amount of radioactive element disintegrates in unit time is known as rate of radioactive decay which is directly proportional to the amount present at that time. The rate of radioactive decay is expressed mathematically in the following way—

$-\frac{dN}{dt} \propto N$ where N = number of radioactive atoms or nuclei at any instant

dN = number of atoms disintegrating in a very small time dt.

$\frac{dN}{dt}$ = rate of disintegration. In the decay process the amount of radioactive atoms or nuclei decrease with time. Hence negative sign is placed before the rate $(\frac{dN}{dt})$.

or $-\frac{dN}{dt} = \lambda N$ where λ = disintegration constant.

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

On integrating the above equation

$\text{In}N = -\lambda t + C$ where C = integration constant

Now when $t = 0$, $N = N_0$

Putting these value in the above equation we get

$\text{In}N_0 = C$.

So we can write

$\text{In}N = -\lambda t + \text{In}\ N_0$

or, $\text{In}\ \frac{N_0}{N} = \lambda t$

or, $\lambda t = 2.303 \log \frac{N_0}{N}$ or, $\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$

or, $t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$ or, $\frac{N_0}{N} = e^{\lambda t}$ or, $N = N_0 e^{-\lambda t}$

4.1.3 Units of radioactivity

The radioactivity of a radioactive element (isotope) can be calculated at what rate it is converted into its daughter element. This is done by counting number of disintegration per unit (generally in second) with the help of Gieger Müller counter or scintillation counter. The rate of decay of a radioactive element is generally expressed in curie (ci) which is defined as the amount of any radioactive isotope which gives 3.7×10^{10} disintegration per second (dps). This rate is equal to the disintegration of one gram of radium (mass no 226)

The disintegration rate of ^{226}Ra = $\lambda \times$ no. of atoms in 1g radium

$$1\text{g radium} = \frac{1}{226}\text{mole Ra} = \frac{1}{226} \times 6.023 \times 10^{23} \text{ radium atom}$$

$$t_{1/2} = \frac{0.693}{\lambda} \text{ (where } t_{1/2} = \text{half life of } ^{226}\text{Ra)}$$

$$\lambda \quad = \frac{0.693}{t_{1/2}} = \frac{0.693}{1600} \times \frac{1}{226} \times 6.023 \times 10^{23} \text{ disintegrations per year}$$

$$= \frac{0.693}{1600 \times 365 \times 24 \times 60 \times 60} \times \frac{1}{226} \times 6.023 \times 10^{23} \text{ disintegration per second (dps)}$$

$= 3.7 \times 10^{10}$ dps = 1 ci

$\therefore$ 1 millicurie = 1×10^{-3} ci

1 μ curiec = 1×10^{-6} ci

The SI unit of radioactivity is becquerel (or Bq) which is defined as one disintegration per second.

$\therefore$ 1 ci = 3.7×10^{10} Bq

Another unit of radioactivity is Rutherford which is defined as 10^6 dps.

From above equation it is evident that rate of radioactive decay decreases with time.

4.1.4 Characteristics of radioactive decay

(i) Rate of radioactive decay decreases with time. (ii) The number of atoms decay in unit time is the rate of decay (iii) Any radioactive decay follows the first order reaction rate (iv) The time taken for the decay of a definite fraction of a radioactive element is independent of its initial concentration. (v) Radioactive disintegration is a random process and number of atoms that disintegrate per second is directly proportional to the number of radioactive atoms present at that time.

4.1.5 Half life period

The time required by a given amount of the radioactive element (having same mass number) to decay one half of its initial value is known as half life period ($t_{1/2}$) of that radioactive element.

Half life period is expressed by $t_{1/2}$.

The half life period is deduced by the following equation—

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N} \qquad \text{when } t = t_{1/2},\ N = \frac{N_0}{2}$$

$$\therefore\ t_{1/2} = \frac{2.303}{\lambda} \log \frac{N_0}{\frac{N_0}{2}} \qquad \text{where } N_0 = \text{initial number of atoms.}$$

$$= \frac{2.303}{\lambda} \log 2 \qquad \log 2 = 0.301$$

$$= \frac{0.693}{\lambda}$$

λ = decay constant, therefore $t_{1/2}$ is a constant and is independent of the initial concentration or amount of radioactive element.

For a particular radioisotope the value of $t_{1/2}$ is constant and depends only on its decay constant. So we can calculate the decay constant of a radio isotope very easily. Let us take an example; the $t_{1/2}$ of radium (mass number 226) is 1600 years. So value of its decay constant (λ).

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{1600} \text{ year}^{-1}.$$

Radioactive isotopes are toxic in nature due to thier ionic and non-ionic radiations. The toxicity of radioactive isotope on human being is the main disadvantage of using the radio-isotopes as tracers or any other work.

Because these radiations cause ionization and produce free radicals which will react with the cells of the living being causing mutation of DNA and affecting proteins and other macromolecules present in the cells. These radiations can induce cancer on prolong exposure or in high doses.

4.1.6 Dosimetry

The dosimetry is the method to determine the dose of different kind of radiations particularly emitted by radioactive substances on living and non-living substances. The dosimetry also determines the effects of different radiations both ionic (α, β) and non-ionic (γ) radiations on living and non-living substances. It also determines the radiation hazards on living being particularly human beings working with radioactive substances in the laboratory or factories, in mines of radioactive ores. Dosimetry is also used in radiotherapy.

The action of ionizing radiation on any matter both living and non-living is directly proportional to absorbed dose of radiation. The absorbed dose is defined as the amount of ionizing radiation energy aborbed by the unit mass of substance being exposed to this radiation. Unit of absorbed dose in SI unit is joules per kilogram of substance. For practical purposes unit of absorbed dose is the **rad** (radiation absorbed dose) and one rad is equal to 100 ergs of energy absorbed by one gram of substance being exposed to the ionizing radiation. One rad is also equal to 6.24×10^{13}eV per cm^3 and rad shows total quantity of radiation energy absorbed by the tissues or any substances.

Nowadays rad has been replaced by SI unit gray (Gy) which is equivalent to 100 rad. Because strength of X-rays or γ-rays decreases as they traversed through the tissue or substance.

Exposer dose of radiation is used in the cases of X-rays and γ-rays radiations and exposer dose is defined as the amount of radiation energy in coulomb absorbed by one kilogram of substance being exposed to these radiaions. This is the SI unit of exposer dose. But for practical purposes exposer dose is expressed in roentgen (symbol r) which is defined as the amount of X-or γ-radiation that will produce ions carrying 2.58×10^{-4} coulomb of electricity, of either sign in 1 cm^3 of dry air at normal temperature and pressure (NTP) i.e. on 0.001293 gm of dry air.

Absorbed dose rate : Absorbed dose rate is defined as amount of dose of radiation absorbed by unit mass of substance per unit time. In SI unit, it is joule per kilogram per sec. ($Jkg^{-1}s^{-1}$). It can also be expressed in rad per second [$r\ s^{-1}$] or electron volt per second.

Similarly exposer dose rate for x- or γ-radiations is defined as amount of dose of x- or γ-radiation per unit time. In SI unit, it is coulomb per kilogram per sec [$Ckg^{-1}s^{-1}$] and for practical purposes, rad per sec [$r\ s^{-1}$]. Mathematically it is expressed in the following way—

$D = -pt$ where D = dose

p = dose rate and t = time in second

4.1.7 Radiation intensity

It is the amount of radiation energy per unit time crossing unit area perpendicular to the propagation of radiation.

Its unit is ergs percm^2 persec [erg cm^{-2}s^{-1}] or [eVcm^{-2}s^{-1}]. In SI unit it is Jm^{-2}s^{-1}.

4.1.8 Radiation chemical yield (G)

An ionizing radiation on chemical substance(s) can induce chemical reactions which can be characterized by radiation chemical yield (G) and this is defined as the numbers of molecules, atoms, ions or free radicals formed or destroyed from a substance by absorbing 100 eV of ionizing energy. It is expressed as follows—

$G = \frac{N}{D} \times 100$ where N = no. of molecules ions atoms or free

radicals formed or destroyed from 1cm^3

of substance

D = absorbed does in eV.

Different ionizing and non-ionizing radiations have different effects on living bodies and degree of hazard associated with different radiations on living bodies are different. For this reason a correction factor is introduced for different types of radiations in comparison with that of x-radiations. The correction factor is known as weighting factor (W). The absorbed dose which is considered for weighting factor is known as sievert (Sv) and sievert can be expressed as follows —

$Sv = Gy \times W$

1 Sv ≡ 100 rem

where rem is roentegen equivalent in man and nowaday it is replaced by sievert. where Gy is known as gray.

The effect of β radiation on living bodies is very similar to that of x-radiation. So the weighting factor for β radiation is taken to be 1 and therefore for β-radiation.

Sv = Gy

But harmful effect of α-radiation is 20 times greater than β-radiation. Therefore the weighting factor will be 20 for α-radiation.

The absorbed dose from a radioactive isotope can be calculated by rate of decay of radioactive isotope, energy associated with decay, the penetrating power of the radiation, the distance between the radioactive source and the object being irradiated. Since a radioactive isotope emits radiation in all directions with equal intensity and the intensity of radiations from a radioactive source is inversly proportional to the square of the distance. So we can deduce the following equation—

$D_1 \times l_2^2 = D_2 \times l_1^2$ where D_1 and D_2 are doses
l_1 and l_2 are distances.

The annual permissible limit for a person exposed to radiation is 50 mSv per year for whole body.

4.1.9 Effects of radiations on biological system

Different types of radiations have different effects on biological systems. As for example α-particles have large size for which α-particles have very little penetrating power, even skin can stop the penetration of α-particles in the body. But α-particles can penetrate into the body through the wounds or cuts and if α-particles enter into the body then they cause a heavy damage to body cells by ionizing the cells.

β-particles have greater penetrating power than α-patticles and β-particles can penetrate in body slightly and can cause burn on skin and intensity of burn depends on the flux of β-particles.

γ-rays are electromagnetic radiations like x-rays. These radiations can penetrate deep into the living bodies very easily.

α, β and γ-radiations can ionize the DNA and break the double strand of DNA, can produce free radicals. As a result of these damage, death of cells may take place. Higher the radiation dose, higher will be damage or death of cells. These radiations, particularly γ-radiations, can break the chromosomes and broken chromosomes can unite in a abnormal way causing the mutation of chromosomes.

The effects of radiations may be short term or long term. Due to high dose of radiation death may take place immediately or after sometime. These radiation may cause carcenogenesis dermatitis, blood dyscrasias, leukaemia, chromosome aberration, acute radiation sickness and abnormalities in the development of foetus.

Radiations can be used for the treatment of cancer or tumours. This is known as radiation therapy. Therapeutic radiations also destroy the cells of body tissue in their paths by breaking the single strand of DNA and by producing free radicals from water present in the cells. These free radicals destroy the proteins, cell membranes and various particles present in the cells. These radiations can destroy malignant tumorous cells also. So the therapeutic radiation must be used in a controlled way at the target tissue area, so that they must cross normal cells as minimum as possible.

X-rays and γ-rays are used for cancer treatment. While β-rays of having low penetrating power can be used for the treatment of skin condition.

4.2 Principles and applications of tracer techniques in biology

Tracers are the chemical substances which can be used as a markers to trace the pathway of a chemical reactions or any other physical processes. Tracers can be also used to locate the position of a substance.

A tracer may be radioactive or non-radioactive substance.

A radioactive tracer or radiotracer is a chemical substance that contains a radionuclide. We know that isotopes of an element have same chemical properties. If one of the isotope is radioactive, then these two isotopes (radioactive and non-radioactive) have same chemical properties but the radioactive isotope only emits radiations. Now in a compound in which a non-radioactive (stable) atom can be replaced by a radioactive isotope of that atom and the compound thus obtained is known as labelled compound which can be traced by the radiation emitted by the labelled radioactive atom in order to follow its course in chemical or physical processes of the system under investigation. Radiotracers can be used to follow the metabolic pathways metabolic turnover rates, photosynthesis, biosynthesis of protein and nucleic acid etc.

A radioactive tracer used in a system to follow its path in any process must mix perfectly with system under investigation or the radiotracer must label a particular non-radioactive isotope perfectly in a compound to investigate its fate. In doing so the tracer used must not affect adversely any part of the system. After incorporating the radiotracer in a system it will behave almost exactly same way with the non-radioactive substance under investigating except for its radioactive emission.

A very small amount of radiotracer is used in a system so that its radioactivity does not affect any part or component of the system.

A radiotracer isotope is not only different in mass number from the element to be traced in a compound or system, but the tracer is also radioactive while the other isotope is non-radioactive. Isotopes having different mass numbers react chemically in different rates. The rates of diffusion of these isotopes are also different. Because rate of diffusion is inversely proportional to the square root of their molar concentration at constant temperature and pressure (Graham's law of diffusion). Moreover isotopic labelling in a compound takes place at random which will increase the entrope of the system, thereby changing the equilibrium constant of this exchange reaction. Beside these factors different isotopes of the same element have different energies due to vibrational energy of two dissimilar mass of isotopes and also on different electron binding energies in the atoms of the isotopes. The combination of all these factors for isotope labelling process is known as *isotope effects*.

Isotopic effect in the case of tritium (mass numbers 3) with respect to protium (hydrogen mass number 1) is very large because mass of tritium is three times that of protium (^{1}H). But in case of uranium 238 (mass number 238) has very little isotopic effect with respect to uranium 235 (^{235}U) because mass difference is very small in this case.

4.2.1 Selection of a radiotracer for a particular system

All radiotracers are not suitable for any process or chemical exchange reaction. A tracer must be suitable chemically and physically for a particular process or chemical reactions under investigation.

For the study of biosynthesis of cholesterol and its metabolites carbon-14 (^{14}C) is very suitable radiotracer. ^{14}C tracer is also very useful to study the photosynthesis, biosynthesis of nucleic acids and protein etc. For bone imagining purposes strontium 89(^{89}Sr) is a very useful radiotracer because it can exchange calcium atoms from calcium phosphate molecules present in bone. Similarly thyroid gland produces an iodine containing amino acid thyroxine. For the study of thyroid gland, iodine of mass number 125 (^{125}I) or 131 (^{131}I) are used a tracers. Other radiotracers are not suitable for thyroid studies.

Another important fact for the selection of a radiotracer is the half life ($t_{1/2}$) of radiotracer. The half life of a tracer should not be very long or short. But the half life of a tracer must be long enough so that a particular experiment can be completed during this half life period. Moreover the activity of the radiotracer should be high enough during the course of experiment for its measurement. The specific activity of a tracer having a long half life is very low. This type of tracers has serious problem in storage and disposal. It has a very serious environmental contamination problem too.

Another important factor for the selection of a radiotracer is the type of radiations emitted from it, because all types of radiation are not suitable for all type of tracer studies.

The radiation emitted from a tracer must have suitable penetrating power for the experiment to be studied and the activity of the radiation can be measured easily by some ways. Its damaging potential for the sample should be as low as possible.

γ-emitting tracers are always used in the case of very thick and dense sample.

Some Isotopes used as Tracers

Isotope	Half life	Type of radiation
^{3}He	12.3y	β
^{14}C	5730y	β
^{24}Na	15d	β,γ
^{32}P	14.28d	β
^{35}S	87.1d	β
^{36}Cl	3.1×10^{5}y	β
^{42}K	12.36h	β,γ
^{90}Sr	29.1y	β
^{128}I	25m	β,γ
^{131}I	8d	β,γ
^{60}Co	5.27y	β,γ

α or β radiations has very little penetrating power, so they are not suitable for thick and dense sample, only β-radiation can be used for this purpose in the case of very thin film or a slice of the sample. So that its activity can be counted by scintillation. α-radiation has the least penetrating power, so α-emitter is not very useful in tracer studies, moreover α-radiation enters into the body of a living object through wounds or cuts producing free radicals which will damage the sample very seriously.

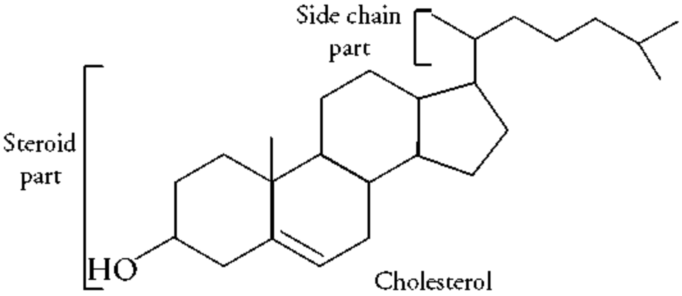
A non-radiotracer can be used in the study of chemical reactions. This non-radioactive tracer is detected by mass spectrograph.

4.2.2 Advantages and disadvantages of radiotracers

A very negligible amount of a radiotracer present in a system can be very efficiently detected and measured by its emitted radiation. But this negligible amount cannot be detected by chemical methods. Negligible amount of radiotracer present in a system minimizes the potential damaging effect of the system or its component, particularly living bodies and biological specimens. The decay of any radiotracer cannot be influenced by the pressure, temperature heat, light pH etc. These are the advantages of radiotracers. All radioactive radiations are toxic in nature. This is one of disadvantages of radiotracer. Handling the radiotracers and disposal of radioactive materials left are the disadvantage of radiotracers.

The metabolite and its transformation products cannot only be detected and measured by the tracer technique method but many important observations can also the made about plants, animals and many biological specimens like isolated organs and tissues. Many definite conclusion can be made with these observations, for example, all the carbon atoms present in the molecule of cholesterol are derived from acetate.

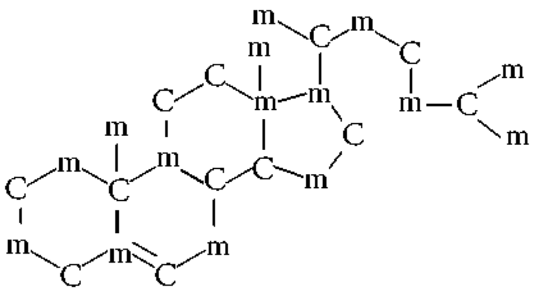
Biosynsthesis of cholesterol is an unique example of the application of tracer technique. By this technique it was conclusively proved that all the carbon atoms present in cholesterol are derived from acetic acid.



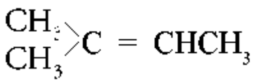
Cholesterol

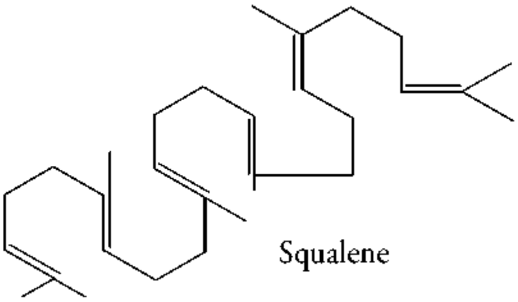
Cholesterol molecule has two part; one is the steroid and another is eight membered side chain. In 1940 Block et.al. proved that all the carbon atoms present in cholesterol (steroid and side chain) are derived from acetate. They fed a rat by labelled acetic acid and found that this labelled carbon atoms (^{14}C) are incorporated in the cholesterol found in the liver of the rat. They used methyl labelled acetate and carboxylate labelled acetate separately to rat and in both cases they found that labelled carbon atoms are present in the cholesterol.

$CH_3\overset{*}{C}OOH$	$\overset{*}{C}H_3COOH$
carboxylate labelled acetic acid	methyl labelled acetic acid



Where m denotes methyl labelled carbon atom and C denotes carboxylate labelled carbon atom.

Cholesterol is synthesized in the liver of animal from labelled acetic acid which by the way of acetoacetic acid and mevalonic acid is converted to five membered isopentanoid  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C = CHCH_3$ units. Six such units on combination give linear labelled squalene which is fed to animal. This labelled squalene by appropriate folding and ring closure, leads to lanosterol, desomosterol and finally to labelled cholesterol. This proves that squalene is a precursor of cholesterol.



Squalene

4.2.3 Autoradiography

Autoradiography is a technique to follow the localization of radiotracer in the metabolic pathway or biological specimens or living objects or any specimen in order to determine its ultimate fate. In this technique any material living or non-living that contains radiotracer is placed in contact with an undeveloped photographic film or plate and the radiation emitted from radiotracer will expose on the photofilm for sometime.

A photographic film is coated with a uniform layer of light sensitive emulsion. This emulsion consists of silver halide cystals (mainly AgBr) embedded on gelatine. Silver halide present in photofilm is reduced to metallic silver on exposure to light (radiation) by chemical reaction of developing and the amount of reduction is proportional to the intensity of light and developers produce black deposit of fine particles of metallic silver on those part of the film that had been exposed to light thus giving a negative image. The unaffected silver halide is removed by the action of sodium thiosulphate solution and then by washing with water. This gives a negative which is free of light sensitive silver halide.

The negative thus obtained will produce an image of the location of the radioactive areas of the object.

This autoradiography technique is very sensitive and it is widely used in a large number of biological specimens for different purposes. Autoradiography is also used to locate the distribution of the radiolabelled drug in the whole body of an experimental animal. To study the metabolic path, radiolabelled metabolites are separated by chromatography and these metabolites can be detected by autoradiography while they are in the chromatography column or in TLC (Thin layer chromatograph) plate even in paper chromatograph. Once the position of the metabolite is located by autoradiography, the metabolite is recovered from that part for counting the activity by Geiger-Müller tube or counting by some other methods.

4.2.4 Preventive measures

The person working with radioactive substances should be very careful to avoid the radioactive substances for the inhalation, swallowing or direct contact with skin. Suitable protecting clothing must be used to prevent the direct contant from these harmful radioactive substance. In the case of x-rays and γ-rays, proper thickness shielding should be used to reduce the exposure below allowable limit. Proper ventilation should be arranged in the factories or in the work place in order to prevent the inhalation of these harmful radioactive dust particles or gases. Empolyees, working in radiation laboratories, in the mines of radioactive ores, in the industries using radioactive substances should be monitoring at regular intervals to determine the absorbed dose. Periodic medical check up and examinations must be done for every workers. If any harmful effects are found to anybody then the person must be transferred to a safe place immediately involving no exposure to radiation.

4.3 Questions

1. What do you mean by radioactivity and radioactive substance?
2. What are the characteristics of α, β and γ rays?
3. How would you express the rate of disintegration of a radioelement mathematically?
4. What are units of radioactivity? Define them.
5. How would you detect α and β-rays?
6. What is end product?
7. Deduce a relation between half life ($t_{1/2}$) and decay constant.
8. What are the characteristics of radioactive decay?
9. What do you mean by dosimetry?
10. Define (i) rad, (ii) rem, (iii) gray, (iv) absorbed dose rate, (v) radiation chemical yield (vi) radiation intensity, (vii) sievert.
11. What are the effects of radiation on biological system? What are the preventives measures?
12. What is a radiotracer?What is a labelled compound? What are the characteristics of a good radiotracer?
13. What is autoradiography?

UNIT 5 ❑ Ionic Product

Structure

- **5.1 Ionic product of water**
- **5.2 Degree of dissociation of water at 25°C**
- **5.3 pH**
- **5.4 pOH**
- **5.5 Buffer solution**
- **5.6 Determination of pH of a buffer solution**
- **5.7 Indicators**
- **5.8 Questions**

5.1 Ionic product of water

Pure water is a very bad conductor of electricity. The specific conductance of water at 25°C is $5.54 \times 10^{-8} \text{ohm}^{-1}\text{cm}^{-1}$. This proves that the water molecule dissociates into H^+ and OH^- ions. Since water conducts very small amount of electricity, so water is a very weak electrolyte. Therefore, dissociation of water molecules will be in equilibrium, i.e.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

because the existence of free H^+ ion is not possible still for our convenience we will write the equation in the following way,

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{... (3.1)}$$

$$\therefore K = \frac{[H^+]\times[OH^-]}{[H_2O]} \quad \text{... (3.2)}$$

where K = equilibrium or dissociation constant and $[H^+]$, $[OH^-]$ and $[H_2O]$ are the concentrations of H^+ ion, OH^- ion and H_2O respectively at the equilibrium. Concentration is expressed in mol. litre^{-1}. Since water is a very bad conductor of electricity, so the dissociation of water molecules into ions will be also very small. Hence the concentration of water will remain practically unchanged, i.e. $[H_2O]$ = constant.

$$\therefore K \times [H_2O] = [H^+] \times [OH^-] = K_w$$

where K_w is known as ionic product of water and it is defined as the product of the concentrations of $[H^+]$ and $[OH^-]$ ions in pure water.

Dissociation constant of H_2O × concentration of H_2O = Ionic product of H_2O.

The value of K_w depends on temperature and it is 1×10^{-14} at 25°C

$\therefore K_w = [H^+] \times [OH^-] = 1 \times 10^{-14}$ at 25°C.

By the dissociation of water molecule equimolar amount of H^+ and OH' are obtained.

$\therefore [H^+] \times [OH^-] = [H^+]^2 = 10^{-14}$

$\therefore [H^+] = \sqrt{10^{-14}} = 10^{-7}$ mol.litre^{-1} at equilibrium at 25°C.

5.2 Degree of dissociation of water at 25°C

At 25°C, $K_w = 10^{-14}$

$\therefore \quad [H^+] \times [OH^-] = 10^{-14}$

or, $\quad [H^+]^2 = 10^{-14} \qquad$ since $[H^+] = [OH^-]$

$[H^+] = \sqrt{10^{-14}} = 10^{-7}$ mole. litre^{-1}.

$\therefore$ $c\alpha = 10^{-7}$ where c = molality (molal concentration) of H_2O and α = degree of dissociation of water. The molecular weight of H_2O is 18. One mole of H_2O = 18 g of H_2O and the volume of 18 g of H_2O = 18 cm^3.

$\therefore$ 1 litre or 1000 cm^3 water contains $= \dfrac{1000}{18} = 55.6$ mole of H_2O.

$c\alpha = 10^{-7}$

$$\alpha = \frac{10^{-7}}{c} = \frac{10^{-7}}{55.6} = 1.8 \times 10^{-9} \text{ mol. litre}^{-1}$$

5.3 pH

pH is a word used to express the activity of hydrogen ion in a system or a solution and pH is equal to $-\log a_H{}^+$, where $a_H{}^+$ is the hydrogen ion activity of a solution or system. In a dilute solution, activity of a solution is generally equal to concentration,

$$\therefore \text{pH} = -\log a_{H^+} = -\log [H^+] = \frac{1}{\log[H^+]} \qquad \dots (3.3)$$

where $[H^+]$ = concentration of hydrogen ion.

The concentration of hydrogen ion in pure water is 10^{-7}mol.litre. So, pH of pure water will be,

$\therefore$ pH = – log[H$^+$] = –log10^{-7} = 7.

The hydrogen ion concentration of any acidic solution is greater than that of pure water. So the pH of any acidic solution will be less than 7 and the pH value of any acid solution will be between 0 to 7 and pH of any alkaline solution will be between 7 – 14. The pH of pure water is 7 and it is neutral, i.e. pure water is not acidic or alkaline.

5.4 pOH

The pOH value of any solution or system may be difined as the negative logarithm of the hydroxyl ion concentration,

pOH = – log[OH$^-$]

But [H$^+$] × [OH$^-$] = 10^{-14} ($K_w = 10^{-14}$)

Taking logarithm on both sides.

log[H$^+$] + log[OH$^-$] = log 10^{-14}

or, –log[H$^+$] – log[OH$^-$] = – log10^{-14}

According to defination

pH + pOH = 14. ... (3.4)

(i) By this equation, pOH value of any solution can be determined provided pH value is known and vice versa, for example, if the pH value of a solution is 2, then the pOH value of this solution is (14 – 2) = 12.

(ii) By decreasing the hydrogen ion by 10 fold the pH value will increase by one unit. The hydrogen ion concentration [H$^+$] of N/100 acid solution is 10^{-2} mol·litre^{-1}.

$\therefore$ pH value of N/100 acid solution = 2.

Similarly pH of N/10 acid solution = 1.

and pH of 1(N) acid solution = 0 because [H$^+$] of 1(N) acid = 1 = 10^0 mol. litre^{-1}.

(iii) pH value of any solution cannot be less than zero or more than 14.

(iv) Since the value of K_w depends on temperature. So the pH value changes with temperature. So, 25°C is taken as standard for the determination of pH or pOH value.

(v) The pH value which is expressed by hydrogen ion concentration (mol·litre^{-1}) is known as pH scale. Similarly the pOH value which is expressed by [OH$^-$] concentration (mol·litre^{-1}] is known as pOH scale.

(vi) pH value of any acid solution will be from 0 to <7 and pH value of any alkaline solution will be 14 to > 7. The pH acid of pure H_2O is 7.

[OH^{-1}] mol.lit	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}
[H$^+$] mol.lit	10^{0}	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
pOH	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0

***pH* range of some substances**

Gastric juice	1.0 – 3.0	Human urine	4.8 – 5.1
Human blood	7.36 – 7.42	Human saliva	6.5 - 7.5

5.5 Buffer solution

A solution which can resist a change of pH by the addition of some acid or alkali is known as buffer solution. A buffer solution is composed of either an acid and its salts or a base and its salts.

Classification of buffers

(1) Simple buffers : A buffer which is composed of salt of weak acid and a base or an acid salt and a neutral salt, for example, CH_3COONH_4, NH_4OH; disodium hydrogen phosphate (Na_2HPO_4) and sodium phosphate (Na_3PO_4). The mixture of protein and amino acid is also an example of simple buffer. The buffer range of simple buffer is between 5.0 – 6.3 pH.

(2) Mixed buffer : *(i) Acid buffer :* A buffer composed of a weak acid and its salt (which on dissociation in solution gives strong base) is known as an acid buffer, for example, acetic acid (CH_3COOH) and sodium acetate (CH_3COONa) solution; sodium bicarbonate ($NaHCO_3$) and carbonic acid solution; boric acid (H_3BO_3) and borax ($Na_2B_4O_7.10H_2O$) solution. The pH range of the acid buffers is between 7 – 14.

(ii) Basic buffer : A buffer composed of weak base and its salt (which is obtained by reacting the base with a strong acid) is known as basic buffer, for example, ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl) solution; glycine (NH_2CH_2COOH) and glycine hydrochloride ($ClH^-.N^+H_3CH_2COOH$) solution. The pH range of basic buffers is between 0 – 7.

Mechanism of buffer action : Let us take a buffer composed of acetic acid and sodium acetate. Acetic acid is weak acid. So it disassociates partially in an aqueous solution into H^+ and CH_3COO^- ions. But in aqueous solution sodium acetate disassociates completely into Na^+ and CH_3COO^- (acetate) ions. Due to this acetate ion (common ion) the dissociation of acetic acid is further suppressed.

The dissociation constant *Ka* of acetic acid is 1.8×10^{-5} mol·litre^{-1}.

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

$$\therefore Ka = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

$$= \frac{[H^+]^2}{[CH_3COOH]} \qquad \text{Because } [H^+] = [CH_3COO^-]$$

The dissociation of acetic acid is negligible. So the concentration of acetic acid remains practically unchanged, i.e. its concentration remains 1 molar.

$[H^+]^2 = 1.8 \times 10^{-5}$

$[H^+] = \sqrt{1.8 \times 10^{-5}} = 4.2 \times 10^{-3}$ mol·lit^{-1}.

$\therefore$ The pH of 1 molar acetic acid $= -\log [H^+] = -\log 4.2 \times 10^{-3}$

$$\begin{aligned} pH &= -\log 4.2 - \log 10^{-3} \\ &= 3 - \log 4.2 \\ &= 2.38. \end{aligned}$$

Now one mole sodium acetate is added into the acetic acid solution, so that the concentration of CH_3COO^- ion in the solution is 1(M). The dissociation of acetic acid is suppressed due to the presence of this acetate common ions. So the concentration of acetic acid in the mixture remains practically unchanged.

$$\therefore Ka = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+] \times 1.0}{1.0}$$

$Ka = [H^+] = 1.8 \times 10^{-5}$

$\therefore pH = -\log[H^+] = -\log 1.8 \times 10^{-5} = 5 - \log 1.8 = 4.78$

The pH of 1(M) acetic acid and 1(M) sodium acetate solution is 4.78.

Now 0.01(M) HCl is added to this solution. The acid reacts with CH_3COO^- ion to give 0.01(M) acetic acid. In this condition the concentration of acetic acid will be 1.01M and concentration of acetate ion will be 0.99M.

$$\therefore Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]\times 0.99}{1.01}$$

$$1.8 \times 10^{-5} = \frac{[H^+]\times 0.99}{1.01}$$

$$\text{or} \qquad [H^+] = \frac{1.01}{0.99} \times 1.6 \times 10^{-5}$$

$\therefore$ pH = 4.74

If 0.01M HCl is added to pure water, then its pH will change from 7 to 2.

Similarly if we add 0.01(M) alkali to this buffer than the pH will be 4.79 because alkali (OH^-) will react with CH_3COOH acid to give CH_3COO^- and water. So the concentration of acetic acid will be 0.99 (M) and acetate ion will be 1.01 (M).

5.6 Determination of pH of a buffer solution

A buffer is composed of weak acid HA and its salt NaA in an aqueous solution. So,

$$HA \rightleftharpoons H^+ + A^- \quad \text{and} \quad NaA \rightleftharpoons Na^+ + A^-$$

$$\therefore Ka = \frac{[H^+]\times[A^-]`}{[HA]} \quad \text{where } Ka = \text{dissociation constant of the acid}$$

$$\therefore [H^+] = \frac{Ka\times[HA]}{[A^-]}$$

The concentration of A^- depends on the dissociation of NaA mainly, because the concentration of A^- due to dissociation of HA is negligible. The dissociations of HA is further depressed due to the common ion. So the concentration of HA practically remains same.

$\therefore$ $[A^-]$ = [NaA] and [HA] = Acid.

$$[H^+] = \frac{Ka\times[HA]}{[A^-]}$$

Taking logarithm on both sides

$$\log[H^+] = \log Ka + \log \frac{[HA]}{[A^-]}$$

$$\therefore -\log [H^+] = -\log Ka - \log \frac{[HA]}{[A^-]}$$

$$\text{or, } pH = pKa + \log \frac{[A^-]}{[HA]} \quad \text{where } pKa = -\log Ka$$

$$\text{or, } pH = pKa + \log \frac{[salt]}{[acid]} \qquad \ldots (3.6)$$

This equation (3.6) is known as Handerson's equation.
Now if [salt] = [acid]
pH = pKa

Again $\frac{[salt]}{[acid]} = 10$there pH = pKa + 1

and $\frac{[salt]}{[acid]} = \frac{1}{10}$ there pH = pKa – 1

Buffer capacity : Number of gm equivalent amount of acid or base required for 1 litre of a buffer solution to change its pH by one unit is known as its buffer capacity.

5.7 Indicators

Indicators are organic compounds, generally organic dyes. An indicator indicates the completion of a chemical reaction, i.e. end point in a volumetric analysis by the sharp change of its colour. It also indicates the pressence or absence of certain substance in a solution. A very small amount of indicator is used in volumetric titration. In an acid base titration litmus, phenolphthalein, methyl orangeti are used as indicators. In permanganometric titration permanganate itself is used as an indicator and in iodometic titration starch solution is used as an indicator.

The colour of these organic dyes depends on the hydrogen ion concentration, that means on pH of the solution, for example, the colour of phenolphthalein is colourless in acid medium but pink in alkaline medium. These organic dyes in water generally behave as acids or bases by dissociating in ions in solutions. The colour of the disassociated molecule may be different from its undissociated form. Now if the amount of undissociated form is in excess then we see a particular colour of the solution and if the amount of dissociated form is in excess than we see another colour of solution. The undissociated or dissociated form will depend on the pH of the solution. The dissociation of an indicator has no effect on the pH of the solution because indicator is used in a very small amount. The equilibrium of a weak acidic organic dye indicator [HIn] may be expressed as,

$$\mathrm{HIn} \rightleftharpoons \mathrm{H^+} + \mathrm{In^-}$$

$$K_{\mathrm{In}} = \frac{[\mathrm{H^+}]\times[\mathrm{In^-}]}{[\mathrm{HIn}]} \text{ or } \frac{[\mathrm{HIn}]}{[\mathrm{In^-}]} = \frac{[\mathrm{H^+}]}{K_{\mathrm{In}}}$$

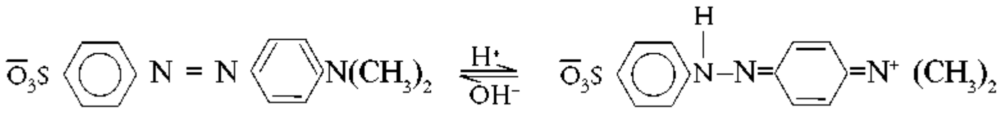
where K_{In} = dissociations constant of the indicator. HIn = undissociated indicator, $\mathrm{In^-}$ = dissociated anion part of the indicator.

If the value of ratio $[\mathrm{HIn/In^-}]$ is in between 0.1 to 10 then we can understand the colour change. In such case the value of *Ka* should be very close to hydrogen ion concentration $[\mathrm{H^+}]$. The colour change of an indicator takes place over a pH range such that it can indicate the end point of a titration.

Acid base indicators and their pH range

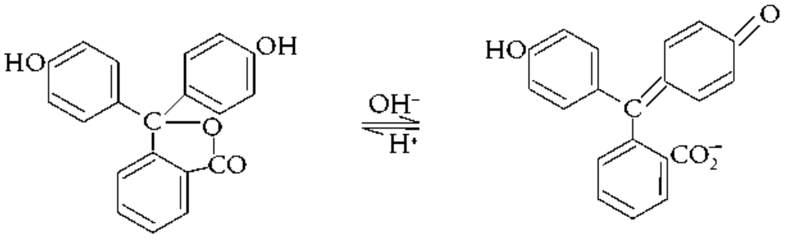
Indicators medium	Colour in acid medium	Colour in alkaline	pH-range
Methyl Orange	Orange red	Yellow	2.1-4.4
Methyl red	Red	Yellow	4.2-6.3
Litmus	Pink	Blue	5.0-8.0
Bromothymol blue	Yellow	Blue	6.0-7.6
Phenolphthalein	Colourless	Pink	0.3-10.0

The colour change of methyl orange due to its change in structure is given below,



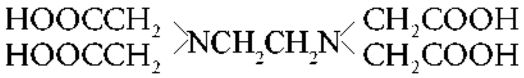
$\mathrm{In^-}$ (yellow in alkaline medium) HIn (orange red in acid medium)

In case of phenolphthalein



HIn (colourless in acid medium) In$^-$ (pink in alkaline medium)

Different types of indicators are used in different titrations, for example, in permanganometry titration $KMnO_4$ itself used as an indicator (self indicator). In iodometry titration starch solution is used as an indicator. In complexometry titration by EDTA (ethylene diaminetetraacetic acid) Eriochrome black T is used as an indicator.



$$\begin{array}{l}HOOCCH_2\\HOOCCH_2\end{array}\!\!>NCH_2CH_2N<\!\!\begin{array}{l}CH_2COOH\\CH_2COOH\end{array}$$

(EDTA)

Problems :

1. Calculate the pH of 0.001(N) H_2SO_4 solution. The concentration of H^+ ion in 0.001 (N) H_2SO_4 and solution is 0.001 mol·litre^{-1}.

   $\therefore$ pH $= -\log [H^+]$
   $= -\log (0.001)$
   $= -\log 10^{-3}$
   $= 3$

2. What is the pH of 0.1(N) NaOH solution?

   The OH^- ion concentration of 0.1N NaOH = 0.1 mol·litre^{-1}.

   $\therefore$ p(OH) $= -\log [OH^-]$
   $= -\log [0.1]$
   $= -\log 10^{-1}$
   $= 1$

   But pH + pOH = 14
   $\therefore$ pH= 14 – pOH
   = 14 – 1
   = 13.

3.8 Questions

1. What do you mean by ionization and ionic product of H_2O ?
2. What is the degree of dissociation of water at 25°C ?
3. Define pH and pOH of a solution or a system. What is pH scale ?
4. What is a buffer solution? Classify buffer solutions.
5. Explain the mechanism of buffer action.
6. How do you determine the pH of a buffer solution ?
7. What is Handerson's equation ?
8. What is buffer capacity ?
9. What is an indicator? Give examples of some acid base indicators and their pH-range with colour in acid and alkaline medium.
10. What is a self indicator ?
11. Write the structures of phenolphthalein in acid and alkaline medium.