Course Title- **PHYSICAL CHEMISTRY II (ADVANCE PHYSICAL CHEMISTRY)**

**Course Code- DCECHE-105**

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# UN IT 1 CHEMICAL EQUILIBRIUM AND PHASE EQUILIBRIUM

Structure

## 1.1 INTRODUCTION

There exist a definite relationship between the concentration of reactants and products . The concept of ‘chemical equilibrium’ is an approach towards studying such relationships .The equilibrium system may involve one or more chemical species and one or more states of matter. System can be broadly divided into two classes based on the presence of either one (homogenous)or more phases (heterogeneous). Phase equilibrium deals with the behavior of heterogeneous system ,it governs phase rule which made possible to predict qualitatively by means of a diagram , the effect of changing pressure , temperature and concentration on a heterogeneous system in equilibrium.

## 1.1.1 Objectives

After studying this unit you should be able to :

- Compute equilibrium constant ,distribution constant
- Apply Phase rule
- Predict favourable conditions for the reactions
- Predict at particular temperatue and pressure how many phases can co –exist.
- Compute solubility in two solvents.
- Solve problems related to extraction of dissolved solute.

## 1.2 CHEMICAL EQUILIBRIUM

It is our experience that all chemical reactions are reversible upto some degree .The reaction proceeding in both the directions are called reversible reactions. Further , it is also well noted fact that many reactions do not go to completion, they usually leave considerable amount of unaffected reactants even after lapse of a sufficient time. In such cases, we can define chemical equilibrium as " it is a dynamic process in which the forward and reverse reactions occur simultaneously at equal rates in opposite direction reversibly so that the concentration of each species present remain constant at constant temperature and also there is no observable change in the properties of the system".

### 1.2.1 Equilibrium Constant and Free Energy

We may define the equilibrium constant as follows ," At equilibrium the ratio of the products of activity terms of the products to those of the reactants, each term being raised to the power equal to the number of times the molecules of that substances occur in the equation representing the chemical

For homogeneous equilibrium in ideal solutions and ideal gases,the activities may be represented by the molar concentration (as f=1 ; a =C ) or mole fractions (X's).

Let us consider a reversible reaction attaining equilibrium i.e.,

$$aA \ + \ bB \ \rightleftharpoons pP + qQ$$

$$K_c = \frac{[P]_P^p \ . \ [Q]_Q^q \ . \ \ldots\ldots}{[A]_A^a \ . \ [B]_B^b . \ \ldots\ldots} \qquad K_X = \frac{X_P^p \ . \ X_Q^q \ . \ \ldots\ldots}{X_A^a \ . \ X_B^b . \ \ldots\ldots}$$

for homogeneous gaseous reactions molar concentrations of a substance is proportional to its partial pressure (P) at constant temperature.

$$K_P = \frac{P_P^p \, . \, P_Q^q \, . \quad \ldots\ldots}{P_A^a \, . \, P_B^b . \quad \ldots\ldots}$$

Properties of equilibrium constant:

1. These are not the true constants.
2. The expression for $K_P$ or $K_C$ or $K_X$valid only for reversible processes at equilibrium.
3. Temperature dependent
4. Give an idea about the extent to which particular reaction can takes place under specified conditions
5. Help in predicting quantitatively the effect of change of pressure, temperature and concentration.

**SAQ 1** Write the equilibrium constant expression for the synthesis of nitric oxide.

$$N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g)$$

$$K_P = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})}$$

$\Delta H^0$and $\Delta S^0$determine the magnitude of $\Delta G^0$and because K is a measure of the ratio of the concentration of products to the concentration of reactant , we should be able to express K in terms of $\Delta G^0$and vice -versa. $\Delta G$ is equal to the maximum amount of work that a system can perform on its surrounding while doing a spontaneous change .For a reverse process that does not involve external work,we can express the change in free energy in terms of volume,pressure, entropy and temperature .The relationship is

$$\Delta G = V\Delta P - S\Delta T \qquad (2.2.1)$$

at constant temperature $\Delta T = 0$ then

$$\Delta G = V\Delta P \qquad (2.2.2)$$

under normal condition , the pressure dependence of free energy is not important for solids and liquids because of their small molar volume but for gases the effect of pressure on free energy is very important.

Assuming ideal gas behavior V we can be replaced by $\frac{nRT}{P}$ (where n is a number of moles of gas and R is the ideal gas constant) andexpress $\Delta G$in terms of the initial and final pressure ($P_i$ and $P_f$ respectively )

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P = nRT\frac{\Delta P}{P} = nRT \ln\left(\frac{P_f}{P_i}\right) \qquad (2.2.3)$$

if the initial state is the standard state with $P_i$ = 1 atm , then the change in free energy of a substance when going from the standard state to another state with a pressure P can be written as follows :

$$G - G^0 = nRT \ln P$$

$$\text{Or } G = G^0 + nRT \ln P$$

Considering the reaction we can write

$$\Delta G = \Delta G^0 + nRT \ln K_p \qquad (2.2.4)$$

$\Delta G = 0$ in reversible reaction therefore the equation becomes

$$\Delta G^0 = - nRT \ln K_p \qquad (2.2.5)$$

Equation (2.2.5) represents the relation between standard free energy and equilibrium constant.

**SAQ 2** Calculate K for reaction which has $\Delta G^0$ value -20 kcal at $25^0$ C .

$$\Delta G^0 = - 2.303\ RT \log K$$

If $\Delta G^0$ is given in calories then R= 1.99 T= 273+25 =298 K

$$-\log K = \frac{\Delta G^0}{(2.3o3)(1.99)(298)} = \frac{-20000}{1365.75} = -14.7$$

$$\log K = 14.7$$

Taking antilog $K = 5 \times 10^{14}$

### 1.2.2 Thermodynamic Derivation of Law of Mass Action

The law of mass action and hence the expression for equilibrium constant, K can be derived from thermodynamic considerations as follows:

Consider a general reaction

$$aA + bB + \ldots\ldots \rightleftharpoons pP + qQ\ldots\ldots.$$

The change in free energy of the reaction is given by

$$\Delta G = \sum(G)_{\text{Products}} - (G)_{\text{Reactants}}$$

$$= (pG_p + qG_Q + \ldots\ldots\ldots) - (aG_A + bG_B + \ldots\ldots\ldots)$$

$$= (p\mu_p + q\mu_Q + \ldots\ldots\ldots) - (a\mu_A + b\mu_B + \ldots\ldots\ldots) \qquad (2.3.1)$$

Where $\mu_A$, $\mu_B$ ,$\mu_p$ ,$\mu_Q$ etc. represent the chemical potentials (i.e. free energy per mole) of the various species. We know that the chemical potential of a substance in the mixture is related to its activity (a) by the relation.

$$\mu = \mu^o + RT \ln a \qquad (2.3.2)$$

where μ° is the chemical potential of the pure substance in standard state of unit activity at 298 K. Substituting the value of chemical potentials from (2.3.1) to (2.3.2), we have,

$$\Delta G = [p(\mu^o_p + RT \ln a_p) + q(\mu^o_q + RT \ln a_q) + \ldots\ldots\ldots]$$

$$- [a(\mu^o_A + RT \ln a_A) + b(\mu^o_B + RT \ln a_B) + \ldots\ldots\ldots]$$

$\Delta G = [(p\mu^{o}_{p} + q\mu^{o}_{Q} + \ldots\ldots) \square (a\mu^{o}_{A} + b\mu^{o}_{B} + \ldots\ldots)]$

$+ RT[(p \ln a_p + q \ln a_Q + \ldots\ldots) \square (a \ln a_A + b \ln a_B + \ldots\ldots)]$

$$\text{Or} \qquad \Delta G = \Delta G^{\circ} + RT \ln \frac{a_P^p \,.\, a_Q^q \,.\, \ldots\ldots}{a_A^a \,.\, a_B^b . \ \ldots\ldots} \qquad (2.3.3)$$

Where $a_A$, $a_B$, $a_P$, $a_Q$ etc. are the activities of A, B , P, Q etc., respectively. The quantity $\Delta G^{\circ}$ is the free energy change of the reaction when all the reactants and products in their standard state (i.e. at unit activity and at 298 K).

Now, At equilibrium the change in free energy of the system at constant temperature and pressure should be zero, i.e.$\Delta G = 0$. Hence, we get

$$0 = \Delta G^{\circ} + RT \ln \frac{a_P^p \,.\, a_Q^q \,.\, \ldots\ldots}{a_A^a \,.\, a_B^b . \ \ldots\ldots}$$

$$\Delta G^{0} = \square RT \ln \frac{a_P^p \,.\, a_Q^q \,.\, \ldots\ldots}{a_A^a \,.\, a_B^b . \ \ldots\ldots} \qquad (2.3.4)$$

For a given reaction at constant temperature,$\Delta G^0$ is constant, thus right hand side of the

$$\ln \frac{a_P^p \,.\, a_Q^q \,.\, \ldots\ldots}{a_A^a \,.\, a_B^b . \ \ldots\ldots} = \frac{\square \Delta G^0}{RT} = Z \text{ (constant, since T is constant)}$$

Therefore

$$K_a = \frac{a_P^p \,.\, a_Q^q \,.\, \ldots\ldots}{a_A^a \,.\, a_B^b . \ \ldots\ldots} \qquad (2.3.5)$$

Where$K_a$ is the thermodynamics equilibrium constant .It is expressed in terms of activities of constituents and hence it is valid for both ideal and non-ideal system. Equation (2.3.5) can be rewritten in terms of concentration (when f= 1; a=C ) ,mole fraction (X) and partial pressure(P, for gaseous reactions ) to obtain corresponding expression for $K_C$, $K_X$ ,$K_P$respectively as a stated earlier ..

### 1.2.3 Le Chatelier's Principle

It is concluded from the studies that physical and chemical equilibrium in a system depends on various factors like temperature, pressure, concentration of one or more of the substances involved in equilibrium, addition of foreign substances etc. These factors are called ‘parameters’. A change in any one of these parameters may change the composition of an equilibrium mixture. This is sometimes called “shift in the equilibrium”

The general principle governing qualitatively the effect of various parameters on the equilibrium was proposed by Le chatelier and it is also called the principle of **mobile equilibrium** or the Le **Chatelier's Principle.** According to this principle " if a system in equilibrium is disturbed by changing the pressure or the temperature of the overall system or by the concentration of one or more of the substances involved in the equilibrium , the system adjust itself in such a way that tends to undo the effect of the change as far as possible ". The system relieves its stress by shifting the equilibrium towards right or left that is towards forward or reverse direction .The effect of various parameters on a few well known physical and chemical equilibria has be discussed below.

## CHEMICAL EQUILIBRIUM

### Effect Of Pressure : Homogeneous Chemical Equilibria In Gas Phase

Pressure variations only affect equilibrium in gas phase reactions for which n(product)≠ n (reactant) ($\Delta n \neq 0$). An increase in pressure will shift the equilibrium towards the side having a few moles (low pressure) of gas and decrease in pressure will shift the equilibrium to the side having more moles (high pressure) of the gas. Thus, for example, an increase in pressure for the reaction

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)\ ;\ \Delta n = -1$$

will favour the formation of $NH_3$ that is the equilibrium will shift towards right because along this direction the system has tendency to reduce the number of moles.

when n (product) = n (reactant) , $\Delta n = 0$ in gas-phase reactions, changing the pressure will have no effect on the equilibrium

$$N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g)\ ;\ \Delta n = 0$$

### Heterogeneous Chemical Equilibria

The effect of pressure on equilibrium reactions involving gases and liquids or solids is usually due to change in gaseous molecules only because molar volume of gases are too much larger than of solids and liquids .Similarly in equilibrium reaction of solids or liquids with no gases, the pressure effect is usually very small .

$$\text{(i)}\ CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

$$\text{(ii)}\ CH_3COOH\ (\ell) + C_2H_5OH\ (\ell) \rightleftharpoons CH_3COOC_2H_5\ (\ell) + H_2O\ (\ell)$$

Inthe first case, ifthepressure is increased,the system will tend to consume $CO_2$to form$CaCO_3$, thereby decreasing its number of moles (or pressure). Thus, the equilibrium will shift towards left that is backward direction .In the second case the change of pressure does not alter the state of equilibrium

## Effect of Temperature

When the temperature of a system at equilibrium is raised, the equilibrium is displayed in the direction which absorbs heat. Every equilibrium system involves one endothermic and one exothermic reaction. An increase in the temperature of the system will favour the endothermic reaction.Thus for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad ; \quad \Delta H^0 = -12.2 \text{ KJ}$$

The forward reaction is exothermic while reverse is endothermic. Thus,an increase in temperature would favour the endothermic (reversible) reaction that is decomposition of HI, so as to consume the added heat. In other words, increase in temperature will shift equilibrium in the direction of formation of $H_2$ and $I_2$ and vice-versa on decreasing temperature.

**Effect of Concentration**

In a chemical equilibrium,an increase in reactants concentration or decrease in product concentration will shift the equilibrium of a gas phase or liquid phase reaction towards the product side. A decrease in reactant concentration or an increase in the product concentration will shift the equilibrium towards the reactant side. Consider the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Adding $H_2$ or $I_2$ (or removing HI) will shift the equilibrium towards the right. While removing $H_2$ or $I_2$ (or adding HI ) will shift the equilibrium towards left . This is all due to the fact that the value of equilibrium constant (K) is constant at constant temperature. Thus the added substance is consumed (equilibrium is shifted) in such a way (either to the left or right) so as to maintain the value of K constant.

**Effect of Catalyst**

Catalyst only accelerate both forward and backward reaction rates equally .Thus they speed up the approach to equilibrium , but do not alter the equilibrium concentration that is the value of equilibrium constant (K) In other words a catalyst help in establishing the equilibrium quickly without affecting the state of equilibrium or equilibrium constant (K).

**SAQ 3** With the help of Le chatelier's principle work out the conditions which would favour the formation of Ammonia by Haber's process?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad ; \quad \Delta H^0 = -99.38 \text{ KJ}$$

According to Le Chatelier's Principle addition of either $N_2$ or $H_2$ or both , removal of $NH_3$ , high pressure , low temperature will favour the formation of ammonia .

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## 1.3 PHASE EQUILIBRIUM

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A state of **true equilibrium** or **phase equilibrium** is said to exist in a system when the same state can be obtained by approach from either direction. Thermodynamically true equilibrium is attained when the free energy content of the system is at a minimum for the given values of the variables for example equilibrium between Ice and liquid water at $0^0$and 1 atm pressure is a true equilibrium. At the given pressure, the temperature at which the two phases are in equilibrium is the same whether it is obtained by partial melting of ice or by partial freezing of water.

### 1.3.1 Statement and meaning phase, component and degree of freedom

#### 1.3.1.1 PHASE

A phase is defined as "any homogenous, physically distinct part of a system which is mechanically separated from other parts of the system by definite bounding surfaces".

A phase can exist in either state of matter, viz., solid liquid or gas. In general we have:

(i) **For gaseous system:** Only one phase is possible as gases are completely miscible with one another in all proportions.

**(II)For liquid system:** The number of phases is equal to the number of layers present in the system. For completely miscible liquids, the number of phases is equal to one.

**(III) For solid system**: In general, every solid constituent a single phase except when a solid solution is formed. So, the number of phases in the solid system is equal to the number of solids present. In solid solution, the number of phases is equal to one. Each polymorphic form and allotropic modification constitutes a separate phase.

A system consisting of one phase only is called **homogeneous system** and a system consists consisting of two or more phases is called a **heterogeneous system**.

Let us consider the equilibrium system for the decomposition of calcium carbonate when calcium carbonate is heated in a closed vessel, we have

$$CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

There are two solid phases and one gas phase .Hence it is a three phase system.

#### 1.3.1.2 COMPONENT

The number of components of a system is defined as, "the smallest number of independently variable constituents by means of which the composition of each phase can be represented by means of a chemical equation".

Constituents can either be elements or compound, to understand the above definition and to use it for finding the number of component of a system remember that:

(a) The chemical formula representing the composition of a phase is written on LHS.

(b) The rest of the chemical constituents existing independently in the system as represented by the chemical formulas are placed on RHS.

(c) The quantities of constituent on RHS can be made minus (-)or zero (0) to get at the composition of the phase on LHS.

(a) **One component system**: We know that water system consists of three phases **solid**(ice),**liquid**(water),**gas**(water vapours)

Solid water (ice) ⇌ Liquid water
Solid water ⇌ Water vapour
Liquid water ⇌ Water vapour
Solid water ⇌ Liquid water ⇌ Water vapour

Each of the three phases is nothing else but water. Hence, all the three phases can be represented in terms of the composition of only one constituent that is by the formula $H_2O$. So, water system is a one component system.

**(b)Two component system**: The case of dissociation of calcium carbonate is rather complicated. Its equilibrium can be represented as:

$$CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

The composition of all the three phases can be expressed in terms of either of the two components.Any two out of three substances can be chosen as the two components and this is clearly understood as follows :

(1) **When $CaCO_3$ and CaO are the two components :**

Phase Components
$CaCO_3 = CaCO_3 + 0\ CaO$
$CaO = 0CaCO_3 + CaO$
$CO_2 = CaCO_3 - CaO$

(2) **When $CaCO_3$ and $CO_2$ are the two components:**

Phase Components
$CaCO_3 = CaCO_3 + 0\ CO_2$
$CaO = CaCO_3 - CO_2$
$CO_2 = 0CaCO_3 + CO_2$

**(3) When CaO and $CO_2$ are the two components:**

Phase Components
$CaCO_3 = CaO + CO_2$
$CaO = CaO + 0CO_2$
$CO_2 = 0CaO + CO_2$

Hence, from the above three cases it is clear that only two constituents are needed to express the composition of each of the three phases. So,it is a two component system.

### 1.3.1.3 DEGREE OF FREEDOM OR VARIANCE

There are three variable factors, viz., temperature, pressure and concentration on which the equilibrium of a system depends. In some cases we have to mention only one factor to define the system completely sometime two or three. So the degree of freedom (or variance) of a system is defined as:

"The minimum number of independent variables such as temperature, pressure and concentration that must be ascertained so that a given system in equilibrium is completely defined".
A system with F =0 is known as **nonvariant** or having no degree of freedom.
A system with F =1 is known as **univariant** or having one degree of freedom.
A system with F =2 is equal is known as **bivariant** for having two degree of freedom.
Let us consider some example to explain degree of freedom:
(1) **For ice ⇌water⇌ vapour system ,F=0**: In this system the three phases ice ⇌water ⇌ vapour coexist at the freezing point of water . Since the freezing temperature of water has a fixed value,the vapour pressure of water has also a definite value. The system has two variables (temperature and pressure)and both these are already fixed. Thus the system is completely defined automatically, there being no need to specify any variable .Hence it has no degree of freedom (F=0).

(2) **For water ⇌ water vapour, F=1.**The system water in equilibrium with water vapour has two variables temperature and pressure. At a definite temperature the vapour pressure of watercan haveonly one fixed value. Thus if one variable (temperature or pressure) is a specified,the other is fixed automatically. Hence the water system has one degree of freedom (F=1).

(3)**For Pure gas, F=2**. For a given sample of any pure gas PV=RT. If the values of pressure (P) and temperature (T) be specified, volume (V) can have only one definite value, or that the volume (the third variable) is fixed automatically. Any other sample of the gas under the same pressure and temperature as a specified above will be identical with the first one. Hence a system containing a pure gas has two degree of freedom (F=2).

(4) **For a mixture of gases, F =3**. A system containing a mixture of two or more gases is completely defined when its composition, temperature and pressure is specified. If pressure and temperature only are specified, the third variable that is composition could be varied. Since it is necessary to specify three variables to define the system completely, a mixture of gases has three degree of freedom F=3.

### 1.3.2Derivation of Gibbs Phase rule

After understanding the definitions of phase, component and degree of freedom, we can now easily proceed to define the Phase rule given by **J. W. Gibbs.** According to it , if the equilibrium of a heterogeneous system is not affected by electrical or magnetic forces or by gravity, then the degree of freedom (F) , number of components (C) and number of phases (P) are connected by means of equation ,

$$F = C - P + 2$$

The mass of the phase does not enter into the equation, as it has no effect on the state of equilibrium. Above equation can be derived as follows.
Consider a heterogeneous system in equilibrium consisting of C components distributed in P phases .The degree of freedom of the system is equal to the number of independent variable which must be fix arbitrarily to define the system completely. The number of variables is equal to the total number of variables minus the number of variables which are defined automatically by virtue of the system being in equilibrium.
At equilibrium, each phase has the same temperature and pressure, so there is one temperature variable and one pressure variable for the whole system. So, these variables total two only.The number of composition (or concentration)variables, however is much more. In order to define the composition of each phase,it is necessary to mention (C – 1)

composition variables because the composition of the remaining component may be obtained by difference.Thus, for P phases the total number of concentration or composition variable will beP(C-1).

Total number of variables = P(C-1) + 1 + 1

For composition for temperature for pressure

= P(C-1) + 2

According to thermodynamics when heterogeneous system is in equilibrium at constant pressure and temperature, the chemical potential (μ) of any given component must be same in every phase. Therefore, if there is one component in three phases x, y and z and one of the of these phases, say x is referred to as standard phase, then this fact may represented in the form of two equations:

$$\mu 1\ (x) = \mu 1\ (y)$$
$$\mu 1\ (x) = \mu 1\ (z)$$

Each component in equilibrium in three phases two equations are known. In general, therefore for each component in P phases, (P – 1) equations are known. For C components, thus the number of equations or variables that are known from the condition of equilibrium are C (P-1) .Since chemical potential is a function of pressure,temperature and concentration, it means that each equation represent one variable. Therefore,the number of unknown variable (which should be fixed) or degree of freedom.

F = Total number of variables - Number of equations or variables

$$F = [\ P\ (C-1) +2\ ] – [\ C(P-1)]$$

$$F = C - P + 2$$

This equation is the phase rule equation as given by Gibbs.

**SAQ 4** How many phases are present in mixture of three gases $O_2$, $N_2$ and $CO_2$?

Ans. Is a one phase system.

**SAQ 5** Calculate the degree of freedom and number of components for a system of sodium Chloride solution in water containing undissolved salt , in equilibrium with water vapour?

**Ans.** Component 2(water and NaCl), Phases 3 (solution of NaCl, undissolved Salt, water vapour). Therefore degree of freedom is 1 using Gibbs phase rule.

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## 1.4 PHASE EQUILIBRIUM OF ONE COMPONENT SYSTEM

For a one component system we can write the phase rule equation as

$$F = C - P + 2 = 1 - P + 2 = 3 - P$$

Three cases may arise :

**Case 1 :** When only one phase is present

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

Thus the system is bivariant. It can be completely define by specifying the two variables temperature and pressure or that , both the temperature and pressure can be varied independently . Therefore a single phase is represented by **anareaon PT graph.**

**Case 2 :** When only two phases are in equilibrium .

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

The system has one degree of freedom and is termed as monovariant. This means that the pressure cannot be changed independently if we change the temperature. The pressure is fixed automatically for a given temperature. A two phase system is depicted by **a line on a PT graph.**

**Case 3 :** When only three phases are in equilibrium .

$F = C - P + 2 = 1 - 3 + 2 = 0$

The system has zero degree of freedom and is termed as nonvariant or invariant. This special condition can be attained at a definite temperature and pressure. The system is, therefore defined completely and no further statement of external conditions is necessary. A three phase system is depicted by **apoint on the PT graph**. At this point the three phases (solid,liquid,vapour ) are in equilibrium and therefore ,it is referred to as the **Triple point .**

**Phase Diagrams**

A phase diagram is a plot showing the conditions of temperature and pressure under which two or more physical states can exist together in a state of dynamic equilibrium. The diagram consists of regions or areas, lines or the curves and triple point. We will discuss phase diagram of one component system of Water, Sulphur and Helium.

### 1.4.1 The Water System

Under normal conditions the system‘water’ is a **three phase, one componentsystem**. The three phases involved are liquid water,ice, water vapour. All these phases can be represented by one chemical identity $H_2O$ and hence one component of the system.The number of phases which can coexist in equilibrium at any time depends on the conditions of temperature and pressure. The phase diagram or PT graph of the system water /ice /vapour is shown in figure 1.4.1. The silent features of the phase diagram are listed below.

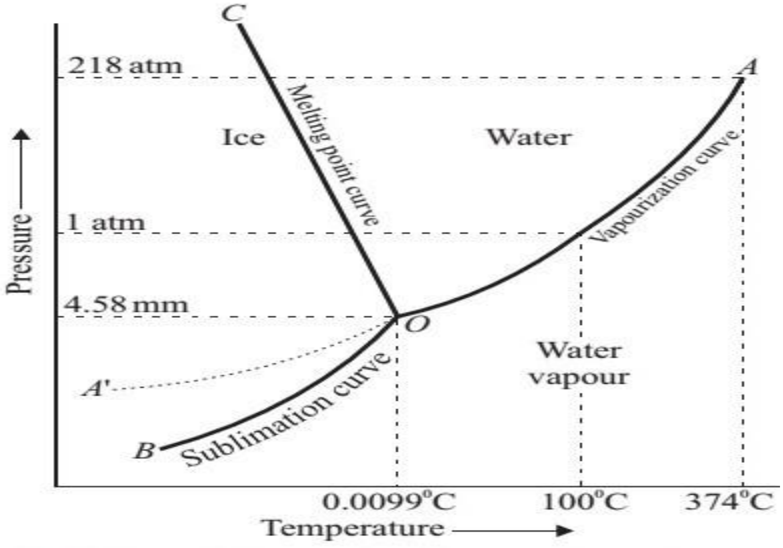

**Fig 1.4.1 The phase diagram of the system ‘Water’**

(1) The Curves OA,OB,OC
(2) The Triple Point O
(3) The Areas AOC,AOB,BOC
(4) Metastable System

Let us discuss the significance of each of these features.

**(1) The Curves OA, OB, OC**

These three curves meet at point O and divide the diagram into three regions or areas.

**Curve OA, the vapour pressure curve of water**. It represents the vapour pressure of liquid water at different temperatures. The two phases water and water vapour coexist in equilibrium along this curve.The curve OA terminates at A the critical point (218 atm, temp 347$^0$C) when the liquid and vapour are indistinguishable from each other and there is left one phase only. When the vapour pressure is equal to 1 atmosphere,the corresponding temperature as indicated on the phase diagram is the boiling point (100$^0$C ) of water

**Curve OB, the sublimation curve of ice**. It shows the vapour pressure of solid ice at different temperatures . The two phases solid ice and vapour coexist in equilibrium along this curve. At the lower limit the curve OBterminates at absolute zero (-273$^0$ C ) where no vapour exists

**Curve OC ,the fusion of Ice.** It depicts the effect of pressure on the melting of ice. Here ice and water coexist in equilibrium. The fact that OC slopes to the left indicates that the melting point of ice decreases with increase of pressure. Since ice melts with decrease in volume by Le Chatelier's principle the melting point is lowered by an increase of pressure. It may be noted that the 1 atmosphere line meets the fusion curve at 0$^0$C which is the normal melting point of ice.
Along the curves OA, OB , OC there are two phases in equilibrium and one component therefore.
$F = C - P + 2 = 1 - 2 + 2 = 1$
Hence each two – phase system :
Water / water vapour represented by OA
Ice / water vapour represented by OB
Ice / water represented by OC has one degree of freedom that is monovariant.

**(2) The triple point 'O' .** The curves OA, OB ,OC meet at triple point 'O' where all the three phases liquid water/ ice /vapour are in equilibrium .This occur at 0.0099$^0$ C and vapour pressure 4.58 mm Hg . Since there are three phases and onecomponent,we have
$F = C - P + 2 = 1 - 3 + 2 = 0$
That is the system at the triple point is nonvariant. Thus if either the pressure or temperature is changed, the three phases would not exist and one of the phases would disappear.

**(3) The Areas AOC,AOB,BOC**
The areas or regions between the curves show the conditions of temperature and pressure under which a single phase –**ice, water or vapour** is capable of stable existence. Thus
Area AOC represents conditions for the one- phase system **water**.
Area AOB represents conditions for the one- phase system **water vapour**.
Area BOC represents conditions for the one- phase system**ice**.
In all the three areas there being one- phase and one-component, we have
$F = C - P + 2 = 1 - 1 + 2 = 2$
Thus each system water, water vapour or Ice has 2 degrees of freedom that is the system is **bivariant**.

(4) **Metastable system : supercooled water / vapour system**
The vapour pressure curve of water OA can be continued past the triple point as shown by the dashed line OA' . That is,water can be supercooled by carefully eliminating solid particles. The supercooled water/ vapour system is metastable (unstable) .It at once reverts to the stable system ice / vapour on the slightest disturbance or introducing a crystal of ice.

**Summary**

- Solid water is less dense than liquid water just above the freezing point.
- The critical temperature ($T_c$) of a substance is the highest temperature at which the substance can possibly exist as a liquid.
- The critical pressure ($P_c$) is the pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid.

- The critical point is the intersection point of the critical temperature and the critical pressure.

**SAQ6** Why does the melting point of ice get lower at higher pressures?

Water has an unusual phase diagram: its melting point decreases with increasing pressure because ice is less dense than liquid water.

**SAQ 7** Can you compress steam to form a liquid if the temperature is above 374°C?

It cannot exist as a **liquid above** this **temperature**, regardless **of** the pressure. .

**SAQ 8**What is the critical pressure of water?

218 atm is the critical pressure of water.

### 1.4.2 The Sulphur System

It is a **one component,four phase system**.

The four phases are:

(a) Two solid polymorphic forms: Rhombic Sulphur ($S_R$) and Monoclinic Sulphur ($S_M$)

(b) Sulphur Liquid ($S_L$)

(c) Sulphur vapour ($S_V$)

All the four phases can be represented by the only chemical individual'sulphur' itself and hence one component of the system .The two crystalline forms of sulphur $S_R$ and $S_M$ exhibit in enantiotropy with a transition point at $95.6^0$C. Below this temperature $S_R$ is stable, while above $S_M$ is the stable variety. At $95.6^0$C each form can be gradually transform to the other and the two are in equilibrium. At $120^0$ C , $S_M$melts . Thus

$$S_R \overset{95.60\ C}{\Longleftrightarrow} S_M \overset{120\ C}{\Longleftrightarrow} S_L$$

The phase diagram for the sulphur is shown in the figure 1.4.2 .The salient features of the phase diagram are described below.
(a) The six curves AB, BC, CD, BE, CE, EG
(b) The three triple points B, C, E
(c) The four areas:
ABG marked 'solid Rhombic'
BEC marked 'solid Monoclinic'
GECD marked 'liquid sulphur'
ABCD marked 'sulphur vapour'
(d) Metastable equilibria
Let us explain the significance of these features:

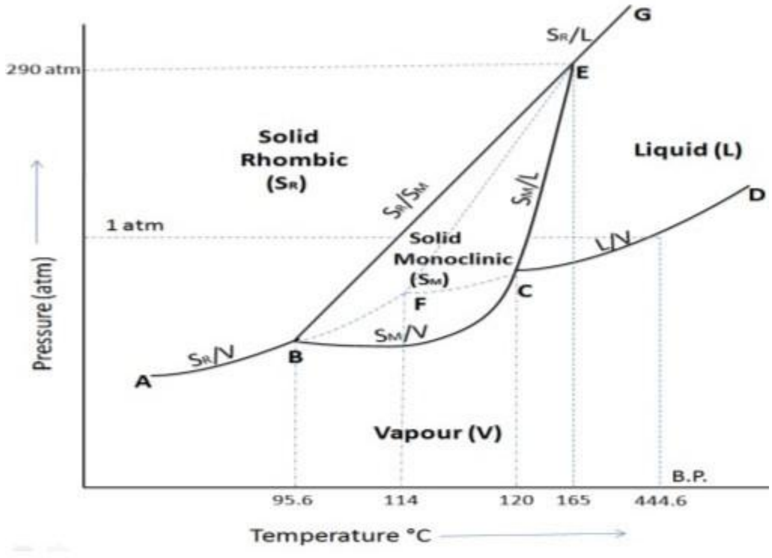

**Fig: 1.4.2 The phase diagram of Sulphur System**

**(a) The curves AB, BC, CD, BE, CE, EG**

These six curves divide the diagram into four areas.

**Curve AB, Vapour Pressure curve of $S_R$ .** It shows that the vapour pressure of solid rhombic Sulphur ($S_R$) at different temperature. Along this curve the two phases $S_R$ and sulphur vapour ($S_V$) are in equilibrium. The System $S_R$/ $S_V$ has one degree of freedom.
$F = C - P + 2 = 1 - 2 + 2 = 1$ that is , it is monovariant.

**Curve BC , Vapour Pressure curve of $S_M$ .** It shows variation of the vapour pressure of solid monoclinic Sulphur ($S_M$ ) with temperature. Along this curve the two phases $S_M$ and sulphur vapour ($S_V$ ) coexist in equilibrium. The System $S_M$ / $S_V$ has one degree of freedom (monovariant).

**Curve CD , Vapour Pressure curve of $S_L$ .** It depicts the variationof the vapour pressure of liquid Sulphur (SL ) with temperature. Along this curve the two phases SL and sulphur vapour ($S_V$ ) coexist in equilibrium. The System SL / SV has one degree of freedom (monovariant). One atmosphere line meets this curve at a temperature ($444.6^0$C) which is the boiling point of Sulphur.

**Curve BE, The Transition curve .**It shows that effect of pressure on the transition temperature for $S_R$ and $S_M$. As two solid phases are in equilibrium along the curve, the system $S_R$/ $S_M$ is monovariant . The transformation of SRand SM is accompanied by increase of volume (density of $S_R$= 2.04 : $S_M$ = 1.9) and absorption of heat that is

$$S_R + Q \text{ ( heat energy )} \rightleftharpoons S_M$$

Thus the increase of pressure will shift the equilibrium to the left(Le Chatelier'sprinciple) and the transition temperature will , therefore be raised. This is why the line BFslopes away from the pressure axis showing thereby that the transition temperature is raised with increase of pressure.

**Curve CE, the fusion curve of $S_M$.** It represents the effect of pressure on the melting point of $S_M$. The two phases in equilibrium along this curve are $S_M$ and $S_L$ . The system $S_M$ / $S_L$ is monovariant .As the melting or fusion of $S_M$is accompanied by slight increase of volume , the melting point will rise by increase of pressure ( Le chatelier's principle ) . Thus theCurve CE slopes slightly away from the pressure axis. The curve ends at E because $S_M$ceases to exist beyond this point.

**Curve EG, the fusion curve for $S_R$.** Here the two phases in equilibrium are $S_R$ and $S_L$. The number of phases being two, the system $S_R$ / $S_L$ is monovariant .

**(b)The Triple points B, C, and E**

**Triple point B**. This is the meeting. of the three curves AB , BC and BE .Three phases , solid $S_R$ ,solid $S_M$ and $S_V$ are in equilibrium at point B .There being three phases and one component .The system is $S_R$ / $S_M$ /$S_V$ is nonvariant.

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

At B, $S_R$ is changed to $S_M$ and the process is reversible. Thus the temperature corresponding to B is the transition temperature (95.6$^0$ C ).

**Triple point C.** The curves BC, CD, CE meet at this point. The three phases in equilibrium are $S_M$,$S_L$ and $S_V$.There being three phases and one component, the system $S_M$ / $S_L$ /$S_V$ is nonvariant. The temperature corresponding to C as indicated on the phase diagram is 120$^0$C. This is the melting point of $S_M$.

**Triple point E.** The two lines CE and BE, having different inclination away from the pressure axis, meet at E where a third line EG also joins. The three phases $S_R$, $S_M$ and $S_L$ .are in equilibrium and the system at a point E is nonvariant is. This points gives the condition of existence of the systemS$_R$ / $S_M$/ $S_L$at155$^0$ C and 1290 atmospheric pressure.

**(c)The Areas**

The phase diagram of the sulphur system has **four areas** Or**regions** .These are labeled as rhombic sulphur, monoclinicsulphur, liquid sulphur and vapour. These represent single phase system which has two degree of freedom.

$F = C - P + 2 = 1 - 1 + 2 = 2$ that is each of the systems $S_R$ ,$S_M$ , $S_L$ and $S_V$are bivariant .

**(d) Metastable Equilibria**

The change of $S_R$ to $S_M$ takes place very slowly. If enough time for the change is not allowed and $S_R$ is heated rapidly, it is possible to pass well above the transition temperature without getting a $S_M$ .In that case , there being three phases( $S_R$ , $S_L$ ,$S_V$) only and one component , the phase diagram , like that of water system , will consist of three curves ,one triple point and three areas .

**The dashed curve BF , the Vapour Pressure curve of metastable $S_R$ .** This is the continuation of the vapour pressure curve AB of stable the metastable $S_R$ .The metastable phases $S_R$ and $S_V$are in equilibrium along this curve. It is nonvariant system.

**The dashed curve CF , the Vapour Pressure curve ofsupercooled $S_L$** .On supercooling liquid sulphur , the dashed curve of CF is obtained .It is in fact the back prolongation of DC. The curve CF represents the metastable equilibrium between supercooled $S_L$ and $S_V$.Thus it may be designated as a vapour pressure curve of supercooled $S_L$ .It meets the dashed BF at F .

**The dashed curve EF,the Fusion curve of metastable $S_R$ .** The two metastable phases $S_R$and $S_L$ are in equilibrium along this curve and the system is monovariant . This shows that the meltingpoint of metastable $S_R$ is increased with pressure. Beyond E this curve depicts the condition for the stable equilibrium $S_R$ / $S_L$ as the metastable $S_R$ disappears .

**The metastable Triple point F.** At this point,three metastable phases $S_R$, $S_L$and $S_V$are in equilibrium. The system is a metastable triple point with no degree of freedom. Thecorresponding temperature is the melting point of metastable $S_R$ (114$^0$C).

**SAQ9 How many triple point exit in Sulphur system?**

Ans: There are 4 triple point in Sulphur system out of which one is metastable triple point.

### 1.4.3 The Helium System

Helium is a remarkable and unique element. He atoms attract each other so weakly that He remains a gas until 4.2 K or so at ordinary pressures, and the liquid does not solidify until the pressure is raised to about 2.5 MPa (or about 25 atm) at temperatures of<1.5 K. Liquid helium is also fascinating in that the weak interactions coupled with the small mass of He leads to the appearance of a liquid-liquid phase transition at around 2.1 K and 1 atm pressure. The normal liquid undergoes a transition to a superfluid phase at and below 2.1 K;

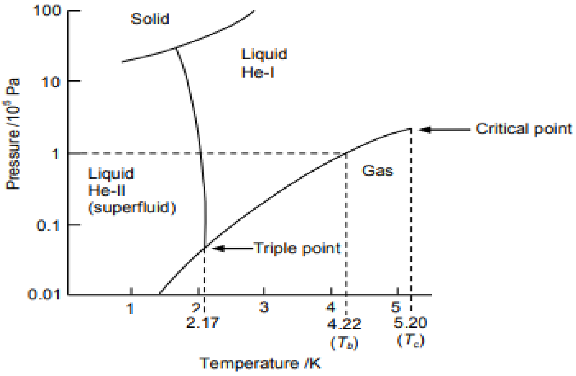

Fig 1.4.3 The Phase Diagram of Helium System

The unique properties of helium-3 come from not only its small mass, roughly 75% that of helium-4, but also to quantum mechanical consequences that are unexpected. The proton and neutron both have nuclear spins with spin quantum numbers of 1/2 (recall how proton NMR works). In 4He, these inherent nuclear angular momenta must add to a total quantum number that is an even integer, and in fact, the sum is zero. But in 3He, the sum must be half integral (its 1/2, in fact), and that makes a huge difference.This leads to appearance of two superfluid liquids having different magnetic behavior.

Phase diagram includes 4 areas having two superfluid liquids, vapour helium and solid helium. Areas have only one phase thus degree of freedom is two according to phase rule for one component system (Helium). Lines includes following equilibriums between two phases – helium gas / superfluid liquid (I),helium gas / superfluid liquid (II),superfluid liquid (I)/ superfluid liquid (II),helium solid /superfluid liquid (I),heliumsolid /superfluid liquid (II). As here two phases coexist thus dergree of freedom is one for having one component system. Beside this there exit two triple point - superfluid liquid (I)/ superfluid liquid (II) / helium gas andsuperfluid liquid (I)/ superfluid liquid (II) / helium solid. Here degree of freedom is zero as three phases coexist together.

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**SAQ 10** Describe two unusual properties of helium (other than the “superfluid” He-II phase) that are not shared by most substances.

The unusual properties of helium that can be deduced from the phase diagram include:

(i) It has 2 triple points.

(ii) There is no gas/solid equilibrium line (i.e. helium does not sublime).

(iii) There is a liquid/liquid equilibrium line.

(iv) The triple points involve 2 liquid phases.

(v) Helium cannot exist as a solid at atmospheric pressure.

**SAQ 11** Is it possible to liquefy helium above 5.20 K? Explain your answer
No. If T > 5.2 K, helium exists as a supercritical fluid above ~2 × 105 Pa and as a gas below this pressure.

**SAQ 12** Why is the liquefaction of He very difficult, even at low temperatures?
Intermolecular forces between He atoms are extremely weak. The electrons are held very tightly in the small 1s orbital. The atom is therefore very small and the electron cloud is not very polarizable. As a result, the interatomic dispersion forces required for liquefaction are very weak and they can only sufficient to keep He atoms in a liquid phase at temperatures approaching absolute zero.

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## 1.5 PHASE TRANSITION

The following conditions must be satisfied for the existence of equilibrium between two phases in a system:

**(1) Thermal equilibrium:** All phases must be at the same temperature, otherwise heat will flow from one phase to another. Consider two phases A and B at temperature $T_A$ and $T_B$respectively . Let $S_A$ and$S_B$the entropy of the two phases and let be dq be the heat transferred from phase A to B at equilibrium.The entropy change of the system is given by

$dS = d S_A + d S_B = 0$

We know,$d S_A = -\frac{dq}{T_A}$ and $d S_B = +\frac{dq}{T_B}$

$\left(\frac{-dq}{T_A}\right)+\left(\frac{+dq}{T_B}\right)+ = 0$or $T_A = T_B$

**(2) Mechanical Equilibrium:** All the phases must be at the same pressure , otherwise the volume of one phase will increase at expense of the other phase . Suppose A-phase is expanded to B-phase and volume change dV . Then the change of helmholtz free energy (A) at constant temperature is given by.

$dA = -d A_A + d A_B = 0$ (at equilibrium )

Weknow,$d A_A = - P_A\, dV$ $d A_B = - P_B\, dV$ (At constant T )

At equilibrium,$d A_A = d A_B$ , so $P_A = P_B$.

**(3) Chemical Equilibrium :** For a system of two or more phases at equilibrium , the chemical potential of a component will be the same in both or all phases.

The term phase transition is most commonly used to describe transitions between solid, liquid, and gaseous states of matter, as well as plasma in rare cases. A phase of a thermodynamic system and the states of matter has uniform physical properties. During a phase transition of a given medium, certain properties of the medium change, often discontinuously, as a result of the change of external conditions, such as temperature, pressure, or others. For example, a liquid may become gas upon heating to the boiling point, resulting in an abrupt change in volume. The measurement of the external conditions at which the transformation occurs is termed the phase transition.

At the phase transition point (for instance, boiling point) the two phases of a substance, liquid and vapor, have identical free energies and therefore are equally likely to exist. Below the boiling point, the liquid is the more stable state of the two, whereas above the gaseous form is preferred.

It is sometimes possible to change the state of a system diabatically (as opposed to adiabatically) in such a way that it can be brought past a phase transition point without undergoing a phase transition. The resulting state is metastable, i.e., less stable than the phase to which the transition would have occurred, but not unstable either. This occurs in superheating, supercooling, and supersaturation.

Phase transitions often involve the development of some type of order with an associated symmetry breaking. The broken symmetry is described by an order parameter which usually increases on moving deeper into the ordered phase, and which measures the degree of order as the phase transition proceeds. The order parameter is a physical observable, usually related to a first derivative of G. Examples of order parameters are magnetisation M for a ferromagnet, electrical polarisation P for a ferroelectric, and the degree of alignment of the molecules in a liquid crystal.

## 1.5.1 First Order Phase Transition

First-order phase transitions are those that involve a latent heat. During such a transition, a system either absorbs or releases a fixed (and typically large) amount of energy per volume. During this process, the temperature of the system will stay constant as heat is added: the system is in a "mixed-phase regime" in which some parts of the system have completed the transition and others have not. Familiar examples are the melting of ice or the boiling of water (the water does not instantly turn into vapor, but forms a turbulent mixture of liquid water and vapor bubbles).

It is actually discontinuous phase transitions which are being characterized by a discontinuous change in entropy at a fixed temperature. The change in entropy corresponds to latent heat $L = T\,\Delta S$. Examples are solid–liquid and liquid–gas transitions at temperatures below the critical temperature.

First order transitions have discontinuities in the first derivatives of G

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$

First order transitions are therefore discontinuous

## 1.5.2 Second Order Phase Transition

**Second-order phase transitions**are also called "continuous phase transitions".Continuous phase transitions involve a continuous change in entropy, which means there is no latent heat. Examples are liquid–gas transitions at temperatures above the critical temperature, metal–superconductor transitions and many magnetic ordering transitions. It also exist between normal conductivity and super conductivity in certain metals ; for example Hg ,Sn,Pb , Al on being cooled to characteristic temperature (4.2 K for Hg at 1 atm ; 7.2 K for Pb at 1 atm ) become supercoductors with zero electrical resistance.

Second order transitions have discontinuities in the second derivatives of G.

$$\left[\frac{\partial^2 G}{\partial T^2}\right]_P = \frac{-C_p}{T}, \left[\frac{\partial^2 G}{\partial P^2}\right]_T = -Vk_T \quad , \left[\frac{\partial^2 G}{\partial T \partial P}\right] = V\,\beta_P$$

**SAQ 13**Differentiate first and second order phase transition in terms of continuity ?

First-order phase transitions are discontinuous in the first derivative whereassecond-order phase transitions are continuous in the first derivative (the order parameter, which is the first derivative of the free energy with respect to the external field, is continuous across the transition) but exhibit discontinuity in a second derivative of the free energy.

**SAQ 14** Give salient features of First-order phase transitions ?
Salient features of First-order phase transitions are

- Entropy (S) changes discontinuously
- Volume (V) changes discontinuously
- Gibbs free energy (G) doesn't changes

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## 1.6 PHASE EQUILIBRIUM OF TWO COMPONENT SYSTEM

When single phase is present in two components the degree of freedom is three.

$$F = C - P + 2 = 2 - 1 + 2 = 3$$

This means that three variables must be specified in order to describe the condition of the phase . Thus in such a case system,in addition to pressure and temperature the concentration of one of the components has also to be given. For graphical representation of these variables, three coordinate axes at right angles to each other would be required.Therefore the phase diagram of obtained would be a solid model.

### 1.6.1 Solid liquid equilibria

For the sake of having simple plane diagrams we generally consider only two variables ,the third one being a constant .For example for solid / liquid equilibrium , the gas is usually absent and the effect of pressure on the equilibrium is very small . Thus when a two component system consists of solid and liquid phases only, the effect of pressure may be disregarded. Thenit is necessary to take into account the remaining variables viz., temperature and concentration. **Such a solid / liquid system with the gas phase absent is called a condensed system.**

The experimental measurements of temperature and concentration in condensed systems are usually carried out under atmospheric pressure. Since the degree of freedom in such case is reduced by one,we may write the **Reduced Phase rule** as

$$F' = C - P + 1$$

Where F'gives the remaining degrees of freedom of the system. The reduced phase rule is more convenient to apply to solid / liquid two component condensed system.

Since the only variable for two component solid / liquid equilibrium systems are temperature and composition, the phase diagram for such systems consists of Temperature - Concentration graphs (TC graphs).

### 1.6.2 Simple eutectic system Pb-Ag System

This system has **two components** and **four phases**. The phases are solid silver, solid lead,solution of molten silver and lead and vapour. The boiling points of silver and lead being considerably high, the vapour pressure is practically absent. Thus Pb / Ag is a condensed system with three phases. In such a case, pressure can have no effect on the system. Therefore we need to consider only two remaining variables, namelythe temperature (T) and concentration (C). The complete TC diagram of the system Pb / Ag is shown in figure 1.6.2

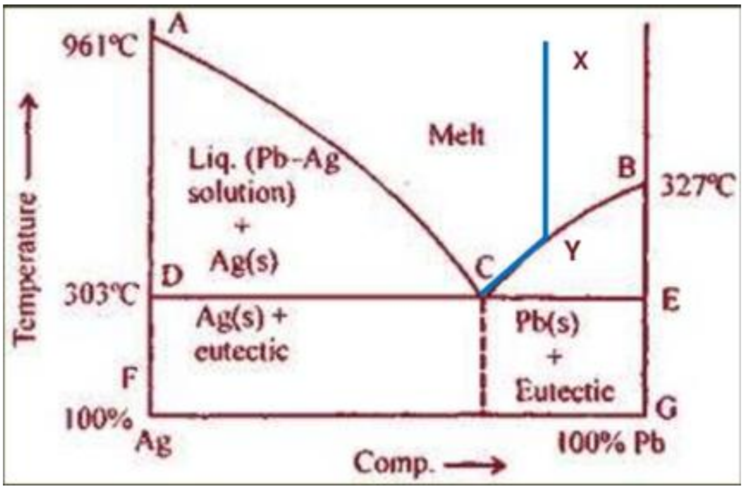

**Fig. 1.6.2 The Phase diagram of Pb/Ag system**

**The salient features of the diagram are**:

(a) Two curves AC and BC
(b) Eutectic point C
(c) Three areas (I) above ACB (II) below AC (III) below BC

**Curve AC: the freezing point curve of Ag**. A represents the freezing point or melting point of solid silver ($961^0$C) and the curve AC shows that the addition of lead lowers the melting point along it . The phases in equilibrium along AC are solid silver and solution of silver and lead. Applying the reduced Phase rule equation

$F' = C - P + 1 = 2 - 2 + 1 = 1$

Thus the system Ag / solution (Ag / Pb) is monovariant.

**Curve BC: the freezing point curve of Pb**. B represents the melting point of solid lead ($327^0$C) and the curve BC shows that the melting point is lowered by addition of silver. The phase in equilibrium along BC are solidlead and solution ( Pb /Ag ) . The system is monovariant .

**The Eutectic point C**. The curves AC and BC intersect at C, which is called the **eutectic point**. Here three phases solid Ag, solid Pb and solutions Pb/Ag are in equilibrium. Applying the reduced Phase rule equation

$F' = C - P + 1 = 2 - 3 + 1 = 0$

Thus the system Ag/ Pb/ solution ( Pb /Ag) at C is nonvariant. Both the variables, temperature ($303^0$C) and composition (97.5 % Pb , 2.5 % Ag) are fixed . If you change the temperature above the eutectic temperature the solid phases Ag and Pb disappear and if you cool below it, you will land in the solid Ag/ PB area where solution phase is nonexistence.

**The area above AOC**. This region represents the single phase system, the solution of molten Ag and PB . Applying the reducedphaserule equation. We have

$F' = C - P + 1 = 2 - 1 + 1 = 2$

Thus the System Solution Ag / Pb is bivariate.

The area below AC represents the phases Ag + solution, while that below BC the phases Pb + solution.The area below the temperature $303^0$C represents solid Pb + solid Ag. All these areas have two phases and one degree of freedom.

$F' = C - P + 1 = 2 - 2 + 1 = 1$

## 1.6.3 Desilverisation of lead

The process of recovery of silver from argentiferous lead is based on the facts contained in the **Fig. 1.6.2.** The argentiferous lead containing small amount of silver (less than 0.1%) is melted well above the melting temperature ofpure lead (327$^0$C ).Let the point X represent the system 'molten lead' in the diagram .It is then allowed to cool when the temperature of the melt falls along the dashed lineXY. As the temperature correspond to Y on the curve BC is reached solid lead begins to separate and the solution would contain relatively larger amount of silver. On further cooling more of the lead separates and we travel along the curve BC until the eutectic point C is reached. Lead is continuously removed by means of ladles and the percentage of silver in the meltgoes on increasing. At C,an alloy containing 2.5 % Ag and 97.5 % Pb is obtained . This is treated for the recovery of silver profitability.

**SAQ 15** What do you mean by eutectic point?
The point in a phase diagram indicating the chemical composition and temperature corresponding to the lowest melting point of a mixture of components.

## 1.7 SYSTEM INVOLVING COMPOUND FORMATION

So far we have studied systems in which two components exit as separate entities whether it in the solid or solution phase. There are a number of systems know, in which two metals form an intermetallic compound or a salt and water from a solid hydrate.
Let us considered a general case with two components A and B which form a stable compound AB. The system will involve three solid phases A, B and AB .The fourth phase will be liquid (or solution)containing varying concentration of A and B.

**What is a congruent melting point ?**
When the solid compound AB and the liquid phase have identical composition at the maximumpoint,on the freezing point curve, the corresponding temperature is called to be the congruent Melting Point of the compound.
At that point since both the phases have the same composition. The system has one component only.Hence it is mono variant.
$F' = C - P + 1 = 1 - 2 + 1 = 0$
Their phase diagram has an appearance of two simple eutectic diagrams join together, the diagram on the left represents the eutectic system A/AB, while that on the right the system AB/B.

### 1.7.1 A congruent melting point (Mg-Zn)

It is typical two component system which involves the formation of an intermetallic compound $MgZn_2$.It hasfour phases:solid magnesium (Mg), solid Zinc (Zn), solid $MgZn_2$ and the liquid solution of Mg and Zn.

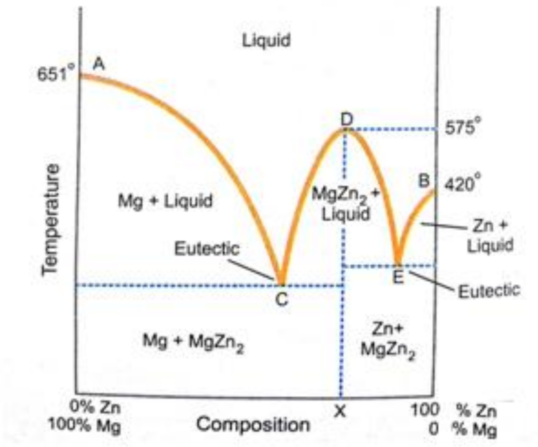

**Fig.1.7.2 The Phase Diagram of Mg / Zn System**

The complete phase diagram of the system magnesium - zinc is shown in the figure 1.7.2. It appears to be made up of two simple eutectic diagrams. The one towards the left represents the eutectic system Mg - $MgZn_2$, while the one to the right the system Zn-$MgZn_2$.

**The curves AC, CDE and BE.** AC is the freezing point curve of magnesium.BE is the freezing pointcurve of zinc and CDE is that of the compound $MgZn_2$.

**The curve AC** shows that the melting point of magnesium ($651^{0}$C) is loweredon the addition of zinc.This continuesuntil the point C is reached. Here a new phase, solid $MgZn_2$appears.

**The curve CD** shows the increase of concentration of zinc in the melt with rise of temperature. At the maximum point D,the composition of the melt and the solid compound $MgZn_2$becomes the same. The point D,therefore, represents the melting point of $MgZn_2$($575^{0}$C). **The curve DE** now shows the lowering of the melting point with addition of zinc until the lowest point is attained. Here solid zinc appears.

**The curve BE** exhibits that the melting point of zinc ($420^{0}$C) falls with the addition of magnesium until the point E is reached.

Along the freezing point curves AC, CDE and BE, there are two phases in equilibrium, viz., one solid phase (Mg , Zn or $MgZn_2$)and the other liquid phase. Applying the reduced phase rule equation, we have

$$F' = C - P + 1 = 2 - 2 + 1 = 1$$

This shows that the system Mg/liquid, Zn/liquid, $MgZn_2$/ liquid are all monovariant .

**Eutectic point C and E.**There are two eutectic points in the phase diagram .The systems at the point C and E have two components and three phases in equilibrium .

C Phases: Solid Mg , Solid $MgZn_2$, liquid
E Phases: Solid Zn , Solid $MgZn_2$, liquid

These systems are therefore nonvariant.

$$F' = C - P + 1 = 2 - 3 + 1 = 0$$

**Congruent Melting Point** As already stated, the composition of the compound $MgZn_2$ and the melt at D is identical. The corresponding temperature is the congruent melting point of the compound. Here the system has two phases viz., the solid compound and the melt. Both these can be represented by one component ($MgZn_2$). Therefore the system at D is nonvariant .

$$F' = C - P + 1 = 1 - 2 + 1 = 0$$

**The Areas**: The area above the curves AC , CDE and BE represents the solution of magnesium and Zinc (the melt) .The single phase system at any point in this area is bivariant .The phases present in the other regions of the phase diagram are as labelled.

**SAQ 16** What is the congruent melting point of the Zn – Mg System and how many phases can exist in that system?

Zn-Mg System is a two-component system and possesses a congruent melting point. 575°C is the congruent melting point of the system. In the reduced form, the system has the following four phases: Solid magnesium, solid zinc, solid $MgZn_2$ and liquid solution of Zn and Mg.

## 1.7.2 An incongruent melting point ($CuSO_4 – H_2O$ )

There are several systems in which components combine together to form one or more compounds which are unstable and do not possess congruent melting points.

A system (compound) is said to possess incongruent melting point, if on heating it decomposes much below its melting point and forms a new solid phase and a solution having different composition from the corresponding solid state. It has no sharp melting point, the decomposition at this temperature is known as transition on meritectic or peritectic reaction and the temperature (the incongruent melting point) is known as transition on meritectic orperitectic temperature.

Original solid ⇌ new solid + solution

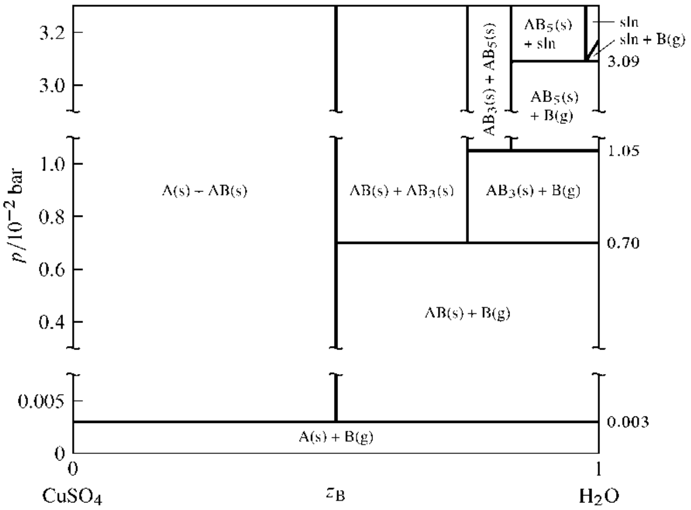

Fig 1.7.3 Pressure–composition phase diagram for the binary system of $CuSO_4$ (A) and $H_2O$ (B) at 25°C

As an example of a two-component system with equilibrated solid and gas phases, consider the components $CuSO_4$ and $H_2O$, denoted A and B respectively. In the pressure–composition phase diagram shown in Fig.1.7.3, the composition variable $Z_B$ is as usual the mole fraction of component B in thesystem as a whole.

The anhydrous salt and its hydrates (solid compounds) form the series of solids $CuSO_4$, $CuSO_4{\cdot}H_2O$, $CuSO_4{\cdot}3H_2O$ , and $CuSO_4{\cdot}5H_2O$. In the phase diagram these formulas are abbreviated A, AB, $AB_3$, and $AB_5$. The following dissociation equilibria (dehydration equilibria) are possible:

$CuSO_4{\cdot}H_2O(s) \rightleftharpoons CuSO_4(s) + H_2O(g)$

$\frac{1}{2}CuSO_4{\cdot}3H_2O(s) \rightleftharpoons \frac{1}{2}CuSO_4{\cdot}H_2O(s) + H_2O(g)$

$\frac{1}{2}CuSO_4{\cdot}5H_2O(s) \rightleftharpoons \frac{1}{2}CuSO_4{\cdot}3H_2O(s) + H_2O(g)$

The equilibria are written above with coefficients that make the coefficient of $H_2O(g)$ unity. When one of these equilibria is established in the system, there are two components and three phases; the phase rule then tells us the system is univariant and the pressure has only one possible value at a given temperature. This pressure is called the *dissociation pressure* of the higher hydrate.

The dissociation pressures of the three hydrates are indicated by horizontal lines in Fig. 1.7.3. For instance, the dissociation pressure of $CuSO_4·5H_2O$ is $1.05\times10^{-2}$bar. At the pressure of each horizontal line, the equilibrium system can have one, two, or three phases, with compositions given by the intersections of the line with vertical lines. A fourth three-phase equilibrium is shown at $p=3.09\times10-2$bar; this is the equilibrium between solid $CuSO_4·5H_2O$, the saturated aqueous solution of this hydrate, and water vapor.

Consider the thermodynamic equilibrium constant of one of the dissociation reactions. At the low pressures shown in the phase diagram, the activities of the solids are practically unity and the fugacity of the water vapor is practically the same as the pressure, so the equilibrium constant is almost exactly equal to $P_d/P°$, where $P_d$ is the dissociation pressure of the higher hydrate in the reaction. Thus, a hydrate cannot exist in equilibrium with water vapor at a pressure below the dissociation pressure of the hydrate because dissociation would be spontaneous under these conditions. Conversely, the salt formed by the dissociation of a hydrate cannot exist in equilibrium with water vapor at a pressure above the dissociation pressure because hydration would be spontaneous.

If the system contains dry air as an additional gaseous component and one of the dissociation equilibria is established, the partial pressure $P_{H2O}$ of $H_2O$ is equal (approximately) to the dissociation pressure$P_d$ of the higher hydrate. The prior statements regarding dissociation and hydration now depend on the value of$P_{H2O}$ . If a hydrate is placed in air in which $P_{H2O}$ is less than $P_d$, dehydration is spontaneous; this phenomenon is called **efflorescence** (Latin: *blossoming*). If $P_{H2O}$ is greater than the vapor pressure of the saturated solution of the highest hydrate that can form in the system, the anhydrous salt and any of its hydrates will spontaneously absorb water and form the saturated solution; this is **deliquescence** (Latin: *becoming fluid*).

If the two-component equilibrium system contains only two phases, it is bivariant corresponding to one of the areas in Fig. 1.7.3. Here both the temperature and the pressure can be varied. In the case of areas labeled with two *solid* phases, the pressure has to be applied to the solids by a fluid (other than $H_2O$) that is not considered part of the system.

**SAQ17** State difference between congruent and incongruent melting point ?

**Congurent melting** It is actually the melting of solid in such a way that the composition of the resultant liquid remain the same as was in the melted solid. Congurent melting point shows the definite temperature of a compound.

Incongurent melting is not a uniformly melting of compound, instead of this solid substance changes in to the liquid or solid such that the composition do not remain the same.

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## 1.8 NERNST DISTRIBUTION LAW

Nernst studied the distribution of several solutes between different appropriate pairs of solvents. He gave a generalization which governs the distribution of a solute between two immiscible solvents. This is Nernst Distribution law which says that if a solute X distribute itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents.

$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = K_D$$

If $C_1$ denotes the concentration of the solute in solvent A and $C_2$ denotes the concentration of the solute in solvent B. Nernst Distribution law can be expressed as

$$\frac{C_1}{C_2} = K_D$$

The constant $K_D$ is called the Distribution coefficient or Partition coefficient or Distribution ratio.

### 1.8.1 Limitations of Distribution Law

The conditions to be satisfied for the application of Nernst distribution law are:

- **Constant temperature**: The temperature is kept constant throughout the experiment
- **Same molecular state**: The molecular state of the solute is the same in the two solvents. This does not hold if there is any association or dissociation of the solute in one of the solvents .
- **Equilibrium concentration**: Concentration of the solutes are noted after the equilibrium has been established.
- **Dilute solution**: The concentration of the solute into solvent is low .The law does not hold when the concentrations are high.
- **Non-miscibility of solvents:** The two solvents are non-miscible or only slightly soluble in each other. The extent of mutual solubility of the solvents remains unaltered by the addition of salute to them.

### 1.8.2 Application of Nernst distribution law

- **Solvent Extraction** This is the process used for separation of organic substances from aqueous solution. The process of extraction is more efficient if the solvent is used in number of small proportions then in one whole lot. This multiple extraction is referred to simple extraction. The multiple extractions are also the basis of the industrial **counterflow solvent extraction**. We can use formula given below which enables the calculation of the amount of substance left on extracted (**$x_n$**)after a specified number of extraction with v ml portion of the solvent each time.

  $$x_n = A\left(\frac{KV}{KV+v}\right)^n$$

  Here A is the initial amount taken, K being the distribution constant and V in the initial amount of solvent (aqueous)in which solute which is to be extracted is dissolved.

- **Partition Chromatography** This is a modern technique of separating a mixture of small amount of organic material. A paste of the mixture is applied at the top of the column of silica soaked in water. Another immiscible solvent,say hexane is allowed to flow down the column. Each component of the mixture is partitioned between the stationary liquid phase (water) and the mobile liquid phase (hexane). The various components of the mixture are extracted by hexane in order of their distribution coefficients. Thus the component with the highest distribution coefficient is first to move down in the flowing hexane which is collected separately. Similarly, a component with lower distribution ratio comes down later and is received in another vessel.
- **Determination of Association** If this equation holds good for any system $\frac{\sqrt[n]{C_A}}{\sqrt[n']{C_B}}$ then it is experimentally proved that association takes place over there. Here $C_A$and $C_B$ are concentration of layer A and B and n and n’ are number of molecules which combine to form associated molecules in layer A and B.

- **Determination of dissociation** Suppose a substance X is dissociated in aqueous layer and exist as single molecules in ether. If x is the degree of dissociation, the distribution law is modified as

  $\frac{C_1}{C_2(1-x)} = K_D$ $C_1 = c\text{oncentration of X in benzene,}C_2 = \text{concentration of X in aqueous layer}$

  The value of x can be determined from conductivity measurements. If this equation holds good for the above system then it is proved that dissociation takes place there.

- **Determination of solubility** Suppose the solubility of iodine in Benzene is to be determine. Iodine is shaken with water and benzene. At equilibrium concentration of iodine in benzene ($C_b$)and water ($C_w$)are found experimentally and the value of distribution coefficient calculated.

  $$\frac{C_b}{C_w} = K_D \text{but} \frac{S_b}{S_w} = K_D$$

  Where $S_b$= solubility in benzene, and $S_w$ = solubility in water
  If the solubility of iodine in water ($S_w$) is known, the solubility in benzene can be calculated.

**SAQ 18** A solid X is added to a mixture of benzene and water.10 ml of the benzene layer was found to contain 0.13 g of X and 100ml of water layer contained 0.22 g of X. Calculate the value of distribution coefficient?

Concentration of X in benzene ($C_B$) =$\frac{0.13}{10}$ = 0.013 g $ml^{-1}$

Concentration of X in water ($C_w$) =$\frac{0.22}{100}$ = 0.002 g $ml^{-1}$

According to distribution law $\frac{C_B}{C_w} = \frac{0.013}{0.002} = 5.9$

## 1.8.3 Thermodynamic Derivation of the Distribution Law

The thermodynamic derivation of the distribution law is based upon he principle that if there are two phases in equilibrium (i.e. two immiscible solvents containing the same solute dissolved in them), the chemical potential* of a substance present in them must be same in both the phases.

From thermodynamics, we know that the chemical potential $(\mu)$ of a substance is a solution given by

$\mu = \mu^0 + RT \ln a$

Where$\mu^0$is the standard chemical potential and 'a' is the activity of the substance (solute) in the solution.

Thus for the solute in liquid A, we have

$\mu_A = \mu_A^0 + RT \ln a_A$

Similarly for the solute in liquid B we have

$\mu_B = \mu_B^0 + RT \ln a_B$

But as already stated, since the liquids A and B are in equilibrium,

$\mu_A = \mu_B$

$\mu_A^0 + RT \ln a_A = = \mu_B^0 + RT \ln a_B$

$RT \ln a_A - RT \ln a_B = \mu_B^0 - \mu_A^0$

$\ln \left(\frac{a_A}{a_B}\right) = \mu_B^0 - \mu_A^0 \cdot \frac{1}{RT}$

Furtherat a given temperature, $\mu_A^0$and $\mu_B^0$are constant for given substance in the particular solvents. Hence at constant temperature, we have

$\ln \left(\frac{a_A}{a_B}\right) =$ constant

And therefore

$\frac{a_A}{a_B} =$ constant

This is the exact expression of the distribution law. However, if the solutions are dilute, the activates are equal to the concentrations so that the above expression becomes

$$\frac{C_A}{C_B} = \text{constant}$$

which is the original form of the distribution law.

## 1.9 SUMMARY

- The relation between standard free energy and equilibrium constant is given by

$\Delta G^0 = - nRT \ln K_p$

- **Le chatelier's principle** say that " if a system in equilibrium is disturbed by changing the pressure or the temperature of the overall system or by the concentration of one or more of the substances involved in the equilibrium , the system adjust itself in such a way that tends to undo the effect of the change as far as possible".
- **Phase rule is** $F = C - P + 2$

- The triple point of a substance is the temperature and pressure at which the three phases of that substance coexist in thermodynamic equilibrium. Water has one triple point where as Sulphur has three triple point in its phase system.
- A **phase diagram** is a type of chart **used to** show conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct **phases** (such as solid, liquid or gaseous states) occur and coexist at equilibrium.
- **Metastable equilibrium** is an unstable equilibrium;it at once reverts to the stable system on the slightest disturbance.
- **First-order phase transitions** are discontinuous in the first derivative whereas**second-order phase transitions** are continuous but exhibit discontinuity in a second derivative of the free energy.
- For two component (Solid liquid equilibria) reduced phase rule is used that is $F' = C - P + 1$
- A solid / liquid system with the gas phase absent is called a **condensed system.**
- When the solid compound and the liquid phase have identical composition at the maximumpoint, on the freezing point curve, the corresponding temperature is called to be the **congruent Melting Point** of the compound.
- A system (compound) is said to possess**incongruent melting point**, if on heating it decomposes much below its melting point and forms a new solid phase and a solution having different composition from the corresponding solid state.
- **Nernst Distribution law**which says that if a solute X distribute itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents. $\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = K_D$
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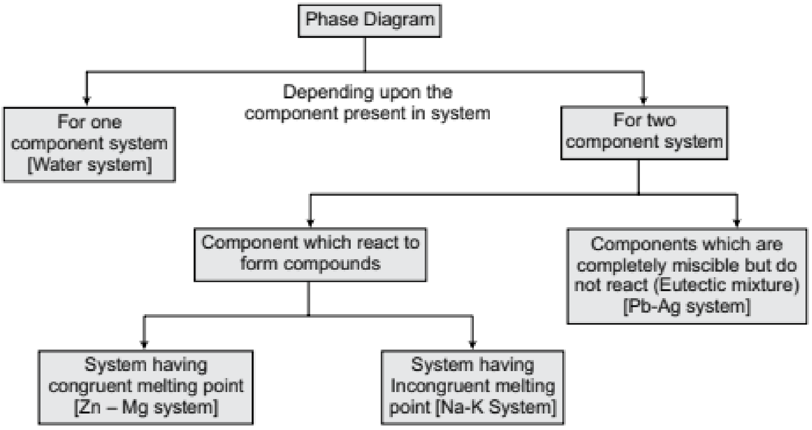

## 1.10 TERMINAL QUESTIONS

**SAQ 1** In a vessel having $N_2$ and $H_2$ in the ratio 1:3 by volume is heated at $400^0$ C at 1000 atm. At equilibrium 0.2491 mole fraction of $NH_3$ was formed. Determine $K_p$ for this reaction.

**SAQ 2** The equilibrium constant$K_P$ for the reaction $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$ is $5.04 \times 10^{17}$ atm$^{-1}$ at $25^0$ C . Calculate $\Delta G^0$ .

**SAQ 3** Apply Le chatelier's principle to predict the effect of change of temperature and change of pressure on the following reactions :

(i) $PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g) \quad \Delta H = -100$ K cal

(ii) $4HCl\ (g) + O_2(g) \rightleftharpoons 2\ H_2O\ (g) + 2Cl_2\ (g)$ $\Delta H = -7$ K cal
(iii) $2C\ (g) + 2H_2(g) \rightleftharpoons C_2H_4(g)$ $\Delta H = +55$ K cal

**SAQ 4** Derive some conclusions from Gibbs Phase Rule

**SAQ 5** Can the Phase rule equation in its original form can be applied to a condensed system ? Write the reduced Phase rule equation .

**SAQ 6** At what temperature becomes liquid

**SAQ 7** Which of the following phases of Sulphur is most dense ?

**SAQ 8** Define critical point in terms of phase diagram.

**SAQ 9** Define eutectic point**.**

**SAQ 10** An aqueous solution of iodine containing 0.0516 g/ lit is in equilibrium with a carbon tetra chloride ($CCl_4$) solution containing 4.412 g/lit at $25^0$ C. The solubility of iodine in water at $25^0$ C is 0.34 g/lit. Find the solubility of iodine in carbon tetrachloride.

**SAQ 11** The distribution coefficient of isobutyric acid between ether and water is3 at $25^0$ C .What will be the amount of isobutyric acid removed if 4 g of isobutyric acid in 100 ml of water is extracted with 100 ml ether at $25^0$ C.What would be the effect if two successive 50 ml portion of ether has been used to extract the aqueous layer.

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## 1.11 ANSWERS

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**SAQs**

1.The reaction is $N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$
partial pressure = mole fraction × Total pressure
$P_{NH_3} = 0.2491 \times 1000 = 249.1$ atm
$P_{Total} = P_{N_2} + P_{H_2} + P_{NH_3}$
$P_{N_2} + P_{H_2} = 1000 - 249.1 = 750.9$ atm
Since $P_{N_2} : P_{H_2} = 1 : 3$
Partial pressure of Nitrogen = $\frac{1}{4} \times 750.9 = 187.72$ atm
Partial pressure ofHydrogen = $\frac{3}{4} \times 750.9 = 563.18$ atm

Since $K_P = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

$$K_P = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{(249.1)^2}{(187.72)\ (563.18)^3} = 1.8 \times 10^{-6} \text{atm}$$

2.$\Delta G^0$ = ⍰ nRT ln $K_p$ Here R= 8.314; T= 25+273 = 298 K; $K_P = 5.04 \times 10^{17}$ $atm^{-1}$

Substituting the values in the above expression

$\Delta G^0 = -2.303\ (8.314)\ (298) \log (5.04 \times 10^{17})$

$= -\ 5706 \times \log (5.04 \times 10^{17})$

$= -5706 \times (17.702)$

$= -\ 1.010 \times 10^5$ J

$\Delta G^0 = -\ 101$ kJ

3. (i) Δn = 2-1 =1 therefore on increasing pressure backward reaction will be favour , As the reaction is exothermic thus on increasing temperature , backward reaction is again favourable. Low temperature and low pressure is favourable condition for decomposition of $PCl_5$.

(ii) Δn = 4-5 = -1 therefore on increasing pressure forward reaction will be favour, As the reaction is exothermic thus on increasing temperature, backward reaction is favourable. Low temperature and high pressure is favourable condition for the formation of chlorine gas.

(iii) Δn = 1-4 = -3 therefore on increasing pressure forward reaction will be favour , As the reaction is endothermic thus on increasing temperatue , forward reaction is again favourable. High temperature and high pressure is favourable condition for the formation of ethene

4. Some conclusions are

(a) For a system having a specified number of components, the greater the number of phases, the lesser is a number of degree of freedom.

(b) A system having a given number of components and the maximum possible number of phases in equilibrium is non- variant.

(c) For a system having a number of phases, the larger the number of components, the greater will be the number of degree of freedom of the system.

5. No,When single phase is present in two components the degree of freedom is three.

$$F = C - P + 2 = 2 - 1 + 2 = 3$$

This means that three variables must be specified in order to describe the condition of the phase.Therefore the phase diagram of obtained would be a solid model. For the sake of having simple plane diagrams we generally consider only two variables, the third one being a constant. Such a system is known as condensed system where reduced phase rule is used that is $F' = C - P + 1$.

6. At standard pressure, the chemical element helium exists in a liquid form only at the extremely low temperature of −269 °C (about 4 K or −**452.2 °F**).

7. From **phase** diagram Rhombic is the **densest phase**, because the monoclinic-rhombic equilibrium line has a positive slope and the solid-liquid equilibrium lines also has positive slopes.

8. In a phase diagram, a point at which both liquid and gaseous state of the substance having in distinguishable density is known as critical point of that substance.

9. ***Eutectic point*** - the point on a phase diagram where the maximum number of allowable phases is in equilibrium. When this point is reached, the temperature must remain constant until one of the phases disappears. It is an invariant point.

10. Concentration of $I_2$ in water ($C_w$) = 0.0516 g/lit

Concentration of $I_2$ in carbon tetrachloride ($C_C$) = 4.412 g/lit

Therefore The value of Distribution coefficient is

$$\frac{C_C}{C_w} = \frac{4.412}{0.0516} = 85.5$$

Applying Distribution Law $\frac{\text{Solubility of Iodine in Carbon tetrachloride}}{\text{Solubility of Iodine in water}} = 85.5$

$$\frac{\text{Solubility of Iodine in Carbon tetrachloride}}{0.34} = 85.5$$

Solubility of Iodine in Carbon tetrachloride = 85.5 × 0.34 = 29.07 g/ lit

11. (a) Extraction with 100 ml of ether

$$\frac{C_{\text{ether}}}{C_{\text{water}}} = 3$$

Let x be the amountof the acidextracted with 100 ml of ether

Therefore $\frac{x/100}{4-x/100} = 3$ Hence x= 3 g

Thus we can separate 3g (75%) of isobutyric acid from the aqueous layer using 100 ml of ether.

(b) Two extraction using 50 ml of ether in each extraction.

Let $x_1$ be the amount of acid removed in the first extraction

$\frac{x_1/50}{4-x_1/100} = 3$ where come out to be $x_1$ = 2.4 g

The acid left unextracted in water layer after first extraction 4-2.4 = 1.6 g

The 1.6 g of the acid is then extracted with a second 50 ml portion of ether. If $x_2$ is the amount removed from ether during second extraction.

$\frac{x_2/50}{1.6-x_2/100} = 3$ where come out to be $x_2$=0.96 g

Thus in two successive extraction we can extract 2.4 + 0.96 = 3.36 g (84%) of isobutyric acid from aqueous layer.

## Suggested reading

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### Reference Books

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- Atkins, Peter & Julio De Paula, Physical Chemistry 9th Ed., Oxford University Press (2010).

- Castellan, G. W. Physical Chemistry, 4th Ed., Narosa (2004)..
- Engel, T. & Reid, P. Physical Chemistry 3rd Ed., Prentice-Hall (2012).
- Zumdhal, S.S. Chemistry concepts and applications, Cengage India (2011).
- Mortimer, R. G. Physical Chemistry 3rd Ed., Elsevier: NOIDA, UP (2009).
- Levine, I. N. Physical Chemistry 6th Ed., Tata McGraw-Hill (2011).
- Metz, C. R. Physical Chemistry 2nd Ed., Tata McGraw-Hill (2009).

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**Text Books**

- **Puri B.R., Sharma L.R. & Pathania Madan S., Principles of physical chemistry, Vishal publishing Company ,(2013)**
- **Mukerjee, R.C., Modern approach to Physical Chemistry, Bharati Bhawan(2016)**
- **Raj Gurdeep, Advanced Physical Chemistry, Krishna Prakashan(2016)**
- **Bahl, A., Bahl, B.S. & Tuli, G.D., Essential of Physical Chemistry, S. Chand & Company (2012)**
- **Sahgal, S., Numerical Analysis of Physical Chemistry, Victorious Publishers (2018)**

# UNIT 2: THERMODYNAMICS -II

Structure

## 1.1 INDRODUCTION

Analyse the word Thermodynamics, it splits into two: thermos means heat and dynamics means motion, resulting into mechanical work. Thus, thermodynamics can be defined as that branch of science which is concerned with converting heat into mechanical work and vice-versa. This term was coined by mechanical engineers who were chiefly concerned with the study related to the conversion of heat into mechanical work. However, in the light of latest developments, the word thermodynamics has acquired far wider meaning. It is not only limited to heat and mechanical work but with practically all forms of energy appearing in various processes including physical and chemical.

It includes all kind of energies for example Potential energy (due to position or condition of a body likes wounds spring), Kinetic energy (due to body's motion), Radiant energy (visible light), Chemical energy (energy stored in all the substances), Electrical energy (exhibited by flow of electrons).All form of energy can be transformed into heat and as such, they are interlinked with one another quantitatively .In light of above facts thermodynamics can be redefine with a bit of modification as under:

"Thermodynamics is that sub field of science which deals with the quantitative relationship between heat and other form of energy". Exhaustive study of thermodynamics is based on three generalisations first, second and third law of thermodynamics. These three laws are based on the experience of scientists and as such no theory can be presented in support of these laws. However the validity of these laws lies in the fact that nothing against these laws has been found and nothing contrary is anticipated.

### 1.1.1 Objectives

After studying this unit you should be able to know:

- Need for second law of thermodynamics.
- Relation between first and second law.
- First law deals with the balance of energy whereas the second law tells the direction of flow of heat or energy.
- It also helps us to lay down the criteria for predicting feasibility of a process including a chemical reaction under a given set of condition.
- Required conditions for a reaction to be spontaneous in terms of Entropy, Helmholtz free energy and Gibb's free energy.
- Increase in randomness favours a spontaneous change.
- Various aspects related to Entropy.
- Purpose of introducing Free energy functions.
- Various aspects related to Helmholtz and Gibb's free energy.
- Maximum work obtained is Helmholtz free energy where as useful work obtained is Gibb's free energy.
- Partial molal properties and the way they can be obtained.
- The term chemical potential and its significance.

## 1.2 SECOND LAW OF THERMODYNAMICS

The first law states that energy can change from one form to another, but the total amount of energy of a system remains constant. Though this law has given us two important state functions E and H, yet it suffers from the following limitations or drawbacks.

### 1.2.1 Need for second law of thermodynamics

- This law does not explain why chemical reactions do not proceed to completion.
- This Law does not answer why natural (spontaneous) processes are unidirectional.
- This law does not say anything about source of heat and direction of flow of heat.
- This law says that all form of energy change into one another but does not define the ease or extent of convertibility of one form of energy into another.
- Work can be completely transformed into heat but heat cannot be completely converted into work,without leaving permanent change in the system or surroundings. This observation could not be explained by first law.
- The difference between spontaneous and non-spontaneous processes is of no significance from the viewpoint of first law of thermodynamics.
- All naturally occurring processes always tends to change spontaneously in a direction which leads to equilibrium. This fact cannot be answered by the first law of thermodynamics.
- The first law does not contradict the existence of heat engine of 100% efficiency or self-acting machine. But human experiences tell us that such heat engines and machine are not attainable in practice.

Thus above observations led to the formulation of another law, called second law of thermodynamics.

### 1.2.2 Statement of the second law of thermodynamics

The second law has been stated in various ways. All the statements have the same meaning.

1. **Clausius Statement** : “It is not possible for a self-acting machine ,unaided by an external agency ,to convey heat from a body at lower temperature to another at higher temperature”.
2. **Thomson statement:** “The heat of the coldest body among those participating in a cyclic process cannot serve as a source of work”.
3. **Kelvin-Planck statement:**“It is impossible to construct a heat engine which operating in a complete cycle, will abstract heat from a single body and convert the whole of it into work, without leaving any changes in the working system that is it is impossible to build heat engine of 100 % thermal efficiency”.
4. “All the natural and spontaneous processes take place in one direction only and cannot be reserved”.
5. “The energy of universe remains constant but available energy is decreasing and entropy of the universe is increasing to a condition of maximum randomness (Chaos). When there is a maximum chaos, order will prevail itself”.

### Conclusions drawn from second law

1. First law deals with the balance of energy whereas the second law tells the direction of flow of heat or energy.
2. There is no mathematical derivation of this law. It is based on experience about heat engines and refrigerators.

3. Increase in randomness favours a spontaneous change.

**SAQ 1** Is there any proof in support of second law of thermodynamics?
While mathematical statements can have **proof**, fundamentally, physical **laws** can only be consistent with experimental **evidence**. It sounds weak, but in the case of the **second law of thermodynamics there** is **a** monumental amount of consistent experimental **evidence**.

**SAQ 2** What is the basic difference between first and second law of thermodynamics?
First law deals with the coservation of energy whereas the second law tells the direction of flow of heat or energy.

## 1.3 CONCEPT OF ENTROPY

For reversible Carnot Cycle working between temperatures $T_2$ and $T_1$ ($T_2>T_1$) , We have

$$⍰ = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \text{........ (1.3.1)}$$

Where$T_2$ = Temperature of heat source with corresponding heat quantity $q_2$ .

$T_1$ = Temperature of heat sink with corresponding heat quantity $q_1$ .

$$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

$$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

$$\frac{q_1}{T_1} = \frac{q_2}{T_2}$$

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} = 0 \qquad \text{.........(1.3.2)}$$

$$\frac{q_2}{T_2} + \frac{-q_1}{T_1} = 0 \qquad \text{.........(1.3.3)}$$

The ratio q/T is called reduced heat. Equation (1.3.3) shows that the algebraic sum of reduced heats for a reversible Carnot Cycle is zero .

For any reversible Carnot Cycle, we have

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2}$$

$$1 - \frac{q_1}{q_2} < 1 - \frac{T_1}{T_2}$$

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} < 0$$

$$\left\{\frac{q_2}{T_2} + \left(\frac{-q_1}{T_1}\right)\right\} < 0$$

Hence, the algebraic sum of reduced heat is less than zero for anirreversible Carnot Cycle. For an infinitely small reversible Carnot Cycle the equation (1.3.2) becomes

$\frac{dq_2}{T_2}$ -$\frac{dq_1}{T_1}$ = 0 .........(1.3.4)

Where dq/T is called elementary reduced heat.

Any reversible cycle is made of number of infinitesimally small Carnot Cycle, hence by summating equation (1.3.4)for all infinitesimally small cycles, we get for any reversible Carnot Cycle,

$$\int \frac{dq_2}{T_2} - \int \frac{dq_1}{T_1} = 0$$ .........(1.3.5)

The above equation (1.3.5) can also be expressed as

$\oint \frac{dq}{T}$ =0.........(1.3.6)

Where $\oint$ = represents cyclic integration.

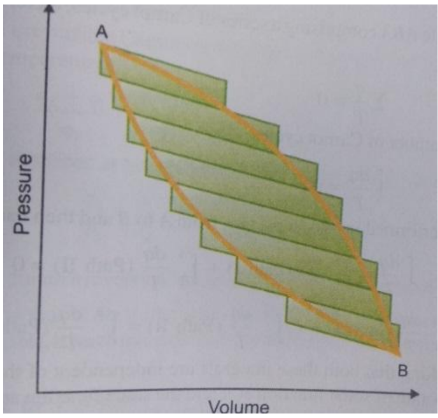

Fig 1.3.1 Reversible cycle consisting of infinitely small cycles

For an irreversible cycle $\oint \frac{dq}{T} < 0$

Hence in general $\oint \frac{dq}{T} \leq 0$ .........(1.3.7)

The equation (1.3.6) is known as ***Clausius inequality .***

The cyclic integral is the sum of two integrals.

1. one from direct process that is from state 1 to state 2
2. Other for reversible process that is from state 2 to state 1.

This way the sum completes the cycle that is we reach the point from where we started. Hence equation (1.3.6) is written as

$\oint \frac{dq}{T} = \int_1^2 \frac{dq_{(a)}}{T} + \int_2^1 \frac{dq_{(b)}}{T} = 0$.........(1.3.8)

Where a= Path through which transition of system from state 1 to 2 takes place

b = = Path through which transition of system from state 2 to 1

$$\int_1^2 \frac{\delta q_{(a)}}{T} = - \int_2^1 \frac{\delta q_{(b)}}{T}$$

$\int_1^2 \frac{\delta q_{(a)}}{T} = \int_1^2 \frac{\delta q_{(b)}}{T}$.........(1.3.9)

From equation(1.3.9), it follows that the integral of dq/T is same for a change in state from 1 to 2 whether the system follows path a or path b. Hence dq/T is an exact differential. That is , it represents a change in some state function of system. This state function has been called **entropy** and is denoted by S. The definition of S is therefore

$$\int_1^2 \frac{\delta q}{T} = S_2 - S_1 = \int_1^2 dS \text{.........(1.3.10)}$$

Therefore we can say $\frac{\delta q}{T} = dS$.........(1.3.11)

Equation (1.3.10) and (1.3.11) are the definition of Entropy. It can be defined in the following ways :

1.Entropy of a system is a function of state and its change is equal to the ratio of heat change to the temperature at which heat change occurs in a reversible (or equilibrium) cyclic process.

2. Entropy is such a state function that the change in its value is equal to the sum of reduced heat absorbed by a system in a reversible cyclic process.

If the reversible cyclic process is adiabatic then

$dq = 0$

$dS = \frac{\delta q}{T} = 0$

$S = \text{Constant}$

Thus in an adiabatic cyclic process does change in entropy is zero. That is entropy does not change in such processes. In other words, the entropy of the adiabatic reversible process remain constant. Hence entropy may also be defined as the thermal property of the substance which remains constant during an adiabatic cyclic change.

For a small change :$dS = \frac{\delta q}{T}$

For macro change : $\Delta S = \frac{q}{T}$

**SAQ3** Who introduced the concept of entropy?

In the early 1850s, Rudolf Clausius set forth the **concept** of the thermodynamic system and proposed the argument that in any irreversible process a small amount of heat energy dq is incrementally dissipated across the system boundary. Clausius continued to develop his ideas of lost energy, and coined the **term entropy**.

## 1.3.1Entropy as a state function

For reversible cyclic process , we know that

$$\oint \frac{\delta q}{T} = \int_1^2 \frac{\delta q_{(a)}}{T} + \int_2^1 \frac{\delta q_{(b)}}{T} = 0$$

$$\int_1^2 \frac{\delta q_{(a)}}{T} = - \int_2^1 \frac{\delta q_{(b)}}{T}$$

$$\int_1^2 \frac{\delta q_{(a)}}{T} = \int_1^2 \frac{\delta q_{(b)}}{T} \text{............(1.3.12)}$$

$\int_1^2 dS_{(a)}$ = $\int_1^2 dS_{(b)}$ …………..(1.3.13)

Equation (1.3.13) means that change in entropy from state 1 to 2 is same whether the system follows the path a or part b. That is change in entropy does not depend on the path of process but only on initial and final stages. Consequently dSis exact differential. Entropy is a single valued, continuous and finite function of state. Thus mathematically:

dS $=\frac{\delta q}{T}$ = An exact differential

This equation shows that δq is not an exact differential that is q is not a state function, but after division by T, the quantity(δq/T) become a differential of a function that is it become an exact differential. Thus from mathematical view point the quantity (1/T) serves as an integrating factor for δq or (T serve as a integrating divisior).

**SAQ 4 Is entropy a path function?**

Since **entropy** is a state **function**, the **entropy** change of the system for an irreversible **path** is the same as for a reversible **path** between the same two states.In classical thermodynamics, the **entropy** of a system is defined only if it is in thermodynamic equilibrium.

**SAQ 5 Give some examples of entropy in our daily life?**

We see evidencesin our life that the universe tends toward highest entropy.A campfire is an example of entropy. The solid wood burns and becomes ash, smoke and gases, all of which spread energy outwards more easily than the solid fuel.Ice melting, salt or sugar dissolving, making popcorn and boiling water for tea are processes with increasing entropy in our kitchen.

## 1.3.2 Entropy as a function of V& T

We know that

δq = dE + PdV (First law) ………..(1.3.14)

We know that $\frac{dE}{dT}$=n$C_v$

Or dE = n $C_v$dT………..(1.3.15)

Putting the value of dE in equation (1.3.14) from equation (1.3.15)

dq =n $C_v$dT + PdV

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

δq =n $C_v$dT $+ nRT\frac{dV}{V}$………..(1.3.16)

Since dS =$\frac{\delta q}{T}$

dS = n $C_V \frac{dT}{T}$+ n R $\frac{dV}{V}$

Integrating this equation between states 1 and 2 , we get

$$\int_{S_1}^{S_2} dS = n\,C_V\int_{T_1}^{T_2}\frac{dT}{T} + nR\int_{V_1}^{V_2}\frac{dV}{V}$$

$$\Delta S = n\,C_V\ln\left(\frac{T_2}{T_1}\right) + nR\ \ln\left(\frac{V_2}{V_1}\right)\text{..........}(1.3.17)$$

**Case 1.** When volume is constant (Isochoric Process)

That is dV = 0 or $V_1 = V_2$

Hence equation (1.3.17) becomes

$$\Delta S = n\,C_V\ln\left(\frac{T_2}{T_1}\right) = 2.303\ n\,C_V\log\left(\frac{T_2}{T_1}\right)\text{..........}(1.3.18)$$

**Case 2.** When temperature is constant (Isothermal Process)

That is dT = 0 or $T_1 = T_2$

Hence equation (1.3.17) becomes

$$\Delta S = nR\ \ln\left(\frac{V_2}{V_1}\right) = 2.303nR\log\left(\frac{V_2}{V_1}\right)\text{..........}(1.3.19)$$

**Case 3.**When entropy is constant (Adiabatic Reversible Process)

Δ S = 0dS= 0 then equation (1.3.17) becomes

$$C_V\ln\left(\frac{T_2}{T_1}\right) = -R\ \ln\left(\frac{V_2}{V_1}\right) \quad \text{or} \quad C_V\ln\left(\frac{T_2}{T_1}\right) = R\ \ln\left(\frac{V_1}{V_2}\right)$$

$$C_V\log\left(\frac{T_2}{T_1}\right) = R\ \log\left(\frac{V_1}{V_2}\right)\text{..........}(1.3.20)$$

Equation (1.3.17) gives entropy change of ideal gas with volume and temperature together.

**SAQ 6** Calculate the entropy change involved in thermodynamic isothermal reversible expansion of 1 mole of an ideal gas from an initial volume of 2 litres to final volume of 20 litres.

$\Delta S = 2.303\ nR\ \log\left(\frac{V_2}{V_1}\right)$

Here n=1, $V_1$ = 2 litres, $V_2$ = 20 litres, R= 8.313 Joules $K^{-1}$ mole $^{-1}$

$\Delta S = 2.303 \times 1 \times 8.313\ \log\left(\frac{20}{2}\right)$

Δ S= 19.15 Joules $K^{-1}$ mole $^{-1}$

**SAQ 7** Water is heated on a stove. Which of the following temperature changes results in the greatest change in entropy?

1. from 10°C to 20°C
2. from 45°C to 55°C

3. from $80^oC$ to $90^oC$

4. all have the same entropy change

$\Delta S= \int_i^f \frac{dq}{T} = \int_i^f \frac{M_{water}C_w\ dT}{T} = M_{water}C_w \int_i^f \frac{dT}{T} = M_{water}C_w \ln\left(\frac{T_f}{T_i}\right)$

(1) from $10^oC$ to $20^oC$ => 283K to 293K => ln(293/283) = 0.035

(2) from $45^oC$ to $55^oC$ => 318K to 328K => ln(328/318) = 0.031

(3) from $80^oC$ to $90^oC$ => 353K to 363K=> ln(363/353) = 0.028

Therefore option one is correct.

**SAQ 8** Calculate the change in entropy when one mole of Helium gas at constant volume suffered heating from 200K to 400K. (Given $C_v$= 2 Cal $K^{-1}$ $mole^{-1}$)

$\Delta S = n C_V \ln\left(\frac{T_2}{T_1}\right) = 2.303\ n C_V \log\left(\frac{T_2}{T_1}\right) = 2.303 \times 1 \times 2 \log\left(\frac{400}{200}\right) = 1.39$ Cal $K^{-1}$ $mole^{-1}$

## 1.3.3 Entropy as a function of P& T

We know that

$\delta q = dE + PdV$ (First law) ...........(1.3.14)

For n mole of an ideal gas

$PV = nRT$

$Pdv + VdP = nRdT$

$PdV = nRdT - VdP$ ...........(1.3.21)

We know that $\frac{dE}{dT} = nC_v$

Or $dE = n C_v dT$...........(1.3.15)

From equation (1.3.14) ,(1.3.15) and (1.3.21) , we get

$\delta q = n C_v dT + nRdT - VdP$

$\delta q = n (C_V + R) dT - VdP$

$C_P - C_V = R$

$C_P = R + C_V$

$\therefore \delta q = n C_P dT - VdP$ ...........(1.3.22)

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

Equation (1.3.22) becomes

$\delta q = n C_P dT - nRT\frac{dP}{P}$ ...........(1.3.23)

Since $dS = \frac{dq}{T}$

$dS = n\ C_P \frac{dT}{T} - nR\frac{dP}{P}$

Integrating this equation between states 1 and 2 , we get

$$\int_{S_1}^{S_2} dS = n\ C_P \int_{T_1}^{T_2} \frac{dT}{T} - nR \int_{P_1}^{P_2} \frac{dP}{P}$$

$\Delta S = n\ C_P\ \ln\left(\frac{T_2}{T_1}\right) - nR\ \ln\left(\frac{P_2}{P_1}\right)$...........(1.3.24)

**Case 1.** When pressure is constant (Isobaric Process)

That is $dP = 0$ or $P_1 = P_2$

Hence equation (1.3.24) becomes

$\Delta S = n\ C_P\ \ln\left(\frac{T_2}{T_1}\right) = 2.303\ n\ C_P\ \log\left(\frac{T_2}{T_1}\right)$...........(1.3.25)

**Case 2.** When temperature is constant (Isothermal Process)

That is $dT = 0$ or $T_1 = T_2$

Hence equation (1.3.24) becomes

$\Delta S = -nR\ \ln\left(\frac{P_2}{P_1}\right) = -\ 2.303\ nR\log\left(\frac{P_2}{P_1}\right) = 2.303\ nR\log\left(\frac{P_1}{P_2}\right)$...........(1.3.26)

**Case 3.** When entropy is constant (Adiabatic Reversible Process)

$\Delta S = 0 dS = 0$

$C_P\ \ln\left(\frac{T_2}{T_1}\right) = R\ \ln\left(\frac{P_2}{P_1}\right)$ or

$C_P\ \log\left(\frac{T_2}{T_1}\right) = R\ \log\left(\frac{P_2}{P_1}\right)$...........(1.3.27)

Equation (1.3.24) gives entropy change of ideal gas with pressure and temperature together.

**SAQ 9** Calculate the change in entropy when one mole of Helium gas at constant pressure suffered heating from 200K to 400K. (Given $C_P$ = 5 Cal $K^{-1}$ $mole^{-1}$)

$\Delta S = n\ C_P\ \ln\left(\frac{T_2}{T_1}\right) = 2.303\ n\ C_P\ \log\left(\frac{T_2}{T_1}\right) = 2.303 \times 1 \times 5 \log\left(\frac{400}{200}\right) = 3.47$ Cal $K^{-1}$ $mole^{-1}$

**SAQ 10** Calculate the change in entropy when 2 moles of an ideal gas are allowed to expand isothermally at 293K from a pressure of 10 atm to a pressure of 2 atm.

$\Delta S = 2.303\ nR\ \log\left(\frac{P_1}{P_2}\right) = 2.303 \times 2 \times 8.314 \log\left(\frac{10}{2}\right) = 26.77$ J $K^{-1}$ $mole^{-1}$

## 1.3.4 Entropy change in physical process

A process of change in state, for example melting of solid or vaporization of liquid may be carried out at constant temperature reversibly as the two phases are in equilibrium at all times during the change. Suppose the process of change of state of 1 mole of substance is carried out reversibly, the amount of heat absorbed will be equal to the molar heat of fusion or vaporisation and the temperature will be the melting point or the boiling point.

**Entropy change in change of phase**

**(a) Melting of solids to liquids phase :** when1 mole of substance is melting reversibly at its fusion point T, at a constant pressure, the entropy change of the process will be

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

Where $\Delta H_f$ is the molar heat of fusion which is equal to the heat absorbed (latent heat of fusion ) during the process.

**(b) Vaporization of liquids in its vapour phase :** when1 mole of substance is boiling (changing from liquid to vapour state) at its boiling point, at a constant pressure, the entropy change of the process will be

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

Where $\Delta H_v$ is the molar heat of vaporization which is equal to the heat absorbed (latent heat of vaporization) during its process.

**(c) Change in entropy when one crystalline transforms to another :** The entropy change$\Delta S_t$, when1 mole of solid substance change reversibly from one crystalline form (say rhombic sulphur) to another crystalline form (say monoclinic sulphur) at transition temperature $T_t$ , it is given by the following equation

$$\Delta S_t = \frac{\Delta H_t}{T_t}$$

Where $\Delta H_t$ is the molar heat of transition which is evolved or absorbed during the process.
Since $\Delta H_f$ and $\Delta H_v$ are both positive, an increase in entropy takes place during the process of fusion and vaporization.
In the change of state from vapour to liquid or from liquid to solid $\Delta H_v$ and $\Delta H_f$ will be negative and during processes of condensation of vapour or freezing of a liquid , decrease in entropy takes place.

**SAQ11** Calculate entropy change accompanying the transfer of 10460 joules of heat from a body A at 300$^0$C to a body B at 77$^0$C.

$$\Delta S = -\frac{q}{T_1} + \frac{q}{T_2} = q\left(\frac{T_1 - T_2}{T_1 . T_2}\right)$$

$\Delta$ S $= \frac{10460\ J\,(573K-350K)}{(573K)(350K)}$ = 11.63 Joule $K^{-1}$

**SAQ12** What happens when entropy becomes zero?
**Entropy** is nothing but disorderness of molecules. Change in **Entropy** must be greater or equals to zero. If it is zero there is no change in **entropy** with respect to previous state and the process can be stated as reversible process. If it is greater than zero the process is irreversible.

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## 1.4 GIBBS AND HELMHOLTZ FUNCTIONS

In thermodynamics, two new functions have been introduced to explain various physical and chemical processes occurring at constant temperature and at constant pressure. These functions are called free energy functions .These are

- Helmholtz free energy (work content, maximum work function or work function )
- Gibb's free energy (Gibb's function, free enthalpy, thermodynamics potential or Gibb's potential)

### 1.4.1 Purpose of introducing Free energy functions

Most of thermodynamics processes can be explained using state functions like E, H and S , but there were so many processes which could not be explained with the help of these functions . For example, the spontaneous processes have a tendency to attain the maximum entropy and minimum energy at equilibrium. In selecting the entropy as criteria of spontaneity, one must consider the entropy changes for both the system and surroundings together. That is, for spontaneity the system must achieve both minimum energy and maximum entropy simultaneously. But in practice it is not always convenient for the system to achieve these conditions of irreversibility .This situation can be made clear by taking following examples

- Evaporation of liquid (which is endothermic process) is a spontaneous process .
- There are many processes in which no heat change occurs (i.e. thermal process) are spontaneous

  $AgClO_2\ (s) \rightarrow Ag\ (s) + \frac{1}{2}\ Cl_2 + O_2\ (g) \qquad \Delta H = 0$

in all these processes entropy of the system increases ($\Delta S_{sys}$= +ive ) and it dominates the enthalpy change (or energy change)of the system.

- There are many well-known processes which are spontaneous and the entropy of the system decreases ($\Delta S_{sys}$= -ive ). For example dissolution of HCl gas in water.

  $HCl\ (g) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$

$\Delta H_{sys}$= - 150 KJ $mole^{-1}\Delta S_{sys}$ = - 78 $JK^{-1}$ $mole^{-1}$

Here enthalpy change outweighs the decrease in entropy.

**Conclusions:** In view of above examples, it becomes very much clear that none of $\Delta H$, $\Delta$ E and $\Delta S_{sys}$ alone is sufficient to decide the direction of occurrence of spontaneous (Irreversible process) if we concentrate our attention on the system only. In usual practice the processes are studied either at constant T and constant P or at constant T and constant V. Therefore it is a desirable to introduce new functions in thermodynamics as criteria of spontaneity. It is common observation regarding all the spontaneous processes, that

(a) for endothermic changes, $\Delta S_{sys}$= +ive and very high .

(b) for exothermic changes$\Delta S_{sys}$= -ive

Thus there is always a compromise between heat of reaction ($\Delta H$ or $\Delta E$) and $\Delta S$sys.

1. Compromise between $\Delta E$ and $\Delta S$ is represented by $\Delta A$ such that

$$\Delta A = \Delta E - T\Delta S$$

2. Compromise between $\Delta H$ and $\Delta S$ is represented by $\Delta G$ such that

$$\Delta G = \Delta H - T\Delta S$$

In the above representations

A = Helmholtz Free Energy

G = Gibb's Free Energy

Thus A and G are defined as

$A = E - TS$ and $G = H - TS$

**SAQ 13** Is negative entropy spontaneous?

The second law of thermodynamics states that for any spontaneous process, the overall $\Delta S$ must be greater than or equal to zero; yet, spontaneous chemical reactions can result in a negative change in entropy. This leads to the formulation of concept of Gibbs and Helmholtz free energy.

## 1.4.2 Gibbs Free Energy Function (G)

**1.4.2.1 Definition of G.** We know that

$$dS \geq \frac{\delta q}{T}$$

$$dS \geq \frac{dE + PdV}{T}$$

$$dE + PdV - TdS \leq 0$$

If P and T are constant then above equation becomes

$$\delta(E + PV - TS)_{P,T} \leq 0 \quad \text{...........( 1.4.1)}$$

The quantity (E + PV - TS ) is referred to as the Gibb's free energy and is represented by G. Hence G is define as

$$G = E + PV - TS$$

Since $H = E + PV$

Hence $G = H - TS$ ...........( 1.4.2)

Therefore, for a given process, from equation (1.4.1)

$$(d\,G)_{P,T} \leq 0$$

Thus , state function G is useful in explaining the physical or chemical processes occurring at constant pressure and constant temperature.

**1.4.2.2 G is a state function** We know that $G = H - TS$

In the above equation H, S and T are state function. It follows that G will also be a state function and dG will be an exact differential.

**1.4.2.3 G is an Extensive Property** We know that $G = H - TS$

Since H and S are extensive properties , G will also be an extensive property. That is , value of G also depends on the mass of substance.

**1.4.2.4 Variation of G with Temperature and Pressure** We know that

$G = H - TS$

On differentiation $dG = dH - TdS - S\,dT$ ---------(1.4.3)

We know that $H = E + PV$

On differentiation $dH = dE + PdV + VdP$ ---------(1.4.4)

From equation (1.4.3) and (1.4.4) we get

$dG = dE + PdV + VdP - TdS - S\,dT$ ---------(1.4.5)

From First and second law of thermodynamics, for a reversible process

$TdS = dE + PdV$ or we can say

$dE = TdS - P\,dV$ ---------(1.4.6)

Putting the value of dE from equation (1.4.6) into equation (1.4.5) we get

$dG = TdS - P\,dV + PdV + VdP - TdS - S\,dT$

$dG = VdP - S\,dT$ ---------(1.4.7)

Equation (1.4.7) shows the variation of G with pressure and temperature.

**Case 1** When pressure is constant ($dP = 0$)

At constant P equation (1.4.7) becomes $dG = - S\,dT$

$\left(\frac{dG}{dT}\right)_p = - S$ ---------(1.4.8)

**Case 2** When temperature is constant ($dT = 0$)

Under this conditionequation (1.4.7) becomes $dG = VdP$

$$\left(\frac{dG}{dP}\right)_T = V \quad \text{---------} \ (1.4.9)$$

**Value of ΔG for n mole of an ideal gas**

Integrating equation (1.4.9)

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

$$\int_{G_1}^{G_2} dG = nRT\int_{P_1}^{P_2} \frac{dP}{P}$$

$$G_2 - G_1 = nRT \ln\left(\frac{P_2}{P_1}\right)$$

$$\Delta G = 2.303 \ nRT \ \log\left(\frac{P_2}{P_1}\right) \text{---------} \ (1.4.10)$$

Since T is constant

$$P_1V_1 = P_2V_2$$

$\frac{P_2}{P_1} = \frac{V_1}{V_2}$ Putting the values in equation (1.4.10)

$$\Delta G = 2.303 \ nRT \ \log\left(\frac{V_1}{V_2}\right) \text{---------} \ (1.4.11)$$

**1.4.2.5 Change in G for an isothermal Process**

$G = H - TS$

For initial state (1) : $G_1 = H_1 - TS_1$

For final state (2) : $G_2 = H_2 - TS_2$

∴ For change in G

$G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$

$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$

$\Delta G = \Delta H - T\Delta S$ …………………. (1.4.12)

**1.4.2.6 Significance of G**

We know that
$dG = dE + PdV + VdP - TdS - SdT$ ---------(1.4.5)
For a reversible process occurring at constant temperature and pressure , we have

$dT = 0$ and $dP = 0$ Hence equation (1.4.5) becomes

$(dG)_{P,T} = dE + PdV - TdS$ ---------(1.4.13)

For reversible process

$dS = \frac{\delta q_{rev}}{T}$ or $TdS = \delta q_{rev}$---------(1.4.14)

But $\delta q_{rev} = dE + dw_{rev}$

Since in reversible process work obtained ismaxmimum , hence

$w_{rev} = w_{max}$

$\delta q_{rev} = dE + \delta w_{max}$---------(1.4.15)

From equation (1.4.13), (1.4.14) and (1.4.15), we get

$(dG)_{P,T} = \delta q_{rev} - \delta w_{max} + PdV - \delta q_{rev}$

$(dG)_{P,T} = - \delta w_{max} + PdV$

$-(dG)_{P,T} = + \delta w_{max} - PdV$ ---------(1.4.16)

In equation (1.4.16)

$\delta w_{max}$ = Maximum work obtained in reversible process

$PdV$ = Work wasted against constant pressure

∴ Usefulwork = Maximum work - Work wasted

$\delta w_{useful} = \delta w_{max} - PdV$ ---------(1.4.17)

comparing equation (1.4.16) and (1.4.17) we get

$-(dG)_{P,T} = + \delta w_{useful}$---------(1.4.18)

Equation (1.4.18) means that decrease in Gibb's free energy is equal to useful work that can be obtained from reversible process taking place at costant pressure and temperature. Hence another definition of G is as follows :

"The fraction of total energy which is isothermally available for converting into useful work is called Gibb's free energy of the system".

**SAQ 14** Given the following data at 298 K, calculate $\Delta G^o$at 298 K for the following reaction:

$C_2H_4 (g) + H_2 (g) \rightarrow C_2H_6 (g)$

| **Substance** | **$\Delta G_f^0$ (kJ/mol)** |
|---|---|
| $C_2H_4(g)$ | 68.4 |
| $C_2H_6(g)$ | -32.0 |

The $\Delta G_f^0$ values can be used to calculate $\Delta G^0$ or the reaction in exactly the same method as $\Delta H^0$ can be used to calculate a reaction enthalpy.

$\Delta G^0$=(1mol)(−32.0kJ/mol)−(1mol)(68.4kJ/mol)

$\Delta G^o$=100.4kJ

*Note*: $H_2$ (g) is not included in the calculation since for $\Delta G_f^0$ $H_2$ (g) is 0 since it is an element in its standard state.

**SAQ 15** Calculate the change in free energy (in calories). Which occurs when 2 moles of a perfect gas expands reversibly and isothermally at $37^0$C from an initial volume of 55 litres to 1000 litres.

$\Delta G = 2.303 \ nRT \ \log \left(\frac{V_1}{V_2}\right) = 2.303 \times 2 \times 1.987 \times 310 \log \left(\frac{55}{1000}\right) = -3.574$ calories

## 1.4.3 Helmholtz Free Energy Function (A)

**1.4.3.1 Definition of A.** We know that

$$dS \geq \frac{dq}{T}$$

$$dS \geq \frac{dE + PdV}{T}$$

$$TdS \geq dE + PdV$$

$$dE + PdV - TdS \leq 0$$

If V is constant then above equation becomes

$(\delta E - T\delta S)_V \leq 0$ ...........(1.4.19)

If T also remains constant then equation ( 1.4.19) becomes

$\delta(E - TS)_{V,T} \leq 0$ ...........(1.4.20)

The quantity (E - TS) is referred to as Helmholtz Free Energy and is represented by A.

Hence , A is defined as

$A = E - TS$ ...........(1.4.21)

Therefore, for a given process, from equation (1.4.20)

$(dA)_{V,T} \leq 0$...........(1.4.22)

**1.4.3.2 A is a state function** We know that $A = E - TS$

In the above equation E, S and T are state function. It follows that A will also be a state function and dA will be an exact differential.

**1.4.3.3 A is an Extensive Property** We know that $A = E - TS$

Since E and S are extensive properties , it follows that A will also be an extensive property. That is , value of A also depends on the mass of substance. Thus we can say that state function A is more useful for processes at constant volume and at constant temperature.

**1.4.3.4 Relationship between G and A** We know that

G = H - TS ( ∴ H = E + PV )

G = E + PV - TS

G = ( E - TS ) + PV

G = A + PV ---------(1.4.23)

### 1.4.3.5 Variation of A with Temperature and Volume

We know thatA = E - TS

On differentiation

dA = dE - TdS - SdT---------(1.4.24)

From first law of thermodynamics

δq = dE + P dV---------(1.4.25)

For a reversible process , according to second law of thermodynamics

dS $=\frac{\delta q}{T}$ or dq = TdS ---------(1.4.26)

Putting the value of dEfrom equation (1.4.25) in equation (1.4.24) we get

dA = δq - P dV - TdS - SdT---------(1.4.27)

Putting the value of dqfrom equation (1.4.26) in equation (1.4.27) we get

dA = TdS - P dV - TdS - SdT---------(1.4.27)

dA = - P dV - SdT---------(1.4.28)

**Case 1** When volume is constant (dV = 0)

At constant V equation (1.4.28) becomes dA = - S dT

$\left(\frac{dA}{dT}\right)_V$ = - S ---------(1.4.29)

**Case 2** When temperature is constant (dT = 0)

Under this condition equation (1.4.28) becomes dA = - PdV

$\left(\frac{dA}{dV}\right)_T$ = - P --------- (1.4.30)

### 1.4.3.6 Value of ΔA for n mole of an ideal gas

We know that for an ideal gas

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

dA = - PdV (At constant T )

Putting the value of P in the above equation

dA = - nRT$\left(\frac{dV}{V}\right)$

On integrating above equation we get

$$\int_{A_1}^{A_2} dA = -\ nRT\int_{V_1}^{V_2} \frac{dV}{V}$$

$$A_2 -\ A_1 = -\ nRT\ \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta A = -\ 2.303 nRT\ \log\left(\frac{V_2}{V_1}\right)$$

$$\Delta A = 2.303\ nRT\ \log\left(\frac{V_1}{V_2}\right) \text{ --------- (1.4.31)}$$

### 1.4.3.7 Change in A for an isothermal Process

A = E– TS

For initial state (1): $A_1 = E_1 - TS_1$

For final state (2) : $A_2 = E_2 - TS_2$

∴ For change in A

$A_2 - A_1 = (E_2 - TS_2) - (E_1 - TS_1)$

$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$

ΔA = ΔE - T ΔS …………………. (1.4.32)

### 1.4.3.8 Significance of A

dA = dE - TdS - SdT---------(1.4.24)

At constant T the equation becomes

$dA = dE - TdS$---------(1.4.33)

From first law of thermodynamics

$\delta q_{rev} = dE + \delta w_{rev}$---------(1.4.34)

For a reversible process , according to second law of thermodynamics

$dS = \frac{\delta q_{rev}}{T}$ or $\delta q_{rev} = TdS$---------(1.4.26)

Equation (1.4.33) can be written as

$-\delta w_{rev} = dE - \delta q_{rev}$

$-\delta w_{rev} = dE - TdS$---------(1.4.35)

On comparing equation (1.4.33) and (1.4.35)

$dA = -\delta w_{rev}$

Since in reversible process work obtained ismaxmimum , hence

$W_{rev} = W_{max}$

$\therefore dA = - W_{max}$ or $- dA = W_{max}$---------(1.4.36)

Where $- dA =$ decrease in work fumction

Equation (1.4.36) means that decrease in work function in an isothermal process is equal to maximum work that can be obtained from the process. Hence by this statement it is justified to call A as maximum work function of the system.

### 1.4.4 Gibbs- Helmholtz Equation

#### (a) In terms of free energy and enthalpy

$dG = VdP - S\,dT$ ---------(1.4.7)

$\Delta G = \Delta H - T\,\Delta S$ …………………. (1.4.12)

Equation (1.4.7) at constant P becomes

$dG = - S\,dT$ orfor a small change $\left(\frac{dG}{dT}\right)_p = - S$ ---------(1.4.8)

For initial state (1) above equation becomes $\left(\frac{dG_1}{dT}\right)_p = - S_1$

For final state (2) above equation becomes $\left(\frac{dG_2}{dT}\right)_p = - S_2$

For change $\left(\frac{dG_2}{dT}\right)_p$ - $\left(\frac{dG_1}{dT}\right)_p$ = (- $S_2$ ) - (- $S_1$ ) = - ($S_2$ - $S_1$)

$\left[\frac{d(G_2 - G_1)}{\partial T}\right]_P$ = - ($S_2$ - $S_1$)

$\left[\frac{\partial \Delta G}{\partial T}\right]_P$ = -ΔS ...........(1.4.4.1)

Putting the value of -ΔS in equation (1.4.12), we get

$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_P$...........(1.4.4.2)

Equation (1.4.4.2) is **Gibbs- Helmholtz Equation** in terms of free energy and enthalpy at constant pressure.

**(b) In terms of internal energy and work function**

dA = - P dV - SdT---------(1.4.28)

ΔA = ΔE- T ΔS ...................... (1.4.32)

Equation (1.4.28) at constant V becomes

dA = - S dT orfor a small change $\left(\frac{dA}{dT}\right)_V$ = - S ---------(1.4.8)

For initial state (1) above equation becomes $\left(\frac{dA_1}{dT}\right)_V$ = - $S_1$

For final state (2) above equation becomes $\left(\frac{dA_2}{dT}\right)_V$ = - $S_2$

For change $\left(\frac{\partial A_2}{dT}\right)_V$ - $\left(\frac{\partial A_1}{\delta T}\right)_V$ = (- $S_2$ ) - (- $S_1$ ) = - ($S_2$ - $S_1$)

$\left[\frac{\partial(A_2 - A_1)}{\partial T}\right]_V$ = - ($S_2$ - $S_1$)

$\left[\frac{\partial \Delta A}{\partial T}\right]_V$ = -ΔS ...........(1.4.4.3)

Putting the value of -ΔS in equation (1.4.32), we get

$\Delta A = \Delta E + T\left[\frac{\partial \Delta A}{\partial T}\right]_V$...........(1.4.4.4)

Equation (1.4.4.4) is **Gibbs-Helmholtz Equation**in terms of internal energy and work function at constant volume.

**SAQ 16** Calculate the change in helmholtz free energy (in calories). Which when 5 moles of a perfect gas expands reversibly and isothermally at $37^0$C from an initial volume of 100litres to 1000 litres.

$\Delta A = 2.303 \ \ nRT \ \ \log \left(\frac{V_1}{V_2}\right) = 2.303 \times 5 \times 1.987 \times 310 \log \left(\frac{100}{1000}\right) = -7.092$ K calories

**SAQ 17** What is the difference between Gibb's and Helmholtz free energy?

The Gibbs' free energy is the energy available to do non-PV work in a thermodynamically-closed system at constant pressure and temperature. The Helmholtz free energy is the maximum amount of work that can be extracted from a thermodynamically-closed system at constant volume and temperature.

**SAQ 18** Give Helmholtz free energy applications?

In explosives research, **Helmholtz free energy** is often used since explosive reactions by their nature induce pressure changes. It is also frequently used to define fundamental equations of state in accurate correlations of thermodynamic properties of pure substances.

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## 1.5 CRITERIA FOR THERMODYNAMIC EQUILIBRIUM AND SPONTANEITY IN TERMS OF CHANGESIN ENTROPY, GIBBS AND HELMHOLTZ FUNCTIONS

These are the following thermodynamics conditions for spontaneity and equilibrium.

(i) Spontaneous change is unidirectional that is irreversible. No work has to be done for spontaneous change. It occurs by itself whereas in case of reversible change it is bidirectional. For reversible change to take place, work has to be done. Reversible process is unreal.

(ii) There is no time limitation for spontaneous change to occur, it may take place rapidly or very slowly. Irreversible or spontaneous processis real.

**(iii) Conditions in terms of entropy change**

$dS \geq \frac{\delta q}{T}$ (second law)

$\delta q = dE + P\,dV$ (First law)

$dS \geq \frac{dE + PdV}{T}$

$TdS \geq dE + PdV$

If E = Constant, then dE = 0 ---------(1.5.1)

If V = Constant, then dV = 0 ---------(1.5.2)

Hence from equation (1.5.1) and (1.5.2), we get

$(dS)_{E,V} \geq 0$ or $(dS)_{E,V} \geq 0$---------(1.5.3)

On the bases of expression (1.5.3) we can conclude that

(a) If $(\partial S)_{E,V}= 0$ , then process is reversible

(b) If $(\delta S)_{E,V} > 0$ , that is +ive ; then process is spontaneous (real). In the spontaneous process entropy goes on increasing and become maximum at equilibrium.

**(iv) Conditions in terms of Gibb's free energy change.**

G = H - TS

On differentiation dG =dH - TdS - S dT ---------(1.4.3)

We know that H = E + PV

On differentiation dH =dE + PdV + VdP ---------(1.4.4)

From equation (1.4.3) and (1.4.4) we get

dG =dE + PdV + VdP - TdS - S dT ---------(1.4.5)

dG -VdP+ S dT= dE + PdV- TdS---------(1.5.4)

TdS≥ $dE + PdV$ (combination of first and second law )

Or 0≥ $dE + PdV$ -TdS---------(1.5.5)

On comparing equation (1.5.4) and (1.5.5) we can say that

dG -VdP+ S dT≤0---------(1.5.6)

If P = Constant, then dP = 0 ---------(1.5.7)

If T = Constant, then dT = 0 ---------(1.5.8)

Hence from equation (1.5.7) and (1.5.8), we get

$(dG)_{P,T} \leq 0$ or $(\partial G)_{P,T} \leq 0$ ---------(1.5.9)

Conclusion

(a) For spontaneity $(\partial G)_{P,T} < 0$

(b) For equilibrium $(dG)_{P,T} = 0$

(c) For reversibility $(dG)_{P,T} = 0$

**(v) Conditions in terms of Helmholtz free energy change.**

We know that A = E - TS

On differentiation

dA = dE - TdS - SdT---------(1.4.24)

dA + SdT = dE - TdS ---------(1.5.10)

But we know that

TdS$\geq dE + PdV$ (combination of first and second law )

-PdV$\geq dE$- TdS---------(1.5.11)

On comparing equation (1.5.10) and (1.5.11) we get

- PdV≥dA + SdT

dA + SdT+PdV$\leq$ 0 ---------(1.5.12)

If V = Constant, then dV = 0 ---------(1.5.13)

If T = Constant, then dT = 0 ---------(1.5.14)

Hence from equation (1.5.13) and (1.5.14), we get

$(dA)_{V,T} \leq 0$ or $(\partial A)_{V,T} \leq 0$ ---------(1.5.15)

Conclusion

(a) For spontaneity $(\partial A)_{V,T} < 0$

(b) For equilibrium $(\partial A)_{V,T} = 0$

(c) For reversibility $(\partial A)_{V,T} = 0$

**SAQ 19** Give criteria for thermodynamic equilibrium and spontaneity in terms of changes inenthalpy.
We know that H = E + PV
On differentiation dH =dE + PdV + VdP ---------(1.4.4)
dH-VdP = dE + PdV
TdS $\geq dE + PdV$ (combination of first and second law )
TdS $\geq$ dH-VdP
0 $\geq$ dH-VdP– TdS At constant P and S
We get $(dH)_{P,S} \leq 0$
(a) For spontaneity $(dH)_{P,S} < 0$
(b) For equilibrium $(\partial H)_{P,S} = 0$
(c) For reversibility $(\partial H)_{P,S} = 0$

**SAQ 20** Give criteria for thermodynamic equilibrium and spontaneity in terms of changes in energy.
TdS $\geq dE + PdV$ (combination of first and second law )
0 $\geq dE + PdV$- TdSAt constant V and S

We get $(dE)_{V,S} \leq 0$
(a) For spontaneity $(dE)_{V,S} < 0$
(b) For equilibrium $(\partial E)_{V,S} = 0$
(c) For reversibility $(\partial E)_{v,S} = 0$
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## 1.6 CONCEPT OF CHEMICAL POTENTIAL

### 1.6.1 Partial molal quantity

Before knowing chemical potential we must know what **partial molal quantity** is.

Let us consider a system which is undergoing small changes in all its variables, including the amounts of the system. The net change in thermodynamic property say X will be given by partial differentiation as given below.

X = ƒ (P, T, $n_1$ , $n_2$ , $n_3$, …….$n_i$ )---------(1.6.1)

$$dX = \left(\frac{\partial X}{\delta P}\right)_{T,\ n_{1,},\ n_2\ ,\dots} dP + \left(\frac{\partial X}{\delta T}\right)_{P,\ n_{1,},\ n_2\ ,\dots} dT + \left(\frac{\partial X}{\partial n_1}\right)_{T,\ P,\ n_2\ ,\dots} dn_1$$
$$+\left(\frac{\partial X}{\partial n_2}\right)_{T,\ P,\ n_1\ ,\dots} dn_2 + \dots\dots\dots\dots + \left(\frac{\partial X}{\partial n_i}\right)_{T,\ P,\ n_1\ ,\ n_2\ ,\dots} dn_i \text{---------(1.6.2)}$$

The term $\left(\frac{\partial X}{\partial n_1}\right)_{T,\ P,\ n_2\ ,\dots}$ is called Partialmolal property or quantity for the component 1. This is usually denoted by putting a bar over the symbol of thermodynamic property. Hence

$$\left(\frac{\partial X}{\partial n_1}\right)_{T,\ P,\ n_2\ ,\dots} = \overline{X_1}\text{---------(1.6.3)}$$

$$\left(\frac{\partial X}{\partial n_2}\right)_{T,\ P,\ n_1\ ,\dots} = \overline{X_2}\text{---------(1.6.4)}$$

$$\left(\frac{\partial X}{\partial n_i}\right)_{T,\ P,\ n_1\ ,\ n_2\ ,\dots(n1-1)} = \overline{X_i}\text{---------(1.6.5)}$$

Thus $\overline{X_1}$ , $\overline{X_2}$ , $\overline{X_3}$ … … … $\overline{X_i}$denotes Partialmolal properties for the components 1 , 2, 3 , ….., i respectively.

Hence the Partial molal property denotes the rate of change of the given thermodynamic extensive property of the system on account of addition of one mole of the given component , when moles of all other components, temperature and pressure remain constant .

Similarly for i$^{th}$ component in a system

Partial molal internal energy $\overline{E_i} = \left(\frac{\partial E}{\partial n_i}\right)_{T,\ P,\ n_1\ ,\ n_2\ ,\dots(n1-1)}$

Partial molal enthalpy $\overline{H_i} = \left(\frac{\partial H}{\partial n_i}\right)_{T,\ P,\ n_1\ ,n_2\ ,\dots(n1-1)}$

Partial molal Gibb's potential $\overline{G_i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,\ n_1\ ,n_2\ ,\dots(n1-1)}$

Partial molal work function $\overline{A_i} = \left(\frac{\partial A}{\partial n_i}\right)_{T,\ P,\ n_1\ ,n_2\ ,\dots(n1-1)}$

Partial molal Volume $\overline{V_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,\ P,\ n_1\ ,n_2\ ,\dots(n1-1)}$

**SAQ 21** What kind of property is partial molal property?
The partial molal properties are intensive properties. They do not depend on the size (mass) of the system. For example, if the value of $n_i$ is increased at constant pressure and temperature, the partial molal property $\overline{X_i}$will remainconstant because the corresponding extensive thermodynamic property $\overline{X_i}$increases in the same proportion.

### 1.6.2 Chemical Potential

The Partial molal Gibb's free energy (or Partial molal Gibb's potential) of a constituent in a mixture at constant pressure and constant temperaureis known aschemical potentialby Willard Gibbs. It is symbolized by μ. Hence we can say

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,\ n_1\ ,n_2\ ,\dots} = \overline{G_i}\text{---------}(1.6.6)$$

In an open system the Gibbs potential is expressed as

$G = f(P, T, n_1, n_2, n_3, \dots\dots n_i)$

By partial differentiation

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,\ n_{1,},\ n_2\ ,\dots} dP + \left(\frac{\partial G}{\partial T}\right)_{P,\ n_{1,},\ n_2\ ,\dots} dT + \left(\frac{\partial G}{\partial n_1}\right)_{T,\ P,\ n_2\ ,\dots} dn_1$$
$$+\left(\frac{\partial G}{\partial n_2}\right)_{T,\ P,\ n_1\ ,\dots} dn_2 + \dots\dots\dots\dots\dots + \left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,\ n_1\ ,n_2\ ,\dots(n1-1)} dn_i$$

At constant pressure (dP= 0) and at constant temperature (dT= 0) the above equation becomes

$(dG)_{P,T} = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots\dots\dots\dots + \mu_i dn_i$

### 1.6.3 Physical significance of Chemical Potential

1. The chemical potential is independent of the masses but not independent on the composition of the system. Thus we can say that chemical potential is an intensive property of the system which has same value within the entire system in equilibrium.

2. If a small amount ‘$dn_i$’ moles of the component *i* is added to the system (keeping P, T and moles of other components of the system constant ), the increase in free energy per mole of i^th component added is given by

$(dG)_{P,T,n_1,,n_2,...} = \mu_i dn_i$

Where $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,\ n_1\ ,n_2\ ,...}$ ---------(1.6.6)

From equation (1.6.6) we can say that chemical potential of i^th component is the increase in the Gibbs free energy of the system , which occurs due to the addition of 1 mole of i^th component , at constant pressure and temperature , on the condition that other component remain unaltered.

3. Matter flows from the region of high chemical potential to low chemical potential in spontaneous processes.

4. For a pure substance the chemical potential is equal to molar free energy that is

$\mu = G / n$ where n = number of moles

5. **Escaping tendency** is anothername of chemical potential. That is $\mu_i$stands for escaping tendency of component i. This signifies that if $\mu_i$is high,then componenti has large escaping tendency and vice – versa.

**SAQ 22** What is the unit of chemical potential?
Chemical potential is expressed in **energy** units per unit of the substance **mass** (**Joule**/kg) or per **mole** of the substance (**Joule/mole**) or per molecule of the substance.

## 1.7 SUMMARY

- Second law of thermodynamics say that “It is impossible to construct a heat engine which operating in a complete cycle, will abstract heat from a single body and convert the whole of it into work, without leaving any changes in the working system that is it is impossible to build heat engine of 100 % thermal efficiency”.
- Entropy of a system is a function of state and its change is equal to the ratio of heat change to the temperature at which heat change occurs in a reversible (or equilibrium) cyclic process.
- Entropy as a state function.
- Entropy as a function of V and T is given by $\Delta S = n C_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$
- Entropy as a function of P and T is given by $\Delta S = n C_P \ln\left(\frac{T_2}{T_1}\right) - nR \ln\left(\frac{P_2}{P_1}\right)$
- Natural processes in universe areirreversible (spontaneous )process . Hence entropy of the universe is increasing. That is $\Delta S_{universe} > 0$

  Entropy of reversible(non -spontaneous )process is constant . That is $\Delta S_{universe} = 0$

  Combining above two statements we can conclude$\Delta S_{process} \geq 0$
- Both Helmholtz and Gibb’s free energies are state function and behave extensive in nature..

| Helmholtz free energy | Gibbs free energy |
|---|---|
| It is defined as the maximum work that is obtained from a particular system | It is defined as the useful work other than P ΔV that is obtained from a particular system |
| It is the energy required to create a system at constant temperature and volume | It is energy required to create a system at constant pressure and temperature |
| Helmholtz free energy finds lesser application as the volume of the system should be constant | Gibbs free energy finds more application as the pressure of the system is constant |

- **Gibbs- Helmholtz Equation** in terms of free energy and enthalpy at constant pressure.

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_P$$

- **Gibbs-Helmholtz Equation** in terms of internal energy and work function at constant volume.

$$\Delta A = \Delta E + T\left[\frac{\partial \Delta A}{\partial T}\right]_V$$

- Summary of Criteria

| S. No. | Spontaneity (irreversible) | Equilibrium in real process | Reversibility |
|---|---|---|---|
| 1. | $(\partial S)_{E,V} > 0$ | $S = \text{Max. i. e.}, (\partial S)_{E,V} = 0$ | $(\partial S)_{E,V} = 0$ |
| 2. | $(\partial G)_{P,T} < 0$ | G = Min. i.e.,$(\partial G)_{P,T} = 0$ | $(\partial G)_{P,T} = 0$ |
| 3. | $(\partial A)_{V,T} < 0$ | A= Min. i.e., $(\partial A)_{V,T} = 0$ | $(\partial A)_{V,T} = 0$ |
| 4. | $(\partial H)_{P,S} < 0$ | H= Min. i.e.,$(\partial H)_{P,S} = 0$ | $(\partial H)_{P,S} = 0$ |
| 5. | $(\partial E)_{V,S} < 0$ | E= Min i.e., $(\partial E)_{V,S} = 0$ | $(\partial E)_{V,S} = 0$ |

- The Partial molal property denotes the rate of change of the given thermodynamic extensive property of the system on account of addition of one mole of the given component , when moles of all other components, temperature and pressure remain constant .

Similarly for i$^{th}$ component in a system

$$\left(\frac{\partial X}{\partial n_i}\right)_{T,\ P,\ n_1\ ,n_2\ ,\ldots} = \overline{X_i}$$

- The Partial molal Gibb's free energy (or Partial molal Gibb's potential) of a constituent in a mixture at constant pressure and constant temperatureis known aschemical potential. It is denoted by the symbol μ.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,\ n_1\ ,n_2\ ,\ldots}$$

- **Escaping tendency** is another name of chemical potential. That is $\mu_i$ stands for escaping tendency of component i. This signifies that if $\mu_i$ is high, then component i has large escaping tendency and vice – versa

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## 1.8 TERMINAL QUESTIONS

**SAQ1** Which state in each of the following pairs has the higher entropy per mole of substance?
(I) $H_2$ at $25^0$ C in a volume of 10 L or $H_2$ at $25^0$ C in a volume of 50 L.
(II) $O_2$ at $25^0$ C and 1 atm or $O_2$ at $25^0$ C and 10 atm.
(III) $H_2$ at $25^0$ C and 1 atm or $H_2$ at $100^0$ C and 1 atm.
(IV) $CO_2$ at STP or $CO_2$ at $100^0$ C and 0.1 atm.

**SAQ2** Calculate the standard entropy change of the reaction $N_2$ (g) + $O_2$ (g) → 2NO (g) the values of absolute entropies of $N_2$ , $O_2$ and NO are 191.62 , 205.01 and 210.45 J $K^{-1}$ $mol^{-1}$ respectively.

**SAQ3** Calculate the change in free energy (in calories). Which occurs when 10 moles of a perfect gas expands reversibly and isothermally at $27^0$C from an initial volume of 10 litres to 100 litres.

**SAQ4** Calculate the entropy change( in joules) involved in thermodynamic isothermal reversible expansion of 2.5 mole of an ideal gas at $27^0$C from an initial volume of 2 litres to final volume of 20 litres.

**SAQ5** Calculate the change in entropy when 5 mole of Helium gas at constant pressure suffered heating from 400K to 800K. (Given $C_P$ = 5 Cal $K^{-1}$ $mole^{-1}$)

**SAQ6** What is the relationship between spontaneity and equilibrium?

**SAQ7** Calculate the change in entropy in the evaporation of 1 mole of waterat $100^0$C. Latent heat of evaporation of water is 9.650 cal per mole.

**SAQ8** Calculate the total change in entropy when 5g of ice at 273 K is converted into steam at 373K. Given that the latent heat of vaporisation of water = 540 cal $g^{-1}$ ,$C_p$= 18 $calmol^{-1}$ and latent heat of fusion of ice = 80 cal $g^{-1}$.

**SAQ9** What is the basic difference between $X_i$and $\overline{X_i}$ .

**SAQ10** What will be the effect of temperature on chemical potential at constant pressure?

**SAQ11** What will be the effect of pressure on chemical potential at constant temperature?

**SAQ12** For the following reaction$N_2$ (g) + $O_2$ (g) → 2NO (g) the free energy changes at $25^0$C and $35^0$C are - 33.089 and – 28.018 kJ respectively. Calculate the heat of reaction.

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## 1.9 ANSWERS

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**SAQs**

1. (I) Larger the volume of the gas, greater the tendency of the molecules to set into motion hence randomness increases. $H_2$ at $25^0$ C in a volume of 50 L.

(II) $O_2$ at $25^0$ C and 1 atm.

(III) $H_2$ at $100^0$ C and 1 atm.

(IV) $CO_2$ at $100^0$ C and 0.1 atm.

2. $\Delta S^o = \sum S^0_{products} - \sum S^0_{reactants}$

$= (2mol \times 210.45\ J\ K^{-1}\ mol^{-1}) - (1mol \times 191.62\ J\ K^{-1}\ mol^{-1} + 1mol \times 205.01\ J\ K^{-1}\ mol^{-1})$

$= 24.27\ J\ K^{-1}\ mol^{-1}$

3. $\Delta G = 2.303\ nRT\ \log\left(\frac{V_1}{V_2}\right) = 2.303 \times 10 \times 1.987 \times 300 \log\left(\frac{10}{100}\right) = -13.72$ k calories

4. $\Delta S = 2.303\ nR\ \log\left(\frac{V_2}{V_1}\right)$

Here n=2.5, $V_1$ = 2 litres, $V_2$ = 20 litres, R= 8.313 Joules $K^{-1}$ mole $^{-1}$

$\Delta S = 2.303 \times 2.5 \times 8.313\ \log\left(\frac{20}{2}\right)$

$\Delta S = 47.86$ Joules $K^{-1}$ mole $^{-1}$

5. $\Delta S = n\ C_P\ \ln\left(\frac{T_2}{T_1}\right) = 2.303\ n\ C_P\ \log\left(\frac{T_2}{T_1}\right) = 2.303 \times 5 \times 5 \log\left(\frac{800}{400}\right) = 17.33$ Cal $K^{-1}$ mole$^{-1}$

6. Conversely, if ΔG° > 0, then $K_p < 1$, and reactants are favoured over products. If ΔG° = 0, then Kp is equal to 1, and neither reactants nor products are favoured: the system is at **equilibrium**. For a **spontaneous** process under standard conditions, Keq and Kp are greater than 1.

7. Entropy change in evaporation of 1 mole of water is obtained by dividing the latent heat of evaporation of 1mole of water by the absolute temperature.

$\Delta S = \frac{9.650}{373} = 25.87$ cal $K^{-1}mol^{-1}$

8. Ice at 273 K can be converted into steam at 373K through the following steps:

For $H_2O$ (s) (at 273 K) → $H_2O$ (l) (at 273 K)

$\Delta S_1 = \frac{\Delta H^0_f}{T_f} = \frac{80\times5}{273} = 1.465 calK^{-1}$

For $H_2O$ (l) (at 273 K) → $H_2O$ (l) (at 373 K)

$\Delta S_2 = 2.303\ n\ C_P\ \log\left(\frac{T_2}{T_1}\right) = 2.303 \times \frac{5}{18} \times 18 \log\left(\frac{373}{273}\right) = 1.560 Cal\ K^{-1}$

For $H_2O$ (l) (at 373 K) → $H_2O$ (v) (at 373 K)

$\Delta S_3 = \frac{\Delta H^0_v}{T_b} = \frac{540\times5}{373} = 7.239 calK^{-1}$

Total entropy change = $\Delta S_1 + \Delta S_2 + \Delta S_3$ = 1.465 + 1.560 + 7.239 = 10.264 cal $K^{-1}$

9. $X_i$ are thermodynamic properties which are extensive in nature where as $\overline{X_i}$ symbolizes partial molal properties which are intensive in nature , being the ratio of two extensive properties . Hence thermodynamic properties (X) depends on the number of moles where as partial molal properties

($\bar{X}$) do not depend on the number of moles , provided the composition practically remains same . However both properties (X) and partial molal properties ($\bar{X}$) at constant T and P depend on the composition (mole fraction ) of the system.

10. Fori-th component of a system,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,n_i}$$

Differentiating this equation with respect to T at constant P and composition, we get

$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j} = \frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,n_\mathrm{i}}\right]_{P,\ \mathrm{ni}}$ But we know that G ia a state function , so we can say

$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j} = \frac{\partial}{\partial n_i}\left[\left(\frac{\partial G}{\partial T}\right)_{P,\mathrm{ni}}\right]_{T,P,\mathrm{ni}}$ ….(1.8.1)From the equation dG = VdP – SdT at constant P , we get
$\left(\frac{\partial G}{\partial T}\right)_P = -S$ ….(1.8.2)on compairing equation (1.8.1)and (1.8.2) , we get
$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j} = \left(\frac{\partial S_i}{\partial n_i}\right)_{T,P,n_i} = -\overline{S_\iota}$
As S is always positive, **μ decreases with the increase in temperature**. The rate of change of μ with T is different for solids, liquids and gases ; minimum for the solids and maximum for the gases.

11.Fori-th component of a system,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,n_i}$$

Differentiating this equation with respect to P at constant T and composition, we get

$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \frac{\partial}{\partial P}\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,n_\mathrm{i}}\right]_{T,n_\mathrm{i}}$ But we know that G ia a state function , so we can say

$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j} = \frac{\partial}{\partial n_i}\left[\left(\frac{\partial G}{\partial p}\right)_{T,n_\mathrm{i}}\right]_{T,P,n_\mathrm{i}}$ ….(1.8.3)From the equation dG = VdP – SdT at constant T, we get
$\left(\frac{\partial G}{\partial P}\right)_T = V$ ….(1.8.4)on comparing equation (1.8.3)and (1.8.4) , we get
$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_\mathrm{i}} = \left(\frac{\partial V_i}{\partial n_i}\right)_{T,P,n_\mathrm{i}} = \overline{V_\iota}$
For an ideal gas, the partial molar volume is equal to partial volume ($V_m$)
$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j} = \overline{V_\iota} = V_m = \frac{RT}{P}$
Thus the rate of change of μ of a component I with P at constant T and composition is equal to the partial molar volume.

12. $\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_P$
$G_1 = -33.089$ kJ  $T_1 = 273+25 = 298$ K
$G_2 = -28.018$ kJ  $T_2 = 273+35 = 308$ K
$T\left[\frac{\partial \Delta G}{\partial T}\right]_P = \frac{-28.018-(-33.089)}{308-298} = 0.507\text{kJ}$
At $35^0$C $\Delta G = -28.018$ kJ  $T = 273+35 = 308$ K
$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_P$

$-28.018 = \Delta H + 308 \times 0.507$
$\Delta H = 28.018 + 156.16 = 184.17$ kJ

**Suggested reading**

**Reference Books**

- **Peter, A. & Paula, J. de. Physical Chemistry 9th Ed., Oxford University Press (2011)**
- **Engel, T. & Reid, P. Physical Chemistry 3rd Ed., Prentice-Hall (2012).**
- **McQuarrie, D. A. & Simon, J. D. Molecular Thermodynamics Viva Books Pvt. Ltd.: New Delhi (2004).**
- **Levine, I .N. Physical Chemistry 6th Ed., Tata Mc Graw Hill (2010)**
- **Metz, C.R. 2000 solved problems in chemistry, Schaum Series (2006)**
- **Assael, M. J.; Goodwin, A. R. H.; Stamatoudis, M.; Wakeham, W. A. & Will, S.**

**Commonly Asked Questions in Thermodynamics. CRC Press: NY (2011).**

**Text Books**

- **Puri, B.R., Sharma L.R. & Pathania Madan S., Principles of Physical Chemistry, Vishal Publishing Company ,(2013)**
- **Mukerjee,R.C., Modern approach to Physical Chemistry, Bharati Bhawan(2016)**
- **Raj Gurdeep, Advanced Physical Chemistry, Krishna Prakashan(2016)**
- **Bahl, A., Bahl, B.S. & Tuli,G.D., Essential of Physical Chemistry, S. Chand &Company (2012)**
- **Sahgal, S., Numerical Analysis of Physical Chemistry, Victorious Publishers (2018)**

# UNIT -3 ELECTROCHEMISTRY- II

**Structure**

## 3.1 INTRODUCTION

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Redox reactions are everywhere! Your body uses redox reactions to convert food and oxygen to energy plus water and carbon dioxide, which we then exhale. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. The batteries in your electronics also rely on redox reactions, which you will hear more about when we learn electrochemistry. Can you find other examples of redox reactions happening around you?

All electrochemical system involves a heterogeneous process in which the reactions occur in a region known as the cell, where the transfer of electrons between the electrode surface and molecules in the solution adjacent to the electrode surface.

The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, the study of electrochemistry is important for creating new technologies that are ecofriendly. The transmission of sensory signals through cells to the brain and vice versa and communication between the cells are known to have an electrochemical origin. Electrochemistry, is, therefore, a very vast and interdisciplinary subject. In this Unit, we will cover some of its important elementary aspects and their applications.

***Objectives***

By the end of this unit, you will be able to:

- Describe an electrochemical cell and its components
- Represent an electrochemical cell as per convention
- Differentiate between galvanic and electrolytic cell; reversible cell and irreversible cell
- Understanding of electromotive force and electrode potential
- Learn different types of electrodes
- Construct the reference hydrogen electrode and explain why it is a reference electrode.
- Calculate the standard potential from the reduction potentials.
- Understand electrochemical series and its applications
- Relate cell potentials to free energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants
- Describe the characteristics and the half-cell reactions of various kinds of electrodes used
- Differentiate between primary and secondary cells.

- List different types of dry cells in common use
- Concept of Concentration cell with and without transport,
- Understand liquid junction potential
- Explain corrosion as an electrochemical process.
- Define pH and measure the pH of a solution
- Application of the concept of pH metry and ion -selective potentionmetry
- Draw and level a glass electrode and write the Nernst equation for a glass electrode,
- Describe how the pH meter can be used to measure the pH
- Describe the composition, function and mechanism of acid-base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base
- Learn the concept of salt hydrolysis
- Explain the principle of potentiometric titration
- Learn activity and activity coefficient

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### *3.2 SOME BASIC CONCEPTS*

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#### *3.2.1 Redox reaction*

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which is generated by the movement of electrons from one electrode to another in a reaction is known as an oxidation-reduction (redox) reaction.

Let us consider the reaction between Zn and $CuSO_4$

$\mathbf{Zn + CuSO_4 \rightarrow ZnSO_4 + Cu\downarrow}$

It may also be written as

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

The above redox reaction can be split into two reactions.

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

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

It occurs by the transfer of electrons from Zn to Cu. Zn loses an electron and is said to be oxidized to $Zn^{+}$ ion. At the same time, Cu gains an electron and is reduced to $Cu^{2+}$ ion. Such a reaction which is brought about by the loss of electrons (oxidation) and gain of electrons (reduction) simultaneously, is called an **Oxidation-Reduction reaction or Redox reaction**. It may be noted that in the overall redox reaction no free electrons are generated.

Oxidation is the loss or release of electrons. Reduction is the gain or addition of electrons.

**Oxidation**

$$A \longrightarrow A^{n+} + ne^-$$

**Reduction**

$$B + me^- \longrightarrow B^{m-}$$

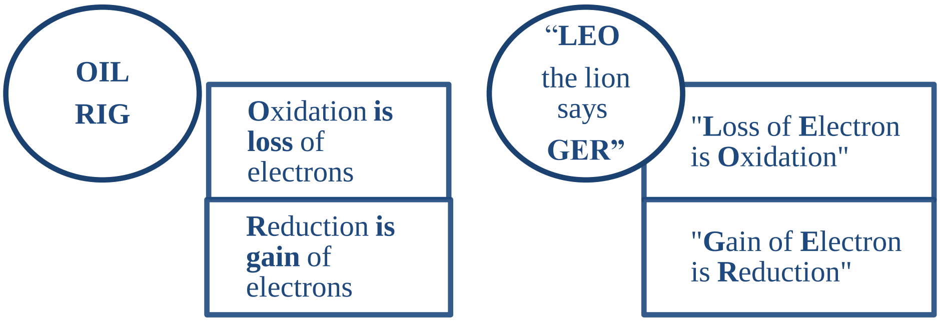


**Fig. 3.1**.Tips to remember Oxidation and Reduction

## *3.3. ELECTROCHEMICAL CELL*

A device used to convert the chemical energy of a reaction into electrical energy is called an electrochemical cell.

***How redox reactions are a source of electric current in electrochemical cells?***

Let us compare the two situations. One in which a zinc rod is dipped in a solution of copper sulphate, as shown in (Fig. 3.2 (A)). In this situation, copper metal is deposited on the Zn rod. Now, let the two half-reactions occur in separate compartments which are connected by a wire (Fig. 3.2 (B)). The electrons produced in the left compartment flow through the wire to the other compartment. However the current will flow for an instant and then stop. The current stops flowing because of the charge build-up in the two compartments. The electrons leave the left compartment and it would become positively charged. The right compartment receives electrons and becomes negatively charged. Both these factors oppose the flow of electrons (electrical current) which eventually stops. This problem can be solved using a **salt bridge (**U-tube filled with an electrolyte such as NaCl, KCl, or $K_2SO_4$), which provides a passage to ions from one compartment to the other compartment without extensive mixing of the two solutions. With this ion flow, the circuit is complete and electrons pass freely through the wire to keep the net charge zero in the two compartments.

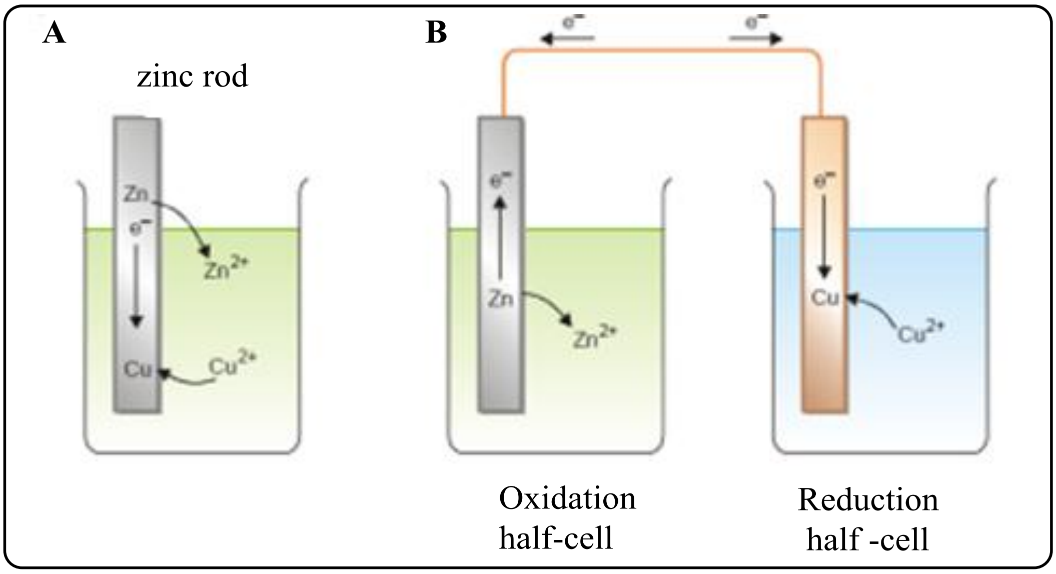


**Fig. 3.2** Redox reactions are a source of electric current (A) Redox reaction taking place on zinc rod itself. (B) two half-reactions occur in separate compartments which are connected by a wire

Thus, Electrochemical cells can be described as *"the device capable of either generating electrical energy as a result of some spontaneous chemical reaction or the device which can carry out a chemical reaction with the help of electric current*". Thus, in an electrochemical cell, a spontaneous red-ox reaction is carried out indirectly and the decrease in free energy during chemical reaction appears as electrical energy. An indirect redox reaction is such that reduction and oxidation processes are carried out in two separate vessels called half-cells.

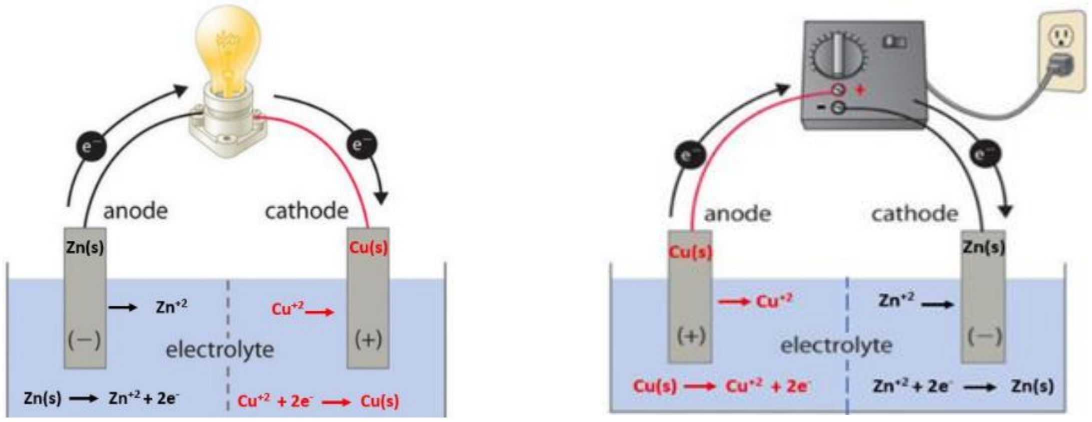
### *3.3.1 Types of Electrochemical cell*

A. (a) Electrolytic Cell and (b) Galvanic Cell or Voltaic Cell.

(a) **Electrolytic Cell:** It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

(b) **Galvanic Cell:** The device used to convert the chemical energy produced on a redox reaction into electrical energy is called an electrochemical cell or simply a chemical cell. These are also called galvanic cells or voltaic cell after the names of Luigi Galvanic and Alessandro Volta who were first to perform experiments on the conversion of chemical energy into electrical energy. These cells operating spontaneously and can be used to provide energy to do work, like the common "battery" we use in flashlights and electrical devices.

Just as we could drive a nonspontaneous reaction by coupling it to a spontaneous reaction, we could hook up an external supply of power with the opposite polarity and drive the reaction in the intrinsically nonspontaneous direction. In this case, the electrochemical cell is operating in the electrolytic mode and being driven by an external source of energy. **Fig. 3.3** show the two modes of functioning of an electrochemical cell. The left mode is the spontaneous redox reaction and can be used to provide energy to do work. The right mode is the electrolytic mode, which will not occur unless an external energy source is added to drive it. That is, the reaction on the electrolytic cell is not spontaneous unless it is driven by an external source.



| ***Galvanic cell*** | **Electrolytic cell** |
|---|---|
| **$Zn(s) + Cu^{2+} \rightarrow Zn^{2+}(aq) + Cu(s)$** | **$Cu (s) + Zn^{2+} \rightarrow Zn(s) + Cu^{2+}$** |
| Operates in spontaneous galvanic mode releases energy that can do work | Operating in non-spontaneous electrolytic mode requires external energy to make it work |

**Figure 3.3** Two modes of functioning of an electrochemical cell

### B. *(a) Reversible cell and (b) Irreversible cell*

**(a)** **Reversible cell:** A reversible cell is a cell in which the driving and opposing force differ infinitesimally small amount from each other and the chemical change taking place in it can be reversed by applying an external force infinitesimally greater than the e.m.f. of the cell. Example: **Daniel cell** is a reversible cell. The reaction of the Daniel cell is

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$

The cell reaction can be adjusted to forward or reverse direction by adjusting the external e.m.f. of the cell.

**A reversible cell should satisfy the following conditions:**

i)When the external e.m.f. of the cell is infinitesimally greater than the e.m.f. of the cell, then- current should flow through the cell and the cell reaction of the cell should get reversed.

ii) When the external e.m.f. of the cell is infinitesimally less than the e.m.f. of the cell, then- current should flow from the cell.

iii) When the external e.m.f. of the cell is exactly equal to the e.m.f. of the cell, then no current should flow through the cell.

**(b) Irreversible cell:** Cell which does not satisfy the condition of reversibility is irreversible. Consider the following cell set up by dipping copper and zinc electrodes in a solution of sulphuric acid. When the cell operates, the following reaction takes place

$$\mathbf{Zn + 2H^{+} \longrightarrow Zn^{2+} + H_2}$$

When this cell is connected to an external e.m.f. which is slightly greater than the e.m.f. of the cell, the following reaction occurs

$$\mathbf{Cu + 2H^{+} \longrightarrow Cu^{2+} + H_2}$$

Thus the first reaction is not reversed than that of the second. Hence it is an irreversible cell.

**Differences between the reversible cell and irreversible cell**

| | **Reversible cell** | **Irreversible cell** |
|---|---|---|
| 1. | Cell reaction is reversible | 1. Cell reaction is irreversible |
| 2. | E.m.f. is generated by the cell reaction of its own. | 2. An external potential greater than the ce e.m.f. is required for the cell reaction t occur. |
| 3. | Cell reaction occurs only when the two electrodes are connected externally. | 3. Cell reaction may occur even if the tw electrodes are not connected externally. |
| 4. | It is a galvanic cell | 4. It is an electrolytic cell. |
| 5. | | |

## omponents of Electrochemical Cells

An electrochemical cell splits the oxidant and reductant in a manner that allows electrons to flow through an external circuit from the reductant (which gets oxidized) to the oxidant (which causes reduction) while preventing them from physically touching each other. **Fig. 3.3** represent electrochemical cells and you should look at those images while reading this section. The two compartments of an electrochemical cell where the half-reactions occur are called the anode and the cathode, and they must have an electrode that you can connect the external circuit to.

i. **Anode:** Oxidation occurs at the anode. This is always the case, but the sign of the anode switches between galvanic and electrolytic modes (see Fig. 3.3).
   - In a galvanic cell, this is the negative electrode. This can be understood from two perspectives. From the reaction perspective, as the reductant (Zinc) loses electrons and enter the solution the electrode gains these electrons and thus acquires a negative charge, which can be transferred to something positive. The second is from the perspective of the external circuit, where the negative electrons flow to the positive terminal, which is the other electrode, making the anode the negative electrode.
   - In an electrolytic cell, this is the positive electrode. Here the electrode sign is not being determined by the cell reaction, but by the external power supply that is driving the reaction in

the nonspontaneous direction. The right side of figure 3.3 shows the Daniel Cell being driven by an external power supply which has its [+] electrode connected to the cell with the copper. This causes the nonspontaneous reaction of electrons leaving the copper and moving towards the positive electrode. Since the wire connecting this to the power source has negligible resistance, this electrode is at roughly the same potential and is thus the positive electrode. It must be emphasized that the reaction is being driven by the coupling of an external power supply that produces negative free energy in the nonspontaneous direction, and this must be greater in magnitude than the spontaneous free energy that occurs in the galvanic cell, resulting in a net negative free energy that causes the intrinsically nonspontaneous reaction to occur. Because of this, the electrode sign is dictated by the external power supply. But the anode is still where oxidation occurs.

ii. **Cathode:** Reduction occurs at the cathode.

- The cathode has the opposite signs of the anode, so it is [+] in a galvanic/voltaic cell, and [-] in an electrolytic cell.

Always remember for a galvanic cell

(**An Ox Red Cat**: Anode Oxidation; Reduction Cathode).

iii. **Electrodes**: To hook up an external circuit you need to have something to physically connect the wire to. There are two types of electrodes, active and inert.

- **Active electrode**: This is an electrode that takes part in the half-reaction, and thus must be solid. In the Daniels ($Zn^{+2}$/Cu) cell both electrodes are active, and as the reaction proceeds the anode loses mass (as Zn converts to $Zn^{+2}$ and enters the solution), while the cathode gains mass (as $Cu^{+2}$ gains electrons from the external circuit and becomes Cu(s).
- **Inert electrode**: This is an electrode that is made of a substance that does not undergo oxidation or reduction. Often oxidants or reductants are not solids but gases or solutes, like in the hydrogen electrode, which has no solid material that can function as an electrode, and would thus require an additional substance like platinum or graphite, that would function as an inert electrode. We shall discuss it in detail in a later section of this unit.

iv. **Electrolyte:** An electrolyte is a charged mobile ion that functions as a conducting medium and in the case of "wet cells" is typically an aqueous solution of ionic compounds. In the case of active electrodes, this will often by a soluble salt that has a common ion that also makes a soluble salt with the metal of that half-cells electrode. For example, copper (II) sulfate is a soluble salt, so sodium sulfate would be a good electrolyte for that half-cell. Sodium phosphate would not work because copper (II) phosphate would precipitate out.

v. **External Circuit:** The external circuit allows electrons to flow from the anode to the cathode. In the case of a galvanic cell, this is a spontaneous flow and can be used to provide energy that can produce heat or do work. In the case of an electrolytic cell, this requires an energy source to make it work.

vi. **Salt Bridge:** Salt bridge is usually an inverted U-tube filled with a concentrated solution of inert electrolytes. An inert electrolyte is one whose ions neither involved in any electrochemical change nor do they react chemically with the electrolytes in two half-cells. Generally salts like KCl, $KNO_3$, and $K_2SO_4$ etc. are used. For the preparation of salt bridge, gelatin or agar-agar is dissolved in a hot concentrated aqueous solution of an inert electrolyte and solution thus formed is filled in the U-tube. On cooling the solution set in the form of a gel in the U-tube. The ends of the U-tube are plugged with cotton wool to minimize diffusion effects.

**The function of the salt bridge:**

(a) It connects the solutions of two half cells and completes the cell circuit.

(b) It prevents transference or diffusion of the solutions from one-half cell to the other.

(c) It keeps the solutions in the two half-cells, electrically neutral. In anodic half-cell, positive ions pass into the solution and there shall be an accumulation of extra positive charge in the solution around the anode, which will prevent the flow of electrons from anode. Similarly in the cathodic half cell accumulate around cathode due to deposition of positive ions by reduction. To neutralize these ions, sufficient numbers of positive and negative ions are provided by a salt bridge. Thus salt bridge maintains electrical neutrality of the solution.

(d) It prevents liquid-liquid junction potential i.e. the potential difference which arises between two solutions when contact with each other.

From the above discussion, it is clear that electrolytic cells are very similar to voltaic (galvanic) cells in the sense that both require a salt bridge, both have a cathode and anode side, and both have a consistent flow of electrons from the anode to the cathode. However, there are also striking differences between the two cells. The main differences are outlined below:

**Table 3.**1: Differences between Galvanic and Electrochemical Cells

| **Electrochemical cell (Galvanic Cell)** | **Electrolytic cell** |
|---|---|
| A Galvanic cell converts chemical energy into electrical energy. | An electrolytic cell converts electrical energy into chemical energy. |
| Here, the redox reaction is spontaneous and is responsible for the production of electrical energy. | The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction. |
| The two half-cells are set up in different containers, being connected through the salt bridge or porous partition. | Both the electrodes are placed in the same container in the solution of a molten electrolyte. |
| Here the anode is negative and a cathode is a positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction. | Here, the anode is positive and a cathode is a negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction. |
| The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit. | The external battery supplies the electrons. They enter through the cathode and come out through the anode. |

**SAQ 1**

How do we define anode and cathode? What sign - positive or negative - would you assign to anode and cathode in (a) a galvanic cell (b) an electrolytic cell?

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**SAQ2**

Why is a salt bridge necessary in galvanic cells?

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### 3.3.3. Cell Notation

A cell notation is an abbreviated symbolic depiction of an electrochemical cell. For this purpose, we will consider that a cell consists of two half-cells. Each half-cell is again made of a metal electrode contact with metal ions in solution. The IUPAC (1953) recommended the following conventions for writing cell notations. We will illustrate these regarding Zinc-Copper cell

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

I. Anode half-cell is written on the left and cathode half-cell on the right.

II. By convention, within the half-cell, the reactants are written before the products.

III. A **single vertical line ( | )** represents a phase boundary between a metal electrode and an ion solution (electrolyte). Thus the two half-cells in a voltaic cell are indicated as

Phase boundary

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

Anode Half-cell $\qquad$ Cathode Half-cell

IV. A **double vertical line ( || )** represents the elimination of potential at the junction of two electrolyte solutions or represent the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.

V. Finally, the concentrations of aqueous solutions may be written in parenthesis after the symbol of the ions. If the ion concentrations were known the (aq) would be changed with the molarity. The line notation, therefore, corresponds to the direction of the flow of electrons. It must be kept in mind that these do not represent balanced equations, but identify what is being oxidized and what is being reduced.

In the complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between.

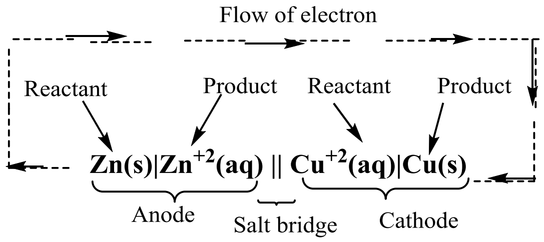

*Fig.* 3.*4 Cell notation for zinc copper cell operating in a galvanic mode*

So at standard one molar conditions, the zinc-copper cell would be written as
**$Zn(s)|Zn^{+2}(1M)||Cu^{+2}(1M)|Cu(s)$**

If the above cell was operating in the electrolytic mode it would be written as

**$Cu(s)|Cu^{+2}(aq)||Zn^{+2}(aq)|Zn(s)$**

***Cell construction from cell reaction***

Now we shall discuss the steps involved in constructing a cell from a given chemical reaction:

**Step I:** From the given chemical equation, write the balanced ionic equation.

**Step II:** Separate this ionic equation into two parts, one in which oxidation takes place and, another, in which reduction takes place. Balance each part using electrons. Sometimes $H^-$, $OH^-$, or $H_2O$ also may have to be added to either side of the equation for proper balancing.

**Step III:** The oxidation part must appear on the left side of the cell. The reduction part must appear on the right side of the cel1. Usually, electrons and $H_2O$ are not indicated in the representation of the cell. Also, stoichiometric numbers must not appear in the representation.

**Step IV:** The electrodes are shown at the extreme left and right positions. These are shown distinctly separated from the corresponding electrolytes using single vertical lines. In case of gas electrodes and many redox systems (which we shall study in detail in Sec. 3.6), inert electrodes such as Pt wire or carbon rod are used for electrical contact.

**Step V:** A pair of vertical lines or a dotted line must be used to show the barrier, between

the left side and right side parts. Two vertical lines indicate the use of a salt bridge and a dotted line shows a porous barrier.

**Step VI:** It is usual to represent the pressure of the gases, the concentration of the electrolytes and the physical state of the electrodes within parenthesis.

**EXAMPLE 1**: Using the above steps, let us try to construct a cell for the reaction

**$Cu(s) + 2Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$**

**Solution**: This can be broken into the following oxidation reactions

Oxidation: **$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$**

Reduction: **$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$**

Which gives the cell of

**$Cu|Cu^{2+} \| Fe^{3+}, Fe^{2+}|Pt$**

There are three things to note in the above Equation

1. First, the reduction half-reaction involves two ions and so there is no solid, and an inert electrode had to be added (Pt) to the end of the cathode half-reaction.
2. Second, the $Fe^{+2}$ and $Fe^{+3}$ are in the same phase and so you use a comma to separate them and not a vertical line (the vertical line represents a phase boundary).
3. And third, you are only identifying what is being oxidized (in the anode) and reduced (in the cathode), and so the cell notation does not represent a balanced chemical equation.

**SAQ3**

Consider a galvanic cell consisting of
$5Fe^{2+}(aq)+MnO_4^{-}(aq)+8H^{+}(aq) \longrightarrow 5Fe^{3+}(aq)+Mn^{2+}(aq)+4H_2O(l)$
Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

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**SAQ4**

Use cell notation to describe the galvanic cell where copper (II) ions are reduced to copper metal and zinc metal is oxidized to zinc ions.

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## *3.4 ELECTRODE POTENTIAL*

At each electrode-electrolyte interface, there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode tend to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged concerning the solution. A potential difference develops between the electrode and the electrolyte which is called **electrode potential**. Let take the example of Zn-Cu voltaic cell, in this cell electrons are released at the anode and it becomes negatively charged. The negative electrode pushes electrons through the external circuit by electrical repulsions. The copper electrode gets a positive charge due to the discharge of $Cu^{2+}$ ions on it. Thus electrons from the outer circuit are attracted into this electrode. The flow of current through the circuit is determined by the 'push', of electrons at the anode and 'attraction' of electrons at the cathode. These two forces constitute the 'driving force' or 'electrical pressure' that sends electrons through the circuit. This driving force is called the **electromotive force** (abbreviated **emf**) or **cell potential.** The emf of cell potential is measured in units of volts (V) and is also referred to as **cell voltage.** The emf generated by an electrochemical cell is given by the symbol E. It can be measured with the help of a potentiometer.

### *Convention regarding the sign of emf value*

The magnitude of the emf of a cell reflects the tendency of electrons to flow externally from one electrode to another. The electrons are transported through the cell solution by ions present and pass from the positive electrode (Cu in case of Daniel cell) to the negative electrode. This corresponds to a clockwise flow of electrons through the external circuit. Thus the emf of the cell is given the +ve sign. If the emf acts in the opposite direction through the cell circuit, it is quoted as –ve value. For example, Daniel cell has an emf of 1.1V and the copper electrode is positive. This can be expressed in two ways :

**$Zn(s)|Zn^{+2}(1M)||Cu^{+2}(1M)|Cu(s)$ E=+1.1V**

**$Cu(s)|Cu^{+2}(aq)||Zn^{+2}(aq)|Zn(s)$ E= -1.1V**

The negative sign indicates that the cell is not feasible in the given direction. The reaction will take place in the reverse direction. At each electrode-electrolyte interface, there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode tend to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged to the solution. A potential difference develops between the electrode and the electrolyte which is called **electrode potential**. Let take the example of Zn-Cu voltaic cell, in this cell electrons are released at the anode and it becomes negatively charged. The negative electrode pushes electrons through the external circuit by electrical repulsions. The copper electrode gets a positive charge due to the discharge of $Cu^{2+}$ ions on it. Thus electrons from the outer circuit are attracted into this electrode. The flow of current through the circuit is determined by the 'push', of electrons at the anode and 'attraction' of electrons at the cathode. These two forces constitute the 'driving force' or 'electrical pressure' that sends electrons through the circuit. This driving force is called the **electromotive force** (abbreviated **emf**) or **cell potential.** The emf of cell potential is measured in units of volts (V) and is also referred to as **cell voltage.** The emf generated by an electrochemical cell is given by the symbol E. It can be measured with the help of a potentiometer.

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The negative sign indicates that the cell is not feasible in the given direction. The reaction will take place in the reverse direction.

## 3.4.1 Measurement of electrode potential

The capacity to do electrical work by a cell is called the cell potential. It is expressed in volt (V). We could use a voltmeter to measure the cell potential. However, this would not give us the correct value of cell potential. The reason is that the cell potential is dependent upon the concentration of the electrolyte which would change if we allow the current to flow in the circuit through the voltmeter. Hence, we must measure the potential difference between the two half-cells when the cell is held at almost constant composition and no current is flowing. The potential difference of a cell when no current is drawn out and when the cell is operating reversibly is called the emf (electromotive force) of the cell. The measurement of the emf can be done by using a potentiometer. More recently emf is found with the help of an electronic digital voltmeter which draws negligible current.

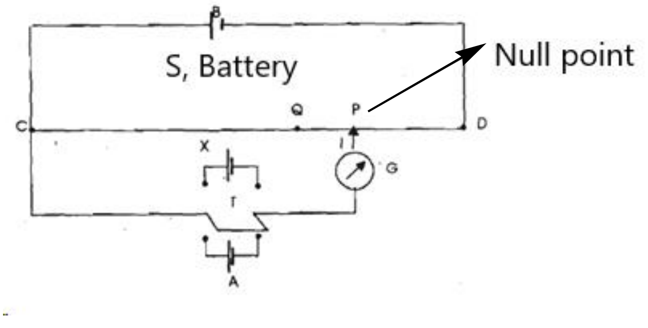

**Fig. 3.5** Potentiometric measurement of cell EMF

**Fig. 3.5** shows a simple set-up to measure the emf of a cell. The potentiometer consists of a wire of uniform cross-section and high resistance. This wire is stretched between two terminals, **C** and **D**. It is connected to a storage battery **B**. The terminal **C** is connected to a sliding point **I** which can be moved from **C** to **D**. In between C and D, there is a double throw-switch **T** and a galvanometer **G**. The function of the switch is to bring either a standard (Weston) cell, **A**, or the test cell **X** (for which emf is to be determined) in the circuit. First, we connect **A** in the circuit and move **I** to such a position **P** that there is no deflection in the galvanometer. The exact length of the wire from **C** to **P** is recorded. Let us suppose this length is $l_1$. Next, using the switch **T,** we remove **A** but bring cell **X** in the circuit. The emf of * A and X may not be the same, hence on replacement of A by X, the galvanometer will show a deflection. We move the contact point to such a position Q that there is again no deflection in the galvanometer. Measure the length of the wire $l_2$, from C to Q. Under the conditions of no deflection, the drop in the potential of the battery **B** across the slide wire is balanced by the emf of the cell (A or X).

Hence, we can write,

$$\frac{\text{emf of X}}{\text{emf of A}} = \frac{\text{Drop}-\text{in potential from C to Q }(E2)}{\text{Drop}-\text{in potential from C to P }(El)} = \frac{\text{Resistance due to wire length CQ}}{\text{Resistance due to wire length CP}} = \frac{l2}{l1}$$

In general,

$$E_2 = E_1 . \frac{l_2}{l_1}$$

Where, $E2$ and $E1$ are the emf values of the test cell and the standard cell, respectively. We make use of a standard cell in the procedure described above for the standardization of a potentiometer. We describe here, Weston cadmium cell, which is a commonly used standard cell.

**Weston Cell**

The Weston cell is a wet-chemical cell that produces a highly stable voltage suitable as a laboratory standard for calibration of voltmeters. Invented by Edward Weston in 1893, it was adopted as the International Standard for EMF from 1911.

Its voltage remains constant for a long period and is reproducible. The change in voltage with temperature is also small. Due to these advantages, the Weston cell is widely used as a standard cell. The basic cell reaction can be represented as

$$\text{Cd} + \text{HgSO}_4 \rightleftharpoons \text{CdSO}_4 + \text{Hg}$$

It is prepared in the form of an H-shaped container as shown in **Fig. 3.6.** In one arm of the container, mercurous sulphate - mercury paste is in contact with mercury. In the other arm, some crystals of cadmium sulphate are dropped over the surface of cadmium amalgam (12.5%). The container is then filled with a saturated solution of cadmium sulphate. The cell produces an emf of 1 .01845 V at 293 K.

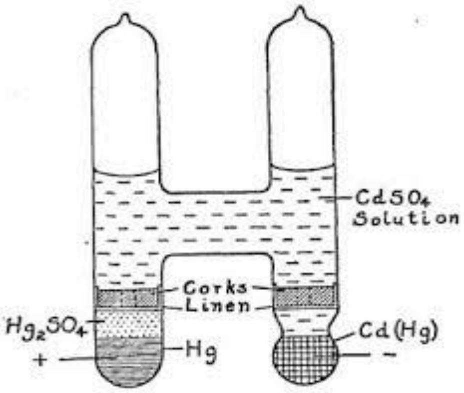

**Fig. 3.6** Weston cell

The cell reaction can be represented as:

**Anode reaction:** $Cd(s) \rightarrow Cd^{2+}(aq) + 2e^{-}$

**Cathode reaction:** $(Hg^{+})_2SO_4^{2-}(s) + 2e^{-} \rightarrow 2Hg(l) + SO_4^{2-}(aq)$

Reference cells must be applied in such a way that no current is drawn from them.

### 3.4.2 *Single electrode potential*

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops the potential to the solution. The potential of a single electrode in a half-cell is called the **Single electrode potential.** Thus in a Daniel cell in which the electrodes are not connected externally, the anode $Zn/Zn^{2+}$ develops a negative charge and the cathode $Cu/Cu^{2+}$, a positive charge. The amount of the charge produced on the individual electrode determines its single electrode potential. The single electrode potential of a half-cell depends on the concentration of ions in solution; tendency to form ions and temperature.

### *3.4.3 Standard Electrode Potential*

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, Concentrated solutions of salts (about 1 M) generally do not exhibit ideal behaviour, and the actual standard state corresponds to an activity of 1 rather than a concentration of

1 M. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C. For a simple Zn-Cu voltaic cell, the standard emf, E°, is 1.10 V. This means that the emf of the cell operated with [$Cu^{2+}$] and [$Zn^{2+}$] both at 1 M and 25°C is 1.10 V. That is,

**$Zn(s)|Zn^{+2}(1M)||Cu^{+2}(1M)|Cu(s)$   $E° = +1.1V$**

### *3.4.4 Determination of Standard Electrode Potential*

Daniell cell discussed earlier section is an electrochemical cell in which the following redox reaction occurs:

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

The reactions taking place in the two compartments known **as** half-cell reactions can be written as :

$$Zn \rightleftharpoons Zn^{2+} + 2e^- \text{ ...... oxidation}$$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu \text{...... reduction}$$

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

In such type of cell, at each electrode-electrolyte interface, there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode tend to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged to the solution. Thus we see that there will be a potential difference known as electrode potential developed at the junction of the metal and the solution. However, the potential difference between the two phases cannot be readily measured. Therefore, instead of measuring the electrode potentials, we usually measure the total cell potential.

The cell potential can be written as the sum of the two electrode potentials, neglecting other effects which contribute to the potential difference between the phases. Thus,

$$E_{cell} = E_{cathode} + E_{anode}$$

The total cell potential is a measure of the driving force of a chemical reaction whereas $E_{cathode}$ and $E_{anode}$ are representative of oxidizing and reducing capabilities of the concerned reactants, respectively. Hence, to obtain a large cell potential, we must use a strong oxidizing agent along with a strong reducing agent. Now the question arises as to how do we decide which is a better oxidising agent and which is a better reducing agent?

To determine the comparative oxidising or reducing the capacity of any substance, we must use some standard against which all other electrode potentials are measured. We shall now explain the necessity of having such a standard.

Let us consider an example, say Daniell cell, the standard cell potential of which is 1.1 V. It just tells us that zinc is a better reducing agent than copper since zinc gets oxidised to $Zn^{2+}$ ion and it reduces $Cu^{2+}$ ions to metallic copper. However, it will not tell us whether a third substance, say, Fe is a better reducing agent than zinc or copper. To get some idea regarding the relative oxidising and reducing abilities of different substances, we must measure the cell potentials keeping one half-cell the same in every case. This is necessary since we cannot measure directly the potential of a half-cell. It is like saying that for a reducing agent to give off its electrons, surely you must have an oxidising agent to accept that electron. It cannot function as an oxidising agent on its own without the presence of a reducing agent. Further, for comparing the reducing powers of different substances, we must use the same oxidising agent. The standard against which all other potentials are measured is a hydrogen electrode. We now describe a standard hydrogen electrode.

**SAQ 5**

Distinguish between cell potential and electromotive force.

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### *3.4.5 Standard Hydrogen Electrode (SHE)*

The chemical reaction taking place at the hydrogen electrode is given by the equation:

$$2H^{+} + 2e^{-} \longrightarrow H_2$$

The electrode potential for the standard hydrogen electrode is arbitrarily assigned a value of zero. **Fig.3.7** shows a standard hydrogen electrode where hydrogen gas is bubbled through a

glass hood over the surface of the **Pt** electrode at a pressure of 1 bar* (≈≈ 1 atm). The electrode is immersed in an acid in which $[H_3O^+] = 1$ M. The whole set-up is kept at 298 K.

The reduction half-reaction chosen as the reference is

$$2\mathrm{H}^+\,(aq, 1M) + 2\mathrm{e}^- \rightleftharpoons \mathrm{H}_2\,(g, 1\,\mathrm{atm}) \qquad E^\circ = 0\,\mathrm{V}$$

$E^\circ$ is the standard reduction potential. The superscript **“°”** on the $E$ denotes standard conditions (1 bar or 1 atm for gases, 1 $M$ for solutes). The voltage is defined as zero for all temperatures.

There are, however, a few points to be kept in mind before we set out to calculate the standard cell potentials.

- Since the cell potentials are a measure of the tendency of a particular reaction to go in a particular direction, these potentials are cited in volt and not as volt per mole.
- The calculation of the standard cell potential from the standard potentials of the two half-cells will not be affected by the stoichiometric coefficients used to balance the overall reaction.

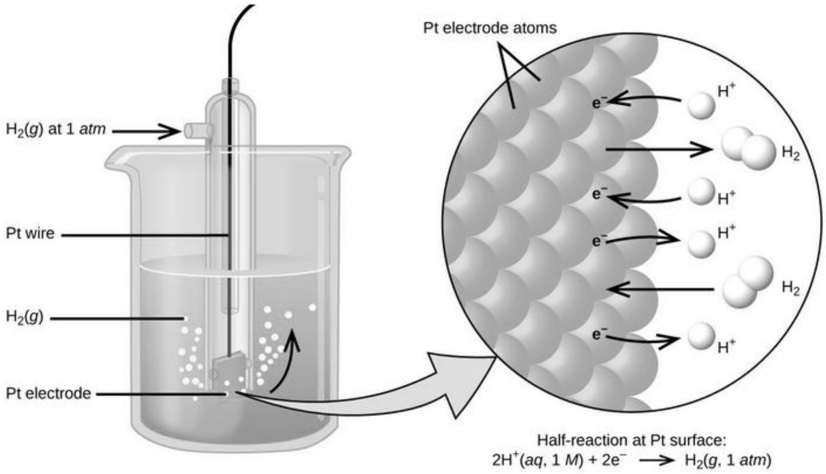
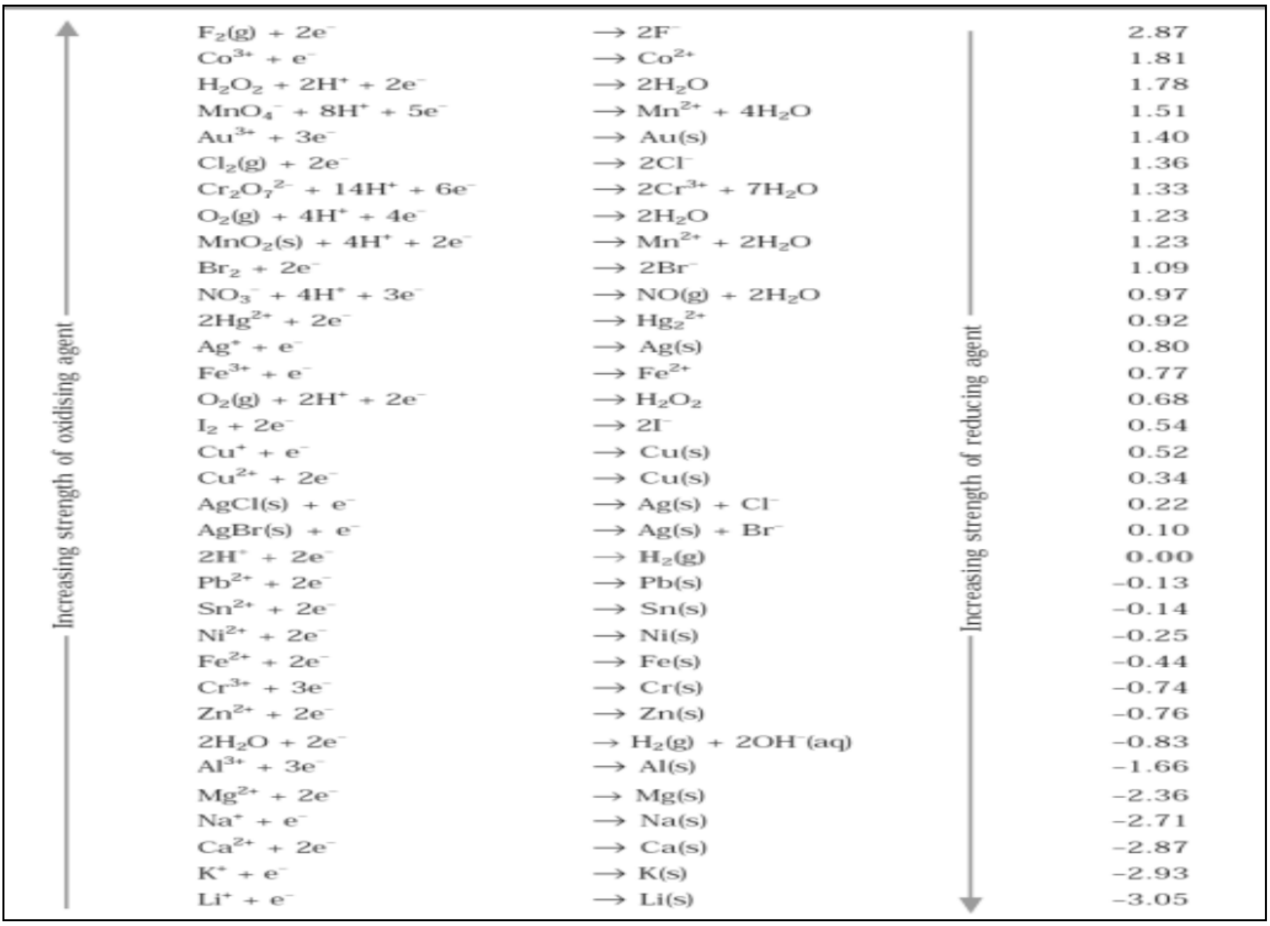


**Fig. 3.7** Standard Hydrogen Electrode (SHE): Electrons on the surface of the electrode combine with $H^+$ in solution to produce hydrogen gas.

In the convention adopted by the IUPAC (International Union of Pure and Applied Chemistry), the

SHE is always placed on the left-hand side of the half-cell under study. The electrons flow from left-to-right and the given half-cell electrode gains electrons (reduction). The observed emf of the combined electrochemical cell is then the emf of the half-cell on the right-hand. Such emf values of half-cells, or half-reactions, are known as the **Standard reduction potentials or Standard potentials.** However, if the SHE be placed on the right- hand side of the given half-cell, the potential so obtained is called the **Standard oxidation potential.** The latter potentials are the standard potentials with the sign reversed, the only difference being that cells have been turned around. According to IUPAC convention, the standard reduction potentials alone are the standard potentials. The values of the standard potentials at 25°C (298 K) for some common Reduction Half- reactions are listed in Table **3.2.**

**Table 3.2**: **'The Electrochemical Series' (**Standard Electrode Potentials at 298 K)



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

You must remember that **Table 3.2** gives the standard reduction potentials for some half-cell reactions. But at the anode, a particular species gets oxidised. To get the standard potential for the oxidation reaction at the anode, the sign of the standard reduction potential for that reaction must be reversed.

i.e., $E_{anode} = -E°$ as per **Table 3.2**

For example, let us calculate the standard cell potentlal tor the reaction :

$Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$

for which the half-cell reactions and corresponding potentials are given below :

$\mathbf{Cu \rightarrow Cu^{2+} + 2e^-}$ $(E°_{anode} = -E°_{Cu^{2+}/Cu} = -0.34V)$

$\mathbf{Ag^+ + e^- \rightarrow Ag}$ $(E°_{cathode} = -E°_{Ag^+/Ag} = 0.80V)$

We shall not multiply the $Ag^+/Ag$ cell potential by two which is a number used to balance the overall reaction. Secondly, we must keep in mind that in the overall reaction, copper metal is getting oxidised to $Cu^{2+}$ ion. Hence, when we are adding the cathodic and anodic potentials to find the total cell potential, we must reverse the sign of the potential for $Cu^{2+} / Cu$ couple. Thus the standard cell potential for the reaction would be

$$\mathbf{E°_{cell} = E°_{anode} + E°_{cathode}}$$

$$\mathbf{= -E°_{Cu^{2+}/Cu} + E°_{Ag^+/Ag}}$$

$$\mathbf{= [(-0.34) + (0.80)]\ V}$$

$$\mathbf{= 0.46\ V}$$

### *3.4.6. Electrochemical Series*

When the electrodes (metals and non-metals) in contact with their ions are arranged based on the values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the **electrochemical** or **electromotive** or **activity series** (**Table 3.2)** of the elements.

By international convention, the standard potentials of electrodes are tabulated for reduction half-reactions, indicating the tendencies of the electrodes to behave as cathodes towards SHE. Electrodes with positive E° values for reduction half-reactions do in fact act as cathodes versus SHE, while those with negative E° values of reduction half-reactions behave instead as anodes versus

SHE. The negative sign of standard reduction potential indicates that an electrode when joined with SHE, acts as anode and oxidation occurs on this electrode. For example, the standard reduction potential of zinc is -0.76 volt. When zinc electrode is joined with SHE, it acts as the anode (-ve electrode) i.e., oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode, when joined with SHE, acts as cathode and reduction occurs on this electrode.

## Characteristics of Electrochemical Series

- The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials.
- All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.
- The substances which are stronger oxidising agents than $H^+$ ion are placed below hydrogen in the series.
- The metals on the top (having high negative values of standard reduction potentials) tend to lose electrons readily. These are active metals.
- The activity of metals decreases from top to bottom.
- The non-metals on the bottom (having high positive values of standard reduction potentials) tend to accept electrons readily. These are active non-metals.
- The activity of non-metals increases from top to bottom.
-

## Applications of Electrochemical Series

### I. Reactivity of Metals

The activity of the metal depends on its tendency to lose electron or electrons, i.e., tendency to form cation ($M^{n+}$). This tendency depends on the magnitude of standard reduction potential. The metal which has a high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into a cation. Such a metal is said to be chemically active. The chemical reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series. For example,

- Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.
- Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.
- Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

### *II. Electropositive Character of Metals*

The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. Based on standard reduction potential values, metals are divided into three groups:

- **Strongly electropositive metals:** Metals having standard reduction potential near about -2.0 volt or more negative like alkali metals, alkaline earth metals are strongly electropositive.
- **Moderately electropositive metals:** Metals having values of reduction potentials between 0.0

and about -2.0 volt are moderately electropositive. Al, Zn, Fe, Ni, Co, etc., belong to this group.

- **Weakly electropositive metals:** The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive. Cu, Hg, Ag, etc., belong to this group.

### *III. Displacement Reactions ($AB + C \longrightarrow A + BC$)*

- **To predict whether a given metal will displace another, from its salt solution:** A metal higher in the series will displace the metal from its solution which is lower in the series, i.e., the metal having low standard reduction potential will displace the metal from its salt's solution which has a higher value of standard reduction potential. A metal higher in the series has a greater tendency to provide electrons to the cations of the metal to be precipitated.
- **Displacement of one nonmetal from its salt solution by another nonmetal:** A nonmetal higher in the series (towards the bottom side), i.e., having a high value of reduction potential will displace another nonmetal with lower reduction potential i.e., occupying position above in the series. The nonmetal's which possess high positive reduction potentials tend to accept electrons readily. These electrons are provided by the ions of the nonmetal having a low value of reduction potential. Thus, $Cl_2$ can displace bromine and iodine from bromides and iodides.

  $Cl_2 + 2KI \rightarrow 2KCl + I_2$
  $2I^- \rightarrow I_2 + 2e^-$ **(Oxidation half-reaction)**
  $Cl_2 + 2e^- \rightarrow 2Cl^-$ **(Reduction half-reaction)**

  The activity or electronegative character or oxidising nature of the nonmetal increases as the value of reduction potential increases.

- **Displacement of hydrogen from dilute acids by metals:** The metal which can provide electrons to $H^+$ ions present in dilute acids for reduction, evolve hydrogen from dilute acids.
  $Mn \rightarrow Mn^{n+} + ne^-$ **(Oxidation half-reaction)**
  $2H^+ + 2e^- \rightarrow H_2$ **(Reduction half-reaction)**

The metal having negative values of reduction potential possess the property of losing electron or electrons. **Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.** The metals which are below hydrogen in electrochemical series like Cu, Hg, Au, Pt, etc., do not evolve hydrogen from dilute acids.

- **Displacement of hydrogen from water:** Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series. Alkali and alkaline earth metals liberate hydrogen from cold water but Mg, Zn and Fe liberate hydrogen from hot water or steam.

### *IV. Reducing Power of Metals*

Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential more is the tendency to lose electron or electrons. Thus, reducing nature decreases from top to bottom in the electrochemical series. The power of the reducing agent increases as the standard reduction potential becomes more and more negative. Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron. Alkali and alkaline earth metals are strong reducing agents.

### *V. Oxidising Nature of Nonmetals*

Oxidising nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. **Thus, oxidising nature increases from top to bottom in the electrochemical series.** The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive. $F_2$ (Fluorine) is a stronger oxidant than $Cl_2$, $Br_2$ and $I_2$.

### *VI. Thermal Stability of Metallic Oxides*

The thermal stability of the metal oxide depends on its electropositive nature. As the electro positivity decreases from top to bottom, the thermal stability of the oxide also decreases from top to bottom. The oxides of metals having high positive reduction potentials are not stable towards heat. The metals which come below copper form unstable oxides, i.e., these are decomposed on heating.

### *VII. Products of Electrolysis*

In case two or more types of positive and negative ions are present in solution, during electrolysis certain ions are discharged or liberated at the electrodes in preference to others. **In general, in such competition the ion which is stronger oxidising agent (high value of standard reduction potential) is discharged first at the cathode. The increasing order of deposition of few cations is:**

$K^+ < Ca^{2+} < Na^+ < Mg^{2+} < Al^{3+} < Zn^{2+} < Fe^{2+} < H^+ < Cu^{2+} < Ag^+ < Au^{3+}$

Similarly, the anion which is a stronger reducing agent (low value of standard reduction potential) is liberated first at the anode.

**The increasing order of discharge of few anions is:**

$SO_4^{2-} < NO_3^- < OH^- < Cl^- < Br^- < I^-$

### *VIII. Extraction of Metals*

A more electropositive metal can displace a less electropositive metal from its salt's solution. This principle is applied for the extraction of Ag and Au by the cyanide process. Silver from the solution containing sodium argento cyanide, $NaAg(CN)_2$, can be obtained by the addition of zinc as it is more electro-positive than Ag.

$$2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2\,Ag$$

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**SAQ 6**

Predict which of the following reactions will be spontaneous with the help of standard potential values :

……………………………………………………………………………………………………………
……………………………………………………………………………………………………………
……

**SAQ 7**

Find the standard electrode potential of the given cell; and predict the direction of electron flow when the two electrodes are connected.

i) $Fe + 2H^{+} \longrightarrow Fe^{2+} + H_2$

$Cu(s)|\ Cu^{2+}\ |\ Cl^{-}\ ||\ AgCl(s)\ |\ Ag(s)$

ii) $Cu + 2H^{+} \longrightarrow Cu^{2+} + H_2$

iii) $2Fe^{3+} + 2I^{-} \longrightarrow 2Fe^{2+} + I_2$

……………………………………………………………………………………………………………

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**SAQ8**

a) Can you store a copper sulphate solution in a zinc pot?
b) Consult the table of standard electrode potentials given above and suggest three substances that can oxidise ferrous ions under suitable conditions.

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In the previous section, electrochemical cells were introduced, related to redox reactions that could be split into half-reactions, and shown that a cell could be run in a galvanic (voltaic) or electrolytic mode. In this section, we are going to apply some of the fundamentals of thermodynamics that were introduced in unit 2 to the operations of electrochemical cells.

### *3.5. THE NERNST EQUATION*

It was discussed in Unit 2 that the decrease in Gibbs free energy ($-\Delta G$) for any reaction would be equal to the maximum useful work ($-W_{net}$) that can be obtained from the system at constant temperature and pressure. The only kind of work done in an electrochemical cell is the electrical work which can be calculated from Eq. 3.1.

**Electrical work is done by the system ($-W_{net}$)= Quantity of electricity · cell potential**……( Eq. 3.1)

**Cell potential = Electrical energy or work · Quantity of charge**……( Eq. 3.2)

The quantity of electricity carried by 1 mole of electrons is 1F (F stands for Faraday and is equal to 96,500 coulombs). Hence the quantity of electricity carried by n mole of electrons is *nF*. If the cell potential is E, then Eq. 3.5.1 can be written as,

**Electrical work = $-W_{net} = nFE$** ……( Eq. 3.3)

Hence, **$-\Delta G = nFE$** ……( Eq. 3.4)

Under standard state conditions,

$$-\Delta G^\circ = nFE^\circ \qquad \text{......( Eq. 3.5)}$$

For a general reaction of the type,

$$aA + bB \longrightarrow cC + dD + \ldots\ldots.$$

Recall that from unit 2, the actual free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G^\circ + RT \ln Q \qquad \text{......( Eq. 3.6)}$$

$$\text{Where, } Q = \frac{(ac)^c(\,aD)^d}{(aA)^a\,(aB)^b} \ldots\ldots\ldots\ldots \text{ ( Eq. 3.7)}$$

In Eq. 3.7, aC, aD,... etc., refer to the activities of the substances

Substituting the values of $\Delta G$ and $\Delta G^\circ$ from Eqs. 3.4 and 3.5 in Eq. 3.6, we obtain

$$-nFE_{cell} = -nFE^\circ_{cell} + RT \ln Q \qquad \ldots\ldots\ldots\ldots\ldots\text{( Eq. 3.8)}$$

Dividing both sides of this equation by $-nF$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q \qquad \ldots\ldots\ldots\ldots\ldots\text{( Eq. 3.9)}$$

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log Q \qquad \ldots\ldots\ldots\ldots\ldots\text{( Eq. 3.10)}$$

At 298 K, the numerical value of $\left(\frac{2.303RT}{F}\right)$ is 0.059

Hence, at 298 K,

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log Q \qquad \ldots\ldots\ldots\ldots\ldots\text{( Eq. 3.11)}$$

Eqs. 3.5.10 and 3.5.11 are known as **Nernst Equation** in honour of German physicist and chemist Walter Nernst (1864–1941), who first derived this equation. If activity coefficients are equal to unity, the activities given in Eq. 3.5.7 can be replaced by concentrations. Then, Eqs. 3.5.10 and 3.5.11 can be written as

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \ldots\ldots\ldots\ldots\ldots\text{( Eq. 3.12)}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \ldots\ldots\ldots\ldots\ldots\text{( Eq. 3.13)}$$

Eqs. 3.12 and 3.13 are better-known forms of Nemst Equation. Nernst equation brings out the dependence of emf on the concentrations of the substances taking part in the cell reaction.

### 3.5.1 Applications of Nernst Equation

Let us consider some applications of Nernst equation.

**I. The Equilibrium constant of the cell reaction**

At equilibrium, $\Delta G = 0$ and hence from Eq. 3.6 we get

$0 = \Delta G° + RT \ln K$ (At equilibrium, Q is replaced by K)

or $\Delta G° = - RT \ln K$ ……………( Eq. 3.14)

Combining Eqs. Eq. 3.5 and 3.14 we get,

$- nFE° = - RT \ln K$

Hence, $E° = \frac{RT}{nF} \ln K$

or $E° = \frac{2.303\ RT}{nF} \log K$ ………. ( Eq. 3.15)

Hence, from E° value, the equilibrium constant can be calculated. Eq. 3.15 is interesting due the fact that the equilibrium constant of a reaction is related to standard emf of the cell where the reactant and products are in their standard states. Eq. 3.15 can also be written to the following way :

$K = e^{nE°F/RT}$

$\log K = \frac{nFE°}{RT}$

Hence, $2.303 \log K = \frac{nFE°}{RT}$

$\log k = \frac{nFE°}{2{,}303\ RT}$

$\log k = \frac{nFE°}{0.0591}$ (at 298 K)………. ( Eq. 3.16)

**II. Calculation of $E_{cell}$ from the concentration of Electrolytes**

Consider the half-cell reaction:

$M^{n+} + ne^- \longrightarrow M$

Applying Nernst equation (Eq. 3.5.11) to the above reaction

$E_{M^{n+}/M} = E°_{M^{n+}/M} - \frac{0.059}{n} \log \frac{1}{M^{n+}}$ ………. ( Eq. 3.17)

Since [M]=1, Eq. 3.17 can be utilize to write the equation for the two half-cell reactions for the Daniell cell shown below:

$$Zn(s)\ |\ Zn^{+2}(c_1)\ ||\ Cu^{+2}(c_2)\ |\ Cu(s)$$

$$E_{cell} = E_{anode} + E_{cathode}$$

$$= E_{Zn^{2+}/Zn} + E_{Cu^{2+}/Cu} \qquad \text{( Eq. 3.18)}$$

Using Eq. 3.17

$$E_{Zn^{2+}/Zn} = E^{\circ}_{Zn^{2+}/Zn} - \frac{0.059}{2}\ \log\ \frac{1}{[Zn^{2+}]} \quad \text{.......... ( Eq. 3.19)}$$

$$E_{Cu^{2+}/Cu} = E^{\circ}_{Cu^{2+}/Cu} - \frac{0.059}{2}\ \log\ \frac{1}{[Cu^{2+}]} \quad \text{.......... ( Eq. 3.20)}$$

From Eqs. 3.5.18, 3.5.19 and 3.5.20

$$E_{cell} = (E^{\circ}_{Cu^{2+}/Cu}\ E^{\circ} - E^{\circ}_{Zn^{2+}/Zn}) - \frac{0.059}{2}\ \log\ \frac{1}{[Cu^{2+}]} - \ \log\ \frac{1}{[Zn^{2+}]}$$

$$E = E^{\circ} - \frac{0.059}{2}\ \log\ \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad \text{.......... (Eq. 3.21)}$$

$$E^{\circ}_{cell} = \ - E^{\circ}_{Zn^{2+}/Zn} + E^{\circ}_{Cu^{2+}/Cu} \text{.......... (Eq. 3.22)}$$

Note that *Eq. 3.22* could be used to indicate whether a given cell can function *as* a galvanic cell when the substances are in their standard states; that is, when the concentrations of the electrolytes are equal to 1 M. Eq. 3.21 is useful in predicting whether a given cell can function as a galvanic cell when the concentrations of the substances are not equal to 1 M.

We have derived Eqs. 3.21 and 3.22 for Daniel1 cell. We can write generalized expressions for any electrochemical cell as follows:

$$E = E^{\circ} - \frac{2.303\ RT}{nF}\ \log_{10} \frac{[RHS]}{[LHS]} \text{.......... (Eq. 3.23)}$$

Where,

[RHS] Product of concentrations of substances in the right-hand side raised to suitable powers

[LHS] Product of concentrations of substances in the left-hand side raised to suitable powers

n = number of electrons required to balance the oxidation and the reduction reactions

The term 'suitable powers' refers to stoichiometric coefficients in the cell reaction.

### *3.5.2 Thermodynamic quantities of cell reaction*

We shall now study how ΔH, ΔS, and ΔG for the cell reaction can be calculated using modified forms of Nernst equation.

#### (i) Relationship between *ΔG* and cell emf

Eq. 3.4 gives the relationship between **Δ**G and ***E*** values Hence, if ***E<sub>cell</sub>*** value is known, *ΔG*, for the cell reaction can be calculated.

$$-\Delta G = nFE \qquad \text{......( Eq. 3.4)}$$

**(ii) Relationship between entropy change (*ΔS)* and cell emf**

The change in entropy accompanying the cell-reaction can also be determined. In unit II, you have learnt that the temperature coefficient of the free energy change at constant pressure related to the decrease in entropy (- *ΔS*).

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = (-\Delta S) \quad \text{........ (Eq. 3.24)}$$

By differenciating *ΔG* and $E_{cell}$ *in Eq.* 3.4 with respect to temperature with constant pressure, we can write

$$-\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = nF\left(\frac{\partial E}{\partial T}\right)_P \quad \text{........ (Eq. 3.25)}$$

Since *n* and F are constant

Using *Eq. 3.24* and *3.25,* we get,

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P \text{........ (Eq. 3.26)}$$

*i.e.,* $\Delta S = nF\left(\frac{E_{2-E_1}}{T_{2-T_1}}\right)_P$ ........ *(Eq. 3.27)*

In case $E_2$ and $E_l$ (the emfs of the cell at temperatures $T_2$ and $T_1$) are known, *ΔS* can be calculated.

$\left(\frac{\partial E}{\partial T}\right)_P$ is known as the ***"temperature coefficient"*** of emf at constant pressure.

**(iii) Relationship between enthalpy change (*ΔH)* and cell emf**

At constant temperature and pressure, the **change in Gibbs free energy (*ΔG)*** is defined as

$\Delta G = \Delta H - T\Delta S$

or $\Delta H = \Delta G + T\Delta S$

*Using Eq.* 3.5.4 and *3.5.26* we can write,

$$\Delta H = -nFE + T\,nF\left(\frac{\partial E}{\partial T}\right)_P \qquad \text{........ (Eq. 3.28)}$$

Hence, if E, T and $\left(\frac{\partial E}{\partial T}\right)_P$ is known, then the enthalpy change accompanying the cell-reaction can also be determined.

**Example 2:** What is the standard free energy change and equilibrium constant for the following reaction at 25 °C?

**$2Ag^+(aq) + Fe(s) \rightleftharpoons 2Ag(s) + Fe^{2+}(aq)$**

**Solution:** The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Table 3.2

anode (oxidation): $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$ $\quad E^\circ_{Fe2+/Fe} = -0.447$ V

cathode (reduction): $2\times(Ag^+(aq) + e- \longrightarrow Ag(s))$ $\quad E^\circ_{Ag+/Ag} = 0.7996$ V

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= E^\circ_{Ag+/Ag} - E^\circ_{Fe2+/Fe} = +1.247$ V

Remember that the cell potential for the cathode is not multiplied by two when determining the standard cell potential. With *n* = 2, the equilibrium constant is then

$E^\circ = \frac{0.0592}{n} \log K$ or $K = e^{nE^\circ F/RT}$

$$F = \frac{6.022\times10^{23} e^-}{mol} \times \frac{1.602\times10^{-19} C}{e^-} = 9.648 \times 10^4 \frac{C}{mol} = 9.684 \times 10^4 \frac{J}{V \cdot mol}$$

$K = 10^{nE^\circ F/RT}$

$= 10^{2\times1.247 \text{ V}/0.0592 \text{ V}}$

$= 10^{42.128}$

$= 1.3\times10^{42}$

$\Delta G^\circ = -nFE^\circ$

$= -2 \times 96,485\ J/V.mol \times 1.247 \text{ V} = -240.6$ kJ/mol

Thus, a positive standard cell potential means a spontaneous reaction, so the standard free energy change should be negative, and an equilibrium constant should be >1.

**Example 3:** Calculate the equilibrium constant at 298 K for the cell reaction taking place in the cell,

**$Al(s)|Al^{+3}(c_1)||Cu^{+2}(c_2)|Cu(s)$**

**Solution**

**$Al \rightarrow Al^{3+} + 3e^-$** (Anode; Oxidation)…..1

**$Cu^{2+} + 2e^- \rightarrow Cu$** (Cathode; Reduction) ……2

Before combining equation (1) and (2), we have to multiply (1) by 2 and (2) by 3 so that six mole electrons are exchanged between the electrodes; i.e.,

**$2Al \rightarrow 2Al^{3+} + 6e^-$ …..3**

**$3Cu^{2+} + 6e^- \rightarrow 3Cu$ …..4**

Adding (3) and (4) we get the cell reaction for this cell is,

**$2Al + 3Cu^{+2} \rightleftharpoons 2Al^{+3} + 3Cu$**

Hence, n = 6.

$E°_{cell} = E°_{anode} + E°_{cathode}$

$= E°_{Al^{3+}/Al} + E°_{Cu^{2+}/Cu}$

$= [-(-1.66) + 0.34]$ V

$= 2.0$ V

$E° = \frac{0.0592}{n} \log K$

$\log K = \frac{12}{0.0592} = 203.390$;  Hence, **$K = 2.5 \times 10^{20}$**

**Example 4:** Calculate the cell potential of a Daniell cell at 298 K when the concentrations of $zn^{2+}$ and $Cu^{2+}$ are **1.5** M and **0.5** M, respectively.

**Solution:**

For Daniell cell, $E°_{cell} =$ **1.1** V and ***n*** = **2**

From *Eq. 3.5.21,* $E = E° - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$

$= (1.1 - \frac{0.059}{2} \log \frac{1.5}{0.5})$ V

$= (1.1 - \frac{0.059}{2} \times 0.4771)$ V

$= 1.09$ V

**SAQ 9**

Calculate the potential of a copper electrode immersed in 0.044 M CuSO4

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**SAQ 10**

Calculate the potential of a zinc electrode immersed in 0.060 M ZnSO4.

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**SAQ 11**

Calculate the cell potential for the cell made by combining the half-cell in SAQs 1 and 2 in the following way:

$$\mathrm{Zn}\left|\mathrm{Zn}^{2+}(0.060\,\mathrm{M})\right\|\mathrm{Cu}^{2+}(0.044\,\mathrm{M})\left|\mathrm{Cu}\right.$$

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**SAQ 12**

The potential for the following cell is 0.462 V. Calculate the concentration of Ag+ in its half-cell:

$$\mathrm{Cu}\left|\mathrm{Cu}^{2+}(0.010\,\mathrm{M})\right\|\mathrm{Ag}^{2+}\left|\mathrm{Ag}\right.$$

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**SAQ 13**

Calculate the equilibrium constant at 298 K for the following reaction :

$$\mathrm{Zn}^{2+} + 4\mathrm{NH}_3 \rightleftharpoons \left[\mathrm{Zn}\,(\mathrm{NH}_3)_4\right]^{2+}$$

Use the standard potentials given below:

$$\mathrm{Zn}^{2+} + \mathrm{e}^- \longrightarrow \mathrm{Zn} \qquad E^\circ = -0.76\ \mathrm{V}$$

$$\left[\mathrm{Zn}\,(\mathrm{NH}_3)_4\right]^{2+} + 2\mathrm{e}^- \longrightarrow \mathrm{Zn} + 4\mathrm{NH}_3 \qquad E^\circ = -1.03\ \mathrm{V}$$

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**SAQ 14**

Write down the equations relating ΔH°, ΔS°, and ΔG° to temperature coefficient of emf at constant pressure.

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### *3.6 TYPES OF ELECTRODES*

A large number of electrodes are known and these can be conveniently divided into several categories depending upon the nature of the half-cell reactions. We shall now look at some of the commonly used electrodes.

**3.6.1 Metal-metal ion electrode**: An electrode of this type consists of metal rod dipping in a solution containing its own ions. For example zinc rod dipping in zinc sulphate solution or copper rod dipping in copper sulphate solution.

The general electrode reaction is represented by

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

If the metal rod behaves as positive electrode (i.e., the reaction at the electrode involves reduction), the equilibrium will shift towards the right. The concentration of $M^+$ ions in solution will, therefore, decrease. If on the other hand, the metal rod behaves as negative electrode (i.e., the electrode reaction involves oxidation), the above equilibrium shifts towards the left. The concentration of the $M^+$ ion in the solution will therefore, increase.

The electrode potential is given by Eq. 3.17

$$E_{M^{n+}/M} = E°_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]} \quad \text{………. (Eq. 3.17)}$$

$Cu^{2+}/Cu$, $Zn^{2+}/Zn$, $Ag^{+}/Ag$, $Pb^{2+}/Pb$ etc. are common examples of metal-metal ion electrodes.

**3.6.2 Gas Electrodes** : Hydrogen electrode (Fig.3.7) is a typical example of this type of electrode where a gas is in equilibrium with its ions in solution. The gas/electrolyte equilibrium takes place on the surface of an inert metal or any other inert conductor. The commonly used inert electrode materials are platinum and carbon.

The electrode potential for the reaction is given below:

$$2H^+ + 2e^- \longrightarrow H_2$$

$$\mathbf{E_{cell} = E°_{cell} - \frac{0.059}{n} \log Q} \quad \text{……………( Eq. 3.11)}$$

g Eq. 3.7 to the reduction of $H^+$ ions,

$Q = \frac{aH_2}{a^2 H^+}$ ………… ( Eq. 3.29)

In case of a solution, the activity can be replaced by concentration, while for a gas, activity can be substituted by its partial pressure.

Thus, $aH^+ = [H^+]$ and $aH_2 = pH_2$

Using these in Eq. 3.11, we get at 298 K,

$E_{H^+/H2} = E°_{H^+/H2} - \frac{0.059}{2} \log \frac{pH_2}{[H^+]^2}$ (since n =2)

i.e $E_{H^+/H2} = E°_{H^+/H2} + 0.059 \log [H^+] - \frac{0.059}{2} \log pH_2$

$E_{H^+/H2} = - 0.059\, pH - \frac{0.059}{2} \log pH_2$ ……………………( Eq. 3.30)

[since $E°_{H^+/H2} = 0$ and $- \log [H^+] = pH$

If $pH_2$= 1atm, then $E_{H^+/H2} = -0.059pH$………………( Eq. 3.31)

Hence *pH* of the solution will decide the electrode potential of a hydrogen eltctrode, when hydrogen gas pressure is 1 atm. This principle is made use of in Sec. 3.9 for determining the *pH* of a solution using hydrogen electrode.

**3.6.3 Amalgam Electrode** : Active metals of Group IA and IIA which react with water can be used in amalgam form. The reaction can be represented as:

$M^{n+} + ne^- \longrightarrow M(Hg)$

The electrode potential is given by Eq. 3.32

$E_{M^{n+}/M} = E°_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{M(Hg)}{[M^{n+}]}$ ………. ( Eq. 3.32)

where [M(Hg) ] indicates the concentration of the metal M dissolved in Hg.

**3.6.4 Metal-Insoluble Salt Electrode**: The typical examples of such electrodes are calomel electrode and silver-silver chloride electrode. These are represented as :

$Hg/Hg_2C1_2$ (s), KC1 (c) and

Ag/AgCl (s), KC1 (c)

It can be seen from the above half-cells that a metal (Hg or Ag) is in contact with a saturated solution of its sparingly soluble salt ($Hg_2Cl_2$ or AgCl) and another soluble salt (KCl) having common anion ($Cl^-$).

The saturated calomel electrode is often used as a reference electrode in place of hydrogen electrode which is inconvenient and difficult to prepare. As a reference electrode, a saturated calomel electrode is reversible and has a fixed potential. It can be represented as

$Hg \mid Hg_2Cl_2(s) \mid KCl$ (saturated)

Fig. 3.8 shows a simple construction of a saturated calomel electrode (SCE). It consists of mercury in contact with mercurous chloride (calomel) and chloride ions (from saturated KC1). Mercurous chloride is reduced to mercury, when the saturated calomel electrode is used as a cathode, according to the equation:

$Hg_2C1_2 + 2e^- \longrightarrow 2Hg + 2C1^-$

The half-cell potential for saturated calomel electrode is 0.2682 V at 298 K.

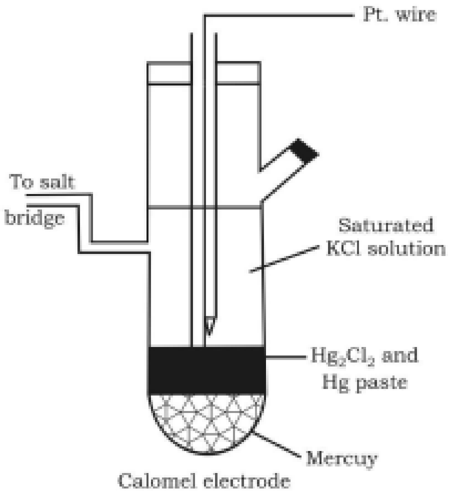


**Fig. 3.8** Saturated calomel electrode (SCE).

In the silver-silver chloride electrode, Ag is in equilibrium with Ag ion in solution:

$$Ag+ \;+\; e^- \rightleftharpoons Ag$$

As the solution is saturated with AgCl, silver ion produced will combine with chloride ions to give insoluble AgCl and the electron is transferred to the electrode.

The standard half-cell potential for this electrode is 0.2223 V.

**3.6.5 Membrane Electrode:** In this type of electrode (Fig. 3.9), a semipermeable membrane (X) separates two solutions containing different concentrations of the salt, **MA** and is permeable to one of the ions say, **$M^+$.** This ion will tend to diffuse into a more dilute solution.

but the anion, $A^-$, cannot follow and therefore, a difference of potential is set up. This will retard the migration of $M^+$ and after sometime equilibrium will be established. Under these conditions, the standard potential difference is given by

$$E° = \frac{2.303RT}{nF} \log \frac{[M^+]\alpha}{[M^+]\beta} \quad \text{……… ( Eq. 3.33)}$$

where $[M^+]_\alpha$, and $[M^+]_\beta$, represent $[M^+]$ in the two halves of the cell across the membrane. The most useful and common electrode of this kind is a **glass electrode**. This is used for measuring the $H^+$ ion concentration of solutions. Other ion-selective electrodes have been developed for the measurement of concentrations of $Na^+$, $K^+$ etc.

**3.6.6 Redox Electrodes**: it is usually referred to as a system in which a species exists in solution in two different oxidation states. The electrodes are nonreactive with a solution and are just carriers of electrons. A typical example is Pt/$Fe^{3+}$, $Fe^{2+}$, where a platinum electrode is immersed in a solution containing $Fe^{3+}$ and $Fe^{2+}$ ions. The half-cell reaction can be represented by

$$Fe^{3+} \;+\; e^- \rightleftharpoons Fe^{2+}$$

with a potential given by

$$E = E° - \frac{0.059}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \quad \text{………. ( Eq. 3.34)}$$

### 3.7 TYPES OF GALVANIC CELLS

In the previous section, we have studied about different kinds of electrodes, which may combine in many different ways to give a large number of galvanic cells. Hence, it would be desirable and useful to classify them into two broad groups: **(1)** chemical cells or **battery** (2) concentration cells.

#### 3.7.1 Chemical Cells or battery

Any cell in which the two half-cell reactions use different reactants is called a chemical cell. A typical example is Daniel1 cell. When these cells are connected in series to obtain a higher voltage the arrangement is called Battery. In simple words, a **battery** is an electrochemical cell or series of cells that produce an electric current. In principle, any galvanic cell could be used as a battery. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity.

Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone but would be rejected for this application because of its mass. Thus, no single battery is “best” and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind as well security factor.

**3.7.1.1** Electrochemical batteries are classified into 3 broad categories:

**(A). Primary batteries:** Primary batteries are single-use batteries because they cannot be recharged. When the cell reaction reaches an equilibrium state, there is no further flow of current and the cell ceases to function. It is then called a 'dead' cell. The more common types are zinc-carbon, silver oxide zinc, zinc-mercury etc. and they are commonly called dry cells.

**(i) Leclanche Cell:** It is also Called zinc-carbon dry cell. This type of cell is commonly used in toys, flashlights etc. It contains a zinc cup which acts as an anode and is filled with a moist paste of ammonium chloride, manganese dioxide, zinc chloride in starch and finely divided carbon. A central carbon rod immersed in the paste acts as a cathode. The whole-cell is enclosed in either cardboard or metal, which seals it against the atmosphere as shown in **Fig. 3.9.** The actual reactions which take place in the cell are quite complicated and not completely understood. However, a simplified version of the reactions is given below:

**At the anode**

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{(Oxidation)}$$

$$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$$

**At the cathode**

$$2MnO_2 + 2NH_4^+ + 2e^- \longrightarrow Mn_2O_2 + 2NH_3 + H_2O \quad \text{(Reduction)}$$

This cell produces about 1.5V but drops to about 0.8V as the reaction proceeds. This drop is because the reaction products cannot diffuse away from the electrolyte. If such a cell is left unused for a short time, the voltage may rise back again to about 1.3V. The cell appears to be dead because large excess of $[(Zn(NH3)_4)]Cl_2$ formed crystallizes out around the anode. The electrolyte becomes unable to conduct electricity effectively. A little warming of the cell may restore the voltage due to the diffusion of the complex.

Fig. 3.9. Leclanche Cell

**(ii) Alkaline Cells**: These are similar to Leclanche cell except that the electrolyte, ammonium chloride, is replaced by potassium or sodium hydroxide. They can withstand under heavy use, have longer shelf-life and deliver more current. Main reasons for the better performance of alkaline cells are: (i) larger effective area since the anode is made porous and (ii) absence of acid atmosphere; due to the acid atmosphere caused by the presence of $NH_4^+$ ions in Leclanche cell, the electrodes in it get corroded easily. The cell ( **Fig. 3.9)** produces approximately 1.5 V and basic reactions that take place in alkaline cells are given below:

**At the anode**

$$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^-$$

**At the cathode**

$$2MnO_2 + 2H_2O + 2e^- \longrightarrow 2MnO(OH) + 2OH^-$$

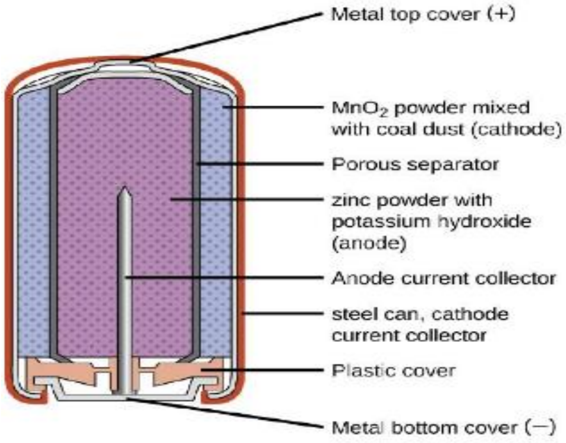


Fig. 3.9. **Alkaline Cells**

**(iii) Button-Cells**: These are small button like cells which are used in watches, calculators, cameras etc. The main advantage is a small size and stable voltage of about 1.3 to 1.5 V. Some cells use a mixture of

HgO, $Zn(OH)_2$ and KOH while others use $Ag_2O$, $Zn(OH)_2$ and KOH. In the mercury cell, the cathode is steel, while, in the other cell, it is a silver oxide (**Fig. 3.10**). The anode in both cases is zinc. The reactions are given below:

**At the anode**

$$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^-$$

**At the cathode**

$$\left.\begin{array}{l} Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^- \\ \text{or } HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^- \end{array}\right\}$$

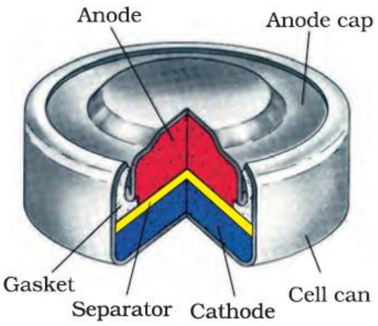


Fig. 3.10. Button-Cell

(B) **Secondary Batteries**

The cells in which the cell reaction is reversed by passing direct current in the opposite direction i.e. it can operate both as a voltaic cell and as an electrolytic cell. The secondary batteries can be used through a large number of cycles of discharging and charging. They are used as a source of DC power. Eg. Lead-acid storage cell, Ni-Cd battery and Lithium-ion batteries.

(i) **Lead-acid storage cell**

The lead storage cells are used to supply current for electrical vehicles, gas engine ignition, telephone exchanges, electric trains, mines, laboratories, hospitals, broadcasting stations, automobiles and power station. It consists of lead-antimony alloy coated with lead dioxide (PbO2) as a cathode and spongy lead as an anode. The electrolyte is a 20% solution of H2SO4. The storage cell can operate both as voltaic cell and electrolytic cell. It acts as a voltaic cell when supplying energy and as a result eventually becomes rundown. The cell operates as an electrolytic cell when being recharged. The cell consists of a series of Pb-plates (negative plates) and PbO2 plates (positive plates) connected in parallel. The plates are separated from adjacent one by insulators like wood, rubber or glass fibre. The cell reactions are as follows:

**Discharging (**voltaic cell**):** During the discharging the battery, $H_2SO_4$ has consumed the density of $H_2SO_4$ falls to 1.20g/cm$^3$, then the battery needs recharging. In discharging, the cell acts as a voltaic cell where oxidation of lead occurs. In charging, the cell is operated like an electrolyte cell and electric energy is supplied to it.

At Anodic (-): $\mathbf{Pb(S) \rightarrow Pb^{2+} + 2e^-}$

$\mathbf{Pb^{2+} + SO_4^{2-}(aq) \rightarrow PbSO_4(S)}$

At Cathodic (+): $\mathbf{PbO_2(S) + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O}$

$\mathbf{Pb^{2+} + SO_4^{2-}(aq) \rightarrow PbSO_4(S)}$

---

Net reaction: $\mathbf{Pb(S) + PbO_2(S) + 4H^+ + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(S) + 2H_2O +}$ Elect.Energy

---

**Charging (**electrolytic cell**):** During this process, lead is deposited at the cathode, $PbO_2$, is formed at the anode and $H_2SO_4$ is regenerated in the cell.

At Anodic (+): $\mathbf{PbSO_4(S) + 2H2O \rightarrow PbO_2(S) + 4H^+ + SO_4^{2-}(aq) + 2e^-}$

At Cathodic (-): $\mathbf{PbSO_4(S) + 2e^- \rightarrow Pb(S) + SO_4^{2-}(aq)}$

---

Net reaction: Elect. Energy $\mathbf{+ 2PbSO_4(S) + 2H_2O \rightarrow Pb(S) + PbO_2(S) + 4H^+ + 2SO_4^{2}(aq)}$

---

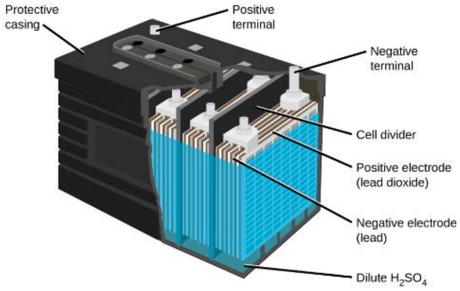


**Fig. 3.11.** Lead-acid storage cell

### (ii) Nickel-Cadmium cell

It is used - in flashlights, photoflash units, portable electronic equipment, In emergency lighting systems, alarm systems, in aircraft and space satellite power systems and for starting large diesel engines and gas turbines etc. This battery consists of Cd anode and cathode is composed of a paste of nickel dioxide [$NiO_2$]. The electrolyte is 20-28% aqueous KOH jelled with a jelling agent. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a “jelly-roll” design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. These cells are rechargeable and give a voltage of 1.4V each. They can be connected in series to give Ni-Cd battery. The cell reactions are:

**Discharging** (voltaic cell):

Anode(-): $\mathbf{Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + 2e^-}$

Cathode(+): $\mathbf{NiO_{2(s)} + 2H_2O + 2e^- \longrightarrow Ni(OH)_{2(s)} + 2OH^-_{(aq)}}$

Net Reaction: $\mathbf{Cd_{(s)} + NiO_{2(s)} + 2H_2O \longrightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)} + Elect.Energy}$

**Charging** (electrolytic cell):

Cathode (-): $\mathbf{Cd\ (OH)_{2(s)} + 2e^- \longrightarrow Cd_{(s)} + 2OH^-_{(aq)}}$

Anode (+): $\mathbf{2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \longrightarrow NiO_{2(s)} + 2H_2O + 2e^-}$

Net reaction: $\mathbf{Elect.Energy + Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \longrightarrow Cd_{(s)} + NiO_{2(s)} + 2H_2O}$

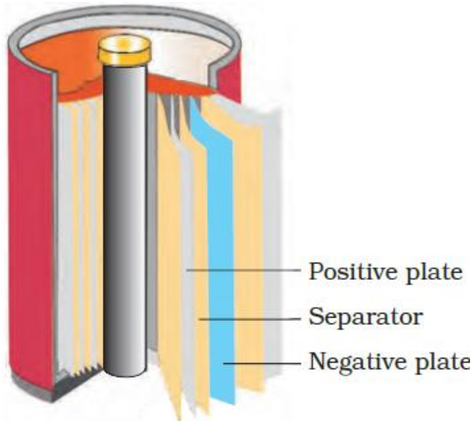


**Fig. 3.12.** Nickel-Cadmium cell

### (C) Fuel cells

A fuel cell is a galvanic cell in which chemical energy of a fuel – oxidant system is converted directly into electrical energy in a continuous electrochemical process. The chemical energy provided by the fuel cell is stored outside the cell. The fuel and oxidants are continuously and separately supplied to the electrodes of the cell where they undergo reactions. Fuel cells are capable of supplying current as long as reactants are supplied.

Eg. Hydrogen - oxygen fuel cell and Methanol - oxygen fuel cell

#### (i) Hydrogen – Oxygen Fuel cell

It is used as an energy source in space shuttles, submarines and other military vehicles. Both anode and cathode consists of porous graphite electrodes impregnated with finely divided Pt/Pd. The electrolyte is 25% KOH held in an asbestos matrix. The reactants (fuel + oxidant) are constantly supplied from outside and the products are removed at the same rate as they are formed. The product discharged is water and the standard EMF of the cell is 0.8 V to 1.0V.

**Cell reactions:** Anode: $2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(l)} + 4e^-$

Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Net Reaction: $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} + \text{Elect.Energy}$

Fig. 3.12. Hydrogen – Oxygen Fuel cell

#### (ii) Methyl Alcohol – Oxygen Fuel cell

The cell consists of methanol and used as the fuel and oxygen (or) air as the oxidant. Anode: Nickel sheet covered by Pt-Pd catalyst, Cathode: Silver on nickel sheet Electrolyte: KOH solution. In this cell methanol and oxygen are fed to the electrolyte. CO2 produced is absorbed by the electrolyte KOH and converted in carbonates. Formation of carbonates decreases the cell efficiency because of the increasing, concentration and polarization at the electrode surface and decreases the conductivity of the electrolyte. The cell reactions are as follows:

At Anode: $CH_3OH_{(l)} + 6OH^- \rightarrow CO_{2(g)} + 5H_2O_{(l)} + 6e^-$

At Catho $+ 6e^- \rightarrow 6OH^-_{(aq)}$

Net React

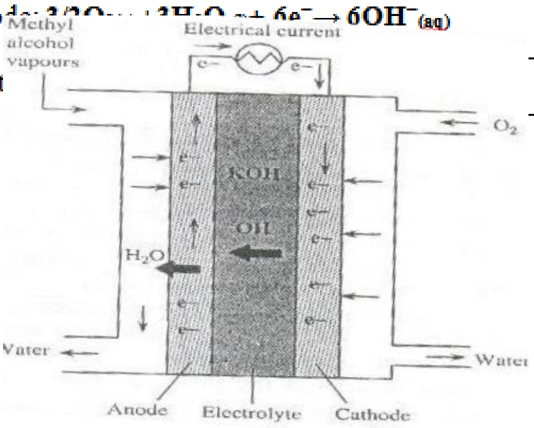


**Fig. 3.13.** Methyl Alcohol – Oxygen Fuel cell

**Elect. Energy Advantages of methyl alcohol-oxygen fuel cell:**

1. Easy to transport.
2. Do not require complex steam reforming operations.
3. These fuel cells are targeted to portable applications
4. It is excellent fuel due to the presence of a high concentration of hydrogen in methanol.
5. There is zero-emission by the cells hence the fuel cells are eco friendly.

### Applications:

1. Because of lightweight, these fuel cells are preferred for space crafts and product H2O is a valuable freshwater source for astronauts.
2. The major application of methyl alcohol-oxygen fuel cells is fuel for fuel cell motor vehicles like NECAR-5 in Japan, USA.

**Advantages of Fuel cells over other cells**

1. High efficiency in energy conversion.
2. The product H2O is a drinking water source for astronauts.
3. Noise and thermal pollution are low.
4. Low maintenance cost.
5. It is an energy storage system for space applications.

---

**SAQ 15**

The chlorine gas electrode is represented as Pt(s) | $Cl_2$ (p) | $C1^-$(c). Write an expression for its

Half-cell potential.

…………………………………………………………………………………………………………………………………………………………
……………………………………

**SAQ16**

**Explain why** :

a) a dry cell comes back to life if left idle for a while.

b) fuel cells are considered better than an electrical power plant using the same fuel.

c) alkaline cells are considered better than Leclanche cell.

---

### 3.7.2 Concentration Cells

If the chemical reactions in two half-cells are the same, but the concentrations of the electrolyte solutions or electrode materials are different, then the net reaction is the transfer of species from higher concentration to lower concentration. There is no net chemical reaction in the cell. Such cells are known as concentration cell.

For example, consider a cell consisting of two half-cells at different $Zn^{+2}$ concentrations ($c_1$ and $c_2$).

**$Zn(s)|ZnSO_4\ (c_1)||\ ZnSO_4\ (c_2)|Zn(s)$**

The overall reaction involves the passage of $Zn^{+2}$ from a solution of higher concentration ($c_2$) to that of lower concentration ($c_1$).

**At the anode**

$Zn(s) \longrightarrow Zn^{2+}(c_2) + 2e^-$

(aq)

**At the cathode**

$Zn^{2+}(c_2) + 2e^- \longrightarrow Zn(s)$

(aq)

Cell reaction : $Zn^{2+}(\ c_2) \longrightarrow Zn^{2+}(\ c_1)$

(aq) (aq)

You must remember that, $E°_{cell}$ for a concentration cell is zero. This can be shown as follows :

**$E° = E°_{anode} + E°_{cathode}$**

$$\mathbf{E}° = (\mathbf{E}°_{Zn^{+2}/Zn}) + (\mathbf{E}°_{Zn^{+2}/Zn})$$

Hence,

$E° = 0$

The emf of the above concentration cell can be calculated using Eq. 3.12

$$E_{cell} \;=\; -\frac{2.303RT}{2F}\, log \frac{c_1}{c_2} \quad \text{..............( Eq. 3.35)}$$

At 298K, this expression becomes

$$E_{cell} \;=\; \frac{0.059}{2}\, log\; log \frac{c_1}{c_2} \quad \text{..............( Eq. 3.36)}$$

In general, there are two types of concentration cells

A. Electrode Concentration Cells
B. Electrolyte- Concentration Cells

### A. Electrode Concentration Cells

In these cells, the potential difference is developed between two like electrodes at different concentrations dipped in the same solution of the electrolyte.

For example, two hydrogen electrodes at different pressure in the same solution of hydrogen ions constitute a cell of this type can be presented as:

<table>
<tr><td colspan="3">(Pt, $H_2$ (Pressure $p_1$))| Anode |$H^+$ | ($H_2$ (Pressure $p_2$) Pt) |Cathode<br>or Pt; $H_2(p_1)$ | $H^+$ | $H_2(p_2)$; Pt</td></tr>
<tr><td><b>RHE</b></td><td><b>LHE</b></td><td><b>Overall</b></td></tr>
<tr><td>$2H^+ + 2e^- \rightarrow H_2(p_2)$</td><td>$H_2(p_1) \rightarrow 2H^+ + 2e^-$</td><td>$H_2 (p) \rightarrow H_2 (p_2)$</td></tr>
<tr><td colspan="3">$Ecell = 0.02955 log \frac{p1}{p2}$<br>In the above cell, both electrodes are hydrogen electrodes immersed in the same solution of $H^+$ ions but the $H_2$ gas passed in the two electrodes is at different pressure. In the above cell, there is no transference of electrolyte and hence, this is called <b>concentration cell without transference.</b></td></tr>
</table>

### B. Electrolyte- Concentration Cells

In these cells, electrodes are identical but these are immersed in solutions of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the start the emf of the cell is maximum and it gradually falls to zero. Such a cell is represented in the following manner:

M | $M^{n+}$ ($C_1$) | | $M^{n+}$ ($C_2$) | M ($C_2$ is greater than $C_1$)
(aq) (aq)

### Examples of Electrolyte- Concentration Cells

**Type A** Those cell in which the two electrodes are same, having different concentrations of the electrolytes and connected by a salt bridge. These cells are **concentration cell without transference.**

Example: (Zn|$Zn^{2+}$ ($C_1$))/Anode || ($Zn^{2+}$ ($C_2$ )|Zn)/Cathode

(aq) (aq)

Zn → $Zn^{2+}$($C_1$) + 2e (**Anode )**

(aq)

$Zn^{2+}$($C_2$) + $2e^-$ → Zn(s) (**Cathode)**

(aq)

The emf of the cell is given by the following expression at 25° C:

$$E_{cell} = \frac{0.0591}{n} log \frac{C_1}{C_2}$$

**Type B** The two electrodes are the same, having different concentrations of the electrolytes but the two solutions are directly in contact with each other. This can be done by putting the two solutions in a tube very carefully so that there is no mixing of the two solutions. In such cases the cell, the cells are represented as

**Zn|Zn$^{2+}$ (a$_1$): (Zn$^{2+}$ (a$_2$ )|Zn**
(aq) (aq)

i.e. the double line is replaced by a dotted line. The junction where the two solution meet is called the ***liquid junction***. In this type of concentration cell, there is a direct transference of electrolyte from one solution to the other through the liquid junction. Hence, these cells are called **concentration cell with transference.**

**Example 5 :** EMF of the cell Cu | CuSO4 (0.001M) || CuSO4 (X) | Cu

(aq) (aq)

is 0.0595V at 25°C. Find X value.

It is clear that $C_1 = 0.001$M, $C_2 = X$ and n = 2; Apply Nernst equation for concentration cell

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1} \text{ at 298K}$$

$$\frac{E_{cell} \times n}{0.0591} = \log \frac{X}{C_1}$$

$$\text{Antilog}\left(\frac{E_{cell} \times n}{0.0591}\right) = \frac{X}{C_1}$$

$$0.001 \times \text{Antilog}\left(\frac{0.0595 \times 2}{0.0591}\right) = X$$

$$0.001 \times 103 = X$$

$$\mathbf{X = 0.103M}$$

**Example 6:** A concentration cell is constructed by dipping copper rods in 0.001M and 0.1M copper sulphate solutions. Calculate the EMF of the cell at 298K.

**Cell representation:**

$$\mathrm{Cu} \mid \mathrm{Cu}^{2+}_{C_1=0.001\mathrm{M}} \parallel \mathrm{Cu}^{2+}_{C_2=0.1\mathrm{M}} \mid \mathrm{Cu}$$

**Cell reactions:**

$$\textbf{Anode (–ve):}\ \mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+}_{C_1=0.001\mathrm{M}} + 2e^-$$

$$\textbf{Cathode (+ve):}\ \mathrm{Cu}^{2+}_{C_2=0.1\mathrm{M}} + 2e^- \longrightarrow \mathrm{Cu}$$

$$\textbf{Overall reaction:}\ \mathrm{Cu}^{2+}_{C_2=0.1\mathrm{M}} \longrightarrow \mathrm{Cu}^{2+}_{C_1=0.001\mathrm{M}}$$

Apply Nernst equation for concentration cell,

$$E_{cell} = \frac{0.0591}{n}\log\frac{C_2}{C_1}$$

$$E_{cell} = \frac{0.0591}{2}\log\frac{0.1}{0.001}$$

$$= 0.0591\mathrm{V}$$

### 3.7.3 Liquid junction potential

**W**hen two electrolytic solutions of different concentrations are brought in contact with each other, a potential difference develops at the junction of two solutions. This potential difference is called Liquid junction potential.

The liquid junction potential arises mainly due to unequal rates of diffusion of ions across the interface. In other words, it is due to the difference in migration velocities of ions.

For example, consider the following cell

$$\mathrm{Pt, H_2(g)} \;\Big|\; \overset{I}{\underset{(a_1)}{\mathrm{HCl}}} \;\vdots\; \overset{II}{\underset{(a_2)}{\mathrm{HCl}}} \;\Big|\; \mathrm{H_2(g), Pt} \qquad (a_1 > a_2)$$

The more concentrated solution will tend to diffuse into the comparatively less concentrated one. The rate of diffusion of each ion will be roughly proportional to its speed in an electric field, or their ion mobility. Both H+ and $Cl^-$ ions diffuse from the concentrated solution to the dilute solution. The ionic velocity of $H^+$ ion will be greater than $Cl^-$ ion. So, $H^+$ will diffuse more rapidly from $a_1$ to $a_2$. The dilute solution in the II compartment will thus become positively charged to solution in I. As a result of this concentrated solution is left with an excess of $Cl^-$ ions and thus acquires a negative charge. Hence, an electrical double layer of positive and negative charges at the junction of the two solutions forms, with a potential difference known as liquid junction potential or diffusion potential. It is a non-equilibrium potential which depends on the relative speeds of the ions' movement.

**Calculation of the Liquid junction potential**

The liquid junction potential cannot be measured directly but calculated. The electromotive force (EMF) of a concentration cell with transference includes the liquid junction potential.

The EMF of a concentration cell without transport is:

……………( Eq. $E_{\mathrm{nt}} = \frac{RT}{F} \ln \frac{a_2}{a_1}$ 3.37)

where $a_1$ and $a_2$ are activities of HCl in the two solutions, R is the universal gas constant, T is the temperature and F is the Faraday constant.
The EMF of a concentration cell with transport (including the ion transport number) is:

……………( Eq. 3.38)

$$E_{\mathrm{wt}} = t_M \frac{RT}{F} \ln \frac{a_2}{a_1}$$

where $a_2$ and $a_1$ are activities of HCl solutions of right and left-hand electrodes, respectively, and $t_M$ is the transport number of $Cl^-$.

Liquid junction potential is the difference between the two EMFs of the two concentration cells, with and without ionic transport:

$$E_{\mathrm{lj}} = E_{\mathrm{wt}} - E_{\mathrm{nt}} = (t_M - 1)\frac{RT}{F} \ln \frac{a_2}{a_1}$$ ……………( Eq. 3.39)

The emf of the cell is thus not only the sum of the oxidation potential ($E_1$) of the electrode where oxidation occurs and reduction potential ($E_2$) of the electrode where reduction occurs, but also includes the junction potentials ($E_j$).

In other words, the emf of the cell is

$E = E_1 + E_2 + E_j$

**Expression for the Liquid junction potential**

Let us consider following concentration cell with transport (where dotted lines show liquid junction potential.

$$\mathrm{Pt, H_2(g)} \left| \begin{array}{c} I \\ \mathrm{HCl} \\ (a_1) \end{array} \right\vdots \begin{array}{c} II \\ \mathrm{HCl} \\ (a_2) \end{array} \Big| \mathrm{H_2(g), Pt} \qquad (a_1 > a_2)$$

The overall reaction of cell is

$H^+ (a_2) \longrightarrow H^+ (a_1)$

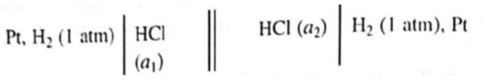
Also $t_a$.HCl ($a_2$) = $t_a$.HCl ($a_1$)

$E = E_1 + E_2 + E_j$

$$= \frac{-\mathrm{RT}}{F}\, ln\, \frac{(a_{H^+})_1}{(a_{H^+})_2} = \frac{\mathrm{RT}}{F}\, ln\, \frac{(a_{H^+})_2}{(a_{H^+})_1}$$

$$E_1 + E_2 + E_j = \frac{2 \times 2.303.\mathrm{ta.RT}}{F}\, log\, \frac{(m_2\gamma_2)}{(m_1\gamma_1)} \text{ ...............( Eq. 3.40)}$$

The same cell without transport



Pt, H$_2$ (1 atm) | HCl ($a_1$) || HCl ($a_2$) | H$_2$ (1 atm), Pt

(aq) (aq)

The cell without transport containing salt bridge (KCl), If we assume that the $K^+$ ions and $Cl^-$ move almost with equal speed, the junction potential is almost reduced to zero. In such a case, the emf of the cell can be simply taken as

$E_1 + E_2$

The overall reaction of cell is

$$\underset{(aq)}{H^+(a_2)} \longrightarrow \underset{(aq)}{H^+(a_1)}$$

$$E = E_1 + E_2 = \frac{2.303\mathrm{RT}}{F}\, log\, \frac{(a_2)}{((a_1))}$$

$$= \frac{2.303\mathrm{RT}}{F}\, log\, \frac{(m_2\gamma_2)}{(m_1\gamma_1)} \text{ ...............( Eq. 3.41)}$$

Subtracting Eq. 3.41 from Eq. 3.40, we get

$$E_T - E_{WT} = E_j = \left[\frac{2 \times 2.303.\mathrm{ta.RT}}{F} - \frac{2.303\mathrm{RT}}{F}\right] log\, \frac{(m_2\gamma_2)}{(m_1\gamma_1)}$$

$$E_j = \frac{2.303\mathrm{RT}}{F} (2t_a - 1)\, log\, \frac{(m_2\gamma_2)}{(m_1\gamma_1)}$$

**Since, $t_a + t_c = 1$, Therefore $(2t_a - 1) = 2t_a - (t_a + t_c) = (t_a + t_c)$**

$$E_j = \frac{2.303\mathrm{RT}}{F} (t_a - t_c)\, log\, \frac{(m_2\gamma_2)}{(m_1\gamma_1)} \text{...............( Eq. 3.42)}$$

**Conclusions**: From Eq. 3.42, we can draw the following conclusion:

(i) Sign as well as the magnitude of $E_j$ depends on transport numbers of anions and cations.
(ii) If $t_a = t_c$, the $E_j$ will be zero.
(iii) If $t_a > t_c$, then $E_j$ will be positive. Hence, it will add to the *emf* of the cell.

(iv) If $t_a < t_c$, then $E_j$ will be negative. Hence, it will operate to yield the *emf* of the cell less than ($E_1 + E_2$).

**Elimination of junction potential**

The liquid junction potential interferes with the exact measurement of the electromotive force of a chemical cell, so its effect should be minimized as much as possible for accurate measurement. The most common method of eliminating the liquid junction potential is to place a salt bridge consisting of a saturated solution of potassium chloride (KCl) and ammonium nitrate ($NH_4NO_3$) with lithium acetate ($CH_3COOLi$) between the two solutions constituting the junction. When such a bridge is used, the ions in the bridge are present in large excess at the junction and they carry almost the whole of the current across the boundary. The efficiency of $KCl/NH_4NO_3$ is connected with the fact that in these salts, the transport numbers of anions and cations are the same.

### 3.7.4 Application of Concentration Cells

### A. Determination of Solubility of Sparingly soluble salts

The ionic concentration of a solution can be calculated from the emf of a concentration cell. In case of a sparingly soluble salt, the salt can be supposed to be completely ionised even in saturated solutions. Hence the ionic concentration is proportional to the solubility of the salt.

Suppose we want to find the solubility of silver chloride. This can be done by measuring the emf, E, of the cell.

Ag | N/100 $AgNO_3$ | Glass || Saturated AgCl | Ag

The emf of the cell at 25°C is given by

$$E = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Here, *n*, the valence of $Ag^+$ ion is 1 and the concentration of $Ag^+$ in N/100 $AgNO_3$ solution is 0.01 gram ion per liter.

Hence,

$$E = \frac{0.0591}{1} \log \frac{0.01}{C_1}$$

From the above expression, the concentration of AgCl in gram ions of silver per litre can be calculated. Multiplying this by 143.5, the molecular weight of silver chloride, we get the solubility of AgCl in grams per liter.

**Example 7** The emf of the cell

Ag | AgI in 0.045 M KI || 0.045 M $AgNO_3$ | Ag

is 0.788 at 25°C. Calculate (*i*) the solubility product of AgI and (*ii*) the solubility of AgI in water at 25°C.

**Solution: Calculation of $K_{SP}$**

At 25°C the concentration of $Ag^+$ in the cathodic half-cell is 0.045M and the concentration of $I^-$ ion in anodic half-cell is 0.045 M KI.

Let the concentration of $Ag^+$ ion in the anodic half-cell due to solubility of AgI be $C_1$.

$$\therefore \quad E = \frac{0.0591}{1} \log \frac{0.045}{C_1}$$

$$0.788 = \frac{0.0591}{1} \log \frac{0.045}{C_1}$$

$$\log \frac{0.045}{C_1} = \frac{0.788}{0.0591} = 13.33$$

$$\frac{0.045}{C_1} = 2.138 \times 10^{13}$$

$$C_1 = \frac{0.045}{2.138 \times 10^{13}} = 2.105 \times 10^{-15}$$

**Calculation of Solubility**

Solubility of AgI $= \sqrt{K_{sp}}$

$= \sqrt{0.9472 \times 10^{-18}}$

$= 0.9732 \times 10^{-9}$ g mol litre$^{-1}$

$= 0.9732 \times 10^{-9} \times 188$ g litre$^{-1}$

$= \mathbf{1.829 \times 10^{-6}}$ **g litre**$^{\mathbf{-1}}$

### B. Determination of Valence of ions

The valancy of ions in doubtful cases can be verified with the help of emf measurement. The expression for the emf, *E*, of a concentration cell is

$$E = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

where n is the valence of the metallic ion in solution, while $C_1$ and $C_2$ are the concentrations of the ions in the two half-cells. Knowing the experimental values of E, $C_1$ and $C_2$, n can be calculated.

### 3.8 Corrosion

Corrosion is a general term used to describe various interactions between a material and its environment leading to degradation in the material properties.

This term generally used for metals and in simple words, we can say that it is an electrochemical spontaneous process through which metals in manufactured states return to their natural oxidation states. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper and bronze are all examples of corrosion.

As per IUPAC,

“Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in its consumption or dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusively physical or mechanical processes such as melting and evaporation, abrasion or mechanical fracture are not included in the term corrosion”.

**Types of Corrosion**:

Corrosion takes place in several different ways and it can be classified based on one of the three factors:
I.**Nature of the corrodent**: This classification is based on “wet” or “dry” conditions in which corrosion occurs. The presence of moisture is essential for wet corrosion and dry corrosion usually involves reaction with gases at high temperatures.

II. **Mechanism of corrosion**: Corrosion can occur either electrochemically or with direct chemical reactions.

III. **Appearance of the corroded metal**: Corrosion can be either uniform or localized. The metal corrodes at the same rate over the entire surface of the metal called generalized corrosion while only small areas are affected in localized corrosion.

**Mechanism of corrosion:**

In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Mechanism of oxide formation is based on electrochemical theory which can explain by taking the example of rusting of iron. Iron will rust when it is exposed to oxygen and water. At a particular spot , ( Fig. 3.14) of an object made of iron, when exposed to the atmosphere, oxidation takes place and that spot behaves as anode and we can write the reaction

$Fe\ (s) \longrightarrow Fe^{2+}(aq) + 2e^{-} \qquad E^{\circ}_{Fe^{2+}/Fe} = -0.44\ V \qquad$ (anode)

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in the presence of $H^+$ (which is believed to be available from H2CO$_3$ formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction.

$O_2(g) + 2H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \qquad E^\circ_{H^+|O_2|H_2O} = +1.23\text{ V}$ (cathode)

The overall reaction being: $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l) \qquad E^\circ_{cell} = +1.67\text{ V}$

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$4Fe^{2+}(aq) + O_2(g) + (4 + 2x)H_2O(l) \longrightarrow 2Fe_2O_3{\cdot}xH_2O(s) + 8H^+(aq)$

The number of water molecules is variable, so it is represented by *x*. The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide (Fe2O3. *x* H2O) and with further production of hydrogen ions.

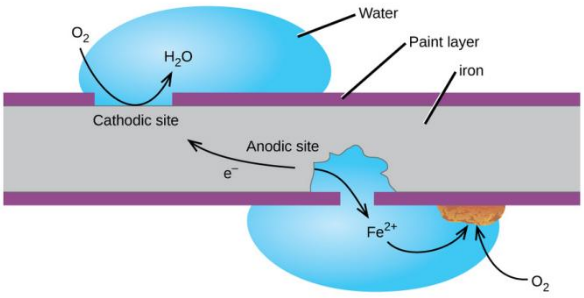


**Fig. 3.14**. Mechanism of rusting of iron.

**Factors responsible for Corrosion:**

(a) Reactivity of the metal: more active metals having high oxidation potential are readily corroded.
(b) Presence of Air and Moisture: Air and moisture accelerate the corrosion. Presence of gases like $SO_2$ and $CO_2$ in air enhances the process of corrosion. Iron does not rust when placed in vacuum.
(c) Presence of Electrolyte: Electrolytes increases the rate of corrosion. For example, iron rusts faster in saline water than in pure water.
(d) Strains in metals: Corrosion takes place readily at bends, scratches and cuts in the metal.
(e) Presence of impurities: Presence of impurities in metals enhances the chances of corrosion. Pure metal do not corrode.

**Corrosion prevention:**

Prevention of metals from corrosion is of very important. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion.It can be prevented through using multiple products and techniques including :

- **Protective coatings:** Metallic structures can be protected from corrosion in many ways. A common method involves the application of protective coatings made from paints, plastics or films of noble metals on the structure itself (e.g., the coating on tin cans). These coatings form an impervious barrier between the metal and the oxidant but are only effective when the coating completely covers the structure. Flaws in the coating have been found to produce accelerated corrosion of the metal.
- ***Alloying***: The alloying the iron with other metals is also useful. For example, stainless steel is mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.
- **Polarize or shift the potential of the metal:** Another method of reducing corrosion is to polarize or shift the potential of the metal enabling it to act as a cathode (rather than an anode) in an electrochemical cell. One example is the galvanizing of steel with a coating of zinc. The iron and zinc then function as the electrodes of a cell. Zinc is the more readily oxidized metal of the pair and functions as the anode and corrodes, while the iron functions as the cathode. The zinc is used up and protection is effective as long as some zinc remains.
- ***Sacrificial anodes**:* Sacrificial anodes work on the same principal as dissussed for shift the potential of the metal but use an external electrode made from a readily oxidized metal; this form of protection is commonly used on buried pipelines. The sacrificial anode (Zn, Mg and Al) can be replaced as needed.
- ***Passivation**:* Some corrosion processes will create solid metal compounds that will coat the initial site of corrosion and prevent further corrosion at that site.
- **Cathodic protection**: Cathodic protection using an impressed current derived from an external power supply is a related form of protection in which the metal is forced to be the cathode in an electrochemical cell. For example, most cars now use the negative terminal on their batteries as the ground. Besides being a convenient way to carry electricity, this process shifts the electrical potential of the chassis of the car, thereby reducing (somewhat) its tendency to rust.
- **Corrosion inhibitors**: Corrosion inhibitors can be added to solutions in contact with metals (e.g. inhibitors are required in the antifreeze solution in automobile cooling systems). These compounds can prevent either the anode or the cathode reaction of corrosion cells; one way that they can do this is by forming insoluble films over the anode or cathode sites of the cell. Examples of anodic inhibitors are sodium phosphate or sodium carbonate while zinc sulfate and calcium or magnesium salts act as cathodic inhibitors. New forms of paints are being developed which take advantage of similar properties. These paints promise to nearly eliminate corrosion in applications like painted car fenders, etc.

## 3.9 ELECTROMETRIC MEASUREMENT OF pH

An electroanalytical method can be defined as one, in which the electrical response of a chemical system or sample is measured. These methods can be classified into a number of types characterized by measuring the electrical response in terms of different electrical quantities such as: potential, current, quantity of current, resistance and voltage etc. and bear the corresponding names as potentiometry, amperometry, coulometry, conductometry and voltammetry etc.

There is a widespread usage of electrochemical methods in general and of potentiometric determination of pH and concentration of several ions in particular. Measurement of pH is one of the most important and widely used test in water analysis. For natural water treatment as well as for waste water treatment a large number of reactions e.g. coagulation, disinfection, water softening, acid base neutralisation etc. are all pH dependent. Most of chemical laboratories are equipped with pH meters. Modernization of potentiometry by the development of ion selective electrodes has increased the interest in the study of environmental samples.

The principle of potentiometry is applied to measure the potential difference in terms of pH unit on pH scale by suitably modifying the common voltmeter to high input impedance mV meter and such pH measurement can be termed as pH metry instead of potentiometry. In pH metry, pH meter is used to measure the pH. Before going in further details of potentiometric measurement of pH, let us know the basic concept of pH.

### 3.9.1. THE concept of pH

The hydrogen ion concentration plays an important role in many areas of chemistry and its determination and control is of great practical value in the electroanalytical methods. The shorthand notation of hydrogen ion concentration is given in terms of pH for ***'puissance de hydrogen'*.** **(French: power of hydrogen**). The pH value, originally formulated in 1909 by S.P. Sorensen, is defined as “the negative logarithm of hydrogen ion concentration”.

Mathematically it may be expressed as

$$\boldsymbol{pH = -log\,[H^+]} \quad …….(3.43)$$

Where [ ] represents equilibrium concentration and logarithm is taken to the base 10.

Alternative and more useful forms of pH definition are:

$\boldsymbol{pH = -log\,\frac{1}{[H^{+}]}}$............(3.45)

$[\boldsymbol{H^{+}}] = \mathbf{10}^{-\boldsymbol{pH}}$............(3.46)

In practice 'p' preceding a variable is used to express the negative logarithm of that variable. Likewise, pOH is to designate the negative logarithm of hydroxyl ion concentration.

In aqueous solutions the product of $[\boldsymbol{H^{+}}]$ and $[\boldsymbol{OH^{-}}]$ is always a constant at a particular temperature. Thus,

$K_w = [\boldsymbol{H^{+}}][\boldsymbol{OH^{-}}]$ ............(3.47)

where *K*w is the ionic product constant of water, its value is $1\times10^{-14}$ at 25°C.

Taking logarithm of both sides of equilibrium of equation 3.47 and substituting 'p' for

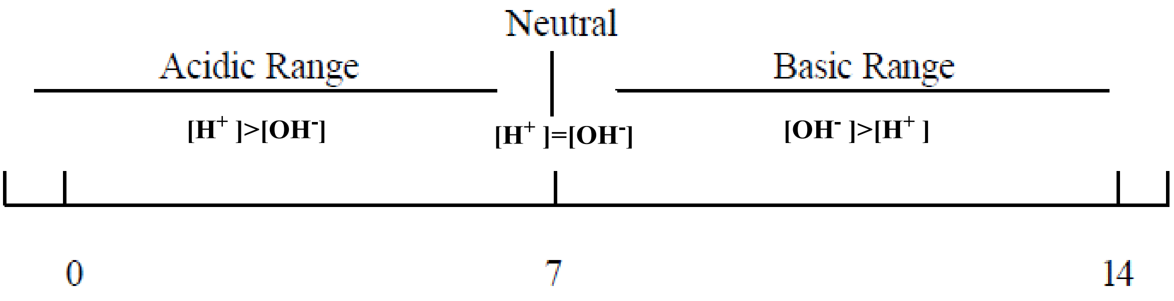
negative logarithm we get

pH + pOH = p*K*w = 14, at 25°C............(3.48)

For pure water $[H^{+}] = [OH^{-}] = 1\times10^{-7}$ (at 25°C), which gives the pH value of pure water equal to 7 at this temperature.

For an acidic solution $[\boldsymbol{H^{+}}] > [\boldsymbol{OH^{-}}]$ and pH is below 7, whereas

for a basic solution $[\boldsymbol{OH^{-}}] > [\boldsymbol{H^{+}}]$ and pH is above 7.



**pH Scale**

**SAQ 17**

Find the concentration of $H_+$ ions of a solution for which pH value is 4.5.

### 3.9.2 Measurement of pH

The pH of a solution is commonly found by the use of either an indicator or a pH meter. Because of their accuracy and speed, pH meters have superseded the older indicator method in many applications. However, the indicator method remains in use because it is simple and convenient especially for fieldwork in pollution analysis.

#### 3.9.2.1 Colorimetric Measurement of pH

For the approximate and rapid estimation of pH and in studies in non-aqueous media, it is convenient to make use of coloured indicators. Colourimetric measurement can be carried out visually or photometrically.

- **Visual Measurement of pH**

The use of coloured indicators for the visual measurement of pH is well known. The approximate pH of a solution can be determined by comparing its reaction with different indicators or on papers impregnated with the indicator solution. In this method, the colour change is observed in a particular pH range. The chief advantage is the low cost and also the method is suitable for routine pH measurement. A very common example is litmus which is red below pH 5 and blue above pH 8. The colour changes from red to blue when pH changes from 5 to 8. To find colour changes in a wide range of pH, the mixtures of indicators, the so-called universal indicators are to be used. For example, the Kolthoff universal indicator is a mixture of five indicators and gives a conspicuous colour change within unit pH values. The colours at different pH values are given in Table 3.9.1.

Table 3.9.1. **Variation of the colour of Kolthoff Universal Indicator with the change in pH.**

| | | | | | |
|---|---|---|---|---|---|
| pH | 1 | 2 | 3 | 4 | 5 |
| Colour | R | R-P | R-O | O | Y-O |
| pH | 6 | 7 | 8 | 9 | 10 |
| Colour | L-Y | Y-G | G | G-B | V |

Abbreviations: R=Red, P=Pink, O=Orange, Y=Yellow, LY=Light Yellow, G=Green, B=Blue & V=Violet

- **Photometric Measurement of pH**

The visual method for pH measurement using indicators has low accuracy due to difficulties of light intensity estimation. The accuracy can be increased by instrumental means using a colorimeter or a spectrophotometer to measure the absorbance at a particular wavelength. Indicators are considered to behave as weak acids or weak bases and the degree of dissociation of indicator substance depends on hydrogen ion concentration in solution. Consider, e.g. an indicator acid, HIn, which dissociates as

HIn $\rightarrow H^{+} + In^{-}$………(3.48)

Colour A Colour B

The dissociation constant K of indicator HIn is

$$K = \frac{[H^{+}]\,[In^{-}]}{[HIn]} \quad \text{………(3.49)}$$

$$\log K = \log\,[H^{+}] + \log\frac{[In^{-}]}{[HIn]} \quad \text{………(3.50)}$$

or

$$pH = pK + \log\frac{[In^{-}]}{[HIn]} \quad \text{………(3.51)}$$

Indicator colours are indicated by the $In^{-}$ and HIn concentration ratio which depends on degree of dissociation and hence the pH can be indicated by the intensity of either colour A or colour B with the assumption that the Beer's law is obeyed. To get satisfactory results by photometric measurement, it is necessary to keep the indicator concentration as small as possible.

#### 3.9.2.2. Potentiometric Measurement of pH

The electrometric method of pH determination is based on the measurement of potential of a pH cell, whereby the potential of a hydrogen sensitive electrode is directly proportional to pH, and pH is defined in an operational manner on a potentionmetric scale.

The pH meter is calibrated potentiometrically with an indicator electrode (glass) and a reference electrode using a standard buffer. The operational pH is defined as:

$$(pH)_u = (pH)_s \pm \frac{(E_{(cell)})u - (E_{(cell)})s}{0.0591} \quad \text{………(3.52)}$$

where

(pH)u = potentiometrically measured pH of the sample (unknown solution)

(pH)s = assigned pH of the standard buffer used for calibration

(*E*cell)u = cell potential of glass electrode and reference electrode system with unknown solution

($E$cell)s = cell potential of glass electrode and reference electrode system with standard buffer

In order to understand this operational definition of pH, we will take up general principles of potentiometry.

### 3.9.3 **Principle of Potentiometry**

Potentiometry deals with the measurement of difference in potential between two electrodes which have been combined to form an electrochemical cell. The difference in potential between the two electrodes in electrochemical cell is known as cell potential. The cell potential depends on the composition of the electrodes, concentration of the solution or more correctly activity of a species in solution (or pressure of gases) and the temperature. Relationship connecting the cell potential with the activity of the species involved in the concerned chemical reaction, known as **Nernst equation**, can be derived using thermodynamic principles. Based on the dependence of cell potential on the activity or concentration of the species in the electrochemical cell, we use this concept to obtain the activity or concentration, and pH of a species in solution from potential difference measurements using potentiometer or pH meter.

The potential difference between the electrode and solution in a half cell is referred to as the electrode potential. In general, the potential difference of a cell is given by the difference between the two electrode reduction potentials $E1$ and $E2$, of the cathode and anode, respectively

$E\text{cell} = E_1 + E_2$

The junction potential developed at the junction between the two half cells are also contributing to the cell potential, the $E$cell calculation can be rewritten as:

$E(\text{cell}) = [E_1 + E_2\ ] + E\text{j}$

Where $E$j is the liquid junction potential and can be a positive or negative quantity. By using salt bridge between two half- cell the liquid junction potential can be minimized. Using Nernst equation, the relationship between cell potential and activity of species involved can be developed.

The Nernst equation is:

$$E = E^{\circ}_{cell} - \left(\frac{RT}{nF}\right) ln \frac{a(reduced)}{a(oxidised)} \text{.........}(3.53)$$

Where $R$ is the universal gas constant, $T$ is the absolute temperature, $n$ is the numbers of electron involved in the transfer, $F$ is Faraday's constant and $a$(reduced) and $a$(oxidized) are the activities of the reduced and oxidized species of each half cell.

For example the Copper (Copper II) half-cell of the galvanic cell mentioned earlier it is written as

$$E_{Cu^{2+}/Cu} = E^{\circ}_{Cu^{2+}/Cu} - \left(\frac{RT}{2F}\right) ln \frac{a(Cu)}{a(Cu^{2+})}$$

But we can take the activity of a pure substance to be unity, so

$$E_{Cu^{2+}/Cu} = E^{\circ}_{Cu^{2+}/Cu} - \left(\frac{RT}{2F}\right) ln \frac{1}{a(Cu^{2+})}$$

or $E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} - \left(\frac{RT}{2F}\right) \ln a(Cu^{2+})$

A similar expression could be written for the left-hand half-cell:

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \left(\frac{RT}{2F}\right) \ln a(Zn^{2+})$$

If the liquid junction potential is negligible, the potential of the cell is then given by:

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

Clearly the potential of the cell will depend upon the activity of both the copper(II) and zinc(II) ions. In such situation it is not possible to determine the activity or concentration of the two ions from the cell potential. In practice, we determine the activity or concentration of a single substance, rather than a combined value for two or more substances. For this reason if we keep the activity of zinc(II) ions at a fixed value so that its potential also remains constant. Then,

$$E_{cell} = E^\circ_{Cu^{2+}/Cu} + \left(\frac{RT}{2F}\right) \ln a(Cu^{2+}) - E_{Zn^{2+}/Zn}$$

As $E^\circ_{Cu^{2+}/Cu}$ and $E_{Zn^{2+}/Zn}$ are both constant, they can be combined into one value *E'*.

Then,

$$E_{cell} = E' + \left(\frac{RT}{2F}\right) \ln a(Cu^{2+})$$

Now, the measurement of cell potential is proportional to the natural logarithm of the activity of the Copper (II) ion. This equation relates the activity of the oxidized form of the metal to potential. However, a general equation can be written for both oxidized and reduced forms of electrodes.

$$E_{cell} = E' \pm \left(\frac{RT}{2F}\right) \ln a_i \text{………}(3.54)$$

Where *n* is the charge on the ion, I, and *E*' is a constant incorporating the potential of the first half cell which is kept constant and the standard potential of the second half cell containing the solution under investigation and the first half cell. Note the ± sign in the equation is used to signify that it will be positive if I is a cation and negative if I is an anion. This equation can be applied to a typical cell used in potentiometric analysis and shown in **Fig. 3.15**.

This is the common practice in potentiometric measurements. The first half cell which is having constant potential is referred to as a **reference electrode**. The second electrode in combination with the reference electrode is called an **indicator electrode** and its response should be dependent upon changes in activity or concentration of the species of interest.

Before considering electrodes in detail, let us now discuss the measurement of cell potential. If a current is drawn from a cell as discussed above, in the course of measurement of cell potential, the cell reaction proceeds and the concentration of the solutions change in the two half-cells. Hence, it is important to measure the cell potential without allowing current to flow. The cell potential measured nearly under zero or negligible current flow is called **electromotive force (e.m.f)** of the cell. The instruments which used for accurate measurement of potential are potentiometer and pH meter. These instruments draw only negligible current.

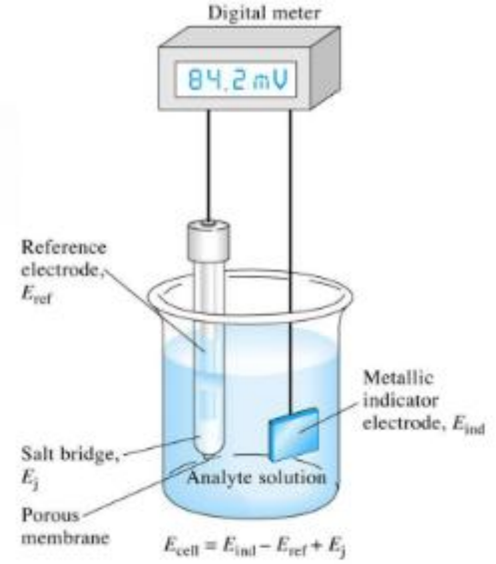


**Fig.3.15.** Diagrammatic representation of a cell used for potentiometric analysis

### 3.9.3.1**Reference Electrode**

Now we are going to take up some reference electrodes which are commonly used in potentiometry. But before that, you should know the features to be considered when constructing or selecting a reference electrode. Some important one is:

- The potential of the electrode should remain constant; even some current is passed through it.
- The potential should be reproducible. The electrode should be easily prepared from readily available materials.
- The potential of the electrode should not change with temperature.
- It should be cheap.

You know well that all the standard electrode potentials are quoted about the standard Hydrogen Electrode, which is the most important primary reference electrode and whose potential is equal to zero under fixed conditions namely hydrogen gas at 1 atm. We have already discussed it in the previous section.

Even though the hydrogen electrode is first and primary reference electrode developed, nowadays, many other subsidiary standard electrodes, which can be easily prepared and permanently set up, are available for practical use and are preferred because of easiness to set up in comparison with hydrogen electrode, which is more complicated and requires rigorous experimental conditions. Hydrogen electrode is inconvenient for use in practical routine laboratory experiments since it has got the following practical problems.

1. It requires a large gas cylinder.

2. Hydrogen and air mixture is highly explosive.

3. Catalyst is easily poisoned.

Hence for routine laboratory use some other reference electrodes are commonly employed for measuring the potentials of other half-cells. The potentials of these reference electrodes have been measured against standard hydrogen electrode (SHE) and in potentiometry, the potential of any system is expressed as if it is measured with reference to the potential of standard hydrogen electrode (SHE). The simple and common reference electrodes widely used are calomel electrode and silver-silver chloride electrode. These two are preferred because of their easy fabrication and maintain a constant and reproducible potential were discussed in the previous section.

### 3.9.3.2 **Indicator Electrodes**

The electrodes that respond to a specific ion are referred to as indicator electrodes and the selection and use of such electrodes is the key to modern potentiometry. Several metals can be served as indicator electrodes. But they are not selective as these electrodes can respond to its ions and can also respond to some other metal ions. There are several other indicator electrodes which are selective to particular ions. Many of them are very valuable in potentiometric analysis and are collectively referred to as ion-selective electrodes (ICE). The most common of these is the glass electrode, which is selective to $H^+$ ions and, consequently, pH.

### Glass Electrode

The most convenient way for determining pH has been by the use of the glass electrode. It is an ion-selective electrode. Glass electrode is a membrane-type electrode whose membrane is made by a special type of glass. A potential develops across a thin glass membrane separating two solutions of different acidities. The measurement of potential difference can thus be related to hydrogen ion concentration.

This phenomenon was first recognized by Cremer in 1906 and systematically explored by Haber in 1909 with the construction of a glass bulb electrodes. After the work of Sorenson (1909) to determine hydrogen ion concentration in terms of pH and the use of vacuum tube voltmeter by A. Beckmann (1930) made the use of glass pH electrodes more practical. Development of transistor-based pH meters and the special purpose glass for the measurement of high pH values have further improved the technology. The glass electrodes of various sizes, shapes and for different pH ranges are commercially available. Fig. 3.9.2 illustrates the construction of a common type of glass electrode. It consists of a thin, H+ sensitive glass membrane bulb at the end of a heavy-walled glass tubing. A buffer solution (or 0.1*M* HCl) is filled in the glass membrane bulb. A reference electrode (usually silver-silver chloride electrode) is placed in contact with the inner solution. It is connected to one terminal of the pH meter. The bottom portion (bulb) of the glass electrode is immersed in the external solution whose pH is to be measured. An external reference electrode (usually an SCE) is immersed in the external solution and is connected to the other terminal of the pH meter.

Schematic diagram of cell containing a pH glass electrode can be represented as in **Fig.3.16**:

| **Internal Reference Electrode** | **Internal buffer** $a(H^+)_1$ | $H^+$**sensitive glass membrane** | **External Solution** $a(H^+)_2$ | **External Reference Electrode** |
|---|---|---|---|---|

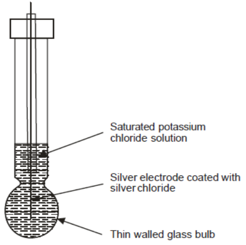


**Fig.3.16. A typical glass electrode for pH measurements**

The potential for this cell response is related to the logarithm of hydrogen ion activities on the two sides of the glass membrane and is given by Nernst equation:

$\boldsymbol{E_{cell} = K + 0.0591\ \log \frac{a(H^+)_1}{a(H^+)_2}}$………(3.55)

Where *k* is a constant. The constant includes the difference in junction potential between the reference electrode and solution and the asymmetry potential for the glass membrane. The asymmetry potential is due to the difference in the surface of the inner and outer layers of the glass membrane. Since the pH on the internal side of the glass membrane is held constant using a buffer, the potential of the glass membrane electrode will depend upon the pH of the external solution.

Since **pH =** $-\log \boldsymbol{a}\,(\boldsymbol{H}^+)$

This substituting into Eq. 3.9.13gives,

$\boldsymbol{E_{cell} = k1 + 0.0591\ pH}$ …….. (3. 56)

Where *k*1 now includes the constant factor related to $aH^+$. Thus, the emf produced in the glass electrode system varies linearly with pH. From the Eq. 3.56 the constant *k*1 can be eliminated by measuring potential, first with standard buffer solution whose pH is precisely known and then with unknown sample solution. Thus for the standard buffer

$(E\text{cell})_s = k1 + 0.0591\ (\text{pH})_s$

For the unknown sample solution

$(E\text{cell})\text{u} = k1 + 0.0591\ (\text{pH})\text{u}$

Then the difference in both the cell potentials

$(E\text{cell})\text{u} - (E\text{cell})\text{s} = 0.0591\ (\text{pH})\text{u} - 0.0591\ (\text{pH})\text{s}$

or

$(\text{pH})\ \text{u} = (\text{pH})\text{s} + \frac{(E\text{cell})\text{u} - (E\text{cell})\text{s}}{0.0591}$........ (3. 57)

This is the operational definition of the pH.

As said above, the constant *k* 1 includes the asymmetry potential which exists across the glass membrane even if the two sides of the cell are of identical composition. For this reason, a pH meter is to be calibrated from time to time (preferably whenever pH measurements are done) with standard buffers.

In pH meter, the voltmeter is used to measure the potential of the cell. The voltage scale is calibrated in pH units so that 0.0591V correspond to 1pH Unit at 25°C. This value will change with temperature and modern pH meters have a temperature compensation device. This may be set before taking pH readings.

**Quinhydrone Electrode**

It is a widely used secondary standard electrode. It involves the redox reaction between quinone (Q) and hydroquinone (QH2),

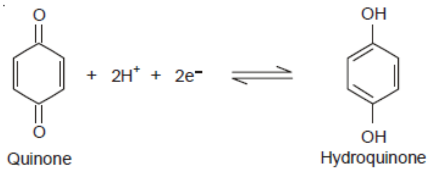
$$\text{Q} + 2\text{H}^+ + 2e^- \rightleftharpoons \text{QH}_2$$

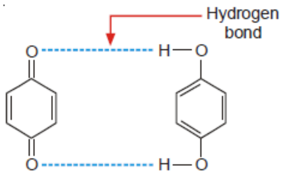
The hydroquinone half-cell consists of a platinum strip immersed in a saturated solution of quinhydrone at a definite H+ ion concentration (buffered solution). Quinhydrone is a molecular compound which gives equimolar amounts of quinone and hydroquinone in solution.

The electrode system may be represented as

$$\text{Pt} \mid QH_2, Q, H^+$$

The potential developed is measured against a hydrogen electrode or calomel electrode. The emf to a standard hydrogen electrode is 0.2875 V at 25°C.





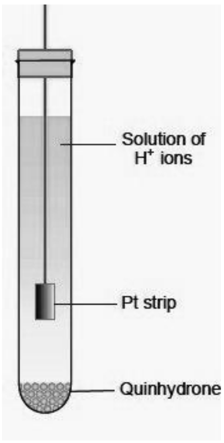


**Fig.3.17. The Quinhydrone Electrode**

## Combination Electrodes

For the purpose of convenient both an indicator and a reference electrodes (with salt bridge) can be combined into a single probe to make a complete cell or combination electrodes. For such electrodes only small volume is needed for potentiometric measurements. A typical assembly of combination electrodes is shown in Fig. Fig.3.18. It consists of a tube within a tube, the inner one having the pH indicator electrode and the outer one having the reference electrode and its salt bridge.

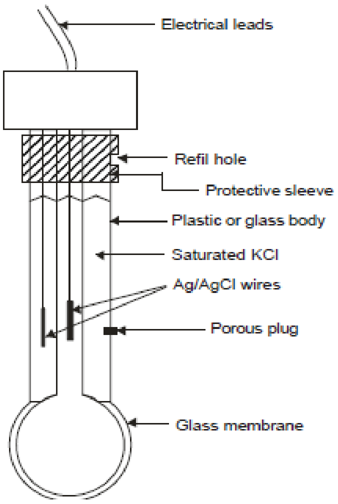


**Fig.3.18**. Combination pH reference electrode

### 3.9.4 Measurement of pH Using pH Meter

A pH meter is an electronic voltmeter of requisite sensitivity having a scale calibrated directly in pH units. The scale is normally taken as extending from 0 to 14 pH units. A pointing needle moves across the graduated scale and the pH of the solution can be read directly on the scale. Numerous pH meters of various designs are marketed by several instrument manufactures. General purpose pH meters are either line operated instruments that are readable to 0.05 pH unit or battery operated instruments suitable for field job. These days digital pH meters readable to 0.01 pH unit are more popular as compared to scale-needle instruments.

Measurement of pH of a solution with the instrument (analog meter) shown in **Fig. 3.19.** can be made following the procedure given below in a step-wise manner.

1. Keep the selector switch on 'zero' position and adjust the zero position by a screwdriver if the pointer does not indicate zero.

2. Mount the electrodes (a glass electrode and a saturated calomel electrode or a combined glass-calomel electrodes) in the clip on the stand. Wash the electrode(s) well with distilled water.

3. Connect the power cable to a 220V AC supply. Switch on the instrument and wait for a few minutes till the instrument warms up.

4. Adjust the temperature/solution temperature value.

5. Take the standard buffer solution of desired range (e.g. buffer of pH 4 for acidic solutions) in a beaker. The electrode assembly is immersed in the pH reference buffer and the solution is agitated gently by swirling the solution in the region of the glass electrode surface so as to bring it into pH equilibrium. It should be ascertained that the glass electrode membrane is completely immersed in the solution. The electrodes should not touch each other or the side or the bottom of the beaker.

6. Put the selector switch to suitable pH range (0-7 for acidic or 7-14 for basic solutions) and adjust set buffer knob in manner that the pointer reads the pH of the standard buffer solution (placed in the beaker).

7. Put the selector switch back to zero position. Remove the electrodes from the buffer solution, wash the electrodes with distilled water and wipe them gently with tissue paper.

8. Transfer the standard buffer back to the storage bottle and wash the beaker well with distilled water.

9. Take the sample solution in the beaker. Introduce the electrodes in the solution and swirl it gently.

10. Set the selector switch in the suitable range position and read the pH on the scale.

11. Put the selector switch back to zero position. Remove the electrodes from the solution, wash them with distilled water and keep the electrodes in distilled water, when not in use.

**Precautions**

(i) Never touch the membrane of the glass electrode with anything else except soft tissue paper since it is fragile and is easily ruined if scratched or bumped.

(ii) The electrode(s) must not be removed from the solution unless the selector switch is at zero.

(iii) Never dip the glass electrode in a solution with a dehydrating action.

(iv) If used for measuring pH of albuminous substances, the glass electrode must be cleaned with suitable solvents and th en the electrode is placed in distilled water for a few hours before it is used to measure the pH of the other solution.

(v) For basic solutions with pH more than 11, glass electrodes of special composition are required to avoid interference due to sodium ion.

(vi) The glass electrode may be covered with a sleeve to save it from jerks.

(vii) The standard buffer of pH value as close as possible to the sample pH value must be taken for the calibration of the system. Commercially available standard buffers of pH values 4, 7 and 9.2 are commonly used.

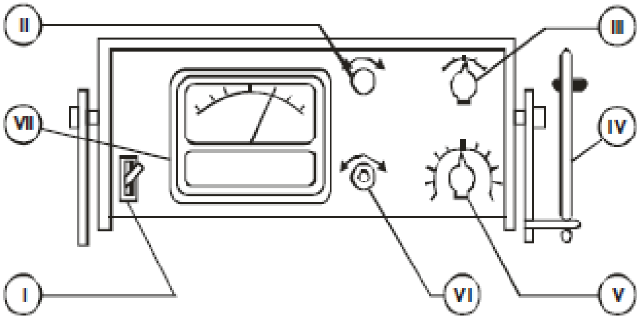


**Fig. 3.19.** A direct reading pH meter (front view) legend: I. On/off switch II. Set zero III. Selector IV. Electrode support V. Temperature compensation VI. Set buffer VII. Meter

**Example 9:**

A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of $10^{-6}$ M hydrogen ions. The emf of the cell is *0.118* volt at 25° C. Calculate the concentration of hydrogen ions at the positive electrode.

**Solution:**

The cell may be represented as

$Pt|H_2(1\ atm)|H^+||H^+|H_2(1\ atm)|Pt$

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $2H^+ + 2e \rightarrow H_2$

$E_{cell} = 0.0591/2\ \log([H^+\ ]_{cathode}{}^2)/[10^{-6}\ ]^2$

$0.081 = (0.0591)\ \log\ ([H^+])/10^{-6}$

$\log[H^+\ ]_{cathode}/10^{-6} = 0.118/0.0591 = 2$

$[H^+\ ]_{cathode}/10^{-6} = 10^2$

$[H^+]_{cathode} = 10\text{-}^6 = 10^{-4}$ M

## 3.10. Buffer

What do you think will happen if the pH of our blood changes drastically from its normal pH of 7.35? Yes, the cells of our body will not function properly and our body systems will fail! Human blood contains a 'buffer' that allows it to maintain its pH at 7.35 to ensure normal functioning of cells. Buffer solutions are also important in chemical and biochemical processes where the control of pH is very important. Let's understand buffer solutions in more detail.

A buffer is a solution that can resist pH change upon the addition of an acidic or basic components. It is able to neutralize small amounts of added acid or base, thus maintaining the pH of the solution relatively stable. This is important for processes and/or reactions which require specific and stable pH ranges. Buffer solutions have a working pH range and capacity which dictate how much acid/base can be neutralized before pH changes, and the amount by which it will change.

### Types of Buffer Solution

The two primary types into which buffer solutions are broadly classified into are acidic and alkaline buffers.

### Acidic Buffers

As the name suggests, these solutions are used to maintain acidic environments. Acid buffer has acidic pH and is prepared by mixing a weak acid and its salt with a strong base. An aqueous solution of an equal concentration of acetic acid and sodium acetate has a pH of 4.74.

- pH of these solutions is below seven
- These solutions consist of a weak acid and a salt of a weak acid.
- An example of an acidic buffer solution is a mixture of sodium acetate and acetic acid (pH = 4.75).

### Alkaline Buffers

These buffer solutions are used to maintain basic conditions. Basic buffer has a basic pH and is prepared by mixing a weak base and its salt with strong acid. The aqueous solution of an equal concentration of ammonium hydroxide and ammonium chloride has a pH of 9.25.

- The pH of these solutions is above seven
- They contain a weak base and a salt of the weak base.
- An example of an alkaline buffer solution is a mixture of ammonium hydroxide and ammonium chloride (pH = 9.25).

Buffer solutions help maintain the pH of many different things as shown in the Fig.3.20 below.

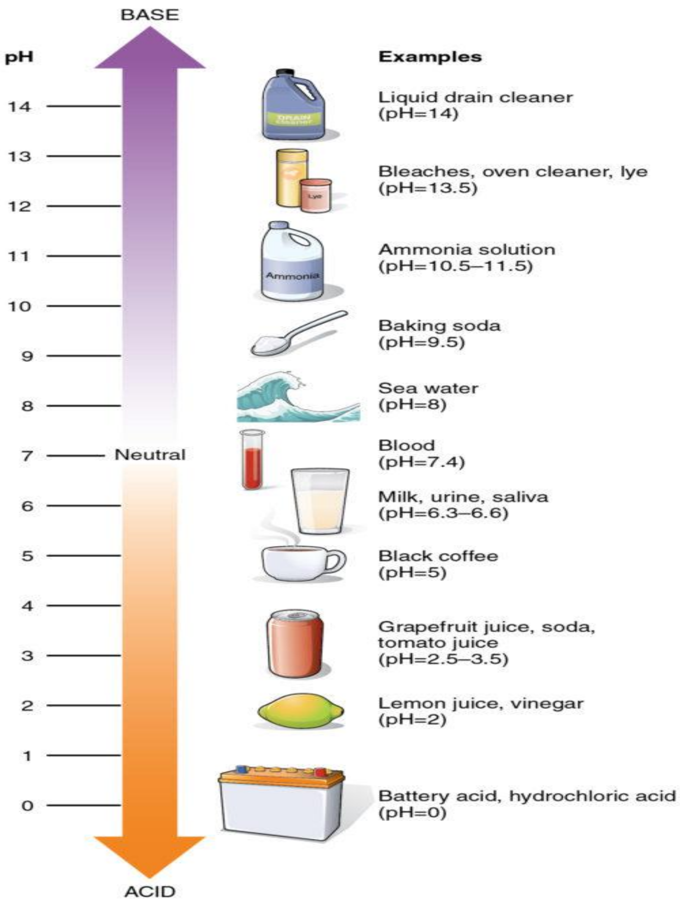


**Fig. 3.20.** . Buffer solutions help maintain the pH of many different things

### 3.10.1 Mechanism of Buffering Action

**Mechanism of buffering action of acidic buffer**

A mixture of acetic acid and sodium acetate is acidic because the $K_a$ of acetic acid is greater than the $K_b$ of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value.

$$CH_3COOH\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq)\ +\ CH_3COO^-\ (aq)$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+\ (aq)\ + CH_3COO^-\ (aq) \longrightarrow CH_3COOH\ (aq) + H_2O\ (l)$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (**Fig. 3.21.** ).

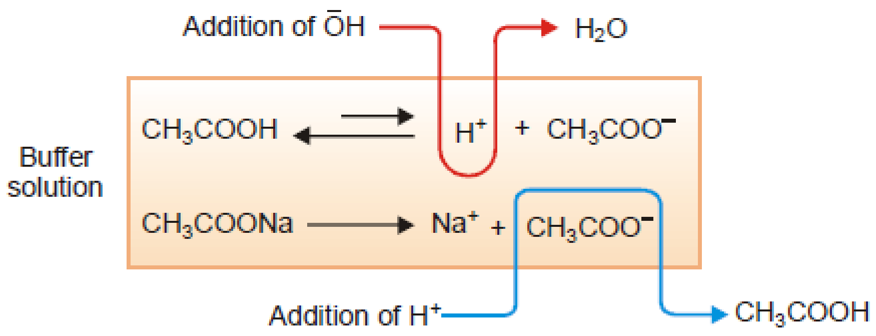


**Fig.3.21.** Mechanism of buffering action of acidic buffer

**Mechanism of buffering action of basic buffer**

A mixture of ammonia and ammonium chloride is basic because the $K_b$ for ammonia is greater than

the $K_a$ for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:
$NH_4^+$ (aq) +$OH^-$ (aq) ⟶ $NH_3$ (aq) + $H_2O$ (l)

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:
$H_3O^+$ (aq) + $NH_3$ (aq) ⟶ $NH_4^+$ (aq)+ H2O (l)

The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

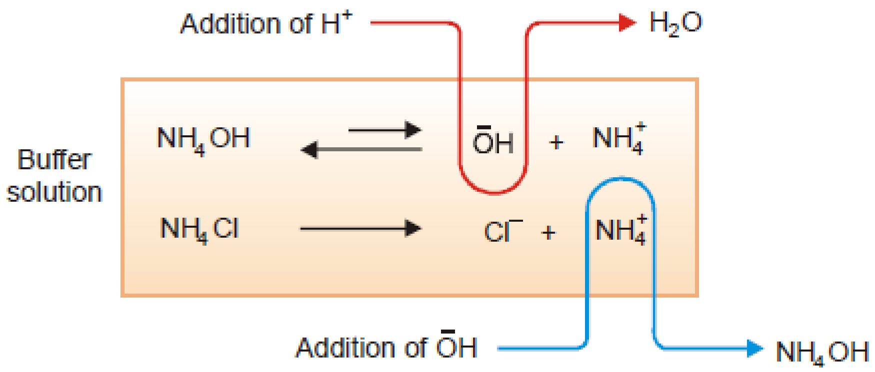


**Fig. 3.22.** Mechanism of buffering action of basic buffer

### 3.10.3. Henderson-Hasselbalch equation

The pH of an acid buffer can be calculated from the dissociation constant, *Ka*, of the weak acid and the concentrations of the acid and the salt used. The dissociation expression of the weak acid, HA, may be represented as

$$HA \rightleftharpoons H^+ + A^-$$

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

$$[H^+] = K_a \times \frac{[HA]}{[A^-]} \text{.........(3.58)}$$

The weak acid is only slightly dissociated and its dissociation is further depressed by the addition of the salt ($Na^+A^-$) which provides $A^-$ ions (Common ion effect). As a result the equilibrium concentration of the un-ionised acid is nearly equal to the initial concentration of the acid. The equilibrium concentration [$A^-$] is presumed to be equal to the initial concentration of the salt added since it is completely dissociated. Thus we can write the equation (3.58) as

$$[H^+] = K_a \times \frac{[acid]}{[salt]} \text{.........(3.59)}$$

where [acid] is the initial concentration of the added acid and [salt] that of the salt used.

Taking negative logs of both sides of the equation (3.59), we have

$$-\log [H^+] = -log\ K_a - log \frac{[acid]}{[salt]} \text{.........(3.60)}$$

But – log [$H^+$] = pH and log $Ka$ = p$Ka$

Thus from (3.60) we have

$$-\log [H^+] = -log\ K_a - log \frac{[acid]}{[salt]}$$

pH = $\mathrm{p}Ka - log \frac{[acid]}{[salt]}$ or

$$\text{pH} = \mathrm{p}Ka + log \frac{[salt]}{[acid]} \text{.........(3.61)}$$

This relationship is called the **Henderson-Hasselbalch equation** or simply **Henderson equation.**

In a similar way, the Henderson-Hasselbalch equation for a basic buffer can be derived. This can be stated as :

$$\text{pOH} = \mathrm{p}Kb - log \frac{[base]}{[salt]} \text{ .........(3.62)}$$

## Significance of the Henderson-Hasselbalch equation

With its help :

(1) The pH of a buffer solution can be calculated from the initial concentrations of the weak acid

and the salt provided *Ka* is given. However, the Henderson-Hasselbalch equation for a basic buffer will give pOH and its pH can be calculated as (14 – pOH).

(2) The dissociation constant of a weak acid (or weak base) can be determined by measuring the pH of a buffer solution containing equimolar concentrations of the acid (or base) and the salt.

$$\text{pH} = \text{p}Ka + log\frac{[salt]}{[acid]}$$

$$[\text{salt}] = [\text{acid}],\ log\frac{[salt]}{[acid]} = log1 = 0$$

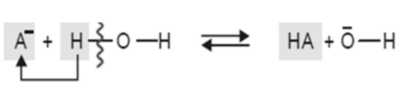
∴ p*Ka* = pH

The measured pH, therefore, gives the value of p*Ka* of the weak acid. Likewise, we can find the p*Kb* of a weak base by determining the pH of the equimolar basic buffer.

(3) A buffer solution of the desired pH can be prepared by adjusting the concentrations of the salt and the acid added for the buffer. It is noteworthy that buffer solution is most effective when the concentrations of the weak acid (or weak base) and the salt are about equal. This means that pH is close to the value of p*Ka* of the acid (or p*Kb* of the base).

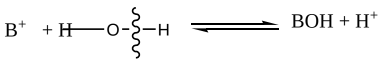
## 3.11. SALT HYDROLYSIS

The salt of a weak acid, HA and a strong base dissolves in water to form the anion $A^-$. The $A^-$ anion tends to react with water by drawing a proton ($H^+$) from its molecule to form the unionised molecule.



……….(3.63)

Similarly, the salt of a weak base, BOH, and a strong acid dissolves in water to form the cation $B^+$. The cation $B^+$ reacts with water by accepting $OH^-$ ions from its molecule.



…………(3.64)

The reaction of an anion or cation with water accompanied by cleavage of O–H bond is called Hydrolysis. The term hydrolysis is derived from hydro, meaning water, and lysis, meaning breaking. It may be noted that in anionic hydrolysis shown in (3.63) the solution becomes slightly basic (pH > 7) due to the generation of excess OH– ions. In cationic hydrolysis shown in (3.64), there is excess of H+ ions which makes the solution slightly acidic (pH < 7).

### BRONSTED–LOWRY CONCEPT OF HYDROLYSIS

HA and $A^-$ are conjugate acid-base pair

$$\underset{\text{weak acid}}{HA} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{conjugate base}}{A^-}$$

Since HA is a weak acid (poor proton donor), its conjugate base, $A^-$ , must be relatively strong (good proton acceptor). Owing to this fact, A– ions tend to react with water by accepting proton from the latter to form HA molecule (anionic hydrolysis),

$$A^- + H_2O \longrightarrow HA + OH^-$$

The presence of $OH^-$ ions makes the solution basic. Similarly, BOH and $B^+$ are a conjugate acid-base pair. Since BOH is a weak base, its conjugate acid, $B^+$, would be relatively strong. Thus $B^+$ would accept $OH^-$ ions from water to form BOH

molecules. The presence of excess $H^+$ ions makes the solution acidic.

$$B^+ + H_2O \longrightarrow BOH + H^+$$

## EXAMPLES OF HYDROLYSIS

The different salts may be classified into the following types according to their hydrolytic behaviour:

(1) Salts of Weak acids and Strong bases
(2) Salts of Weak bases and Strong acids
(3) Salts of Weak acids and Weak bases

It is interesting to know that a salt of strong acid and strong base *e.g.*, NaCl, does not show hydrolysis. NaCl dissociates in water to give the anion $Cl^-$. HCl and $Cl^-$ constitute an acid-base conjugate Pair. Since HCl is a strong acid, $Cl^-$ is very weak base. $Cl^-$ is unable to accept a proton ($H^+$) from an acid, particularly water. That is why $Cl^-$ does not hydrolyse. It cannot generate $OH^-$ ions, The pH of sodium chloride solution remains unaffected.

## Salts of Weak acids and Strong bases

Sodium acetate, $CH_3COONa$, and sodium cyanide, NaCN, are examples of this type of salts.

**Sodium acetate, $CH_3COONa$.** This is a salt of the weak acid, $CH_3COOH$, and strong base, NaOH. It ionises in aqueous solution to form the anion $CH_3COO^-$. Being the conjugate base of a weak acid, $CH_3COOH$, it is a relatively strong base. Thus $CH_3COO^-$ accepts $H^+$ ion from water and undergoes hydrolysis.

$$CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$

The resulting solution is slightly basic due to excess $OH^-$ ions present.

**Sodium Cyanide, NaCN.** It is the salt of a weak acid, HCN, and a strong base, NaOH. It ionizes to form

$CN^-$ anions. Being conjugate base of a weak acid, $CN^-$ is relatively strong base. Thus the anion $CN^-$ accepts a $H^+$ ion from water and undergoes hydrolysis. The solution becomes basic due to the generation of $OH^-$ ions.

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

### Salts of Weak bases and Strong acids

Some salts of weak bases and strong acids undergo cationic hydrolysis and yield slightly acidic solutions.

**Ammonium chloride** is a typical example of this class of salts. It is the salt of a weak base, $NH_4OH$, and strong acid, HCl. It ionises in aqueous solution to form the cation, $NH_4^+$.

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

$NH_4^+$ is a Bronsted conjugate acid of the weak base $NH_4OH$. Therefore, it is a relatively strong acid. It accepts $OH^-$ ion from water ($H_2O$) and forms the unionised $NH_4OH$ and $H^+$ ion.

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

The accumulation of $H^+$ ions in solution makes it acidic. The other examples of this type of salts are ferric chloride, aluminium chloride, and copper sulphate.

### Salts of Weak acids and Weak bases

The examples of this type of salts are ammonium acetate, ammonium cyanide and ammonium fluoride. Both the anion and the cation produced by ionisation of the salt undergo hydrolysis. The resulting solution is neutral, basic or acidic depending on the relative hydrolysis of the anions and the cations.

**Ammonium acetate,$CH_3COONH_4$.** It is the salt of weak acid, $CH_3COOH$, and weak base, NH4OH. In aqueous solution it ionises to form the anion $CH3COO^-$ and the cation $NH_4^+$. Since the acid and the base are both weak, their conjugate base ($CH3COO^-$) and conjugate acid ($NH_4^+$) are relatively strong. They accept H+ and OH– ions respectively from water and undergo considerable hydrolysis.

$$\underset{\text{conjugate base}}{CH_3COO^-} + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$\underset{\text{conjugate acid}}{NH_4^+} + H_2O \rightleftharpoons NH_4OH + H^+$$

The overall hydrolysis may be represented as

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

We have stated above that pH of the resulting solution will depend on the relative extent of anionic hydrolysis and cationic hydrolysis. If both the ions react to the same extent (as shown for $CH_3COONH_4$), $[OH^-] = [H^+]$ and the solution is neutral. If the cation reacts to a greater extent, the solution is slightly acidic. If the anion is a little more reactive, the solution will be basic. Thus, a solution of $CH_3COONH_4$ is neutral, a solution of $NH_4CN$ is slightly basic and a solution of $NH_4F$ is slightly acidic.

## QUANTITATIVE ASPECT OF HYDROLYSIS

Hydrolysis is a reversible reaction. The equilibrium constant derived by application of Law of

Mass action to a hydrolysis (or hydrolytic) reaction is called the **Hydrolysis constant** or **Hydrolytic constant.** The hydrolysis constant is represented by *Kh*.

Now, we proceed to discuss the mathematics of hydrolysis of the various types of salts.

### Salt of a Weak acid and Strong base

The general hydrolysis reaction of a salt of weak acid (HA) and strong acid can be written as

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

This leads to the equilibrium constant expression

$$K_h = \frac{[HA]\,[OH^-]}{[A^-]\,[H_2O]}$$

The concentration of water, $[H_2O]$, is very large and is regarded as practically constant. Thus the hydrolysis constant expression assumes the form:

$$K_h = \frac{[HA]\,[OH^-]}{[A^-]} \qquad \text{................(3.65)}$$

**Relation between *Kh*, *Kw* and *Ka***

We know that the ionic product of water, *Kw*, is expressed as

$Kw = [H^+]\,[OH^-]$ ...(3.11.4)

For the dissociation of a weak acid, HA,

$$HA \rightleftharpoons H^+ + A^-$$

The acid dissociation constant, *Ka*, is expressed as

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad ...(3.11.5)$$

Dividing (3.11.4) by (3.11.5)

$$\frac{K_w}{K_a} = \frac{[OH^-][HA]}{[A^-]} = K_h$$

$$\frac{K_w}{K_a} = K_h \quad ......(Eq\ 3.66)$$

It is clear from (Eq. 3.66) that the hydrolysis constant (*Kh*) of the salt varies inversely as the dissociation constant *Ka* of the weak acid. Therefore, **weaker the acid greater is the hydrolysis constant of the salt.**

**Relation between Hydrolysis constant and Degree of hydrolysis**

The degree of hydrolysis is the fraction of the salt which has undergone hydrolysis when equilibrium is established. It is generally represented by α. Suppose we start with one mole of the salt dissolved in *V* litres of solution. Then the equilibrium

concentrations are :

$$\boldsymbol{A^- + H_2O \rightleftharpoons HA + OH^-}$$

(Equilibrium concentrations)

$$\frac{\mathbf{1-\propto}}{\boldsymbol{V}} \qquad\qquad\qquad \frac{\propto}{\boldsymbol{V}} \qquad \frac{\propto}{\boldsymbol{V}}$$

Hence, the hydrolysis constant *Kh* is given by

$$K_h = \frac{[HA][OH^-]}{[A^-]} = \frac{\alpha/V \times \alpha/V}{1 - \alpha/V} = \frac{\alpha^2}{(1-\alpha)V}$$

If α is small, (1 – α) may be taken as equal to one. Then,

$$K_h = \frac{\alpha^2}{V}$$

$$\alpha^2 = K_h V = \frac{K_w}{K_a} V$$

$$\alpha = \sqrt{\frac{K_w V}{K_a}}$$

$$= \sqrt{\frac{K_w}{K_a C}} \qquad \text{……………Eq. 3.67}$$

where C is the initial concentration of the salt. Knowing the values of *Kw*, *Ka* and C, the degree of hydrolysis can be calculated.

**Derivation of pH.**

The pH of an aqueous solution of weak acid and strong base can be derived as follows :

From earlier discussion, we know that

$$[\mathrm{OH}^-] = \frac{\alpha}{V} = \alpha \mathrm{C}$$

and $$[\mathrm{H}^+] = \frac{K_w}{[\mathrm{OH}^-]}$$

∴ $$[\mathrm{H}^+] = \frac{K_w}{\alpha \mathrm{C}}$$

But $$\alpha = \sqrt{\frac{K_w}{K_a \mathrm{C}}}$$

∴ $$[\mathrm{H}^+] = \frac{K_w}{\mathrm{C}} \sqrt{\frac{K_a \mathrm{C}}{K_w}} = \sqrt{\frac{K_w K_a}{\mathrm{C}}}$$

Taking logarithms and reversing the sign throughout

$$-\log[\mathrm{H}^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log \mathrm{C}$$

$$\mathrm{pH} = \frac{1}{2}\mathrm{p}K_w + \frac{1}{2}\mathrm{p}K_a + \frac{1}{2}\log \mathrm{C}$$

$$= 7 + \frac{1}{2}\mathrm{p}K_a + \frac{1}{2}\log \mathrm{C}$$

……………Eq. 3.68

It is evident that pH of the solution will always be greater than 7. Thus **aqueous solution of salt of weak acid and strong base will be always alkaline.**

**Salts of Weak bases and Strong acids**

The hydrolysis of a salt of a weak base BOH (*e.g*, NH4OH) and a strong acid may be represented by the equation :

$$\mathrm{B}^+ + \mathrm{H_2O} \rightleftharpoons \mathrm{BOH} + \mathrm{H}^+$$

**Hydrolysis Constant** Applying the Law of Mass Action to the above hydrolysis reaction, the hydrolysis constant, $K_h$, is given by

$$K_h = \frac{[\mathrm{H}^+]\,[\mathrm{BOH}]}{[\mathrm{B}^+]\,[\mathrm{H_2O}]}$$

Since [H2O] is very large, it is taken to be constant and the hydrolysis constant expression is reduced to

$$K_h = \frac{[\mathrm{H}^+]\,[\mathrm{BOH}]}{[\mathrm{B}^+]}$$ ……………Eq. 3.69

**Relation between *Kh*, *Kw* and *Kb*.** We know that the ionic product of water *Kw* is expressed as :

$$K_w = [\mathrm{H}^+]\,[\mathrm{OH}^-]$$

For the dissociation of a weak base, BOH

$$\mathrm{BOH} \rightleftharpoons \mathrm{B^+ + OH^-}$$

The dissociation constant, *Kb*, can be expressed as :

$$K_b = \frac{[\mathrm{B^+}]\,[\mathrm{OH^-}]}{[\mathrm{BOH}]}$$

$$\frac{K_w}{K_b} = \frac{[\mathrm{H^+}]\,[\mathrm{BOH}]}{[\mathrm{B^+}]} = K_h$$

$$\frac{K_w}{K_b} = K_h$$

……………Eq. 3.70

Thus the hydrolysis constant, $K_h$, varies inversely as the dissociation constant, *Kb*, of the base. Therefore **weaker the base greater will be the hydrolysis constant of the salt.**

**Relation between Hydrolysis constant and degree of hydrolysis.** Suppose we start with one mole of the salt dissolved in *V* litres of solution. Then the concentrations when equilibrium is attained are :

$$\mathrm{B^+ + H_2O} \rightleftharpoons \mathrm{BOH + H^+}$$

(Equilibrium concentrations) $\frac{1-\propto}{V}$ $\frac{\propto}{V}$ $\frac{\propto}{V}$

Applying the Law of Mass Action, the hydrolysis constant, *Kh* is given by the expression

$$K_h = \frac{[\mathrm{H^+}]\,[\mathrm{BOH}]}{[\mathrm{B^+}]} = \frac{\alpha/V \times \alpha/V}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)V}$$

When α is small, (1 – α) may be considered as equal to one. Then we have

$$K_h = \frac{\alpha^2}{V}$$

$$K_h \times V = \alpha^2$$

$$\alpha = \sqrt{K_h \times V}$$

$$K_h = \frac{K_w}{K_b}$$

$$\alpha = \sqrt{\frac{K_w}{K_b} \times V}$$

$$= \sqrt{\frac{K_w}{K_b \times \mathrm{C}}}$$

$$\left[\because\ C \propto \frac{1}{V}\right]$$ ……………Eq. 3.71

Where “C” is initial concentration of salt.

**Derivation of pH.** From the above discussion it is clear that

$$[H^+] = \frac{\alpha}{V} = \alpha \times C$$

Substituting the value of α from equation ( Eq. 3.71), we have

$$[H^+] = \frac{1}{V}\sqrt{\frac{K_w \times V}{K_b}} = \sqrt{\frac{K_w}{K_b V}} = \sqrt{\frac{K_w \times C}{K_b}}$$

Taking logarithms and reversing the signs

$$-\log[H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log C + \frac{1}{2}pK_b$$

$$pH = 7 + \frac{1}{2}pK_b = \frac{1}{2}\log C$$

**……….**Eq. 3.72

In this case it is evident that pH will always be less than 7. Thus, **the solution of a salt of weak base and strong acid will always be acidic.**

**Salts of Weak acids and Weak bases**

In this type of salt, both the anion of weak acid ($X^-$) and the cation of weak base ($B^+$) undergo hydrolysis simultaneously.

$$B^+ + X^- + H_2O \rightleftharpoons BOH + HX$$

**Hydrolysis constant.** Applying Law of Mass Action to the above hydrolysis reaction we have the hydrolysis constant, *Kh*.

$$K_h = \frac{[BOH]\,[HX]}{[B^+]\,[X^-]\,[H_2O]}$$

[H2O] is very large and is taken to be constant. The hydrolysis constant expression, therefore, becomes

$$K_h = \frac{[BOH]\,[HX]}{[B^+]\,[X^-]}$$

……**……….**Eq. 3.73

**Relation between $K_h$, $K_w$, $Ka$ and $K_b$.** Applying Law of Mass Action to the ionisation of weak acid, HX, weak base, BOH, and water, we can write

$$HX \rightleftharpoons H^+ + X^- \qquad K_a = \frac{[H^+]\,[X^-]}{[HX]}$$

$$BOH \rightleftharpoons B^+ + OH^- \qquad K_b = \frac{[OH^-]\,[B^+]}{[BOH]}$$

$$K_w = [H^+]\,[OH^-]$$

Dividing (4) by (3) and (2), we have

$$\therefore \qquad = \frac{[HX]\,[BOH]}{[X^-]\,[B^+]}$$

$$\frac{K_w}{K_a \times K_b} = K_h$$

**……….**Eq. 3.73

**Relation between Hydrolysis constant and Degree of Hydrolysis**

Let us start with 1 mole of the salt of a weak acid and weak base. If **α** is the degree of hydrolysis (fraction hydrolysed), the equilibrium concentrations are :

Substituting these in the hydrolysis constant expression (3.73)

$$K_h = \frac{\alpha / V \times \alpha / V}{1 - \alpha / V \times 1 - \alpha / V}$$

or

$$K_h = \frac{\alpha^2}{(1 - \alpha)^2}$$

$V \quad V \quad V \quad \frac{x}{V}$

When α is small, (1 – α) may be taken as equal to one. Thus we have

$$K_h = \alpha^2$$

$$\alpha = \sqrt{K_h} \qquad \text{……(3.74)}$$

$$K_h = K_w / K_a \times K_b$$

$$\alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

**Derivation of pH.**

Hydrogen ion concentration of the solution of a salt of weak acid and weak base can be derived from the dissociation equilibrium of the weak acid, HX.

From the hydrolysis reaction of the salt, we know that

Substituting these values we have

$$[H^+] = \frac{K_a \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = K_a\left(\frac{\alpha}{1-\alpha}\right)$$

Ignoring α as compared to unity,

$$[H^+] = K_a \times \alpha$$

Substituting the value of α from equation (3.74),

$$[\mathrm{HX}] = \frac{\alpha}{V} \quad \text{and} \quad [\mathrm{X}^-] = \frac{1-\alpha}{V}$$

Taking logarithms and reversing the sign throughout

$$K_a = \frac{\quad}{[\mathrm{HX}]}$$

$$K \; [\mathrm{HX}]$$

$$[H^+] = K_a \sqrt{\frac{K_w}{K_a \; K_b}} = \sqrt{\frac{K_w \; K_a}{K_b}}$$

$$-\log[H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}K_a + \frac{1}{2}\log K_b$$

$$\mathrm{pH} = \frac{1}{2}\mathrm{p}K_w + \frac{1}{2}\mathrm{p}K_a - \frac{1}{2}\mathrm{p}K_b$$

$$\mathrm{p}K_a = \mathrm{p}K_b$$

i.e., the dissociation constant of the acid is equal to that of the base,

**……….**Eq. $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_w = 7$ 3.75

Thus the solution will be neutral despite the fact that hydrolysis has taken place. Since the dissociation constant of acetic acid is almost the same as that of ammonium hydroxide, the solution of ammonium acetate is neutral *i.e.*, it has a pH of 7.

If p*Ka* > p*Kb* *i.e*., the acid is relatively weaker than the base, the solution will be alkaline as pH is more than 7. If p*Ka* < p*Kb* *i.e*., the acid is relatively stronger, the solution will be acidic as pH will be less than 7.

## 3.12 **POTENTIOMETRIC TITRATIONS**

The potential of a suitable indicator electrode is conveniently employed to establish the equivalence point for a titration (a potentiometric titration). A potentiometric titration provides different information from a direct potentiometric measurement rather than involving absolute potentials or potentials with respect to standard half-cells, the measurements are made while the titration is in progress. The equivalence point of the reaction will be revealed by a sudden change in potential in the plot of emf readings against the volume of the titrating solution. One electrode must be maintained at a constant, but not necessarily known, potential; the other, electrode must serve as an indicator of the changes in ionic concentration and must respond rapidly. The solution must, of course, be stirred during the titration. In contrast to direct potentiometric measurements, potentiometric titrations generally offer increased accuracy and precision. Accuracy is increased because; measured potentials are used to detect rapid changes in activity that occurs at equivalence point of the titration. Furthermore, it is a change in emf versus titre volume rather than absolute value of emf. Thus, the influence of liquid-junction potentials and activity coefficients is minimised. Potentiometric titrations may be applied to a variety of systems including those involving oxidation-reduction, precipitation, acid-base, and complexation equilibria reactions.

We will discuss all these systems in detail in subsequent sections. Further, potentiometric end-point detection also provides more accurate result than the corresponding method employing indicators. It is particularly useful for titration of coloured or opaque solutions and for detecting the presence of unsuspected species in a solution. Titrations of more dilute solutions are possible using potentiometry.

Unfortunately, it is more time consuming than a titration performed with an indicator. Simple arrangement for potentiometric titration is given in **Fig. 3.24**.

Ordinarly the titration involves measuring and recording a cell potential after each addition of a reagent.

The titrant is added in large increments at the outset. As the end-point is approaching (as indicated by larger potential changes per addition), the increments are made smaller. Sufficient time must be allowed for the attainment of equilibrium after each addition of reagent. Precipitation reactions may require several minutes for equilibration, particularly in the vicinity of the equivalence points. A closed approach

to equilibrium is indicated when the measured protential ceases to drift by more than a few millivolts. Good stirring is frequently effective in hastening the achievements of equilibrium.

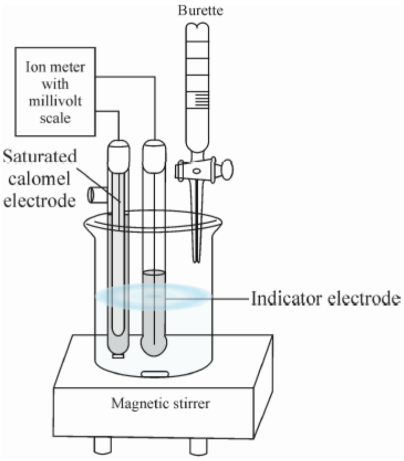


**Fig. 3.24. Typical apparatus for potentiometric titration**

A number of commercial "potentiometric titration units" are available which comprise an electrode system (frequently a selection of electrode is offered) together with a special stand providing supports for the electrodes, and one or two burette holders. The base of the stand incorporates in magnetic stirrer and in some cases a hot plate, so that if necessary the solution to be titrated may be heated. A separate unit embodies a potentiometer and a compact galvanometer or if the potentiometer is designed for the portion from the a.c. mains, the balance point indicator may be 'magic eye' electronic indicates similar to that used in mains operated conductivity bridges.

### 3.12.1 Location of End Points

In potentiometric titration the end-point is detected by determining the volume at which a selectively large change in potential occurs as the titrant is added. The method can be employed for all the reactions used for titrimetric purposes: acid -bases, redox, precipitation and complex formation. The titration may be performed manually or the procedure may be automatic.

In manual titrations, the potential is measured after the addition of each successive increment of titrant and the resulting readings are plotted on graph paper vs the volume of titrant to give the titration curve shown in **Fig. 3.25 a).** You can see, this increase is not linear and a sigmoid shaped curve is obtained as shown the figure. The greater change in emf occurs around the equivalence point. In fact the equivalence

point of maximum change in emf with volume added. This is formed the point of inflexion. The equivalence point is determined by dropping vertical line from this point. **Fig. 3.25 (b)** shows a plot of slope of a titration curve i.e. the rate of change of potential, with a change in volume ($\Delta E/\Delta V$) against volume of titrant, the resulting curve rises to maxima at equivalent point. The volume at equivalence point is determined by dropping a vertical line from the peak to volume axis. The more complete the reaction, the sharper the peak and hence more accurate the location of equivalence point. **Fig. 3.25 (c)** shows a plot of the change in the slope of a titration curve ($\Delta^2E/\ \Delta V^2$) against the volume of titrant. At the point where the slop $\Delta^2E/\ \Delta V^2$ is a maximum, the derivative of the slope is zero. The end-point is located by drawing a vertical line from the point at which $\Delta^2E/\ \Delta V^2$ is zero to the volume axis. Portion of the curve joining the maximum and minimum values of $\Delta^2E/\ \Delta V^2$ is steeper, the more complete the titration reactions.

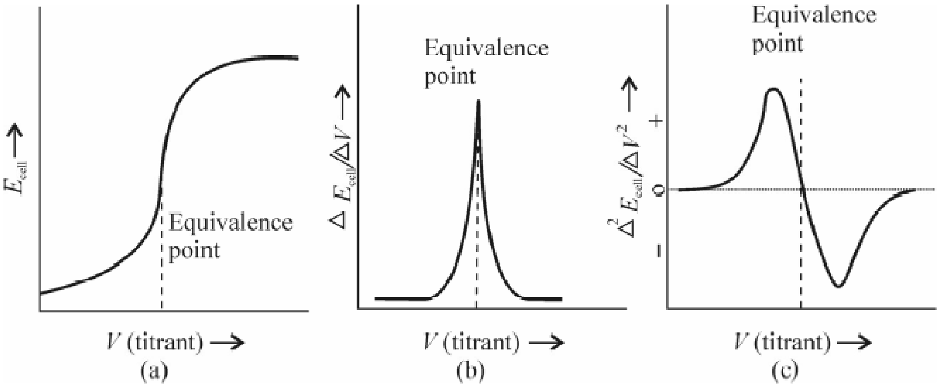


**Fig. 3.25.** Titration curves : (a) typical plot of emf vs volume; (b) typical first derivative

titration curve; and (c) typical second derivative titration curve

### 3.12.2 Types of Potentiometric Titrations

The majority of potentiometric titrations involve chemical reactions such as neutralisation, oxidation-reduction, precipitation and complexation.

1. **Neutralisation Titrations**: Potentiometric neutralisation titrations are particularly useful for the analysis of mixture of acids or polyprotic acids or bases because discrimination between the end-points can often be made. An approximate numerical value for dissociation constant of the reactant species can also be estimated from potentiometric titration curves in theory. This quantity can be obtained from any point along the curve as a practical matter. It is most easily calculated from the pH at the point of half-neutralisation e.g. in the titration of weak acid HA, we may ordinarily assume that at the mid-point

$[HA] = [A^-] + [H+]$ and therefore :

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

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

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

$pK_a = pH - \log \frac{[A^-]}{[HA]}$

At half neutralization of the acid

$[A^-]$[salt]= [HA] [Acid]………… **……….**Eq. 3.76

Therefore, $pK_a = pH - \log 1$

or $pK_a$ = pH……….Eq. 3.77

This is the midway point to the equivalence pint. Therefore, p*K*a values can also be directly read from the titration curves. It is important to note that a dissociation constant determined from a potentiometric titration curve may differ from that shown in the table of dissociation constant in the literature by a factor of 2 or more because the latter is based upon the activities while the former is not.

2. **Oxidation-Reduction Titrations:** Indicator electrodes for oxidation-reduction are generally fabricated from platinum, gold mercury or silver. The metal chosen must be un-reactive with respect to the components of the reaction. It is merely a site for electron transfer. Platinum electrode is most widely used for oxidation-reduction titrations. It should be recalled that the curves for many oxidation-reduction titrations are not symmetric. Thus, the equivalence point potential may be significantly different from the potential corresponding to the point of inflection in the curve. The determining factor in the values of potential is the ratio of the activity or concentration of the oxidised and reduced forms of certain ion species.

Take a general equation

the potential acquired by the indicator electrode at 25°C is given by

$$\text{Oxidised form} + ne \rightleftharpoons \text{reduced form}$$

$$E = E^0 + \frac{0.0591}{n} \log \frac{a_{\text{oxidised form}}}{a_{\text{reduced form}}}$$

where $E^0$ is the standard potential of the system. The potential of the immersed electrode is controlled by the ratio of these activities or concentration. In redox reactions, reducing agent is oxidised or oxidising agent is reduced and the ratio and the potential therefore changes more rapidly at the end point of the reaction. Thus titrations involving such reactions like Fe (II) with potassium

permanganate or potassium dichromate or ceric sulphate may be followed potentiometrically and equivalence points can be obtained.

3. **Precipitation titrations:** Titrations involving the precipitation reactions are not nearly so numerous in titrimetric analysis for as those involving redox or acid-base reactions. One of the reasons for limited

use of such reactions is the lack of suitable indicators. In some cases, particularly in the titration of dilute solution, the rate of reaction is too slow for convenience of titrations. As the equivalence point is approached and the titrant is added slowly, a high degree of supersaturation does not exist and the precipitation may be very slow. Another difficulty is that the composition of the precipitate is frequently not known because of co-precipitation effects. Although the latter can be minimised or partially corrected for by processes such as ageing the precipitate. This is not possible in direct titrations involving the formation of precipitate. The indicator electrode for a precipitation titration is frequently the metal from

which the reacting cation was derived. Membrane electrodes that are sensitive to one of the ions involved in the titration may also be employed. Theoretical curves for a potentiometric titration are readily derived. For example, we may describe the potential of a silver electrode during the titration of iodide with silver ion by the expression.

$$E_{Ag} = -0.151 - 0.0591 \log [Ag^+]$$

Where – 0.151 is the standard potential for the half- reaction

$$Ag\,I\,(s) + e \rightleftharpoons Ag\,(s) + I^-$$

Alternatively, the potential is given by

$$E_{Ag} = 0.799 - 0.0591 \log 1/[Ag^+]$$

where 0.799 is the standard potential for the reduction of silver ion.

**4. Complex Formation Titrations:** Both metal electrodes and the membrane electrodes can be used to detect end point in reactions that involve formation of a soluble complex. The mercury (Hg) electrode given in **Fig. 3.26** is particularly useful for EDTA titrations. It will function as an indicator electrode for the titration of cations forming complexes that are less stable than $HgY2^-$ .

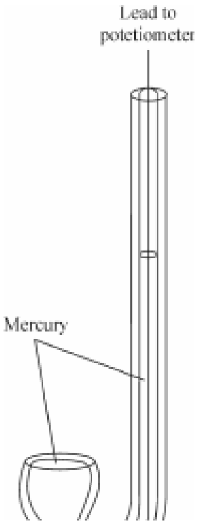


**Fig. 3.26.** Mercury electrode

5. **Differential Titrations:** This titration requires the use of two identical indicator electrodes, one of which is well-shielded from bulk of solution. **Fig. 3.27** given below illustrates a typical arrangement. Here one of the electrodes is contained in a small side-arm test-tube. Contact with the bulk of the solution is made through a small hole in the bottom of the tube. Because of the restricted access, the composition of the solution surrounding the shielded electrode will not be immediately affected by an addition of titrant to the bulk of the solution. The resulting difference in solution composition gives rise to a difference in potential Δ*E* between the electrodes. After each potential measurement, the solution is homogenised by squeezing the rubber bulb several times, where upon Δ*E* again becomes zero. If the volume of the solution in the tube that shields the electrode is kept small, the error arising from failure of final addition of reagent to react with this portion of the solution can be shown to be negligibly small. The main advantage of a differential method is the elimination of the need for the reference electrode and salt bridge.

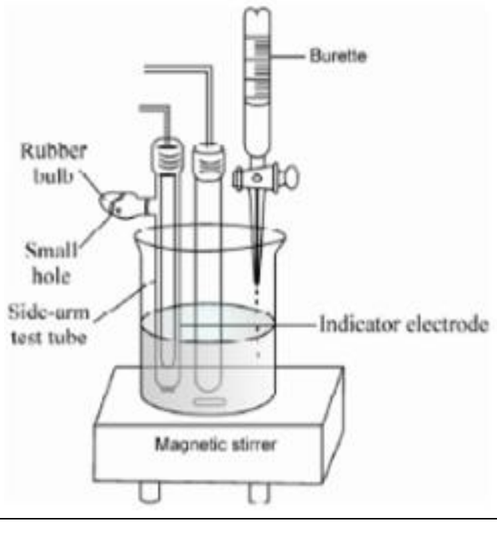


**Fig. 3.27.** Apparatus for differential potentiometric titration

**Automatic Titrations**

Now-a-days large number of automatic titrators based on the principle of potentiometry have come into the market. These are highly useful in those places, where a large number of routine analysis are required. These may not be more accurate than the manual techniques, but are quite rapid and decrease the time needed to perform the experiment and thus offer some economic advantages. Two different automatic titrators are available:

1. The first type gives titration curves of $V$ vs $E$ or D $E$/ D $V$ vs $V$. The end point is obtained from the curve by inspection.

2. In the second type of titrators, the titration is stopped automatically when the potential of the electrode system reaches a predetermined value and the volume of reagent delivered is read at the operators convenience or printed on a tape. These titrators usually employ a burette system with a solenoid-operated value to control the flow or alternately it makes use of a syringe, the plunger of which is activated by a motor driven micrometer screw.

### 3.14 *Concept of Activity and Activity coefficient*

In a solution of a strong electrolyte significant electrostatic interactions (which has a $1/r^2$ dependence) both between ion-ion & ion-solvent exists, Therefore these type of solutions deviate from their ideal behavior and moreover properties of these electrolytic solutions usually deviates from the laws which are used to derive chemical potential of solutions.

The deviation from ideality of a solute particle can be expressed in terms of solute activity, denoted by the letter '*a*'. The term "activity" was introduced by Lewis in 1920's, in order to describe deviation in behaviour of a gas , liquid or solid state from an idealized pressure state of fugacity.

Activity is defined as a measure of the effective concentration of a molecule or ionic species. Activity depends on the temperature, pressure and composition of the mixture of species. Activity of a solute depends on its concentration, being proportional to concentration at sufficient dilution.

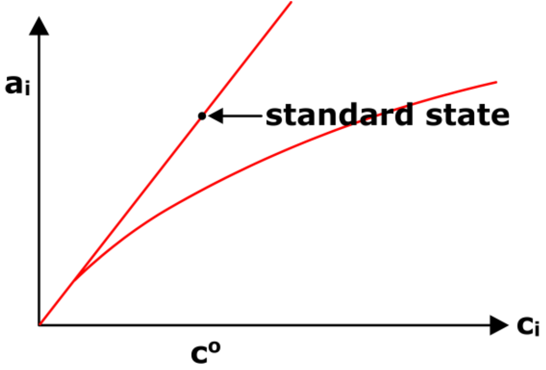


Fig. 3.28: Plot of activity with concentration

In the plot of $a_i$ versus $c_i$, the region of linearity is rather limited, especially for ionic solutes. The standard state is chosen as a hypothetical state – which corresponds to the behaviour of solute at standard conditions $c^O$, in order to maintain the linear relationship upto that concentration. Therefore, in an electrolytic solution, the activity of a solute 'a' is related to concentration, m as :

$a = \gamma m$

Where:

- a = activity
- γ= activity coefficient (concentration dependent)
- m = molality (mol/kg)

$\gamma$ (activity coefficient) is a correction factor (or we can also say proportionality constant) which take into account the departure from linearity (Fig. 1). Here we have used molality as a unit of concentration because it is independent of temperature.

Concentration can be regarded as the number of ions present, while activity can be thought as the availability of the species to take part in chemical reactions and to determine the properties of a particular phase. As concentration approaches zero, activity coefficient approaches to unity i.e

$$\gamma = 1$$

Therefore:

$$\mathbf{a = m}$$

▶ activity becomes equal to concentration.

In very dilute solutions, since the interactions become insignificant, therefore concentration and effective concentration are the same.

*Ionic activity*

Ionic Activity has more importance in case of ionic solutions (electrolytic solutions) than in non-electrolytic solutions. This is due the presence of strong interactive forces among ions in eletrolytic solutions.
For an ionic solute ($A_xB_y$), that dissociates completely, according to the equation:

$$A_xB_y \rightarrow xA^{z^+} + yB^{z^-}$$

Where: x is the number of cations with charge $z^+$ y is the number of anions with charge $z^-$

Let $\upsilon$ denote the total number of ions:

$$\upsilon = x + y$$

We also define stoichiometric molalities of each ion, based on the analytic molality of the solid electrolyte , $m_i$

$$\left.\begin{aligned} m_+ &= x^*m \\ m_- &= y^*m \end{aligned}\right\} \quad \text{……….Eq. 3.77}$$

Absolute activities of cations & anions cannot be determined because activity of a single ion depends on the nature of counter-ion to preserve the overall electroneutrality of the solution. For eg: In a solution of NaCl or $Na_2SO_4$ , the activity of $Na^+$ will depend on the nature of the anion , such as $Cl^-$ or $SO_4^{2-}$. Therefore, we define activity of an electrolyte in terms of the ions into which it dissociates. Since, positive and negative ions coexist we define mean ionic quantities.

If the activity of the cation and anion is $a_+$ and $a_-$ respectively then the mean activity is given as:

$$a_\pm = a_+^x a_-^y \qquad \text{..........Eq. 3.78}$$

The symbol ± refers to a mean ionic variable and is defined in terms of number of ions. We also define mean ionic molality $m_\pm$:

$$m_\pm = (m_+^x m_-^y)^{\frac{1}{(x+y)}} \qquad \text{..........Eq. 3.78}$$

The individual activities of cation a+ can be written as:

$$\left.\begin{aligned} a_+ &= m_+ \gamma_+ \\ &= xm\,\gamma_+ \\ &\text{Similarly for anion} \\ a_- &= m_- \gamma_- \\ &= ym\,\gamma_- \end{aligned}\right\}$$

Substituting above values in equation Eq. 3.78, we get:

$$a_\pm = (xm\gamma_+)^x (ym\gamma_-)^y$$

$$a_\pm = (x)^x (y)^y m^{(x+y)} \gamma_+^x \gamma_-^y \qquad \text{..........Eq. 3.79}$$

Where :-

m = Molality

$\gamma_+$ = activity coefficient for positive ion

$\gamma_-$ = activity coefficient for negative ion

### *Mean activity coefficient*

Activity coefficient of individual ions can never be determined because in a strong electrolytic solution only cations and only anions can never exist, cations are always accompanied by anions and vice-versa. Therefore $\gamma_+$ and $\gamma_-$cannot be determined individually so, we define a new term mean activity coefficient which is represented as: $\gamma_\pm$

Mean activity coefficient ($\gamma_\pm$ ) is a measure of ion-ion interactions in solution. Mathematically it is given as:

$$\gamma_\pm = (\gamma_+^x \gamma_-^y)^{\frac{1}{x+y}}$$

Taking log on both sides we have;

$$(\mathrm{x}+\mathrm{y}) \log \gamma_\pm = (x \log \gamma_+ + y \log \gamma_-)$$

$$\log \gamma_\pm = \frac{1}{x+y} (x \log \gamma_+ + y \log \gamma_-)$$

$$\gamma_\pm^{x+y} = \gamma_+^x \gamma_-^y$$

In this equation the value of x & y depends on the nature of electrolyte.

Using equation Eq. 3.79, we get,

$$a = x^x y^y m^{x+y} \gamma_\pm^{x+y}$$

$$a = x^x y^y (m\gamma_\pm)^{x+y} \qquad \text{…………Eq. 3.80}$$

Debye and Huckel suggested a theory to find out the mean activity coefficient ($\gamma_\pm$) in order to measure the ion-ion interactions present in the solution. This theory is applicable only to strong electrolytes (like salts). These types of solutions are electrically neutral & they dissociate completely (eg: NaCl).

- For ideal solutions Mean activity coefficient ($\gamma_\pm$) =1 as m approaches 0.
- For even low concentration solutions $\gamma_\pm$ value deviates from 1.

  Experimental plot for variation of $\gamma_\pm$ with $\sqrt{I}$ is shown in the Fig **Fig. 3.29**

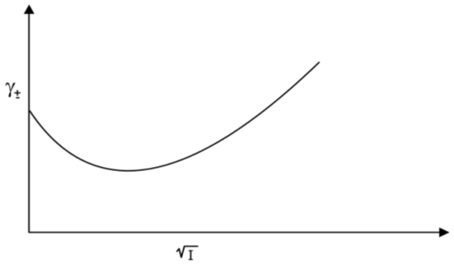


**Fig. 3.29: Graph showing variation of $\gamma_\pm$ with $\sqrt{I}$**

The variation depends on the nature of electrolytes. Debye Huckel theory ultimately accounted for variation of mean activity coefficient with $\sqrt{I}$. Therefore using Debye – Huckel theory, we find $\gamma_\pm$ *and* $\gamma_$theoretically.

**Example 10**: For different types of electrolytes, the activity can be calculated as:

### I. Uni-univalent electrolyte :AB (eg. – NaCl, CuSO4)

$$\boldsymbol{AB \rightarrow A^{+} + B^{-}}$$

$$\boldsymbol{x = 1}$$
$$\boldsymbol{y = 1}$$

$$\boldsymbol{a = (x)^{x}\,(y)^{y}\,(m\gamma_{\pm})^{x+y}}$$
$$\boldsymbol{a = (1)^{1}\,(1)^{1}\,(m\gamma_{\pm})^{2}}$$
$$\boldsymbol{= m^{2}\gamma_{\pm}^{2}}$$

### II. Uni-bivalent electrolyte: AB2 (e.g. BaCl$_2$)

$$AB_2 \rightarrow A^{2+} + 2B^{-}$$

$$\boldsymbol{x = 1}$$
$$\boldsymbol{y = 2}$$

$$\boldsymbol{a = (1)^{1}\,(2)^{2}\,(m\gamma_{\pm})^{3}}$$
$$\boldsymbol{= 4m^{3}\gamma_{\pm}^{3}}$$

### III. AB3 (e.g. – FeCl$_3$)

$$AB_3 \longrightarrow A^{2+} + 2B^{-}$$

$$\boldsymbol{x = 1}$$
$$\boldsymbol{y = 3}$$

$$\boldsymbol{a = (1)^{1}\,(3)^{3}\,(m\gamma_{\pm})^{4}}$$
$$\boldsymbol{= 27m^{4}\gamma_{\pm}^{4}}$$

**IV. $A_2B_3$ (eg: $Fe_2Cl_3$**

$$A_2B_3 \rightarrow 2A^{3+} + 3B^{2-}$$

$$x = 2$$

$$y = 3$$

$$\begin{aligned} a &= (2)^2\,(3)^3\,(m\gamma_{\pm})^5 \\ &= 108m^5\gamma_{\pm}^5 \end{aligned}$$

*Measurement of Activity*

For volatile species, activity can be measured from its equilibrium partial vapour pressure. For non-volatile components such as NaCl, $BaCl_2$ we do not measure activity from the partial vapour pressure because they do not have measurable vapour pressure at most of the temperatures. We, therefore use a different approach that is the vapour pressure of the solvent is measured and using Gibb's Duhem relation the change in solvent vapour pressures is translated with concentration into activities for solute in the solution. The activity ('a') of an electrolyte is a property that can be measured by experiment e.g.: by measuring colligative properties such as osmotic pressure or freezing point depression of the solution.

We can determine the mean ionic activity coefficient ($\gamma_{\pm}$) of ions in solutions using either Debye-Hückel equation or from the solubility product or from electrochemical methods (using Nernst Equation).

# Determination of activity coefficient of electrolytes

To know the activity of the solution corresponding to the given molarity, we must measure the activity coefficient of the electrolyte in the given solution. Suppose we want to determine the activity coefficient of hydrochloric acid. Consider a cell without liquid junction containing HCl. The two electrodes are so chosen that one is reversible concerning the cation of the electrolyte (in this case, $H^+$ ion) and other is reversible concerning the anion (i.e., $Cl^-$ ion). The first electrode is a hydrogen electrode and the other can be the silver- chloride electrode. The cell reaction is given by the equation:

$$\frac{1}{2} H_2 (g) + AgCl(s) \rightleftharpoons Ag (s) + H^+ (m) + Cl^- (m)$$

The cell arrangement of the above chemical cell without transference can be represented as:

$$Pt; H_2 (g) (1atm) |HCl (m) | AgCl (s), Ag(s) \text{ or}$$

$$\frac{1}{2} H_2 (1 \text{ atm}) + AgCl(s) \rightleftharpoons Ag (s) + H^+ (a_H+) + Cl^- (a_{Cl}^-)$$

Where *m* is the molality of HCl solution and *a* is the activity of ions.

The e.m.f. of the cell at $25^0C$ is given by

$$E= E^0 - 0.0591 \log \frac{(a_{H^+})(a_{Cl^-})}{a_{H_2}} \text{……………………(3.81)}$$

or we can write,

$$E= E^0 - 0.0591 \log a\text{……………………(3.82)}$$

Where *a*, is an activity of HCl as a whole.

As the activity (a) of HCl at any molarity (m) is related to mean activity coefficient as:

$$E_{cell} = E°_{Ag/Agcl} - \frac{RT}{F} ln\, m^2 \gamma_\pm^2$$

$$E_{cell} = E°_{Ag/Agcl} - \frac{2RT}{F} ln\, m - \frac{2RT}{F} ln\, \gamma_\pm$$

$$E_{cell} + \frac{2RT}{F} ln\, m = E°_{Ag/Agcl} - \frac{2RT}{F} ln\, \gamma_\pm \text{......................(3.83)}$$

All the quantities on the left hand side of this equation are determined experimentally. To calculate $\gamma_{\pm}$, the values of $E°_{Ag/Agcl}$ is needed. To determine $E°_{Ag/Agcl}$, the quantity $E_{cell} + \frac{2RT}{F}$ *ln m* is plotted against *m* and the result is extrapolated to *m=0*. When *m=0,* $\gamma_{\pm} = 1$, therefore from eq (3)

$E°_{Ag/Agcl} = E_{cell} + \frac{2RT}{F}$ *ln m* i.e. equal to the value of ordinate.

### Example

Calculate the mean ionic activity coefficient of 0.1 molar hydrochloric acid at 25°C given that the *emf* of the cell

$H_2$(1atm)|HCl (a), AgCl (s)|Ag

is 0.3524 V at 25°C and the standard electrode potential of Ag-AgCl is 0.2224 V at25°C.

Solution

For the given cell,

$$E_{cell} + \frac{2RT}{F} \ln m = E°_{Ag/Agcl} - \frac{2RT}{F} \ln \gamma_{\pm} \text{ or}$$

$$E_{cell} + \frac{2\times 2.303RT}{F} \log m = E°_{Ag/Agcl} - \frac{2\times 2.303RT}{F} \log \gamma_{\pm}$$

Putting T=298K, R=8.314$JK^{-1}mol^{-1}$ and F= 96500 C, this equation becomes

$$E_{cell} + 0.01183 \log m = E°_{Ag/Agcl} - 0.1183 \log \gamma_{\pm}$$

Substituting $E_{cell}$ =0.3524V, $E°_{Ag/Agcl}$ = 0.2224V, m = 0.1 mol $kg^{-1}$

We obtain, 0.3524 + 0.1183 log 0.1 = 0.2224 - 0.1183 $\log \gamma_{\pm}$

$$\log \gamma_{\pm} = \frac{-0.3524+0.2224+0.1183}{0.1183}$$

$$\log \gamma_{\pm} = -0.0989$$

$$\gamma_{\pm} = 0.796$$

## 3.14 SUMMERY

We began our study with an elementary account of production of electricity with the help of chemical reactions. Then we looked at how the cell potential is measured under standard conditions. We explained the setting up of standard hydrogen electrode, with reference to which, all other potentials are measured. Then we discussed the importance of the table of standard reduction potentials for some selected half-cell reactions. Measurement of cell potential and its relation with the concentrations of the oxidized and the reduced species was developed in the form of Nernst equation. The different applications of Nernst equation were then discussed. Next we briefly looked at different kinds of galvanic cells and some of the

commercial cells. We finally discussed some of the applications of emf measurements.

Further, in this unit, you have learnt about electrode potentials, principles of potentiometer and measurement of potential, different types of reference electrodes : such as Hydrogen Electrode, Calomel Electrode, Silver-Silver Chloride Electrode and different types of indicator electrodes. You have also learnt about the measurement of potential and location of end points from the graphs obtained from the experimental values of emf and volume of titrant. Different type of tirations such as acid-base titrations, redox titrations, precipitation titrations, complexometric titration and differential titrations were also explained in detail.

## 3.15 TERMINAL QUESTIONS

1. What is an electrode potential?

2. Why the absolute value of electrode potential cannot be determined?

3. What is the reference electrode? Give some examples.

4. Explain liquid-junction potential. How can it be eliminated?

5. What is a Standard Cell? Give the reaction in case of Weston Standard Cell.

6. For the galvanic cell

$\text{Cd} \mid \text{Cd}^{2+}\ (0.05\ \text{M}) \parallel \text{Cl}^{-}\ (0.10\ \text{M}) \mid \text{Cl}_2(1\ \text{atm}) \mid \text{Pt}$,

$E^{o} = 1.76$ V. Calculate

a) the standard electrode potential of the cadmium electrode

b) the equilibrium constant for the cell reaction and

c) the emf at $25\ ^{o}$C.

7. Why is it necessary to calibrate the glass electrode before use?

8. Discuss the source of pH dependence in a glass membrane electrode.

9. Calculate the potential of the indicator electrode at 25°C relative to S.C.E. at the equivalence point of the titration of 25.00 $cm^3$ of 0.010 M $Fe^{2+}$ with 0.010 M $Cr_2O_7^{\ 2-}$ in a sol. that is buffered at pH 3.50.

## 3.16 ANSWERS

**Self Assessment Questions**

### SAQ 1

The electrode, at which oxidation occurs, is called anode, whereas the electrode where reduction takes place, is called cathode.

a) In galvanic cell, the cathode is given a positive sign and the anode, a negative sign.

b) In electrolytic cell, the two signs are reversed. The anode is given a positive sign and the cathode is given a negative sign.

### SAQ2

Without the salt bridge, the circuit would be open (or broken) and no current could flow. With a salt bridge, each half-cell remains electrically neutral and current can flow through the circuit.

### SAQ3

By inspection, $Fe^{2+}$ undergoes oxidation when one electron is lost to form $Fe^{3+}$, and $MnO_4^-$ is reduced as it gains five electrons to form $Mn^{2+}$. Balancing the charge gives
oxidation: $5(Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$
reduction: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O\ (l)$
overall: $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O\ (l)$
Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. It is necessary to use an inert electrode, such as platinum, because there is no metal present to conduct the electrons from the anode to the cathode. No concentrations were specified so:
$Pt(s)|Fe^{2+}(aq), Fe^{3+}(aq)\|\ MnO_4^-(aq), H^+(aq), Mn^{2+}(aq)|Pt(s)$
Oxidation occurs at the anode and reduction at the cathode.

### SAQ4

From the information given in the problem:
anode (oxidation): $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
cathode (reduction): $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
overall: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$
Using cell notation: $Zn(s)|Zn^{2+}(aq)\|Cu^{2+}(aq)|Cu(s)$

### SAQ5

| Basis For | Electromotive Force | Potential Difference |
|---|---|---|

| **Comparson** | | |
|---|---|---|
| Definition | It is the amount of energy supply to one coulomb of charge. | The amount of energy used by one couomb of charge in moving from one point to another. |
| Unit | Volt | Volt |
| Symbol | ε | V |
| Source | Dynamo or Battry | Battery |
| Resistance | Independent from the resistance of the circuit | Proportional to the resistance of the circuit. |
| Current | It transmits current througout the circuit. | It transmits current between any two points. |
| Magnitude | Greater than the potential difference between any two points | Always less than the maximum value of emf when the battery is fully charged. |
| Variation | It remains constant | Does not remain constant. |
| Relation | Cause | Effect |
| No current | Not Zero | Zero |
| Voltage | It is the maximum voltage that the battery can transfer | It is less than the maximum voltage that cell can deliver. |
| Field | Causes in magnetic, gravitational and electric field. | Induces only in electric field |
| Energy | Gain energy | Loss energy |
| Measuring Instrument | EMF Meter | Voltmeter |

**SAQ6**

As explained in Sec. 3.4, if any reaction leads to negative cell potential, that particular reaction will be non-spontaneous. Hence, we have to calculate the cell potentials in each case to know whether a particular reaction is spontaneous or not.

i) $Fe + 2H^{+} \longrightarrow Fe^{2+} + H_2$

$E^{\circ}_{cell} = E^{\circ}_{anode} + E^{\circ}_{cathode}$

$= [-(-0.44) + 0]$ V (since standard potential for $Fe^{2+}/Fe$ is $-0.44$ V)

$= 0.44$ V.

This reaction is spontaneous.

ii) $Cu + 2H^{+} \longrightarrow Cu^{2+} + H_2$

$E^{\circ}_{cell} = E^{\circ}_{anode} + E^{\circ}_{cathode}$

$= [-(0.34) + 0]$ V (since for $Cu^{2+}/Cu$, $E^{\circ} = +0.34$ V)

$= -0.34$ V.

This reaction is non-spontaneous.

iii) $2Fe^{3+} + 2I^{-} \longrightarrow 2Fe^{2+} + I_2$

$E^{\circ}_{cell} = E^{\circ}_{anode} + E^{\circ}_{cathode}$

$= [-(0.54) + 0.77]$ V

$= 0.23$ V. This reaction is spontaneous.

**SAQ7**

The reactions corresponding to this cell will be:

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ Anode reaction (oxidation)

$AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-}(aq)$ Cathode reaction (reduction)

Net Reaction

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

$E_{cell} = E_{Right} - E_{Left}$

$= (0.22 - 0.34)$ V

$= -0.12$ V

Since this potential is negative, then the reaction will proceed to the left, and electrons will be withdrawn from the silver-silver chloride electrode and flow through the external circuit into the copper electrode. Note carefully that in combining these half-cell potentials, we did not multiply the $E^{0}$ for the silver-silver chloride electrode by two.

**SAQ8**

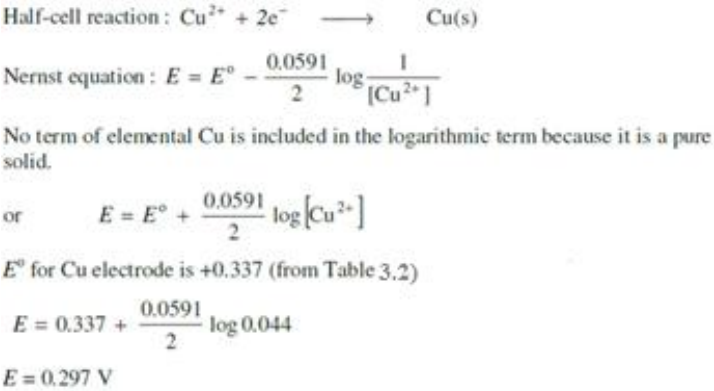
**a)** Copper sulphate cannot be stored in a zinc pot because zinc being more reactive will displace copper and slowly form zinc sulphate and in doing so, the area of the pot which is in contact with copper sulphate will develop holes and the solution will eventually drain out, or leak out from the pot.

**b)** Any substance that has greater standard electrode potential than $Fe^{+3}/Fe^{+2}$ can oxidise ferrous ions.

$$Fe^{3+} \rightarrow Fe^{2+} + e^{-}\ ;\quad E^{\circ} = +0.77\ V$$

This means that the substances that have higher reduction potentials than +0.77 V can oxidise ferrous ions to ferric ions. Examples of three such substances are $O_2$, $F_2$ and $Cl_2$.

**SAQ 9**



Half-cell reaction : $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

Nernst equation : $E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$

No term of elemental Cu is included in the logarithmic term because it is a pure solid.

or $E = E^\circ + \frac{0.0591}{2} \log [Cu^{2+}]$

$E^\circ$ for Cu electrode is +0.337 (from Table 3.2)

$E = 0.337 + \frac{0.0591}{2} \log 0.044$

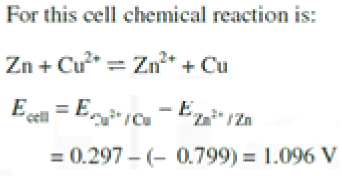
$E = 0.297$ V

**SAQ 10**

You have to follow same steps as shown in SAQ 9.

*E* = – 0.799 V

**SAQ 11**



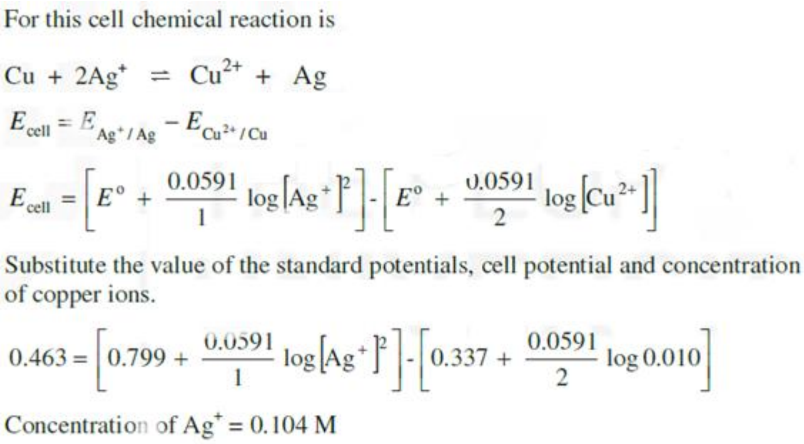
For this cell chemical reaction is:

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$E_{cell} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$

$= 0.297 - (-\ 0.799) = 1.096$ V

**SAQ 12**



For this cell chemical reaction is

$Cu + 2Ag^+ \rightleftharpoons Cu^{2+} + Ag$

$E_{cell} = E_{Ag^+/Ag} - E_{Cu^{2+}/Cu}$

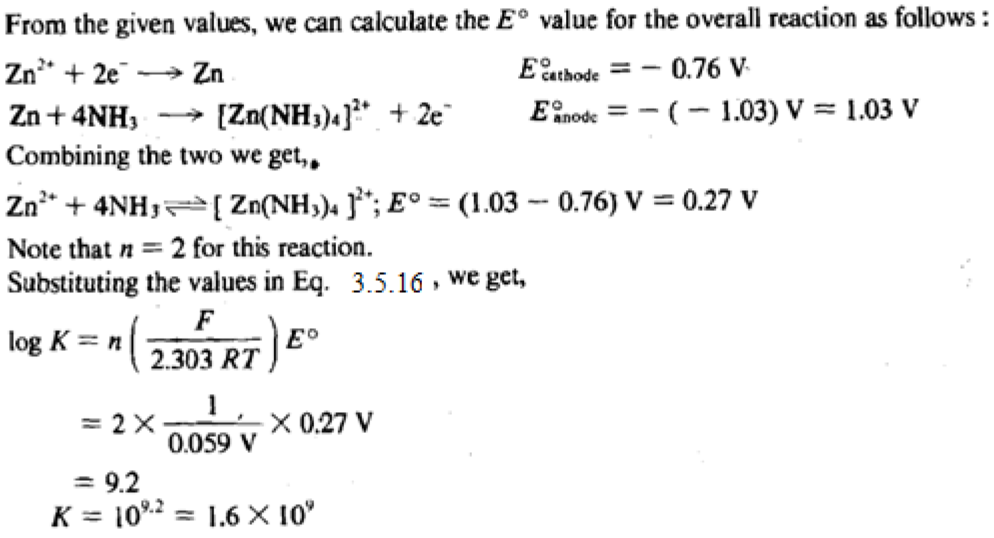
$E_{cell} = \left[E^\circ + \frac{0.0591}{1} \log [Ag^+]^2\right] - \left[E^\circ + \frac{0.0591}{2} \log [Cu^{2+}]\right]$

Substitute the value of the standard potentials, cell potential and concentration of copper ions.

$0.463 = \left[0.799 + \frac{0.0591}{1} \log [Ag^+]^2\right] - \left[0.337 + \frac{0.0591}{2} \log 0.010\right]$

Concentration of $Ag^+$ = 0.104 M

**SAQ 13**



From the given values, we can calculate the $E^\circ$ value for the overall reaction as follows :

$Zn^{2+} + 2e^- \longrightarrow Zn$ $\qquad E^\circ_{cathode} = -0.76$ V

$Zn + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+} + 2e^-$ $\qquad E^\circ_{anode} = -(-1.03)$ V $= 1.03$ V

Combining the two we get,

$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$; $E^\circ = (1.03 - 0.76)$ V $= 0.27$ V

Note that $n = 2$ for this reaction.

Substituting the values in Eq. 3.5.16 , we get,

$$\log K = n\left(\frac{F}{2.303\,RT}\right)E^\circ$$

$$= 2 \times \frac{1}{0.059\text{ V}} \times 0.27\text{ V}$$

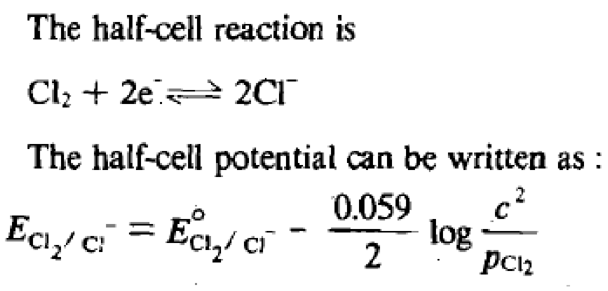
$$= 9.2$$

$$K = 10^{9.2} = 1.6 \times 10^9$$

**SAQ 14**

Kindly refer to the section *3.5.2.*

**SAQ 15**



The half-cell reaction is

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$

The half-cell potential can be written as :

$$E_{Cl_2/Cl^-} = E^\circ_{Cl_2/Cl^-} - \frac{0.059}{2}\log\frac{c^2}{p_{Cl_2}}$$

**SAQ 16**

a) As the reaction products accumulate near the electrodes, the electrode reactions become slow and may finally stop. After leaving it idle for a while, the products diffuse away and the cell starts functioning again.

b) The fuel cells are considered better since reactions take place under nearly reversible conditions and the efficiency is higher in producing more useful work.

c) Alkaline dry cell lasts longer because zinc electrode does not corrode easily (due to absence of acidic conditions).

**SAQ 17**

Using the equation,

$$pH = -\log [H^+]$$

We get, $4.5 = -\log [H^+]$

$$\log [H^+] = -4.5$$

$$[H^+] = 10^{-4.5}\ M \text{ or } 10^{(-5+0.5)}\ M = 10^{0.5} \times 10^{-5}\ M$$

$$= 3.2 \times 10^{-5}\ M$$

**Terminal Questions**

1. This is the tendency of an electrode to get oxidised or reduced. But as per the IUPAC conventions, it is the reduction potential of the electrode.
2. Because oxidation or reduction cannot take place independently.
3. A standard electrode with reference to which the potential of an indicator electrode is determined is called "reference electrode." Some examples are Standard Hydrogen Electrode (S.H.E.); Saturated Calomel Electrode (S.C.E.).
4. This is the potential which is set up at the junction of two solutions because of difference in the speeds of ions moving across the boundary. It can be eliminated by using a salt bridge containing KCl, since K+ and $Cl^-$ move with almost equal speeds.
5. This is a cell which gives constant and reproducible emf and has very small temperature coefficient. An important example is Weston Standard Cell in which the cell reaction is
   Cd (Hg) + Hg2SO4(sat.) + 8/3 H2O (l) _ CdSO4 8/3 H2O (sat.) + 2 Hg (l)

6. The cell reaction is

   $$Cd_{(s)} + Cl_2\,(g,\ 1\text{ atm}) \rightarrow Cd^{2+}\,(0.05\text{ M}) + 2\,Cl^-\,(0.1\text{M})$$

   a) The value of $E^O$ for the cell is 1.76V. The standard electrode potential for the $Cl_2$ | $Cl^-$ | Pt cell is 1.3595 V. Therefore the electrode (reduction) potential for the $Cd^{2+}$ | Cd cell is: 1.76 V = $E^O$ = $E^O_{Cl^-}$

$/Cl_2 - E^{o}_{Cd^{2+}/Cd}$

$E^{o}_{Cd^{2+}/Cd} = 1.3595 - 1.76 = -0.4005$ V

b) The equilibrium constant for the reaction (n = 2) is

$K = \exp[2 \times 96500 \times 1.76 / 8.314 \times 298] = \exp(137.1) = 3.49 \times 10^{59}$

c) The reaction quotient for the reaction is

$Q = [Cd^{2+}] / [Cd(s)] \times [Cl^-]^2 / Cl_2(g)]$

Both the denominators Cd(s) and $Cl_2$(g) at 1 atm pressure are in their standard states.

$\therefore Q = 0.05 \times (0.1)^2 = 0.0005$

$E = E^{o} - (0.02569 / n) \ln Q$

$= 1.76 - 0.012845 \times (-76)$

$= 1.858$ V

7. It is not possible to determine the values of asymmetry potential as well as liquid- junction potential in glass/calomel electrode, therefore, it is necessary to calibrate glass membrane electrode with suitable buffer solutions before use.

8. When glass electrode is placed in a test solution its glass membrane will have an inner and outer hydrated layers and potential difference is developed due to the difference in hydrogen ion activities between test solution and outer hydrated surface of glass electrode as well as inner solution and inner hydrated surface. This potential is called boundary potential and it varies with the activity or pH of the solution. Overall boundary potential is the potential difference between both the boundary potentials. Concentration of inner solution is kept constant, thus the boundary potential is a measurement of the hydrogen ion activity or the pH of the external solution.

9.

The half-cell Potentials in this case are

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^- \ ; \qquad E^{o}_{Fe^{3+}/Fe^{2+}} = 0.771$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2\,Cr^{3+} + 7H_2O; \quad E^{\circ}_{CrO_7^{2-}/Cr^{3+}} = 1.33$$

The overall Potential is

$$6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \rightleftharpoons 6\,Fe^{3+} + 2Cr^{3+} + 7H_2O$$

The potential of the indicator electrode, relative to the S.H.E. is given by,

$$E_{In} = 0.771 - 0.0591 \log \{[Fe^{2+}]\}/\{[Fe^{3+}]\} \quad \textbf{Eq.....1}$$

$$\text{and by} \quad E_{In} = 1.33 - \frac{0.0591}{6} \log \{[Cr^{3+}]^2 / [Cr_2O_7^{2-}]\,[H^+]^{14}\} \quad \textbf{Eq........2}$$

We must combine these two equations in such a manner as to eliminate the concentration of the reactants that cannot be calculated at the equivalence point. In this titration, neither $[Fe^{2+}]$ nor $[Cr2O_7^{2-}]$ can be calculated at the equivalence point without prior knowledge of the equilibrium constant for the reaction. Hence, multiplying Eq. (2) by 6 and then adding with Eq. (1), we obtain,

$$7E_{In} = 8.75 - 0.0591 \log \frac{[Fe^{2+}]\,[Cr^{3+}]^2}{[Fe^{3+}]\,[Cr_2O_7^{2-}]\,[H^+]^1}$$

$$[Fe^{2+}] = 6\,[Cr_2O_7^{2-}]$$

Hence above simplifies to,

$$7E_{\text{cell}} = 8.75 - 0.0591 \log \frac{6[\text{Cr}_2\text{O}_7^{2-}]\ [\text{Cr}^{3+}]^2}{[\text{Fe}^{3+}]\ [\text{H}^+]^{14}} \qquad \ldots (4)$$

$$= 8.75 - 0.0591 \log \frac{6\ [\text{Cr}^{3+}]^2}{[\text{Fe}^{3+}]\ [\text{H}^+]^{14}} \qquad \ldots (5)$$

Let *x* be the volume of $[\text{Cr2O}_7{}^{2-}]$ added at the point of equivalence.

Since at the equivalence point,

$$[\text{Fe}^{2+}] = 6\ [\text{Cr}_2\text{O}_7^{2-}]$$

Hence,

$$(0.01\ \text{mmol/cm}^3) \times 25\ \text{cm}^3 = 6\ (0.01\ \text{mmol/cm}^3) \times x$$

$$x = 4.16 \sim 4.2\ \text{cm}^3$$

$$[\text{Fe}^{3+}] = \frac{0.010\,\text{mmol}/\text{cm}^3 \times 25.0\,\text{cm}^3}{25.0 \times 4.2\ \text{cm}^3}$$

At the equivalence point

$$[\text{Cr}^{3+}] = [\text{Fe}^{3+}] \times 2/6 = 2.9\ x \times 10\ \text{M}$$

since, pH = 3.50, hence $[\text{H}^+] = 3.2 \times 10^{-4}$ M

Substituting these values in Eq. (4) and simplifying, we obtain

$E\text{In} = 0.855$ V

Hence, the potential of the indicator electrode relative to SCE is

$E = 0.855 - 0.242 = 0.613$ V

as reduction potential of saturated calomel electrode is 0.242 V.

## FURTHER READINGS

1. Glasstone, S. (2011). *An introduction to electrochemistry*. Read Books Ltd. Bahl, A., Bahl, B. S., & Tuli, G. D. (2012). Essentials of physical chemistry.
2. Atkins, P. W., De Paula, J., & Keeler, J. (2018). *Atkins' physical chemistry*. Oxford University Press.
3. Zoski, C. G. (Ed.). (2006). *Handbook of electrochemistry*. Elsevier.
4. Eliaz, N., & Gileadi, E. (2019). *Physical Electrochemistry: Fundamentals, Techniques, and Applications*. John Wiley & Sons.
5. Puri, L. B., Sharma, L. R., & Pathania, M. S. (2013). *Principles of Physical Chemistry*. Vishal Publications.
6. Rakshit, P. C. (1997). Physical Chemistry, 4 th reprint. *Calcutta: PM Bagchi, Modern Book Agency Private Limited*, *88*.
7. Sharma, B. K. (1997). *Electro chemistry*. Krishna Prakashan Media.
8. Raj, G. (1978). *Advanced Physical Chemistry*. Krishna Prakashan Media.
9. https://chem.libretexts.org
10. https://courses.lumenlearning.com/chemistryformajors/?s=+Electrochemistry

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# UNIT 4 COLLOIDAL STATE AND MACROMOLECULES

## Structure

## 4.1 Introduction

Colloidal systems consist of finely divided particles of any substance dispersed in any medium. Ink, milky dispersion of sulphur, clays and humus, shaving cream, glue and blood serum are all examples of colloids. The dispersed entities are molecules or aggregates of molecules. Generally, these are smaller than coarse, filterable particles but larger than atoms and small molecules. The colloidal particles have dimensions in the range 0.000001–0.0005 nm i.e. 1 mμ − 500 mμ or 10 − 5000 Å

Colloidal particles are invisible under ordinary microscopes and pass through the pores of ordinary filter paper. The dispersed phase can be liquid, solid or gas. For example: Emulsions are composed of liquid particles dispersed in another liquid. Foams contain bubbles of gas in liquid or solid. The degree of dispersion is a quantity varying reciprocally with size of the particles. Emulsions have low degree of dispersion and this means that the droplets are relatively coarse.

### Objectives

After studying this unit, you should be able to:

- describe the definition of colloids
- describe the types of colloids
- describe the Zeta potential

- describe the sols
- describe the Hardy Schulze Law
- describe the gold number
- describe the emulsions
- describe the gels
- describe the macromolecules
- describe the determination of molecular weight
- describe the Donnan membrane theory and its application

## 4.2 Definition of colloids

A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

The essential difference between a solution and a colloid is that of particle size. While in a solution, the constituent particles are ions or small molecules, in a colloid, the dispersed phase may consist of particles of a single macromolecule (such as protein or synthetic polymer) or an aggregate of many atoms, ions or molecules. Colloidal particles are larger than simple molecules but small enough to remain suspended. Their range of diameters is between 1 and 1000 nm (10–9 to 10–6 m).

Colloidal particles have an enormous surface area per unit mass as a result of their small size. Consider a cube with 1 cm side. It has a total surface area of 6 cm2. If it were divided equally into 1012 cubes, the cubes would be the size of large colloidal particles and have a total surface area of 60,000 cm2 or 6 m2.

## 4.3 Classification of Colloids

Colloids are classified on the basis of the following criteria:

4.3.1 Physical state of dispersed phase and dispersion medium

4.3.2 Nature of interaction between dispersed phase and dispersion medium

4.3.3 Type of particles of the dispersed phase.

### 4.3.1 Classification Based on Physical State of Dispersed Phase and Dispersion Medium

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The examples of the various types of colloids along with their typical names are listed in Table 4.1.

**Table 4.1: Types of Colloidal Systems**

| Dispersed phase | Dispersion medium | Type of colloid | Examples |
|---|---|---|---|
| Solid | Solid | Solid sol | Some coloured glasses and gem stones |
| Solid | Liquid | Sol | Paints, cell fluids |
| Solid | Gas | Aerosol | Smoke, dust |
| Liquid | Solid | Gel | Cheese, butter, jellies |
| Liquid | Liquid | Emulsion | Milk, hair cream |
| Liquid | Gas | Aerosol | Fog, mist, cloud, insecticide sprays |
| Gas | Solid | Solid sol | Pumice stone, foam rubber |
| Gas | Liquid | Foam | Froth, whipped cream, soap lather |

Many familiar commercial products and natural objects are colloids. For example, whipped cream is a foam, which is a gas dispersed in a liquid. Firefighting foams, used at emergency airplane landings are also colloidal systems. Most biological fluids are aqueous sols (solids dispersed in water). Within a typical cell, proteins and nucleic acids are colloidal-sized particles dispersed in an aqueous solution of ions and small molecules.

Out of the various types of colloids given in Table 5.4, the most common are **sols** (solids in liquids), gels (liquids in solids) and emulsions (liquids in liquids). However, in the present Unit, we shall take up discussion of the ‘sols’ and ‘emulsions’ only. Further, it may be mentioned that if the dispersion medium is water, the sol is called aquasol or hydrosol and if the dispersion medium is alcohol, it is called alcosol and so on.

## 4.3.2 Classification Based on Nature of Interaction between Dispersed Phase and Dispersion Medium

Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, lyophilic (solvent attracting) and lyophobic (solvent repelling). If water is the dispersion medium, the terms used are hydrophilic and hydrophobic.

### 4.3.2.1 Lyophilic colloids:

These are the colloidal solutions in which the particles of the dispersed phase have great affinity (love) for the dispersion medium. In case water acts as the dispersed phase, the lyophilic colloid is called hydrophilic colloid. These are generally stable due to the strong attractive forces operating between the two phases. These are reversible in nature. On evaporating the sol, the dispersed phase obtained can be easily reconverted into the solution by simply agitating it with the dispersion medium. Gums, gelatine and starch form lyophilic (hydrophilic) colloids.

### 4.3.2.2 Lyophobic colloids:

These are the colloidal solutions in which particles of the dispersed phase have no affinity for the dispersion medium. Such solutions are relatively less stable and are not easily prepared. These can be easily precipitated by heating the sol or on adding small amount of electrolyte to it. These are irreversible. The solid obtained by precipitation cannot be reconverted into colloidal solution by simply shaking it with the dispersion medium. Colloidal solutions of gold, silver, $Fe(OH)_3$, $As_2S_3$ etc. are lyophobic. Lyophobic sols need stabling agents for their preservation.

## 4.3.3 Classification Based on Type of Particles of the Dispersed Phase, Multimolecular, Macromolecular and Associated Colloids

Depending upon the type of particles of the dispersed phase, colloids are classified as: multimolecular, macromolecular and associated colloids.

### 4.3.3.1 Multimolecular colloids:

These are the sols in which the particles of dispersed phase consist of aggregate of large number of atoms or small molecules having molecular size less than 1 nm (1 nm $=10^{-9}$ m) and the aggregate has dimensions of colloidal size. In these colloids, the particles are held together by van der Waal's forces. Some examples of such colloids are (i) Sols of gold atoms (ii) Platinum of (iii) Sulphur sol. Sulphur sol consists of particles containing a thousand or more $S_8$ molecules.

### 4.3.3.2 Macromolecular colloids:

In this type of colloids, individual molecules have very large size, which is of colloidal dimensions. The macromolecules constituting the dispersed phase are generally polymers having very high molecular weights. Naturally occurring macromolecules are proteins, enzymes, gelatin, starch, cellulose, etc. Artificial macromolecules are polythene, polystyrene, nylon etc. Since the particle size in case of macromolecules is comparable to those of colloids, solutions of macromolecular substances are macromolecular colloidal solutions. Dispersions of macromolecules are quite stable and resemble true solutions in many respects. Thus, common examples of macromolecular colloids are (i) Proteins (ii) Starch (iii) Cellulose (iv) Plastics (v) Enzymes.

### 4.3.3.3 Associated Colloids or Micelles:

These are the substances which behave as normal electrolytes at low concentrations but as colloids at higher concentrations. It is because these form aggregated (associated) particles called micelles at higher concentration. The micelle formation takes place only above a particular concentration called critical micelle concentration (CMC) and above a particular temperature called Kraft temperature (Tk). On dilution, these colloids again behave as electrolytes. These colloids have lyophilic as well as lyophobic parts. Micelles may contain as many as 100 molecules are more. Common examples of this type are surface active agents such as soaps and synthetic detergents. For soaps, the CMC is $10^{-4}$ to $10^{-3}$ mol $L^{-1}$.

## Mechanism of micelle formation

Let us take the example of soap solutions. Soap is sodium or potassium salt of a higher fatty acid and may be represented as $RCOO^-Na^+$ (e.g., sodium stearate $CH_3(CH_2)_{16}COO^-Na^+$, which is a major component of many bar soaps). When dissolved in water, it dissociates into $RCOO^-$ and $Na^+$ ions. The $RCOO^-$ ions, however, consist of two parts — a long hydrocarbon chain R (also called non-polar 'tail') which is hydrophobic (water repelling), and a polar group $COO^-$ (also called polar-ionic 'head'), which is hydrophilic (water loving).

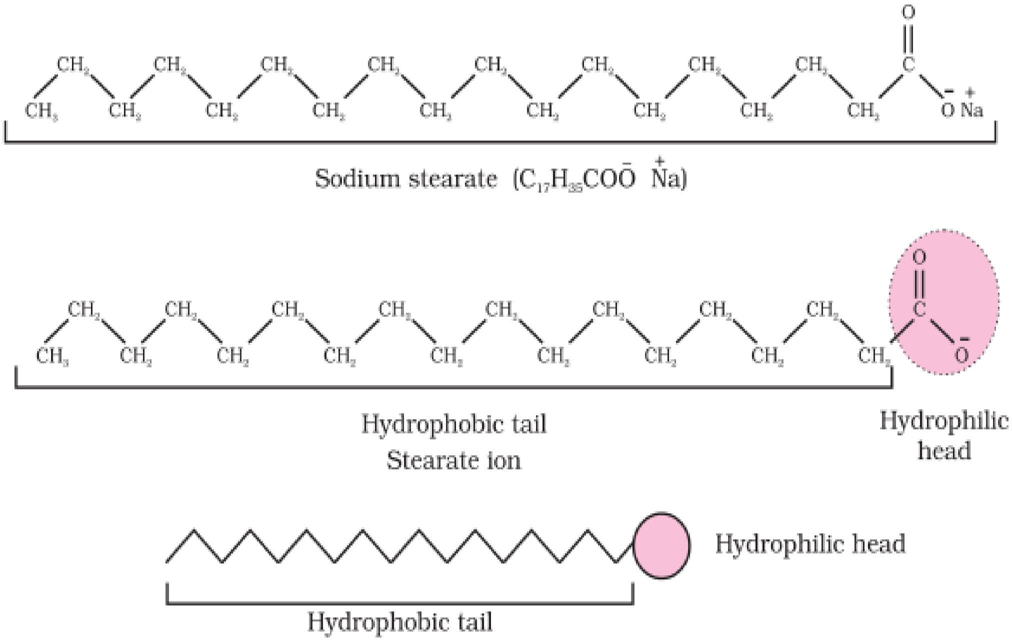


*Fig. 4.1 : Hydrophobic and hydrophilic parts of stearate ion*

The $RCOO^-$ ions are, therefore, present on the surface with their $COO^-$ groups in water and the hydrocarbon chains R staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with $COO^-$ part remaining outward on the surface of the sphere. An aggregate thus formed is known as 'ionic micelle'. These micelles may contain as many as 100 such ions.

Similarly, in case of detergents, e.g., sodium laurylsulphate, $CH_3(CH_2)_{11}SO_4^-Na^+$, the polar group is $-SO_4^-$ along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is same as that of soaps.

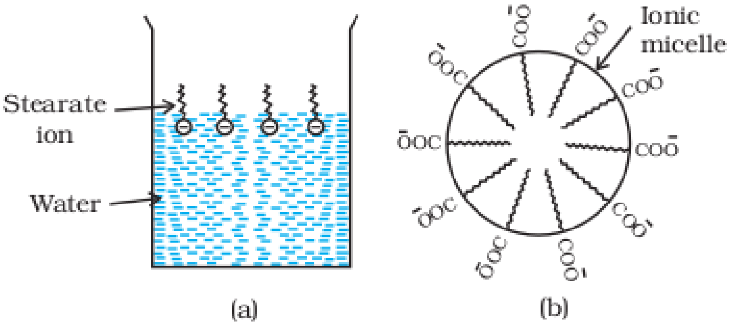


Fig. 4.2: (a) Arrangement of stearate ions on the surface of water at low concentrations of soap
(b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap

## Cleansing action of soaps

It has been mentioned earlier that a micelle consists of a hydrophobic hydrocarbon – like central core. The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles. Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

# 4.4 Preparation of Colloids

A few important methods for the preparation of colloids are as follows:

## 4.4.1Chemical Methods

Colloidal solution can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction or hydrolysis. These molecules then aggregate leading to formation of sols.

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decomposition}} As_2S_3(sol) + 3H_2O$$

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$$

$$2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au(sol) + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\ (sol) + 3HCl$$

## 4.4.2 Electrical disintegration or Bredig’s Arc method

This process involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared by this method. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium (Fig. 4.3). The intense heat produced vapourises the metal, which then condenses to form particles of colloidal size.

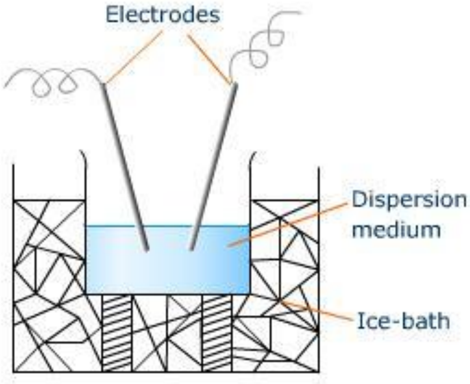


Fig. 4.3: Bredig's Arc method

### 4.4.3 Peptization

Peptization may be defined as the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called peptizing agent. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol. During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates, which ultimately break up into smaller particles of the size of a colloid.

## 4.5 Purification of Colloidal Solutions

Colloidal solutions obtained by chemical methods contain appreciable amounts of electrolytes. To obtain pure sol, it is necessary to remove those electrolytes which tend to coagulate the colloidal particles. The methods employed for this purpose are:

4.5.1. Dialysis

4.5.2. Electro dialysis

4.5.3. Ultra filtration

### 4.5.1. Dialysis:

We know that the particles of the colloidal solution cannot pass through the parchment paper, cellophane or animal membrane while those of the ture solution can easily pass through them. It is due to the difference in their particle size. The process of separating a crystalloid from a colloid by diffusion throug a parchment paper or animal membrane is called dialysis. The apparatus which is employed to effect such separation is called Dialyser.

Dialyser used by Graham is known as Graham's dialyser. It consists of a hollow cylinder open at both ends. One end of this cylinder is closed by a membrane. A bag made of animal membrane can also be used in place of hollow cylinder (Figure 4.4). Impure colloidal sol is placed in the dialyser, which is then suspended in a large vessel containing distilled water. The pores of the membrane permit the ions and small molecules to pass through but not the large colloidal particles. By using a continuous flow of fresh water, the concentration of the electolyte in the outside vessel is maintained at a negligible level. Thus diffusion of the ions into pure water takes place at a reasonable rate. In this way, practically all the electrolyte present in the sol can be removed easily. Dialysis can be used to remove HCl from ferric hydroxide sol.

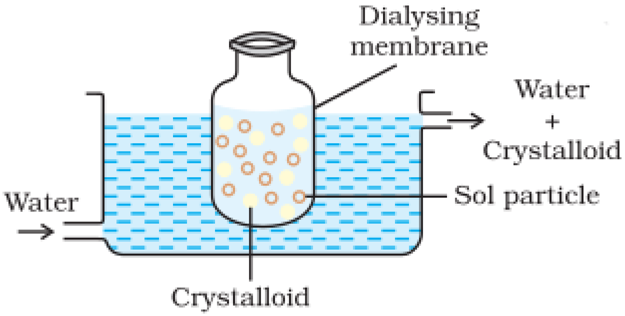


*Fig. 4.4 : Dialysis*

## 4.5.2 Electro dialysis

Dialysis is a slow process. To hasten the process, dialysis is carried out under the influence of an electric field. The cations and anions of the electrolyte will be attracted owards the oppositely charged electrodes (Figure 4.5).

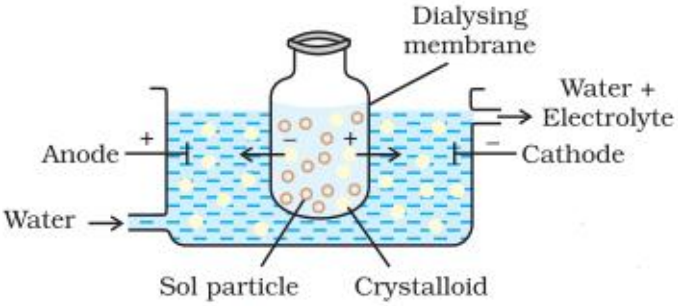


*Fig. 4.5 : Electro-dialysis*

**Limitation:** Electrodialysis is not suitable for the removal of non-electrolyte impurities such as sugar and urea.

## 4.5.3. Ultra filtration

Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles. Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with collodion solution to stop the flow of colloidal particles. The usual collodion is a 4% solution of nitrocellulose in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the filter paper in a collodion solution, hardening by formaldehyde and then finally drying it. Thus, by using ultra-filter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process.

To speed up the process, pressure or suction is applied. The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

## 4.6 Properties of Colloids

Various properties exhibited by the colloidal solutions are described below:

### 4.6.1 Colligative properties:

Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a true solution. Hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentrations.

### 4.6.2 Tyndall effect:

If a homogeneous solution placed in dark is observed in the direction of light, it appears clear and, if it is observed from a direction at right angles to the direction of light beam, itappears perfectly dark. Colloidal solutions viewed in the same way may also appear reasonably clear or translucent by the transmitted light but they show a mild to strong opalescence, when viewed at right angles to the passage of light, i.e., the path of the beam is illuminated by a bluish light. This effect was first observed by Faraday and later studied in detail by Tyndall and is termed as Tyndall effect. The bright cone of the light is called Tyndall cone (Fig. 4.6).

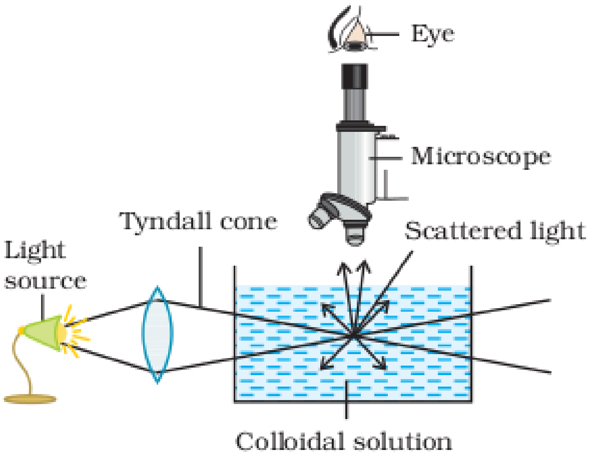


*Fig. 4.6 : Tyndall effect*

The Tyndall effect is due to the fact that colloidal particles scatter light in all directions in space. This scattering of light illuminates the path of beam in the colloidal dispersion. Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. Tyndall effect is observed only when the following two conditions are satisfied.

(i) The diameter of the dispersed particles is not much smaller than the wavelength of the light used; and

(ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

Tyndall effect is used to distinguish between a colloidal and true solution. Zsigmondy, in 1903, used Tyndall effect to set up an apparatus known as ultramicroscope. An intense beam of light is focussed on the colloidal solution contained in a glass vessel. The focus of the light is then observed with a microscope at right angles to the beam. Individual colloidal particles appear as bright stars against a dark background. Ultramicroscope does not render the actual colloidal particles visible but only observe the light scattered by them. Thus, ultramicroscope does not provide any information about the size and shape of colloidal particles.

### 4.6.3 Colour:

The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. The colour of colloidal solution also changes with the manner in which the observer receives the light. For example, a mixture of milk and water appears blue when viewed by the reflected light and red when viewed by the transmitted light. Finest gold sol is red in colour; as the size of particles increases, it appears purple, then blue and finally golden.

### 4.6.4 Brownian movement:

When colloidal solutions are viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous zig-zag motion all over the field of view. This motion was first observed by the British botanist, Robert Brown, and is known as Brownian movement (Fig. 4.7). This motion is independent of the nature of the colloid but depends on the size of the particles and viscosity of the solution. Smaller the size and lesser the viscosity, faster is the motion. The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.

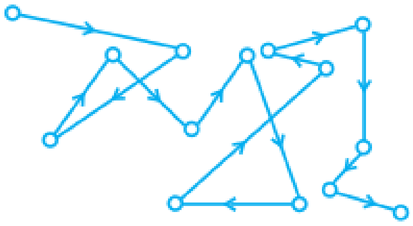


*Fig. 4.7 : Brownian movement*

### 4.6.5 Charge on colloidal particles:

Colloidal particles always carry an electric charge. The nature of this charge is the same on all the particles in a given colloidal solution and may be either positive or negative. A list of some common sols with the nature of charge on their particles is given below:

| **Positively charged sols** | **Negatively charged sols** |
|---|---|

| | |
|---|---|
| Hydrated metallic oxides, e.g., $Al_2O_3.xH_2O$, $CrO_3.xH_2O$ and $Fe_2O_3.xH_2O$, etc.<br>Basic dye stuffs, e.g., methylene blue sol.<br>Haemoglobin (blood)<br>Oxides, e.g., $TiO_2$ sol. | Metals, e.g., copper, silver, gold sols.<br>Metallic sulphides, e.g., $As_2S_3$, $Sb_2S_3$, CdS sols.<br>Acid dye stuffs, e.g., eosin, congo red sols.<br>Sols of starch, gum, gelatin, clay, charcoal, etc. |

The charge on the sol particles is due to one or more reasons, viz., due to electron capture by sol particles during electrodispersion of metals, due to preferential adsorption of ions from solution and/or due to formulation of electrical double layer. Preferential adsorption of ions is the most accepted reason. The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions. When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:

**(a)** When silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal solution results. However, when KI solution is added to $AgNO_3$ solution, positively charged sol results due to adsorption of $Ag^+$ ions from dispersion medium.

| | |
|---|---|
| $AgI/I^-$ | $AgI/Ag^+$ |
| Negatively charged | Positively charged |

**(b)** If $FeCl_3$ is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of $Fe^{3+}$ ions. However, when ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of OH- ions.

| | |
|---|---|
| $Fe_2O_3.xH_2O/Fe^{3+}$ | $Fe_2O_3.xH_2O/OH^-$ |
| Positively charged | Negatively charged |

Having acquired a positive or a negative charge by selective adsorption on the surface of a colloidal particle as stated above, this layer attracts counter ions from the medium forming a second layer, as shown below.

| | |
|---|---|
| $AgI/I^- K^+$ | $AgI/Ag^+I$ |

The combination of the two layers of opposite charges around the colloidal particle is called Helmholtz electrical double layer. According to modern views, the first layer of ions is firmly held and is termed fixed layer while the second layer is mobile which is termed diffused layer. Since separation of charge is a seat of potential, the charges of opposite signs on the fixed and diffused parts of the double layer results in a difference in potential between these layers. This potential difference between the fixed layer and the diffused layer of opposite charges is called the electrokinetic potential or zeta potential. The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution, because the repulsive forces between charged particles having same charge prevent them from coalescing or aggregating when they come closer to one another.

### 4.6.6 Electrophoresis:

The existence of charge on colloidal particles is confirmed by electrophoresis experiment. When electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode. The movement of colloidal particles under an applied electric potential is called electrophoresis. Positively charged particles move towards the cathode while negatively charged particles move towards the anode. This can be demonstrated by the following experimental setup (Fig. 4.8). When electrophoresis, i.e., movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed electroosmosis.

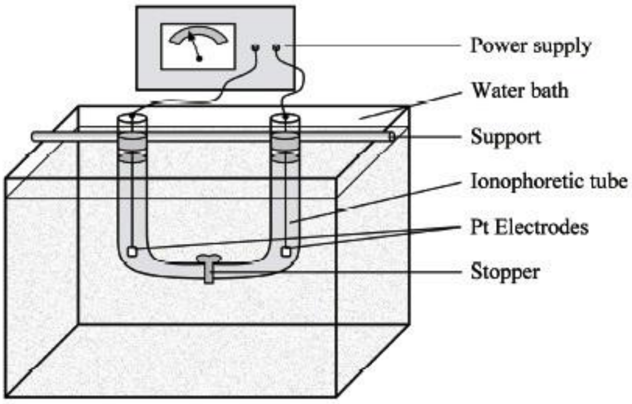


Fig. 4.8 Electrophoresis

### 4.6.7 Coagulation or precipitation:

The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If, somehow, the charge is removed, the particles will come nearer to each other to form aggregates (or coagulate) and settle down under the force of gravity. The process of settling of colloidal particles is called coagulation or precipitation of the sol. The coagulation of the lyophobic sols can be carried out in the following ways:

**(i) By electrophoresis:** The colloidal particles move towards oppositely charged electrodes, get discharged and precipitated.

**(ii) By mixing two oppositely charged sols:** Oppositely charged sols when mixed in almost equal proportions, neutralise their charges and get partially or completely precipitated. Mixing of hydrated ferric oxide (+ve sol) and arsenious sulphide (–ve sol) bring them in the precipitated forms. This type of coagulation is called mutual coagulation.

**(iii) By boiling:** When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately lead to settling down in the form of a precipitate.

**(iv) By persistent dialysis:** On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable and ultimately coagulate.

**(v) By addition of electrolytes:** When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation. The ion responsible for neutralisation of charge on the particles is called the coagulating ion. A negative ion causes the precipitation of positively charged sol and vice versa.

It has been observed that, generally, the greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as Hardy-Schulze rule. In the coagulation of a negative sol, the flocculating power is in the order: $Al^{3+} > Ba^{2+} > Na^{+}$

Similarly, in the coagulation of a positive sol, the flocculating power is in the order: $[Fe(CN)6]^{4-} > PO4^{3-} > SO4^{2-} > Cl^{-}$

The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value. The smaller the quantity needed, the higher will be the coagulating power of an ion.

## 4.7 Coagulation of Lyophilic Sols

There are two factors which are responsible for the stability of lyophilic sols. These factors are the charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. This is done (i) by adding an electrolyte and (ii) by adding a suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sols, the dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

## 4.8 Protective Action of Sols

Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloids are extensively solvated, i.e., colloidal particles are covered by a sheath of the liquid in which they are dispersed. Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect the latter from electrolytes. Lyophilic colloids used for this purpose are called protective colloids.

### 4.8.1 Gold number:

The protective power of different lyophilic sols is different. The protective action of different colloids is expressed in terms of gold number introduced by Zsigmondy. It is defined as: The number of milligrams of a hydrophilic colloid which just prevents the precipitation of 10 mL of a gold sol on the addition of 1 mL of ten per cent sodium chloride solution. The onset of precipitation of gold sol is indicated by change in colour from red to blue. Thus gold number is a measure of the quantity of protective colloid which just fails to prevent the coagulation of the sol by the electrolyte. It is obvious, therefore, that smaller the gold number, greater is the protective power of the given protective colloid. The gold numbers of a few protective colloids are as follows:

**Table 4.2**

| **Substance** | **Gold number** | **Substance** | **Gold number** |
|---|---|---|---|
| Gelatine | 0.005–0.01 | Gum Arabic | 0.15–0.25 |
| Haemoglobin | 0.03–0.07 | Dextrin | 6–20 |
| Albumin | 0.1–0.2 | Potato Starch | 20–25 |
| Sodium Oleate | 0.4–1.0 | Casein | 0.01 |

**Experimental Procedure to find Gold Number**

The procedure is as follows: After determining the approximate concentration of protecting colloids required, 0.01, 0.1, 1.0 mL proportion of sol are put into the beakers and 10 mL of gold sol is added to each. After shaking for three minutes, 1 mL of 10% NaCl is added to each. If the colour changes in first beaker but not in others, then gold number lies between 0.01 mL and 0.1 mL of protecting colloid. By repeating concentrations between these limit more exact values are obtained. The gold number found in this way by Zsigmondy and Gortner for several hydrophilic colloids are given in Table 4.2.

**Stability of Colloids**

The lyophobic sols are stabilized by electric double layer interations. Solvation always has good influence on their stability.

### 4.8.2 The Schulze-Hardy Rule

This rule of coagulation states that (1) The effective ions in the preparation of sol by electrolytesis the ion opposite in sign to the charge on the colloidal particles and (2) the precipitating powerof the effective ion increases greatly with increasing valence of the ion. The effective ion is sometimes referred to as the precipitating ion of an electrolyte, whereas the ion having the same sign of charge as the particle is called stabilizing ion.

According to Schulze-Hardy Rule higher the valency of the flocculating ion added, the greater is its power to cause coagulation. Thus, for precipitating an $As_2S_3$ sol (negative), the precipitating powerof positively charged ions is in the order: $Al^{3+} > Ba^{2+}$ $Na^{+}$.

Use of the potash alum in the purification of water is based on the strong power of $Al^{3+}$ ions to coagulate negatively charged colloidal impurities present in natural water. Similarly, in the coagulation of the positively charged ferric hydroxide sol, the flocculating power decreases in the order $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$. It may be noted that the rule is only approximate and several departures are known.

Generally, the precipitating power of a trivalent ion is nearly 500 to 1000 times as high as that of the monovalent ion. The precipitating power of a bivalent ion is about 100–500 times as high as that of univalent ion.

## 4.9 Emulsions

These are liquid-liquid colloidal systems, i.e., the dispersion of finely divided droplets in another liquid. If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called emulsion. Generally, one of the two liquids is water. There are two types of emulsions.

(i) Oil dispersed in water (O/W type) and

(ii) Water dispersed in oil (W/O type).

In the first system, water acts as dispersion medium. Examples of this type of emulsion are milk and vanishing cream. In milk, liquid fat is dispersed in water. In the second system, oil acts as dispersion medium. Common examples of this type are butter and cream. Emulsions of oil in water are unstable and sometimes they separate into two layers on standing. For stabilisation of an emulsion, a third component called emulsifying agent is usually added. The emulsifying agent forms an interfacial film between suspended particles and the medium. The principal emulsifying agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc., and for W/O, heavy metal salts of fatty acids, long chain alcohols, lampblack, etc. Emulsions can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed, forms a separate layer. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes. They also show Brownian movement and Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

## 4.10 Gels

Lyophilic colloids that is normally stable but may be induced to coagulate partially under certain conditions (e.g. lowering the temperature). This produces a pseudo-solid or easily deformable jelly-like mass enclosing the entire amount of the liquid within itself. Such a product is called a gel, in which entertaining particles endorse the whole dispersing medium. Gel is a liquid-solid system in which a liquid is dispersed in a solid. Gels may be further subdivided into elastic gels (e.g. gelatin) and rigid gels/inelastic gels (e.g. silica gel). They are distinguished form each other by the process of dehydration and rehydration.

### 4.10.1 Elastic Gels:

An elastic gel is obtained by cooling a lyophlic colloid, such as as gelatin or agar solution prepared by warming these substance with water. Starch gelatin, agar-agar and pectinsols belong to this class. Solutions of soap also belong to elastic gels. The elastic gels are reversible. In these cases, dehydration and rehydration on exposure to water vapour are most reversible, even then the process is carried out more than one.

### 4.10.2 Inelastic Gels:

The best known example of inelastic gel is silicic acid or silica gel. This is prepared by the addition of hydrochloric acid to sodium silicate at an appropriate concentration. The system sets to gel almost immediately. In some cases the setting may be delayed. Other examples are $Fe(OH)_3$, $Al(OH)_3$, and $Cr(OH)_3$. The inelastic gels are irreversible. If silica gel is dehydrated, addition of water will not reset it into the gel. Among the lyophilic sols the well known gels are gelatin, agar-agar, gum arabic, mastic and gamboge sol, etc. Amongst the lyophobic sols, the well known gels are silicic acid, ferric hydroxide, ferric phosphate sols. The sols should be in sufficiently high concentration to facilitate the gelation process. Both gels and gelation are very important in medicine and biology because the plants and animals are composed of naturally occurring gels. Gelatin made up of macromolecular solutions have got great importance in technological field. In food and technological field industries make use of gelatin.

## 4.11 Preparation of Gels

Gels may be prepared by the following process.

### 4.11.1 Cooling of sols at Moderate Concentration:

Agar-agar, gelatin gels are made by cooling their sols having moderate concentrations prepared in hot water. As we know that hydrophilic sols are extensively hydrated, when cooled, the hydrated particles agglomerate together to form larger aggregates and finally led to form a semi-solid network structure of gel.

### 4.11.2 Double-Decomposition:

Hydrophobic gel such as silicic acids (commonly known as silica gel) and aluminium hydroxide (commonly known as alumina gel) are prepared by doubledecomposition method) HCl is added to sodium silicate solution. As a result, a highly hydrated silicic acid gets precipitated. When this is allowed to stand to set, it forms a gel. By similar method alumina gel is prepared by adding NaOH on $AlCl_3$ solution. A highly hydrated salt is obtained. On standing for few minutes, it changes to gel.

### 4.11.3 Change of solvents:

Certain hydrophobic gels are prepared by this method. When ethanol is added instantly to a solution of calcium acetate of high concentrations, the salts separates out to form a colloidal solution. On standing the solution undergoes gelation and finally form a semi rigid gel.

## 4.12 **Inhibition**

The rate of growth of colloidal particles depends upon the surface phase reaction and heat of formation. On the surface the rate of growth of crystallization for glycerol is 0.002 cm/sec, whereas for phosphorous the rate of growth is 100 cm/sec. The growth rate depends on proper orientation of molecule. In general the rate of growth tends to increase with increasing super saturation and decrease with increasing viscosity and loss of mobility of the molecule in liquid. Decreasing the temperature and increasing the supersaturation, the viscosity of liquid increases and growth will become easier. The growth of colloid may be retarded by the presence of impurities which are adsorbed on the surface and prevent the incorporation of additional molecules.

## 4.13 Important Applications of Colloids

The colloids have great application in day-to-day life as well as in industry, agriculture, medicine and biological sciences. Some of its applications are given below:

### 4.13.1 Purification of water:

Sometimes it is noticed that there is some turbidity in water. This is due to the presence of some negatively charged colloidal particles in the form of fine clay. The addition of potash alum ($K_2SO_4$ $Al_2(SO_4)_3$ $24H_2O$) (which furnishes $Al^{3+}$ ) coagulates the clay particles. Finally the clay—$Al^{3+}$ substance settles down at the bottom and leaves water in a clear state.

### 4.13.2 Foods articles:

Most of our foods are colloidal in nature. For example, milk is an emulsion having fat disposed in water. To preserve the smoothness of ice cream some gelatin is added as a protective agent. Whipped cream fruits, jellies, gels, fruit juice, eggs, salads are substances having colloidal nature.

### 4.13.3 Rubber industry:

Using the process of electrophoresis the deposit on the wires or handles of various tools. The article to be rubber-plated is made the anode. The rubber particles migrate in an electric field towards the anode and get deposited on it. This process in known as insulation.

### 4.13.4 Sewage disposal:

The sewage water consists of dirt, mud, and many unwanted particles etc. having the colloidal dimension which carry electric charge and they do not settled down easily. On creating electric field in the sewage tank, those particles migrate to the oppositely changed electrodes, get neutralized and finally settle down at the bottom.

### 4.13.5 Formation of deltas:

The deltas are formed at the mouth of the rivers by the precipitation of the charged clay particles.

### 4.13.6 Artificial rain:

Clouds are charged particles of water dispersed in air. Rain is caused by the aggregation of these particles. Artificial rains are possible by throwing electrified sound from aero planes, which convert water to rainfall.

### 4.13.7 Chrome-tanning:

The Chrome-tanning of leather is done by the penetration of positively charged particles of hydrated chromic oxide into leather. The rate of penetration may be increased by the process of electrophoresis.

### 4.13.8 Industrial applications:

The industry manufactures pairs, soaps, varnishes, gums, glues, many adhesives, enamels, celluloses, rayon, nylon 66, terylene, textiles, leather, papers, opaque glass of high quality, etc all of them are colloidal in nature. Many industrial processes such as dying, tanning, lubrication, polymerisations etc are colloidal in nature. So colloids have great role to play in industry.

### 4.13.9 Smoke Screens:

The smoke screens are used in warfare for the purpose of concealment and camouflage. The smoke screens consist of very fine particles of titanium oxide in air and are ejected from the aeroplanes. The titanium oxide colloid is heavy and form heavy smoke screen like curtain of dazzling whiteness.

### 4.13.10 Blue Colour of the Sky:

Colloidal dust particles along with water suspended in air scatter blue light which reaches our eyes and sky appears blue to us.

### 4.13.11 Curdling of milk:

The sugar present in milk produces lactic acid on fermentation. Ions produced by acid, destroy the charge on the colloidal particles present in milk, which then coagulate and separate as curd.

### 4.13.12 Tail of the comets:

When the comet flies with very high speed, it leaves behind a tail of tiny solid particles suspended in air. These particles scatter light forming Tyndall’s cone, which looks like tail of the comet.

### 4.13.13 Photographic plates and films:

The photographic plates and films are obtained by coating an emulsion of the light sensitive AgBr in gelatin over glass plates or celluloid films.

### 4.13.14 Coagulation of Blood:

Bleeding caused by razor shaving can be stopped by rubbing alum (containing $Al^{3+}$) against the cut which coagulates the blood and seals the blood vessels.

### 4.13.15 Industrial Products:

Paints, rubber, inks, graphite lubricants, cement, etc. are all colloidal solution

## 4.14 Macromolecules

The term macromolecule was coined by Nobel laureate Hermann Staudinger in the 1920s, although his first relevant publication on this field only mentions high molecular compounds (in excess of 1,000 atoms). A macromolecule is a very large molecule commonly created by polymerization of smaller subunits. In biochemistry, the term is applied to the three conventional biopolymers (nucleic acids, proteins and carbohydrates) as well as non-polymeric molecules with large molecular mass such as lipids and macrocycles. The individual constituent molecules of macromolecules are called monomers (mono=single, meros=part).

## 4.14.1 Determination of Molecular Weight of Macromolecules

### 4.14.1.1 Viscosity Method:

The viscosity method, is introduced by Staudinger, is the one most commonly employed in research. Accurate measurement of absolute viscosity being difficult, it is convenient to measure relative viscosity, $\eta_{rel}$, defiend as:

$$\eta_{rel} = \eta / \eta_o \qquad (1)$$

Where $\eta$ and $\eta_o$ are, respectively, the viscosity of the solution and the viscosity of the solvent. The relative viscosity is related to some other quantities as follows:

$$\eta_{sp} = \eta_{rel} - 1 \qquad (2)$$

$$\eta_{red} = \eta_{sp} / c \qquad (3)$$

$$[\eta] = \lim_{c \to 0} = (\eta sp / c) \qquad (4)$$

Where $\eta_{sp}$ is specific viscosity, $\eta_{red}$ is reduced viscosity and $[\eta]$ is intrinsic viscosity (also called the viscosity number or Staudinger index). In these equations, c is the concentration of the polymer. Note that none of these quantities has the unit of viscosity.

In 1906, Einstein derived the following relation between the viscosity of a dilute suspension of hard spherical molecules and the volume fraction, $\phi$, of the solute molecules:

$$\eta = \eta_o (1+2.5\, \phi) \qquad (5)$$

Rearrangement of Eq. 5 gives

$$\eta / \eta_o - 1 = \eta_{sp} = 2.5\, \phi \qquad (6)$$

Hence, from Eqs. 4 and 6,

$$[\eta] = \lim_{c \to 0} = \left( \frac{\eta_{sp}}{c} \right) = \left( \frac{2.5\Phi}{c} \right) \qquad (7)$$

It is, however, very difficult to measure $\phi$, the volume fraction of the polymer molecules in solution. The plots of $\eta_{sp}$/ c and ln $\eta_{red}$/ c versus c give straight lines which confirm to the following equations:

$$\text{Huggin's equation: } \eta_{sp}/\,c = [\eta] + k''[\eta]^2 c \qquad (8)$$

$$\text{Kraemer's equation: } \ln v_{red}/\,c = [\eta] - k'[\eta]^2 c \qquad (9)$$

Both these equations are applicable only in dilute solutions. For many polymers, $k' = 0.4 \pm 0.1$ and $k'' = 0.50 \pm 0.05$.

Fortunately, Staudinger found, in 1950, that for a series of a sample of the same polymer in a given solvent and at a constant temperature, the intrinsic viscosity (or the viscosity number) is related to the molar mass of the polymer by the following equation, known as Mark-Kuhn-Houwink-Sakurda equation, formerly called Staudinger equation:

$$[\eta] = K\,\overline{M}_V^{\,a} \qquad (10)$$

where $\overline{M}_V$ is the viscosity- average molar mass of the polymer and K and a are constants, usually determined by intrinsic viscosity measurements on a series of polymer samples for which the molar mass has been determined by a different method, say, the light scattering method. The value of the exponent a depends upon the geometry or the shape of the macromolecules. The more elongated a molecule, the more effective of the higher molar mass fraction in reducing the viscosity of the solution. The value of a vary from 0.5 to 1. For polymers behaving as random coils, a is about 0.8 and the globular proteins possessing a compact structure, it is about 0.5. Note that $[\eta]$ has the dimensions of reciprocal density and hence its units are $cm^3\ g^{-1}$.

Taking logs of both sides of Eq. 10, we have

$$\ln [\eta] = \ln K + a \ln \overline{M}_V \qquad (11)$$

Eq. 11 shows that a log – log plot of $[\eta]$ versus $\overline{M}_V$ gives a straight line with slope equal to *a* and intercept equal to log *K*. Thus, the constant *a* and *K* can be easily determined. Knowing the values of *a* and *K*, the viscosity- average molar mass $\overline{M}_V$ can be determined from intrinsic viscosity measurements.

## 4.14.1.2 Osmotic Pressure Method:

Let us take the case of a dilute polymer solution of a low finite concentration separated from the pure solvent by a semipermeable membrane. The chemical potential of the solvent ($\mu_s$) in solution is lees than that ($\mu_o$) of pure solvent and therefore, to keep the system in equilibrium, the chemical potential of the solvent on the two sides of the membrane requires to be balanced and made equal. This is readily done by applying an excess pressure, $\pi$, called the osmotic pressure to the solution side to compensate for the difference in chemical potential. The equilibrium condition can thus be expressed as :

$$\mu_o - \mu_s = \Delta\mu_1 = -\pi\,\overline{V}_1$$

$$\text{or,} \qquad RT \ln f_1 x_1 = -\pi \overline{V}_1 \qquad (1)$$

where, $R$ is the universal gas constant, $T$, the absolute temperature, $\overline{V}_1$, the partial molar volume, $f_1$, the activity coefficient of the solvent in solution, and $x_1$, the solvent mole fraction; for a very dilute solution, $f_1 \rightarrow 1$ and $V_1$ may be taken as equal to the molar volume $V_1^0$ of the pure solvent. Replacing solvent mole fraction $x_1$ by $(1 - x_2)$, where $x_2$ is the mole fraction of the (polymer) solute in solution, and expanding the logarithm factor, one obtains

$$\pi V_1^0 = RT \left( x_2 + \frac{x_2^2}{2} + \frac{x_2^3}{3} + \text{----} \right) \qquad (2)$$

If $c$ is the concentration of the solute in gram per unit volume of the solution, then for a very low value of $c$ and very high value of $M_n$, $x_2$ is given by

$$x_2 = \frac{c / \overline{M}_n}{1/V_1^0 + c/\overline{M}_n} \simeq \frac{V_1^0 c}{\overline{M}_n} \qquad (3)$$

Combining equation (2) and (3), one obtains

$$\pi / c = \frac{RT}{\overline{M}_n} \left\{ 1 + \frac{1}{2} \left( \frac{V_1^0}{\overline{M}_n} \right) c + \frac{1}{3} \left( \frac{V_1^0}{\overline{M}_n} \right)^2 c^2 + \text{-----} \right\} \qquad (4)$$

Polymer solutions largely deviate from ideality, thus rendering the value of $f_1$ less than unity; even at a very low finite concentration at which precision osmometric measurement is possible. The real coefficients of concentration terms in equation (4) are somewhat higher than those shown in the equation. Even then, the $\pi / c$ term may be expressed as a power series in $c$ using empirical coefficients:

$$\pi / c = RT \left( A_1 + A_2 c + A_3 c^2 + \text{-----} \right) \qquad (5)$$

Or alternatively,

$$\pi / c = \frac{RT}{\overline{M}_n} \left( 1 + \Gamma_2 c + \Gamma_3 c^2 + \text{-----} \right) \qquad (6)$$

where, $\Gamma_2 = A_2 / A_1$, $\Gamma_3 = A_3 / A_1$ and so on, and $A_1 = ( 1 / \overline{M}_n )$

The coefficient $A_2$, $A_3$ etc. are referred to as second, third, etc. virial coefficients. For most cases and for all practical purposes, the term in $c^2$ and those in higher powers of $c$ may be neglected. Thus, $\pi / c$ is measured as a function of $c$ in unit of g/dl at a given temperature and plotted graphically; extrapolation of the low concentration range linear plot with a positive slope to $c \rightarrow o$ gives an intercept that equals the parameter $(RT / M_n)$.

Alternatively, $(\pi/RTc)$ may be graphically plotted against $c$, Fig. 4.9, and direct evaluation of the number average molecular weight $M_n$, then readily follows from the measure of the intercept. The plots are linear over the low concentration region (very dilute solutions) in each case of (a) and (b) in Fig. 4.9. The slope of each linear portion of the plot may be used to calculate the second virial coefficient. In good solvents and over relatively high concentration range, the plots may turn concave upward, more so, for the plot as in part (a) of fig.4.9.

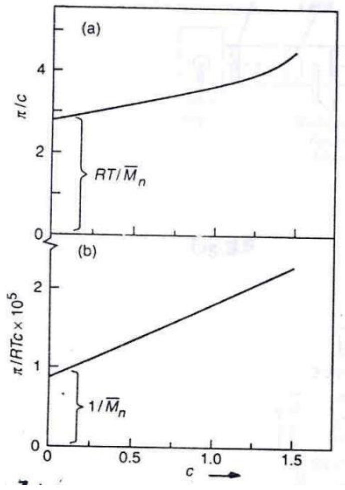


Fig. 4.9: Plots of $\pi / c$ vs. $c$ and $\pi /RTc$ vs. $c$ for Determination of $\overline{M}_n$.

The osmotic pressure equation may be modified to the form

$$\frac{\pi}{RTc} = \frac{1}{M_2} + \frac{\rho_1}{M_1\,\rho_2^{2}}\left(\frac{1}{2} - \chi_1\right) c + \text{-----} \qquad (7)$$

where subscripts 1 and 2 stand for solvent and polymer solute respectively, $\rho$ for the density parameter, and $\chi_1$ is the polymer – solvent interaction constant according to the Flory – Huggins theory. Equation (7) permits plot of ($\pi / RTc$) vs $c$ where the intercept gives the polymer molecular weight (number overage) and the value of the slope may be used to calculate the value of Flory –Huggins polymer – solvent interaction constant $\chi_1$.

## 4.14.2 Donnan Membrane Equilibrium

The molar masses of charged macromolecules (e.g., proteins), determined by osmotic pressure measurement in electrolytic media were found to be considerably smaller than those determined by other methods. This was found to be due to an electrical phenomenon, known as Donnan membrane equilibrium, which occur when a large non diffusible, charged ion (e.g., a protein ion), is separated by a semipermeable membrane from a diffusible salt.

Suppose a solution of a salt $Na^+P^-$ of concentration $c_1$ (where $P^-$ is a protein particle carrying a negative charge) is separated by a semipermeable membrane from a solution of sodium chloride of concentration $c_2$. During osmosis, the chloride ions tends to diffuse from a region of higher concentration $c_2$ on the right to a region of lower concentration $c_1$ on the left. However, the protein ions $P^-$ cannot pass through the membrane. In order to maintain electrical neutrality, an equal number of $Na^+$ ions would pass from right to left across the membrane.

*Initial State*

| $Na^+$ | $P^-$ | | $Na^+$ | $Cl^-$ |
|---|---|---|---|---|
| $c_1$ | $c_1$ | | $c_2$ | $c_2$ |

*Equilibrium State*

| $Na^+$ | $P^-$ | $Cl^-$ | $Na^+$ | $Cl^-$ |
|---|---|---|---|---|
| $c_1 + x$ | $c_1$ | $x$ | $c_2 - x$ | $c_2 - x$ |

The osmotic pressure measurement would thus get complicated by a additional number of particles present on the left side i.e., on the protein side of the membrane. Let x be the concentration change due to the diffusion of NaCl across the membrane. In both the positive ions should be equal to that of the negative ions in each solution.

At equilibrium, the chemical potential of NaCl which is present on both sides of the membrane must be the same on each side. Accordingly,

$$\mu^0 + RT \ln (a_{\mathrm{NaCl}})_l = \mu^0 + RT \ln (a_{\mathrm{NaCl}})_r \qquad (1)$$

where $a_{\mathrm{NaCl}}$ represents the activity of sodium chloride and the subscripts *l* and *r* refer to the solution on the left and the right of the semipermeable membrane. Thus, we have for the left compartment,

$$(a_{\mathrm{NaCl}})_l = (a_{\mathrm{Na}^+})_l\, (a_{\mathrm{Cl}^-})_l = (\gamma_\pm)^2_l\, (\mathrm{Na}^+)_l\, (\mathrm{Cl}^-)_l \qquad (2)$$

and for the right compartment,

$$(a_{\mathrm{NaCl}})_r = (a_{\mathrm{Na}^+})_r\, (a_{\mathrm{Cl}^-})_r = (\gamma_\pm)^2_r\, (\mathrm{Na}^+)_r\, (\mathrm{Cl}^-)_r \qquad (3)$$

Assuming that the mean ionic activity coefficients in the left and right compartments are equal, i.e., $(\gamma_\pm)^2_l = (\gamma_\pm)^2_r$, which is usually the case since the ionic strengths are equal, we can express the Donnan membrane as:

$$(\mathrm{Na}^+)_l\, (\mathrm{Cl}^-)_l = (\mathrm{Na}^+)_r\, (\mathrm{Cl}^-)_r$$

$$\text{or} \qquad (c_1 + x)\, x = (c_2 - x)\,(c_2 - x) = (c_2 - x)^2$$

$$\text{or} \qquad c_1x + x^2 = c_2^2 + x^2 - 2c_2x$$

$$\text{or} \qquad x(c_1 + 2c_2) = c_2^2$$

$$x = c_2^2 / (c_1 + 2c_2) \qquad (4)$$

It is evident from Eq. 4 that the magnitude of x depends on $c_2$, the concentration of salt as well as on $c_1$, the concentration of the protein. This means that the extent of diffusion of sodium chloride, viz., x, is distinctly affected by the presence of the non-diffusible protein ion $P^-$. If the solution behaves ideally, the osmotic pressure can be calculated with the help of the Van't Hoff equation, viz., $\Pi = RTc$; the concentration term c, in the present case, being the difference in the molar concentrations on the two sides of the membrane. Thus at equilibrium,

$$\Pi = RT\ \{[(c_1 + x) + (c_1 + x)] - [(c_2 - x) + (c_2 - x)]\}$$

$$\Pi = 2RT\,(c_1 - c_2 + 2x) \qquad (5)$$

If the concentration of the salt $c_2$ is small as compared to the concentration of the non-diffusible ion, $c_1$, the osmotic pressure would be given by $\Pi = 2RT\,(c_1 - c_2 + 2x)$. Since the pressure is higher than the actual pressure which should have been given by $\Pi = 2RTc_1$, the molar mass determined from osmotic pressure measurement would be smaller than than the actual value.

If the concentration of the salt $c_2$ is small as compared to the concentration of the non-diffusible ion, $c_1$, then according to Eq. 4, $2x = c_2$. Eq. 5, therefore, takes the form

$$\Pi = 2RTc_1 \qquad (6)$$

This equation does not involve the concentration of chloride ion. In other words, the effect of Donnan membrane in osmotic pressure is practically eliminated by using a high concentration of salt in solution. This is precisely the condition under which molar masses of such macromolecules should be determined from osmotic pressure measurements.

## 4.14.3 Concepts of Micelles

A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle centre. This phase is caused by the packing behavior of single-tailed lipids in a bilayer. The difficulty filling all the volume of the interior of a bilayer, while accommodating the area per head group forced on the molecule by the hydration of the lipid head group, leads to the formation of the micelle. This type of micelle is known as a normal phase micelle (oil-in-water micelle). Inverse micelles have the head groups at the centre with the tails extending out (water-in-oil micelle). Micelles are approximately spherical in shape. Other phases, including shapes such as ellipsoids, cylinders, and bilayers, are also possible. The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micelles is known as micellisation and forms part of the Phase behaviour of many lipids according to their polymorphism.

### 4.14.3.1 Critical Micelle Concentration

In colloidal and surface chemistry, the critical micelle concentration (CMC) is defined as the concentration of surfactants above which micelles form and all additional surfactants and to the system go to micelles. The CMC is an important characteristic of a surfactant. Before reaching the CMC, the surface tension changes strongly with the concentration of the surfactant. After reaching the CMC, the surface tension remains relatively constant or changes with a lower slope. The value of the CMC for a given dispersant in a given medium depends on temperature, pressure, and (sometimes strongly) on the presence and concentration of other surface active substances and electrolytes. Micelles only form above critical micelle temperature.

For example, the value of CMC for sodium dodecyl sulfate in water (no other additives or salts) at 25 °C, atmospheric pressure, is $8 \times 10^{-3}$ mol/L.

The study of the aggregation of lipids (amphiphiles) is known as lipid polymorphism.

Upon introduction of surfactants (or any surface active materials) into the system, they will initially partition into the interface, reducing the system free energy by:

1. lowering the energy of the interface (calculated as area times surface tension), and
2. removing the hydrophobic parts of the surfactant from contact with water.

Subsequently, when the surface coverage by the surfactants increases, the surface free energy (surface tension) decreases and the surfactants start aggregating into micelles, thus again decreasing the system's free energy by decreasing the contact area of hydrophobic parts of the surfactant with water. Upon reaching CMC, any further addition of surfactants will just increase the number of micelles (in the ideal case).

There are several theoretical definitions of CMC. One well-known definition is that CMC is the total concentration of surfactants under the conditions:

if $C$ = CMC, $(d^3F/dC_t^3) = 0$

$F = a$[micelle] + $b$[monomer]: function of surfactant solution

$C_t$: total concentration

$a$, $b$: proportional constants

The CMC generally depends on the method of measuring the samples, since $a$ and $b$ depend on the properties of the solution such as conductance and photochemical characteristics. When the degree of aggregation is monodisperse, then the CMC is not related to the method of measurement. On the other hand, when the degree of aggregation is polydisperse, then CMC is related to both the method of measurement and the dispersion. The CMC is the concentration of surfactants in the bulk at which micelles start forming. The word *bulk* is important because surfactants partition between the bulk and interface and CMC is independent of interface and is therefore a characteristic of the surfactant molecule. In most situations, such as surface tension measurements or conductivity measurements, the amount of surfactant at the interface is negligible compared to that in the bulk and CMC can be approximated by the total concentration.

There are important situations where interfacial areas are large and the amount of surfactant at the interface cannot be neglected. For example if we take a solution of a surfactant above CMC and start introducing air bubbles at the bottom of the solution, these bubbles, as they rise to the surface, pull out the surfactants from the bulk to the top of the solution creating a foam column thus bringing down the concentration in bulk to below CMC. This is one of the easiest methods to remove surfactants from effluents (foam flotation). Thus in foams with sufficient interfacial area there will not be any micelles. Similar reasoning holds for emulsions. The other situation arises in detergency. One initially starts off with concentrations greater than CMC in water and on adding fabric with large interfacial area and waiting for equilibrium, the surfactant concentration goes below CMC and no micelles are left. Therefore the solubilization plays a minor role in detergency. Removal of oily soil occurs by modification of the contact angles and release of oil in the form of emulsion.

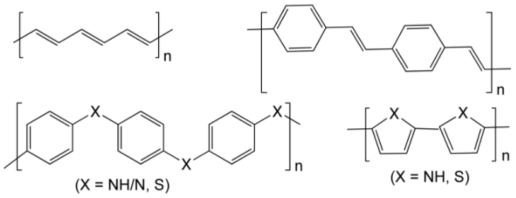
### 4.14.3.2 Uses

When surfactants are present above the CMC (Critical micelle concentration), they can act as emulsifiers that will allow a compound that is normally insoluble (in the solvent being used) to dissolve. This occurs because the insoluble species can be incorporated into the micelle core, which is itself solubilized in the bulk solvent by virtue of the head groups' favorable interactions with solvent species. The most common example of this phenomenon is detergents, which clean poorly soluble lipophilic material (such as oils and waxes) that cannot be removed by water alone. Detergents also clean by lowering the surface tension of water, making it easier to remove material from a surface. The emulsifying property of surfactants is also the basis for emulsion polymerization.

Micelle formation is essential for the absorption of fat-soluble vitamins and complicated lipids within the human body. Bile salts formed in the liver and secreted by the gall bladder allow micelles of fatty acids to form. This allows the absorption of complicated lipids (e.g., lecithin) and lipid soluble vitamins (A, D, E and K) within the micelle by the small intestine. Micelles are used for targeted drug delivery.

## 4.14.4 Conducting Polymers.

Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, *i.e.*, they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.



Chemical structures of some conductive polymers. polyacetylene; polyphenylene vinylene; polypyrrole (X = NH) and polythiophene (X = S); and polyaniline (X = NH/N) and polyphenylene sulfide (X = S).

### 4.14.4.1 Properties and Applications

Due to their poor processability, conductive polymers have few large-scale applications. They have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have had limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process. Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, chemical sensors and biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide. Another use is for microwave-absorbent coatings, particularly radar-absorptive coatings on stealth aircraft. Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly, augment this field with their higher surface area and better dispersability. With the availability of stable and reproducible dispersions, PEDOT and polyaniline have gained some large scale applications. While PEDOT (poly(3,4-ethylenedioxythiophene)) is mainly used in antistatic applications and as a transparent conductive layer in form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.

## 4.14.5 Light Emitting Polymer

It is a polymer that emits light when a voltage is applied to it. The structure comprises a thin-film of semiconducting polymer sandwiched between two electrodes (anode and cathode) as shown in fig.1. When electrons and holes are injected from the electrodes, the recombination of these charge carriers takes place, which leads to emission of light that escapes through glass substrate. The bandgap, i.e. energy difference between valence band and conduction band of the semiconducting polymer determines the wavelength (colour) of the emitted light.

### 4.14.5.1 Applications

Polymer light-emitting diodes (PLED) can easily be processed into large-area thin films using simple and inexpensive technology. They also promise to challenge LCD's as the premiere display technology for wireless phones, pagers, and PDA's with brighter, thinner, lighter, and faster features than the current display.

### 4.14.5.2 Advantages

- Require only 3.3 volts and have lifetime of more than 30,000 hours.
- Low power consumption.
- Self luminous.
- No viewing angle dependence.
- Display fast moving images with optimum clarity.
- Cost much less to manufacture and to run than CRTs because the active material is plastic.
- Can be scaled to any dimension.
- Fast switching speeds that are typical of LEDs.
- No environmental draw backs.
- No power in take when switched off.
- All colours of the visible spectrum are possible by appropriate choose of polymers.
- Simple to use technology than conventional solid state LEDs and lasers.
- Very slim flat panel.

### 4.14.5.3 Disadvantages

- Vulnerable to shorts due to contamination of substrate surface by dust.

- Voltage drops.
- Mechanically fragile.
- Potential not yet realized.

## 4.15 Summary

In this unit you have studied about .the colloidal solution intermediate between true solutions and suspensions. The size of the colloidal particles range from 1 to 1000 nm. A colloidal system consists of two phases - the dispersed phase and the dispersion medium. Colloidal systems are classified in three ways depending upon (i) physical states of the dispersed phase and dispersion medium (ii) nature of interaction between the dispersed phase and dispersion medium and (iii) nature of particles of dispersed phase. The colloidal systems show interesting optical, mechanical and electrical properties. The process of changing the colloidal particles in a sol into the insoluble precipitate by addition of some suitable electrolytes is known as coagulation. Emulsions are colloidal systems in which both dispersed phase and dispersion medium are liquids. These can be of: (i) oil in water type and (ii) water in oil type. The process of making emulsion is known as emulsification. To stabilise an emulsion, an emulsifying agent or emulsifier is added. Soaps and detergents are most frequently used as emulsifiers. Colloids find several applications in industry as well as in daily life. A macromolecule is a very large molecule commonly created by polymerization of smaller subunits, and determination of molecular weight of macromolecule by viscosity and osmotic pressure method.

## 4.16 Terminal Questions

1. What is the Schulze-Hardy rule ?
2. How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?
3. What are lyophilic and lyophobic sols? Give one example of each type. Why are hydrophobic sols easily coagulated ?
4. What are emulsions? What are their different types? Give example of each type.
5. What are micelles? Give an example of a micellers system.
6. Determination of molecular weight of macromolecules on the basis of viscosity method.

## 4.17 Answers

**1.** This rule of coagulation states that (1) The effective ions in the preparation of sol by electrolytesis the ion opposite in sign to the charge on the colloidal particles and (2) the precipitating powerof the effective ion increases greatly with increasing valence of the ion. The effective ion is sometimes referred to as the precipitating ion of an electrolyte, whereas the ion having the same sign of charge as the particle is called stabilizing ion. According to Schulze-Hardy Rule higher the valency of the flocculating ion added, the greater is its power to cause coagulation. Thus, for precipitating an As2S3 sol (negative), the precipitating powerof positively charged ions is in the order: $Al^{3+} > Ba^{2+}$ $Na^{+}$.

Use of the potash alum in the purification of water is based on the strong power of Al3+ ions to coagulate negatively charged colloidal impurities present in natural water. Similarly, in the coagulation of the positively charged ferric hydroxide sol, the flocculating power decreases in the order $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$. It may be noted that the rule is only approximate and several departures are known.

Generally, the precipitating power of a trivalent ion is nearly 500 to 1000 times as high as that of the monovalent ion. The precipitating power of a bivalent ion is about 100–500 times as high as that of univalent ion.

**2.** Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The examples of the various types of colloids along with their typical names are listed in Table.

**Table Types of Colloidal Systems**

| **Dispersed phase** | **Dispersion medium** | **Type of colloid** | **Examples** |
|---|---|---|---|
| Solid | Solid | Solid sol | Some coloured glasses and gem stones |
| Solid | Liquid | Sol | Paints, cell fluids |
| Solid | Gas | Aerosol | Smoke, dust |
| Liquid | Solid | Gel | Cheese, butter, jellies |
| Liquid | Liquid | Emulsion | Milk, hair cream |
| Liquid | Gas | Aerosol | Fog, mist, cloud, insecticide sprays |
| Gas | Solid | Solid sol | Pumice stone, foam rubber |
| Gas | Liquid | Foam | Froth, whipped cream, soap lather |

Many familiar commercial products and natural objects are colloids. For example, whipped cream is a foam, which is a gas dispersed in a liquid. Firefighting foams, used at emergency airplane landings are also colloidal systems. Most biological fluids are aqueous sols (solids dispersed in water). Within a typical cell, proteins and nucleic acids are colloidal-sized particles dispersed in an aqueous solution of ions and small molecules.

Out of the various types of colloids given in above table, the most common are **sols** (solids in liquids), gels (liquids in solids) and emulsions (liquids in liquids). However, in the present Unit, we shall take up discussion of the ‘sols’ and ‘emulsions’ only. Further, it may be mentioned that if the dispersion medium is water, the sol is called aquasol or hydrosol and if the dispersion medium is alcohol, it is called alcosol and so on.

**3.** Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, lyophilic (solvent attracting) and lyophobic (solvent repelling). If water is the dispersion medium, the terms used are hydrophilic and hydrophobic.

### Lyophilic colloids:

These are the colloidal solutions in which the particles of the dispersed phase have great affinity (love) for the dispersion medium. In case water acts as the dispersed phase, the lyophilic colloid is called hydrophilic colloid. These are generally stable due to the strong attractive forces operating between the two phases. These are reversible in nature. On evaporating the sol, the dispersed phase obtained can be easily reconverted into the solution by simply agitating it with the dispersion medium. Gums, gelatine and starch form lyophilic (hydrophilic) colloids.

**Lyophobic colloids:**

These are the colloidal solutions in which particles of the dispersed phase have no affinity for the dispersion medium. Such solutions are relatively less stable and are not easily prepared. These can be easily precipitated by heating the sol or on adding small amount of electrolyte to it. These are irreversible. The solid obtained by precipitation cannot be reconverted into colloidal solution by simply shaking it with the dispersion medium. Colloidal solutions of gold, silver, $Fe(OH)_3$, $As_2S_3$ etc. are lyophobic. Lyophobic sols need stabling agents for their preservation.

**4.** These are liquid-liquid colloidal systems, i.e., the dispersion of finely divided droplets in another liquid. If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called emulsion. Generally, one of the two liquids is water. There are two types of emulsions.

(i) Oil dispersed in water (O/W type) and

(ii) Water dispersed in oil (W/O type).

In the first system, water acts as dispersion medium. Examples of this type of emulsion are milk and vanishing cream. In milk, liquid fat is dispersed in water. In the second system, oil acts as dispersion medium. Common examples of this type are butter and cream. Emulsions of oil in water are unstable and sometimes they separate into two layers on standing. For stabilisation of an emulsion, a third component called emulsifying agent is usually added. The emulsifying agent forms an interfacial film between suspended particles and the medium. The principal emulsifying agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc., and for W/O, heavy metal salts of fatty acids, long chain alcohols, lampblack, etc. Emulsions can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed, forms a separate layer. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes. They also show Brownian movement and Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

**5.** A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle centre. This phase is caused by the packing behavior of single-tailed lipids in a bilayer. The difficulty filling all the volume of the interior of a bilayer, while accommodating the area per head group forced on the molecule by the hydration of the lipid head group, leads to the formation of the micelle. This type of micelle is known as a normal phase micelle (oil-in-water micelle). Inverse micelles have the head groups at the centre with the tails extending out (water-in-oil micelle). Micelles are approximately spherical in shape. Other phases, including shapes such as ellipsoids, cylinders, and bilayers, are also possible. The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micelles is known as micellisation and forms part of the Phase behaviour of many lipids according to their polymorphism.

**6.** The viscosity method, is introduced by Staudinger, is the one most commonly employed in research. Accurate measurement of absolute viscosity being difficult, it is convenient to measure relative viscosity, $\eta_{rel}$, defiend as:

$$\eta_{rel} = \eta / \eta_o \qquad (1)$$

Where $\eta$ and $\eta_o$ are, respectively, the viscosity of the solution and the viscosity of the solvent. The relative viscosity is related to some other quantities as follows:

$$\eta_{sp} = \eta_{rel} - 1 \qquad (2)$$

$$\eta_{red} = \eta_{sp} / c \qquad (3)$$

$$[\eta] = \lim_{c \to 0} =(\eta sp / c) \qquad (4)$$

Where $\eta_{sp}$ is specific viscosity, $\eta_{red}$ is reduced viscosity and $[\eta]$ is intrinsic viscosity (also called the viscosity number or Staudinger index). In these equations, c is the concentration of the polymer. Note that none of these quantities has the unit of viscosity.

In 1906, Einstein derived the following relation between the viscosity of a dilute suspension of hard spherical molecules and the volume fraction, $\phi$, of the solute molecules:

$$\eta = \eta_o (1+2.5\ \phi) \qquad (5)$$

Rearrangement of Eq. 5 gives

$$\eta / \eta_o - 1 = \eta_{sp} = 2.5\ \phi \qquad (6)$$

Hence, from Eqs. 4 and 6,

$$[\eta] = \lim_{c \to 0} = \left(\frac{\eta_{sp}}{c}\right) = \left(\frac{2.5\Phi}{c}\right) \qquad (7)$$

It is, however, very difficult to measure $\phi$, the volume fraction of the polymer molecules in solution. The plots of $\eta_{sp}$/ c and ln $\eta_{red}$/ c versus c give straight lines which confirm to the following equations:

$$\text{Huggin's equation: } \eta_{sp}/ c = [\eta] + k''[\eta]^2 c \qquad (8)$$

$$\text{Kraemer's equation: } \ln v_{red}/ c = [\eta] - k'[\eta]^2 c \qquad (9)$$

Both these equations are applicable only in dilute solutions. For many polymers, $k' = 0.4 \pm 0.1$ and $k'' = 0.50 \pm 0.05$.

Fortunately, Staudinger found, in 1950, that for a series of a sample of the same polymer in a given solvent and at a constant temperature, the intrinsic viscosity (or the viscosity number) is related to the molar mass of the polymer by the following equation, known as Mark-Kuhn-Houwink-Sakurda equation, formerly called Staudinger equation:

$$[\eta] = K\,\overline{M}_V^{\,a} \qquad (10)$$

where $\overline{M}_V$ is the viscosity- average molar mass of the polymer and K and a are constants, usually determined by intrinsic viscosity measurements on a series of polymer samples for which the molar mass has been determined by a different method, say, the light scattering method. The value of the exponent a depends upon the geometry or the shape of the macromolecules. The more elongated a molecule, the more effective of the higher molar mass fraction in reducing the viscosity of the solution. The value of a vary from 0.5 to 1. For polymers behaving as random coils, a is about 0.8 and the globular proteins possessing a compact structure, it is about 0.5. Note that $[\eta]$ has the dimensions of reciprocal density and hence its units are $\mathrm{cm^3\ g^{-1}}$.

Taking logs of both sides of Eq. 10, we have

$$\ln[\eta] = \ln K + a \ln \overline{M}_V \qquad (11)$$

Eq. 11 shows that a log – log plot of $[\eta]$ versus $\overline{M}_V$ gives a straight line with slope equal to *a* and intercept equal to log *K*. Thus, the constant *a* and *K* can be easily determined. Knowing the values of *a* and *K*, the viscosity- average molar mass $\overline{M}_V$ can be determined from intrinsic viscosity measurements.

## Reference Books

1. Physical chemistry of macromolecules: basic principles and issues (2nd Edition) by Sun, S.F., Hoboken, N.J. : John Wiley & Sons.
2. Physical Chemistry by Gordon M. Barrow; Mc-Graw Hill.
3. Atkins' Physical Chemistry by Peter Atkins & Julio De Paula; Oxford University Press.
4. Physical chemistry (4th Edition) by Silbey, Robert J., Alberty, Robert A., Bawendi, Moungi G., Hoboken, NJ: Wiley.
5. Physical chemistry by Ball, David W., Australia: Thomson, Brooks/Cole.

# UNIT 5 SURFACE CHEMISTRY

## Structure

## 5.1 Introduction

Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface or surface is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas. Due to complete miscibility, there is no interface between the gases. The bulk phases that we come across in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends on the size of the particles of bulk phases. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

To accomplish surface studies meticulously, it becomes imperative to have a really clean surface. Under very high vacuum of the order of $10^{-8}$ to $10^{-9}$ pascal, it is now possible to obtain ultra clean surface of the metals. Solid materials with such clean surfaces need to be stored in vacuum otherwise these will be covered by molecules of the major components of air namely dioxygen and dinitrogen.

### Objective

After studying this Unit, you will be able to

- describe interfacial phenomenon and its significance;
- define adsorption and classify it into physical and chemical adsorption;
- explain mechanism of adsorption;
- explain the factors controlling adsorption from gases and solutions on solids;
- explain the Freundlich adsorption isotherms;
- explain the Langmuir adsorption isotherm;
- explain the Gibbs adsorption equation;

- explain the BET equation;
- explain the determination of surface area;

## 5.2 Adsorption

There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. The molecular species or substance, which concentrates or accumulates at the surface is termed adsorbate and the material on the surface of which the adsorption takes place is called adsorbent. Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents.

**Adsorption in action**

1. If a gas like $O_2$, $H_2$, CO, $Cl_2$, $NH_3$ or $SO_2$ is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.
2. In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.
3. Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.
4. The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by virtue of adsorption. The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.

## 5.3 Distinction between Adsorption and Absorption

In adsorption, the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent, while in absorption, the substance is uniformly distributed throughout the bulk of the solid. For example, when a chalk stick is dipped in ink, the surface retains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption. On breaking the chalk stick, it is found to be white from inside. A distinction can be made between absorption and adsorption by taking an example of water vapour. Water vapours are absorbed by anhydrous calcium chloride but adsorbed by silica gel. In other words, in adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid. Both adsorption and absorption can take place simultaneously also. The term sorption is used to describe both the processes.

## 5.4 Mechanism of Adsorption

Adsorption arises due to the fact that the surface particles of the adsorbent are not in the same environment as the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides, and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface.The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words, $\Delta H$ of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to decrease in the entropy of the gas after adsorption, i.e., $\Delta S$ is negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, $\Delta G$ must be negative, i.e., there is a decrease in Gibbs energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, $\Delta G$ can be negative if $\Delta H$ has sufficiently high negative value as $-T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes $\Delta G$ negative. As the adsorption proceeds, $\Delta H$ becomes less and less negative ultimately $\Delta H$ becomes equal to $T\Delta S$ and $\Delta G$ becomes zero. At this state equilibrium is attained.

## 5.5 Types of Adsorption

There are mainly two types of adsorption of gases on solids. If accumulation of gas on the surface of a solid occurs on account of weak van der Waals’ forces, the adsorption is termed as physical adsorption or physisorption. When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed chemical adsorption or chemisorption. The chemical bonds may be covalent or ionic in nature. Chemisorption involves a high energy of activation and is, therefore, often referred to as activated adsorption. Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, dihydrogen is first adsorbed on nickel by van der Waals’ forces. Molecules of hydrogen then dissociate to form hydrogen atoms which are held on the surface by chemisorption. Some of the important characteristics of both types of adsorption are described below:

**Characteristics of physisorption**

1. **Lack of specificity:** A given surface of an adsorbent does not show any preference for a particular gas as the van der Waals’ forces are universal.
2. **Nature of adsorbate:** The amount of gas adsorbed by a solid depends on the nature of gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed as van der Waals’ forces are stronger near the critical temperatures. Thus, 1g of activated charcoal adsorbs more sulphur dioxide (critical temperature 630K), than methane (critical temperature 190K) which is still more than 4.5 mL of dihydrogen (critical temperature 33K).
3. **Reversible nature:** Physical adsorption of a gas by a solid is generally reversible. Thus, Solid + Gas l Gas/Solid + Heat

More of gas is adsorbed when pressure is increased as the volume of the gas decreases (Le–Chateliers's principle) and the gas can be removed by decreasing pressure. Since the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increasing temperature (Le-Chatelier's principle).

4. **Surface area of adsorbent:** The extent of adsorption increases with the increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.
5. **Enthalpy of adsorption:** No doubt, physical adsorption is an exothermic process but its enthalpy of adsorption is quite low (20– 40 kJ mol-1). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals' forces.

**Characteristics of chemisorption**

1. **High specificity:** Chemisorption is highly specific and it will only occur if there is some possibility of chemical bonding between adsorbent and adsorbate. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.
2. **Irreversibility:** As chemisorption involves compound formation, it is usually irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, adsorption often increases with rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually high pressure is also favourable for chemisorption.
3. **Surface area:** Like physical adsorption, chemisorption also increases with increase of surface area of the adsorbent.
4. **Enthalpy of adsorption:** Enthalpy of chemisorption is high (80-240 kJ mol-1) as it involves chemical bond formation.

## 5.6 Difference between Physisorption and Chemisorption

| **Physisorption** | **Chemisorption** |
|---|---|
| **1.** It arises because of van der Waals' forces. | **1.** It is caused by chemical bond formation. |
| **2.** It is not specific in nature. | **2.** It is highly specific in nature. |
| **3.** It is reversible in nature. | **3.** It is irreversible. |
| **4.** It depends on the nature of gas. More easily liquefiable gases are adsorbed readily. | **4.** It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption. |
| **5.** Enthalpy of adsorption is low (20-40 kJ mol–$^{1}$ )in this case. | **5.** Enthalpy of adsorption is high (80-240 kJ mol–$^{1}$) in this case. |
| **6.** Low temperature is favourable for adsorption. It decreases with increase of temperature. | **6.** High temperature is favourable for adsorption. It increases with the increase of temperature. |
| **7.** No appreciable activation energy is needed. | **7.** High activation energy is sometimes needed. |
| **8.** It depends on the surface area. It increases with an increase of surface area. | **8.** It also depends on the surface area. It too increases with an increase of surface area. |

|  |  |
|---|---|
| **9.** It results into multimolecular layers on adsorbent surface under high pressure. | **9.** It results into unimolecular layer. |

## 5.7 Freundlich adsorption isotherm

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm.

Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation:

$$\frac{X}{m} = k.p^{1/n} \; (n > 1) \qquad (1)$$

where $x$ is the mass of the gas adsorbed on mass $m$ of the adsorbent at pressure $P$, $k$ and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature. The relationship is generally represented in the form of a curve where mass of the gas adsorbed per gram of the adsorbent is plotted against pressure (Fig. 5.1). These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.

Taking logarithm of eq. (1)

$$\log \frac{X}{m} = \log k + \frac{1}{n} \log p \qquad (2)$$

The validity of Freundlich isotherm can be verified by plotting log $\frac{X}{m}$ on $y$-axis (ordinate) and log $p$ on x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid, otherwise not (Fig. 5.2). The slope of the straight line gives the value of $\frac{1}{n}$. The intercept on the $y$-axis gives the value of log $k$. Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor $\frac{1}{n}$ can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation (2) holds good over a limited range of pressure.

When $\frac{1}{n} = 0$, $\frac{X}{m}$ = constant, the adsorption is independent of pressure.

When $\frac{1}{n} = 1$, $\frac{X}{m} = k\,p$, i.e. $\frac{X}{m} \propto p$, the adsorption varies directly with pressure.

Both the conditions are supported by experimental results. The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.

### 5.7.1 Adsorption from Solution Phase

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution. Similarly, the litmus solution when shaken with charcoal becomes colourless. The precipitate of Mg(OH)2 attains blue colour when precipitated in presence of magneson reagent. The colour is due to adsorption of magneson. The following observations have been made in the case of adsorption from solution phase:

(i) The extent of adsorption decreases with an increase in temperature.

(ii) The extent of adsorption increases with an increase of surface area of the adsorbent.

(iii) The extent of adsorption depends on the concentration of the solute in solution.

(iv) The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

The precise mechanism of adsorption from solution is not known. Freundlich's equation approximately describes the behaviour of adsorption from solution with a difference that instead of pressure, concentration of the solution is taken into account, i.e.,

$$\frac{X}{m} = k\,C^{1/n} \qquad (3)$$

($C$ is the equilibrium concentration, i.e., when adsorption is complete). On taking logarithm of the above equation, we have

$$\log \frac{X}{m} = \log k + \frac{1}{n} \log \qquad (4)$$

Plotting log $\frac{X}{m}$ against log $C$ a straight line is obtained which shows the validity of Freundlich isotherm. This can be tested experimentally by taking solutions of different concentrations of acetic acid. Equal volumes of solutions are added to equal amounts of charcoal in different flasks. The final concentration is determined in each flask after adsorption. The difference in the initial and final concentrations give the value of $x$. Using the above equation, validity of Freundlich isotherm can be established.

### 5.7.2 Applications of Adsorption

The phenomenon of adsorption finds a number of applications. Important ones are listed here:

1. Production of high vacuum: The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.
2. Gas masks: Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.
3. Control of humidity: Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

4. Removal of colouring matter from solutions: Animal charcoal removes colours of solutions by adsorbing coloured impurities.
5. Heterogeneous catalysis: Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of $H_2SO_4$ by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.
6. Separation of inert gases: Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.
7. In curing diseases: A number of drugs are used to kill germs by getting adsorbed on them.
8. Froth floatation process: A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent.
9. Adsorption indicators: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.
10. Chromatographic analysis: Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

## 5.8 Langmuir Adsorption Isotherm

In 1916 Langmuir proposed this theory of adsorption of a gas on the surface of solid. He considered the surface of the solid to be made up of elementary sites of which could adsorb one gas molecule. It is assumed that all adsorption sites are equivalent and the ability of the gas molecule to get bound to any one site is independent of whether or not the neighbouring sites are occupied. It is further assumed that a dynamic equilibrium exist between the adsorbed molecules and the free molecules. If A is the gas molecule and M is the surface sites, then

$$A_{(g)} + M(\text{surface}) \underset{k_d}{\overset{k_a}{\rightleftarrows}} AM$$

Where $k_a$ and $k_d$ are the rate constants for adsorption and desorption, respectively. The rate of adsorption is proportional to the pressure of A, viz., $p_A$ and the number of vacant sites on the surface, Viz., $N(1 - \theta)$ where N is the total number of sites and $\theta$ is the fraction of surface sites occupied by the gas molecules, i.e.,

$$\theta = \frac{\text{Number of adsorption sites ocupied}}{\text{Number of adsorption sites available}}$$

Thus, the rate of adsorption = $k_a \, p_A \, N(1 - \theta)$ (1)

The rate of desorption is proportional to the adsorbed molecules, $N\,\theta$.

Thus, the rate of desorption = $k_d \, N \, \theta$ (2)

Since, at equilibrium, the rate of adsorption is equal to the rate of desorption, we can write from equation 1 and 2,

$k_a p_A N(1-\theta) = k_d N \theta$ (3)

or $Kp_A(1-\theta) = \theta$ (4)

where $K = k_a/k_d$

Eq. 4 may, thus, be written as

$$\frac{1-\theta}{\theta} = \frac{1}{Kp_A} \quad (5)$$

or $$\frac{1}{\theta} - 1 = \frac{1}{Kp_A} \quad (6)$$

$$\frac{1}{\theta} = \frac{1}{Kp_A} + 1 = \frac{1+Kp_A}{Kp_A} \quad (7)$$

Hence, $$\theta = \frac{Kp_A}{1+Kp_A} \quad (8)$$

Eq. 8 is called the Langmuir adsorption isotherm.

The following five assumptions are involve in the derivation of the Langmuir adsorption isotherm:

1. The adsorbed gas behaves ideally in the vapour phase.
2. Only a monolayer is formed by the adsorbed gas.
3. The surface of the solid is homogeneous so that each binding sites has the same affinity for the gas molecules.
4. There is no lateral interaction between the adsorbate molecules.
5. The adsorbate gas molecules are localized, i.e., they do not move around on the surface.

The first assumption holds at low pressure; the second assumption breaks down when the pressure of the gas is increased. The third assumption is not strictly true because the real surfaces are quite heterogeneous so that affinity for gas molecules is different at different sites. Crystal imperfection and cracks lead to the creation of different sites on the surface. The fourth and fifth assumptions, too, are not strictly valid.

Now let us consider Eq. 8. At low pressures, $Kp_A \ll 1$ so that

$\theta = Kp_A$ (9)

i.e., the fraction of the surface covered is directly proportional to the partial pressure of the gas molecules. This behaviour corresponds to first order reaction and is depicted by the initial steep rise of the isotherm.

At high pressure, $Kp_A \gg 1$ so that Eq. 8 reduces to

$\theta = 1$ (10)

Thus, at high pressure, the value of θ tends to become unity, i.e., the entire surface gets covered by a monomolecular layer of the gas there by making the reaction rate independent of the pressure. In other words the reaction becomes zero order.

## 5.9 BET theory

The Langmuir theory of adsorption is restricted to the formation of a monomolecular layer of the gas molecules on the solid surface and disregards the possibility that multilayer adsorption may also take place. The theory of adsorption proposed in1938 by Stephen Brunauer, Paul Emmet and Edward Teller and is called BET isotherm. This isotherm derived by them successfully accounts for all types of adsorption.

It assumes that the surface possesses uniform, localised sites and that adsorption on one site does not affect adsorption on neighbouring sites just as in Langmuir theory. Also, molecules can be adsorbed in second, third,… and $n^{th}$ layers with the surface available for layer equal to the coverage of the next lower layer.

The rate constants for adsorption and desorption of the primary layer are $k_a$ and $k_d$ and those of the subsequent layers are all $k_a\,'$ and $k_d\,'$. The number of sites corresponding to zero, monolayer, bilayer, … coverage at any stage are $N_0$, $N_1$, $N_2$, etc. and $N_i$ in general. The condition for equilibrium of the initial layer is the equality of the rates of its formation and desorption,

$$k_a pN_0 = k_d N_1 \qquad (1)$$

**The condition for equilibrium of the next layer is**

$$k'_a pN_1 = k'_d N_2 \text{ and in general } k'_a pN_{i-1} = k'_d N_i\,, \quad i = 2,\ 3, \ldots.$$

This condition may be expressed in terms of $N_0$ as follows:

$$N_i = \left(\frac{k'_a}{k'_d}\right) pN_{i-1}$$

$$= \left(\frac{k'_a}{k'_d}\right)^2 p^2 N_{i-2} \quad = \left(\frac{k'_a}{k'_d}\right)^{2-1} p^{i-1}.N_1 \quad = \left(\frac{k'_a}{k'_d}\right)^{i-1}\left(\frac{k_a}{k_d}\right) p^i N_0$$

$$N_i = \left(\frac{k'_a}{k'_d}\right)^{i-1}\left(\frac{k_a}{k_d}\right) p^i N_0 \qquad (2)$$

writing $\frac{k'_a}{k'_d} = x$ and $\frac{k_a}{k_d} = cx$, then

$$N_i = x^{i-1} cxp^i \ N_0$$

$$N_i = c(xp)^i N_0 \qquad (3)$$

Now, we calculate the total volume, V, of adsorbed material. V is proportional to the total number of particles adsorbed, and so

$$V = N_1 + 2N_2 + 3N_3 + .... = \sum_{i=1}^{\infty} iN_i \qquad (4)$$

Because each layer contributes number of particles according to its thickness, i.e., a monolayer one particle, a bilayer site two particles etc.

If there were complete monolayer coverage the volume adsorbed would be $V_{mono}$, with

$$V_{mono} = N_0 + N_1 + N_2 + ... = \sum_{i=1}^{\infty} N_i \qquad (5)$$

Because each site contributes only one particle to the total it follows then

$$V = \sum_{i=0}^{\infty} iN_i = \sum_{i=1}^{\infty} ic(xp)^i N_0$$

$$= cN_0 \sum_{i=1}^{\infty} i(xp)^i$$

$$= cN_0 xp \sum_{i=1`}^{\infty} i(xp)^{i-1}$$

$$= cN_0 xp \frac{1}{(1-xp)^2}$$

$$V = cN_0 xp(1-xp)^{-2} \qquad (6)$$

From equation (5),

$$V_{mono} = \sum_{i=0}^{\infty} N_i = N_0 + N_1 + N_2 + ...$$

$$= N_0 + \sum_{i=1}^{\infty} N_i$$

$$= N_0 + \sum_{i=1}^{\infty} c(xp)^i N_0$$

$$= N_0 + \frac{cN_0 xp}{1-xp}$$

$$= N_0 + cN_o xp\left(1 + xp + (xp)^2 + ...\right) \qquad (7)$$

$$\because (1-xp)^{-1} = 1 + xp + (xp)^2 + ...$$

From equation (6) and (7 ), we have

$$\frac{V}{V_{mono}} = \frac{cN_0xp(1-xp)^{-2}}{N_0 + cN_0xp(1-xp)^{-1}} \tag{8}$$

$$= \frac{cxp}{1+(c-2)xp+(1-c)(xp)^2}$$

$$= \frac{c(p/p*)}{1+(c-2)p/p*+(1-c)p^2/p*^2}$$

$$= \frac{cz}{1+(c-2)z+(1-c)z^2} \tag{9}$$

$$x = \left(\frac{K'_a}{k'_d}\right) = \frac{1}{p*},$$

p* = equilibrium pressure, (ads) $\Leftrightarrow$ vapour

putting $z = p/p*$

$$\frac{V}{V_{mono}} = \frac{cz}{1+cz-2z+z^2-cz^2} = \frac{cz}{(1-z)\{1-(1-c)z\}} \tag{10}$$

$$= \frac{c.p/p*}{(1-p/p*)\{(1-1+c)p/p*\}}$$

$$= \frac{c.p/p^p}{(1-p/p*)\left[1+(c-1)p/p^o\right]}$$

$$\frac{V}{(z/(1-z))} = \frac{V_{mono}c}{1(1-c)z}$$

$$\frac{V}{(z/(1-z))} = \frac{V_{mono}c}{1(1-c)z}$$

$$\frac{z}{(1-z)}.\frac{1}{V} = \frac{1}{cV_{mono}} + \frac{(c-1)z}{cV_{mono}} \tag{11}$$

$\frac{(c-1)}{cV_{mono}}$ can therefore be obtained from the slope of a plot of $\frac{z}{(1-z)V}$ against z, and $cV_{mono}$ can be found from the intercept at z=0, the result being combined to give c and $V_{mono}$ from the corresponding value of $V_{mono}$ at 273 K and 1 atm, number of molecules present in $V_{mono}$ could be calculated. By knowing the contact area of a molecule, surface area of the adsorbent per unit mass could be determined.

## 5.10 Determination of surface area

Knowing $v_{\text{mono},}$ the surface area of the adsorbent can be easily calculated. The assumption is that the molecules of the gas adsorbed in the first layer are closely packed on the surface.

The area of cross section *a* of the molecule can be determined from the density of the liquefied or solidified adsorbate. Thus, if $\rho$ is the density and *M* is the molar mass of the adsorbate, then the volume *v* occupied by a single molecule, assuming the adsorbate to be closely packed with no void volume, is obtained as follows:

$$\rho = M / V = M / (N_A v)$$

$$v = M / (N_A \rho)$$

Assuming the molecule to be spherical with radius *r*, we have

$$v = (4/3)\pi r^3 = M / (N_A \rho) \qquad (1)$$

$$r = \left( \frac{3M}{4\pi N_A \rho} \right)^{1/3} \qquad (2)$$

$$a = \pi r^2 = \pi \left( \frac{3M}{4\pi N_A \rho} \right)^{2/3} \qquad (3)$$

Eq. 3 is only approximate for calculating the area of cross- section of a molecule since it does not take into account the nature of packing at the surface of the adsorbent. Also, the presence of void volume in the crystal lattice has been ignored.

## 5.11 Gibbs adsorption equation

The concentration of a solute at the surface of a solution is, in generally, markedly different from that in bulk. If the surface tension of the solute is lower than that of the liquid, it tends to accumulate at the surface of the liquid thereby decreasing the surface tension (or the surface free energy per unit area) of the liquid. A quantitative treatment of the thermodynamics of adsorption of a solute at the surface of a liquid was given in 1878 by J. W. Gibbs, the greatest 19th century American mathematical physicist.

Considering a system having a plane interface between them the Gibb's free energy of a system containing two components could be written as follows:

$$G = n_1\mu_1 + n_2\mu_2 \qquad (1)$$

Where $n_1$ and $n_2$ are the number of moles and $\mu_1$ and $\mu_2$ are the chemical potentials of the two components respectively. While dealing with the adsorption of one of the components on the surface of another, an additional term of surface energy has to be introduced, and hence, equation (1) modifies to

$$G = n_1\mu_1 + n_2\mu_2 + \gamma\sigma \qquad (2)$$

where $\gamma$ is the surface energy per unit area and $\sigma$ is the surface area. It is now clear that equation (1) is for bulk while equation (2) will be applicable for the surface of the absorbent liquid. The complete differential of (2) may be written as

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \gamma d\sigma + \sigma d\gamma \qquad (3)$$

We find that the total free energy G of the whole system depends on independent variables , namely , T,P,$n_1$,$n_2$ and $\sigma$, thus,

$$G = f(T, P, n_1, n_2, \sigma)$$

and complete differential of G will be,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2,\sigma} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\sigma} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,\sigma} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,\sigma} dn_2 + \left(\frac{\partial G}{\partial \sigma}\right)_{T,P,n_1,n_2} d\sigma$$

or $$dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma \qquad (4)$$

At constant temperature and pressure, above equation reduces to,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma \qquad (5)$$

Comparing equation (3) and (5), we get

$$n_1 d\mu_1 + n_2 d\mu_2 + \sigma d\gamma = 0 \qquad (6)$$

A corresponding equation for the bulk of the system may be,

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0 \qquad (7)$$

Where $n_1^0$ and $n_2^0$ are the number of moles of adsorbent liquid and solute in the bulk. From the equation (6) and (7), we get

$$-\frac{d\gamma}{d\mu_2} = \frac{(n_2 - n_1 n_2^0 / n_1^0)}{\sigma} \qquad (8)$$

Here, the term $\frac{(n_2 - n_1 n / n_1^0)}{\sigma}$ represents the corresponding excess moles of solute per unit area on the surface of the adsorbent and now be represented by $\Gamma_2$

$$\therefore \qquad -\frac{d\gamma}{d\mu_2} = \Gamma_2$$

The chemical potential of solute $\mu_2 = \mu_2^0 +$ RT $ln\ a_2$

or $d\mu_2 =$ RTd $ln\ a_2$

When solution is very dilute activity $a_2$ of solute could be replaced by its concentration.

$$\therefore \qquad \Gamma_2 = -\frac{c_2}{RT}\left(\frac{d\gamma}{\partial c_2}\right)_T$$

or, in general for any solute and liquid adsorbent,

$$\Gamma = -\frac{c}{RT}\left(\frac{\partial \gamma}{\partial c}\right)_T \qquad (9)$$

In the above equation $\gamma$ is essentially surface energy per unit area, which may easily be replaced by surface tension (force/length).

The application of the above equation is as follows. If the detergent (solute or adsorbate) tends to accumulate at the interface its surface excess is positive, and so $\frac{d\gamma}{dc}$ is negative. This means surface tension decreases when a solute accumulates at the surface.

## 5.12 Summary

In this unit you have studied about the surface chemistry, we began by distinguishing between physisorption and chemisorption and also between monolayer adsorption and multiplayer adsorption. The binding energies in physisorption are much smaller and in the range of 8 to 25 kJ/ mole. A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm. We have outlined the main ingredients of some important isotherms such as the adsorption isotherms of Gibbs, Freundlich and Langmuir. A multiplayer adsorption was characterized through the BET isotherm. The heat of a reaction was obtained using an adsorption. We also outlined the mechanisms of unimolecular and bimolecular reactions at surfaces.

## 5.13 Terminal Question

**1.** What is the difference between physisorption and chemisorption?
**2.** What is an adsorption isotherm? Describe Freundlich adsorption isotherm.
**3.** The surface tension of the dilute solution of phenol in water at $27^oC$ were the following:

| | | | | | |
|---|---|---|---|---|---|
| Mass % phenol | 0.024 | 0.05 | 0.125 | 0.25 | 0.40 |
| $\gamma$ x $10^3/(Nm^{-1})$ | 72.7 | 72.2 | 71.3 | 70.3 | 69.3 |

Calculate surface excess concentration ( $\Gamma$) at a concentration of 0.15 mass of phenol. Comment on the significance of the observed value of $\Gamma$.

**4.** The volume of $CH_4$ (corrected to STP) adsorbed per gram of charcoal at 240 K various pressures of $CH_4$ is:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| P/(Torr) | 38 | 55 | 78 | 104 | 133 | 173 | 218 |
| $V/(cm^3.g^{-1})$ | 14.14 | 17.52 | 21.38 | 24.72 | 28.00 | 31.35 | 34.50 |

Verify that the data obey Langmuir adsorption isotherm. Also determine Langmuir constant $K_L$ and the volume corresponding to complete surface coverage. Calculate the fraction of charcoal surface which is covered by $CH_4$ molecules at P=150 torr.

**5.** What are the applications of adsorption in in domestic as well as in industrial processes?

## 5.14 Answers

**1.** Difference between Physisorption and Chemisorption

| **Physisorption** | **Chemisorption** |
|---|---|
| 1. It arises because of van der Waals' forces. | 1. It is caused by chemical bond formation. |
| 2. It is not specific in nature. | 2. It is highly specific in nature. |
| 3. It is reversible in nature. | 3. It is irreversible. |
| 4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily. | 4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption. |
| 5. Enthalpy of adsorption is low (20-40 kJ mol–$^1$ )in this case. | 5. Enthalpy of adsorption is high (80-240 kJ mol–$^1$) in this case. |
| 6. Low temperature is favourable for adsorption. It decreases with increase of temperature. | 6. High temperature is favourable for adsorption. It increases with the increase of temperature. |
| 7. No appreciable activation energy is needed. | 7. High activation energy is sometimes needed. |
| 8. It depends on the surface area. It increases with an increase of surface area. | 8. It also depends on the surface area. It too increases with an increase of surface area. |
| 9. It results into multimolecular layers on adsorbent surface under high pressure. | 9. It results into unimolecular layer. |

**2.** The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm.

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm. Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation:

$$\frac{X}{m} = k.p^{1/n} \ (n > 1) \qquad (1)$$

where *x* is the mass of the gas adsorbed on mass *m* of the adsorbent at pressure *P*, *k* and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature. The relationship is generally represented in the form of a curve where mass of the gas adsorbed per gram of the adsorbent is plotted against pressure (Fig. 5.1). These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.

Taking logarithm of eq. (1)

$$\log \frac{X}{m} = \log k + \frac{1}{n} \log p \qquad (2)$$

The validity of Freundlich isotherm can be verified by plotting log $\frac{X}{m}$ on *y*-axis (ordinate) and log *p* on x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid, otherwise not (Fig. 5.2). The slope of the straight line gives the value of $\frac{1}{n}$. The intercept on the $y$-axis gives the value of log $k$. Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor $\frac{1}{n}$ can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation (2) holds good over a limited range of pressure.

When $\frac{1}{n} = 0$, $\frac{X}{m}$ = constant, the adsorption is independent of pressure.

When $\frac{1}{n} = 1$, $\frac{X}{m} = k\,p$, i.e. $\frac{X}{m} \propto p$, the adsorption varies directly with pressure.

Both the conditions are supported by experimental results. The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.

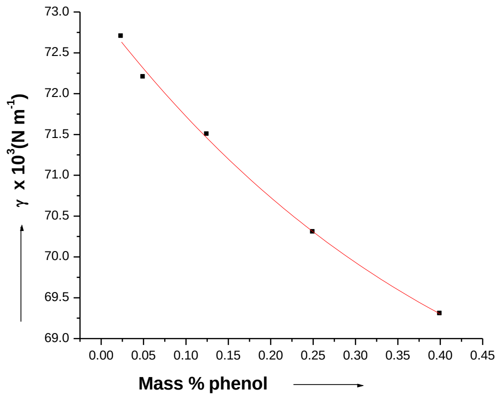
**3.** A plot of $\gamma$ us mole of phenol gives a curvature with negative slope for 0.15 mol of phenol slope is $-\frac{1.7}{0.1875}$, putting values in equation,

$$\Gamma = -\frac{C}{RT}\left(\frac{\partial \gamma}{\partial c}\right)_T$$

$$\text{We get,} \quad \Gamma = -\frac{0.15}{8.31x300^0 k}\left(-\frac{1.7}{0.1875}\right)$$

$$= \ 5.45 \text{ x } 10^{-4} \text{ mol m}^{-2}$$

The positive value of $\Gamma$ signifies that phenol is surface active and accumulates at the interface.



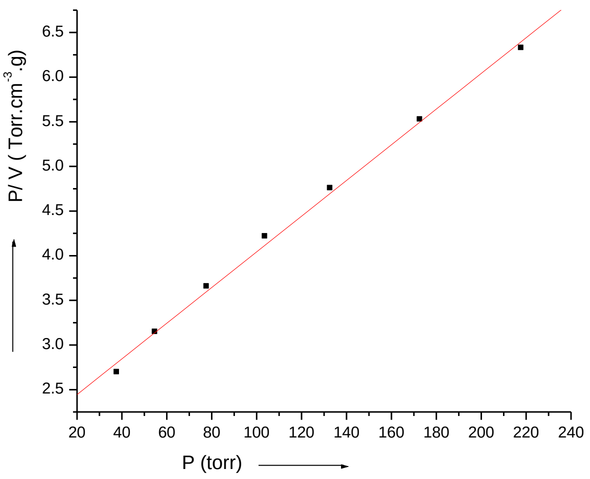
**4.** Plot of p/v vs p as shown below is linear which shows that the data verify the Langmuir monolayer adsorption isotherm.

$$\frac{p}{V} = \frac{p}{V_m} + \frac{1}{K_L V_m}$$

Slope of the curve =0.02 cm$^{-3}$.g

$$\therefore V_m = \frac{1}{slope} = \frac{1}{0.02cm^{-3}g} = 50.0cm^3g^{-1}$$

intercept =2.05 torr cm$^{-3}$ g = $\frac{1}{K_L V_m}$



$$\therefore K_L = \frac{1}{V_m \times intercept} \quad K_L = \frac{1}{(50.0cm^3g^{-1})(2.05\mathrm{torr}\,cm^{-3}g)}$$

$=9.75 \text{ x } 10^{-3}$ torr$^{-1}$

Fraction of the surface covered ($\theta$)

at P=150 torr,

$$\Theta = \frac{K_L p}{1 + K_L p}$$

$$= \frac{(9.75x10^{-3}torr^{-1})(150torr)}{1+(9.75x10^{-3}torr^{-1})(150torr)}$$

$\theta$ = 0.593 $\Rightarrow$ 59.3% of the surface is covered by $CH_4$ molecules.

**5.** The process of adsorption is very important as it has many applications in domestic as well as in industrial processes, to name some of them are follows:

i. **In heterogeneous catalysis:** Surface active material are widely used as catalyst mostly due to adsorption processes. If the surface active materials (adsorbents) have different phase with that of substrates, then the catalysis is called heterogeneous catalysis. A system where both the catalyst and substrate are in same phase is called homogeneous catalysis.

ii. **In removal of colouring material:** Many coloured materials or impurities are removed through adsorption by suitable surface active materials like charcoal. Activated charcoal has been extensively used for this purpose.

iii. **In ion exchange resins:** Several polymeric materials are used for the separation of ionic substances in chromatography through ion-exchange.

iv. **In adsorption indicators:** Several dyes like eosin and fluoresein are used as indicators in the titrations of $Cl^-$, $Br^-$ etc. against $Ag^+$(Fajan's method).

v. **In gas masks**: Activated charcoal is used to remove toxic gases in gas masks.

vi. **In dyeing of cloth:** Many substances work as mordants for dyeing of cloths. Several metal cyanogen complexes, alums work as efficient mordants in dyeing cloths.

vii. **In de humidizers:** Many substances when they adsorb water change their colour. Silica and alumina gels are used as adsorbents for removing moisture. Silica is colourless but after adsorbing water becomes blue. Silica is colourless but after adsorbing water becomes blue.

## Reference Books

6. Physical chemistry of macromolecules: basic principles and issues (2nd Edition) by Sun, S.F., Hoboken, N.J. : John Wiley & Sons.
7. Physical Chemistry by Gordon M. Barrow; Mc-Graw Hill.

8. Atkins’ Physical Chemistry by Peter Atkins & Julio De Paula; Oxford University Press.
9. Physical chemistry (4th Edition) by Silbey, Robert J., Alberty, Robert A., Bawendi, Moungi G., Hoboken, NJ: Wiley.
10. Physical chemistry by Ball, David W., Australia: Thomson, Brooks/Cole.

# UNIT 6 PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

## Structure

## 5.1 Introduction

The physical properties of a substance are those properties that can be observed and measured without changing the composition of the substance. Physical properties include odor, color, density, solubility, boiling point, and melting point. Because they depend on there being no change in composition, physical properties can be used to describe and identify substances. A colorless, odorless liquid that freezes at 0°C is probably water, for example. The chemical properties of a substance are those properties that can only be observed when the substance is undergoing a change in composition. The fact that hydrogen peroxide decomposes to give oxygen gas and water is an example of a chemical property.

### Objective

After studying this Unit, you will be able to

- Describe molar volume;
- explain parachor;
- explain the molar refraction;
- explain the polarization;
- explain the dipole moment of molecule;
- explain the Debye equation;
- explain the Clausius-Mosotti equation;

## 5.2 Molar volume

The **molar volume**, symbol $V_m$, is the volume occupied by one mole of a substance (chemical element or chemical compound) at a given temperature and pressure. It is equal to the molar mass (M) divided by the mass density (ρ). It has the SI unit cubic metres per mole ($m^3/mol$), although it is more practical to use the units cubic decimetres per mole ($dm^3/mol$)

for gases and cubic centimetres per mole ($cm^3$/mol) for liquids and solids. It is an intensive quantity.

The molar volume of a substance can be found by measuring its molar mass and density then applying the relation

$$V_{\mathrm{m}} = \frac{M}{\rho}$$

If the sample is a mixture containing N components, the molar volume is calculated using:

$$V_{\mathrm{m}} = \frac{\sum_{i=1}^{N} x_i M_i}{\rho_{\mathrm{mixture}}}$$

For ideal gases, the molar volume is given by the ideal gas equation: this is a good approximation for many common gases at standard temperature and pressure. For crystalline solids, the molar volume can be measured by X-ray crystallography

The ideal gas equation can be rearranged to give an expression for the molar volume of an ideal gas:

$$V_{\mathrm{m}} = \frac{V}{n} = \frac{RT}{P}$$

**Crystalline solids**

The unit cell volume ($V_{cell}$) may be calculated from the unit cell parameters, whose determination is the first step in an X-ray crystallography experiment (the calculation is performed automatically by the structure determination software). This is related to the molar volume by

$$V_{\mathrm{m}} = \frac{N_{\mathrm{A}} V_{\mathrm{cell}}}{Z}$$

## 5.3 Parachor

Macleod in1823, showed that the equation

$$\gamma^{1/4} / (\rho - \rho') = C \qquad (1)$$

(where $\rho$ is the density of the liquid, $\rho'$ is the density of the saturated vapour of the liquid at the same temperature and $C$ a constant) holds good over a wide range of temperature. Multiplying both sides of equation by $M_{m,}$ the molar mass of the substance, we get

$$\gamma^{1/4} / (\rho - \rho') = M_m C = \text{constant} = [P] \qquad (2)$$

The constant [P] was called the parachor, by Sugden.

Since the density of the saturated vapour can be ignored in comparison with the density of the liquid, the Eq. 2 may be stated as

$$M_m \gamma^{1/4} / \rho = [P] \qquad (3)$$

Suppose, at a particular temperature, $\gamma = 1$. Then, since $M_m / \rho$ is molar volume, the above equation may be written as

$$[P] = \text{Molar volume} \qquad (4)$$

The parachor may, therefore, be defined as the molar volume of a liquid at a temperature at which its surface tension is unity.

The parachor has proved more useful than molar volume in deciding between different alternative structures of compounds. This is supported by the following observations:

1. The isomeric compounds of the same family of organic compounds (such as esters, alcohols, etc.) have almost same parachor. For example, there are six esters having the molecular formula $C_6H_{12}\ O_2$. There parachors, as shown in Table 1, are very close to one another.

**Table 1**

**Parachors of Esters of Formula $C_6H_{12}\ O_2$**

| Ester | Parachor | Esrer | Parachor |
|---|---|---|---|
| Methyl valerate | 292.5 | Iso-Amyl formate | 293.6 |
| Ethyl isobutyrate | 292.2 | Iso-Butyl acetate | 295.1 |
| Ethyl butyrate | 293.6 | n-Propyl propionate | 295.3 |

2. The difference between the parachors of successive numbers of different homologous series is about the same, as shown by hydrocarbons in Table 2.

**Table 2**

**Parachor of Paraffins**

| Paraffins | | Parachor | Difference | Parachor for one $CH_2$ group |
|---|---|---|---|---|
| Name | Formula | | | |
| Ethane | $C_2H_6$ | 110.5 | | |
| Propane | $C_3H_8$ | 150.8 | 40.3 | 40.3 |
| Hexane | $C_6H_{14}$ | 270.1 | 119.3 | 39.8 |
| Heptane | $C_7H1_6$ | 309.3 | 39.2 | 39.2 |
| Octane | $C_8H_{18}$ | 345.0 | 35.7 | 35.7 |
| Decane | $C_{10}H_{28}$ | 424.2 | 79.2 | 39.6 |

The average difference of corresponding to the parachor of the $CH_2$ group, from a similar study of several other homologous series (such as alcohols, ethers, esters, aldehydes ketones, etc.), has been found to be 39.0.

## 5.3.1 Atomic Parachors

Knowing that each - $CH_2$ has a parachor 39, while decane ($C_{10}H_{22}$) has a a prachor 424.2, it follows that

Since $C_{10}H_{22} = 10(CH_2) + 2H$

$\therefore$ $424.2 = 10 \times 39 + 2 \times$ atomic parachor of hydrogen

$\therefore$ Atomic parachor of hydrogen = $\frac{442-390}{2} = 17.1$

Atomic parachor of carbon = 39.0 – 34.2 = 4.8

Knowing atomic parachors of carbon and hydrogen, it has been possible to determine atomic parachors of other elements. For exemple, atomic parachor of oxygen has been obtained from ethers, that of nitrogen from amines and those of chlorine, bromine and iodine from the corresponding halides.

## 5.3.2 Structural Parachors

It was soon found that parachor, like molar volume, through largely an additive property, is partly a constitutive property as well. For instance, the parachor of ethylene ($C_2H_4$), which should be = $2 \times 4.8 + 4 \times 17.1 = 78.0$ is, in reality, 99.5. Thus, the double bond should make a contribution of 21.5. Further careful determinations in the case of unsaturated compounds containing ethylenic double bond have shown that each ethylenic double bond makes a contribution, on an average, of 23.2. Similarly, triple bond is known to make a contribution of 46.6. Some of the atomic and structural parachor are given in Table 3.

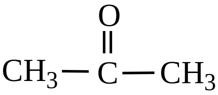
**Table 3 Atomic and Structural Parachors**

| Atoms | Parachor | Structure | Parachor |
|---|---|---|---|
| Carbon | 4.8 | Double bond | 23.2 |
| Hydrogen | 17.1 | Triple bond | 46.6 |
| Nitrogen | 12.5 | Dative bond | -1.6 |
| Oxygen | 20.0 | 3-membered ring | 16.7 |
| Chlorine | 54.3 | 4-membered ring | 11.6 |
| Bromine | 68.0 | 5-membered ring | 8.5 |
| Iodine | 90.0 | 6-membered ring | 6.1 |
| Sulphur | 48.2 | Naphthalene ring | 12.2 |
| Phosphorus | 37.7 | $O_2$ in esters | 60.0 |

## 5.3.3 Calculation of Parachors of Compounds

The parachor of compounds can be calculated with the help of the above table. One example is given below:

Parachor of acetone, It may be calculated as illustrated below:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

3C = 3 $\times$ 4.8 =14.4

6H = 6$\times$ 17.1 = 102.6

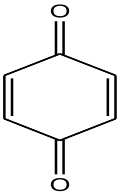
O = 1$\times$ 20.0 = 20.0

1 double bond = 1$\times$ 23.2 = 23.2

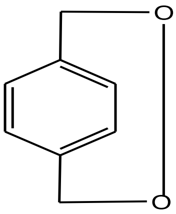
∴ Parachor of acetone = 160.2 (Observed value = 161.1)

## 5.3.4 Application of parachors in deciding structure

Since the structural factors, such as double and triple bonds, benzene ring, the nature of oxygen, etc. Make different contributions towards parachors, the latter may be used to decide, in certain cases, between alternative possible structures. This may be illustrated with reference to the structure of quinone. Two structures have been suggested for quinine ($C_6H_4O_2$). These are:



(I)



(II)

The parachor for the two structures are:

| | |
|---|---|
| 6 C = 6 $\times$ 4.8 = 28.8 | 6 C = 6 $\times$ 4.8 = 28.8 |
| 4 H = 4 $\times$ 17.1 = 68.4 | 4 H = 4 $\times$ 17.1 = 68.4 |
| 2 O = 2 $\times$ 20.0 = 40.0 | 2 O = 2 $\times$ 20.0 = 40.0 |
| 4 double bonds = 4 $\times$ 23.2 = 92.8 | 3 double bonds = 3 $\times$ 23.2 = 69.6 |
| 1 benzene ring = 6.1 | 2(6- membered rings) = 2 $\times$ 6.1 = 12.2 |
| 236.1 | 219.0 |

The observed value is 236.8. Hence, quinine may be regarded as having the first structure, that is, the diketone structure.

## 6.4 Molar refraction

The product of molar mass ($M_m$) of the liquid and specific refraction ($R$) is called molar refraction ($R_m$). Thus,

$$R_m = \frac{M_m\,(n^2 - 1)}{\rho(n^2 + 2)} \qquad (1)$$

Molar refraction of a solid is determined by dissolving it first in a suitable solvent so as to get a solution of known concentration. The refractive index and the density of a solution are then determined experimentally. The molar refraction $R'$ of the solution $R_{m,sol}$, is given by

$$R_{m,sol} = \frac{n_r^2 - 1}{n_r^2 - 1} \left[ \frac{x_1 M_m' + x_2 M_m''}{\rho} \right] \qquad (2)$$

where $M_m'$ and $M_m''$ are the molar masses of the solvent and the solute, respectively and $x_1$ and $x_2$ are their respective mole fractions, while $n_r$ and $\rho$ are the refractive index and density, respectively, of the solution. Since all the quantities on the right hand side of Eq. 2 are known, $R_{m,sol}$ can be evaluated.

The molar refraction of the solution $R_{m,sol}$ is related to molar refraction $R_{1,m}$ and $R_{2,m}$ of the solvent and the solute, respectively, by the following equation:

$$R_{m,sol} = x_1 R_{1,m} + x_2 R_{2,m} \qquad (3)$$

From Eq. 3, the molar refraction of the solid solute, $R_{2,m}$ can be easily calculated.

## 6.5 Polarisation

When a molecule is placed in an electric field, the field polarizes it in the following three ways:

### 6.5.1 Electronic Polarization:

The field distorts the electronic charge cloud of the molecule. This is called electronic polarization and the corresponding polarizability is termed electronic polarizability, $\alpha_e$.

### 6.5.2 Atomic Polarization

The nuclei, or the atoms, are distorted towards the negative end of the field. The corresponding polarizability is called atomic polarizability, $\alpha_a$.

### 6.5.3 Orientation Polarization

The electric field tends to align molecules having a permanent dipole moment along the direction of the field. The corresponding polarizabilty is called orientation polarizability, $\alpha_\mu$.

Thus, the total polarizability ($\alpha$) of a molecule in an electric field is the sum of the three contributions, i.e.,

$$\alpha = \alpha_e + \alpha_a + \alpha_\mu \tag{1}$$

$$\alpha = \alpha_d + \alpha_\mu \tag{2}$$

where $\alpha_d$ (= $\alpha_e + \alpha_a$) is called distortion polarizability.

## 6.6 Dipole moment

As we know in polar molecules like $H_2O$ and HCl the center of negative charge does not coincide with the center of positive charge. These types of molecules which have two equal and opposite charges separated by certain distance are said to possess electric dipole.

The term dipole moment gives an idea about the extent of polarity in polar covalent molecules. It is defined as the product of the magnitude of the charge and the distance of separation between the charges. Mathematically it is represented as:

Dipole moment ($\mu$) = charge (e) x distance of separation (d)

Unit to measure dipole moment is Debye. It is expressed as D

(1Debye = $1\text{x}10^{-18}$ e.s.u. cm). 1D = $3.33564\text{x}10^{-30}$cm

Dipole moment is a vector quantity and represented by a small arrow (→). Tail of the arrow is pointed towards positive center and head towards negative center.

$$\overset{\longrightarrow}{\mathrm{H}\text{———}\mathrm{Cl}}$$

### 6.6.1 Dipole Moment and Molecular Structure

**1. Diatomic Molecules**

It is formed by the combination of two atoms bonded together by covalent bond. Diatomic molecule will be polar if bond formed between the atoms is polar. e. g. Dipole moment of HCl molecule is the same as that of H—Cl bond, ($\mu$ = 1.03 D). The dipole moment increases with the increase in electronegativity.

**2. Polyatomic Molecules**

Dipole moment of polyatomic molecules not only depends upon the individual dipole moment of the bonds but also on the spatial arrangement of the various bonds in the molecules. So the dipole moment of such molecules is the vector sum of the dipole moments of the various bonds.

For example, $CO_2$ and $H_2O$ both these molecules are triatomic but have different dipole moments. $CO_2$ (zero), $H_2O$ (1.84 D) it can be explained on the basis of their structures. $CO_2$ molecule has a linear structure in which two C=O bonds are oriented in the opposite directions at an angle of $180^0$. Each C=O bond has 2.3 D dipole moment but due to linear structure the dipole moment of one C=O bond cancels that of another. In this way resultant dipole moment of $CO_2$ is zero. Hence $CO_2$ is non-polar molecule. But in case of water molecule the two O—H bonds are oriented at an angle of 104.5º and have a bent structure. The dipole moment of $H_2O$ is1.84 D that is the resultant of the dipole moments of two bonds.

Take the case of tetra atomic molecules like $BF_3$ and $NH_3$. Their dipole moments are zero and 1.49 D respectively. This shows that $BF_3$ molecule is symmetrical and all the three bonds are directed at an angle of 120º. All the three bonds are in the same plane and dipole moments cancel one another resulting net dipole moment equal to zero. While ammonia molecule is pyramidal structure, the resultant dipole moment of $NH_3$ molecule given by all the three N-H bonds is 1.49 D.

So we can say that the presence of polar bonds in a polyatomic molecule does not mean that the molecule as a whole will always have a dipole moment. There are some molecules where molecules have dipole moment zero because of the arrangement of the individual bonds in the molecule. For example, $CO_2$, $BF_3$, $CCl_4$ all these molecules have symmetrical structure. But in case of $CHCl_3$, dipole moment is not equal to zero because all the bonds are not same. The resultant of bond dipole moments of three C-Cl bonds is not cancelled by bond dipole moment of C-H bond.

**Interesting case of $NH_3$ and $NF_3$ molecules in relation to net dipole moment:**

Both these molecules are pyramidal in shape having lone pair of electrons on nitrogen atom. The N-F bonds are more polar than N-H bonds because of the presence of the most electronegative fluorine atom. As a result, the resultant dipole moment of $NF_3$ is larger than that of $NH_3$. But actually the dipole moment of $NF_3$ ($\mu$= 0.24 D) is lesser than that of $NH_3$ ($\mu$= 1.46 D). This is due to the presence of lone pair of electron on nitrogen atom.

In $NF_3$, the orbital dipole is in the opposite direction to the resultant dipole moment of the three N-F bonds. Thus, the lone pair moment cancels the resultant N-F bond moments. But in case $NH_3$ it is just opposite to $NF_3$. The orbital is in the same direction as the resultant dipole moment and therefore adds on the resultant dipole of N-H bonds.

### 6.6.2 Applications of Dipole Moment

To understand chemical bond, “dipole moment” plays an important role. For example

1. It helps in distinguishing polar and non - polar molecules. Non -polar molecules have zero dipole moment while polar molecules have somevalue.

2. It also helps in measuring the degree of polarity in diatomic molecules.Greater the dipole moment, greater the polarity. For example: – HF (1.91D) is more polar than HCl (1.03D).
3. Dipole moment is used to find the shapes of the molecule. In Be F2molecule if the dipoles of two Be-F bonds cancel each other, then itsdipole moment will be zero. Or the two bonds must be oriented in oppositedirections. This is possible if the molecule is linear.
4. Dipole moment also gives an idea about the ionic character in a bond or a molecule. Experimentally it is found that the dipole moment of HCl is 1.03and its bond length is 1.257A$^0$ . For 100% ionic character the chargedeveloped on H and Cl atoms would be 4.8x10-10 es.u.Therefor dipolemoment for 100% ionic character can be calculated as;

   μ ionic= 4.8x $10^{-10}$x 1.275x $10^{-8}$e.s.u.-cm

   = 6.12x $10^{-18}$e.s.u. –cm = 6.12D

   The observed dipole moment ($\mu_{obs}$) =1.07 D

   Therefore percentage ionic character= $\mu_{obs}/\ \mu_{ionic}$ x 100 = 1.03 / 6.12x100 = 16.83%

   In general, larger the value of dipole moment more will be the ionic character.

## 6.7 Debye Equation

In 1912, Debye considered the behaviour of polar molecules placed between the plates of a condenser. In the absence of electric field, as a result of a thermal motion, the molecules are randomly oriented so that there is no net dipole moment in any direction. However, on the application of the electric field across the plates of the condenser, the molecules under the combined influence of the electric field and the thermal motion orient themselves.

Debye calculated the average component of permanent dipole moment μ of the molecule in the direction of the electric field as a function of temperature. For a randomly oriented dipole in the absence of electric field, all orientations are equally probable.

In Clausius - Mosotti equation, the term $\alpha_\mu$ had been ignored. Debye, however, took into consideration both $\alpha_d$ and $\alpha_\mu$ when Clausius - Mosotti equation takes the form

$$P_m = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} V_m = \frac{4}{3}\pi N_A \left(\alpha_d + \frac{\mu^2}{3kT}\right) \qquad (1)$$

In SI units,

$$P_m = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} V_m = \left(\frac{N_A}{3\varepsilon_0}\right)\left(\alpha_d + \frac{\mu^2}{3kT}\right) \qquad (2)$$

Eq. 1 or 2 is called Debye equation. According to this equation, $P_m$ varies linearly with 1/ $T$. The slope and the intercept of the linear Debye plot are $(4/\ 9)\pi N_A\mu^2/k$ or $(1/\ 9\varepsilon_0)N_A\mu^2/k$ and $(4/\ 3)\pi N_A\alpha_d$ or $(1/\ 3\varepsilon_0)\ N_A\alpha_d$, respectively. From the slope and the intercept, μ and $\alpha_d$ of the molecule can be determined. The Dutch physicist, Peter Debye (1884- 1966) was awarded the 1936 Chemistry Nobel prize for contributions of molecular structures through his work on dipole moments.

## 6.8 Clausius-Mosotti equation

Suppose the several molecules of a substance in the solid, liquid and gaseous state are introduced into the space between the plates of a condenser which is charged by applying a constant electrostatic field. The substance is called dielectric and is assumed to be a insulator. The charges on the condenser plates are partially compensated by the induced charges on the boundary of the dielectric. The electric field strength in the dielectric is, therefore, reduced to a value $E$ from its value $E_0$ in vacuum, the two quantities being related by the expression

$$E_0 = E + 4\pi P \qquad (1)$$

where $P$, called dielectric polarization, is the induced dipole moment per unit volume of the dielectric. Thus,

$$P = N\mu_{\text{ind}}$$

where $N$ is the number of molecule per unit volume of dielectric.

From Eq. 1, $E0/E = 1 + 4\pi(P/E) = 1 + 4\pi(N\mu_{\text{ind}}/E)$ (2)

or $\varepsilon_r = 1 + 4\pi N\alpha_d$ (3)

where the quantity $\varepsilon_r$ ($=E0/E$) is called the dielectric constant or relative permittivity. Here we have made use of the fact that $\alpha_d = \mu_{\text{ind}}/E$ where $\alpha_d$, are already mentioned, is the distortion polarizability. The relative permittivity of the medium can be measured experimentally by using the relation

$$\varepsilon_r = (C/C_0) \qquad (4)$$

where $C$ and $C_0$ are the capacitances of the condenser with the medium and the vacuum respectively, as the dielectric between the plates.

Suppose that one mole of a substance of molar volume $V_m$, density $\rho$ and molar mass $M$ is used as a dielectric. Then,

$$N = N_A/V_m = N_A\rho/M$$

where $N_A$ is the Avogadro's number. Hence Eq. 3 can be written as

$$(\varepsilon_r - 1)M/\rho = 4\pi N_A\alpha_d \qquad (5)$$

Evidently, the ratio $(\varepsilon_r - 1)/\rho$ is independent of $\rho$ since $\alpha_d$ is constant for a substance.

Eq. 5 holds for gases at very low pressures when a interaction of the dipole moments between neighbouring molecules is negligible since the molecules are far apart. However, at high pressure and for condensed phases (solid or liquids), this relation does not hold since now interactions between induced moments have to be taken into consideration. Clausius and Mosotti, taking into consideration these interactions for condensed phases, introduced the following relation

$$P_m = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} V_m = (4\pi/3) N_A \alpha_d \qquad (6)$$

where the quantity $P_m$ is called molar polarization. Eq. 6, is known as the Clausius - Mosotti equation.

Relative permittivity, $\varepsilon_r$, is also defined as $\varepsilon_r = \varepsilon / \varepsilon_0$ where $\varepsilon$ is the permittivity of the medium and $\varepsilon_0$ is the permittivity of free space. In SI system, the Clausius - Mosotti equation is written as

$$P_m = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} V_m = (N_A/3\,\varepsilon_0)\,\alpha_d \qquad (7)$$

Since $\alpha_d$ (viz., distortion polarizability) is a characteristic constant of a molecule, hence $P_m$, according to equation 7, should be constant, independent of density or temperature. This has been verified experimentally for non-polar molecules such as $H_2$, $CO_2$, $CH_4$, $CCl_4$ etc., which do not have a permanent dipole moment. The Clausius - Mosotti equation is not obeyed by polar molecules such as HCl, $H_2O$, $NH_3$ etc., which posses a permanent dipole moment.

## 6.9 Summary

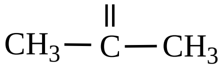
In this unit you have studied about the physical properties and chemical constitution of matter. Molar volume, parachor, atomic parachor, structural parachor, calculation of parachor of compounds, molar refraction, polarisation, dipole moment and molecular structure, Debey equation and Clausius-Mosotti equation.

## 6.10 Terminal question

1. Calculate the parachor value of acetone.
2. Discuss the atomic parachor.
3. What is the molar refraction?
4. What is the dipole moment? Discuss the application of dipole moment.
5. Write the Debye equation.

## 6.11 Answers

**1.** Parachor of acetone, It may be calculated as illustrated below:



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

3C = 3 × 4.8 =14.4

6H = 6× 17.1 = 102.6

O = 1× 20.0 = 20.0

1 double bond = 1× 23.2 = 23.2

∴ Parachor of acetone = 160.2 (Observed value = 161.1)

## 2. Atomic parachor:

Knowing that each - $CH_2$ has a parachor 39, while decane ($C_{10}H_{22}$) has a a parachor 424.2, it follows that

Since $C_{10}H_{22} = 10(CH_2) + 2H$

$\therefore$ $424.2 = 10 \times 39 + 2 \times$ atomic parachor of hydrogen

$\therefore$ Atomic parachor of hydrogen $= \frac{442-390}{2} = 17.1$

Atomic parachor of carbon = 39.0 – 34.2 = 4.8

Knowing atomic parachors of carbon and hydrogen, it has been possible to determine atomic parachors of other elements. For exemple, atomic parachor of oxygen has been obtained from ethers, that of nitrogen from amines and those of chlorine, bromine and iodine from the corresponding halides.

## 3. Molar refraction

The product of molar mass ($M_m$) of the liquid and specific refraction ($R$) is called molar refraction ($R_m$). Thus,

$$R_m = \frac{M_m\,(n^2 - 1)}{\rho(n^2 + 2)} \qquad (1)$$

Molar refraction of a solid is determined by dissolving it first in a suitable solvent so as to get a solution of known concentration. The refractive index and the density of a solution are then determined experimentally. The molar refraction $R'$ of the solution $R_{m,sol}$, is given by

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where $M_m'$ and $M_m''$ are the molar masses of the solvent and the solute, respectively and $x_1$ and $x_2$ are their respective mole fractions, while $n_r$ and $\rho$ are the refractive index and density, respectively, of the solution. Since all the quantities on the right hand side of Eq. 2 are known, $R_{m,sol}$ can be evaluated.

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From Eq. 3, the molar refraction of the solid solute, $R_{2,m}$ can be easily calculated.

## 4. Dipole moment

As we know in polar molecules like $H_2O$ and HCl the center of negative charge does not coincide with the center of positive charge. These types of molecules which have two equal and opposite charges separated by certain distance are said to possess electric dipole.

The term dipole moment gives an idea about the extent of polarity in polar covalent molecules. It is defined as the product of the magnitude of the charge and the distance of separation between the charges. Mathematically it is represented as:

Dipole moment (μ) = charge (e) x distance of separation (d)

Unit to measure dipole moment is Debye. It is expressed as D

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Dipole moment is a vector quantity and represented by a small arrow (→). Tail of the arrow is pointed towards positive center and head towards negative center.

$$\overset{\longrightarrow}{\text{H———Cl}}$$

**Applications of Dipole Moment**

To understand chemical bond, "dipole moment" plays an important role. For example

5. It helps in distinguishing polar and non - polar molecules. Non -polar molecules have zero dipole moment while polar molecules have somevalue.
6. It also helps in measuring the degree of polarity in diatomic molecules.Greater the dipole moment, greater the polarity. For example: – HF (1.91D) is more polar than HCl (1.03D).
7. Dipole moment is used to find the shapes of the molecule. In Be F2molecule if the dipoles of two Be-F bonds cancel each other, then itsdipole moment will be zero. Or the two bonds must be oriented in oppositedirections. This is possible if the molecule is linear.
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   = $6.12x\ 10^{-18}$e.s.u. –cm = 6.12D

   The observed dipole moment ($\mu_{obs}$) =1.07 D

   Therefore percentage ionic character= $\mu_{obs}/\ \mu_{ionic}$ x 100 = 1.03 / 6.12x100 = 16.83%

   In general, larger the value of dipole moment more will be the ionic character.

## 5. Debye Equation

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In SI units,

$$P_m = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} V_m = \left[\frac{N_A}{3\varepsilon_0}\right] \left[\alpha_d + \frac{\mu^2}{3kT}\right] \qquad (2)$$

Eq. 1 or 2 is called Debye equation.

## Reference Books

11. Physical chemistry of macromolecules: basic principles and issues (2nd Edition) by Sun, S.F., Hoboken, N.J. : John Wiley & Sons.
12. Physical Chemistry by Gordon M. Barrow; Mc-Graw Hill.
13. Atkins’ Physical Chemistry by Peter Atkins & Julio De Paula; Oxford University Press.
14. Physical chemistry (4th Edition) by Silbey, Robert J., Alberty, Robert A., Bawendi, Moungi G., Hoboken, NJ: Wiley.
15. Physical chemistry by Ball, David W., Australia: Thomson, Brooks/Cole.
16. Principles of physical chemistry by Puri, Sharma, Pathania; Vishal Publishing Co.

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