

# 4

## USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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Chemistry

### SYLLABUS

(6 Lecturers)

*Thermodynamic functions: energy, entropy and free energy. Estimations of entropy and free energies. Free energy and emf. Cell potentials, the Nernst equation and applications. Acid base, oxidation reduction and solubility equilibria. Water chemistry. Corrosion. Use of free energy considerations in metallurgy through Ellingham diagrams.*

### 4.1 INTRODUCTION

Energy is one of the fundamental parts of the universe. It manifests itself in various forms in nature. Energy is also a fundamental components of our daily lives, and everyday we use energy or power in some form or another. There are many different ways in which the abundant energy around us can be harnessed, converted and exploited for our use. While energy surrounds us in all aspects of life, the ability to harness it and use it for constructive purpose, as economically as possible, is a challenge before mankind. Everything we do is connected to energy in one form or another. Energy from any source, therefore, may be defined as: "*the ability or capacity to do work*". So, work is another form of energy. There are many other forms of energy, just like potential energy which is acquired by any body due to its position. It is expressed as  $mgh$ , where  $m$  is the mass,  $g$  is gravity and  $h$  is height of body from the ground level. Kinetic energy is energy possessed by the body due to its motion. It is expressed as  $\frac{1}{2}mv^2$ , where  $m$  is the mass and  $v$  is the velocity of the body. Besides energy, there are other thermodynamic functions like *isothermal energy, enthalpy, entropy and free energy etc.*

Thermodynamics deals with the energy changes accompanying physical and chemical transformations. Energy may be manifested in several forms; heat, work, light, mechanical and electrical energy etc. These forms of energies are inter convertible. Thus "*the branch of science which deals with the study of the quantitative relationships between heat and other form of energy*" is known as Thermodynamics. When the study is confined to chemical changes only, the branch is known as Chemical Thermodynamics.

The primary objective of chemical thermodynamics is to predict the feasibility of a given transformation which may be physical or chemical.

In this chapter, we will take up the study of some thermodynamic functions and some relations derived from them for the use of chemical equilibria. We will also discuss Illingham Diagram and its applications to metallurgy.

## 4.2 ENERGY

Energy possessed by anybody may be defined as *the ability or capacity of the body to do work under the given set of conditions*. It is expressed in cals or kilocalories in C.G.S. units and in joules or kilo-joules in S.I. units. It can be expressed as pressure-volume work (Mechanical work). Work is a mode of transference of energy between the system and the surroundings.

In thermodynamics, work is defined as any quantity of energy that flows across the boundary of a system during a change in its state and is completely convertible into the lifting of a weight in the surroundings. In general, when a force acting on a body moves it through a certain distance, work is said to be done. If a force  $F$  acting on a body moves it through a distance  $x$ , the work done is expressed as

$$\text{Work} = F \times x$$

$$\omega = P \times a \times dV$$

$$\omega = P dV$$

### 4.2.1 Different Ways To Express Energy Change

#### 1. Pressure-volume work (Mechanical work)

In most of the processes of interest to a chemist is the pressure-volume or mechanical work. This type of work is associated with increase or decrease of the volume either on expansion or compression of the system.

Work of expansion in an isothermal reversible process when it increases its volume by an infinitesimal small  $dV$  against the external pressure  $P$  is given as

$$dw = -PdV \quad \dots(4.1)$$

Therefore, total work done when the gas expands from the initial volume  $V_1$  to final

volume  $V_2$  would be  $w = - \int_{V_1}^{V_2} P dV$

But for an ideal gas  $PV = nRT$

$$\text{or} \quad P = \frac{nRT}{V}$$

Hence

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

$$= -n R T \ln \frac{V_2}{V_1} = -2.303 n R T \log \frac{V_2}{V_1} \quad \dots(4.2)$$

$$= -2.303 n R T \log \frac{P_1}{P_2} \quad \dots(4.3)$$

(We know at constant T,  $P_1 V_1 = P_2 V_2$  or  $\frac{V_2}{V_1} = \frac{P_1}{P_2}$ )

Similarly the work of compression in an isothermal reversible process will be reverse in sign.

### Sign of w

According to the latest S.I. conventions  $w$  is taken as negative if work is done by the system, whereas it is taken as positive if work is done on the system. Thus for expansion we write  $w = -P dV$

In general, the expression for PV work should be written as:  $W = -P dV$

For work done by the system (i.e. expansion work),  $dV$  has a +ive value as  $V_2 > V_1$ .

For work done on the system (i.e. contraction work),  $dV$  has a -ive value as  $V_2 < V_1$ .

### LATEST IUPAC RECOMMENDATION

Work done on the system =  $w$  positive

Work done by the system =  $w$  negative

Heat absorbed by the system =  $q$  positive

Heat evolved by the system =  $q$  negative

It may be of interest to note here that the magnitude of the opposing (external) pressure determines the amount of work done by the system in expansion. The smaller the difference between the opposing (external pressure) and the pressure of the gas (system) contained in the cylinder, the greater will be the work done by it in expansion. *Thus, if the difference between the magnitudes of two pressures is infinitesimally small which is a condition for ideal reversible process, work done is maximum.*

In thermodynamics, energy can also be expressed in terms of thermodynamic function i.e. Internal Energy (E) and Enthalpy or Heat content (H) as explained below:

### 2. Internal Energy (E)

A substance may be associated with different types of energies such as translation energy ( $E_t$ ), rotational energy of molecule ( $E_r$ ), vibrational energy of molecules ( $E_v$ ), electronic energy ( $E_e$ ), nuclear energy ( $E_n$ ), molecular interaction energy ( $E_i$ ), etc. Internal energy is actually the sum of all possible types of energies associated with the atoms or molecules of the given substance. It is a thermodynamic function and is represented by E. It may be defined as follows:

The total amount of energy associated with a definite amount of a substance under a given set of conditions is referred to as the internal energy or intrinsic energy of that substance. That is :

$$E = E_i + E_r + E_v + E_n + E_i$$

Different substances possess different values of internal energy due to a difference between nature of constituent particles and their modes of bonding. For example, internal energy of one mole of hydrogen is different from that of one mole of nitrogen under identical conditions of temperature and pressure. Even the internal energy of a particular substance may be different under different sets of conditions.

### Internal Energy Change ( $\Delta E$ )

The internal energy of a system depends upon state of the system and not upon how the system attains that state. This means that a change of internal energy (represented as  $\Delta E$ ) depends only upon initial and final state of the system and not upon the intermediate states. Therefore, while determining the value of  $\Delta E$ , we are not concerned with the path or the way by which a system changes from one state to another. But change in internal energy ( $\Delta E$ ) is defined as the difference in the internal energies between the final and the initial states. Thus,

$$\Delta E = E_{\text{final state}} - E_{\text{initial state}}$$

When a chemical reaction occurs, the internal energy of the system before the reaction is usually different from the internal energy after the reaction. This is because the nature of the molecules of products obtained in the reaction is different from that of the molecules of the reactants. The change in internal energy in chemical reaction is given by

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

$$\text{or } \Delta E = E_p - E_R$$

where  $E_p$  represents the internal energy of products while  $E_R$  that of reactants.

It is to be noted that the absolute value of internal energy cannot be determined accurately because it is not possible to determine the exact values of the various constituent energies as required. However, the change in internal energy i.e.  $\Delta E$  can easily be measured with the help of first law of thermodynamics as discussed in the forthcoming subsections.

### 3. Enthalpy or Heat Content (H)

We have already seen that the heat, change associated with a chemical reaction occurring at constant temperature and constant volume can be measured in terms of the change in the internal energy of the system. However, it is not always possible to carry out reactions at constant volume in the laboratory, most of the chemical reactions are carried out in open test tubes and beakers which are open to atmosphere and the pressure remains constant (equal to the atmospheric pressure). When a reaction is carried out at *constant pressure*, there may be a change in the volume of the reacting system. The change in the volume involves some work either done by the system (in case of increase in volume) or done on the system (in case of decrease in volume). Therefore, the amount of heat exchanged with surroundings at constant

pressure is not the same as at constant volume because at constant volume there is no change in volume and therefore, no work is done. In order to study the heat changes at constant pressure, a new thermodynamic function called *enthalpy* has been introduced.

Enthalpy is represented by  $H$ . It is regarded as the total heat content of a system at constant pressure. It may be defined as follows:

*The sum of internal energy and pressure-volume energy of a system, under a particular conditions, is referred to as enthalpy of the system.*

Mathematically,

$$H = E + PV \quad \dots(4.5)$$

where  $E$  is the internal energy of the system.  $P$  and  $V$  respectively represent the pressure and volume of the system.

*Enthalpy is a state function.* Therefore, the change in enthalpy ( $\Delta H$ ) depends only upon initial and final states of the system i.e.

$$\Delta H = H_{\text{final state}} - H_{\text{initial state}} \quad \dots(4.6)$$

For a chemical reaction occurring at constant temperature and pressure, the change in enthalpy is equal to the difference in the enthalpies of products and reactants i.e.

$$\begin{aligned} \Delta H &= H_{\text{products}} - H_{\text{reactants}} \\ \text{or } \Delta H &= H_P - H_R \end{aligned} \quad \dots(4.7)$$

From the definition of  $H$  (equation (4.5)), it follows that change in enthalpy ( $\Delta H$ ) will be given by

$$\begin{aligned} \Delta H &= \Delta E + \Delta(PV) \\ \text{or } \Delta H &= \Delta E + P\Delta V + V\Delta P \end{aligned} \quad \dots(4.8)$$

If a change takes place at constant pressure (i.e.  $\Delta P = 0$ ), then we have

$$\Delta H = \Delta E + P\Delta V \quad (\text{at constant pressure}) \quad \dots(4.9)$$

According to the first law of thermodynamics,

$$\Delta E = q + w$$

If the work done is the work of expansion,  $w = -P\Delta V$ , and we have

$$\Delta E = q - P\Delta V$$

Substituting the above values of  $\Delta E$  in equation (4.9), we have

$$\Delta H = (q - P\Delta V) + P\Delta V = q$$

$$\text{or } \Delta H = q_P \quad \dots(4.10)$$

where  $q_P$  refers to the heat change occurring at constant pressure.

Equation (4.10) signifies that the change in enthalpy in a process occurring at constant

pressure is equal to the heat change involved in the process. Therefore,  $\Delta H$  is regarded as a measure of heat evolved or absorbed in a process occurring at constant pressure. Equation 4.10 shows that when we measure a heat change at constant pressure, we actually measure a change in the enthalpy.

### Relationship between $\Delta H$ and $\Delta E$

As seen above,  $\Delta H$  and  $\Delta E$  are related as

$$\Delta H = \Delta E + P \Delta V$$

The difference between  $\Delta H$  and  $\Delta E$  is not of much significance for solids or liquids. However for gases, the difference between  $\Delta H$  and  $\Delta E$  is of great importance. A more useful relation between the two can be derived as follows.

Let us consider a relationship which involves gases and occurs at a constant pressure  $P$  and at constant temperature  $T$ . Let  $V_A$  be the total volume of gaseous reactants and  $V_B$  the total volume of the gaseous products. If  $n_A$  is the total number of moles of gaseous reactants and  $n_B$  is the total number of gaseous products, then according to the ideal gas equation, we have

$$PV_A = n_A RT$$

and

$$PV_B = n_B RT$$

So,

$$PV_B - PV_A = n_B RT - n_A RT$$

or

$$P(V_B - V_A) = (n_B - n_A) RT$$

or

$$P\Delta V = \Delta n RT$$

....(4.11)

where  $\Delta n$  represents the difference between the number of moles of gaseous products and number of moles of gaseous reactants i.e.

$$\Delta n = \sum n_{\text{gaseous products}} - \sum n_{\text{gaseous reactants}}$$

Substituting the value of  $P\Delta V$  from equation (4.11) in equation (4.9), we have

$$\Delta H = \Delta E + \Delta n RT \quad \dots(4.12)$$

Equation 4.12 represents a relation between  $\Delta H$  and  $\Delta E$  for a reaction involving gases and is used for converting  $\Delta H$  into  $\Delta E$  or vice versa. The difference between  $\Delta H$  and  $\Delta E$  depends upon the magnitude as well as the sign of  $\Delta n$ . For example,

When  $\Delta n = 0$ ,  $\Delta H = \Delta E$

when  $\Delta n$  is negative,  $\Delta H < \Delta E$ , and

when  $\Delta n$  is positive,  $\Delta H > \Delta E$

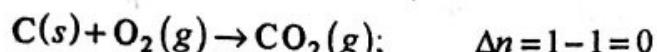
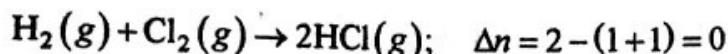
Since  $\Delta H$  measures the heat change at constant Pressure ( $q_P$ ) and  $\Delta E$  the heat constant volume ( $q_v$ ), Equation (4.12) can also be written as

$$q_P = q_v + \Delta n RT \quad \dots(4.13)$$

### Conditions under which $\Delta H$ equals to $\Delta E$

$\Delta H$  or  $q_p$  is equal to  $\Delta E$  or  $q_v$ , under following conditions:

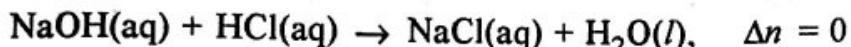
- (i) When  $\Delta n = 0$  i.e. the number of moles of gaseous products is the same as gaseous reactants e.g.



- (ii) When  $\Delta V = 0$  i.e. the reaction is carried out at constant volume. In this case,

$$P\Delta V = \Delta H = \Delta E$$

- (iii) When the reaction does not involve any gaseous reactant or product, e.g.

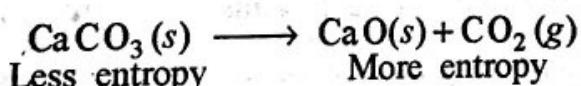
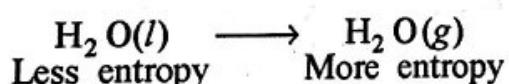


### 4.3 ENTROPY

It is defined as the property of a system which measures the randomness, or the amount of disorder of a system. Like internal energy and enthalpy, entropy is also a state function.

It is a thermodynamic measure for randomness and represented by letter S. The entropy of a system is equal to the sum of the components of that system.

The greater the randomness or disorder in a system, the higher is its entropy, e.g.,



Unlike internal energy, enthalpy, and free energy, the absolute entropy can be calculated.

The concept of entropy as a measure of disorder or randomness has led to the conclusion that all substances in their normal crystalline state at the absolute zero of temperature would be in the condition of maximum orderly arrangement because all motion has essentially ceased at 0 K. In other words entropy of a substance at 0 K is minimum. This led plank to put forward another universal empirical law, the *third law of thermodynamics*, which states:

"The entropy of a pure perfectly crystalline substance is zero at absolute zero (0K) of temperature".

Applying third law of thermodynamics, the absolute entropy of solids can be calculated at a temperature T can be calculated from the formula

$$S_T = \int_{T=0}^{T=T} C_p \frac{dT}{T} = \int_0^T C_p (d \ln T) \quad \dots(4.12)$$

Absolute entropy of substance in the liquid as well as in the gaseous state at a particular temperature can also be calculated by taking into account the entropy phase changes discussed below.

### Units of Entropy

Entropy is usually expressed in terms of calories per degree, sometimes called as entropy units (e.u.). Entropy is an extensive property. It, therefore, mentions the quantity of the substance involved. The quantity is usually taken as 1 mol of the substance. So the entropy units are cal per degree per mole ( $\text{cal K}^{-1}\text{mol}^{-1}$ ) in C.G.S. system and joule per degree per mole ( $\text{JK}^{-1}\text{mol}^{-1}$ ) is S.I. units.

#### 4.3.1 Mathematical Explanation of Entropy

For a reversible Carnot Engine working between a higher temperature  $T_2$  and a lower temperature  $T_1$  with the heat absorbed  $q_2$  and heat evolved  $q_1$ , we have:

$$\begin{aligned} \frac{q_2 - q_1}{q_2} &= \frac{T_2 - T_1}{T_2} \\ \text{or } 1 - \frac{q_1}{q_2} &= 1 - \frac{T_1}{T_2} \\ \text{or } \frac{q_1}{T_1} &= \frac{q_2}{T_2} \\ \text{or } \frac{q_2}{T_2} - \frac{q_1}{T_1} &= 0 \end{aligned} \quad \dots(4.13)$$

Then term  $\frac{q}{T}$  is called the reduced heat. Thus, *for a reversible Carnot cycle, the algebraic sum of the reduced heats is equal to zero.*

For an irreversible cycle, we have

$$\begin{aligned} \frac{q_2 - q_1}{q_2} &< \frac{T_2 - T_1}{T_2} \\ \text{or } \frac{q_2}{T_2} - \frac{q_1}{T_1} &< 0 \end{aligned} \quad \dots(4.14)$$

Therefore, for an irreversible cycle, the sum of  $\frac{q}{T}$  terms is less than zero.

For an infinitely small reversible cycle, Eq. 4.13 can be written as

$$\frac{\delta q_2}{T_2} - \frac{\delta q_1}{T_1} = 0 \quad \dots(4.15)$$

Since a reversible cycle is made of a large number of infinitely small reversible Carnot cycles (Fig. 4.1), therefore for a reversible cycle, equation 4.15 should be written as

$$\int \frac{\delta q_2}{T_2} - \int \frac{\delta q_1}{T_1} = 0$$

or

$$\int \frac{\delta q}{T} = 0 \quad \dots(4.16)$$

where  $\oint$  represents a closed or contour integral.

For an irreversible cycle, from equation (4.14), we have

$$\oint \frac{\delta q}{T} < 0 \quad \dots(4.17)$$

The expression represented by equation (4.17) is called the *Clausius inequality*.

Suppose the reversible cycle is so performed that the system passes from state A to state B by path X and then from state B to state A by path Y. For such a cycle, equation (4.16) can be written as

$$\int_A^B \frac{\delta q(x)}{T} + \int_B^A \frac{\delta q(y)}{T} = 0$$

or

$$\int_A^B \frac{\delta q(x)}{T} = - \int_B^A \frac{\delta q(y)}{T} = \int_A^B \frac{\delta q(y)}{T} \quad \dots(4.18)$$

Therefore the term  $\int \frac{\delta q}{T}$  is the same for a change from state A to state B whether the

system follows path x or path y. This implies that the term  $\int \frac{\delta q}{T}$  represents a function of state. This function is termed as Entropy and is represented by symbol S. Therefore,

$$\int_A^B \frac{\delta q_{rev}}{T} = S_B - S_A = \Delta S$$

Consequently,  $dS = \frac{\delta q_{rev}}{T} \quad \dots(4.19)$

Hence, the change in entropy  $dS$  may be defined as equal to the heat absorbed reversibly by the system divided by the temperature (in Kelvin) at which the heat is being absorbed.

### 4.3.2 Entropy change in a chemical reaction

The entropy change  $\Delta S$  for a chemical change is equal to the sum of the entropies of the products of that change minus the sum of entropies of the reactants.

Let us consider a hypothetical reaction,

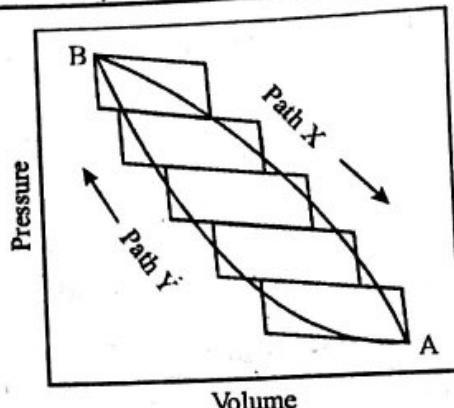


Fig. 4.1. A reversible cycle is composed of a large number of reversible Carnot cycles

The entropy change,

$$\Delta S = \sum S_{\text{products}} - \sum S_{\text{reactants}} \\ = [x \times S_C + y \times S_D] - [m \times S_A + n S_B]$$

where  $S_A$ ,  $S_B$ ,  $S_C$  and  $S_D$  are the entropies of A, B, C and D respectively.

A positive value for  $\Delta S$  ( $\Delta S > 0$ ) indicates an increase in randomness, or disorder. A negative value for  $\Delta S$  ( $\Delta S < 0$ ) indicates decrease in randomness, or decrease in order.

#### 4.3.3 Physical Significance of Entropy

Entropy has been regarded as a measure of disorder or randomness of a system. Thus, when a system goes from a more orderly to less orderly state, there is an increase in its randomness and hence entropy of the system increases. Conversely, if the change is one in which there is an increase in orderliness, there is decrease in entropy. For example, when a solid changes to a liquid an increase in entropy takes place because with the breaking of the orderly arrangement of the molecule in the crystal to the less orderly liquid state, the randomness increases. Conversely, the process of solidification brings about more orderly state and consequently there is a decrease in entropy. The process of vaporization produces an increase in entropy.

Evidently expansion of a gas in vacuum and diffusion of a solute from a concentrated to a dilute solution when the two are connected together, etc. are accompanied by increase of disorder (more of randomness) and hence there is increase in entropy.

#### 4.3.4 Entropy Change Accompanying Change of Phase

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

- Entropy of fusion:** It is defined as the change in entropy when one mole of a solid substance transforms into the liquid form at its melting point. The molar entropy change accompanying a fusion process is given by:

$$\Delta S_f = \frac{\Delta H_f}{T_f} \quad \dots(4.20)$$

where  $\Delta S_f$  is the molar entropy change (for 1 mol of a solid) accompanying fusion process,  $\Delta H_f$  is the molar heat of fusion and  $T_f$  is the freezing or melting point on the absolute scale.

- Entropy of vaporization:** It is defined as the entropy change when one mole of a liquid changes into vapour at its boiling point. Similarly, the molar entropy change  $\Delta S_v$  accompanying a vaporization process (for 1 mol of a liquid) is given by:

$$\Delta S = \frac{\Delta H_v}{T_b} \quad \dots(4.21)$$

where  $\Delta H_v$  is the molar heat of vaporization and  $T_b$  is the boiling point on the absolute scale.

Since  $\Delta H_f$  and  $\Delta H_v$  are both positive, an increase in entropy takes place during the processes of fusion and vaporization.

In the change of state from vapour to liquid or from liquid to solid,  $\Delta H_f$  will be negative and during processes of condensation of vapour or freezing of a liquid decrease in entropy takes place.

- 3. Entropy of sublimation :** *It is defined as the entropy involved in the transformation of a solid directly into vapour at a particular temperature called sublimation temperature.*

It is represented by  $\Delta S_{\text{sub}}$  and is given as.

$$\Delta S_{\text{vap}} = S_{\text{vap}} - S_{\text{liquid}} = \frac{\Delta H_{\text{sub}}}{T} \quad \dots(4.22)$$

where  $\Delta H_{\text{sub}}$  is the enthalpy of sublimation per mole of a solid at temperature T (in Kelvin).

- 4. Entropy of Transition:** It may be defined as the change in entropy when *one mole of a solid changes from one crystalline state into the other at the transition temperature.*

$$\Delta S = \frac{\Delta H_t}{T_t} \quad \dots(4.23)$$

where  $\Delta H_t$  is the molar heat of transition and  $T_t$  is the transition point.

#### 4.3.5 Entropy Changes in Reversible Processes

When a system gains heat, the surroundings lose heat and hence their entropies also change. The total change in entropy will, therefore, be equal to the algebraic sum of entropy changes of the system and the surroundings i.e.  $\Delta S = \Delta S_{\text{sys.}} + \Delta S_{\text{sur.}}$ . Consider an isothermal reversible expansion of an ideal gas. The gas absorbs  $Q_{\text{rev.}}$  heat at temperature T. The entropy change of the gas, i.e., system is given by

$$\Delta S_{\text{sys.}} = \frac{Q_{\text{rev.}}}{T}$$

Since expansion is reversible, the system is in equilibrium with its surroundings at all times during the expansion. Hence the surroundings lose an amount of heat equal to  $Q_{\text{rev.}}$ , or we can say that the surroundings absorb  $-Q_{\text{rev.}}$  of heat. The entropy changes of the surrounding is given by

$$\Delta S_{\text{sur.}} = -\frac{Q_{\text{rev.}}}{T}$$

So, total entropy change of the universe:

$$\Delta S = \Delta S_{\text{sys.}} + \Delta S_{\text{sur.}} = \frac{Q_{\text{rev.}}}{T} - \frac{Q_{\text{rev.}}}{T} \quad \text{or} \quad \Delta S = 0.$$

*It is concluded that for a reversible process the total entropy change of the universe is zero.*

#### 4.3.6 Entropy Changes in Irreversible Processes

When any part of the process is Irreversible, the process as a whole becomes irreversible. Suppose that the heat lost by the surroundings is  $Q_{\text{irrev.}}$ . This amount of heat will be absorbed by the system, but entropy change of the heat absorbed reversibly ( $Q_{\text{rev.}}$ ), and not upon the heat actually absorbed. If the heat is absorbed isothermally by the system at temperature  $T$ , the entropy change of the system will be

$$\Delta S_{\text{sys.}} = \frac{Q_{\text{rev.}}}{T}$$

This is due to the fact that entropy is a state function and hence entropy increase of the system will be the same no matter whether the change has been brought in a reversible or an irreversible manner. But the heat actually lost by the surroundings is  $Q_{\text{irrev.}}$ . The loss of heat by the surroundings to the system can be adjusted to take place reversibly and therefore the decrease in entropy is given by

$$\Delta S_{\text{sur.}} = -\frac{Q_{\text{irrev.}}}{T}$$

Hence, the net change in entropy is given by:

$$\Delta S = \Delta S_{\text{sys.}} + \Delta S_{\text{sur.}}$$

$$\Delta S = \frac{Q_{\text{rev.}}}{T} - \frac{Q_{\text{irrev.}}}{T}$$

We know that  $Q_{\text{irrev.}} < Q_{\text{rev.}}$  or  $\Delta S > 0$ .

*Thus, in an irreversible process, there is a net increase in entropy of the universe (system + surroundings).*

#### Entropy Change of the Universe

It is interesting to note that since all the natural spontaneous processes (such as, the transfer of heat from a hot to a cold body) are irreversible and hence they must be associated with a net increase of entropy.

The result about the spontaneous processes is so important that it is sometimes taken as the definition of the Second law of thermodynamics.

Hence, the second law may be stated as,

*"All spontaneous processes are accompanied by a net increase of entropy." OR  
"The net entropy of the universe tends to increase."*

Clausius summed up the statements of the first and second laws of thermodynamics as: "The energy of the universe remains constant; the entropy of the universe tends towards a maximum."

#### 4.3.7 Entropy as Criterion of Spontaneity

From the above discussion, we conclude that the entropy of the system and its surroundings taken together increase in a thermodynamically irreversible process at constant pressure but it remains constant in a thermodynamically reversible process.

This provides us with a criterion of distinction between an irreversible and a reversible process.

Mathematically,

$$\Delta S_{\text{sys.}} + \Delta S_{\text{sur.}} = 0 \text{ (for a reversible process)} \quad \dots(4.24)$$

$$\Delta S_{\text{sys.}} + \Delta S_{\text{sur.}} > 0 \text{ (for a irreversible process)}$$

$$\Delta S_{\text{sys.}} + \Delta S_{\text{sur.}} \geq 0 \quad \dots(4.25)$$

Hence 'equal to' sign refers to a reversible process and the 'greater than' sign refers to an irreversible process.

These conclusions are quite significant as these help us to predict whether a given process is thermodynamically feasible or not i.e., whether it can take place or not.

#### 4.3.8 Entropy Changes For An Ideal Gas

Consider a mol of an ideal gas contained in a cylinder fitted with a frictionless piston. Suppose an infinitesimal small amount of heat ( $q_{\text{rev}}$ ) is supplied reversibly at constant temperature T, to the system which would undergo expansion involving pressure - volume work. From first law of thermodynamics,

$$dE = q + w \quad dE = \epsilon - PV$$

$$q_{\text{rev}} = dE + PV$$

$$\boxed{\text{We know that } C_v = \frac{dE}{dT} \text{ or } dE = C_v dT}$$

$$\text{and } PV = RT \quad \text{or} \quad P = \frac{RT}{V}$$

Putting the values in the above equation, we get

$$q_{\text{rev}} = C_v dT + RT \frac{dV}{V}$$

Dividing throughout by T, we get

$$\frac{q_{\text{rev}}}{T} = C_v \frac{dT}{T} + R \frac{dV}{V}$$

$$\text{But } \frac{q_{\text{rev}}}{T} = dS$$

$$\text{Therefore, } dS = C_v \frac{dT}{T} + R \frac{dV}{V}$$

This gives the total entropy change for a mol of an ideal gas when temperature and volume changes both take place reversibly. When the temperature changes from  $T_1$  to  $T_2$ , and the volume from  $V_1$  to  $V_2$ , then the entropy change accompanying the process would be:

$$\Delta S = S_2 - S_1 = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V} = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \dots(4.26)$$

It is assumed that  $C_v$  is constant over the temperature limit  $T_1$  and  $T_2$ . Again for an ideal gas  $P_1 V_1 = RT_1$  and  $P_2 V_2 = RT_2$  for the initial and final state respectively. Therefore,

$$\frac{V_2}{V_1} = \frac{T_2 P_1}{T_1 P_2}$$

Putting this value in the above equation, we get

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{T_2 P_1}{T_1 P_2}$$

Knowing  $C_p - C_v = R$  or  $C_v = C_p - R$

$$\begin{aligned} \therefore \Delta S &= (C_p - R) \ln \frac{T_2}{T_1} + R \ln \frac{T_2 P_1}{T_1 P_2} \\ &= C_p \ln \frac{T_2}{T_1} - R \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \\ &= C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \\ &= C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \end{aligned} \quad \dots(4.27)$$

Equation (4.26) gives the entropy change for a mol of an ideal gas when temperature and volume are varied, whereas equation (4.27) gives the entropy change when temperature and pressure are varied.

These equations can be modified depending upon the conditions of constancy of temperature, pressure and volume as under:

### Case I (For an Isothermal process)

Since there is no change in temperature i.e.  $T_1 = T_2$

The above two equations take the form

$$(\Delta S)_T = R \ln \frac{V_2}{V_1} = -R \ln \frac{P_2}{P_1} = R \ln \frac{P_1}{P_2}$$

If  $V_2 > V_1$ ,  $(\Delta S)_T$  will be positive. This means that isothermal expansion of an ideal gas gives an increase in entropy and vice versa.

**Case II (For an Isobaric process)**

For a process taking place at constant pressure,  $P_1 = P_2$ , the equation (4.26) becomes

$$(\Delta S)_P = C_p \ln \frac{T_2}{T_1} \quad \dots(4.28)$$

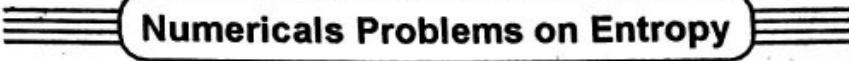
It means that the increase in temperature of an ideal gas at constant pressure gives an increase of entropy of the ideal gas.

**Case III (For an Isochoric process)**

For a process taking place at constant volume,  $V_1 = V_2$ , the equation (4.25) becomes

$$(\Delta S)_V = C_v \ln \frac{T_2}{T_1} \quad \dots(4.29)$$

The equation tells that increase in temperature of an ideal gas at constant volume also shows an increase in entropy.


**Numericals Problems on Entropy**

**Example 1.** Calculate the entropy for the conversion of 1 mole of ice at 274 K and 1 atm into steam at 350K and 1 atm, the molar heat of fusion of ice  $\Delta H_f = 7\text{ kJ mol}^{-1}$  and molar heat of vaporization of water,  $\Delta H_v = 45\text{ kJ mol}^{-1}$  and  $C_p = 76\text{ J K}^{-1}$ . (Assume  $C_p$  is constant within this temperature) (K.U. Jan. 2005)

**Solution.** (i) Entropy change for 1 mole of ice at 274 K

$$\Delta S_1 = \frac{\Delta H_f}{\Delta T_f} = \frac{7000}{274} = 25.54 \text{ J K}^{-1} \text{ mol}^{-1}$$

(ii) Entropy change of m mole of water at 274 to water at 350 K at 1 atm

$$\Delta S_2 = 2.303 \times C_p \log \frac{T_2}{T_1}$$

$$\Delta S_2 = 2.303 \times 76 \times \log \frac{350}{274} = 18.61 \text{ J K}^{-1} \text{ mol}^{-1}$$

(iii) Entropy change of 1 mole of water at 350 K to steam at 350 K at 1 atm.

$$\Delta S_3 = \frac{\Delta H_v}{\Delta H_f} = \frac{42000}{350} = 120 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Total entropy change} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 164.15 \text{ J K}^{-1} \text{ mol}^{-1}$$

**Example 2.** One mol of an ideal gas at 300 K expands reversibly from  $3 \times 10^{-2} \text{ m}^3$  to  $5 \times 10^{-2} \text{ m}^3$ . Calculate the entropy change for the gas. (K.U. Jan. 2005)

**Solution.** The entropy change  $(\Delta S)_T$  for one mol of an ideal gas during isothermal reversible expansion is given as:

$$(\Delta S)_T = 2.303 R \log \frac{V_2}{V_1}$$

Here  $R = 1.987 \text{ cals}$ ,  $V_1 = 3 \times 10^{-2} \text{ m}^3$  and  $V_2 = 5 \times 10^{-2} \text{ m}^3$

$$\text{So, } (\Delta S)_T = 2.303 \times 1.987 \log \frac{5 \times 10^{-2}}{3 \times 10^{-2}}$$

$$= 2.303 \times 1.987 \times [\log 5 - \log 3] = 1.0154 \text{ cals/degree/mol}$$

**Example 3.** Five moles of an ideal gas expands isothermally and reversibly at  $27^\circ\text{C}$  from an initially volume of  $5 \text{ dm}^3$  to  $50 \text{ dm}^3$  against a pressure that is gradually reduced. Calculate  $\Delta G$  and  $\Delta S$  for the process ( $L R = 8.314 \text{ J K}^{-1}$ ). (K.U. June 2008)

**Solution.** We have that  $(\Delta S)_T = 2.303 nR \log \frac{V_2}{V_1}$

$$\text{Putting the given values, } (\Delta S)_T = 2.303 \times 5 \times 8.314 \times \log \frac{50}{5} = 98.74 \text{ JK}^{-1}$$

$$\text{We also know that } \Delta G = 2.303 nRT \log \frac{V_2}{V_1}$$

Putting the values we get:

$$\begin{aligned}\Delta G &= 2.303 \times 5 \times 8.314 \times \log \frac{5}{50} \times 300 \\ &= -28720 \text{ j mol}^{-1} = -28.72 \text{ kJ mol}^{-1}\end{aligned}$$

## 4.4 GIBB'S FREE ENERGY FUNCTION

Another useful function derived from entropy is called the *free energy* function ( $G$ ) defined by:  

$$G = H - TS$$

*The free energy of a system is a measure of its capacity for doing useful work. OR*

*The free energy of a system may be defined as the net available energy of the system, which can be converted into useful work.*

Out of the total energy of a system, a part of it is unavailable (being the entropy), a part of it has to be utilized in performing P-V work and the remaining part is the net available energy (energy available for useful work) known as free energy of the system. Free energy is also known as **Gibb's free energy** and is represented by the symbol  $G$ .

*It is a part of the energy of the system which is available for conversion to useful work and is, therefore, called free energy.*

Free energy may be compared with the potential energy of a system. In mechanical systems, decrease in potential energy takes place. Similarly, during chemical reactions reactants lose energy in the form of non-expansion work known as useful work to form products corresponding to more stable state. This energy is also known as free energy.

## Physical Significance of Free Energy

According to the first law of thermodynamics

$$\text{or } q = \Delta E + w \quad \dots(i)$$

$\Delta$  where  $q$  is heat absorbed by the system,  $w$  is work done by the system on the surroundings and  $\Delta E$  is increase in the internal energy of the system.

$$\therefore w_{\text{expansion}} = P \Delta V \text{ (at constant pressure)}$$

$$\therefore q = \Delta E + P \Delta V + w_{\text{non-expansion}} \quad \dots(ii)$$

$$\text{or } q = \Delta H + w_{\text{non-expansion}} \quad (\because \Delta H = \Delta E + P \Delta V)$$

$$\therefore \Delta S = \frac{q}{T} \quad \dots(iii)$$

$$\therefore q = T \Delta S \quad \dots(iv)$$

where  $w$  is heat supplied to a reversible process at  $T$ .

Putting the value of  $q$  in equation (iii)

$$T \Delta S = \Delta H + w_{\text{non-expansion}}$$

$$\text{or } -w_{\text{non-expansion}} = \Delta H - T \Delta S \quad \dots(v)$$

$$\text{Now } \Delta G = \Delta H - T \Delta S \text{ (At constant temperature and pressure)} \quad \dots(vi)$$

From equation (v) and (vi)

$$-w_{\text{non-expansion}} = \Delta G$$

$$\text{or } w_{\text{non-expansion}} = -\Delta G \quad \dots(4.30)$$

Thus, decrease in the free energy of a system during any change is a measure of the useful work or net work or work of non-expansion.

### 4.4.1 Helmholtz Free Energy or Work Function (F or A)

Although the entropy concept is the fundamental consequence of the second law of thermodynamics, there are two other functions, which utilize the entropy in their derivation, that are more convenient for use in many instances.

The work function represented by the symbol F or A, is defined by:

$$F = E - TS \quad \text{or} \quad A = E - TS \quad \dots(4.31)$$

where E is the energy content of the system i.e. internal energy, T is its temperature and S is entropy. Since E, T and S are characteristic properties of the system, depending only on its thermodynamic state and not on its path, it is evident that the same considerations must apply to the work function. Hence A is to be regarded as a single valued function of the state of the system, and dA can be treated as a complete differential. Further, since E and S are both extensive properties, A will also be extensive in character, its value being proportional to the quantity of matter constituting the system under consideration.

## Physical significance of Helmholtz Free Energy

Consider an isothermal change from the initial state indicated by the subscript 1 to final state indicated by 2; thus:

$$A_1 = E_1 - TS_1 \quad \text{and} \quad A_2 = E_2 - TS_2$$

So that  $\Delta A$ , the increase in the work function accompanying the process at constant temperature is given by

$$\begin{aligned} A_2 - A_1 &= (E_2 - E_1) - T(S_2 - S_1) \\ \Delta A &= \Delta E - T\Delta S \end{aligned} \quad \dots(4.32)$$

Suppose the above change is carried out reversibly at constant temperature  $T$ . Let the heat absorbed by the system be  $q_{rev}$ , then

$$\Delta S = \frac{q_{rev}}{T} \quad \text{or} \quad T\Delta S = q_{rev}$$

Substituting this value of  $T\Delta S$  in equation (4.32), we get

$$\Delta A = \Delta E - q_{rev} \quad \dots(4.33)$$

According to the first law of thermodynamics assuming a reversible isothermal process,

$$q_{rev} = E + w_{rev} \quad \dots(4.34)$$

or

$$-w_{rev} = E - q_{rev}$$

Comparison of equation (4.33) and (4.34) shows that

$$-\Delta A = w_{rev} \quad \dots(4.35)$$

It follows that *in an isothermal process the decrease of the work function is a measure of the maximum work obtainable from that change in state*. It is this fact which justifies the term "work function". It is also called as **Helmholtz Free Energy (F)** after the name of Helmholtz.

It should be noted that any given process, isothermal or otherwise, is accompanied by a definite change in the value of the work function  $A$  but it is only for an isothermal process that this change is a measure of the maximum work available.

### 4.4.2 Relationship between free energy change, enthalpy change and entropy change

Free energy ( $G$ ) is related to enthalpy ( $H$ ), entropy ( $S$ ) and absolute temperature as follows:

$$G = H - TS \quad \dots(4.36)$$

Consider a system passing from the initial thermal state at constant temperature and pressure. For the initial state of the system;

$$G_1 = H_1 - TS_1$$

For the final state of the system

$$G_2 = H_2 - TS_2$$

Here  $G_1$ ,  $H_1$  and  $S_1$  are the free energy, enthalpy and entropy of the system in the initial state respectively and  $G_2$ ,  $H_2$  and  $S_2$  are the corresponding values in the final state.

The change in free energy,  $\Delta G$ , is then given by

$$\begin{aligned}\Delta G &= G_2 - G_1 \\ \text{or} \quad \Delta G &= (H_2 - TS_2) - (H_1 - TS_1) \\ \text{or} \quad \Delta G &= (H_2 - H_1) - T(S_2 - S_1) \\ \text{or} \quad \Delta G &= \Delta H - T\Delta S\end{aligned}\dots(4.37)$$

where  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are free energy change, enthalpy change and entropy change respectively,  $T$  is the temperature on Kelvin scale.

#### 4.4.3 Free Energy as Criterion of Spontaneity (Feasibility) of a Process

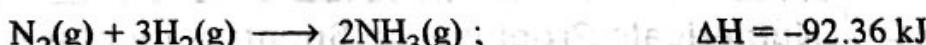
The overall criterion of a process to occur spontaneously, i.e., *driving force* is expressed in terms of free energy change,  $\Delta G$  which is a thermodynamic quantity. Knowing the value of  $\Delta G$  it can be predicted whether the reaction or the process is spontaneous or not.

(a) If  $\Delta G$  is negative ( $\Delta G < 0$ ), the process is spontaneous,  $\Delta G$  can be negative, if

(i) Both the energy and entropy factors are favourable, i.e.,  $\Delta H$  is negative and  $T\Delta S$  is positive, e.g.,

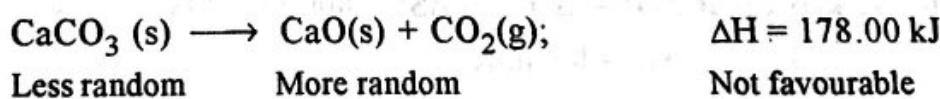


(ii) Both the energy and entropy factors have negative sign but  $\Delta H > T\Delta S$ . i.e., the energy factor favourable while the entropy factor is not favourable and the magnitude of  $\Delta H$  is more than that of  $T\Delta S$ , e.g.,



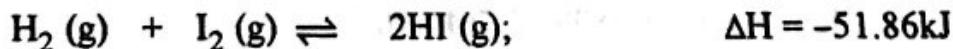
More random      Less random      Favourable

(iii) Both the energy and entropy factors have positive sign but  $\Delta H < T\Delta S$  or  $T\Delta S > \Delta H$ , i.e., the entropy factor is favourable while the energy factor is not favourable and magnitude of  $T\Delta S$  is more than or  $\Delta H$ .



Less random      More random      Not favourable

(b) If  $\Delta G$  is zero, the process is in the equilibrium state and thus there is no net change in either direction. This happens when one of the factor is favourable and the other is opposing but they are equal in magnitudes.



In this reaction, the energy factor favours but the entropy factor (randomness factor) opposes up to the same extent. Thus equilibrium exists.

(c) If  $\Delta G$  is positive, the process does not occur in the forward direction.  $\Delta G$  can be positive, if:

- (i) Both the energy and entropy factors oppose, i.e.,  $\Delta H$  has positive sign and  $T\Delta S$  has negative sign.
- (ii) Both the factors have positive sign but  $\Delta H > T\Delta S$ ,
- (iii) Both the factors have negative sign but  $T\Delta S > \Delta H$ .

#### 4.4.4 Conditions under which $\Delta G$ can be Negative

- (i) Both the energy and entropy factors are favourable, i.e.,  $\Delta H$  is negative and  $T\Delta S$  is positive.
- (ii) Energy factor is favourable (i.e.,  $\Delta H$  is negative) while the entropy factor is not favourable (i.e.,  $T\Delta S$  is also negative) but the magnitude of  $\Delta H$  is more than that of  $T\Delta S$ .
- (iii) Energy factor is not favourable (i.e.,  $\Delta H$  is positive) while the entropy factors favourable (i.e.,  $T\Delta S$  is also positive) but the magnitude of  $T\Delta S$  is more than that of  $\Delta H$ .

In general, the influence of  $\Delta G$  on the spontaneity of a process may be summed up as follows:

- (i)  $\Delta G$  is negative, the process is spontaneous.
- (ii)  $\Delta G$  is zero, the process does not occur and is in equilibrium.
- (iii)  $\Delta G$  is positive, the process does not occur in forward direction. It may, however, proceed in reverse direction.

It may be pointed out that  $\Delta G$  merely serves as a criterion for the feasibility of a process. It does not give any information regarding the conditions, rate or mechanism of the reaction.

### Numerical Problems on Spontaneity of Reactions

**Example 4.** Calculate the equilibrium constant, K for the following reaction at 400K.



Given  $\Delta H^\circ = 80 \text{ kJ mol}^{-1}$ ,  $\Delta S^\circ = 120 \text{ JK}^{-1} \text{ mol}^{-1}$ . (K.U. Jan. 2004)

**Solution.** We know that  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 80000 - 298 \times 120 = 44240 \text{ J}$ .

Now

$$\Delta G^\circ = RT \ln K$$

or

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

or

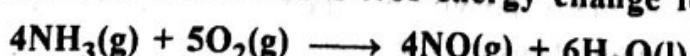
$$44240 = -2.303 \times 8.314 \times 400 \times \log K$$

or

$$\log K = -5.7763 = 6.8899$$

$$\therefore K = \text{Antilog } 6.8899 = 7.761 \times 10^{-6}$$

**Example 5.** Calculate the standard free energy change for the reaction



Predict whether the reaction is feasible at standard state or not.  $\Delta G_f^\circ$  for  $\text{NH}_3\text{(g)}$ ,  $\text{NO(g)}$  and  $\text{H}_2\text{O(l)}$  are  $-16.8$ ,  $+86.7$  and  $-237.2 \text{ kJ mol}^{-1}$  respectively.

**Solution.** Standard free energy change

(K.U. Jan. 2004)

$$\begin{aligned}\Delta G^\circ &= (\Delta G_f^\circ)_{\text{Products}} - (\Delta G_f^\circ)_{\text{Reactants}} \\ &= [4 \times \Delta G_f^\circ(\text{NO}) + 6 \times \Delta G_f^\circ(\text{H}_2\text{O})] - [4 \times \Delta G_f^\circ(\text{NH}_3) + 5 \times \Delta G_f^\circ(\text{O}_2)] \\ &= [4 \times 86.7 + 6 \times -237.2] - [4 \times -16.8 + 5 \times (0)] \quad (\because \Delta G_f^\circ \text{ for oxygen is zero}) \\ &= 346.8 - 1423.2 + (67.2) = -1009.2 \text{ kJ}\end{aligned}$$

Since  $\Delta G^\circ$  is negative, the reaction is feasible at standard state.

**Example 6.** For a reaction at 298K,  $2\text{A} + \text{B} \rightarrow \text{C}$ ,  $\Delta H = 100$  kcal and  $\Delta S = 0.50$  kcal K $^{-1}$ . Assuming  $\Delta H$  and  $\Delta S$  to be constant over the temperature change, at what temperature the reaction will become spontaneous. (M.D.U. May 2007)

**Solution.** It is given that,  $\Delta H = 100$  k cal and  $\Delta S = 0.50$  k cal/K.  $\Delta G$  is related to  $\Delta H$  as

$$\text{We know that } \Delta G = \Delta H - T\Delta S$$

A reaction is spontaneous when  $\Delta G$  is negative i.e.  $\Delta G < 0$ .

Putting  $\Delta G = 0$  and the values of  $\Delta H$  and  $\Delta S$ , we have

$$0 = 100 - (T \times 0.50)$$

$$\text{or } T = \frac{100}{0.50} = 200 \text{ K}$$

Thus  $\Delta G$  is negative at temperature above 200K. Hence, the given reaction will be spontaneous above 200K.

#### 4.4.5 Relationship Between $\Delta G$ and $\Delta A$

$$\text{We know } \Delta G = \Delta H - T\Delta S$$

$$\text{and } \Delta A = \Delta E - T\Delta S$$

Subtracting, we get

$$\Delta G - \Delta A = \Delta H - \Delta E$$

$$\text{or } \Delta G = \Delta H - \Delta E + \Delta A$$

$$\text{But } \Delta H = \Delta E + P\Delta V$$

$$\text{or } \Delta H - \Delta E = P\Delta V$$

$$\text{Hence } \Delta G = \Delta A + P\Delta V \quad \dots(4.38)$$

If the volume remains constant,  $\Delta V = 0$

$$\Delta G = \Delta A$$

Hence, when the volume is constant

$$\Delta G = \Delta A$$

#### 4.4.6 Free Energy change in an Isothermal Process

When the pressure changes from  $P_1$  to  $P_2$ , the change in free energy, ( $\Delta G$ ) in an isothermal process can be obtained by integrating equation  $dG = VdP$

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP$$

$$(G_2 - G_1) = \Delta G = \int_{P_1}^{P_2} VdP$$

where  $G_1$  and  $G_2$  denote respectively the free energy of the system in the initial and final states.

For  $n$  moles of an ideal gas,

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

Putting the value of  $V$  in equation , we get

$$\Delta G = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$$

where  $V_1$  and  $V_2$  are the initial and final volumes.

For 1 mol of an ideal gas, it follows from equation above

$$\Delta G = RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_1}{V_2} \quad \dots(4.39)$$

## 4.5 CELL POTENTIAL OR E.M.F. OF A CELL

An electrochemical cell consists of two electrodes which have different electrode potentials.

The difference in electrode potential which causes the current to flow from the electrode at a higher potential to the electrode at lower potential is known as the cell potential or e.m.f. of the cell.

The differences of potential between the electrodes of a cell can be measured by using a voltmeter. It is the potential differences due to which the cell is sending the current to the circuit. This potential differences is called the electromotive force (e.m.f.) of the cell, if no or very little current is allowed to flow at the time of measurement. It is measured by a potentiometer.

The differences between e.m.f. of a cell and potential difference are summarized below:

Cell Potential or e.m.f	Potential difference
1. It is the difference between electrode potentials of two electrodes <i>when no current is flowing through the circuit i.e. open circuit.</i>	1. It is the difference between electrode potentials of two electrodes <i>when current is flowing through the circuit i.e. closed circuit.</i>
2. It is determined by means of the potentiometer.	2. It is determined by means of a simple voltmeter.
3. It is the maximum voltage obtainable from a cell.	3. It is less than maximum voltage obtainable from a cell.
4. The work calculated from e.m.f. is the maximum work obtainable from a cell.	4. The work calculated from potential difference is less than maximum work obtainable from a cell.
5. It is responsible for the flow of steady current through the circuit.	5. It is not responsible for the flow of steady current through the circuit.

### 4.5.1 Free Energy and E.M.F.

The cell potential is simply related to the free energy change ( $\Delta G$ ) for the reaction. Therefore, measurement of the cell potential is often a convenient way to obtain free energy changes (useful work done) and consequently equilibrium constants.

In an electrochemical cell, the system does work by transferring electrical charge through an external circuit. For an electrochemical cell to work reversibly, it is ensured that while operating the cell only in an infinitesimal current from the cell is to be drawn. The free energy change,  $\Delta G$ , is equal to the electrical work done which is written as:

$$\Delta G = W_{\text{elect}}$$

If free energy change,  $\Delta G$ , of the system is negative, the system does electrical work on its surroundings. If  $\Delta G$  is positive, the change can be affected only if the surroundings does electrical work on the system.

For a reaction occurring in an electrochemical cell, the work done when amount of charge,  $nF$ , is transferred is given by  $-nFE$ . Thus:

$$\Delta G = -nFE_{\text{Cell}}$$

Here  $F$  is the Faraday Constant and  $n$  is the number of moles of electrons transferred in the reaction. For comparing cell voltage on a common basis, standard cell potential ( $E^{\circ}_{\text{cell}}$ ) is used. The free energy associated with standard cell potential is the standard free energy for the reaction denoted by  $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$ .

## Criteria for spontaneity in terms of cell EMF

The value of standard free energy change ( $\Delta G^\circ$ ) can be evaluated knowing the standard e.m.f. ( $E^\circ$ ) of the cell experimentally by applying the above relation. Thus, the criteria of spontaneity is given as:

- (i) If  $\Delta G < 0$  i.e. negative or  $E > 0$  i.e. positive, the reaction will be spontaneous.
- (ii) If  $\Delta G = 0$  or  $E = 0$ , the reaction will be in equilibrium.
- (iii) If  $\Delta G > 0$  i.e. positive or  $E < 0$  i.e. negative, the reaction will be non-spontaneous. However, it will be spontaneous in the reverse direction.

## Calculation of equilibrium constant $K_C$ from $\Delta G^\circ$

Knowing the value of standard free energy  $\Delta G^\circ$ , the equilibrium constant can also be calculated by the relation,

$$E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K_C$$

$$-nF E_{\text{cell}}^\circ = -nF \times \frac{RT}{nF} \ln K_C = -RT \ln K_C$$

$$\text{i.e. } \Delta G^\circ = -RT \ln K_C$$

Substituting the value of  $\Delta G^\circ$ , R and T, the value of equilibrium constant  $K_C$  is calculated. In case of Daniel cell  $K_C = 2 \times 10^7$  which shows that very little of  $\text{Cu}^{2+}$  will be in solution at equilibrium.

**Example 7.** For the cell reaction  $\text{Ni} | \text{Ni}^{2+} \parallel \text{Ag}^+ | \text{Ag}$ . Calculate the equilibrium constant at  $25^\circ\text{C}$ . How much maximum work would be obtained by operation of this cell?

$$(E_{\text{Ni}}^{2+/2} = -0.25 \text{ V}, E_{\text{Ag}^+/\text{Ag}}^\circ = 0.80 \text{ V})$$

**Solution.**  $E_{\text{cell}}^\circ = E_{\text{right}}^\circ - E_{\text{left}}^\circ = 0.80 - (-0.25) = 1.05 \text{ V}$

Now  $\log K_C = \frac{E_{\text{cell}}^\circ \times n}{0.059} = \frac{1.05 \times 2}{0.059} = 35.59$

$$K_C = 3.8 \times 10^{35}$$

Maximum work obtained,  $\Delta G^\circ = -nFE_{\text{cell}}^\circ$   
 $= 2 \times 96500 \times 1.05 = 202650 \text{ J} = 202.650 \text{ kJ}$

**Note:**  $\Delta G^\circ$  and  $K_C$  are also related as:

$$\Delta G^\circ = -2.303 R \log K_C$$

Thus,  $K_C$  can be calculated from  $\Delta G^\circ$  also.

## 4.6 THERMODYNAMIC FUNCTIONS FROM CELL EMF MEASUREMENT

It is only in case of reversible cells that thermodynamic principles can be employed to obtain a definite relation between electrical energy and chemical energy. According to Gibb's and Helmholtz, the electrical energy of a reversible cell is determined by the free energy decrease of the reaction that takes place in the cell. Gibb's Helmholtz equation in terms of free energy and enthalpy changes can be derived as:

Free energy function  $G$  is given by the relation:

$$G = H - TS$$

And we know

$$H = E + PV$$

$$G = E + PV - TS$$

On complete differentiation

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

From first law of thermodynamics

$$dq = dE + dw = dE + PdV$$

or

$$PdV = dq - dE$$

$$\therefore dG = dq + VdP - TdS - SdT$$

For a reversible process, the change in entropy is given by

$$dS = dq/T \text{ or } TdS = dq$$

$$\therefore dG = dq + VdP - dq - SdT$$

or

$$dG = VdP - SdT \quad \dots(4.40)$$

If the pressure remains constant, i.e.,  $dP = 0$

$$\text{Then } dG = - SdT$$

Let  $G_1$  be the initial free energy of a system at  $T$  and

$G_1 + dG_1$  = Free energy of the system at  $T + dT$ , where  $dT$  is infinitesimally small temperature change at constant pressure.

$$\therefore dG_1 = - S_1 dT \quad \dots(4.41)$$

where  $S_1$  is the entropy of the system in the initial state.

Now suppose that the free energy of the system in final state is  $G_2$  at  $T$  and  $G_2 + dG_2$  is the free energy of the system at  $T + dT$  in the final state at constant pressure.

$$\therefore dG_2 = - S_2 dT \quad \dots(4.42)$$

where  $S_2$  is the entropy of the system in the final state.

Subtracting (4.41) from (4.42), we get

$$dG_2 - dG_1 = - (S_2 - S_1) dT$$

or

$$d(\Delta G) = - \Delta S dT$$

$$\therefore \text{At constant pressure} \quad \left( \frac{\partial \Delta G}{\partial T} \right)_P = - \Delta S \quad \dots(4.43)$$

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

$$\text{or} \quad -\Delta S = \frac{\Delta G - \Delta H}{T} \quad \dots(4.44)$$

From (4.43) and (4.44), we get:

$$\frac{\Delta G - \Delta H}{T} = \left( \frac{\partial \Delta G}{\partial T} \right)_P \quad \text{or} \quad \Delta G - \Delta H = T \left( \frac{\partial \Delta G}{\partial T} \right)_P$$

$$\text{or} \quad \Delta G = \Delta H + T \left( \frac{\partial \Delta G}{\partial T} \right)_P \quad \dots(4.45)$$

According to the Gibbs – Helmholtz equation, the change in free energy of system at constant pressure is given by the equation (4.45) where  $\Delta H$  is the change in heat content of the system or the heat of reaction at constant pressure.

The value of electrical energy supplied by the cell is  $n FE$ , where  $n$  is the number of electrons liberated at one electrode ( $n$ , the valency of the ion),  $E$  is the E.M.F of the cell and  $F$  is faraday ( $= 96,500$  coulomb.)

$$\text{So, decrease in the free energy, } -\Delta G = n FE \quad \dots(4.46)$$

Putting the value of  $-\Delta G$  from equation (4.46) in equation (4.45), we get

$$\therefore nFE = \Delta H - T \left( \frac{\partial (-nFE)}{\partial T} \right)_P \quad \text{or} \quad nFE = -\Delta H + TnF \left( \frac{\partial E}{\partial T} \right)_P$$

$$\text{or} \quad E = -\frac{\Delta H}{nF} + T \left( \frac{\partial E}{\partial T} \right)_P \quad \dots(4.47)$$

The term  $\left( \frac{\partial E}{\partial T} \right)_P$ , represent the temperature coefficient of E.M.F. at constant pressure.

It is clear that electrical energy ( $nFE$ ) can be equal to, less than or greater than the enthalpy change ( $\Delta H$ ) depending upon the magnitude and sign of  $\Delta H$ .

The following cases may arise:

- (i) In case of Daniel cell,  $\frac{\partial E}{\partial T}$  is extremely small and may be taken to be zero. So the electrical energy produced ( $nFE$ ) is equal to the enthalpy change ( $\Delta H$ ). The value of E.M.F. ( $E$ ) can be calculated as :  $E = \frac{-\Delta H}{nF}$

Putting the value of  $-\Delta H = 50100$  cals.,  $n = 2$  and  $F = 96500$  Coulomb

$$E = \frac{50100 \times 4.185}{2 \times 96500} = 190 \text{ volts} \quad [\text{Since } 1 \text{ cal} = 4.185 \text{ Volt per coulomb}]$$

- (ii) When  $\frac{\partial E}{\partial T}$  is positive, the electrical energy produced is greater than the heat of reaction at constant pressure. The additional energy required is being absorbed from the surroundings.
- (iii) When  $\frac{\partial E}{\partial T}$  is negative, the electrical energy produced is less than the heat of reaction at constant pressure. The difference of energy being lost as heat to the surroundings.

#### 4.6.1 Calculation of $\Delta H$ , $\Delta G$ And $\Delta S$ From emf Data

Knowing the value of  $E$  as calculated in the (i) case above, the value of  $\Delta G$  can be calculated ( $-\Delta G = nFE$ ). Knowing the value of  $E$  and  $\frac{\partial E}{\partial T}$  the value of  $\Delta H$  can be calculated.

The entropy change ( $\Delta S$ ) accompanying the reaction can then be calculated from the relationship  $\Delta G = \Delta H - T\Delta S$ .

By Equation (4.46),  $\Delta G = -nFE$

Hence  $\Delta G$  is known, when EMF is known.

Again, according to the equation (4.47),

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_P \quad \text{or} \quad \Delta H = nF \left[ T \left( \frac{\partial E}{\partial T} \right)_P - E \right] \quad \dots(4.48)$$

Hence  $\Delta H$  can be calculated if the EMF,  $E$  and the temperature coefficient of the EMF,  $\left(\frac{\partial E}{\partial T}\right)_P$  are known.

The entropy change can then be calculated by using the relation;

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

or

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

or

$$T\Delta S = nF \left[ T \left( \frac{\partial E}{\partial T} \right)_P - E \right] + nFE$$

or

$$T\Delta S = nFT \left( \frac{\partial E}{\partial T} \right)_P - nFE + nFE$$

or

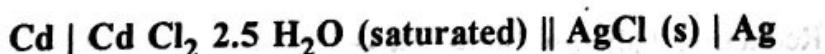
$$T\Delta S = nFT \left( \frac{\partial E}{\partial T} \right)_P$$

or

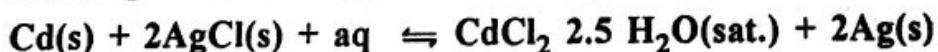
$$\Delta S = nF \left( \frac{\partial E}{\partial T} \right)_P \quad \dots(4.49)$$

Hence  $\Delta S$  can be calculated from knowledge of the temperature coefficient of the E.M.F,  $\left(\frac{\partial E}{\partial T}\right)_P$

#### Example 8. The E.M.F of the following cell



involved the following reaction:



is 0.6753 and 0.6915 at 25° and 0°C respectively. Calculate the heat of the reaction ( $\Delta H$ ), free energy change ( $\Delta G$ ) and entropy change ( $\Delta S$ ) at 25°C. (P.T.U. June 2003)

**Solution. (i) Enthalpy change ( $\Delta H$ )**

Here  $n = 2$ ,  $E = 0.6753$  volt,  $F = 96,500$  coulomb,  $T = 273 + 25 = 298$

$$\left(\frac{\partial E}{\partial T}\right)_P = \frac{0.3915 - 0.6753}{25K} = 0.000065 \text{ volts per Kelvin at atmospheric pressure}$$

Now since E.M.F. decreases with increase in temperature the value of  $\left(\frac{\partial E}{\partial T}\right)_P$  is negative in the present case.

$$\text{Thus } \left(\frac{\partial E}{\partial T}\right)_P = -0.000065 \text{ volt / degree}$$

$$\text{Now } E = \frac{-\Delta H}{nF} = T \left(\frac{\partial E}{\partial T}\right)_P$$

$$0.6753 = \frac{-\Delta H}{2 \times 96500} + 298(-0.000065)$$

$$\Delta H = -167.717 \text{ joules} = -167.717 \text{ KJ K}^{-1}$$

**(ii) Free energy change ( $\Delta G$ ):**

$$-\Delta G = nFE$$

$$\text{So } \Delta G = -2 \text{ mol} \times 96500 \text{ C mol}^{-1} \times 0.3753 \text{ V} \\ = -130332.9 \text{ J} = -130.33 \text{ KJ}$$

**(iii) Entropy change (DS):**

$$\text{Since } \Delta G = \Delta H - T\Delta S$$

$$-\Delta S = \frac{\Delta G - \Delta H}{T} = \frac{-130.33 \text{ KJ} - (-167.72 \text{ KJ})}{298} \\ = 0.1238 \text{ KJ K}^{-1} = 123.8 \text{ J K}^{-1}$$

**Example 9.** The e.m.f. of the cell reaction  $3\text{Sn}^{+4} + 2\text{Cr} \rightarrow 3\text{Sn}^{+2} + 2\text{Cr}^{+3}$  is 0.89. Calculate the standard free energy change for the reaction. (P.T.U. Dec. 2006, May 2007)

**Solution.** The standard free energy change of a redox reaction is given as  $\Delta G^\circ = -nFE^\circ$

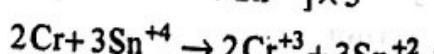
From the given cell reaction,  $3\text{Sn}^{+4} + 2\text{Cr} \rightarrow 3\text{Sn}^{+2} + 2\text{Cr}^{+3}$

The number of electrons involved ( $n$ ) can be calculated as:

$$\Delta G^\circ = -nFE^\circ$$

$$\text{Oxidation half } [\text{Cr} \rightarrow \text{Cr}^{+3} + 3e^-] \times 2$$

$$\text{Reduction half } [\text{Sn}^{+4} + 2e^- \rightarrow \text{Sn}^{+2}] \times 3$$



The value of  $n = 6$

Putting the given values in the above equations, we get

$$\Delta G^\circ = -6 \times 96500 \times 0.89 = -515310 \text{ J} = -515.31 \text{ KJ}$$

## 4.7 NERNST EQUATION OR CONCENTRATION DEPENDENCE OF ELECTRODE POTENTIAL

The e.m.f. of a cell depends both on (i) Standard e.m.f. of cell i.e. its nature (ii) the concentrations of the species involved in the cell reaction and (iii) temperature.

For a general cell reaction of the type,



In thermodynamics, the free energy ( $\Delta G$ ) accompanying the above general equation is given as:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

where  $\Delta G^\circ$  is the free energy change of the reaction under standard conditions.

Since  $\Delta G = -nFE$  and  $\Delta G^\circ = -nFE^\circ$

$$\text{So, } -nFE = -nFE^\circ + RT \ln \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

$$\text{or } E = E^\circ - \frac{RT}{nF} \ln \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

where  $E$  is the e.m.f. of the cell,  $E^\circ$  is the standard e.m.f. of the cell:

$[A]$ ,  $[B]$ ,  $[L]$  and  $[M]$  are the molar concentration of the species A, B, L and M respectively.

$a$ ,  $b$ ,  $l$  and  $m$  are the stoichiometric co-efficients in the chemical equation,  $n$  is the number of electrons involved,  $R$  is the gas constant,  $T$  is the absolute temperature,  $F$  is one faraday (96500 coulombs).

This equation is known as Nernst Equation.

At  $25^\circ\text{C}$ ,  $R = 8.314$  Joules/ kelvin/ mole,  $T = 25^\circ\text{C} + 273 = 298$  K (at Standard conditions) and  $F = 96500$  coulombs

$$\frac{2303RT}{F} = \frac{2.303 \times 8.314 \times 298}{96500} = 0.0591$$

Substituting the value of  $\frac{2303RT}{F}$  in equation above, we get:

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[L]^l [M]^m}{[A]^a [B]^b} \dots(4.50)$$

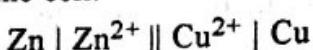
or 
$$E = E^\circ + \frac{0.0591}{n} \log \frac{[A]^a [B]^b}{[L]^l [M]^m}$$

It is seen from Nernst equation, that if the product of the molar concentration of products is more than the product of the reactants, e.m.f.,  $E$  is less than the standard e.m.f.,  $E^\circ$ . On the other hand, if the product of the molar concentration of the reactants is greater than that of the molar concentration of products,  $E$  is greater than  $E^\circ$ .

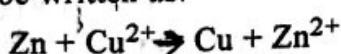
#### 4.7.1 Applications of Nernst Equation

##### (i) Calculation of the e.m.f. of a cell.

Consider for example the cell:



The cell reaction may be written as:



Applying Nernst equation (4.55):

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Cu}] [\text{Zn}^{2+}]}{[\text{Zn}] [\text{Cu}^{2+}]}$$

Here, number of electrons involved in the half cell reaction is 2.

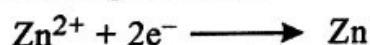
In the standard state, the activity of a solid is taken as unity.

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

From this equation, it is obvious that  $E$  may be equal to  $E^\circ$  or may be greater or less than  $E^\circ$ .  $E$  depends on the ratio of the concentration of  $\text{Zn}^{2+}$  ions and  $\text{Cu}^{2+}$  ions.

##### (ii) Calculation of the Single Electrode Potential

Although the standard electrode potential is fixed, the concentration of the ion in the half-cell affects its single reduction electrode potential. This is also given by Nernst's equation.



$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Zn}]}{[\text{Zn}^{2+}]} = E^\circ - \frac{RT}{nF} \ln \frac{1}{[\text{Zn}^{2+}]} = E^\circ + \frac{RT}{nF} \ln [\text{Zn}^{2+}]$$

[ ∵ Zn being solid, its concentration is taken as unity ]

$$E = E^\circ + \frac{RT}{nF} \ln [\text{Zn}^{2+}] = E^\circ - \frac{2.303RT}{nF} \log [\text{Zn}^{2+}] = E^\circ + \frac{0.0591}{n} \log [\text{Zn}^{2+}]$$

where  $E$  and  $E^\circ$  are the single electrode potential and standard potential,  $n$ ,  $R$  and  $F$  have the usual significance.

The general expression for electrode potential of a metal in contact with  $M^{n+}$  ions reaction involving the electrode may be written as

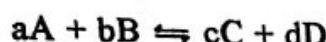


$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}]$$

### (iii) Calculation of equilibrium constant

At the equilibrium concentration of the two metal ions, there is no potential difference between the two electrodes and the e.m.f. of the cell becomes zero.

Consider a reaction at equilibrium



$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The Nernst equation can be represented as

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At the stage of equilibrium,  $E_{\text{cell}} = 0$

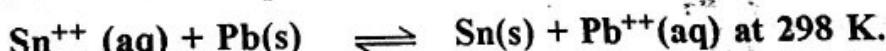
Therefore, the above equation can be written as

$$\text{Zero} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log K_c$$

or  $E_{\text{cell}}^\circ = \frac{0.0591}{n} \log K_c$ , where  $K_c$  is the equilibrium constant for the reaction.

Knowledge of standard cell potential can thus be employed for calculating the equilibrium constant for the reactions.

**Example 10.** Calculate the equilibrium constant for the reaction.

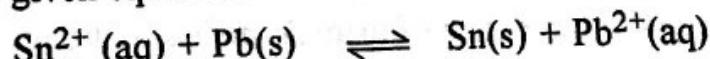


Given  $E^\circ(Sn^{++}/Sn) = -0.14$ , and  $E^\circ(Pb^{++}/Pb) = -0.13 \text{ V}$  (PTU. Dec. 2004)

**Solution.** According to Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log K$$

For the given equation:



$$E_{\text{cell}}^\circ = E_{Sn^{2+}/Sn}^\circ - E_{Pb^{2+}/Pb}^\circ \quad (\text{as Pb is being oxidised in the given equation})$$

$$= -0.14 - (-0.13) = -0.01 \text{ V.}$$

As, at equilibrium,  $E_{\text{cell}}$  becomes zero:

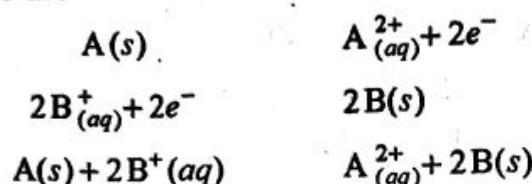
$$E_{\text{cell}}^\circ = \frac{0.059}{n} \log K$$

$$\text{or } -0.01V = \frac{0.059}{n} \log K = \frac{0.059}{2} \log K$$

$$-0.3389 = \log K \quad \text{or} \quad 0.4581 = K$$

**Example 11.** For a cell reaction  $A(s) + 2B(aq) \rightarrow A + 2(aq) + 2B(s)$  at 298K, the equilibrium constant is  $1.0 \times 10^4$ . Calculate  $E_{\text{cell}}^{\circ}$ . (PTU. Dec. 2006, May 2007)

**Solution.** The half cell reactions are



According to Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[A^{2+}_{(aq)}][B(s)]^2}{[A(s)][B^{2+}_{(aq)}]^2}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log K$$

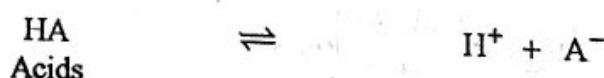
At equilibrium  $E_{\text{cell}} = 0$

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log(1 \times 10^4) = \frac{0.0591}{2} \times 4 = 0.1182V$$

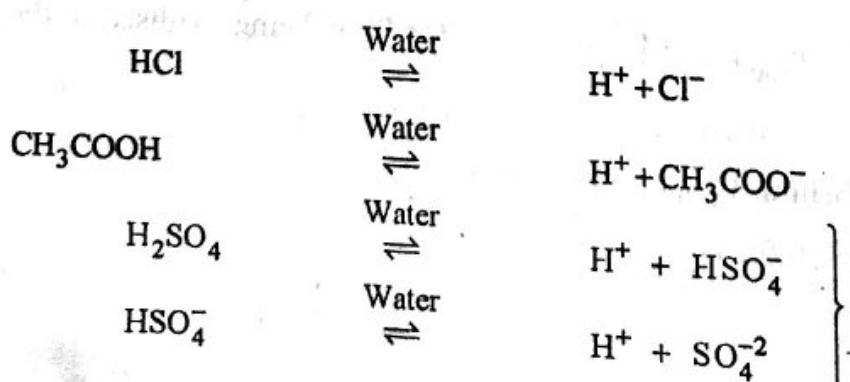
## 4.8 ARRHENIUS CONCEPT OF ACIDS AND BASES

In the light of the behaviour of electrolytes in solution, Arrhenius provided a well-defined basis for the concept of acids and bases.

**ACIDS:** According to him, an acid may be defined as a hydrogen containing substance which gives  $H^+$  ions in aqueous solution. Obviously the presence of ionisable hydrogen is an essential feature of all acids; Thus



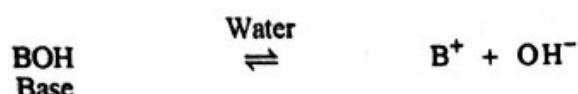
This definition could easily explain why the substances such as HCl,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  etc. are recognised as acids, since each of them furnishes hydrogen ions in solution. For instance:



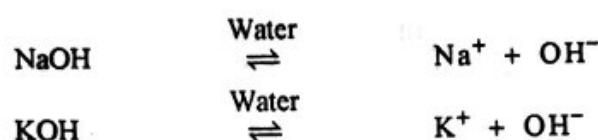
It should be noted that acids like  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  which contain two or more ionisable hydrogen atoms dissociate in more than one stage giving  $\text{H}^+$  ions in each case.

The common characteristics of acids such as sour taste, turning blue litmus red, reaction with bases to form salt and  $\text{H}_2\text{O}$  were attributed to the presence of  $\text{H}^+$  ions in aqueous solution.

**BASES:** A similar concept was put forward for bases. A base is defined as a substance which contains one or more hydroxyl groups and furnishes hydroxyl ( $\text{OH}^-$ ) ions in aqueous solution.



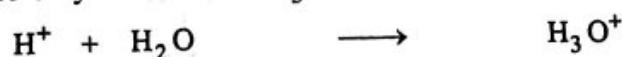
Thus, all commonly known bases such as  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{NH}_4\text{OH}$  ionizes in aqueous solution to give  $\text{OH}^-$  ions.



The hydroxyl ion is responsible for the basic properties exhibited by the bases.

### Nature of hydrogen ion in aqueous solution

According to Arrhenius, an acid gives  $\text{H}^+$  ions in aqueous solution. But a hydrogen ion is only a free proton which has a very small size and an extremely high charge density. It is very strongly attracted by the negative end of water molecules and as a result it gets very readily hydrated or attracted to water molecules. Therefore, it is not very appropriate to speak of the formation of free  $\text{H}^+$  ions or protons in solution. On the other hand, the  $\text{H}^+$  ion always exists in solution in the more stable hydrated form,  $\text{H}_3\text{O}^+$ , known as *hydronium ion* or hydrated proton.



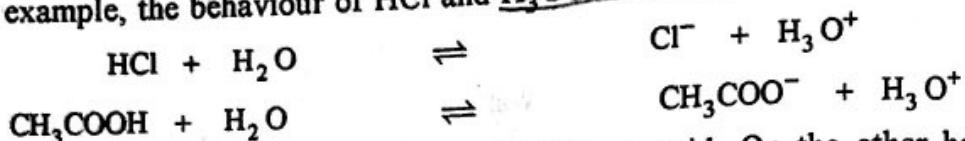
In fact, even this may be an over-simplification. It has been suggested recently that hydrated proton may not be as simple as  $\text{H}_3\text{O}^+$ . Rather it may be further hydrated to form species such as  $\text{H}_9\text{O}_4^+$ . But in the absence of any definite evidence about the exact number of water molecules involved, the hydronium ion is commonly represented as  $\text{H}_3\text{O}^+$  or  $\text{H}^+(\text{aq})$  or  $\text{H}_3\text{O}^+(\text{aq})$ .

### Limitations of Arrhenius Concept

Soon after Arrhenius had proposed his concept of acids and bases, it was realized, that his concept has a limited scope only. This is because it attributes all acidic and basic properties to the formation of hydrogen and hydroxyl ions *in aqueous solution only*. However, there are substances such as  $\text{NH}_3$ ,  $\text{CaO}$  etc. which do not contain the hydroxyl group but can still act as bases since they are known to neutralise acids. Similarly, there are substances such as carbon dioxide which cannot by themselves dissociate to form hydrogen ions but even then act as acids in aqueous solution.

### 4.8.1 Bronsted-Lowry Concept of Acids and Bases

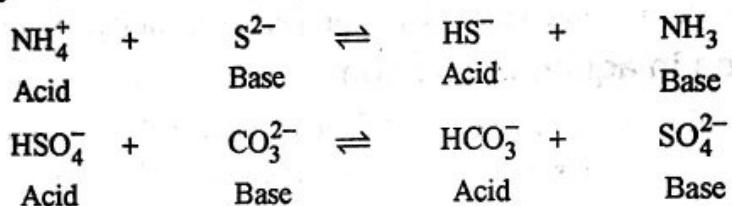
In view of the limitations of Arrhenius concept, Bronsted and Lowry proposed more general definition for acids and bases. According to their concept *an acid is a substance (molecular or ionic) which has a tendency to donate a proton. On the other hand, a base is a substance (molecular or ionic) that has a tendency to accept a proton from any other substance.* For example, the behaviour of HCl and ~~H<sub>3</sub>COOH~~ in water is shown below:



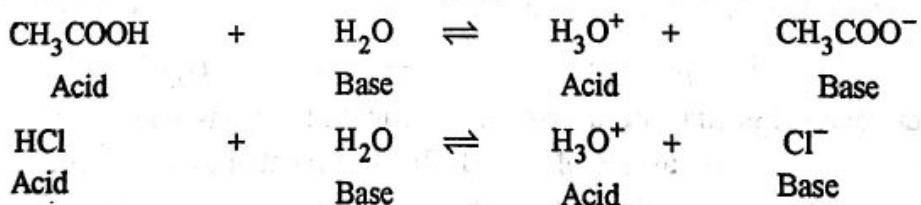
As HCl donates a proton to water, hence HCl is an acid. On the other hand, H<sub>2</sub>O accepts a proton from HCl, hence H<sub>2</sub>O is a base. Similarly H<sub>3</sub>COOH donates a proton to H<sub>2</sub>O and acts as an acid, whereas H<sub>2</sub>O accepts a proton and acts as a base.

The main features of Bronsted-Lowry concept are given as under:

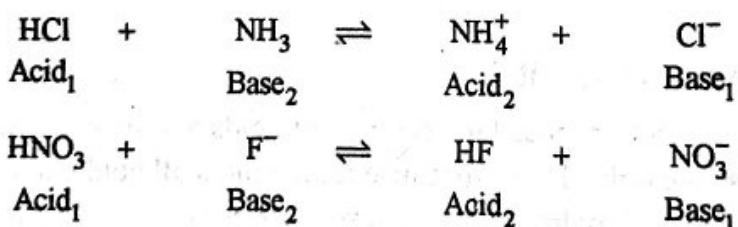
1. An acid-base reaction involves the transference of a proton from a proton donor (acid) to a proton acceptor (base). Thus this concept is also called proton transfer theory of acids and bases.
2. Not only molecules but ions are also capable of acting as acids and bases. For example,



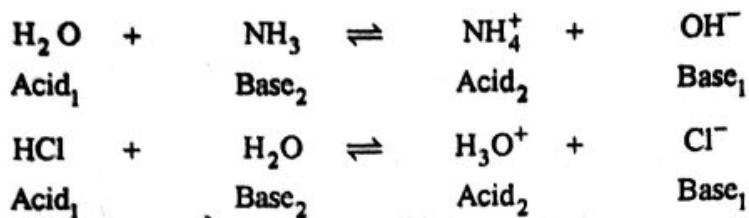
3. For an acid to act as a proton donor, a base (proton acceptor) must be present to receive proton. For example, acetic acid or HCl acts as an acid in water but not in benzene because benzene does not accept proton.



4. Whenever an acid and a base reacts another pair of acid-base is formed e.g.,

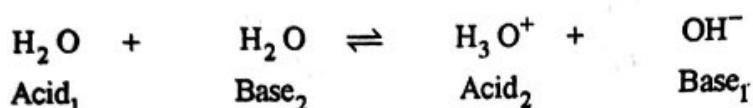


5. **Amphoteric compounds:** Certain molecules and ions may exhibit both acidic or basic behaviour under the appropriate conditions. Such species are known as amphiprotic or amphoteric. For example, water may lose a proton to a base such as NH<sub>3</sub> or gain a proton from an acid such as HCl and so it is classified as amphiprotic.



Species like  $\text{HSO}_3^-$ ,  $\text{HS}^-$ ,  $\text{HCO}_3^-$  are amphoteric in nature.

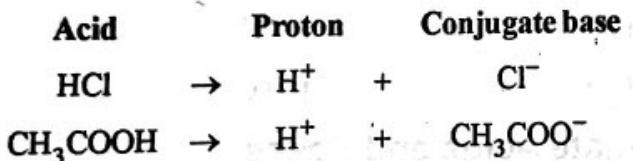
6. Water has a dual character. It can behave as a base in presence of acid (say HCl) and as an acid in presence of a base (say  $\text{NH}_3$ ) as shown above. Its dual behaviour can be represented as:



7. All Bronsted acids are Arrhenius acids but Bronsted bases are not Arrhenius bases. Bronsted acids are proton donors. In other words, it releases proton to some substance acting as base. Arrhenius acids also release  $\text{H}^+$  ions (protons) in aqueous solutions. Thus Bronsted acids are Arrhenius acids. But Bronsted bases are proton acceptors, whereas Arrhenius bases should release  $\text{OH}^-$  ions in aqueous solution. A Bronsted base may or may not have  $\text{OH}^-$  ions.

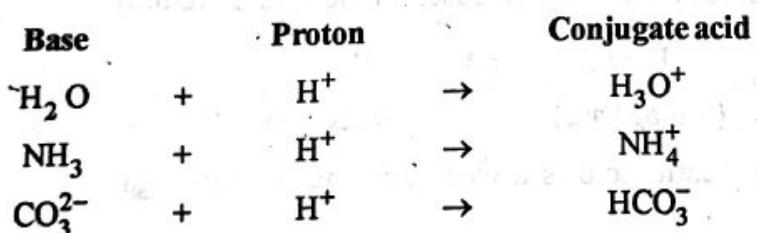
### Conjugate acid-base pairs

When an acid loses a proton, it forms what is called conjugate base of the acid. For example,

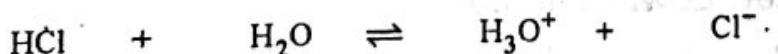


When a base accepts a proton, it forms what is called the conjugate acid of the base.

For example,



Now an acid does not form its conjugate base unless a second base ( $\text{Base}_2$ ) is present to accept a proton. When the second base ( $\text{Base}_2$ ) accepts the proton, it forms its conjugate acid, i.e.,  $\text{Acid}_2$ . For example,



In the forward reaction, HCl donates a proton and thus behaves as an acid, water accepts a proton and thus behaves as a base. In the reverse reaction,  $\text{H}_3\text{O}^+$  donates a proton to chloride ion and thus  $\text{H}_3\text{O}^+$  is an acid while  $\text{Cl}^-$  is a base. Such pairs of substances which are

formed from one another by gain or loss of a proton are known as conjugated acid-base pairs. Thus hydrochloric acid is a conjugate acid of chloride ion while water is a conjugate base of hydronium ion.

In general, each acid base reaction involves two pairs of acids and bases as shown below:

$$\text{Bronsted Acid} + \text{Bronsted Base} = \text{Conjugate Acid} + \text{Conjugate Base}$$

This is illustrated with the following examples:

Bronsted Acid	Bronsted Base		Conjugate Acid		Conjugate Base	
HCl	+	H <sub>2</sub> O	⇒	H <sub>3</sub> O <sup>+</sup>	+	Cl <sup>-</sup>
HCl	+	NH <sub>3</sub>	⇒	NH <sub>4</sub> <sup>+</sup>	+	Cl <sup>-</sup>
H <sub>2</sub> O	+	CO <sub>3</sub> <sup>2-</sup>	⇒	HCO <sub>3</sub> <sup>-</sup>	+	OH <sup>-</sup>
H <sub>2</sub> O	+	H <sub>2</sub> O	⇒	H <sub>3</sub> O <sup>+</sup>	+	OH <sup>-</sup>

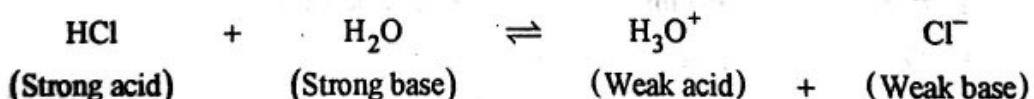
### Polyprotic acid

Some acids can furnish two or more protons. These are called polyprotic acid, e.g. H<sub>2</sub>SO<sub>4</sub> is a diprotic acid while H<sub>3</sub>PO<sub>4</sub> is a triprotic acid. These acids always dissociate in stages. Each stage furnishes only one proton so that Bronsted concept is applied to each stage of dissociation of such acids. For example dissociation of H<sub>3</sub>PO<sub>4</sub> takes place in three stages:

Conjugate Acid	Conjugate Base		Conjugate Acid	Conjugate Base		
H <sub>3</sub> PO <sub>4</sub>	+	H <sub>2</sub> O	⇒	H <sub>3</sub> O <sup>+</sup>	+	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	+	H <sub>2</sub> O	⇒	H <sub>3</sub> O <sup>+</sup>	+	HPO <sub>4</sub> <sup>2-</sup>
HPO <sub>4</sub> <sup>2-</sup>	+	H <sub>2</sub> O	⇒	H <sub>3</sub> O <sup>+</sup>	+	PO <sub>4</sub> <sup>3-</sup>

### Relative Strengths of Conjugate Acids and Bases

It is observed that if an acid is strong its conjugate base is weak and vice versa. For example, HCl is a strong acid, its conjugate base, Cl<sup>-</sup> ion, is a weak base.

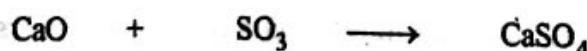


On the other hand, acetic acid is a weak acid but its conjugate base, acetate ion, is a strong base.



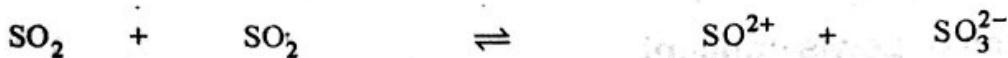
### Limitation of Bronsted-Lowry Theory

The theory fails to explain acid-base reactions in which no proton transfer takes place, e.g., the reaction:



involves the neutralisation of basic oxide (CaO) with acidic oxide ( $\text{SO}_3$ ) to form a salt ( $\text{CaSO}_4$ ) without any transfer of proton between them.

Similarly, reactions taking place in non-aqueous solvents cannot be explained by this theory, e.g.:



#### 4.8.2 Lewis Concept of Acids and Bases

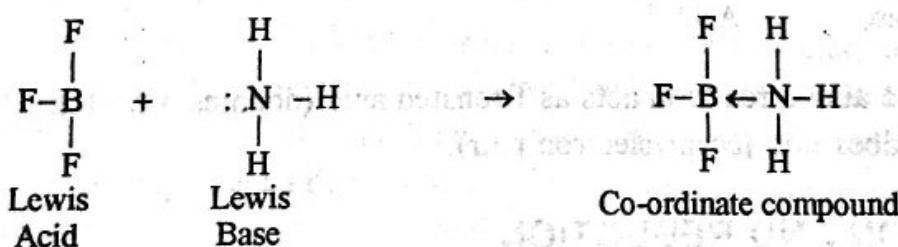
The Arrhenius as well as Bronsted-Lowry concepts limit classification of acid as substances which contain hydrogen. But G.N. Lewis put forward a more general concept which does not require hydrogen to be an essential constituent of all acids. According to Lewis, *an acid is a substance which can accept a pair of electrons while a base is a substance which can donate a pair of electrons to form a coordinate or dative bond.*

In other words, a base is an electron donor while an acid is an electron acceptor. This is the most fundamental of acid-base concepts and includes all other concepts.

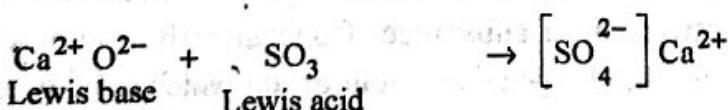
A base according to Lewis, is any substance with one or more lone pairs of electrons. It may be a neutral molecule such as:  $\text{NH}_3$  or a negative ion such as:  $\text{CN}^-$  ion. It may be noted that any substance which can donate a pair of electrons can easily accept a proton. This means that a Lewis base is a Bronsted base.

#### Examples of Acid-base reactions:

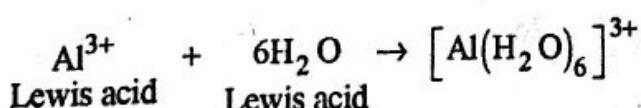
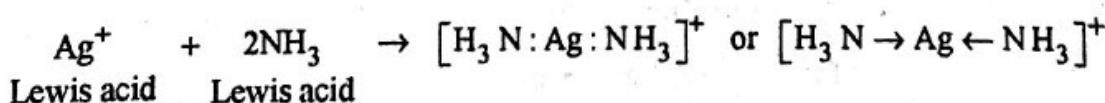
- (i) The molecule of a Lewis acid with a central atom having incomplete octet, and a Lewis base with one or more unshared pairs of electrons,  $\text{BF}_3$  and  $\text{AlCl}_3$  are examples of Lewis acids of this type.



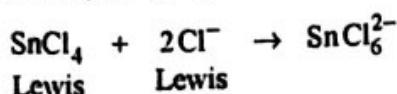
- (ii) The molecule of a Lewis acid containing multiple bonds, e.g.,  $\text{SO}_3$  has multiple bonds. It is not an Arrhenius or Bronsted acid. It is a Lewis acid and neutralizes bases.



- (iii) Simple cations: Simple cations like  $\text{Al}^{3+}$ ,  $\text{Ag}^+$ , act as lewis acids, because they have empty orbitals in their outermost energy levels.



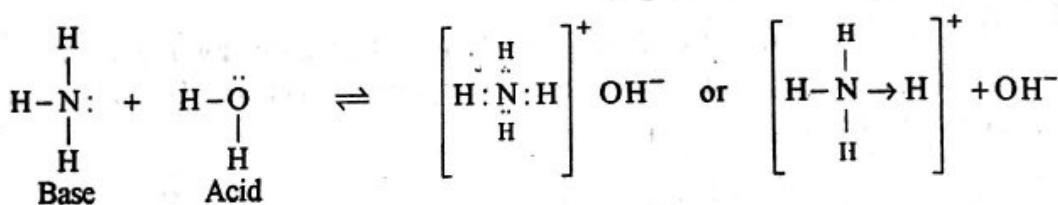
- (iv) The molecule of a Lewis acid having central atom with empty d-orbitals, Sn in  $\text{SnCl}_4$  has empty d-orbitals which are used up to make  $\text{SnCl}_4$  a Lewis acid, the base is a negative ion,  $\text{Cl}^-$ ,  $\text{F}^-$ .



### Limitations of Lewis concept:

- It is very general and includes all the co-ordination compounds and reactions. Protic acids do not form co-ordinate bond with bases.
- Acid-base reactions are quite fast. But the reactions taking place forming co-ordinate compound are very slow. Thus it does not fit in normal acid-base concept.
- The catalytic action of acids in different reactions is due to  $\text{H}^+$  ions. Lewis acid may not contain hydrogen, so, they cannot act as catalysts.
- The essential requirement or the main feature of Lewis concept of acid is the formation of co-ordinate bond with bases. However, protic acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ) do not form co-ordinate bond with bases. This is against Lewis theory.

**Lewis – Bases are essentially Bronsted Bases** because all such substances, e.g.,  $\text{NH}_3$ ,  $\text{CN}^-$ , etc., are also capable of accepting a proton. But Bronsted acids are not Lewis-acids.

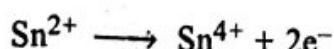
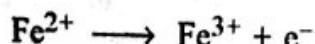
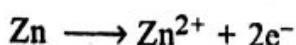


Water in the above reaction acts as Bronsted acid (donates a proton). However, water is not Lewis acid (does not accept electron pair).

## 4.9 OXIDATION AND REDUCTION

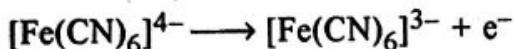
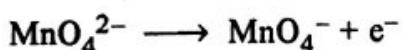
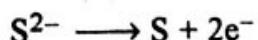
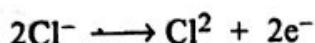
**Oxidation :** Earlier oxidation was treated as any process involving addition of oxygen or removal of hydrogen from a substance. However, these days oxidation is defined as a process which involves the loss of electrons by a substance. Consequently, there is an increase in positive charge or decrease in negative charge of the atom or ion which undergoes oxidation. For example,

- (i) *Loss of electrons resulting in an increase in positive charge*



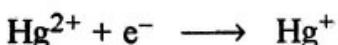
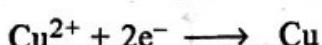
## USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

(ii) *Loss of electrons resulting in a decrease in negative charge*

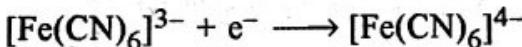
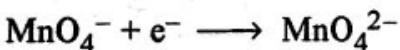


**Reduction:** Earlier, reduction was treated as a process involving addition of hydrogen or removal of oxygen from a substance. However, these days, reduction is defined as a process which involves the gain of electrons by a substance. Consequently, there is a decrease in positive charge or increase in negative charge of the atom or ion which undergoes reduction. For example,

(i) *Gain of electrons resulting in a decrease in positive charge*

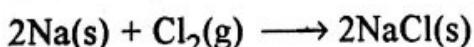


(ii) *Gain of electrons resulting in a increase in negative charge*



Further, in a chemical reaction, there is no net loss or gain of electrons. Therefore, loss and gain of electrons from one substance to another must take place simultaneously. In other words, in a chemical reaction, a substance can gain electrons only if another substance which can lose electrons is also present in the system. This means oxidation can take place only if reduction also takes place at the same time and vice versa.

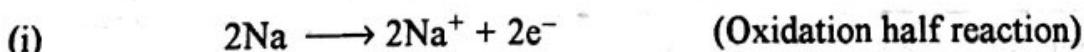
Therefore, oxidation and reduction always occurs side by side. To illustrate this, let us consider reaction between sodium metal and chlorine gas to form sodium chloride.



Now this reaction consists of two distinct, though simultaneous processes, which take place in such a way that:

$$\text{Number of electrons lost} = \text{Number of electrons gained}$$

These are represented below:

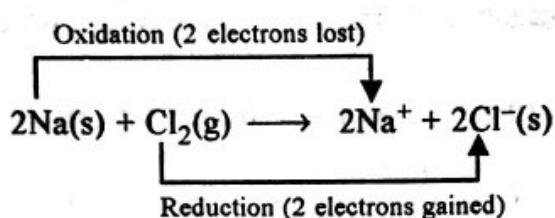


Thus, the overall reaction involves the transfer of electrons from sodium metal to chlorine. It means that sodium metal gets oxidized to  $\text{Na}^+$  ion while chlorine gets reduced to  $\text{Cl}^-$  ions so that overall reaction involves oxidation and reduction and is known as *redox reaction*.

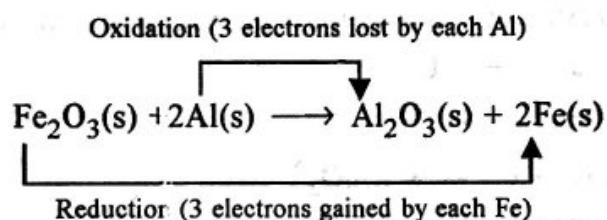
Therefore, a redox reaction may be defined as a reaction in which electrons are transferred from one to another reactant.

Every electron transfer reaction or redox reaction is the sum of oxidation half reaction in which electrons are lost and a reduction half reaction in which electrons are gained as shown above. The sum of the two half reactions is the total or net reaction known as redox reaction.

We may depict the above redox reaction in another way



Another example of the redox reactions is :



## Oxidising and Reducing agents

On the basis of electron transfer, an oxidizing agent may be defined as the substance which can accept electrons and a reducing agent as that which can lose electrons. The oxidizing agent itself, however, gets reduced while the reducing agent gets oxidized. In the formation of  $\text{NaCl}$  from sodium and chlorine, chlorine acts as oxidizing agent and sodium acts as reducing agent.

Some common examples of oxidising agents also called *oxidants* are  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , oxygen, ozone,  $\text{HNO}_3$  and  $\text{SO}_2$  etc.

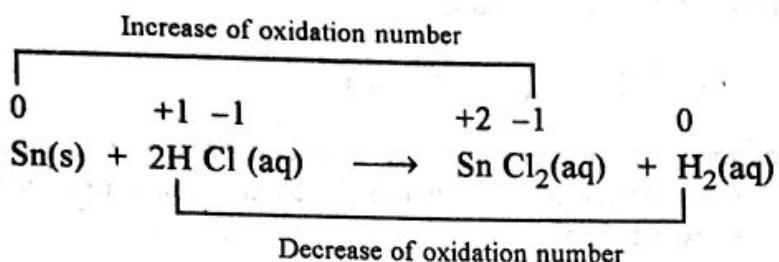
Some common examples of reducing agents also called *reductants* are: Ferrous salt, oxalic acid and oxalates,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{H}_2\text{S}$  and  $\text{C}$  etc.

There are some substances which act as *oxidants as well as reductants* depending upon the conditions of the reaction e.g.  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_2$  etc.

### 4.9.1 Redox Reaction in terms of Oxidation Number

An atom undergoes *oxidation* when it increases its oxidation number. It undergoes *reduction* when its oxidation number decreases. Since the number of electrons in a chemical reaction remains the same, reduction of one atom must accompany the oxidation of another.

Therefore, any reaction involving changes in oxidation numbers is an oxidation reduction or Redox reaction. For example, consider the reaction



As may be seen, Sn is converted to  $\text{Sn}^{2+}(\text{aq})$  by losing two electrons and gets oxidized. On the other hand  $\text{H}^+$  ions gained one electron and gets reduced. It may also be seen that oxidation number of Sn increases from 0 to +2 when it gets oxidized. The oxidation number of  $\text{H}^+$  decreases from +1 to 0 when it gets reduced. Therefore, *oxidation is an increase in oxidation number while reduction is decrease in oxidation number*. In the above reaction, HCl acts as *oxidising agent* while Sn acts as *reducing agent*.

## 4.10 SOLUBILITY EQUILIBRIA

When dissolved in suitable solvents electrolytes undergo dissociation to form charged chemical species known as *ions*. But this dissociation into ions seldom takes place to completion due to reversible nature of the process. In fact, the extent of dissociation is different in different cases. Electrolytes such as NaCl and HCl which are almost completely ionised into ions are called strong electrolyte.

On the other hand, electrolytes such as acetic acid ( $\text{CH}_3\text{COOH}$ ) where the degree of dissociation is low. Such substances which dissociate to a small extent in aqueous solution and hence conduct electricity to a small extent are called weak electrolytes.

In the solutions of weak electrolytes, an equilibrium is established between the ions in solution and the undissociated molecules. This is known as *ionic equilibrium*. Therefore, *ionic equilibrium is the equilibrium which is established between the undissociated molecules and the ions in the solution of weak electrolytes*.

The fraction of the total number of molecules which is ionised at the equilibrium state is known as the *degree of dissociation or ionisation*. It is usually represented by the symbol  $\alpha$ .

$$\alpha = \frac{\text{No. of dissociated molecules}}{\text{Total No. of molecules}}$$

$$\text{and Percentage dissociation} = \frac{\text{No. of dissociated molecules}}{\text{Total No. of molecules}} \times 100$$

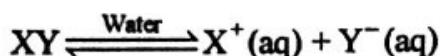
### Different types of Ionic Equilibria

Reactions involving ionic equilibrium may be classified as follows:

1. Equilibria involving soluble ionic compounds such as weak acids and weak bases.
2. Equilibria involving sparingly soluble ionic compounds: solubility product.

In this chapter, we shall be discussing them as under:

- 1. Equilibria involving soluble ionic compounds such as weak acids and weak bases.:**  
Let a weak electrolyte XY be dissolved in water, its ionisation may be represented as:



Let the original concentration of XY prior to dissociation be  $c$  moles per litre and let  $\alpha$  be the degree of dissociation at equilibrium. Then the concentrations of the various species will be as shown below :

Initial concentration (mol/l)	$c$	0	0
		$\text{XY} \xrightleftharpoons{\text{Water}} \text{X}^+(\text{aq}) + \text{Y}^-(\text{aq})$	
Equilibrium concentration (mol/l)	$c(1-\alpha)$	$c\alpha$	$c\alpha$

Applying the law of chemical equilibrium, we have

$$K_c = \frac{[\text{X}^+][\text{Y}^-]}{[\text{XY}]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

where  $K_c$  is known as *dissociation constant*.

If  $\alpha$  is very small as compared to unity, the value of  $\alpha$  may be neglected in the denominator, i.e.,  $1-\alpha$  may be taken equal to 1. In that case :

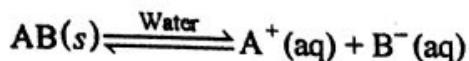
$$K_c = c\alpha^2 \quad \text{or} \quad \alpha^2 = \frac{K_c}{c}$$

$$\text{or} \quad \alpha = \sqrt{\frac{K_c}{c}} \quad \text{or} \quad \alpha \propto \sqrt{\frac{1}{c}}$$

Thus, it may be seen that the degree of ionisation of a weak electrolyte is inversely proportional to the concentration of the solution. This means that the degree of ionisation would increase with dilution and would approach unity in very dilute solutions. This means that all electrolytes are almost completely ionised in very dilute solutions.

- 2. Equilibria involving sparingly soluble ionic compounds : Solubility Product:** All electrolytes dissolve in water. Substances like  $\text{AgCl}$ ,  $\text{BaSO}_4$ , etc. which dissolve to a very small extent are called sparingly soluble. When a sparingly soluble salt like  $\text{AgCl}$  is treated with water, an extremely small amount of it dissolves. The solution is, therefore, saturated with respect to  $\text{AgCl}$  although it is very very dilute. But whatever little  $\text{AgCl}$  dissolves, splits into ions and an equilibrium is set up between the undissolved  $\text{AgCl}$  and its ions. Thus, even very dilute solutions of sparingly soluble salts are saturated and there exists an equilibrium between the undissolved salt and its ions.

Let us now consider a general case of a sparingly soluble salt, say AB. When this salt is dissolved in water to get a saturated solution at a particular temperature, there exists an equilibrium between the undissolved solid salt and the ions  $\text{A}^+$  (aq) and  $\text{B}^-$  (aq) in solution. This can be represented as :



Applying the Law of Mass Action, we have :

$$K_c = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]_{\text{solid}}}$$

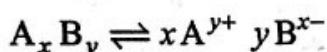
Since the molar concentration or active mass of a solid is taken as constant (say  $k$ ), we may rewrite the above equation as :

$$K_c = \frac{[\text{A}^+][\text{B}^-]}{k}$$

or  $K \times k = [\text{A}^+][\text{B}^-] = K_{sp}$

The constant  $K_{sp}$  is known as *solubility product*. It is equal to the product of ionic concentrations, termed as *ionic product*, for a saturated solution.

In general, for any sparingly soluble salt  $\text{AxBy}$ , which dissociates to set up the equilibrium



The solubility product may be expressed as :

$$K_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$$

where  $\text{A}^{y+}$  and  $\text{B}^{x-}$  denote the positive and negative ions respectively and  $x$  and  $y$  represent the number of these ions in the formula or the electrolyte.

Thus, the solubility product of a salt at a given temperature may be defined as the product of the concentrations of its ions, in a saturated solution, each concentration raised to a power equal to the number of times each ion occurs in the equation for the dissociation of the salt.

It may be borne clearly in mind that both the terms ionic product and solubility product represent the product of the concentrations of the ions of the salt in the solution. But the term ionic product applies to all kinds of solutions whether unsaturated or saturated so that its value is not definite. The term solubility product, however, applies only to a saturated solution and has a definite value. It is, therefore, the ionic product of a saturated solution.

It may be noted that the  $K_{sp}$  of any electrolyte is independent of the source of the ions. However, the product of the concentration of the ions in any solution cannot be more than  $K_3$  irrespective of the nature of the source of the ions. If the concentration of either one or both types of ions is increased so that the ionic product temporarily exceeds the solubility product the excess ions at once combine with oppositely charged ions and the solid salts separate out. Thus, the concept of solubility product fixes the relative values of ionic concentrations in a saturated solution even when the ions are furnished by different electrolytes producing the required ions.

#### 4.10.1 Calculation of Solubility Product

The value of solubility product can be easily calculated if the concentration of ions present in saturated solutions are known as illustrated below.

**Example 13.** The solubility of  $\text{Mg}(\text{OH})_2$  is  $1.518 \times 10^{-4}$  moles per litre at 285 K. Calculate its solubility product at this temperature.

**Solution.** We know that :  $\text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$

It is obvious that the concentration of  $\text{Mg}^{2+}$  ions is the same as that of  $\text{Mg}(\text{OH})_2$  while that of  $\text{OH}^-$  ions is twice that of  $\text{Mg}(\text{OH})_2$ .

$$[\text{Mg}^{2+}] = [\text{Mg}(\text{OH})_2] = 1.518 \times 10^{-4} \text{ moles/litre}$$

$$[\text{OH}^-] = 2 \times [\text{Mg}(\text{OH})_2]$$

$$= 2 \times 1.518 \times 10^{-4} = 3.036 \times 10^{-4} \text{ moles/litre}$$

$$\text{Hence } K_s = [\text{Mg}^{2+}][\text{OH}^-]^2 = [1.518 \times 10^{-4}] [3.036 \times 10^{-4}]^2 = 1.4 \times 10^{-11}$$

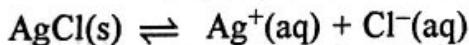
#### 4.10.2 Applications of Solubility Product

The concept of solubility product has been very helpful in studying the reactions involving ionic equilibria. The more important applications are discussed below :

(i) **Calculation of Solubility.** Knowing the solubility product of a salt at a particular temperatures, its solubility can be readily calculated as explained below.

**Example 14.** Calculate the solubility of silver chloride in water at room temperature if solubility product of  $\text{AgCl}$  is  $1.6 \times 10^{-10}$ .

**Solution.** The solubility equilibrium may be shown as :



Let the solubility of silver chloride in water be  $c$  moles per litre. Therefore, the solution would contain  $c$  moles of  $\text{Ag}^+$  ions and  $c$  moles of  $\text{Cl}^-$  ions per litre, since one mole of  $\text{AgCl}$  produces one mole each of  $\text{Ag}^+$  and  $\text{Cl}^-$  ions. Hence, the solubility product,  $K_{sp}$  of silver chloride would be given by the expression :

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = c \times c = c^2$$

But the actual value of solubility product is  $1.6 \times 10^{-10}$

$$\text{So, } c^2 = 1.6 \times 10^{-10}$$

$$c = \sqrt{1.6 \times 10^{-10}} = 1.26 \times 10^{-5} \text{ moles/litre.}$$

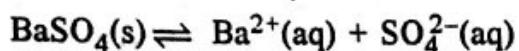
As one mole of  $\text{AgCl}$  is equal to 143.5 g, therefore  $c$  may also be expressed as :

$$c = 143.5 \times 1.26 \times 10^{-5} \text{ g/litre} = 0.0018 \text{ g/litre.}$$

(ii) **Predicting the Precipitation of Reactions.** As already pointed out, the solubility product represents the upper limit of ionic product for a saturated solution of a salt and this value cannot be exceeded if the ions are to remain in solution. In other words, if the ionic product exceeds the solubility product even momentarily, the excess ions immediately combine with oppositely charged ions and the solid salt precipitates

out. This serves as an important guiding principle in following the course of ionic reactions. For instance, let us find out what happens when 10 ml of 0.2 M solution of sodium sulphate is mixed with an equal volume of 0.1 M barium chloride solution. Will a precipitate of barium sulphate be formed or will it not be formed?

The solubility equilibrium of  $\text{BaSO}_4$  may be written as :



To start with, the solution of sodium sulphate contains 0.2 mole per litre of  $\text{SO}_4^{2-}$  ions while the solution of barium chloride contains 0.1 mole per litre of  $\text{Ba}^{2+}$  ions. But on mixing the two solutions, the total volume is doubled and as a result the concentration of each of the ions is reduced to one half. Therefore, the resulting solution contains 0.1 mole per litre of  $\text{SO}_4^{2-}$  ions and 0.05 mole per litre of  $\text{Ba}^{2+}$  ions.

$$\text{Product of ionic concentration} = [0.1] [0.05] = 0.005 = 5 \times 10^{-3}$$

$$\text{But the solubility product of } \text{BaSO}_4 \text{ is } 1.0 \times 10^{-10}$$

Since the ionic product far exceeds the solubility product, barium sulphate gets precipitated. In short,

*A precipitate is formed if ionic product is greater than  $K_{sp}$ .*

*A solution is just saturated if ionic product is equal to  $K_{sp}$ .*

*A solution is unsaturated (no ppt. formed) if ionic product is less than  $K_{sp}$ .*

- (iii) **Inorganic Qualitative Analysis.** The solubility product concept plays a very important role in inorganic qualitative analysis. It enables us to effect the selective precipitation of salts in different groups which forms the basis of the scheme for the analysis of cations. For example, the basis of grouping  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Hg}^+$  together in group I is that their chlorides have very low solubility products. As such they are practically insoluble in water and are, therefore, readily precipitated on adding dilute hydrochloric acid to the solution of the salt.

#### 4.10.3 Comparison of Solubility Product with Ionic Product

The main points of difference between solubility product and ionic product are listed in Table 4.2.

Table 4.2. Comparison of solubility product with ionic product

Solubility product	Ionic product
1. It is product of the concentrations of the ions of an electrolyte, each raised to the appropriate power in a saturated solution.	1. It is the product of the concentration of the ions of an electrolyte each raised to the appropriate power in any solution.
2. It is applicable to only saturated solutions.	2. It is applicable to all types of solutions which may be unsaturated or saturated.