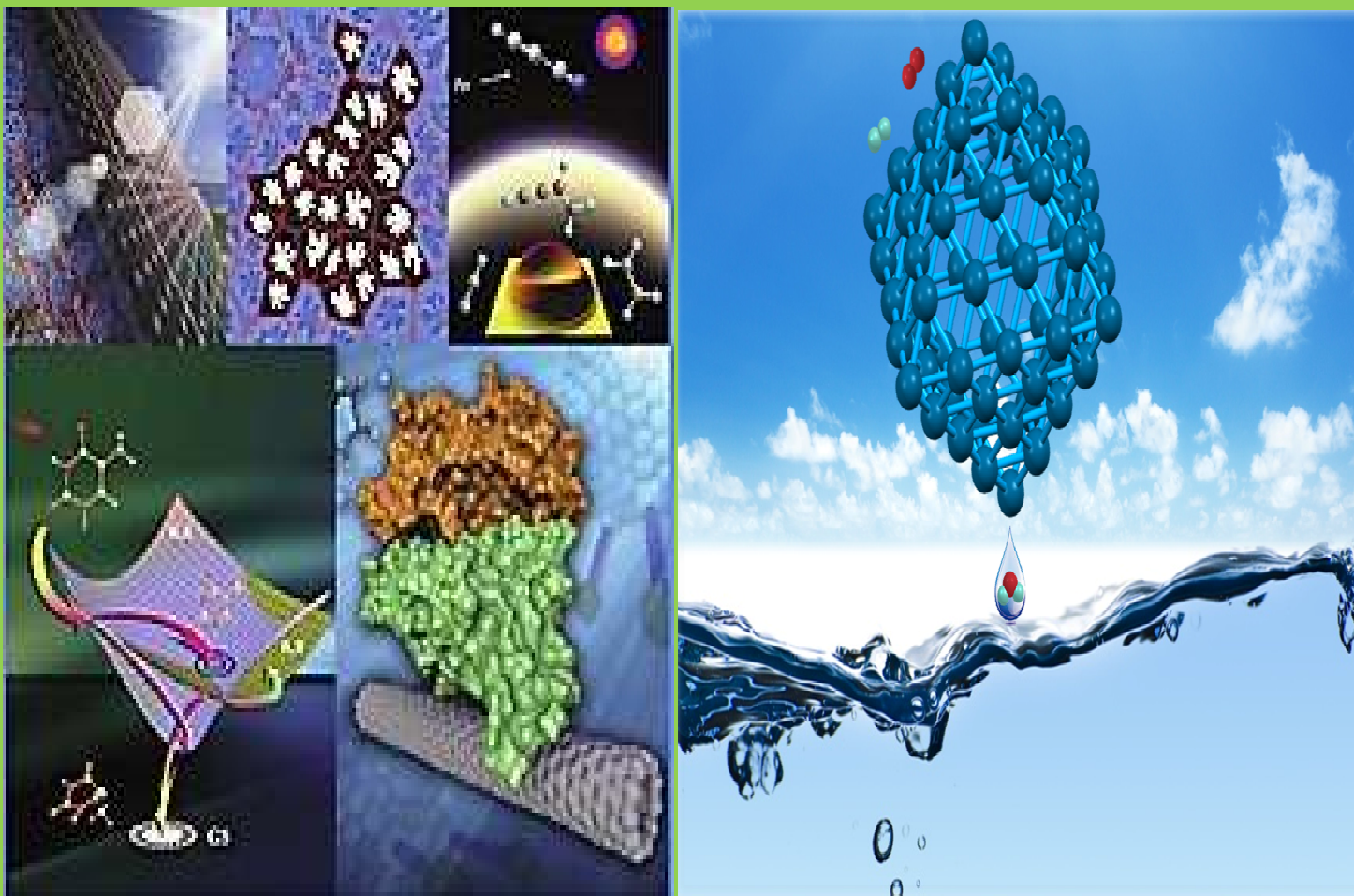BSCCH- 203

B. Sc. II YEAR

PHYSICAL CHEMISTRY-II

SCHOOL OF SCIENCES

DEPARTMENT OF CHEMISTRY

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UNIT -1 THERMODYNAMICS-II

CONTENTS:

1.1 OBJECTIVES

As we know thermodynamics concern itself with the flow of heat and it deals with relation between heat and work. The science of thermodynamics governs not only the transformation of heat or any other form of energy into work but also all types of interconversion of one kind of energy into another.

1.2   INTRODUCTION

The first law summarizes our experience regarding the transformation of energy. It states that (i) the different form of energy is inter convertible and (ii) when one form of energy disappears, an equivalent amount of energy of another kind must appear. But there some limitations of the first law. The first law does not indicate whether the change would at all occur and, if it occurs, to what extent. It also does not indicate the direction in which the change would take place.

Few examples are listed below:

1. Suppose two bodies A and B are brought in contact of each other. Then according to first law, according to first law q amount of heat is lost by A, exactly q amount of heat will be gain by B or vice versa. First law does not indicate which body A or B will lose the heat. For this to know the direction of flow of heat we need another information, namely temperature of A and B.

2. The dissociation of PCl_5 takes place in the following equilibrium

    PCl_5 $= PCl_3 + Cl_2$:
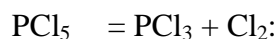
    The first law tells us only that if q amount of heat be evolved in the direct process in the dissociation of pentachloride, then in the opposite reaction of combination of trichloride and chlorine exactly q amount of heat would be absorbed. If we have an arbitrary mixture of PCl_5, PCl_3 and Cl_2, we cannot ascertain from the first law alone there would be dissociation of pentachloride or not. To determine the direction in which the chemical change would occur, we require the knowledge of the equilibrium constant of the reaction.

3. The first law states that energy of one form can be converted into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work. There is thus need for another law, the second law of thermodynamics.

    These examples illustrate the insufficiency of the first law. To ascertain the direction of a chemical or physical process we need something more beyond first law; before we can state second law of thermodynamics in a usable form, we must define some terms.

1.3   IRREVERSIBLE OR SPONTANEOUS PROCESSES

Changes taking place in a system without the aid of any external agency is termed as spontaneous processes several examples of such processes can be given. Some of these are follows.

(i)   Water flows downhill spontaneously. We cannot reverse the direction of flow without some external aid

(ii)   Suppose a vessel containing a gas at higher pressure P_1 be connected by a tube to another vessel where the pressure is less say P_2; $(P_1 > P_2)$. Now the gas would spontaneously move from the higher pressure to lower pressure. The process will continue until the two pressures are equalized. The process is unidirectional i.e., irreversible. When equilibrium is attained, the gas, by itself, will not rush back to the first vessel to increase the pressure to its original higher value.

(iii)   If a bar of metal is hot at one end and cold at the other and, heat flows spontaneously from the hot end to the cold end until the temperature of the rod become uniform throughout. The process cannot be reversed. Our experience does not show that a metal bar having uniform temperature can become hot at one end and cold at other end spontaneously.

(iv)   Electricity flows spontaneously flows from a point at higher potential to a point at a lower potential. The direction of flow of current can be reversed only by applying an external field to the opposite direction.

(v)   Metallic copper is deposited with evolution of heat when copper sulphate solution is brought in contact with zinc, and the reaction continues until the chemical equilibrium is attained.

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$
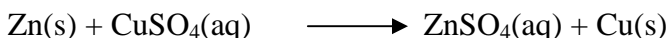
The above reaction can be reversed only by passing electrical current between a copper rod and a zinc rod immersed in aqueous zinc sulphate. But electrical energy is required to do so will be more than the heat energy in the direct reaction.

1.4 *CRITERIA OF SPONTANEITY*

Some important criteria of spontaneous physical and chemical changes are given below.

(i)   A spontaneous reaction is one way or unidirectional, for reverse change to occur, work has to be done.

(ii)   For a spontaneous change to occur time is no factor. A spontaneous reaction may take place rapidly or very slowly.

(iii)   If the system is not in equilibrium state, a spontaneous change is inevitable. The change will continue till the system attains the state of equilibrium.

(iv)   Once a system is in equilibrium state, it does not undergo any further spontaneous change in state if left undisturbed. To take the system away from equilibrium, some work must be done on the system.

(v)   A spontaneous change accrues by decrease of internal energy or enthalpy. In addition to enthalpy an additional factor, entropy is also responsible for spontaneity.

The second law of thermodynamics which is formulated to record our experience about the direction of change may be therefore be stated as;

"All spontaneous processes are irreversible."

Or we may also say

"All spontaneous processes tend to equilibrium."

We may continue our attention to a specific case, namely the flow of heat as in our illustration 1.3(iii) we can express our experience by the statement given by Clausius.

"Heat itself will not flow from a lower to a higher temperature."

Or   more elegantly stated; by Kelvin-Plank

"It is impossible for a self acting machine unaided by any external agency, to convey heat from a body at a low temperature to one at a higher temperature."

1.5   *SECOND LAW OF THERMODYNAMICS*

We have studied in the previous unit (1.4) the basis of the second law for the guidance of a process in a definite direction. It is also a human experience that when every form of energy, including mechanical work, has a natural tendency to be transformed into thermal energy. The thermal energy shows no natural indication to be transformed into any other form. Only through the introduction of some mechanism, or machine, we can convert heat into other forms. Even then this conversion occurs to a limited extent and not completely. Since heat is readily

available, a good deal of human ingenuity is employed to find out the conditions and circumstances under which it would be possible to change heat into work.

The guidance as to the conditions under which heat changes into the direction of work would obviously come under the second law. For this reason, in enunciating second law we often find statements refer to the conversion of heat into work. It is now known that two conditions must be fulfilled to utilize heat into useful work.

1. A mechanism commonly called the thermodynamic engine, is essential. Without the aid of an engine the conversion of heat into work is impossible. Further the engine must work in a reversible cyclic process.

2. The engine must operate between two temperatures. It will take up heat at a higher temperature, convert a portion of it into work and give up the rest of the heat to a body at lower temperature.

Now suppose we have an engine, a cylinder with piston containing x gm moles of an ideal gas, at temperature T same as that of surroundings. Let the gas expands isothermally from a volume V_1 to volume V_2. There will be no change in internal energy, as the gas is ideal. The heat absorbed from the surroundings will be completely converted into work dw($= x RT \ln V_2/V_1$) in accordance with the first law. Here in this case q quantity of heat from the surroundings is completely converted into work w. but when this has been achieved, the external agency (the engine), has suffered a change in volume from V_1 to V_2

It is thus an experience that complete conversion of heat into work is impossible without leaving a permanent change elsewhere.

If we want to repeat the performance, the gas must be made to come back to its original volume and pickup heat a gain from the surroundings during expansion. To bring the gas to its original volume V_1 from V_2, we must perform isothermal work of compression equal to $x RT \ln \frac{V_2}{V_1}$, the same work that we obtained before. The net result is that the engine, working in a cycle at a temperature same as that of source of supplier of heat, would produce no work. Thus under isothermal conditions no engine can convert heat into work. That is why we cannot run our tramcars or motorcars with the heat of surrounding air, or we cannot utilize vast amount of ocean-heat to move our ships.

If we could produce a machine which could continuously take up heat from the reservoir and convert it partially or fully into work, we could achieve what is called the perpetual motion of second kind.

Suppose we install a machine in our drawing room, which would take up heat from the air of the room and do mechanical work (say, run a fan). The air will automatically cool from the loss of heat. Hence no supply of electric energy from the electric supply company would be needed. All attempts to produce such a perpetual motion machine of second kind have failed.

Ostwald said "It is impossible to construct a perpetual motion machine of the second kind."

"It is impossible to construct a machine operating in cycles that will convert heat into work without producing any other changes in the surroundings."

This is Plank's statement of second law.

According to Clausius:

"It is impossible to construct a heat engine which will continuously abstract heat from a single body and convert the whole of it to work without leaving changes in the working system."

Some statements of second law have been given in 1.4.

1.6 HEAT ENGINES

The flow of heat from a hotter body to a colder body is spontaneous process. The heat that flows out spontaneously can be used to do work with the help of suitable device.

A machine which can do work by using heat that flows out spontaneously from a higher temperature source to a low-temperature sink, is called an engine.

A heat engine takes heat energy from a body of high temperature (reservoir) and converts some of it into work, returning the unconverted heat to a body of a low-temperature (sink). A basic heat engine is illustrated in Fig 1.1. A steam engine is a typical heat engine.
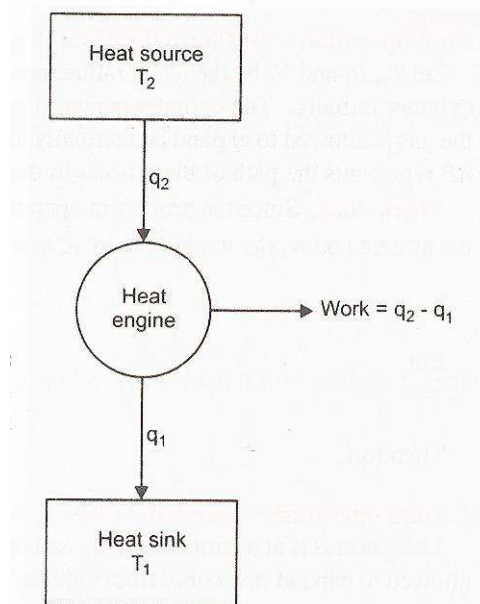
Fig 1.1Principle of heat engine

It takes heat from the boiler (high-temperature source) convert some heat to work and return the unused heat to the surroundings (low temp sink).

A heat engine running on a periodic cyclic process can yield work continuously.

1.7 CARNOT CYCLE

The brilliant French engineer Sadi Carnot in 1824 explained clearly how and to what extent work is obtainable from heat. Carnot started with two essential pre-requisites. Firstly, to estimate the work obtained from heat during its passage from higher to a lower temperature, the external agency (the engine) must come back to its original state so as to exclude any work involved in its own change. That is, the engine must operate is complete cycles. Secondly, to obtain maximum work in a cycle of operation, every step should be carried out in a reversible manner.

The typical Carnot's cycle consists of four hypothetical successive operations using one gm mole of a perfect gas as the working substance. We take gas enclosed in a cylinder fitted with a frictionless piston. To start with, the cylinder containing the gas is kept in a large thermostat at

a higher temperature T_1 (source) and suppose volume of the gas be V_1. Then we proceed with the following operations.

1. Isothermal reversible expansion
2. Adiabatic reversible expansion
3. Isothermal reversible compression
4. Adiabatic reversible compression

The above four processes are shown in the indicator diagram of Carnot cycle fig 1.2
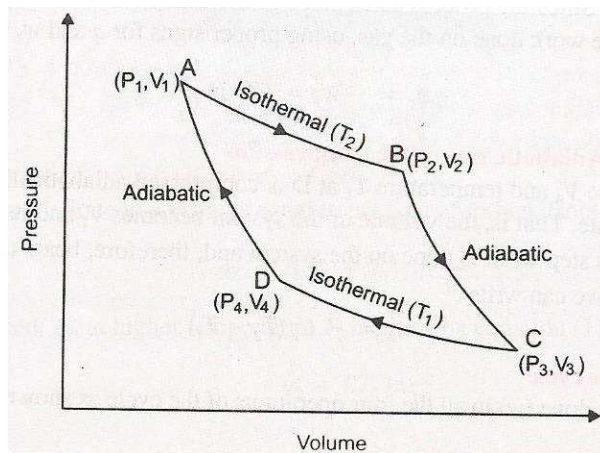
Fig 1.2 Indicator diagram of Carnot cycle

1.7.1   First operation-Isothermal reversible expansion:

Let T_2, P_1 and V_1 be the temperature, pressure and volume respectively of the gas enclosed in the cylinder initially. The cylinder is placed in the heat reservoir at the higher temperature (T_2). Now the gas is allowed to expand isothermal and reversibly so that volume increases from V_1 to V_2. A B represents the path of the process in the diagram.

Being isothermal process $\Delta E=0$. If q_2 be heat absorbed by the system and w_1 the work done by it, according to first law of thermodynamics   ($\Delta E = q-w$).

$$q_2 = w_1$$

but $w_1 = RT_2 \ln \dfrac{V_2}{V_1}$

hence $q_2 = RT_2 \ln V_2/V_1$ ………..1.1

1.7.2   Second operation-Adiabatic reversible expansion:

The gas at B is at a temperature T_2 and volume V_2 under the new pressure P_2. The gas now is allowed to expand adiabatically and reversibly from volume V_2 to V_3 when the temperature drops from T_2 to T_1 (along BC).

The process is adiabatic q=0. If w_2 be the work done, according to the first law equation ($\Delta E=q-w$),

$$\Delta E = - w_2$$

$$\text{or } w_2 = - \Delta E$$

But $\qquad \Delta E = -C_V (T_1-T_2)$

Therefore $w_2 = C_V (T_2-T_1)$ $\qquad\qquad\qquad$ ..…1.2

1.7.3   Third operation- isothermal reversible compression:

Now the cylinder is placed in contact with a heat reservoir at a lower temperature T_1, the volume of the gas is compressed isothermally and reversibly from V_3 to V_4 (respectively by CD in diagram).

Now during compression, the gas produces heat, which is transferred to the low temperature reservoir. Since the process takes place isothermally, $\Delta E=0$, if q_2 is the heat given to the reservoir and w_3, the work done on the gas, using proper sign for w and q, we have

$$-q = -w_3 = RT_1 \ln V_4/V_3 \qquad \ldots\ldots\ldots..1.3$$

1.7.4   Fourth operation- Adiabatic reversible compression:

The gas with volume V_4 and temperature T_1 at D compressed adiabatically along DA until it regains the original state. That is volume of the system becomes V_1 and temperature T_2.

In this process the work is done on the system and, therefore, bears negative (-ve) sign.

It is denoted by w_4, we can write

$$-w_4 = -w(T_2-T_1) \qquad\qquad \ldots\ldots\ldots..1.4$$

Adding up the work done(w) in all the four operations of the cycle as shown in equation (12.1), (12.2), (12.3) and (12.4) we have

$W=w_1+w_2+(-w_3)+(-w_4)$

$=RT_2 \ln V_2/V_1 + C_V(T_2-T_1) +RT_1 \ln V_4/V_3 - C_V(T_2-T_1)$

$=RT_2 \ln V_2/V_1 + RT_1 \ln V_4/V_3$ ……1.5

If q is the net heat absorbed in the whole cycle

$q= q_2-q_1$

$= RT_2 \ln V_2/V_1 - RT_1 \ln V_4/V_3$ ……1.6

For adiabatic changes for points B and C

$T_2V_2^{\gamma-1} = T_1V_3^{\gamma-1}$ …….1.7

For points A and D

$T_2V_1^{\gamma-1} = T_1V_4^{\gamma-1}$ ………..1.8

Dividing equation 1.7 by equation 1.8

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$

or $\dfrac{V_3}{V_4} = \dfrac{V_2}{V_1}$

substituting the value in equation 1.6 we have

q $= RT_2 \ln \dfrac{V_2}{V_1} - RT_1 \ln \dfrac{V_2}{V_1}$

$=R(T_2-T_1) \ln \dfrac{V_2}{V_1}$ ……1.9

1.7.5 Calculation of efficiency:

Since total work done in a cycle is equal to net heat absorbed, from equation 1.9 and 1.5 we can write

$W= R(T_2-T_1) \ln V_2/V_1$ …..1.10

The heat absorbed, q_2 at higher temperature T_2 is given by the equation 12.1,

$$q_2 = RT_2 \ln V_2/V_1 \qquad\qquad .....1.11$$

Dividing 1.10 by 1.11

$$w/q_2 = R(T_2-T_1) \ln (V_2/V_1)/ RT_2 \ln (V_2/V_1)$$

$$= (T_2-T_1)/T_2 \qquad\qquad ..….1.12$$

The term w/q_2 is called thermodynamic efficiency of engine. It is denoted by η and gives the fraction of the heat taken from the high-temperature reservoir which it is possible to convert into work by a heat engine. The larger the temperature difference (T_2-T_1) between the high and low temperature reservoirs, the more the heat converted to work by the heat engine.

Now $w/q_2 = (T_2-T_1)/T_2 = \Delta T/T_2$

or $w= q_2\Delta T/T_2$ $\qquad\qquad …………..1.13$

This relation expresses the maximum amount of work obtainable from the heat flowing from T_2 to T_1, this is then the mathematical form of the second law.

The following points are to be noted.

(i) Between two given temperatures, only $\Delta T/T_2$ fraction of the total heat supplied at T_2 is obtainable as work.

(ii) $W=q_2$, only when $T_1=0$. That is if the engine works between absolute zero and a higher temperature, complete conversion of heat into work would be possible. Since working at 0^0K cannot be realized in practice, the complete transformation of heat into work is impracticable; the efficiency is thus always less than unity.

(iii) The efficiency of the engine depends only on the temperature of the source and sink (eqn 1.12). For a given source, the lower the temperature of the sink the greater will be the yield of work. Very often the sink is at the room temperature. In such a case, for greater output of work, the temperature of source should be high. This is the reason for using high pressure steam in boilers for production of power.

(iv) When $T_2=T_1$, work w becomes zero. No work is available by operating an engine under isothermal conditions.

Example:

A Carnot engine working between 0^0C and 100^0C takes up 840 joules from high temperature reservoir. Calculate the work done, the heat rejected and the efficiency.

(a) Work done: $w = q_2\, \Delta T/T$

$$= 840 \times 10^7 \frac{100}{373} = 2.25 \times 10^9 \text{ ergs}$$

(b) Heat rejected: $q_1 = q_2\, T_2/T_1$

$$= 840 \times 273/373 = 6.14 \times 10^9 \text{erg}$$

(c)   Efficiency η: $= \frac{T_2 - T_1}{T_2} = \frac{100}{373} = 0.268$ or

             η = work done/Total amount of heat absorbed from source

             $= 2.2510^9/8.14 \times 10^9 = 0.268$

1.8 THE CARNOT THEOREM

According to equation 1.12 the efficiency of an engine working reversibly depends only on the temperature of the source and the sink. It is independent of that nature of the substance or substances used for operations.

Two important deductions are easily arrived at on the assumptions of the validity of the second law. These deductions comprise Carnot theorem. The theorem states working between the same temperature limits.

(i)   a reversible engine is more efficient than an irreversible one and

(ii)   all reversible engines are equally efficient.

We can establish them in the following way.

To establish them we proceed in the following way.

(i)   Suppose we have an irreversible engine I and a reversible engine R. Let us assume that efficiency of I is greater than that of R, i.e., $\eta_I > \eta_R$. This means that if a source supplies same quantity of heat to both the engines, greater amount of work will be obtained from I than R. suppose the engines operate between the source at temperature T and sink at temperature T'. Now the energy changes with the two engines would be as follows as shown in Fig 1.3
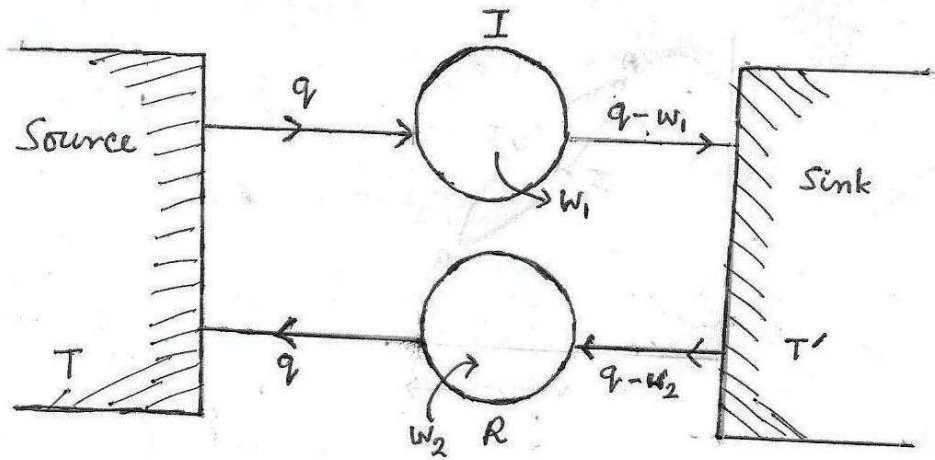
Fig 1.3 Comparison of efficiency of two engines.

Engine I			Engine R	
Heat supplied by source		q	Heat supplied by source	q
Work performed		w_1	work performed	w_2
Heat rejected to sink	$q-w_1$		Heat rejected to sink	$q-w_2$
We know $w_1 > w_2$		hence	$q-w_1 < q-w_2$	

Now let us carry out a cyclic process in which engine I would perform the forward process. It will be supplied with heat q from the source it will yield w_1 work and reject the rest of the heat to the sink. The reverse process will be done by the engine R which taking up heat $q-w_2$ from the sink and having w_2 units of work done on it, would return heat q to the source. In this cyclic process, the source has not ultimately lost any heat. The sink has suffered a heat loss. $(q-w_2) - (q-w_1)$. The coupled engine have yielded work= w_1-w_2, which is equal to heat lost by the sink. That means we have been able to convert completely the heat taken from the sink at the lower temperature fig 1.4. This is contrary to the second law and is improbable.

Hence efficiency of the reversible engine cannot be less than the efficiency of the irreversible one.

(ii) Second part of the theorem can also be proved in a similar way. Suppose two reversible engines R_1 and R_2 work between the source (T) and sink (T`) let us assume one of the engines,

say R_1 is more efficient than R_2. As before, let us couple the two engines to carry out a cyclic process. The engine R_1 takes up heat q from the source, yields work w_1 and rejects $(q-w_1)$ heat to the sink, while the engine R_2 perform the opposite process taking $(q-w_2)$ units of heat from the sink, with w_2 units of work done on it, and returning heat a back to the source. Since $\eta_{R1}>\eta_{R2}$, therefore $w_1>w_2$. At the completion of the cyclic process the source has not lost any heat. The net result is that w_1-w_2 units of work has been produced. There is a loss of $(q-w_2)$ – $(q-w_1)$ = w_1-w_2 units of heat from the sink. The heat of the lower temperature sink is thus completely converted into work, which is against the second law. Thus engine R_1 cannot be more efficient than R_2. Similarly R_2 also cannot have greater efficiency than R_2. That is, both engines are equally efficient. Hence, all reversible engines working between the same temperatures must be equally efficient.

1.9 THERMODYNAMIC SCALE OF TEMPERATURE:

Ordinarily the measurement of temperature is based on some property of the thermometric substance, such as linear or volumetric expansion, electrical resistance etc. There is one difficulty in such measurements. The variation in the property studied is not the same for different substances nor is it regular in different ranges of temperature. Thus, a constant-volume nitrogen thermometer will record a somewhat different value from that of the constant-volume helium thermometer for measuring T_1/T_2, the ratio of temperatures of two given reservoirs.

We have seen that the efficiency of the reversible engine is dependent only on the temperature of the source and the sink and is in dependent of the materials used. Hence

$$\eta = w/q$$

$$= (T_2-T_1)/T_2$$

or $(q_2-q_1)/q_1 = (T_2-T_1)/T_2$

or $q_2/q_1 = T_1/T_2$

Where q_2 and q_1 are the heat received from the source at T_2 and rejected to the sink at temperature T_1 respectively, T_2 and T_1 being expressed in ideal gas scale.

Kalvin proposed that a knowledge of heat (q_2) absorbed from the source and heat (q_1) rejected to the sink in a Carnot's engine would enable us to define the ratio of the temperature of

the two reservoirs. Thus we would be able to define a scale of temperature independent of any property of substance as q_2 and q_1 are independent of the materials used in the engine. It would then be a thermodynamical scale of measurement in which the principle of thermometry is being really replaced by that of calorimetry.

Let us take three reservoirs A, B and C in decreasing order of temperatures. Let us also denote by the symbol, τ, a quantity which is measure of the temperature or degrees of hotness of reservoirs fig 1.4
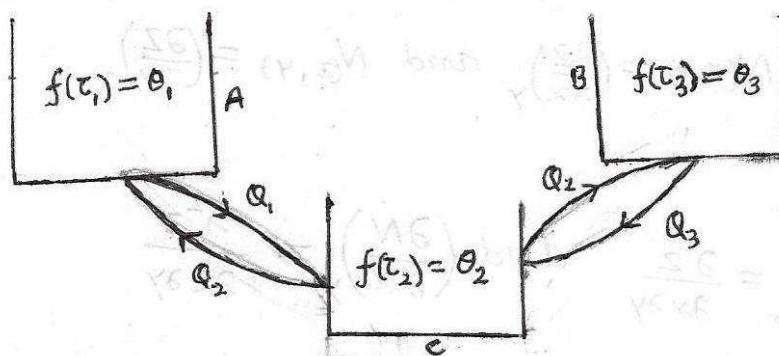
Fig 1.4 Thermodynamic scale of temperature

Now suppose a reversible Carnot's engine works between the boths A and B, receiving q_1 heat from A and rejecting q_2 heat to B then the ratio q_1/q_2 will be function of temperature of A and B, i.e., function of τ_1 and τ_2.

So $q_1/q_2 = F(\tau_1.\tau_2)$ …….1.14

If we have now second Carnot's engine working between B and C taking heat q_2 from B and rejecting q_3 heat to C, then, as before,

$q_2/q_3 = F(\tau_2.\tau_3)$ 1.15

When these two engines are coupled together to work between A and C, naturally we have

$q_1/q_3 = F(\tau_1.\tau_3)$.….1.16

dividing 12.16 by 12.15 we get

$q_1/q_2 = F(\tau_1,\tau_3)/F(\tau_2,\tau_3)$ …..1.17

comparing 1.14 and 1.17

$$F(\tau_1,\tau_2) = F(\tau_1,\tau_3)/F(\tau_2,\tau_3) \qquad\qquad \ldots\ldots 1.18$$

The left hand side of this equation does not contain τ_3 which occurs on the right-hand side. This is possible only when the function F is a ratio having identical forms in both the numerator and denominator.

i.e., $F(\tau_1,\tau_3) = f(\tau_1)/f(\tau_3)$ and $F(\tau_2,\tau_3) = f(\tau_2)/f(\tau_3)$

then we have $F(\tau_1,\tau_2) = F(\tau_1,\tau_3)/F(\tau_2,\tau_3)$

$$= \frac{f(\tau_1)}{f(\tau_3)} \cdot \frac{f(\tau_3)}{f(\tau_2)} = f(\tau_1)/f(\tau_2)$$

Hence from 1.14 $\dfrac{q_1}{q_2} = \dfrac{f(\tau_1)}{f(\tau_2)}$

        Let this undermined function $\int(\tau)$ represent the temperature in this new thermodynamics scale and let it be denoted by θ then $q_1/q_2 = \theta_1/\theta_2$, where are the temperature in the thermodynamic scale of reservoirs A and B respectively and these do not depend on any property of the working substance of the engine.

        Since $q_1/q_2 = \theta_1/\theta_2$ then $(q_1-q_2)/q_1 = (\theta_1-\theta_2)/\theta_1$

        or $\eta = (\theta_1-\theta_2)/\theta_1$, i.e., if $\theta_2=0$, $\eta = 1$

        the ratio of the thermodynamic scale has been defined to be the temperature of the sink working down to which the engine would completely convert heat into work. Similarly, in Carnot cycle also

        $\eta = (T_1-T_2)/T_1$, i.e.,   if $T_2=0$, $\eta = 1$

        Hence the zero in the two scales are also identical. To honour this fundamental contribution of Lord Kelvin, the thermodynamic scale is called Kelvin Scale, with symbol ^{0}K. It relates the centigrade scale as, 0^0K$=-273.16$C and $273.16\ ^0$K$= 0^0$C.

1.10 SUMMARY

        In this unit we have studied the limitations of first law of thermodynamics and hence the need of second law. In nature all processes are spontaneous and all spontaneous processes tend to

equilibrium. Flow of heat from high temperature to low temperature region is a spontaneous process. If we stall a device say an engine to obtain work when heat flows from high temperature to low temperature comes under second law of thermodynamics. Carnot employed a reversible cycle to demonstrate the maximum convertibility of heat into work. Although the reversible cyclic processes are merely theoretical and imaginary, but the concept is highly useful in deriving certain important relationships.

1.11 TERMINAL QUESTIONS

A. Objective type questions:

1. For an adiabatic process:
(a) T=constant   (b) q=0(c) q=constant (d) w=0

2. The tendency of a process to occur naturally is called
(a) Momentum of the reaction   (b) spontaneity of the reaction

    (b) Equilibrium of the reaction   (d) capacity of a reaction

3. The efficiency of a heat engine operation between 400K and 300K is:
    (a) 0.25   (b) 1.0 (c) 0.75   (d) 0.50

B. Short answers type questions:

4.   What is a cyclic process? Explain.
5.   Write a note on Carnot Theorem.
6.   Give two statements of second law of thermodynamics.

C. Long answer type questions:

7. What is meant by efficiency of an engine? Derive expression for the same.
8. (a) What do you understand by the term enthalpy?

(b) "It is not profitable to carry out a process reversibly though maximum work can be obtained by doing so". Comment on the statement.

9.   (a) Derive a relation between pressure and volume for an adiabatic reversible expansion of an ideal gas.

     (c) Write a note on spontaneous reactions.

1.12. ANSWER

1. (b) 2. (b) 3. (a)

Source of study material

1. Principles of Physical Chemistry. By Puri, Sharma, Pathania
2. Essentials of Physical Chemistry By B.S. Bahl, Arun Bahl G.D. Tuli
3. Physical Chemistry by P.C. Rakshit

Books recommend for further study

1. Physical Chemistry By Adkins
2. Thermodynamics By P.C. Rakshit
3. Thermodynamics for chemists By S Glasstone

UNIT -2 CONCEPT OF ENTROPY

CONTENTS:

2.1 OBJECTIVES

First law of thermodynamics is law of conservation of energy. It states that one form of energy can change into another form, but the total amount of energy remains the same. If energy of an isolated system remains constant then whole of the universe can be divided into very large number of isolated systems. For each system energy remains constant then energy of the universe remains constant. This law introduced two important state functions E and H, even then the law does not explain the following facts

    i.   Why chemical reaction does not proceed to completion.

    ii.   Why the natural processes are unidirectional.

    iii.   It does not give anything about the source and direction of flow of heat.

    iv.   It does not explain the extent of conversion of one form of energy to another form.

Any process which gives us an idea to which direction the reaction will proceed and to what extent, comes under second law of thermodynamics. According to Kelvin it is impossible to use a cyclic process to extract heat from a reservoir and to convert it into work without transferring at the same time, certain amount of heat from a hotter to colder part of the body

2.2 INTRODUCTION

In unit-1 you have studied spontaneous processes. All natural processes are spontaneous and irreversible. In spontaneous processes there is decrease of internal energy or enthalpy. It implies that only such reaction will occur which are exothermic. But the melting of ice and evaporation of water are endothermic processes which proceed spontaneously (in exothermic processes heat is released and in endothermic processes heat is absorbed.) Clearly, there is some other factor in addition to ΔH which governs spontaneity. If is the second law of thermodynamics which introduces this new factor called entropy.

2.3 SPONTANEITY AND RANDOMNESS

Careful examination shows that in processes like melting of ice and evapouration of water, there is an increase of randomness or disorder of the system. The water molecule in ice are arranged in a highly organised crystal pattern which permits little movement. As the ice melts, the water molecules become disorganized and can move more freely. The movement of molecules becomes freer still when the water evaporates into space and now they can roam about throughout the entire atmosphere. In other words, we can say that the randomness of the water molecules increases as ice melts into water or water evaporates into space.

The efficiency of an engine is given by the relation

$$\eta = (q_1 - q_2)/q_1 = (T_1 - T_2)/T_1 \qquad \qquad \text{……..2.1}$$

q_1 is the amount of heat absorbed at temperature T_1 from the source and q2 is the amount of heat rejected at temperature T_2 to the sink.

This equation can be rearranged in the following form.

$$1 - q_2/q_1 = 1 - T_2/T_1 \qquad \qquad \text{……..2.2}$$

Equation 2.2 may also be written in general form.

$$q_{rev}/_T = \text{constant} \qquad \qquad \text{………2.3}$$

Where q_{rev} is the quantity of heat exchanged in a process carried out reversibly at a temperature T. It may be noted that each step in the Carnot cycle is considered to be carried out reversibly. This is an important generalization since the quantity $q_{rev}/_T$ represents a definite quantity, which is state function, is the entropy change of the system.

2.3.1 Concept of entropy:

The equation 2.2 has been derived by assigning positive sign to heat absorbed (q_2) and negative sign to the heat given out (q_1) by the system. Describing q_1 and q_2 merely as heats exchanged (may be evolved or absorbed). Then equation 2.2 can be written as

$$q_1/T_1 + q_2/T_2 = 0 \qquad \qquad \text{…………2.4}$$

Thus, when the isothermal and adiabatic processes in a Carnot cycle are carried out, reversibly, the summation of q/T terms is equal to zero.

Let there is a cyclic process carried out reversibly which consists of a series of Carnot cycles. In this cyclic process the change from the state A to state B and back to A is carried out reversibly as shown in Fig 2.1
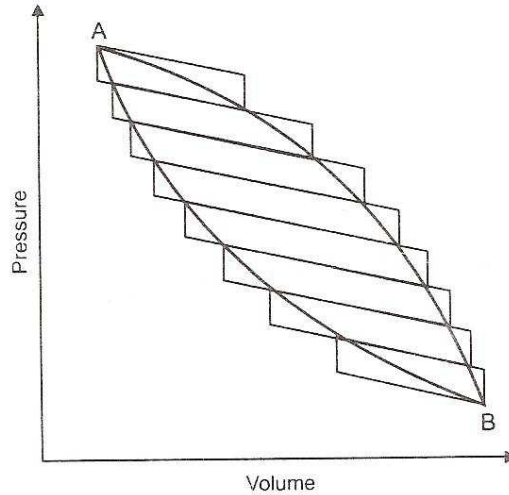
Fig 2.1 Reversible cycle

The path ABA may be considered to comprise of a number of small Carnot cycles, i.e., of a series of isothermals and adiabatic as shown in the figure. If each isothermal and adiabatic change is made extremely minute, i.e., each Carnot cycle is made extremely small by increasing their number, the path inside the loop cancel one another and the cycle corresponds to continuous curve ABC. Thus, any reversible cycle can be regarded as being made up of infinite number of small Carnot cycles.

For each Carnot cycle $\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$, it follows that in the case of the reversible cycle ABA, comprising of series of Carnot cycles, the summation term takes the form.

$$\sum \frac{q}{T} \qquad\qquad \text{......2.5}$$

When the changes are infinitesimal, the above equation can be put as,

$$\sum dq/T = 0 \qquad\qquad \text{......2.6}$$

Since the cycle is performed in two steps, viz., from a A to B and back from B to A, it follows that

$$\sum dq/T = \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0 \qquad\qquad \text{.......2.7}$$

The integral $\int_A^B \frac{dq}{T}$ is the summation of all the dq/T terms when the system changes from A to B along the path I and $\int_B^A \frac{dq}{T}$ is the summation when the system returns from state B to the original state A along path II.

From equation 2.7

$$\int_A^B dq/_T = - \int_B^A dq/_T$$

or $\int_A^B dq/_T \ (path\ I) = \int_A^B \frac{dq}{T} \ (path\ II)$ ……2.8

It follows from equation 2.8 that $\int_A^B dq/_T$ is a definite quantity independent of the path followed for the change and depends only upon the initial and final states of the system. This quantity, therefore like ΔE and ΔH, should represent the change in some single-valued function of the states A and B of the system. This function is called entropy and is denoted by the symbol S. if S_A is the entropy of the system in state A and S_B entropy in the final state B, then the change in entropy, ΔS is given by the equation.

    $\Delta S = S_B - S_A = \int_A^B dq/_T$ ..….2.9

For each infinitesimal change,

    dS = dq/T   .….2.10

At constant temperature, for a finite change dS becomes ΔS and dq becomes q

    Hence $\Delta S = q/T$ ..…2.11

It may be emphasized that since entropy is a state function, the change of entropy (ΔS) for the change of state from A to B will invariably be the same whether change is reversible or not. However, mathematically, it can be given by the equation

    $\Delta S = \int_A^B dq/_T$ ……..2.11

Only when the change has been brought reversibly. This is because the above equation has been derived from Carnot cycle in which all the changes are brought about reversibly.

2.3.2 Definition of entropy:

In the above discussion gives only the physical definition of entropy. But classical thermodynamics does not require a physical explanation of the concept of entropy. All that we need is an operational definition so that we can calculate the entropy change of the system and the surroundings.

In 1850 Clausius introduced a numerical definition of entropy. According to him entropy of a system (not undergoing physical or chemical changes), is a constant quantity when there is no communication of heat. When heat (q) flows into a system at temperature T, the entropy increases by q/T. Heat flowing out of a system produces a corresponding decrease. The entropy could be precisely defined as:

For a reversible change taking place at fix temperature T, the entropy change ΔS is equal to heat energy absorbed or evolved divided by the temperature T.

That is ΔS= q/T   ………….2.12

If heat is absorbed than ΔS will be positive and there will be increase in entropy. If heat is evolved, ΔS will be negative and there is decrease in entropy. From second law in transfer of heat certain portion of energy (available energy) is used for work. The remaining energy is called unavailable energy which is related with the entropy.

Entropy = <u>Unavailable energy</u>

                      Temperature

2.3.3 Unit of entropy:

Since entropy change is expressed by a heat term divided by the absolute temperature, entropy is expressed in terms of calories per degree per mole i.e., cal $mole^{-1}K^{-1}$ in entropy units eu. In the SI system, the units are joules per mole per degree, i.e., $Jmole^{-1}K^{-1}$. These are represented by EU.

1 eu= 4.184 EU

2.3.4 Standard entropy:

We know that the entropy of a pure crystal is zero at absolute zero because there is most orderly arrangement of particles (or least disorder). Therefore, it is possible by measurement and calculation to find the actual amount of entropy that a substance possesses at any temperature above K^0. It is often referred to as standard entropy.

Substance	Entropy, $S°$		Substance	Entropy, $S°$	
	cal mol^{-1} K^{-1}	J mol^{-1} K^{-1}		cal mol^{-1} K^{-1}	J mol^{-1} K^{-}
Ag (s)	41.32	172.9	H$_2$ (g)	31.21	130.6
AgCl (s)	58.5	24.5	H$_2$O (g)	45.11	188.7
Al (s)	6.77	28.3	H$_2$O (l)	16.72	69.96
Al$_2$O$_3$ (s)	12.19	51.0	HCl (g)	44.62	186.7
C $(s$, graphite$)$	0.58	2.4	HNO$_3$ (l)	37.19	155.6
CO (g)	47.30	197.9	H$_2$SO$_4$ (l)	37.5	157.0
CO$_2$ (g)	51.06	213.6	Hg (l)	18.2	76.1
CH$_4$ (g)	44.50	186.2	K (s)	38.30	160.2
CH$_3$OH (l)	30.3	126.8	KCl (s)	57.24	239.5
CO(NH$_2$)$_2$ (s)	25.0	104.6	K$_2$SO$_4$ (s)	42.0	176.0
C$_2$H$_2$ (g)	48.0	200.8	N$_2$ (g)	45.77	191.5
C$_2$H$_6$ (g)	54.85	229.5	NH$_3$ (g)	46.01	192.5
Ca (s)	36.99	154.8	Na (s)	36.72	153.6
CaCO$_3$ (s)	22.2	92.9	NaCl (s)	17.30	72.88
Cl$_2$ (g)	53.29	223.0	O$_2$ (g)	49.0	205.0
Fe (s)	6.5	27.0	S (s)	7.62	31.9
Fe$_2$O$_3$ (s)	21.5	90.0	SO$_2$ (g)	59.40	248.5

Table 2.1 Standard entropies of some substances (25^0C, 1 atm)

The absolute entropy of a substance at 25^0C (278K) and one atmosphere pressure, is called the standard entropy; S^0

The absolute entropy of elements is zero only at 0K in a perfect crystal, and standard entropies of all substances at any temperature above 0K always have positive values Table 2.1 shows standard entropies of some elements and compounds. Entropy is an extensive property. Its value therefore, depends upon the amount of the substance involved. it is necessary, therefore, to make a mention of the quantity of the substance taken. This quantity usually taken as one mole.

2.4 ENTROPY CHANGE IN ISOTHERMAL EXPANSION OF AN IDEAL GAS

In isothermal expansion of an ideal gas carried out reversibly, there will be no change in the internal energy, i.e., $\Delta E=0$ and hence from first law equation $\Delta E=q-w$

$$q_{rev} = w \qquad\qquad\qquad ….2.13$$

In such a case, the work done in the expansion of n moles of a gas from volume V_1 to V_2 at constant temperature T, is given by

$$q_{rev}= nRT\ln V_2/V_1 \qquad\qquad\qquad …..2.14$$

now $\quad \Delta S = q_{rev}/T$

hence $\quad \Delta S \quad = \frac{1}{T} nRT\ln V_2/V_1$

$$= nR\ln V_2/V_1 = nR\ln P_1/P_2$$

$$= 2.303nR\log V_2/V_1 = 2.303nR\log P_1/P_2 \qquad …2.15$$

Solved problems

Question 1:

Calculate the entropy change involved in thermodynamic expansion of two moles of an ideal gas from a volume 5 litres to a volume 50 litres isothermally at 303K

Solution: $\qquad$ Formula $\qquad \Delta S_T = 2.303\ n\log V_2/V_1$

$$= 2.303 \times 2 \times 8.314\ \log 50/5$$

$$= 2.303 \times 2 \times 8.314\ \log_{10}$$

$$= 38.22 JK^{-1}$$

Question 2:

Calculate the entropy change involved in the evaporation of one mole of water at 100^0C. latent heat of evaporation of water is 9650 cals per mole.

Solution:

Formula $\Delta S = H_v/T$

$H_v = 9650$ cals

$T = 273 + 100^0 = 373K$

Hence ΔS $= 9650/378$

$= 25.87$ cal K^{-1} mole^{-1}

2.5 ENTROPY CHANGES IN REVERSIBLE AND IRREVERSIBLE PROCESSES

Consider isothermal expansion of an ideal gas at constant temperature into vacuum. This will, evidently proceed spontaneously, i.e., irreversibly. Since there is no opposing force, the work done (w) by the system will be zero. Further, since there is no change in temperature during the process, there will be no change in the internal energy of the system, i.e., $\Delta E=0$ hence from first law equation q=0, i.e., no heat absorbed or evolved in the process. In other words no heat is supplied to or removed from the surroundings. The entropy of the surroundings, therefore, remains unchanged.

Now entropy of a system is a function only of the state of the system, i.e., its temperature and pressure (or volume) and is independent of previous history of the system. In the process under consideration, the volume of the gas increases, say, from V_1 to V_2 at constant temperature T. hence, entropy increase of the system considering that one mole of the gas is involved, would be given by

$\Delta S = R\ln(V_2/V_1)$ ……………2.16

The total increase in entropy of the system and its surroundings during the spontaneous process of expansion considered above is, thus, $R\ln V_2/V_1$. Since $V_2 > V_1$ it is obvious that the spontaneous (irreversible) isothermal expansion of a gas is accompanied by an increase in the entropy of the system and its surrounding considered together.

Now let us consider isothermal expansion of the ideal gas from V_1 to V_2 carried out reversibly at the same temperature T. the expansion is carried out infinitesimally slowly, i.e., the

pressure on the frictionless piston is so adjusted that is remains always less than that of the gas by an infinitesimal small amount. In this case, the gas does some external work given by w= - PΔV. consequently, an equivalent amount of heat (q_{rev}) is absorbed reversibly by the system from the surroundings at temperature T, hence increase in the entropy of the system is q_{rev}/T.

The heat lost reversibly at temperature T given by surroundings is also q_{rev}. hence decrease in the entropy of the surroundings is q_{rev}/T.

Giving proper sign, giving positive for increase and negative for decrease of entropy, the net entropy change of the system and its surroundings is

$$q_{rev}/_T - q_{rev}/_T = 0 \qquad \text{.......2.17}$$

Thus, in the reversible isothermal expansion of the gas, the total entropy change of the system and surroundings considered together is zero.

Hence net conclusion is that:

A thermodynamically irreversible process is always accompanied by an increase in the entropy of the system and its surroundings taken together while in the thermodynamically reversible process; entropy of the system and its surroundings taken together remains unchanged.

Thus mathematically we can express

$$(\Delta S_{sys} + \Delta S_{sur}) = 0 \qquad \text{for reversible processes}$$

$$\Delta S_{sys} + \Delta S_{sur}) > 0 \qquad \text{for irreversible processes}$$

Combining these two, we have

$$\Delta S_{sys} + \Delta S_{sur} \gtrless 0 \qquad \text{..........2.18}$$

Where equal to sign refers to a reversible process and greater than sign refers to an irreversible process.

We can state equation 2.18 as follows:

In a reversible process, the entropy of the system and the surroundings taken together remains constant while in an irreversible process, the entropy of the system and the surroundings taken together increases.

This statement is of great importance as it helps us to predict whether a given process can take place spontaneously or not, i.e., whether it is thermodynamically feasible or not.

Since all processes in nature occur spontaneously, i.e., irreversibly, it follows that the entropy of the universe is increasing continuously. This is another statement of second law of thermodynamics.

The essentials of the first law and second law of thermodynamics were thus summed up by Clausius as follows:

The energy of universe remains constant and the entropy of the universe tends to maximum.

2.6   PHYSICAL SIGNIFICANCE OF ENTROPY

Entropy is a measure of disorder or randomness of a system. The entropy of the system increases if it goes from orderly state to disorderly state. This concept of entropy has led to the conclusion that all substances in their normal crystalline state at absolute zero would be the most ordered state with zero entropy. At this state, all motions ceases. In case of a perfect crystal the entropy is zero. This is third law of thermodynamics.

2.6.1 Entropy change of an ideal gas with change in P, V and T:

Since entropy of a system varies with the state of a system, its value for a pure gaseous substance will depend upon any two of the three variables T, P and V. since T is taken generally as one of the variables, the second variable to be considered may be V or P. thus the two variables to be considered are either T and V or T and P.

2.6.2 Variation of entropy with temperature and volume:

Let us consider one mole of an ideal gas occupying volume V, pressure P and temperature T. the increase in entropy of the gas in absorbing dq amount of heat reversibly at temperature T is given by

$$ds = dq_{rev}/T \qquad \text{............2.19}$$

According to the equation of first law of thermodynamics

$$dq_{rev} = dE + PdV$$

putting the value of dq_{rev} in equation 12.19 we get

$$ds = \frac{dE + PdV}{T} \qquad \qquad \text{......2.20}$$

we know PV=RT   (for one mole of the gas)

$$P = RT/V$$

and $C_V = \frac{dE}{dT}$ or $dE = C_V dT$

C_V is molar heat capacity at constant volume.

$$ds = [C_V dT + (RT/V)\, dv]/T$$

$$ds = C_V dT/T + RdV/V \qquad \qquad \text{...2.21}$$

Integrating the above equation from initial state when temperature is T_1 and volume is V_1 to final state when temperature is T_2 and volume is V_2 assuming C_v to be constant with in temperature range T_1 and T_2 we have

$$\int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{C_V\, dT}{T} + R \int_{V_1}^{V_2} dV/V \qquad \qquad \text{.....2.22}$$

Thus $\Delta S = S_2 - S_1 = C_V \ln T_2/T_1 + R \ln V_2/V_1$ 2.23

For n moles of an ideal gas the above equation can be written as

$$\Delta S \quad = nC_V \ln T_2/T_1 + nR \ln V_2/V_1 \qquad \qquad \text{.....2.24}$$

$$= 2.303 C_V \log T_2/T_1 + 2.303 nR \log V_2/V_1 \qquad \text{.....2.25}$$

It is evident that the entropy change for the change of state of an ideal gas depends upon the initial and final volumes as well as on the initial and final temperature.

Case I:

At constant temperature for an isothermal process $T_1 = T_2$ then from equation 2.23

$$\Delta S_T \quad = R \ln V_2/V_1$$

$$= 2.303R \log V_2/V_1$$

$$= 2.303 \log P_1/P_2 \qquad \text{(As } P_1V_1=P_2V_2\text{)}$$

In an isothermal expansion $V_2>V_1$ or $P_1>P_2$ hence ΔS_T is positive whereas in isothermal contraction $V_2<V_1$ and $P_1<P_2$ then ΔS_T will be negative.

and for n moles

$$\Delta S_T \quad = nR\ln V_2/V_1$$

$$= 2.303nR \log V_2/V_1$$

Thus subscript T in ΔS_T indicates that temperature remains constant during the process.

Case II:

At constant volume (i.e., isochoric process) the equation 2.23 reduces to:

$$\Delta S_V \quad = C_V \ln T_2/T_1$$

$$= 2.303 \, C_V \log T_2/T_1$$

for n moles:

$$\Delta S_V \quad = nC_V \ln T_2/T_1$$

$$= 2.303 \, n \, C_V \log T_2/T_1$$

The subscript V in ΔS_V indicates that volume remains constant during the process. It follows that increase in temperature of an ideal gas at constant volume is accompanied by increase of entropy.

2.6.3 Variation of entropy with temperature and pressure:

We have from equation 2.23

$$\Delta S= C_V \ln T_2/T_1+R \ln V_2/V_1 \qquad\qquad …2.23$$

If P_1 is the pressure of the ideal gas in the initial state and P_2 in the final state, then

$$P_1V_1 = RT_1 \quad \text{for one mole of the gas in the initial state}$$

$$P_2V_2 = RT_2 \quad \text{for one mole of the gas in the final state}$$

Then $V_2/V_1 = P_1T_2/P_2/T_1$

Substituting this value of V_2/V_1 in equation 2.23 we get

$$\Delta S = C_V \ln T_2/T_1 + R\ln (P_1T_2)/(P_2T_1)$$

$$= C_V \ln T_2/T_1 + R \ln P_1/P_2 + R \ln T_2/T_1$$

$$= (C_V+R) \ln T_2/T_1 - R \ln P_2/P_1$$

$$= C_P \ln T_2/T_1 - R \ln P_2/P_1 \qquad \ldots \ldots 2.26$$

for n moles we have

$$\Delta S = nC_P \ln T_2/T_1 - nR \ln P_2/P_1 \qquad \ldots \ldots 2.27$$

$$= 2.303 \, n \, C_P \log T_2/T_1 - 2.303 \, nR \ln P_2/P_1 \quad \ldots 2.28$$

It is evident from the above equation that the entropy change for the change of state of an ideal gas depends upon the initial and final pressure as well as on the initial and the final temperature.

Case I:

At constant pressure, i.e., when process is isobaric $P_1=P_2$ then equation 2.26 reduces to,

$$\Delta S_P = C_P \ln T_2/T_1$$

$$= 2.303 \, C_P \log T_2/T_1$$

and for n moles

$$\Delta S_P = nC_P \ln T_2/T_1$$

$$= 2.303 \, n \, C_P \log T_2/T_1$$

Evidently increase in temperature of an ideal gas at constant pressure is accompanied by increase in entropy.

Case II:

When temperature remains constant then,

$$\Delta S_T = -R \ln P_2/P_1 = R \ln P_1/P_2$$

$$= 2.303 \, R \log P_1/P_2$$

$$= 2.303 \, R \log V_2/V_1$$

and for n moles

$$\Delta S_T = 2.303 \, n \, R \log P_1/P_2$$

$$= 2.303 \, n \, R \log V_2/V_1$$

as $P_1V_1 = P_2P_2$ so $P_1/P_2 = V_2/V_1$

2.6.4 Entropy change accompanying change of phase:

From solid phase to liquid phase:

Let us consider a case when a solid changes into liquid state at its fusion point. The process requires heat for this purpose, known as heat of fusion.

Consider melting of one mole of a substance reversibly at the fusion point T_f, at constant pressure. Let ΔS_f be the molar heat of fusion. The entropy change of the process, ΔH_f, will then be given by

$$\Delta S_f = \Delta H_f/T \qquad\qquad \text{……..} \quad 2.29$$

2.6.5. From liquid phase to vapour phase:

Suppose one mole of a substance changes from liquid to vapour state reversibly at its boiling point T_b, under a constant pressure. Let ΔH_V be the molar heat of vapourisation. The entropy change accompanying the process will then be given by

$$\Delta S_V = \Delta H_V/T \qquad\qquad \text{…..} 2.30$$

Since ΔH_f and ΔH_V are both positive, the processes of fusion and vapourisation are both accompanied by increase of entropy?

If we consider the change of state from vapour to liquid or from liquid to solid, then ΔH_V and ΔH_f will both be negative and hence the process of condensation of vapour or freezing of a liquid would be accompanied by decrease of entropy.

Example 1:

Calculate the entropy change when one mole of ethanol is evaporated at 351 K. the molar heat of vaporization of ethanol is 39.84 K J mole^{-1}.

Solution: we know ΔS_V $= \Delta H_V / T_b$

                Hence ΔH_V $= 39.84$ KJ mole^{-1}

                                         $= 39840$ J mole^{-1}

                    and T_b $= 351$ K

             then $\Delta S_V = 398.40/351$ C

                          $= 113.5$ J K^{-1} mole^{-1}

Example 2:

Calculate the entropy change in the melting of 1 Kg of ice at 0^0C. Heat of fusion of ice is 334.72 Jg^{-1}

Solution:

                 ΔS_f $= \Delta H_f / T$

                      $= 334.72/273$

                      $= 1.226$ J K^{-1}g^{-1}

For one Kg change of entropy will be 1.226×1000

                                   $= 1226$ JK^{-1} Kg^{-1}

2.6.6 Change of entropy from one crystalline form to another:

The change in entropy when one mole of a solid substance undergoes change of state from one crystalline form (say, rhombic form) to another crystalline form (say, monoclinic form) at the transition temperature T_t, is given by

$$\Delta S_t = \Delta H_t/T_t$$

Where ΔH_t is the molar heat of transition of substance. Molar heat of transition is the amount of heat absorbed or evolved by one mole of a substance when it undergoes change to state from one crystalline form to another at the transition temperature.

2.7 ENTROPY OF MIXTURE OF IDEAL GAS:

From equation 2.21 we have the reaction for entropy change for one mole of an ideal gas

$$dS = C_V dT/T + RdV/V$$

integrating this equation assuming that C_V remains constant for an ideal gas,

$$S = C_V \ln T + R \ln V + S_o \qquad\qquad ….2.31$$

where S_o is constant of integration

now $C_P - C_V = R$

so $C_V = C_P - R$

and $V = RT/P$ we have

$$S = (C_P - R) \ln T + R \ln(RT)/P + S_o$$

$$S = C_P \ln T - R \ln T + R \ln R \ln T - R \ln P + S_o \qquad\qquad …..2.32$$

$$= C_P \ln T - R \ln P + S`_o \qquad \text{where } R \ln R + S_o = S`_0, \text{ another constant.}$$

Entropy of a system consisting of a mixture of gases would evidently be given by the sum of the individual entropies of the constituents at pressure (or concentrations) existing in the mixture. If n_1 and n_2 are the number of moles of two gases present in the mixture and p_1 and p_2 are their partial pressure, then entropy of the mixture is given by

$$S = n_1 (C_P \ln T - R \ln p_1 - S`_o) + n_2 (C_P \ln T - R \ln p_2 + S`_o) \qquad …2.33$$

The partial pressure of p_1 of an ideal gas is given by the expression

$p_1 = x_1 P$ ….2.34

Where x_1 is mole fraction of that particular gas in the mixture and P is total pressure.

Substituting for p_1 and p_2 in equation 2.33 we get

$S = n_1 (C_P \ln T - R \ln x_1 P + S`_o) + n_2(C_P \ln T - R \ln x_2 P + S`_o)$

$= n_1(C_P \ln T - R \ln x_1 - R \ln P + S`_o) + n_2(C_P \ln T - R \ln P + S`_o)$ …..2.35

This equation given entropy of mixture of two ideal gases.

Entropy of mixing:

Entropy of mixing is defined as the difference between the entropy of the mixture of gases and the sum of the entropies of the separate gases, each at a pressure P. Thus

$\Delta S_{mix} = n_1(C_P \ln T - R \ln x_1 P - R \ln P + S`_o) + n_2(C_P \ln T - R \ln x_2 - R \ln P + S`_o)$

$-[n_1(C_P \ln T - R \ln P + S`_o) + n_2(C_P \ln T - R \ln P + S`_o)$

$= -n_1 R \ln x_1 - n_2 R \ln x_2$ …..2.36

Now $x_1 = n_1 /(n_1 + n_2)$ (mole fraction of first gas)

and $x_2 = n_2/(n_1 + n_2)$ (mole fraction of second gas)

for a total of one mole of the gaseous mixture the entropy of mixing is given by

$\Delta S_{mix} = -n1/n_1 + n_2 R \ln x_1 - n_2/n_1 + n_2 R \ln x_2$ …..2.37

Hence $\Delta S_{mix} = -x_1 R \ln x_1 - x_2 R \ln x_2$

Since mole fraction x_1 or x_2 is a fraction, hence entropy of mixing is always positive. Hence entropy of mixing is always positive. Hence mixing of two or more gases is spontaneous process.

Example:

Calculate entropy of mixing of one mole of oxygen gas and one mole of hydrogen gas, assuming that no chemical reaction occurs and the gas mixture behaves ideally (R=8.3145 $K^{-1} mole^{-1}$).

Solution:

Here n_1= 1 mole and n_2=1 mole

Mole fraction of oxygen = 1/(1+1)=1/2=.50

and mole fraction of hydrogen = 1/(1+1)=1/2=.50

ΔS_{mix} = -R($n_1$lnx_1+$n_2$lnx_2)

   = -8.314(ln.50+ln.50)

   = -8.314x2ln.50

   = -8.314x2x2.303log ½

   =-8.314x2x2.303 (-.3010)

   = 11.523 JK^{-1}

2.8 ENTROPY AS A MEASURE OF THE DISORDER OF THE SYSTEM

We have already studied in the above discussion that all spontaneous processes, such as flow of heat from hot end to a cold end of a conductor, expansion of a gas in vacuum, diffusion of solute from a concentrated to a dilute solution, are accompanied by increase in the disorder of the system. Spontaneous processes are accompanied by increase in the entropy a well as increase in the disorder of the system.

We have also studied that melting of a solid or evaporation of liquid is accompanied by increase of entropy. At the same time, it is known that a solid has a definite crystal lattice, i.e., the atoms or ions or molecules in a solid are arranged in a definite order. The order is much less in liquids and least in gases. Thus, increase of entropy implies increase in disorder.

Thus entropy is regarded as a measure of the disorder of a system.

2.9 ENTROPY AS A MEASURE OF PROBABILITY

The thermodynamic probability is the number of ways in which a given system in a specified thermodynamic state can be realized w is the probability of the system. S = f(w).

All spontaneous processes lead to increase in entropy and also increase in disorder. A little consideration will show that when a process is spontaneous it means that it is proceeding from a less probable to more probable state. It appears, therefore, that there is a close relation between entropy S and the thermodynamic probability W of the state of the system, both of which increase at the same time. This relationship was expressed by Boltsman as

$$S = k\ln W + \text{constant} \qquad \text{.......2.38}$$

Where k is Boltzmann constant (=R/N)

According to Planck the constant in the above equation is zero. Hence

$$S = k\ln W \qquad \text{.......2.39}$$

This equation is called Boltzmann entropy equation

A solid at absolute zero temperature is considered to be in most ordered state. In this case, evidently, W is unity and hence $S_o = 0$. The entropy of crystalline solids at absolute zero is, therefore, taken as zero.

2.10 CLAUSIUS INEQUALITY

Entropy change in an irreversible cyclic process

Consider a cyclic process, similar to that of Carnot cycle in which one or more of its stages are performed irreversible. Let ABCD denote the cycle in figure 2.2 in which AB and CD are isothermal stages. Let us further suppose, the absorption of heat δq_1^* by the system at temperature T_1 from the source along AB is irreversible. The rest of the stages are carried out reversibly. The asterisk(*) would indicate the irreversibility, otherwise transformation is reversible. The heat δq_2 is given to the sink at temperature T_2 along CD.
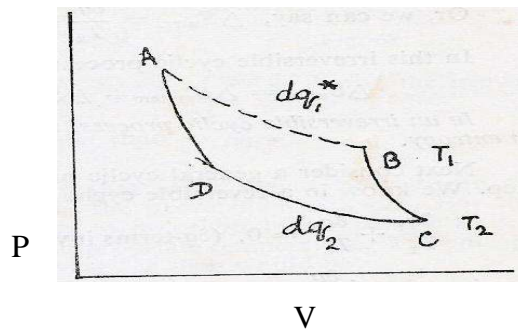

Fig 2.2 entropy change in irreversible cycle.

This is an irreversible cycle and hence the efficiency of the engine is less than that of the Carnot cycle, or,

$(\delta^* q_1 - \delta q_2)/\delta^* q_1 < (T_1-T_2)/T_1$

or $\delta q_2/T_2 < \delta^* q_1/T_1$

When the cycle is completed, the engine has returned to its initial state

$\Delta S_{system} = 0$

Now consider the surroundings and find out the q/T terms. It is $-\delta^* q_1/T_1$ for the source and $\delta q_2/T_2$ for the sink.

Hence for the surroundings

$\sum q/T = \delta q_2/T_2 - \delta^* q_1/T_1$ which is from equation 2.5 is greater than zero, i.e., positive.

The heat change of sink is reversible. The heat $\delta^* q_1$ from the source was taken by the system irreversibly. The source has lost $\delta^* q_1$ and its entropy has decreased. The entropy- change of the source from A to B would be evaluated as stated earlier by supposing the loss of heat δq_1 occurred reversibly and consequently

$\Delta S_{source} = -\delta^* q_1/T_1$

Or we can say,

$\Delta S_{surr} = \delta q_2/T_2 - \delta^* q_1/T_1 > 0$

In this irreversible cyclic process, therefore

$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr} = 0 + \Delta S_{surr} > 0$

In an irreversible cycle process, there would occur a net increase in entropy.

Next consider a general cyclic process involving an irreversible step.

We know in a reversible cyclic process

$= \delta q_1/T_1 + \delta q_2/T_2 = 0$ (δq- terms involve their own signs)

i.e., $\oint \frac{\delta q}{T} = 0$ (revesible)

in an irreversible cycle

$$(\delta q_1 - \delta q_2)/ \delta q_1 < (T_1 - T_2)/T_1$$

Hence $\delta q_1/T_1 + \delta q_2/T_2 < 0$

This is often referred as Clausius enequality.

2.11 WORK FUNCTION AND FREE ENERGY FUNCTION:

The sum of the entropy change of the system and surroundings ($\Delta S_{sys} + \Delta S_{surr}$) serves as a criterion of spontaneity or feasibility of a process. If total entropy change is positive, the process is feasible. If it is zero the system remains in a state of equilibrium. However in order to decide about the feasibility of a process, we shall have to know the entropy change of the system as well as that of the surroundings. This is not always convenient. We may, therefore, consider entropy change in terms of other state functions which may be determined more conveniently. Two such functions are the work function A and free energy function or Gibbs free energy G. These two functions are such that they utilize entropy in their derivation. These are defined by the equations.

$$A = E\text{-}TS \qquad\qquad\qquad ….. \; 2.40$$

$$G = H\text{-}TS \qquad\qquad\qquad …..2.41$$

As E, H and S are state functions hence A and G are also state functions. The exact nature of these functions will be clear from the following

2.11.1 Work function (A):

The work function A is defined as

$$A = E\text{-}TS$$

Let us consider a system which undergoes a change of state from (1) to (2) at constant temperature. As already discussed above A is a state function depends only on initial and final states.

$$A_1 = E_1\text{-}TS_1 \qquad\qquad ……2.42$$

and $\quad A_2 = E_2\text{-}TS_2 \qquad\qquad …..2.43$

substracting 2.42 from 2.43 we get

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

or $\Delta A = \Delta E - T\Delta S$ ...…2.44

2.11.2 Free energy function:

By definition free energy function is given by the equation

$$G= H-TS$$

If the system change from initial state (1) to final state (2) then free equations can be written as

$$G_1= H_1-TS_1 \qquad\qquad ….2.45$$

and $\quad G_2= H_2-TS_2 \qquad\qquad ….2.46$

substracting equation 2.45 from 2.46 we get

$$G_2-G_1 = H_2-H_1 – T(S_2-S_1)$$

$$\Delta G = \Delta H = T\Delta S \qquad\qquad\qquad …..2.47$$

2.11.3 Variation of work function with temperature and volume:

We know work function is represented as

$$A= E-TS$$

Differentiation of this equation gives

$$dA = dE – TdS – SdT$$

but $\qquad dE = TdS-PdV \qquad$ from final and second law of thermodynamics.

$$dA= TdS-PdV-TdS-SdT$$

$$dA= -PdV-SdT \qquad\qquad …..2.48$$

At constant temperature

$$dA_T = -PdV$$

$\left(\frac{\partial A}{\partial V}\right)_T = -P$

And at constant volume

$dA_V = -SdT$

hence $\left(\frac{\partial A}{\partial T}\right)_V = -S$ …..2.49

This relation is utilized for establishing Gibbs-Helmholtz relation.

2.11.4 Variation of free energy with temperature and pressure:

By definition

$G = H-TS$

Since $H = E+PV$

hence $G = E+PV – TS$

upon differentiating

$dG = dE+PdV+VdP-TdS-SdT$ ……2.50

For an infinitesimal stage of reversible process,

$dq = dE+PdV$ (from first law of thermodynamics)

Also $dq = TdS$ (from second law of thermodynamics)

Hence $TdS = dE+PdV$ or $dE = TdS-PdV$ …..2.51

This equation is also known as combined equation of first and second law of thermodynamics as both the laws are included in it. Substituting the value of dE in equation 2.50 we get

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

       $= VdP-SdT$ ….2.52

At constant temperature $dG_T = VdP$

                           or $\left(\frac{\partial G}{\partial T}\right)_T = V$ …..2.53

and at constant pressure

$dG_P = -SdT$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad\qquad \dots\dots 2.54$$

This expression is useful in establishing Gibbs Helmholtz relation.

From equation 2.54

$dG = VdP$

Let the free energy of the system be G_1 at pressure P_1 and G_2 at pressure P_2 then integrating the above equation we get;

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP = \int_{P_1}^{P_2} \frac{RT}{P} dP = RT \int_{P_1}^{P_2} dP/P$$

$G_2-G_1 = RT\ln P_2/P_1 = 2.303RT \log \frac{P_2}{P_1} = 2.303\ln \frac{V1}{V2} \qquad \dots\dots.2.55$

Where V_1 and V_2 are the initial and final volumes respectively.

2.12 GIBB'S HELMHOLTZ EQUATION

These are the two equations derived by Gibbs and Helmholtz and are known as Gibbs-Helmholtz equations. One equation can be expressed in terms of changes in free energy (ΔG) and enthalpy (ΔH), while the other can be expressed in terms of changes in work function(ΔA) and internal energy (ΔE). The former is generally employed and is applicable to all processes, chemical or physical, but in a closed system. From equation 2.52

We know $dG = VdP - SdT$

At constant pressure

$dG = -SdT$

Let G_1 represent free energy of a system in its initial state at temperature T. suppose the temperature rises to T +dT where dT is infinitesimally small. Let the free energy at the new temperature be G_1+dG, then

$dG_1 = -S_1 dT \qquad\qquad \dots..2.56$

where S_1 is entropy in the initial state. Now suppose free energy of the system in the final state be G_2 at temperature T, and G_2+dG_2 is the free energy at temperature T+dT in the final state; then

$$dG_2 = -S_2 dT \qquad\qquad\qquad\qquad .....2.57$$

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

Substracting 2.56 from 2.57 we get

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

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

as the pressure is constant, therefore,

$$\left(\frac{\partial}{\partial T}(\Delta G)\right)_P = -\Delta S \qquad\qquad\qquad ......2.58$$

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

Hence $\Delta G = \Delta H + T\left(\frac{\partial}{\partial T}(\Delta G)\right)_P \qquad\qquad ....2.59$

This equation is known as Gibbs-Helmholtz equation. It is applicable to all processes occurring at constant pressure. It has been used for calculating the heat change ΔH for a process or a reaction taking place at constant pressure provided the values of free energy at two different temperatures are known.

2.13 CLAUSIUS CLAPEYRON EQUATION

An equation of fundamental importance which finds extensive application in one-component two-phase system was derived by Claucius and Clapeyron, from the second law of thermodynamics is known as Clausius Clapeyron equation.

The two phases in equilibrium may be any of the following types:

(i) Solid and liquid   S $\rightleftharpoons$ L   at the melting point of solid
(ii) Liquid and vapour   L $\rightleftharpoons$ V at the boiling point of liquid
(iii)Solid and vapour   S $\rightleftharpoons$ V at the sublimation temperature of solid

(iv) One crystalline form to another crystalline form as rhombic sulphur to monoclinic sulphur.

$S_R \rightleftharpoons S_M$ at the transition temperature of the two allotropic forms.

In deriving the Clausius-Clapeyron equation we must keep in our mind that, when the system is in equilibrium there is no change in free energy. If water is in equilibrium with its vapour the free energy in water phase is equal to free energy in vapour pahse. In general equal amounts of a given substance must have exactly the same free energy in two phases at equilibrium with each other.

Consider the change of a pure substance from phase A to phase B in equilibrium with it at a given temperature and pressure. If G_A is free energy per mole of the substance in the initial phase A and G_B is the free energy per mole in the phase B, then since $G_B = G_A$, there will be no free energy change, i.e.,

$$\Delta G = G_B - G_A = 0 \qquad \dots .2.60$$

If temperature of such a system is raised, say from T to T+dT, the pressure will also have to change, say form P to P+dP, in order to maintain equilibrium.

Let the free energy per mole of the substance in phase A at the new temperature and pressure be $G_A + dG_A$ and that in phase B, $G_B + dG_B$. since two phases are still in equilibrium, hence

$$G_A + dG_A = G_B + dG_B \qquad \dots \dots 2.61$$

From equation 2.60 and 2.61 we have

$$dG_A = dG_B \qquad \dots \dots ..2.62$$

we know $dG = VdP - SdT$

then $dG_A = V_A dP - S_A dT$

and $dG_B = V_B dP - S_B dT$

From equation 2.62 we have

$$V_A dP - S_A dT = V_B dP - S_B dT \qquad \dots \dots 2.63$$

$$dP(V_B - V_A) = dT(S_B - S_A)$$

or $\frac{dP}{dT}$ = (S_B-S_A)/(V_B-V_A) 2.64

It may be noted that V_A and V_B are molar volumes of the pure substance in the two phases A and B respectively.

From definition of entropy $T\Delta S = q$

or $S_B-S_A = \Delta S = q/T$

So   equation 2.64 becomes:

$dP/dT = \dfrac{q}{T(V_B - V_A)}$ 2.65

this equation is known as Clapeyron's equation

this equation gives change in pressure dP which must accompany the change in temperature dT or vice versa, in the case of a system containing two phases of a pure substance in equilibrium with each other. Suppose the system consists of water in two phases, viz., liquid and vapour in equilibrium with each other at temperature T, i.e.,

water (liquid) $\rightleftharpoons$ water (vapour)
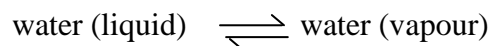
Then q= molar heat of 46aporization ΔH_V

V_B = volume of one mole of water in the vapour phase, say, V_g

V_A = volume of one mole of water in the liquid phase, say V_l

and T will be boiling point of water say T_b

then equation 2.65, will take the form

$dP/dT = \dfrac{\Delta H_V}{(V_g - V_l)}$ 2.66

The molar volume of a substance in the vapour state is considerably greater than in the liquid state. In the case of water, for example, the value of V_g at 100^0C is 18x1670=30060 ml while that of V_l is only a little more than 18 ml. Thus V_g-V_l can be taken as V_g without introducing any serious error. The Clapeyron's equation can be written as

$dP/dT = \Delta H_V/T_g$ 2.67

Assuming that gas law is applicable, i.e., PV=RT or P=RT/P

    Hence $dP/dT = P\Delta H_V/RT^2$ …...2.68

    or $dP/P = \Delta H_V/RT^2\ dT$

    or $d(\ln P) = (\Delta H_v/RT^2)/dT$

Assuming that ΔH_V, remains constant over a small range of temperature, we have

$$\int d\ln P = \frac{\Delta H_V}{R}\int \frac{dT}{T^2} \qquad ….2.69$$

On integrating between limits of pressure P_1 and P_2 corresponding to temperature T_1 and T_2, we get

$$\int_{P_1}^{P_2} d\ln P = \frac{\Delta H_V}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$\ln P_2/P_1 = \frac{\Delta H_V}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad ……2.70$$

This integrated form of Clapeyron's equation is known as Clausius Clapeyron's equation.

2.13.1 Application of Clausius-Clapeyron's equation:

(i) Calculation of molar heat of vaporization

(ii) Effect of temperature on vapour pressure of a liquid

(iii) Effect of pressure on boiling point

(iv) Calculation of molar elevation constant

(v) Calculation of molar depression constant

2.14 SUMMARY

      As you have studied that first law of thermodynamics is law of conservation of energy. It does not tell us about the direction of the reaction. In second law you have studied the direction of a particular process by defining reversible (equilibrium) and irreversible (spontaneous) processes. A thermodynamically irreversible process is always accompanied by an increase in the entropy of the system and its surroundings taken together, while in a thermodynamically reversible process the entropy of the system and its surroundings taken together remains unchanged. By making use of entropy, we have introduced free energy function and work

function. The free energy function is an important function as it gives an idea about feasibility of a reaction. If free energy remains constant the system will be in equilibrium, and if it is negative the process is feasible. Study of Gibbs-Helmholtz equation and Clausius-Clapeyron's equation are of importance for various calculations.

2.15 TERMINAL QUESTIONS

A. Objective type questions:

1. An adiabatic process is an:

(a) isobaric process   (b) isochoric process   (c) isoenthalpic process

(d) isoentropic process

2. Mixing of two or more gases is a:

(a) spontaneous process   (b) non-spontaneous process (c) reversible process

(d) none of these

3. The change in entropy of a reaction is given by:

(a) $\Delta S = \sum S_{reactants} + \sum S_{products}$ (b) $\Delta S = \sum S_{products} - \sum S_{reactants}$

© $I = \sum S_{reactants} - \sum S_{products}$ (d) none of these

4. The free energy function G is defined as :

(a) G=H+TS   (b) G=H-TS   (c) G=TS-H   (d) None of these

5. The change in free energy is measure of

(a) Net work done   (b) Net change in entropy   (c) Net change in enthalpy

(d) Net change in internal energy

A. Short answers type questions:

1. Define entropy

2. Write a note on physical significance of entropy

3. Define expression for the entropy change accompanying variation of temperature   and volume.

4. Show that entropy is a state function.

C. Long answer type questions:

1. Discuss entropy change in reversible and irreversible processes. Comment on the statement "entropy of the universe is always increasing".

2. Derive an expression for the entropy of a mixture of two ideal gases. Define from it an expression for the entropy of mixing of two ideal gases.

3. Derive two important forms of Gibbs-Helmholtz relation. What are its important applications.

4. (a) Write a note on Clasius-Clapeyron's relation.

   (b) Discuss the variation of Gibbs free energy function with temperature.

2.16 ANSWERS

1. (d)   2. (a)   3. (b)   4. (b)   5. (a)

Source of study material

1. Principles of Physical Chemistry. By Puri, Sharma, Pathania
2. Essentials of Physical Chemistry By B.S. Bahl, Arun Bahl G.D. Tuli
3. Physical Chemistry by P.C. Rakshit.

Books recommend for further study:

1. Physical Chemistry by Adkins.
2. Thermodynamics by P.C. Rakshit
3. Thermodynamics for chemists by S. Glasstone

UNIT - 3 CHEMICAL EQUILIBRIUM

CONTENTS:

3.1 OBJECTIVES

After going through this unit, you will be able to know.

- Reversible and irreversible reactions.

- Chemical equilibrium.

- Law of mass action.

- Relation between free energy and equilibrium constant.

- Le Chatelier's principle and its applications.

- Clapeyron equation
- Clapeyron Clausius equation and applications.

3.2 INTRODUCTION

In a chemical reaction, chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time .Usually, this state results when the forward reaction proceeds at the same rate as the reverse reaction. The reaction rates of the forward and backward reactions are generally not zero, but equal. Thus, there are no net changes in the concentrations of the reactants and products. Such a sate is known as dynamic equilibrium.
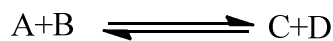
3.3 REVERSIBLE AND IRREVERSIBLE REACTIONS:

Not all chemical reactions proceed to completion .In most reactions two or more substances react to form products which themselves react to give back the original substances.Thus A and B may react to form C and D which react together to reform A and B.
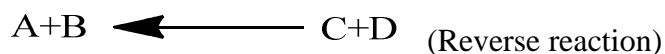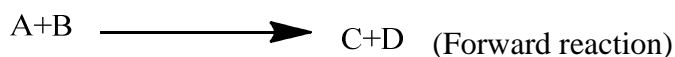
A+B $\longrightarrow$ C+D   (Forward reaction)

A+B $\longleftarrow$ C+D   (Reverse reaction)

A reaction which can go in the forward and backward direction simultaneously is called a Reversible reaction. Such a reaction is represented by writing a pair of arrows between the reactants and products.
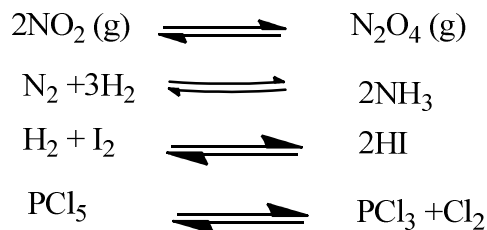
A+B $\rightleftharpoons$ C+D

The arrow pointing right indicates the forward reaction, while that pointing left shows the backward reaction.

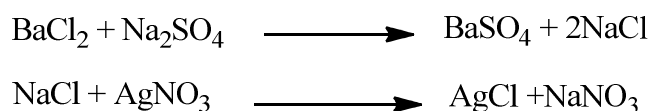Some Examples of Reversible Reactions:

A few common examples of reversible reactions are listed below:

$$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

On the other hand, the reactions which proceed only in one direction are known as irreversible reactions.

Examples:

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$$
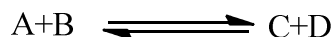
$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

3.4 CHEMICAL EQUILIBRIUM:

Let us consider the rection:

$$A+B \rightleftharpoons C+D$$

If we start with A and B in a closed vessel, the forward reaction proceeds to form C and D. The concentrations of A and B decrease and those of C and D incease continuously. As a result the rate of forward reaction also decrease and rate of backward reaction increases. Ultimately, the rate of two opposing reactions equals and the system attains a state of equilibrium. Thus " The state of reversible reaction in which the concentrations of the reactants and products do not change is called chemical equilibrium".
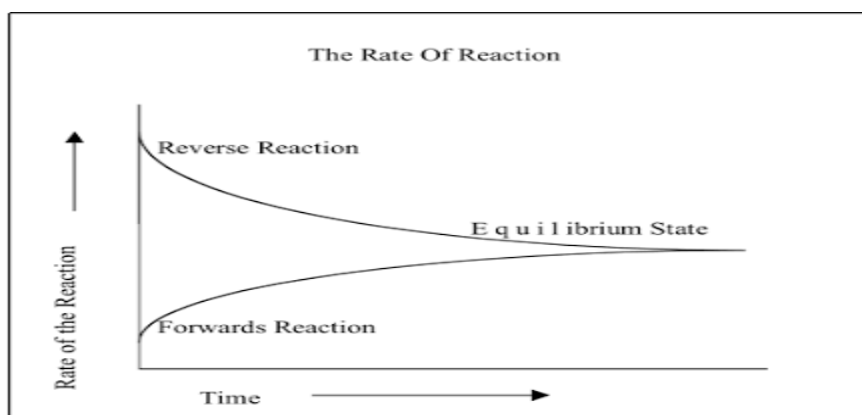
Fig. 3.1 At equilibrium the Forward reaction rate equals the Reverse reaction rate

Characteristics of chemical Equilibrium:

Some of the important characteristics of chemical equilibrium are follows:

(i) At equilibrium, the concentration of each of the reactants and products becomes constant.

(ii) At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction and hence the equilibrium is dynamic in nature.

(iii) A chemical equilibrium can be established only if none of the products is allowed to escape out.

(iv) Chemical equilibrium can be attained from either direction i.e from the direction of reactants as well as from the direction of the products.

(v) A catalyst does not alter the state of equilibrium.

3.5 LAW OF MASS ACTION

Guldberg and Waage, the two Norwegian chemists, in 1864 put forward a law concerning the dependence of rate of reaction on the concentration of the reactants. This law is known as Law os Mass Action. It states as follows: **The rate of chemical reaction is proportional to the active masses of the reactants.**

The term active mass used in the above statement implies activity which, for the sake of simplicity, may be taken as equal to molar concentration.

Consider the following reversible reaction, taking place at constant temperature:

$$A+B \rightleftharpoons C+D$$
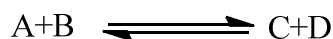
According the law of mass action, the rate (r_1) at which A and B react is given by the equation

$$r_1 \propto [A][B]$$

$$r_1 = k_1 [A][B] \ldots\ldots\ldots (i)$$

Where k_1 is the proportionality constant, called rate constant of the reaction and the square brackets indicate molar concentrations. The rate of backward reaction (r_2) is given by the equation.

$$r_1 = k_2[C][D] \ldots \ldots \ldots (ii)$$

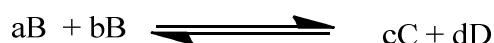Where k_2 is the rate constant of reverse reaction.

Thus ultimately, a dynamic equilibrium is attained when the rate of forward reaction becomes equal to that of the reverse reaction , i.e., $r_1 = r_2$.

3.6 LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

Consider the following reversible reaction:

$$aB + bB \rightleftharpoons cC + dD$$

Where a, b, c and d are numerical quotients of the substance, A , B , C and D respectively.

According to law of mass action,

Rate of forward reaction, $r_1 = k_1 [A]^a[B]^b$

Rate of backward reaction, $r_2 = k_2 [C]^c [D]^d$

Since at equilibrium, $r_1 = r_2$, it follows that

$k_1 [A]^a[B]^b = k_2 [C]^c [D]^d$

or $$\frac{k_1}{k_2} = k_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \ldots \ldots \ldots (i)$$

k_c is known as equilibrium constant and has a fixed value for a certain reaction at a given temperature and pressure and is independent of the amounts of reactants and products. However, its value depends on the temperature and types of reactions.

In a general reaction reprinted by the equation
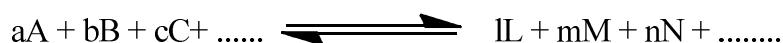
$$aA + bB + cC + \ldots \ldots \rightleftharpoons lL + mM + nN + \ldots \ldots$$

The equilibrium constant is given by

$$K_c = \frac{[L]^l [M]^m [N]^n \cdots}{[A]^a [B]^b [C]^c \cdots} \qquad (ii)$$

For gaseous reactions, it is more convenient to use partial pressures instead of concentrations. The equilibrium constant in that case is represented by K_p.

Thus for a general gaseous reaction

aA + bB + cC+ ...... $\rightleftharpoons$ lL + mM + nN + ...
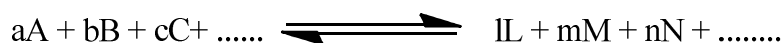
$$K_P = \frac{[P_L]^l \times [P_M]^m \cdots}{[P_A]^a \times [P_B]^b \cdots} \qquad (iii)$$

Where P_L and P_M etc. stand for partial pressures of the products and P_A, P_B, etc for the partial pressures of the reactants.

3.7 RELATIONSHIP BETWEEN K_P AND K_C

For a general reaction,

aB + bB $\rightleftharpoons$ cC + dD
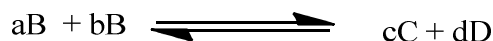
The equilibrium constant in terms of concentrations (moles/liter) is

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad \cdots\cdots\cdots (i)$$

If the reactants and products are gaseous, then the concentration terms may be replaced by partial pressure. The equilibrium constant Kp written as,

$$Kp = \frac{p_C^c \, p_D^d}{p_A^a \, p_B^b} \qquad \cdots\cdots\cdots (ii)$$

For an ideal gas, $pV = nRT \; or \; p = \frac{n}{V}RT = CRT,$

Where C is the molar concentration. For different gases A, B, C, D, we may write

$P_{A} = C_A RT$, $p_B = C_B RT$, $p_C = C_C RT$, $p_D = C_D RT$

Putting these values in equation (ii), we get

$$K_p = \frac{(C_C RT)^c (C_D RT)^d}{(C_A RT)^a (C_B RT)^b}$$

or $$K_p = \frac{C_C^c C_D^d}{C_A^a C_B^b} (RT)^{(c+d)-(a+b)}$$

$$\boxed{K_p = K_c (RT)^{\Delta n}}$$ .... (iii)

Where

$\Delta n = (c + d) - (a + b)$ = [number of moles of products]- [number of moles of reactants]

3.8 THERMODYNAMIC DERIVATION OF THE LAW OF CHEMICAL EQUILIBRIUM

Let us consider a general reaction,

$$aA + bB + ... \rightleftharpoons cC + dD + ...$$
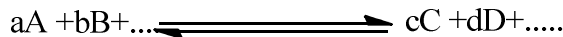
The chemical potential of a substance in a mixture is related to its activity by the expression

$$\mu = \mu^0 + RT \ln a \, ... \, ... (i)$$

Where μ^0 is the chemical potential of pure substance in standard state of unit activity, R is the gas constant and T is the absolute temperature.

For a mole of the substance A we can write using the equation (i)

$$a\mu_A = a(\mu^0 + RT \ln a_A)$$

And similarly,

$$b\mu_B = b(\mu^0 + RT \ln a_B)$$

$$c\mu_C = c(\mu^0 + RT \ln a_C)$$

$$d\mu_D = (\mu^0 + RT \ln a_D)$$

The change in free energy for the reaction is given by

$$\Delta G = G_{products} - G_{reactants}$$

On substitution we get

$$(c\mu_c + d\mu_D + \cdots) - (a\mu_A + b\mu_B = \cdots$$

$$= (c\mu_c + d\mu_D + \cdots) - (a\mu_A + b\mu_B + \cdots)$$

$$= c[\mu_C^0 + RT \ln a_C] + d\{\mu_D^0 + c\}] - [a(\mu_a^0 + RT\ln a_A) + b[\mu_B^0 + RT \ln a_B\}]$$

$$== [\{c\mu_C^0 + d\mu_D^0 + \cdots\} - \{a\mu_A^0 + \mu_B^0 + \cdots\}] + RT\ln\frac{a_C^c \times a_D^d \times \cdots}{a_A^a \times a_B^b \times \cdots}$$

$$\Delta G = \Delta G^0 + RT\ln\frac{a_C^c \times a_D^d \times \cdots}{a_A^a \times a_B^b \times \cdots} \qquad \cdots\cdots(ii)$$

Where ΔG^0 is the difference in free energy of the reaction when all reactants and products are in their standard state. It is given by

$$\Delta G^0 = \{c\mu_C^0 + d\mu_D^0 + \cdots\} - \{a\mu_A^0 + \mu_B^0 + \cdots\}$$

In equation (ii) the factor A is given by

$$\frac{a_C^c \times a_D^d \times \cdots}{a_A^a \times a_B^b \times \cdots}$$

Stands for the reaction quotient of activities of the product and reactants. It may be denoted by J.The equation (ii) becomes,

$$\Delta G = \Delta G^0 + RT \ln J \qquad \cdots\cdots(iii)$$

The equation (iii) is called van't Hoff reaction isotherm

For the reaction at equilibrium

$$\Delta G = 0$$

Therefore, $$\Delta G^0 = -RT \ln J$$

Or $$\Delta G^0 = -RT\ln\frac{a_C^c \times a_D^d \times \cdots}{a_A^a \times a_B^b \times \cdots}$$

As ΔG^0 is the free energy of the reaction in the standard state and is constant at given temperature.

Also, the gas constant R and T are constant, the factor

$$\frac{a_C^c \times a_D^d \times ...}{a_A^a \times a_B^b \times ...}$$ is a constant i.e,

$$\frac{a_C^c \times a_D^d \times ...}{a_A^a \times a_B^b \times ...} = a\ constant = K$$

From equation (iii) we have

$$\Delta G^0 = -RT \ln K \qquad\qquad ......(iv)$$

Or $$c = -2.303 RT \log K \qquad ......(v)$$

The equation (iv) is also called van't Hoff Isotherm. It may be used to calculate the change in free energy of a reaction in the standard (ΔG^0) from the equilibrium constant and vive –versa.

The sign of ΔG^0 indicates whether the forward or reverse reaction is spontaneous. Considering the equation (iv), we can have three possibilities depending on the sign of ΔG^0 for the reaction.

    (1) If ΔG^0 is negative, log K must be positive and the reaction proceeds spontaneously in the forward reaction.

    (2) If ΔG^0 is positive, log K must be negative and K is less than one. The reverse reaction is then spontaneous.

    (3) If $\Delta G^0 = 0, \log K = 0\ and\ K = 1$. The reaction is at equilibrium.

3.9 LE- CHATELIER'S PRINCIPLE

The effect of concentration, temperature and pressure on a system in equilibrium can be predicted with the help of a generalization first proposed by a French chemist Le-Chetelier in 1884. After his name, this generalization is known as Le-Chatelier's principle. It states as follows:

If a system is in equilibrium is subjected to change of concentration, temperature or pressure, the equilibrium shifts in a direction that tends to reduce the effect of the change imposed.

Let us now discuss the effect of the various factors one by one.

(1) Effect of Concentration Change on the Position of Equilibrium:

   If the concentration of one of the substances present in an equilibrium reaction is changed without change in any of the other conditions, then by Le-Chatelier's principle, the position of equilibrium will move to decrease the concentration of the added substance. Thus, in the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
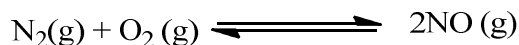
At a given temperature , adding N_2 or O_2 Would shift the equilibrium from left to right, i.e, more nitric oxide (NO) will be formed.

   The effect of changes in concentration of substances on the position pf equilibrium in a chemical reaction may be summarised as follows:

Change in concentration of substance	Effect on equilibrium position of reaction $A + B \rightleftharpoons C + D$
Increase in concentration of A or B	Proportion of C and D increased , i.e., Equilibrium shifts to right.
Decrease in concentration of A or B	Proportion of C and D decreased , i.e., Equilibrium shifts to left.
Increase in concentration of C or D	Proportion of A and B increased , i.e., Equilibrium shifts to left.
Decrease in concentration of C or D	Proportion of A and B decreased , i.e., Equilibrium shifts to right.

Some examples from everyday life:

(1) Clothes dry quicker when there is a breeze or we keep on shaking it. This is because water vapour of the nearby air removed and cloth loses more water vapour to re-establish equilibrium with the surrounding air.

(2) We sweat more on a humid day but it evaporates when we sit under the fan. More sweating takes place because the surrounding air has large amount of water vapour and our skin cannot lose more to it. The fan removes the humid air and evaporation starts from the skin.

(3) Transport of oxygen by hemoglobin in blood. Oxygen breathed in combines with the hemoglobin in the lungs according to the equilibrium
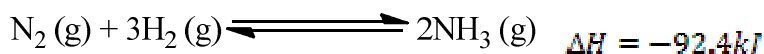
$$Hb\ (s) + O_2 \rightleftharpoons HbO_2\ (s)$$
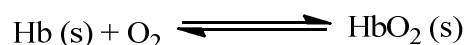
When it reaches the tissues, the pressure of oxygen is low. To readjust the equilibrium, oxyhaemoglobin gives up oxygen. When it returns to lungs where the pressure of oxygen if high, more of oxyhaemoglobin if formed.

(1) Effect of Temperature Change on the Position of Equilibrium:

The change of temperature alters the state of equilibrium for only those reactions in which either heat is evolved (exothermic) or heat is absorbed (endothermic). In fact, every such reaction is made up of two opposing reactions. If the forward reaction is exothermic, the backward reaction will be endothermic and vice-versa.

(i) Consider the exothermic reaction

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g) \quad \Delta H = -92.4 kJ$$

Or it may be written as

$$N_2 + 3H_2\ (g) \underset{endo}{\overset{exo}{\rightleftharpoons}} 2NH_3\ (g) + 92.4\ kJ$$
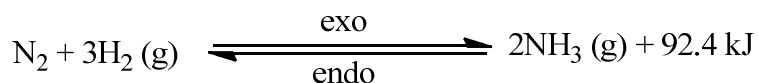
Obviously, the the forward reaction is exothermic while the backward reaction is endothermic. Now, if the temperature is increased i.e. heat is supplied to the system, and then according to Le Chatelier's principle, the equilibrium will shift to the side that absorbs heat i.e in the backward direction. Similarly, decrease in temperature will shift the equilibrium in the forward direction.

(ii) Again , consider the endothermic reaction

$$N_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2NO \text{ (g)} \quad \Delta H = +180.7kJ$$

Or it may be written as

$$N_2 \text{ (g)} + O_2\text{(g)} + 180.7kJ \xrightleftharpoons[\text{exo}]{\text{endo}} 2NO \text{ (g)}$$
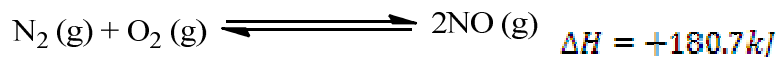
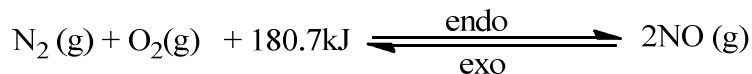Here the forward reaction is endothermic while backward reaction is exothermic .The increase of temperature will favour the forward reaction while the decrease of temperature will favour the backward reaction. Thus in general,

Exothermic reactions are favoured by low temperature whereas endothermic reactions are favoured by high temperature.

Effect of Pressure Change on the Position of Equilibrium:

This factor has a significant role to play only in case of gaseous reactions and those too which proceeds with a change in number of moles.

(i) Consider the dissociation of N_2O_4 into NO_2:

$$\underset{\text{1 mole}}{N_2O_4 \text{ (g)}} \rightleftharpoons \underset{\text{2 moles}}{2NO_2 \text{ (g)}}$$
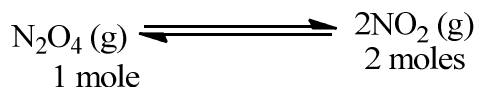
Here, the forward reaction occurs with increase in number of moles. Therefore backward reaction must proceed with decrease in number of moles. If now the pressure on the system is increased, the volume of the system will decrease correspondingly. Hence the total number of moles per unit volume will now be more than before. Therefore according to Le Chatelier's principle, the equilibrium will shift in that direction in which the total number of moles decreases. Since backward reaction takes place with decrease in number of moles so an increase in pressure will favour the formation of N_2O_4. Conversely, if the pressure on the system is decreased, the equilibrium will shift in the forward direction which is accompanied by increase in total number of moles. In other words, decrease in pressure favours the formation of NO_2.

(ii) Consider another gaseous reaction involving formation of ammonia.

$$\underset{\substack{\text{1 mole} \quad \text{3 moles}}}{N_2 \text{ (g)} + 3H_2 \text{ (g)}} \rightleftharpoons \underset{\text{2 moles}}{2NH_3}$$
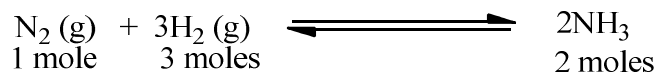
In this equilibrium reaction, the forward reaction is accompanied by a decrease in the total number of moles. On increasing pressure number of moles per unit volume will increase as result equilibrium will shift to the product side i.e it favours the formation of ammonia. Thus, higher the pressure, the better would be the yield of ammonia. On the other hand, a decrease in pressure will favour the dissociation of NH_3 into N_2 and H_2.

(iii)Lastly, consider the following equilibrium reaction involving the formation of hydrogen iodide.

$$H_2 (g) +\ I_2 (g) \rightleftharpoons\ 2HI (g)$$
$$1mole\quad 1mole \qquad\qquad 2\ moles$$

This reaction place in either direction without change in number of moles. So according to Le Chatelier's princilple, pressure will have no effect on this equilibrium. In general,

Low pressure favours those reactions which are accompanied by increase in total number of moles and high pressure favours those reactions which take place with decrease in total number of moles. However, pressure has no effect on an equilibrium reaction which proceeds with no change in total number of moles.

Effect of addition of inert gas on the position of equilibrium:

The effect of addition of addition of inert gas can be studied under two different conditions:

(i) Addition of inert gas at constant volume: when an inert gas is added to the equilibrium state at constant volume, then the total pressure will increase. But the partial pressure of each component will remain unchanged. Under these conditions, there will no effect on the equilibrium on addition of the inert gas.

(ii) Addition of an inert gas at constant pressure: when an inert gas is added to the system at constant pressure there will be increase in the volume. As a result, the number of moles per unit volume of different components will decrease. The equilibrium will shift to the side where the numbers of moles are increased. For example consider the following equilibrium.

$$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)\ \ \text{at constant pressure}$$
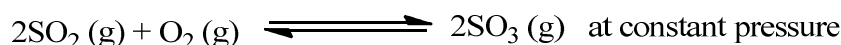
The addition of inert gas at constant pressure will shift the equilibrium to backward direction.

For the equilibrium

$$PCl_5 \text{ (g)} \rightleftharpoons PCl_3 \text{ (g)} + Cl_2\text{(g)} \quad \text{at constant pressure}$$
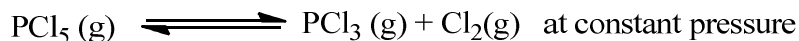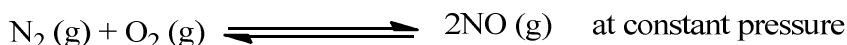
The addition of inert gas at constant pressure will shift the equilibrium to the forward direction.

However , addition of an inert gas to the following equilibrium

$$N_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2NO \text{ (g)} \quad \text{at constant pressure}$$

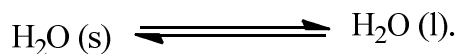Will have no effect because the number of moles of reactants and products are same.

Effect of catalyst on the position of equilibrium:

There is no effect of addition of a catalyst on the equilibrium state. This is because catalyst increases the rate of forward reaction as well as rate of backward reaction to the same extent. It simply helps to achieve the equilibrium quickly. It may be further noted that catalyst has no effect on the equilibrium concentration of a reaction mixture.

Applications of Le Chatelier's Principle:

(1) Physical Equilibria

(a) Melting point of ice: Ice melts with decrease in volume as well as absorption of heat, e.g.,

$$H_2O \text{ (s)} \rightleftharpoons H_2O \text{ (l)}.$$

It is represented as:

$$\text{Ice} \underset{}{\overset{0^0C}{\rightleftharpoons}} \text{Water} - \text{Heat}$$
$$\text{(More volume)} \qquad \text{(Less volume)}$$
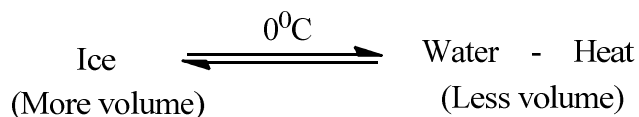
Increase of pressure or temperature will shift the equilibrium from left to right. In other words, melting point of ice is lowered by an increase of pressure or temperature.

(b) Vaporization of water: The equilibrium between water and steam is represented as:

$$\text{Water} \rightleftharpoons \text{Water vapour} - \text{Heat}$$
$$\text{(Less volume)} \qquad \text{(More Volume)}$$

On increasing the temperature, the equilibrium will shift in that direction in which heat is absorbed, i.e., forward reaction. So, more steam will be produced. Similarly, on increasing the pressure, the equilibrium will shift in that direction in which volume is decreased, i.e., backward reaction. So, steam will condense into liquid. In other words, formation of steam will be favored by increase of temperature and decrease of pressure.
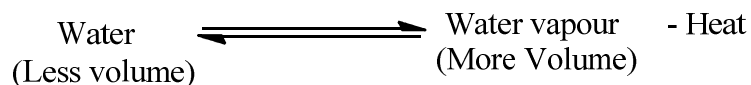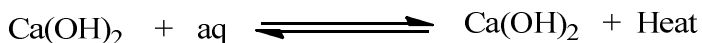
(c) Solubility of substances: Certain substances like sugar, NaCl etc dissolve with an absorption of heat, e.g.,

$$Sugar + aq \rightleftharpoons Sugar\,(aq) \ - \ Heat$$

So, increase of temperature will shift equilibrium to the right. So, the solubility of such substances increases on increase the temperature.
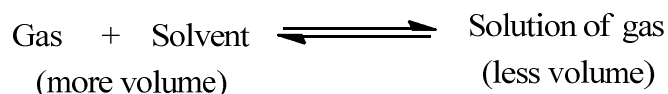
Certain substances like $Ca(OH)_2$ etc. Dissolve with an evolution of heat, e.g.,

$$Ca(OH)_2 + aq \rightleftharpoons Ca(OH)_2 + Heat$$

So, increase of temperature will shift the equilibrium to the left, i.e., direction in which heat is absorbed. So, the solubility of such substances decreases on increasing the temperature.

(d) Solubility of gases in liquids: Consider the solution of a gas in equilibrium with the gas.

The equilibrium can be represented as:

$$\begin{array}{cc} Gas \ + \ Solvent & \rightleftharpoons \quad Solution\ of\ gas \\ (more\ volume) & (less\ volume) \end{array}$$

If pressure is increased, volume will reduced without affecting the pressure and some of the gas will dissolve in the solvent. Thus, the solubility of gas increases on increasing the pressure.

(2) Chemical Equilibria:

(a) Synthesis of ammonia by Haber's process: Haber's process involves the reaction.

$$\begin{array}{ccccc} N_2\,(g) & + & 3H_2\,(g) & \rightleftharpoons & 2NH_3\,(g)., \\ 1\ vol. & & 3\ vol & & 2\ vol \end{array}$$
$$\Delta H = -22\ kcal$$
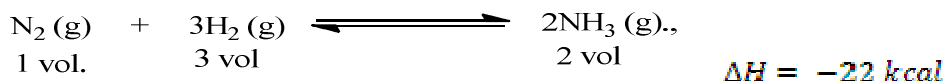
(i) Effect of temperature: If the temperature of the reaction is lowered, the equilibrium must shift so as to tend to raise the temperature again (Le Chatelier's principle). That is, heat must be liberated by the production of ammonia. That is low temperature favours

the formation of ammonia. But lowering of temperature reduces the rate of reaction, so it is necessary to use a catalyst which will give a sufficient reaction rate inspite of a relatively low temperature.

(ii) Effect of pressure. Ammonia is produced from its elements with reduction of volume. Therefore, if the system is in equilibrium and the pressure is then raised, the equilibrium must shift so as to tend to lower the pressure (Le Chatelier's principle). To do this, the volume must be reduced by the production of more ammonia. That is, high pressure favours the formation of ammonia.

(iii) Effect of concentration. If the system is in equilibrium and more N_2 is added to increase its concentration, then according to Le Chatelier's principle, the equilibrium will shift so as to tend to reduce N_2 concentration. That is, more ammonia will be produced to use up N_2. This increase the yield of ammonia relative to H_2, and vice-versa if the H_2 concentration is increased.

The formation of ammonia is favoured by:

(i) Low temperature

(ii) High pressure, and

(iii) High concentration of the reactants.

(b) Formation of sulphuric acid by the contact process: The first step in the production of sulphuric acid is the conversion of sulphur dioxide into sulphur trioxide according the reaction

$$2SO_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2SO_3 \text{ (g)}$$

   2 vol   1 vol   2 vol

$$\Delta H = -47 \ kcal$$
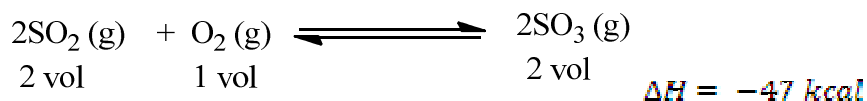
This reaction is just similar to the synthesis of ammonia described above. So, the effect of pressure, temperature and concentration will be the same as mentioned in the synthesis of ammonia. Low temperature, high pressure and increased concentrations of SO_2 and O_2 will favour the formation of sulphur trioxide.

The SO_3 is removed from the equilibrium mixture by dissolving it in fairly concentrated sulphuric acid, forming oleum which is then diluted to get the acid of the required concentration.

(c) Formation of nitric oxide: The reaction is represented as,

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

1 vol   1 vol   2 vol

$$\Delta H = +43.2\ k\,cal$$
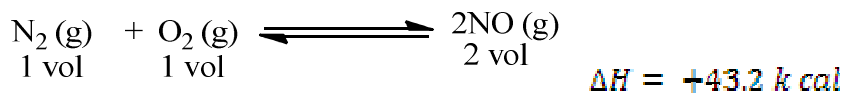
(i) Effect of pressure: As no change of volume occurs during the formation of nitric oxide, there will be no effect of pressure on the equilibrium.

(ii) Effect of temperature: if the temperature is increased then the equilibrium will shift in that direction in which heat is absorbed, i.e., in the forward direction. So , high temperature favours the formation of nitric oxide.

(iii) Effect of concentration: If to the system in equilibrium N_2 is added, the equilibrium will shift in that direction so as to reduce the concentration of N_2. So, more nitric oxide will be formed. Similar is the effect of adding oxygen.

So, the formation of nitric oxide is favoured by

(i) High temperature and

(ii) High concentrations of N_2 or O_2.

3.10 VAN'T HOFF ISOTHERM OR MAXIMUM WORK OBTAINED FROM GASEOUS REACTIONS

Consider the following reaction

$$aA \;+\; bB +....... \;\rightleftharpoons\; lL + mM +......$$
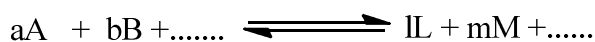
Taking palce under any conditions of temperature, pressure and composition. The free energy change of the reaction is given by the expression

$$\Delta G = (G)_{products} - (G)_{reactants} \cdots \cdots \cdots (1)$$

$$= (l\mu_L + m\mu_M + \cdots) - (a\mu_A + b\mu_B + \cdots)$$

Where μ_A, μ_B, μ_L, μ_M, etc represents chemical potentials of the species concerned.

Let us suppose the various reactants and products are in gaseous state. Chemical potential of a gaseous substance in any state is given by the equation

$$\mu_{i(p)} = \mu^0_{i(p)} + RT\ ln p_i \qquad \cdots \cdots \cdots (ii)$$

Where $\mu^{0}_{i(p)}$ is the chemical potential of gaseous component i, in the standard state (partial pressure = 1 atm) and $\mu_{i(p)}$ is the chemical potential of the gaseous component i in any state of partial pressure p_i.

Substituting the values of chemical potentials of various species at their partial pressures from eq (ii) in equation (i)

$$\Delta G = \{l\left(\mu^{0}_{L(p)} + RT\ \ln p_{L}\right) + m\left(\mu^{0}_{M(p)} + RT\ \ln p_{M}\right) + \cdots\} - \{a\left(\mu^{0}_{A(p)} + RT\ \ln p_{A}\right) + b\left(\mu^{0}_{B(p)} + RT\ \ln p_{B}\right) + \cdots\} \qquad \ldots\ldots\ldots(iii)$$

Re arranging we have

$$\Delta G = \{l\mu^{0}_{L(p)} + m\mu^{0}_{M(p)} + \cdots\} - (a\mu^{0}_{A(p)} + b\mu^{0}_{B(p)} + \cdots)\}$$
$$+ RT\ln\frac{(P_{L})^{l}(P_{M})^{m}\ldots}{(P_{A})^{a}(P_{B})^{b}\ldots} \qquad \ldots\ldots\ldots(iv)$$

The first expression on thr right hand side, evidently, is the free energy change of the reaction when the products and the reactants are all in their respective standard states. This expression may be substituted by ΔG^{0}.Hence,

$$\Delta G = \Delta G^{0} + RT\ln Q_{p} \qquad \ldots\ldots\ldots\ldots(v)$$

Where Q_{p} stands for the reaction quotient of partial pressures of the products and reactants, viz,

$$\frac{(P_{L})^{l}(P_{M})^{m}\ldots}{(P_{A})^{a}(P_{B})^{b}\ldots}$$

Equation (v) is known as van't Hoff reaction isotherm. This gives the free energy change of a reaction at any given temperature, pressure and composition of the reacting system,

Q_{p} is different from K_{p}. Here the values p_{L}, p_{M}, p_{A}, p_{B}....etc are not the partial pressures at equilibrium, but for any state. If the partial pressure values correspond to equilibrium state, then Q_{p} will become equal to K_{p}. As we have

$$\Delta G^{\circ} = -RT\ \ln K_{p}$$

Substituting for ΔG° in eq (v), we have

$$\Delta G = -RT\ \ln K_{p} + RT\ln Q_{p} \qquad \ldots\ldots\ldots(vi)$$

Equation (v) and equation (vi) are two forms of van't Hoff reaction isotherm.

Example: At 25^0, the ΔG° for the reaction

$$H_2(g) \ + \ I_2 \ (g) \ \longrightarrow \ 2HI \ (g),$$

is -3.1 kcal. Calculate ΔG when hydrogen gas at 0.1 atm and iodine vapour at 0.1 atm react to form hydrogen iodide at 10 atm, and 25^0.

Solution: For the given reaction,

$$K = \frac{p^2(HI)}{p(H_2)p(I_2)}$$

Where p terms represent partial pressures of the various species in the reaction mixture.

$$\Delta G = \Delta G^\circ + RT \ln K = \Delta G^\circ + 2.303 \ RT \ log \frac{p^2(HI)}{p(H_2)p(I_2)}$$

$$= -3100 \ cal + 2.303 \ (1.987 cal \ K^{-1}mol^{-1})(298K) log \frac{(10)^2}{(0.1)(0.1)}$$

$$= -3100 \ cal + 1363.7 \log(10^4) \ cal = -3100 \ cal + 4 \ (1363.7) cal$$

$$= +2354.8 \ cal = 2.355 \ kcal.$$

3.11 VAN'T HOFF EQUATION FOR THE TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANT (VAN'T HOFF REACTION ISOCHORE)

The equation for reaction isotherm when the reactants as well as the products are gaseous and are also in their standard states, is represented as

$$\Delta G^0 = -RT \ lnK\_(p \hspace{4cm} ……… (i)$$

Differentiating with respect to temperature at constant pressure, we have

$$\left\{\frac{\partial(\Delta G^\circ)}{\partial T}\right\}_p = -RlnK_p - RT \frac{d(lnK_p)}{dt}$$

Multiplying throughout by T, we get

$$T\left\{\frac{\partial(\Delta G^0)}{\partial T}\right\}p = -RT\ lnK_p - RT^2\frac{d(lnK_p)}{dT} \qquad\qquad \dots\dots\dots(ii)$$

Substituting ΔG^o for $-RT\ lnK_p$, we have

$$T\left\{\frac{\partial(\Delta G^0)}{\partial T}\right\}p = \Delta G^o - RT^2 lnK_p - RT^2\frac{d(lnK_p)}{dT} \qquad\qquad \dots\dots\dots(iii)$$

The well known Gibbs-Helmholtz equation for substances in standard states may be written as

$$\Delta G^o = \Delta H^o + T\left\{\frac{\partial(\Delta G^0)}{\partial T}\right\}p \qquad\qquad \dots\dots\dots(iv)$$

Comparing equations (iii) and (iv), we get

$$RT^2\frac{d(lnK_p)}{dT} = \Delta H^o$$

$$or \qquad \frac{d(lnK_p)}{dT} = \frac{\Delta H^o}{RT^2} \qquad\qquad \dots\dots\dots(v)$$

Equation (v) is known as the van't Hoff's equation. ΔH^o is the enthalpy change for the reaction at constant pressure when the reactants as well as products are in their standard states.

It is well known from experiments that the enthalpy change, ΔH, accompanying a chemical reaction does not vary appreciably with change in partial pressures of the reactants and products . Therefore, we may take $= \Delta H^o$ as equal to ΔH , where ΔH is the enthalpy change of the reaction whatever may be the partial pressures of the reactants or products. Hence, the van't Hoff equation may be written as

$$\frac{d(\ln(K_p))}{dT} = \frac{\Delta H}{RT^2} \qquad\qquad \dots\dots\dots(vi)$$

Integrating equation (vii) between temperatures T_1 and T_2 at which the equilibrium constants are K_p' and K_p'' respectively and assuming that ΔH remains constant over this range of temperature, we get:

$$\int_{K_p'}^{K_p''} d(lnK_p) = \frac{\Delta H}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$\ln K_p{}'' - \ln K_p{}' = \frac{-\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad \ldots\ldots\ldots(vii)$$

$$\log K_p{}'' - \log K_p{}' = \log\frac{K_p{}''}{K_p{}'} = \frac{\Delta H}{2.303\ R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad \ldots\ldots\ldots(viii)$$

Knowing the equilibrium constant at a temperature it is possible to calculate the equilibrium constant at another temperature provided the heat of reaction (ΔH) is known.

Alternatively, knowing the equilibrium constants of a reaction at two temperatures, the heat of reaction ((ΔH) can be calculated.

Example: The equilibrium constant K_p, for the reaction

$$H_2(g) + S(g) \rightleftharpoons H_2S(g)$$
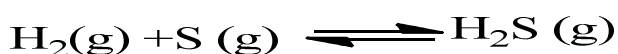
Is 20.2 atm at 945°C and 9.21 atm at 1065⁰C. Calculate the heat of reaction.

Solution: Applying van't Hoff equation

$$\log K_p{}'' - \log K_p{}' = \frac{\Delta H}{2.303\ R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$T_1 = 945 + 273 = 1218\ K$$

$$T_2 = 1065 + 273 = 1338\ K$$

$$K_p{}' = 20.2\ atm$$

$$K_p{}'' = 9.21\ atm$$

Substituting the values, we have

$$\log 9.21 - \log 20.2 = \frac{\Delta H}{(2.303)(8.314\ JK^{-1}mol^{-1})}\left[\frac{1338 - 1218}{(1218K)(1338K)}\right]$$

$$\Delta H = -88126.3\ J = -88.826\ kJ$$

3.12 THE CLAPEYRON EQUATION

Clapeyron equation is an important equation applicable to the equilibrium between any two phases of the same substance. This equation can be derived from second law of thermodynamics as follows:

Suppose a single substance exists in two phases A and b in equilibrium with each other at constant temperature and pressure. If one mole of substance is transferred from one phase A to the other phase B without altering the temperature and pressure , then there will be no work done other than that of expansion. So from equation ($\Delta G = VdP - SdT$), we get,

$$dG = 0, as\ dP = 0\ and\ dT = 0$$

i.e., $G_B - G_A = 0\ or\ G_A = G_B$

In other words, the molar free energy of a substance is the same in the two phases which are in equilibrium.

In a phase change, ($\Delta G = VdP - SdT$, can be written as

$$dG_A = V_A dP - S_A dT \qquad\qquad ....(i)$$

And

$$dG_B = V_B dP - S_B dT \qquad\qquad ....(ii)$$

Subtracting equations (i) from (ii), we get,

$$dG_B - dG_A = (V_B dP - S_B dT) - (V_A dP - S_A dT)$$

Or $\quad 0 = (V_B dP - S_B dT) - (V_A dP - S_A dT) \qquad (As\ G_A = G_B)$

Or $V_B dP - S_B dT = V_A dP - S_A dT$

Or $(V_B - V_A)dP = (S_B - S_A)dT$

Or $\Delta V dP = \Delta S dT$

Or $\qquad \dfrac{dP}{dT} = \dfrac{\Delta S}{\Delta V}$

Where, ΔS and ΔV have their usual significance.

Recognizing further that at equilibrium we have the change in entropy (ΔS), given by

$$\Delta S = \frac{\Delta H}{T}$$

(As $\Delta G = 0$, at equilibrium)

Therefore,

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \qquad \qquad \dots \dots \dots (iii)$$

Equation (iii) was first derived by a French engineer Clapeyron in 1834. It gives the variation of equilibrium pressure (P) with temperature for any two phases of a given substance.

Application (iii) is applicable to various equilibria such as solid-liquid equilibria, liquid-vapour equilibria and equilibria between two solid modifications. The Clapeyron's equation for these various equilibria can be easily obtained as follows:

(1) Solid-liquid equilibrium: We know that solid and liquid forms of a substance can exist in equilibrium only at the freezing or melting point. Hence, in equation (iii), T will be the freezing point and P will be the external pressure exerted on the system. So, equation (iii) can also be written in areversed form as:

$$\frac{dT}{dP} = \frac{T \Delta V}{\Delta H} \qquad \qquad \dots \dots \dots (iv)$$

If V_S, and V_L represents the molar volumes of the solid and the liquid phases, respectively at temperature T and pressure P, then,

$$\Delta V = V_L - V_S$$

Where, ΔV represents the increase in volume in transferring 1 mole from solid to liquid phase, ΔH the amount of heat absorbed may be replaced by ΔH_f, i.e., molar heat of fusion. So making these changes in equation (iv), we get the following Clapeyron's equation:

$$\frac{dT}{dP} = \frac{T\ (V_L - V_S)}{\Delta H_f} \qquad \qquad \dots \dots \dots (v)$$

(2) Liquid-vapour equilibrium: In this equilibrium, the increase in volume (ΔV) accompanying the transfer of one mole of liquid to the vapour will be equal to $V_V - V_L$, where V_V and V_L represents the molar volumes of vapour and liquid, respectively. ΔH may then be replaced by ΔH_V, i.e., molar heat of vaporisation.

From the above considerations, equation (iv) becomes:

$$\frac{dT}{dP} = \frac{T \ (V_V - V_L)}{\Delta H_V} \qquad \qquad ....(vi)$$

It is a well known fact that the boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the external pressure.

So, equation (vi) represents the variation of boiling point of a liquid with pressure P. Thus, equation (vi) can also be written as:

$$\frac{dP}{dT} = \frac{\Delta H_V}{T \ (V_V - V_L)} \qquad \qquad ....(vii)$$

Equation (vii) represents the rate of change of vapour pressure (P) of the liquid with temperature.

(3) Equilibrium between two solid modifications: If α represents the stable form of solid above the transition point and β the stable form of the solid below the transition point then equation (iii) becomes:

$$\frac{dT}{dP} = \frac{T \ (V_\alpha - V_\beta)}{\Delta H_t} \qquad \qquad ....(viii)$$

Where, V_α and V_β represents the molar volumes of the two forms respectively and ΔH_t is the molar heat of transition determined at T.

Applications of Clapeyron Equation:

The Clapeyron equation can be applied in numerous ways to several physio-chemical problems.

(i) It can be used for predicting the effect of pressure on the volumes or densities of the solid liquid phases ($V_s \ and \ V_L$) and of heat of fusion (ΔH_f).

if $V_L < V_S$ then $(V_L - V_S)$ will be negative and so dT/dP will be negative . In other words, increase of pressure will decrease the melting point. This is observed in the ice-water equilibrium

if $V_S < V_L$ then $(V_L - V_S)$ will be positive and so dT/dP will be positive . In other words, increase of pressure will increase the melting point.

(ii) It is also possible to calculate the enthalpy of fusion (ΔH_f) of a substance from equation (vi), is dT/dP or rather $\Delta T/\Delta P$ and specific volumes of the solid and liquid phases are known.

(iii) Clapeyron equation can also predict the effect of pressure on the transition temperature with the help of equation (viii). Similarly, we can precisely calculate the enthalpy of transition from the change in volume, i.e., $(V_\alpha - V_\beta)$ and the value of dT/dP, from equation (viii).

(iv) The enthalpy of vaporization (ΔH_V) can also be calculated from equation and also we can easily find the rate of change of boiling point from equation (vi).

Problem 1: The orthobaric specific volumes of ice and water at 0^0C are 1.0907c.c. and 1.0001 c.c., respectively. What will be the change in melting point of ice per atmosphere increase of pressure? The latent heat of fusion is 79.8 cal/g.

Solution: Orthobaric specific volume of ice (V_S) = 1.0001 c.c.

Orthobaric specific volume of water $(V_{L)}$ = 1.0001 c.c.

So $V_L - V_S =$ −0.0906 c.c.

Latent heat of fusion $\Delta H_f =$1 atm $= 76 \times 13.6 \times 981$

$= 1.013 \times 10^6$ dynes/sq.cm.

dT= ?

We know that for solid-liquid equilibrium, we have,

$$\frac{dT}{dP} = \frac{T\ (V_L - V_S)}{\Delta H_f}$$

$$dT = \frac{T\,(V_L - V_S)}{\Delta H_f} \cdot dP$$

$$= \frac{273 \times 0.0906 \times 1.013 \times 10^6}{79.8 \times 4.2 \times 10^7}$$

$$= -0.007476\,^0C$$

The negative sign indicates that melting point of ice decreases by increase of pressure.

3.13 CLAUSIUS-CLAPEYRON EQUATION

If the temperature of the liquid is not too near the critical point then we can easily neglect the volume of the liquid (V_L), compared with that of vapour (V_V).In such a case, the equation

$$\frac{dP}{dT} = \frac{\Delta H_V}{T(V_V - V_L)}$$ reduces to equation (1) on replacing P by p.So

$$\frac{dP}{dT} = \frac{\Delta H_V}{T\,V_V} \qquad\qquad \ldots\ldots\ldots(i)$$

Furthermore, under such conditions the vapour pressure is very small, so it may be assumed that the vapour behave as an ideal gas to which the equation $PV_v = RT$ is applicable.

$$\frac{dP}{dT} = p \cdot \frac{\Delta H_V}{RT^2}$$

or $$\frac{1}{p} \cdot \frac{dP}{dT} = \frac{\Delta H_V}{RT^2}$$

or $$\frac{d\log p}{dT} = \frac{\Delta H_V}{RT^2} \qquad\qquad \ldots\ldots\ldots(ii)$$

Equation (ii) is sometimes known as Clausius-Clapeyron equation and is generally spoken of as first latent heat equation.It was first derived by Clausius (1850) on the thermodynamics basis of Clapeyron equation.

Equation (ii) is valid for evaporation and sublimation processes but not valid for transition between solids or for the melting of solids. Clausius-Clapeyron equation is an approximate equation because the volume of the liquid has been neglected and ideal behavior of the vapour is also taken into account. However equation (ii) has the advantage of greater simplicity because in the calculation of the value dp/dT or dT/dp, it is necessary to know the volumes of the liquid and the vapour.

3.13.1 Integrated form of clausius-clapeyron equation:

Assuming the heat of vaporization to be independent of temperature, if we integrate equation (ii) between the limits T_1 to T_2 (for temperature) and p_1-p_2 (for vapour pressure), we get,

$$\int_{p_1}^{p_2} d\log p = \int_{T_1}^{T_2} \frac{\Delta H_V}{RT^2} dT$$

Or $$\ln\frac{p_2}{p_1} = \frac{\Delta H_V}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

Or $$2.303 \log\frac{p_2}{p_1} = \frac{\Delta H_V}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Or $$\log\frac{p_2}{p_1} = \frac{\Delta H_V}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \dots\dots\dots (iii)$$

If ΔH_V is expressed in cal/mole and R= 1.987 cal/degree/mole, then equation (iii) becomes

$$\log\frac{p_2}{p_1} = \frac{\Delta H_V}{4.576}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \dots\dots\dots (iv)$$

Equation (iv) is the integrated form of Clausius- Clapeyron equation. If the integration is carried out indefinitely (without limits) then we can write the vapour pressure equation as (ii) as,

$$\log p = -\frac{\Delta H_V}{RT} + C \ (contant) \qquad \dots\dots\dots(v)$$

Problem 1: The vapour pressure of water at 95^0C and 100^0C are 634 and 760 mm, respectively. Calculate the latent heat of evaporation of water per gram between 95^0C and 100^0C.

Solution:

$$log\frac{p_2}{p_1} = \frac{\Delta H_V}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Where p_1 and p_2 are vapour pressure at temperature T_1 and T_2 respectively and ΔH_V is the latent heat of evaporation/mole.It is given that:

$$P_1 = 634 m.m.$$

$$P_2 = 760 m.m.$$

$$T_1 = 95 + 273 = 368^0 K, T_2 = 100 + 273 = 373^0 K$$

So, $$log\frac{760}{634} = \frac{\Delta H_V}{2.303 \times 1.987}\left[\frac{373 - 368}{368 \times 373}\right]$$

or $$\Delta H_V = 9886\frac{cal}{mole} = \frac{9886}{18} = 549.4\frac{cal}{g}.$$

Problem 2: At what height must the barometer stand in order that water may boil at 99^0C? Given that the latent heat of vaporization of water per gram is 536 cal.

Solution: As known, the integrated form of Clausius-Clapeyron equation is,

$$log\frac{p_2}{p_1} = \frac{\Delta H_V}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$P_1 = 76$ cm. mercury $\qquad p_2 = ?$

$T_{1=}100 + 273 = 373$ K $\qquad T_2 = 99 + 273 = 372$

$\Delta H_V = 536$ cal/g $= 536 \times 18$ cal/mole

$$log\frac{p_2}{76} = \frac{535 \times 18}{2.303 \times 1.987}\left[\frac{372 - 373}{372 \times 373}\right] = -\frac{536 \times 18 \times 1}{2.303 \times 1.987 \times 372 \times 373}\right]$$

$$log\, p_2 - log\, 76 = -\frac{536 \times 18 \times 1}{2.303 \times 1.987 \times 372 \times 373}$$

or $\qquad log\, p_2 = log76 - \dfrac{536 \times 18 \times 1}{2.303 \times 1.987 \times 372 \times 373}$

$= 1.8806 - 0.0159 = 1.8659,$

taking antilog we get $\qquad p_2 = 73.43\ cm.\ of\ mercury.$

3.13.2 Applications of clausius-clapeyron equation:

(1) Latent heat from vapour pressure data: Suppose the vapour pressures p_1 and p_2 are determined at two temperature T_1 and T_2 respectively, then it is possible to calculate the molar or specific heat of vaporization. It is also possible to calculate the value of HV graphically. It is clear that if log p is plotted against the reciprocal of the absolute temperature,i.e.,1/T, then a straight line will be obtained. The slope of this line will be equal to $-\Delta H/R$.So, knowing the value of R, the value of ΔH can thus be easily determined after measuring the slope.

(2)Deduction of Trouton's law: Equation (ii) can be written in the form,

$$\frac{1}{p} \cdot \frac{pd}{dT} = \frac{\Delta H_V}{RT^2}$$

For liquid vapour equilibrium $\Delta H_V = L_e$, i.e., molar heat evaporation. Hence, the last expression becomes,

$$\frac{1}{p} \cdot \frac{pd}{dT} = \frac{L_e}{RT^2}$$

or $\qquad \dfrac{T}{P} \cdot \dfrac{dP}{dT} = \dfrac{L_e}{RT} \qquad\qquad \ldots\ldots\ldots (vi)$

we know that, $\qquad \dfrac{T}{T_c} = \theta\ and\ \dfrac{P}{P_c} = \pi,$

Where P_C and T_C represent the critical pressure and critical temperature, respectively and π, θ are the educed pressure and reduced temperature, respectively. So equation (vi) becomes,

$$\frac{\theta}{\pi} \cdot \frac{d\pi}{d\theta} = \frac{L_e}{RT} \qquad\qquad (vii)$$

Vander Waals (1888) suggested the empirical relationship,

$$\log \frac{P}{P_c} = k\left[1 - \frac{T_c}{T}\right]$$

Where k is constant which is equal to 3 for many substances. Hence in reduced terms it can be put as,

$$\log \pi = 2.3 k\left[1 - \frac{1}{\theta}\right] \qquad\qquad (viii)$$

Differentiating equation (viii) with respect to θ, we get,

$$\frac{d\log\pi}{d\theta} = 2.3 \frac{k}{\theta^2}$$

$$or \qquad \frac{1}{\pi}\frac{d\pi}{d\theta} = 2.3 \frac{k}{\theta^2}$$

$$or \qquad\qquad\qquad \frac{\theta}{\pi}\cdot\frac{d\pi}{d\theta} = 2.3 \frac{k}{\theta} \qquad\qquad \ldots\ldots(ix)$$

From equation (vii) and (ix), we conclude that,

$$\frac{L_e}{RT} = 2.3 \frac{k}{\theta}$$

$$or \qquad \frac{L_e}{T} = 6.9 \frac{R}{\theta}$$

If the temperature is taken to be the boiling point T_b, then θ which is T_b/T_c is nearly equal to 0.6 and, therefore,

$$\frac{L_e}{T_b} = 23 \qquad\qquad \ldots\ldots\ldots(x)$$

So, the molar heat of vaporization of a liquid divided by its boiling point on absolute scale, i.e., L_e/T_b is constant and is approximately equal to 23, provided the latent heat is expressed in calories. The fact was first observed by Pictet (1876) and rediscovered by Ramsay (1877) and Trouton (1884) and is commonly known as *Trouton's law.* Some substances which obey Trouton's law are ethyl ether, benzene, propyl acetate, mercury, zinc, potassium chloride etc.

This law is an approximate law. For non-associated substances of molecular weight of about 100, the value of (*Le/Tb*) =21, provided the boiling point is not too high. The law breaks down for associated compounds such as water and alcohol and for substances having high boiling points.

   At the normal boiling point the vapour pressure of liquid is equal to 1 atm., hence equation (v) becomes,

$$log l = -\frac{\Delta H_V}{4.576 T_b} + C$$

According to Trounton's law, *for many non-associated substances, $\Delta H_v/T_b$ may be taken as equal to 21.* Hence,

$$C = \frac{21.0}{4.576} = 4.589$$

The expression for the vapour pressure p (in atm) of any substances to which Trouton's law is applicable now becomes,

$$log p(atm) = -\frac{\Delta H_V}{4.576 T} + 4.589 \qquad \text{...... ...}(xl)$$

Problem 1: The normal boiling point of benzene is 80.1^0C; estimate its vapour pressure at 40^0C.

Solution: Since T_b is 80.1+273=353.1, then by Trouton's law

$$H_v = 21 \quad 353.1 = 7415.1 \text{ cal.mole}^{-1}$$

According to equation (xi),

$$log p(atm) = -\frac{7415.1}{4.576 T} + 4.589 = -\frac{7415.1}{4.576 \times 353.1} + 4.589 = -0.586$$

∴ $p = 0.259 atm. = 0.259 \times 76 = 19.6 cm.$

3.14 SUMMARY

- Chemical equilibrium is defined as the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.

- A reaction which can go in the forward and backward direction simultaneously is called a reversible reaction.

- Chemical equilibrium is dynamic equilibrium

- Law of mass action states that the rate of chemical reaction is proportional to the active masses of the reactants.

- Realtion between $K_{p \text{ and }} K_c$

$$K_p = K_c (RT)^{\Delta n}$$

- Thermodynamic Derivation of Law of Chemical equilibrium is given as,

  ΔG^0 = -2.303 RT log K

- Van't Hoff reaction isotherm gives the free energy of a reaction at any given temperature, pressure and composition of the reacting system.

- Van't Hoff reaction isochors gives the temperature dependence of equilibrium constant.

- Le-Chatelier's principle states that if a system at equilibrium is subjected to a change of concentration, pressure and temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.

- Clausius-Clapeyron equation is given as

  dP/dT = ΔH/TΔV

  It can be applied to various physical equilibria like melting, vaporization and sublimation.

3.15 TERMINAL QUESTIONS

1. Long Answer type questions:

1. Derive law of mass action thermodynamically.

2. Derive the following on the basis of thermodynamics.

(a) Van't Hoff isotherm   (b) van't Hoff isochore   (c) Clausius-Clapeyron equation.

3. State and explain Le-Chatelier's principle. Explain the effect of pressure and temperature on equilibrium on the basis of this principle.

4. Derive Le-Chatelier's principle thermodynamically.

2. Short Answer and Very Short Answer type Questions:

1. State law of mass action.

2. Define Le-Chatelier's principle.

3. Derive Clapeyron equation.

4. Derive integrated form of van't Hoff isochore.

5. Write an equation which relates equilibrium constant with temperature.

6. Write an application of Clausius-Clapeyron equation.

7. Explain Trouton's law.

8. State and explain Le-Chatelier's principle.

9. Write a relation between K_P and K_c.

3. Numerical Problems:

1. 1.The melting point of sulphur is 398K and its latent heat of vaporisation is 9.3 cal/gm. Find the change in melting point of sulphur per atmosphere change in pressure if the per gram volume of its α and β forms are 0.732 c.c. and 0.7070 c.c., respectively.

2. The heat of vaporization of water is 40.82 Kj mol^{-1}.The molar volume of liquid water is 0.019 dm^3 mol^{-1} and the molar volume of steam is 30.199 dm^3 mol^{-1},all at 1000C and 1atm.Calculate the change in boiling point of water at 100^0C,if the atmospheric pressure is change by 1 mm? (1atm. = 101325 Nm^{-2}).

3. Calculate the vapour pressure of water at 80^0C if its value at 100^0C is 76.0 cm. The mean heat of vaporization of water in the given temperature range is 540 cal g^{-1}.

4. At what temperature will water boil under a pressure of 790mm? The latent of vaporization of water is 540 cal g^{-1}.R=1.987 cal K^{-1} mol^{-1}.

5. At what temperature should water boil at space station where the atmospheric pressure is 528 mm? Latent heat of vaporization of water is 545.5540 cal g^{-1}.

6. The vapour pressure of water at 100^0C is 760mm. Calculate its vapour pressure at 95^0C. Given: latent of water =548 cal g^{-1}.

4. Objective Type Questions:

1. At equilibrium, ΔG is

   (a) Positive   (b) Negative   (c) Zero   (d) None of these

2. The maximum work done in a reaction is given by :

   (a) Van't Hoff isotherm   (b) Van't Hoff isochore

   (c) Clausius-Clapeyron equation   (d) None

3. The variation of equilibrium constant with temperature is given by:

   (a) Van't Hoff isotherm   (b) Van't Hoff isochore

   (c) Law of mass action   (d) Le-Chatelier's principle

4. The variation of vapour pressure with temperature is given by:

   (a) Van't Hoff isotherm   (b) Van't Hoff isochore

   (c) Law of mass action   (d) Clausius-Clapeyron equation

5. Fill in the blanks:

5. The law of mobile equilibrium was given by..................

6. Van't Hoff equation gives the variation of.................with temperature.

7. The equilibrium constant.............. with increase of temperature.

8. dP/dt =H/T V is known as.............equation.

9. K_p and K_c are related by the equation..............

3.16 ANSWERS

Multiple choice questions

1. (c)   2. (a)   3. (b)   4. (d) 5.Guldberg & Waage 6. Equilibrium constant 7.Increase

8. Clapeyron's equation   9. $K_p = K_c (RT)^{\Delta n}$

Source of study material:

1. Essential of physical chemistry by Bahal, Bahal and Tuli.
2. Principles of physical chemistry By Puri, Sharma and Pathania.
3. Physical chemistry By   P.C. Rakshit. Physical chemistry By Atkins.

UNIT-4 IONIC EQUILIBRIUM

4.1 OBJECTIVES

After going through this unit, you will be able to know.

- Electrolytes and non electrolytes.

- Acids, bases and salts.

- Ionic product of water.

- pH scale and pH calculation.

- Common ion effect and its applications.

- Solubility and solubility product of sparingly soluble salts.

- Salt hydrolysis.

- Acid base titration curves and use of indicators.

- Buffer solution and buffer capacity.

4.2 INTRODUCTION

There are numerous equilibria that involve ions only. In the following sections we will study the equilibrium involving ions. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (NaCl) is added to water it conducts electricity. Also, the conductance of electricity increases with increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called electrolytes while the other do not conduct electricity are, referred to as non electrolytes. Faraday further classified electrolytes into strong and weak electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and hydronium ions. This is because 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak

electrolyte. It should be noted that in weak electrolytes, equilibrium is established between ions and unionized molecules. This type of equilibrium involving ions in aqueous solution is called ionic equilibrium. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes.

4.3 STRONG AND WEAK ELECTROLYTES AND IONIC EQUILIBRIUM

An electrolyte is defined as a compound whose aqueous solution or molten state conducts electricity. On the other hand, a compound whose aqueous solution or molten state does not conduct electricity is called a non electrolyte.

The conductance by an electrolyte is due to the presence of ions produced by the dissociation of the substance. However, different electrolytes dissociate to different extents.

The fraction of the total number of molecules which dissociate into ions is called the degree of dissociation and is usually represented by α.

i. e. $$\alpha = \frac{\text{Numer of moles dissociated}}{\text{Total number of moles taken}}$$

Depending upon the degree of dissociation, the electrolytes are divided into two categories, called 'strong electrolytes' and 'weak electrolytes'.

Strong Electrolytes: These are the substances which dissociate almost completely into ions in aqueous solution and hence are a very good conductor of electricity. Examples are: NaOH, KOH, H_2SO_4, NaCl, KNO_3 etc.

Weak Electrolytes: These are the substances which dissociate to a small extent in aqueous solution and hence conduct electricity also to a small extent. Examples are: NH_4OH, CH_3COOH etc.

As strong electrolytes are completely ionised in the aqueous solution, therefore, their ionisation is represented by putting a single arrow pointing towards right e.g.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$
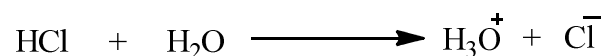
4.4 ACIDS, BASES AND SALTS

There are three concepts of acids and bases in current use. Each has its own peculiar advantages. The student should understand all the three concepts:

(a) Arrhenius concept

(b) Bronsted-Lowry concept

(c) Lewis concept

4.4.1 Arrhenius concept:

Savante Arrhenius (1884) proposed his concept of acids and bases. According to this concept an acid is compound that releases H^+ ions in water; and a base is a compound that releases OH^- ions in water.

Examples: HCl, HNO_3, H_2SO_4, CH_3COOH, H_2CO_3, H_3PO_4.

$$HCl(aq) \longrightarrow H^+(aq) \ + \ Cl^-(aq)$$

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$
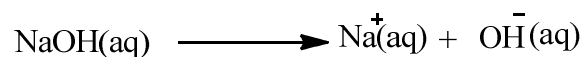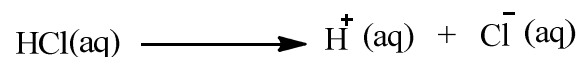
Limitations of Arrhenius Concept

Arrhenius concept of acids and bases proved to be very useful in the study of chemical reactions. However, it has the following limitations:

(1) Free H^+ and OH^- ions do not exist in water. The H^+ and OH^- ions produced by acids and bases respectively do not exist in water in the free state. They are associated with water molecules to form complex ions through hydrogen bonding. Thus the H^+ ion forms a hydronium ion:
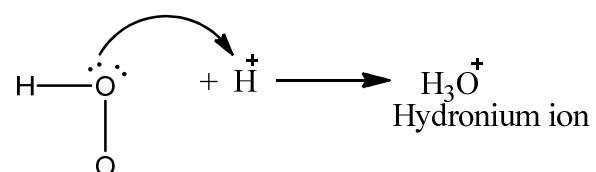

Similarly, OH^- ion forms the complex $H_3O_2^-$.

(2) Limited to water only. Arrhenius defined acids and bases as compounds producing H^+ and OH^- ions in water only. But a truly general concept of acids and bases should be appropriate to other solvents as well.

(3) Some bases do not contain OH^- . Arrhenius base is one that produces OH^- ions in water. Yet there are compound like ammonia (NH_3) and calcium oxide (CaO) that are bases but contain no OH^- ions in their original formulation.

4.4.2 Bronsted-lowry concept:

Lowry and Bronsted suggested a more general definition of acids and bases. According to their concept, an acid is defined as a substance which has a tendency to donate a proton to any other substance and a base as a substance which has a tendency to accept a proton from any other substance. In other words, an acid is a proton-donor and a base is a proton-acceptor.

When an acid loses a proton, the residual part of it has a tendency to regain the proton. Therefore, it behaves as a base. An acid and a base, therefore, be defined by the general equation

$$\text{Acid} \rightleftharpoons \underset{\text{proton}}{H^+} + \text{Base} \qquad ....(i)$$
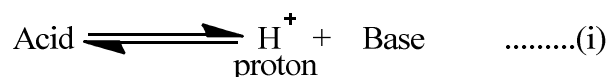
Conjugate Acids and Bases. Consider the dissociation of acetic acid in water which may be represented as

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{CH_3COO^-} ....(ii)$$

It is evident that acetic acid donates a proton to water and thus acts as an acid. Water accepts a proton and, therefore, acts as a base. In the reverse reaction, hydronium ion (H_3O^+) donates a proton to the acetate ion and, therefore, acts as an acid. The acetate ion can accept a proton and, therefore, behaves as a base. Such pairs of substance which can be formed from one another by the gain or loss of proton are known as conjugate acid base pairs. Thus, acetic acid is the conjugate acid of acetate ion and acetate ion is the conjugate base of acetic acid. Similarly, water is the conjugate base of hydronium ion and hydronium ion is the conjugate acid of water.

The following points emerge out of the following discussion:

1. Firstly, it is evident that a substance is able to show acidic character only if another substance capable of accepting a proton is present. For example, acetic acid in benzene is not acidic because benzene is not in a position to take up protons.

2. Secondly, hydrogen ion in aqueous solution does not exist as H^+ ion but as hydrated ion, H_3O^+ ion. It is called hydronium ion because of its resemblance with ammonium ion NH_4^+.

3. Thirdly, not only molecules but even ions may act as a acids and bases.

The dissociation of acetic acid in water can be represented as

$$Acid_1 \ + \ Base_2 \ \rightleftharpoons \ Acid_2 \ + \ Base_1$$
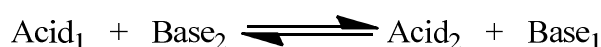
$Acid_1$ and $Base_1$ is a conjugate acid-base pair and so is $Acid_2$ and $Base_2$. In general, the dissociation of an acid HA in water may be represented as

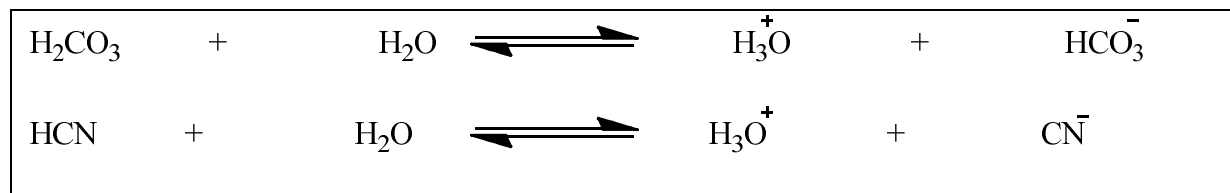$$HA \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ A^-$$

Just as an acid requires a solvent that can take up a proton for its dissociation. Similarly, a base requires a solvent that can give up a proton for its dissociation. Water possesses both acidic and basic properties. Therefore, acids as well as bases can dissociate in water. Thus water acts as an acid (a proton donor) towards ammonia and as a base (a proton acceptor) towards the acetic acid. Such substance are said to be amphiprotic or amphoteric.

Some common cases of equilibria between acids and bases involving proton transfer are given in following table.

Table 4.1 Conjugate Acids and Bases.

$Acid_1$	+	$Base_2$	$\rightleftharpoons$	$Acid_2$	+	$Base_1$
HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-
HNO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_3^-
H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-
H_3PO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$H_2PO_4^-$

$$H_2CO_3 \quad + \quad H_2O \rightleftharpoons H_3\overset{+}{O} \quad + \quad H\overset{-}{CO_3}$$

$$HCN \quad + \quad H_2O \rightleftharpoons H_3\overset{+}{O} \quad + \quad \overset{-}{CN}$$

Relative strengths of Acid-Base pairs: According to concept of Lowry and Bronsted, the strength of an acid depends upon the its tendency to lose protons and the strengths of a base depends upon its tendency to gain protons. If an acid, such as HCl, is a strong acid, it will have a strong tendency to donate protons. Thus, the equilibrium,

$$HCl \ + \ H_2O \rightleftharpoons H_3\overset{+}{O} \ + \ \overset{-}{Cl}$$

Lies very much to the right and the reverse reaction, representing the gain of proton by the chloride ion leading to the reformation of HCl, will take place to a very small amount. Thus, chloride ion is a weak base.

As a general rule, the stronger an acid, the weaker must be its conjugate base and vice versa. If an acid (e.g., HCl) is strong, its conjugate base (Cl⁻) is weak. If a base (e.g., CH_3COO^-) is strong, its conjugate acid (CH_3COOH) is weak.
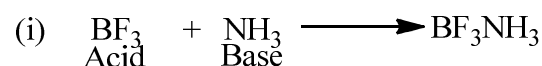
4.4.3 Lewis concept of acids and bases:

In the early 1930s, G. N. Lewis proposed even a more general model of acids and bases. According to Lewis theory,
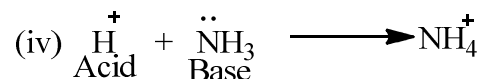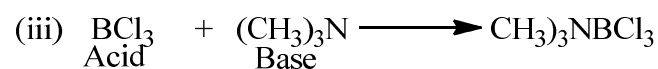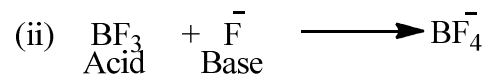
An acid is an electron pair acceptor

A base is an electron pair donor
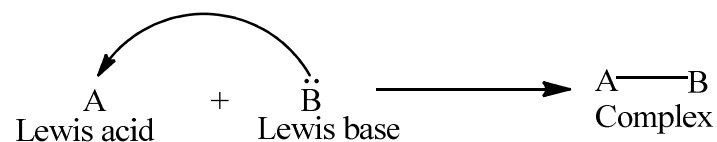
It may be noted that: (1) all cations or neutral electron deficient molecules act as Lewis acids; and (2) all anions or molecules having electron pair act as Lewis base. An a few examples are

(i) $\underset{Acid}{BF_3} \ + \ \underset{Base}{NH_3} \longrightarrow BF_3NH_3$

(ii) $\underset{\text{Acid}}{BF_3}$ + $\underset{\text{Base}}{\overset{-}{F}}$ $\longrightarrow$ $\overset{-}{BF_4}$

(iii) $\underset{\text{Acid}}{BCl_3}$ + $\underset{\text{Base}}{(CH_3)_3N}$ $\longrightarrow$ $CH_3)_3NBCl_3$

(iv) $\underset{\text{Acid}}{\overset{+}{H}}$ + $\underset{\text{Base}}{\overset{..}{N}H_3}$ $\longrightarrow$ $\overset{+}{NH_4}$

4.5 IONIC PRODUCT OF WATER

Pure water is poor conductor of electricity. This shows that water is weak electrolyte i.e., it is ionized to a very small extent as

$$H_2O \rightleftharpoons H^+ + OH^-$$

Applying law of chemical equilibrium, its dissociation constant K_c, is given by

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} \qquad ....(i)$$

Since dissociation takes place to very small constant, the concentration of the undissociated water molecules, $[H_2O]$, may be regarded as constant, say k.

$$\therefore \qquad K_c \times k = [H^+][OH^-]$$

The product of the two constants K_c and k gives another constant which is designated by K_w.

$$K_w = [H^+][OH^-] \qquad ....(ii)$$

Where K_w is called the dissociation constant of water or, more commonly, the ionic product of water.

Hence ionic product of water may be defined as the product of the molar concentration of H^+ and OH^- ions.

The value of K_w at 298K (25^0C) is usually taken as

$$K_w = 1.00 \times 10^{-14}.$$

Effect of temperature on K_w. The ionic product of water (K_w) increases with increase of temperature (as shown by the values given in following table). This is because of the fact that with increase of temperature, the degree of ionization of water increases.

Table 4.2 Values of K_w at different temperatures.

Temperature (^oC)	K_w
0	0.1×10^{-14}
10	0.3×10^{-14}
25	1.0×10^{-14}
30	1.5×10^{-14}
40	3.0×10^{-14}
50	5.5×10^{-14}
60	9.6×10^{-14}

H^+ and OH^- ion concentrations in pure water at 298K, Pure water ionizes as:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Obviously, for any degree of ionization, we will always have

$$[H^+] = [OH^-]$$

But at 298K, we know that

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

$$\therefore \; [H^+][H^+] = 1.0 \times 10^{-14}$$

$$or \quad [H^+]^2 = 1.0 \times 10^{-14}$$

$$or \quad [H^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \, moles/litre$$

Thus in pure water at $25^0 C$,

$$[H^+] = [OH^-] = = \quad 1.0 \times 10^{-7} M$$

4.6 COMMON-ION EFFECT

When a soluble salt (say A^+C^-) is added to a solution of another salt (A^+B^-) containing a common ion (A^+), the dissociation of AB is suppressed.

$$AB \rightleftharpoons A^+ + B^-$$

By the addition of the salt (AC), the concentration of A^+ increases. Therefore, according to Le-Chatelier's principle, the equilibrium will shift to the left, thereby the decreasing the concentration of A^+ ions. Or that, the degree of dissociation of AB will be reduced.

The reduction of the degree of dissociation of a salt by the addition of a common ion is called the common ion effect.

Let us consider a few examples to illustrate the common-ion effect.

Example1. In a saturated solution of silver chloride, we have the equilibrium

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

When NaCl is added to the solution, the concentration of Cl^- ions will be increases. The equilibrium shown above will be shifted to the left to form more of the solid AgCl. Thus the solubility of AgCl, will decrease

Example2. When solid NH_4Cl is added to NH_4OH solution, the equilibrium

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Shift to the left. Thereby the concentration of OH^- decreases.

4.7 IONIC EQUILIBRIA IN WEAK ACIDS AND BASES INCLUDING MULTISTAGE EQUILIBRIA

4.7.1 Dissociation of a weak acid:

Consider the dissociation of a weak monobasic acid in water, represented by the equation

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad ....(i)$$

Applying the law of chemical equilibrium, the equilibrium constant K_c is given by the expression

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad \ldots\ldots\ldots (ii)$$

Since water is present in large excess in dilute solutions, its concentration may be taken as constant, say, k. Further, since the symbol H_3O^+ simply indicates that hydrogen ion is hydrated, it may be replaced by H^+, for simplicity. The above equation may then be put as

$$K_c = \frac{[H^+][A^-]}{[HA] \times k} \quad \ldots\ldots\ldots (iii)$$

Since the product of two constants K_c and k is equal to another constant, say, K_a, eq.(iii) may be written as

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \ldots\ldots\ldots (iv)$$

The significance of equation (iv) is that the product of the concentrations of the hydrogen ion and the anions divided by the concentrations of the undissociated acid., is equal to a constant. The constant (K_a) is characteristic of the acid concerned and is known as the dissociation constant of the acid.

Relative Strengths of Weak Acids: The above equation for the dissociation constant of a weak acid can also be expressed in terms of the degree of dissociation (α) and the total molar concentration (c) of the acid. Consider, for example, the dissociation of acetic acid, represented below:

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

Original concs.   c   0   0

Equim.concs   c(1-α)   cα cα
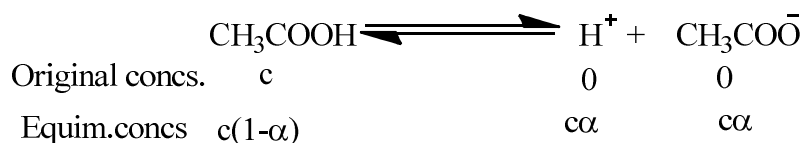
$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$= \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \quad \ldots\ldots\ldots (v)$$

Since for weak acids, α is very small, $(1-\alpha)$ in the denominator may be taken as 1. The above expression, therefore reduces to

$$K_a = c\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{c}} \qquad \text{...... ... (vi)}$$

for two weak acids of dissociation constants K_{a1} and K_{a2}, at the same concentration c, it follows from eq. (vi) that

$$\alpha_1 \Big/ \alpha_2 = \sqrt{K_{a1}} \Big/ K_{a2} \qquad \text{...... ... (vii)}$$

Where α_1 and α_2 are the respective degrees of dissociation of the two acids.

But, degree of dissociation of an acid is a measure of its capacity to furnish hydrogen ions and hence a measure of its strength.

$$\therefore \quad \frac{\text{Strength of one acid, say, } HA_1}{\text{Strength of another acid, say, } HA_2} = \sqrt{\frac{K_{a1}}{K_{a2}}} \qquad \text{...... ... (viii)}$$

Table 4.3 Dissociation constants of some common acids at 25^0C

Acid	Formula	K_{a1}	K_{a2}	K_{a3}
Acetic acid	CH_3COOH	1.75×10^{-5}		
Arsenic acid	H_3AsO_4	5.00×10^{-5}	8.30×10^{-8}	6.30×10^{-11}
Benzoic acid	$PhCOOH$	6.29×10^{-5}		
Boric acid	H_3BO_3	5.80×10^{-10}		
Carbonic acid	H_2CO_3	4.52×10^{-7}	4.69×10^{-10}	
Formic acid	$HCOOH$	1.77×10^{-4}		
Hydrocyanic acid	HCN	7.20×10^{-10}		
	H_2S			

Hydrogen sulphide	HIO_3	5.70×10^{-8}	1.20×10^{-15}	
Iodic acid	$(COOH)_2$	1.67×10^{-8}		
Oxalic acid	H_3PO_4	5.02×10^{-2}	5.18×10^{-5}	
Phosphoric acid	H_2SO_4	7.50×10^{-3}	6.20×10^{-8}	4.20×10^{-13}
Sulphuric acid		Strong		

4.7.2 Dissociation of a Weak Base:

Representing the formula of a weak monoacid base as BOH, its dissociation, in accordance with Arrhenius concept, may be represented by the equation
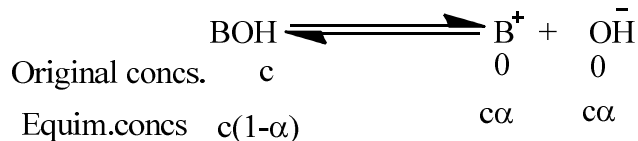
$$BOH \rightleftharpoons B^+ + OH^-$$

Applying the equilibrium law equation, the dissociation constant, K_b, of the base, will be given by

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \text{......... (i)}$$

Assuming that the activity coefficient of the of various species involved are equal to unity each.

If the initial concentration of the base is c moles per liter and if α is the degree of dissociation, then,

$$BOH \rightleftharpoons B^+ + OH^-$$

Original concs.   c   0   0

Equim.concs $c(1-\alpha)$ $c\alpha$ $c\alpha$

$$\therefore \quad K_b = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)} \qquad \text{......... (ii)}$$

Since, for a weak base, α is very small as compared to 1, equation (ii) as before, is reduced to:

$$K_b = c\alpha^2$$

$$or \qquad \alpha = \sqrt{K_b/c}$$

$$\therefore \qquad [OH^-] = c\alpha = c\sqrt{K_b/c} = \sqrt{cK_b} \qquad \dots\dots\dots (iii)$$

The dissociation constants of some common weak bases are given in the table 4.4:

Table 4.4 Dissociation constants of some common Bases at 25^0C

Base	Formula	K_b
Ammonia	NH_4OH	1.81×10^{-5}
Aniline	$C_6H_5NH_2$	3.83×10^{-10}
Dimethyl amine	$(CH_3)_2NH$	5.12×10^{-4}
Ethyl amine	$C_2H_5NH_2$	5.60×10^{-4}
Hydrazine	NH_2NH_2	3.00×10^{-6}

4.8 pH SCALE EXACT TREATMENT OF CALCULATION OF H^+ IONS AND PH FOR HA AND BOH

Knowledge of the concentration of hydrogen ions is one of the greatest importances in chemistry. Hydrogen ion concentrations are typically quite small numbers. Therefore, chemists report the hydrogen ion concentration of solution in terms of pH. It is defined as **the negative of base-10 logarithm (log) of the H^+ ion concentration.** Mathematically it can be expressed as

$$pH = -\log[H^+]$$

Where $[H^+]$ is the concentration of hydrogen ions in moles per litre

Alternative and more useful forms of pH definition are:

$$pH = log\frac{1}{[H^+]}$$

For pure water or neutral solution in which

$$[H^+] = 1 \times 10^{-7} moldm^{-3}$$

$$pH = -log[H^+] = -log(1 \times 10^{-7}) = 7 \text{ at } 25^0C$$

Some other Logarithmic Expressions. Just as pH is used to indicate hydrogen ion concentration, pOH is used to indicate hydroxyl ion (OH^-) concentration. Thus,

$$pH = -log[OH^-] \qquad \ldots\ldots\ldots (i)$$

Ionic product of water, K_w. Is also frequently expressed ina similar manner as

$$pK_w = -logK_w \qquad \ldots\ldots\ldots (ii)$$

Remembering that $[H^+][[OH^-] = K_w$ and taking logs and reversing signs, we have

$$-log[H^+] - log[OH^-] = -logK_w$$

$$\text{or} \quad pH + pOH = pK_w \qquad \ldots\ldots\ldots (iii)$$

This relationship holds well for water as well as for any aqueous solution.

Since K_w at 25^0C is about 10^{-14}, pK_w is is 14.0. Hence,

$$pH + pOH = 14 \qquad \ldots\ldots\ldots (iv)$$

In other words, the sum of pH and pOH is equal to 14 in water or in any aqueous solution at 25^0C.

In pure water, as already stated, a hydrogen ion concentration is equal to hydroxyl ion concentration and each is equal to 10^{-7} moles per liter. Water is, therefore, neutral and its pH is 7. If water is made acidic, its hydrogen ion concentration will increase to a value above 10^{-7} and, therefore, pH will fall below 7. On the other hand, if water is made basic, its hydrogen ion concentration will decrease to a value less than 10^{-7} and, therefore, pH will rise above 7. Thus,

if pH of solution is 7, it is neutral. If pH is less than 7, the solution is acidic and if it is more than 7, the solution is basic.

4.9 HYDROLYSIS

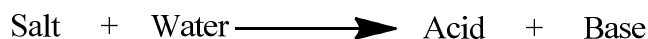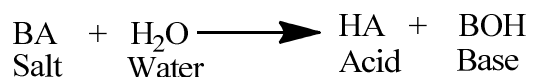The reaction of an anion or cation with water accompanied by cleavage of O-H bond is called hydrolysis.

$$A^- + \text{H-O-H} \rightleftharpoons \text{H-A} + \bar{O}\text{-H} \quad ....(i)$$

$$B^+ + \text{H-O-H} \rightleftharpoons \text{BOH} + H^+ \quad ....(ii)$$

The term hydrolysis is derived from hydro, meaning water, and lysis, means breaking. It may be noted that in anionic hydrolysis shown in (i) the solution becomes slightly basic (pH>7) due to generation of OH$^-$ ions. In cationic hydrolysis shown in (ii) there is excess of H$^+$ions which makes the solution slightly acidic (pH<7).

4.9.1 Salt Hydrolysis:

Salt hydrolysis is defined as the process in which a salt reacts with water to give back the acid and the base.

$$\text{Salt} + \text{Water} \longrightarrow \text{Acid} + \text{Base}$$

Or

$$\underset{\text{Salt}}{\text{BA}} + \underset{\text{Water}}{\text{H}_2\text{O}} \longrightarrow \underset{\text{Acid}}{\text{HA}} + \underset{\text{Base}}{\text{BOH}}$$
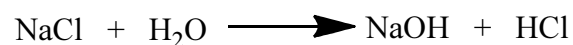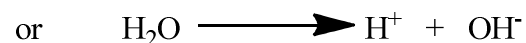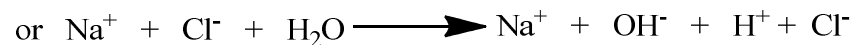
Depending upon the relative strengths of the acid and the base produced, the resulting solution is acidic, basic or neutral.   On this basis, the salts are divided into four categories:

I. Salts of Strong acids and Strong bases:

NaCl, NaNO$_3$, Na$_2$SO$_4$, KCl

As an illustration, let us discuss the hydrolysis of NaCl. We may write:

$$\text{NaCl} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{HCl}$$

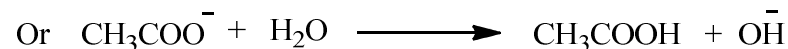or $Na^+ + Cl^- + H_2O \longrightarrow Na^+ + OH^- + H^+ + Cl^-$

or $H_2O \longrightarrow H^+ + OH^-$
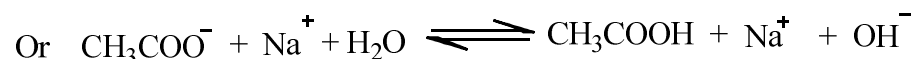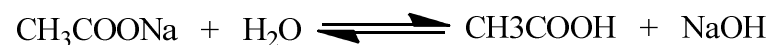
Thus it involves only ionization and no hydrolysis. Further in the resulting solution, $[H^+]$ = $[OH^-]$. So the solution is neutral. Hence it can be generalized that the salts of strong acids and strong bases do not undergo hydrolysis and the resulting solution is neutral.

II. Salts of Weak acids and Strong bases:

Examples are:

CH_3COONa, Na_2CO_3, $NaCN$, K_2CO_3 etc.
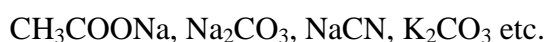
As an illustration, the hydrolysis of sodium acetate ($CH3COONa$) may be represented as follows:

$CH_3COONa + H_2O \rightleftharpoons CH3COOH + NaOH$

Or $CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

Or $CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$

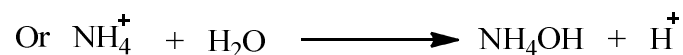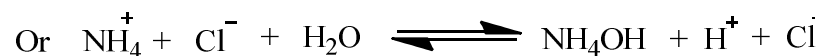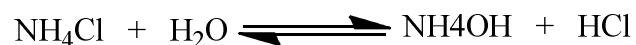As it produces OH^- ions, the solution of such a salt is alkaline in nature.

III. Salts of Strong acids and Weak bases:

Examples are:

NH_4Cl, $CuSO_4$, NH_4NO_3, $AlCl_3$, $CaCl_2$ etc.

As an illustration, the hydrolysis of NH_4Cl may be represented as followes:

$NH_4Cl + H_2O \rightleftharpoons NH4OH + HCl$

Or $NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$
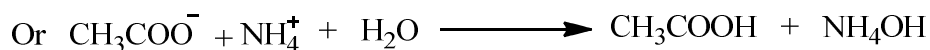
Or $NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$

As it produces H^+ ions, the solution of such a salt is acidic in character.

IV. Salts of Weak acids and Weak bases:

Examples are:

CH_3COONH_4, $(NH_4)_2CO_3$, $AlPO_4$ etc.

As an illustration, the hydrolysis of CH_3COONH_4 may be represented as follows:

$$CH_3COONH_4 \ + \ H_2O \rightleftharpoons \ CH_3COOH \ + \ NH_4OH$$

Or $\ CH_3COO^- + NH_4^+ \ + \ H_2O \longrightarrow \ CH_3COOH \ + \ NH_4OH$

Thus it involves both cationic and anionic hydrolysis. Hence the resulting solution is neutral.

4.9.2 Hydrolysis Constant:

The general equation for the hydrolysis of a salt (BA) may be written as

Applying the law of chemical equilibrium, we get

$$\frac{[HA][BOH]}{[BA][H_2O]} \ = \ K, \ \text{The equillibrium constant}$$
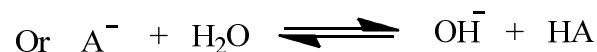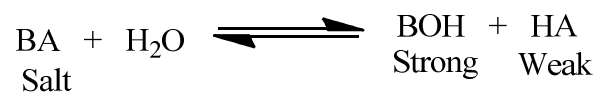
Since water is present in very large excess in aqueous solution, its concentration $[H_2O]$ may be regarded as constant so that we have

$$\frac{[HA][BOH]}{BA} \ = K[H_2O] = \ K_h$$

Where K_h is called the hydrolysis constant.

I .Hydrolysis constant of Salts of weak acid and Strong base:

Representing the salt by BA as usual, the hydrolysis may be represented as follows:

$$\underset{\text{Salt}}{BA} \ + \ H_2O \ \rightleftharpoons \ \underset{\text{Strong}}{BOH} \ + \ \underset{\text{Weak}}{HA}$$

Or $\ B^+ + \ A^- \ + \ H_2O \rightleftharpoons B^+ \ + \ OH^- \ + \ HA$

Or $\ A^- \ + \ H_2O \rightleftharpoons \ OH^- \ + \ HA$

i.e it is a case of anion hydrolysis.

The hydrolysis constant K_h for the above reaction will be given by

$$K_h = \frac{[OH^-][HA]}{[A^-]} \quad\quad\quad \dots\dots\dots (i)$$

For the weak acid HA, the dissociation equilibrium is

$$HA \rightleftharpoons H^+ + A^-$$

∴ The dissociation constant K_a of the acid HA will be given by

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad\quad\quad \dots\dots\dots (ii)$$
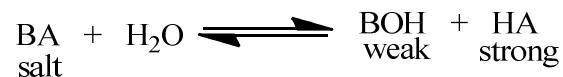
Further the ionic product of water K_w is given by

$$K_w = [H^+][OH^-] \quad\quad \dots\dots\dots\dots (iii)$$

Multiplying eq (i) with (ii) and dividing by (iii), we get

$$K_h = \frac{K_w}{K_a} \quad\quad\quad \dots\dots\dots (iv)$$

II. Hydrolysis constant of Salts of Strong acid and Weak base:

For the salt BA, the hydrolysis may be represented as

$$\underset{\text{salt}}{BA} + H_2O \rightleftharpoons \underset{\text{weak}}{BOH} + \underset{\text{strong}}{HA}$$

i.e it is case of cation hydrolysis.

The hydrolysis constant K_h for the above reaction will be given by

$$K_h = \frac{[BOH][H^+]}{[B^+]} \quad\quad\quad \dots\dots\dots (i)$$

For the weak base BOH, the dissociation equilibrium is

$$BOH \rightleftharpoons B^+ + OH^-$$

∴ The dissociation constant will be given by

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad\quad\quad \dots\dots\dots (ii)$$

Ionic product of water,

$$K_w = [H^+][OH^-] \qquad \qquad \text{........ (iii)}$$

Multiplying eq (i) with (ii) and dividing by (iii), we get

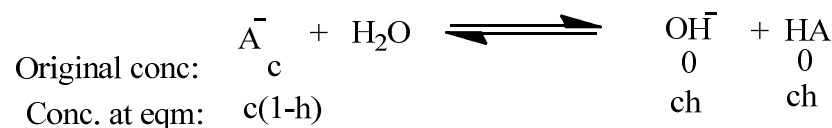$$K_h = \frac{K_w}{K_b} \qquad \qquad \text{.......... (iv)}$$

III. Hydrolysis constant of Salts of Weak acid and Weak base:

$$K_h = \frac{K_w}{K_a K_b} \qquad \qquad \text{......... (i)}$$

4.9.3 pH calculation:

I. pH of Salt of weak acid and strong base:

In this case we have

$$A^- \; + \; H_2O \; \rightleftharpoons \; OH^- \; + \; HA$$

Original conc: c   0   0

Conc. at eqm: c(1-h)   ch   ch

i.e, $[OH^-] = ch$

$$H^+ = \frac{K_w}{[OH^-]} = \frac{K_w}{ch}$$

$$[H^+] = \frac{K_w}{c}\sqrt{\frac{K_a \cdot c}{K_w}}$$

$$or \; [H^+] = \sqrt{\frac{K_w \cdot K_a}{c}}$$

$$pH = -log[H^+] = -log\sqrt{\frac{K_w \cdot K_a}{c}}$$

$$= log \left(\frac{K_w \cdot K_a}{c}\right)^{1/2}$$

$$or \ pH = -\frac{1}{2}[logK_w + logK_a - logc]$$

Thus knowing the molar concentration c of the solution and the dissociation constant K_a of the weak acid involved, the pH of the solution can be calculated.

II. pH of the Salt of weak acid and strong base:

$$pH = -\frac{1}{2}[logK_w - logK_b + logc]$$

III. pH of the Salt of weak acid and weak base:

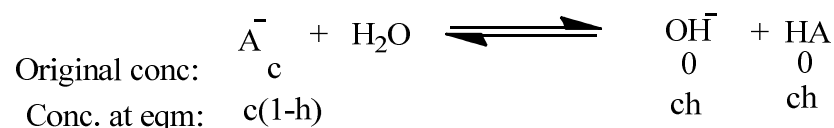$$pH = -\frac{1}{2}[logK_a + logK_w - logK_b]$$

4.9.4. Degree of hydrolysis:

The degree of hydrolysis of a salt is defined as the fraction (or percentage) of the total salt which is hydrolysed.

i.e

$$h = \frac{No.\ of\ moles\ of\ the\ salt\ hydrolysed}{Total\ no.\ of\ moles\ of\ the\ salt\ taken}$$

I. Degree of Hydrolysis of the salts of weak acid and strong base.

Suppose the original concentration of the salt in the solution is c moles/litre and h is the degree of hydrolysis at this concentration. Then we have

$$\begin{array}{ccccccc}
& A^- & + & H_2O & \rightleftharpoons & OH^- & + & HA \\
\text{Original conc:} & c & & & & 0 & & 0 \\
\text{Conc. at eqm:} & c(1-h) & & & & ch & & ch \\
\end{array}$$

The hydrolysis constant (K_h) will, therefore, be given by

$$K_h = \frac{[OH^-][HA]}{[A^-]} = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{1-h}$$

If h is very small as compared to 1, we can take 1-h=1 so that above expression becomes

$$ch^2 = K_h \ or \ h^2 = \frac{K_h}{c}$$

$$h = \sqrt{\frac{K_h}{c}}$$

Substituting the value of K_a, we get,

$$h = \sqrt{\frac{K_w}{K_a . c}}$$

II. Degree of Hydrolysis of the salts of strong acid and weak base:

$$h = \sqrt{\frac{K_w}{K_b . c}}$$

III. Degree of Hydrolysis of the salts of weak acid and weak base:

$$h = \sqrt{\frac{K_w}{K_a . K_b}}$$

4.10. TITRATIONS ACID BASE TITRATION CURVE

Titration is measurement of the volume of a solution of one reactant that is required to react completely with a measured amount of another reactant. Usually the concentration of one of the solution is known (called standard solution) and it is desired to find the concentration of other by titration. The apparatus used is shown in fig. 4.1. A known volume of the solution is taken in the titration flask and the other solution is taken in the burette. The point at which the required volume of one solution has been added to the other to exactly complete the reaction between the two is called **end point** or **equivalence point**.

The process of acid-base titrations is accompanied by a change in pH. A plot between pH of the solution during titration and the amount of acid (or base) added from burette is called a **titration curve.**

Indicators are frequently employed in detecting end points in acid-base titrations. Since, on account of hydrolysis, the pH at the end point depends on the relative strengths of tha acid and the base being titrated and since different indicators have different pH ranges within which they can be used. The pH changes occurring in some acid-base titrations may be first considered.

Titrating a Strong acid with a Strong base:

Fig (a) depicts the titration curve when NaOH is added gradually to HCl. It shows that the pH of the titration solution rises extremely slowly in the beginning. In the vicinity of equivalence point, the pH rises dramatically and the curve becomes vertical. Beyond this, the curve becomes almost flat that shows a slight rise of pH when only excess base is present in the titration solution.

The vertical portion of the curve extends from pH 3 to pH 7. The pH range of methyl orange (3.1-4.4) and phenolphthalein (8.30-10.0) are fairly narrow and fall on the vertical curve. Thus both the methyl orange and phenolphthalein are suitable indicators for strong acid/strong base titrations

Titrating a Weak acid with a Strong base:

Figure (b) represents the titration curve when NaOH (strong base) is added to CH_3COOH (weak acid). The pH curve rises slowly in the beginning but near the equivalence point, the pH changes abruptly from 6 to 11 and the curve becomes vertical. Beyond this the shape of the titration curve is similar to that for strong acid/strong base.

Phenolphthalein has pH range 8.3 to 10.0 that falls on the vertical part of the titration curve as marked in the figure.

Titrating a Strong acid with a Weak base:

The titration curve for HCl (strong acid) NH_4OH (weak base) is shown in fig.(c). As NH_4OH is added, the pH of the titration solution increases gradually. Around the equivalence point, a sharp rise in pH occurs approximately from 3 to 8, when the curve becomes vertical. The pH range of methyl orange (3.1-4.4) falls on the vertical portion of the titration curve.

Titrating a Weak acid with a Weak base:

The titration curve for CH₃COOH (strong acid) NH₄OH (weak base) is shown in fig.(d). The pH of the titration solution rises gradually and there is no sharp change in pH around the equivalence point. The vertical portion is missing in the titration curve. Under these condition, all indicators change colour only gradually and no indicator is suitable.
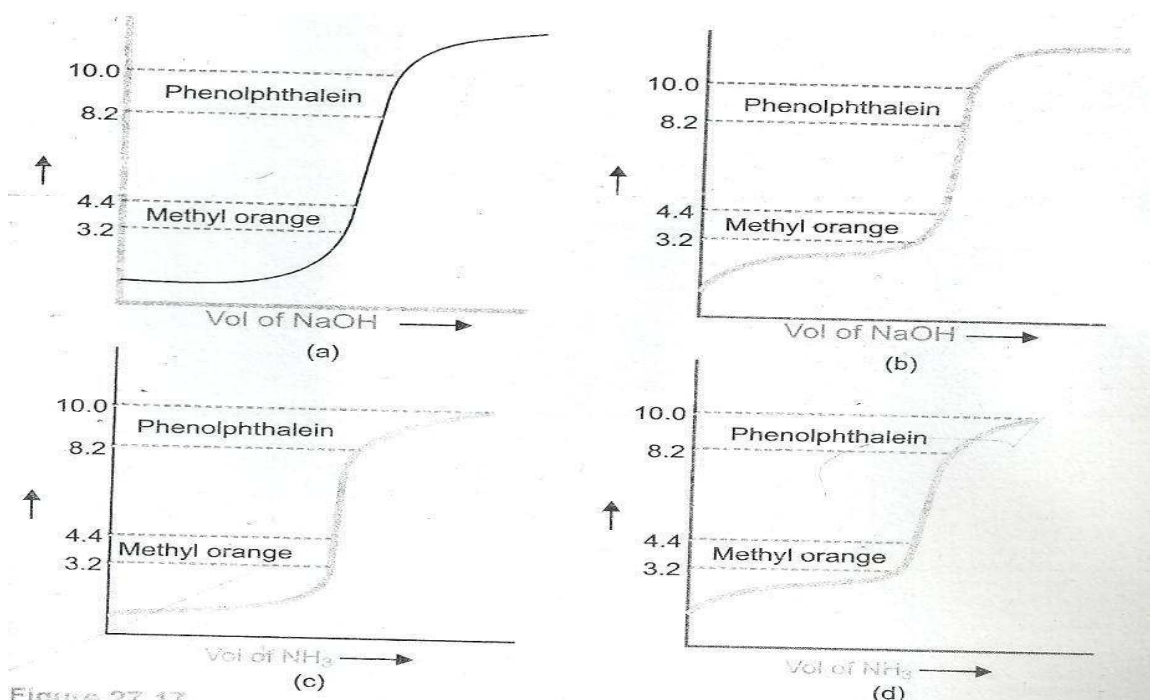
Fig.4.1 To find a suitable indicator from a study of the pH curve for:

(a) **A strong acid and strong base;**   (b) **weak acid and strong base;**

(c) **A Strong acid and weak base;**   (d) **a weak acid and weak base.**

4.11 BUFFER SOLUTION

For many purposes in chemistry, industry and biology, it is necessary to have solutions whose pH does not change much even on the addition of appreciable amounts of strong acids and strong alkalies. Such solutions are called buffer solutions.

A buffer solution is one which can resist change in its pH on the addition of an acid or a base.

Types of Buffer solutions: There are two types of buffer solutions. These are:

(i) Solutions of single substances. The solution of the salt of weak acid and a weak base e.g. ammonium acetate (CH_3COONH_4) acts as a buffer.

(ii) Solutions of Mixtures. These are further of two types:

(a) Acidic Buffer. It is the solution of a mixture of a weak acid and a salt of this weak acid with strong base (e.g. $CH_3COOH + CH_3COONa$).

(b) Basic Buffer. It is the solution of a mixture of a weak base and a salt of this weak base with strong acid (e.g. $NH_4OH + NH_4Cl$).

Buffer action:

The property of a buffer solution to resist any changes in its pH value even when small amounts of the acid or the base are added to it is called Buffer action.

Buffer Action of Acidic Buffer: Let us, for example, consider the buffer action of acidic buffer containing CH_3COOH and CH_3COONa. Acetic acid dissociates to a small extent whereas sodium acetate is almost completely dissociated in the aqueous solution as follows:

$$CH_3COOH \ + \ H_2O \ \rightleftharpoons \ CH_3COO^- \ + H_3O^+$$

$$CH_3COONa \longrightarrow CH_3COO^- \ + Na^+$$
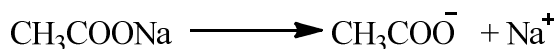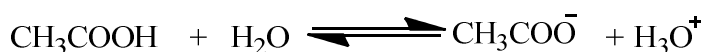
By 'common ion effect' the ionization of CH_3COOH is further suppressed. Thus in the solution, there are excess of acetate (CH_3COO^-) and small amount of H^+ ions.

When a few drops of an acid are added to the above mixture solution, the H^+ ions given by the acid combine with the CH_3COO^- ions to form weakly ionized molecules of CH_3COOH.

$$CH_3COO^- + \ H^+ \longrightarrow CH_3COOH$$
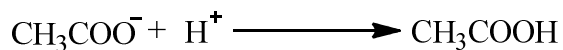
Thus the H^+ ion concentration and hence the pH of the solution remains almost constant.

Similarly, when few drops of a base are added, the OH^- ions given by the base combine with the H^+ ions already present to form weakly ionized molecules of H_2O.

$$H^+ \ + \ OH^- \longrightarrow H_2O$$
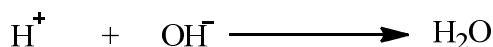
As the H^+ ions are consumed, the equilibrium shifts towards right. Thus more of CH_3COOH dissociates to make up the loss of H^+ ions. Hence the H^+ ion concentration or the pH of the solution does not change.

Buffer action of Basic Buffer:

A mixture containing equimolar solutions of ammonium hydroxide (NH_4OH) and its almost completely dissociated salt, ammonium chloride (NH_4Cl), constitutes another good buffer. The mixture contains undissociated NH_4OH as well as NH_4^+ and Cl^- ions. The buffer action of this mixture may now be considered.

If a strong acid is added, the H^+ ions added are neutralized by the base NH_4OH:

$$H^+ + NH_4OH \longrightarrow H_2O + NH_4^+$$
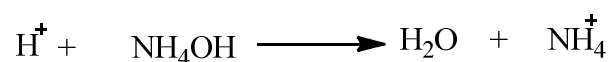
If a strong base is added, the OH^- ions added are neutralized by NH_4^+ ions forming very slightly dissociated NH_4OH.

In this case, evidently reserve acidity is due to the presence of NH_4^+ ions and reserve alkalinity is due to the presence of NH_4OH.

4.12 BUFFER CAPACITY

It is defined as the number of moles of an acid or a base required to be added to one litre of the buffer solution so as to change its pH by one unit. Thus

$$\text{Buffer capacity}(\beta) = \frac{\text{No. of moles of the acid or base added to 1 litre of the buffer}}{\text{Change in pH}} = \frac{n}{\Delta pH}$$

4.13. HENDERSON EQUATION

Consider first a buffer solution containing a weak acid HA and its highly dissociated salt NaA. The hydrogen ion concentration of such a solution is given by the equation

$$[H^+] = K_a [salt]/[acid]$$

Taking logs and reversing the sign, we have

$$-\log[H^+] = -\log K_a + \log [salt]/[acid]$$

or $\quad pH = pK_a + log\,[\text{salt}]/[\text{acid}]$

This equation, known as Henderson's equation, enables the calculation of pH of a buffer solution made by mixing known quantities of a weak acid and its salt.

4.14. SOLUBILITY AND SOLUBILITY PRODUCT

When an ionic substance dissolves in water, it dissociated to give separate cations and anions. As the concentrations of the ions in solution increases, they collide and reform the solid phase. Ultimately, a dynamic equilibrium is established between the solid phases. Ultimately, dyanamic equilibrium is established between the solid phase and the cations and anions in solution. For example, for a sparingly soluble salt, say AgCl, we can write the equilibrium equations as follows:

$$\text{AgCl}\underset{\text{Solid}}{\rightleftharpoons} \text{Ag}^+ + \text{Cl}^-$$

At equilibrium the solute continues to dissolve at a rate that exactly matches the reverse process, the return of solute from the solution. Now the solution is said to be saturated.

A saturated solution is a solution in which the dissolved and undissolved solute is in equilibrium. The solubility (S) of a substance in a solvent is the concentration in the saturated solution. Solubility of solute may be represented in grams per 100ml of solution. It can also be expressed in moles per liter.

Molar solubility is defined as the number of moles of substance per liter of the solution. The value of solubility of a substance depends on the solvent and temperature.

Applying Law of mass action to the above equilibrium for AgCl, we have

$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

The amount of AgCl in contact with saturated solution does not change with time and the factor (AgCl) remains the same. The equilibrium expression becomes

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

Where $[Ag^+]$ and $[Cl^-]$ are expressed in mol/L. The equilibrium constant in the new context is called the Solubility Product Constant and is denoted by K_{sp}. The value of K_{sp} for particular solubility equilibrium is constant at a given temperature. The product $[Ag^+][Cl^-]$ is also called the Ionic Product or Ion product.

TABLE 4.5 Solubility product values for some sparingly soluble salts

Substance	K_{sp} at 25^0C
PbS	3.4×10^{-28}
CdS	3.6×10^{-28}
Fe(OH)$_3$	1.1×10^{-38}
Al(OH)$_3$	8.5×10^{-32}
Mg(OH)$_2$	1.4×10^{-11}
CaCO$_3$	4.8×10^{-9}
PbI$_2$	1.39×10^{-8}

The K_{sp} may be stated as: the product of the concentration of ions in the saturated solution at a given temperature is constant. This is sometimes called the solubility product principle.

4.15. INDICATORS

The substance usually added into the solution taken in the titration flask to detect the equivalence point is called an indicator.

Table 4.6 Common acid-base indicators and their colour changes.

Indicator	pH-range	Acidic colour	Basic colour

Methyl violet	0-2	Yellow	Violet
Methyl yellow	1.2-2.3	Red	Yellow
Methyl orange	3.1-4.4	Red	Yellow
Methyl red	4.2-6.3	Red	Yellow
Litmus	4.5-8.3	Red	Blue
Phenol red	6.4-8.2	Yellow	Red
Cresol red	7.2-8.8	Yellow	Red
Thymol blue	8.0-9.6	Yellow	Blue
Phenolphthalein	8.3-10.0	Colourless	Red
Alizarin yellow	10.1-12.0	Yellow	Violet
Trinirobenzene	12.0-14.0	Colourless	Orange

4.16. COMMON ION EFFECT AND THE SOLUBILITY OF A SPARINGLY SOLUBLE SALT

The common ion effect states that in a chemical solution, if the concentration of any one of the ions is increased, then, according to Le Chatelier's principle, some of the ions in excess should be removed from solution, by combining with the oppositely charged ions. Some of the salt will be precipitated until the ion product is equal to the solubility product. In short, the common ion effect is the suppression of the degree of dissociation of a weak electrolyte containing a common ion.

Solubility effects:

The solubility of a sparingly soluble salt is reduced in a solution that contains an ion in common with that salt. For instance, the solubility of silver chloride in water is reduced if a solution of sodium chloride is added to a suspension of silver chloride in water.

A practical example used very widely in areas drawing drinking water from chalk or limestone aquifers is the addition of sodium carbonate to the raw water to reduce the hardness of the water. In the water treatment process, highly soluble sodium carbonate salt is added to precipitate out sparingly soluble calcium carbonate. The very pure and finely divided precipitate of calcium carbonate that is generated is a valuable by-product used in the manufacture of toothpaste.

The salting out process used in the manufacture of soaps benefits from the common ion effect. Soaps are sodium salts of fatty acids. Addition of sodium chloride reduces the solubility of the soap salts. The soaps precipitate due to a combination of common ion effect and increased ionic strength.

Sea, brackish and other waters that contain appreciable amount of Na+ interfere with the normal behavior of soap because of common ion effect. In the presence of excess sodium ions the solubility of soap salts is reduced, making the soap less effective.

4.17. SUMMARY

- Equilibrium involving ions in aqueous solution is called ionic equilibrium.
- An electrolyte is defined as a compound whose aqueous solution or melt conducts electricity. On the other hand, a compound whose aqueous solution or melt does not conduct electricity is called a non electrolyte
- The fraction of the total number of molecules which dissociate into ions is called the degree of dissociation and is usually represented by α.

$$i.e. \quad \alpha = \frac{Numer\ of\ moles\ dissociated}{Total\ number\ of\ moles\ taken}$$

- **Strong Electrolytes**: these are the substances which dissociate almost completely into ions in aqueous solution and hence are a very good conductor of electricity. Examples are: $NaOH$, KOH, H_2SO_4, $NaCl$, KNO_3 etc
- **Weak Electrolytes**: These are the substances which dissociate to a small extent in aqueous solution and hence conduct electricity also to a small extent. Examples are: NH_4OH, CH_3COOH etc.
- According to Arrhenius concept an acid is compound that releases H^+ ions in water; and a base is a compound that releases OH^- ions in water.

Examples: HCl, HNO_3, H_2SO_4, KOH, NaOH etc.

- According to Bronsted and Lowery an acid is a proton-donor and a base is a proton-acceptor.

- According to Lewis theory, an acid is an electron pair acceptor while a base is electron pair donor.

- Ionic product of water may be defined as the product of the molar concentration of H^+ and OH^- ions. $K_w = [H^+][OH^-]$ The value of K_w at 298K (25^0 C) is usually taken as $K_w = 1.00 \times 10^{-14}$.

- The reduction of the degree of dissociation of a salt by the addition of a common ion is called the common ion effect.

- pH is defined as **the negative of base-10 logarithm (log) of the H^+ ion concentration. .** Mathematically it can be expressed as $pH = -\log[H^+]$.

- $pH + pOH = 14$

- The reaction of an anion or cation with water accompanied by cleavage of O-H bond is called hydrolysis

- Salt hydrolysis is defined as the process in which a salt reacts with water to give back the acid and the base.

- Titration is measurement of the volume of a solution of one reactant that is required to react completely with a measured amount of another reactant.

- A plot between pH of the solution during titration and the amount of acid (or base) added from burette is called a **titration curve.**

- A buffer solution is one which can resist change in its pH on the addition of an acid or a base.

- The property of a buffer solution to resist any changes in its pH value even when small amounts of the acid or the base are added to it is called Buffer action.

- Buffer capacity is defined as the number of moles of an acid or a base required to be added to one liter of the buffer solution so as to change its pH by one unit.

- Molar solubility is defined as the number of moles of substance per liter of the solution.

- The substance usually added into the solution taken in the titration flask to detect the equivalence point is called an indicator.

4.18. TERMINAL QUESTIONS

A. Objective Types Questions:

1. The p^H of an aqueous solution is 4 its $[OH^-]$ is

    a. 10   b. 10^{-4} c. 10^{-10} d. 3

2. The solubility product of sparingly soluble salt at room temperature is 4.0×10^{-6} M^2. its molar solubility is :

    a. 4.0×10^{-6} M   b. 4.0×10^{-3} M   c. 4.0×10^{-6} M^2 d $^.$ $^2.0 \times 10^{-3}$ M^2

3. A buffer solution is one which can resist change in its

    a. p^H b. Concentration   c. Ionization   d. Concentration of salt

4. Ka of weak acid HB is 10-5 the pKb of the conjugate base B^- is a

    a. 2   b. 9   c. 5   d. 7

B. Short Answer Questions

(1) Define the following terms

(a) Ostwald's dilution law   (b) Degree of dissociation

(c) Common ion effect   (d) Solubility equilibria

(e) Solubility product.

(2) What is the Henderson equation?

(3) Define and explain ionic product of water

(4) Explain any two applications of common ion effect.

(5) Define or explain the following terms

(a) Arrhenius acids   (b) Arrhenius bases   (c) Bronsted acids   (d) Bronsted bases   (e) Lewis acids

(f) Lewis bases   (g) pH of solutions   (h) Buffer solution

(6) What are strong and weak electrolytes?

(7) What are conjugate acid-base pairs? Give two examples

(8) What are buffers and how is their capacity measured?

C. Long Answer Type Questions

(9) Define or explain the following terms

(a) Salt hydrolysis   (b) Hydrolysis constant   (c) Degree of hydrolysis.

(10) Derive the relation between hydrolysis constant ionic product of water and dissociation constant of a strong acid and a weak base.

(11) Deduce an expression for the degree of hydrolysis of a salt of a weak acid and a strong base.

(12) calculate the pH of (a) 0.0001M HCl solution (b) 0.04M HNO_3 solution, assuming complete dissociation in each cases.

(13) Calculate the hydrogen ion concentration in moles per litre of a solution whose pH is 5.4

(14) Calculate the pH and pOH of a solution containing hydrogen ion concentration $3.0 \times 10^{-3} mol dm^{-3}$ at 25^0C.

1.19 ANSWER

1. c   2. b   3. a   4.c

Source of study material:

4. Essential of physical chemistry by Bahl, Bahl and Tuli.
5. Principles of physical chemistry By Puri, Sharma and Pathania.
6. Physical chemistry By   P.C. Rakshit.
7. Physical chemistry By Atkins.
8. Mannam Krishnamurthy; Subba Rao Naidu (2012). "8". In Lokeswara Gupta. Chemistry for ISEET - Volume 1, Part A (2012 ed.). Hyderabad, India: Varsity Education Management Limited. p. 298.

UNIT: 5 PHASE EQUILIBRIUM-I

CONTENTS:

5.1 OBJECTIVES

A system consists of parts which have different physical properties (sometime different chemical properties) and which are separated by boundaries, the system is said to be

heterogeneous. The equilibrium between different parts or phases usually explained by four principles.

    i.   Nerest distribution law.

    ii. Law of mass action.

    iii. Clapyron equation

    iv. Phase Rule

5.2 INTRODUCTION

Phase Equilibrium is an important tool of the quantitative treatment of heterogeneous system in equilibrium. The No. of phase that can exist in equilibrium depends upon the condition of temp, pressure and concentration of different phases.

The phase rule can't be express in words. In a hetero generous system at equilibrium, the sum of the number of degree of freedom and the number of phases is equal to the number of components plus two. Mathematically it defined as,

F=C-P+2 Where C = Component, P= No. of Phases, F= No. of degree of Freedom.

5.3 STATEMENT AND MEANING OF THE TERM

5.3.1 Phases:

It is defined as homogeneous part of a system which is physically and chemically different from other part also it is mechanically separable from other part of the system.Completely miscible gas and liquids form a singles phase while immiscible system give different phases i.e., solid + Liquid, solid +gas, have two component. Phases are denoted by P.

5.3.2 Components:

The number of components of a system at equilibrium, the minimum number of independent variable constitutions (chemical species) which are required to express quantitavely the composition of each and every phase either directly or in terms of chemical equation is called components or denoted by C. In the chemical equation negative and zero signs being permitted.

Example: (i) Water system consist of the equilibrium.

Ice= Water = Vapour

(Solid) (Liquid)(Gasecus)

This system consists of one component only, i.e., it is a one component system because the composition of each of the three phases present can be directly expressed as H_2O

(ii) Sulphur system consisting of four phases- Monoclinic (s), Rhombic(s), Liquid (L) and vapors(g) is also one component system because the composition of each phase can be expressed in term of one constituent sulphur.

the no. of component is calculate by

C=S-E-R

Where S= Total No. of constituents or species

E= No. of equation representing equilibrium between the constituents

R= No. of restrictions for electrical neutrality.

Example:

Na_2SO_4-H_2O

    (a) Assuming no dissociation

        S=2

        E=0(No chemical reaction/equilibrium)

        R=0(No. restriction of electrical neutrality or material balance

        C=S-E-R=2-0-0=2 Thus no. of components=2

    (b) Assuming complete dissociation of the salt.

        S=3(Na^+, SO_4^{2-} and H_2O)

        E=0

        R=1(For electrical neutrality, $2Na^+= SO_4^{2-}$)

        C=S-E-R=3-0-1=2, Thus no. of components=2

    (c) Assuming dissociation of *H_2O* also.

        S=6(Na_2SO_4, Na^+, SO_4^{--}, H_2O, H^+, OH^-)

        E=2(Na_2SO_4 -=>$2Na^+$+SO_4^{--} and H_2O=> H^+ +OH^-)

        R=2($2Na^+=SO_4^{2-}$ i.e. number of moles of Na^+ 2 X No. of moles of SO_4^{2-} and $H^+= OH^-$)

C=S-E-R=6-2-2=2 Thus no. of components=2

5.3.3 Degree of Freedom:

It is defined as the no. of independent variables such as temperature, pressure and concentration which must be specified in order to define the system completely. It is denoted by F Greater the no. of component C, greater the degree of freedom F.

Greater the No. of phases P, smaller the number of degree of freedom F. Degree of freedom as also known as variance.

5.4 DERIVATION OF GIBBS PHASE RULE

Consider a heterogeneous system in equilibrium consisting of C "components distributed in P phase, The Degree of freedom of the system are equal to the number of independent variable which must be fixed arbitrarily to define the system completely. The number of such variable is equal to the total number of variable minus the number of variable which are defined automatically by virtue of the system being in equilibrium.

At equilibrium, each phase has the same temperature and pressure, so lbere is one temperature variable and one pressure variable for the whole system. So, these variables total two only. The number of composition (or concentration) variables, however, is much more. In order to define the composition of each phase, it is necessary to mention(C-I) composition variables, because the composition of the remaining component may be obtained by difference. For P phases, thus, the total number of concentration or composition variables will be P(C-1).

 Total number of variables

= P(C-1) for composition   +   1 for temperature   +   1 for pressure

According to thermodynamics as derived in equation (3) (cf. 12.5), when a heterogeneous system is in equilibrium, at constant pressure and temperature, the chemical potential (μ.) of any given component must be the same in every phase. Therefore, if there is one component in three phases x, y and z and one of these phases, say x is referred to as standard phase, then this fact may be represented in the form of two equations:

So, for each component in equilibrium in three phases, two equations are known. In general, therefore, for each component in P phases, (P-1) equations are known. For C components, thus the number of equations or variables that are known from the conditions of equilibrium are C (P-1).

Since chemical potential is a function of pressure, temperature and concentration, it means that each equation represents one variable.

Therefore, the number of unknown variables (which should be fixed) or degree of freedom,

F= number of variable- number of equations

F=[P(C-1+2]-[C(P-I)] or F=C-P+2,................5.1

This equation is the phase rule of Gibbs.

5.5 PHASE EQUILIBRIUM

A System is in equilibrium is the properties like temperature, composition etc. of the various phases do not undergo any change with time.

It is of two type.

 (i) True equilibrium   (ii) metastable equilibrium

(i) True Equilibrium : It defined as:

If the same state can be achieved by approach from either direction. For example, the equilibrium between ice and water at I atm. Pressure and 0 ^{0}C is a true equilibrium, because it can attained by melting of ice or by freezing of water.

(ii) Metastable equilibrium:

If the state of a system can be attained only from one direction and that too by very careful change of conditions. it is called a state of metastabnle equilibrium. For example, water at 2 ^{0}C can be obtained only by very careful cooling of liquid water but not by melting of ice. Hence water at -2 ^{0}C is said to be in a state of metastable equilibrium.

5.5.1 Criteria for phase equilibrium:

There are three equlibria that exist in phase equilibria is a multi component system.

(i) **Thermal Equilibria:**

The temperature is every part of the system must be same as otherwise heat may flow from one part of the system to another.

Suppose a system consist of two phase A and B with temperature T_A and T_B respectively.

At equilibrium, let a small amount of heat dq. flows from phase A to phase B.

Then, Entropy change of phase A $(dS_A)= -\frac{dq}{TA}$

Entropy change of Phase B $(dS_B) = -\frac{dq}{TB}$

So, Total entropy change of system

$dS= -\frac{dq}{TA}$ + $\frac{dq}{TB}$

The condition for equilibrium is terms of entropy change is (dS)E.V.=.0

i.e.,- $\frac{dq}{TA}$ + $\frac{dq}{TB}$ =0 or $\frac{dq}{TA}$ + $\frac{dq}{TB}$ or TA =TB

(ii) Mechanic Equilibrium:

The equilibrium where the pressure in every part of the system must be same as otherwise matter may flow form one part of the system to another. In an as isolated system containing two phase in equilibrium at constant volume and temperature.

A small amount of matter flow from phase A to B so, that volume phase A decrease by small volume d_V and volume of phase B increase by small volume d_V.

The pressures of two phases are P_A and P_B respectively. So, change in Helmoltz free energy of phase A$(dA_A) = P_A$ dv

Change in Helmoltz free energy of phase B$(dA_B)= P_B dV$

But at equilibrium (dA)V.=0

$dA=dA_A+dA_B=-P_AdV+P_BdV=0$ or $P_A=P_B$

(iii) Chemical Equilibrium. At equilibrium, the chemical potential of any component in all the phases must be same. This is called **Thermodynamic criteria for phase equilibrium**. For a solution(or a phases containing a number of constituents, the chemical potential of any

component is the increase of decrease of free energy that takes place, at constant temperature and pressure, for the addition or removal of one mole of that component, keeping the amount of all other components constant it is usually represented by 'μ')

5.6 PHASE EQUILIBRIUM OF ONE COMPONENT SYSTEM

Some of the one component system and their phase diagram's can be given as:

a. Phase diagram of water system:

The system consists of three phases.

Ice (solid)   === Water (liquid) + Vapour (gas)

(s)   (i)   (g)

These three single phases may occur in four possible combinations in equilibrium as

  (i) Liquid === Vapour
  (ii) Solid   ==== Vapour
  (iii)Solid   ====Liquid
  (iv)Solid   ==== Liquid === Vapour

The number of phases that can exist in equilibrium at any point depends upon the conditions of temperature and pressure. These conditions have been determined experimentally and a phase diagram is constructed by plotting pressure against temperature (Fig 5.1). The phase diagram consists of:

  (i) Three stable curves OA, OB, OC and one metastable curve OA'
  (ii) Three areas and
  (iii)Definite point, O.

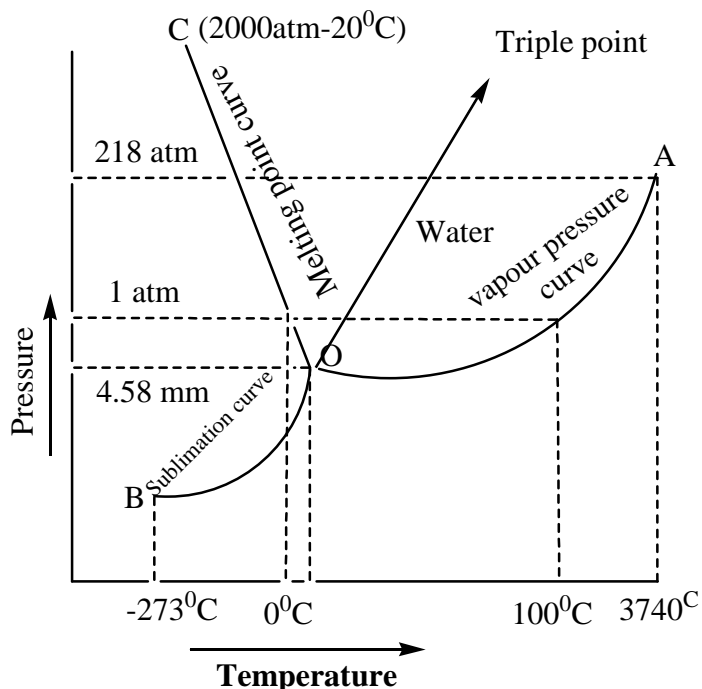   These are separately discussed as under:

Fig. 5.1 Water System

(i) Cureves (i) OA. This is vapour pressure curve of water. It represents the equilibrium between liquid water and vapour at different temperature. At any point on the curve, the two phases are present. The curve starts from the point O, the freezing point of water and ends at A, the critical temperature (374^0C) beyond which the two phases merge into each other. Consider any point on the curve. For a fixed value of pressure, temperature has also a fixed value. if by keeping the pressure constant, an attempt is made to raise the temperature then the liquid phase will disappear and if temperature is lowered then the vapour phase wil disappear, Thus, to define the system completely at any time, it is necessary to mention either temperature or pressure. In other words, pressure being fixed. Therefore, water-vapour system is univariant, or it has one degree of freedom. It also follows from the phase rule equation.

$F=C-P+2$

$F=1-2+2=1$

(ii) OA. The dotted curve OA: a continuation of curve OA represents the vapour pressure curve of super-cooled water. It is metastable curve. On being disturbed, the super cooled phase at once changes to solid ice and curve merges into OB.

(iii) OB. It is the sublimation curve or the vapour pressure curve of ice. It gives values of temperature and pressure at which ice and vapours can exist together. It is obtained by studying the effect of pressure on the freezing point of water. The curve starts from the point O, the freezing point of water and ends at B (-273^0C). As temperature decreases, the vapour pressure of ice tends to become negligible. We find that for a particular temperature, there can be one and only one pressure value and vice versa. In other words, ice- vapour system is univariant, or has one degree of freedom.

(iv)OC. It is melting point curve and represents the equilibrium between ice and liquid water at various pressures. In other words, It shows the effect of pressure on the melting point of ice. It should be noted that the line OC is inclined towards the pressure axis. The slope of the curve OC clearly indicates that melting point of ice is lowered by increase of pressure. There is, however, no limit for the curve OC. It goes up to a point corresponding to 2000 atmospheres and -20^0C. At this point, one type of ice changes into another solid modification but the solid-liquid equilibrium still remains.

At any point on the curve OC, two phases (ice and liquid water) are present in equilibrium. Hence the system is univariant, or degree of freedom is one.

(II) Areas: The areas, i.e., the regions bounded by two lines give the conditions of temperature and pressure under which the single phase i.e., ice or liquid water or vapour is capable of stable existence. Area below AOB has water vapour, are BOC has ice and area COA has liquid water. These areas are bivariant because to locate any point in the area, temperature as well as pressure must be fixed, thus indicating two degress of freedom. This also follows from phase rule equation.

$$F=C-P+2$$

$$F=1-1+2=2$$

(III) Triple point: It is a point where the three curves OA, OB, OC meet. At this point the three phases-ices, water and vapour are in equilibrium. It should be noted that it is only a point indicating that there is only one set of conditions under which it is possible for the three phases to exist together. The point O is a self-defined point corresponding to definite temperature of 0.0098^0C and a definite pressure of 4.58 mm. If either pressure or temperature is changed, then one of the three phases will disappear. Since on changing

either pressure or temperature one of the phases disappear, therefore, the system at the point O has no degree of freedom, that is, it is invariant or nonvariant. The same result follows from phase rule equation.

$$F = C-P+2$$

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

5.6.2. Phase diagram of carbon dioxide system:

Phase diagram of carbon dioxide system resembles that of water system with some differences.

The phase diagram for carbon dioxide system is shown in Fig. It has three distinct areas in which carbon dioxide can exist either as solid, liquid or gas.

Areas

Area on the R.H.S. of the curve ABD consists of vapour phase. Area above the curve CBD consists of the liquid phase while the area on the L.H.S. of the curve ABC consists of solid phase.
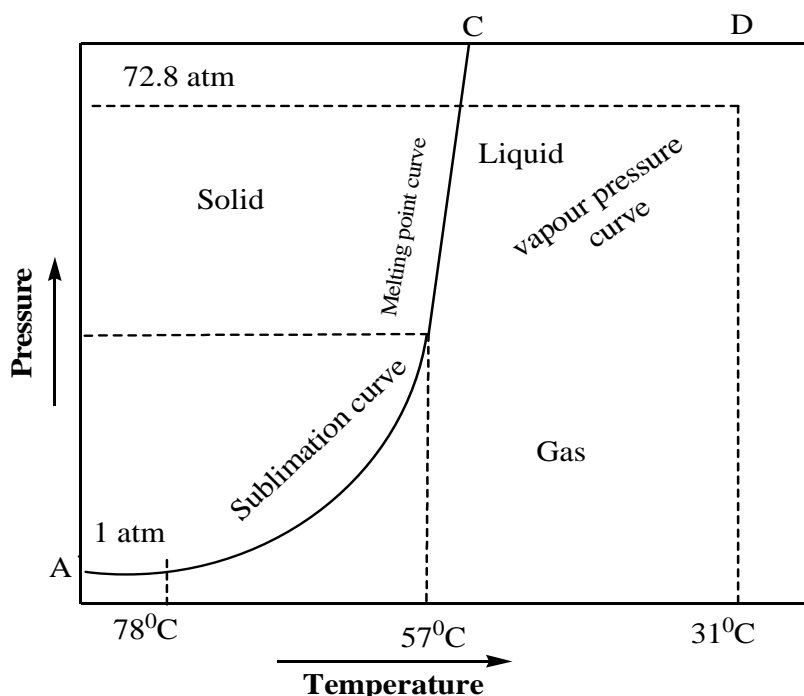
Fig 5.2 The phase diagram for the carbon dioxide system.

Curves:

AB is the sublimation curve along which solid carbon dioxide is in equilibrium with the gas. BD is the vaporization curve along which liquid carbon dioxide is in equilibrium with the gas. This curves ends at 31.1^0C, the critical temperature of CO_2 and corresponding to a pressure of 72.8 atmospheres. The curve BC is the fusion curve along which solid and liquid carbon dioxide are in equilibrium with each other.

Point:

B is the triple point at which all the three phases of carbon dioxide co-exist in equilibrium with one another. The temperature of the system at this point is -57^0C while the pressure is 5.2 atm. A slight variation in temperature or pressure at this point may result in the disappearance of one of the two phase. For example, a slight increase in temperature will result in the disappearance of the solid phase and the equilibrium will shift along the curve BD while a slight decrease in temperature will result in the disappearance of the liquid phase and the equilibrium will shift along the curve BA. Keeping the temperature constant, if the pressure is increased, the gaseous phase will disappear and the equilibrium will shift along the curve BC.

The phase diagram of carbon dioxide resembles that of water in showing three distinct areas for solid, liquid and gaseous phases. But it differs from the latter in several respects. In the first place, the melting point slopes away from the pressure axis. This indicates that increase of pressure raises the melting point of solid carbon dioxide.

The second difference is that solid carbon dioxide can exist in equilibrium with its liquid only at a very high pressure equal to 5.2 atm. This is unlike the water system in which ice and water can exist in equilibrium even at a very low pressure equal to 4.58 mm of Hg (Refer to phase diagram of water).

The third difference is that the vapour pressure of solid carbon dioxide even at extremely low temperature is very high and many times higher than that of ice.

5.6.3. Sulphur system:

We can describe the sulphur system into following steps:
Sublimation curve of rhombic sulphur, represented by AB curve. This curve AB gives the vapour pressure of rhombic sulphur at different temperature. Here, the two phases in equilibrium are (S_R

- S_M) rhombic sulphur and its vapour, is monovarient. Therefore, at one temperature, there can be one vapour pressure only. Point B is the transition temperature (95.6^{o}C) at which rhombic sulphur changes into monoclinic sulphur. B is thus a triple point at which three phase, two solids and the vapour ($S_R - S_M - S_V$) coexist in equilibrium.

Sublimation curve of monoclinic sulphur, represented by BC curve. The curve BC is the sublimation curve of monoclinic sulphur. It gives vapour pressure of monoclinic sulphur at different temperatures. As the number of phase is 2, the system is monovarient. The point C is the melting point (120°C) of monoclinic sulphur. This is another triple point at which three phases, viz., monoclinic sulphur, liquid and vapour ($S_M - S_L - S_V$) are in equilibrium. This is a non – variant point.

Vapour pressure curve of liquid sulphur, represented by CD curve. Here, the two phase ($S_L - S_V$) equilibrium is also monovarient.

Transition curve of rhombic sulphur to monoclinic sulphur, represented by BE curve. The BE curve gives the effect of pressure on the transition temperature of rhombic sulphur into monoclinic sulphur. The equilibrium involved along the curve is ($S_R - S_M$). Both the phases are solid. The system is monovarient. Since transformation of rhombic into monoclinic sulphur is accompanied by increase of volume, the increase of pressure causes a rise in the transition temperature.
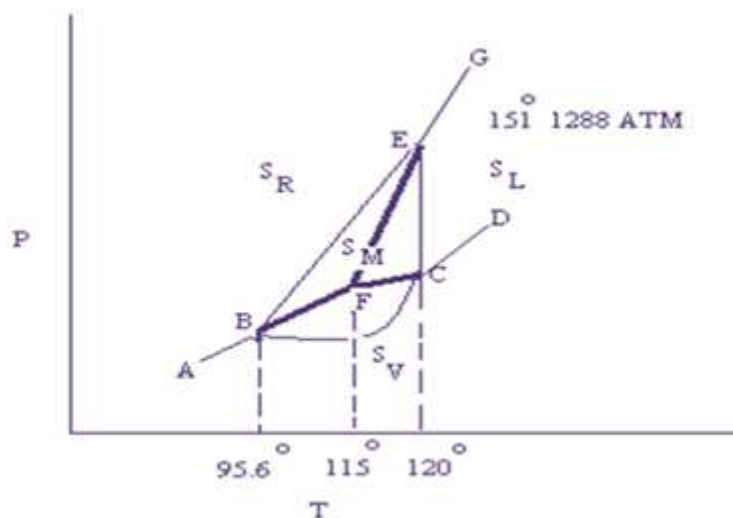
Figure 5.3 Sulphur System

Fusion curve of monoclinic sulphur, represented by CE curve. This gives the effect of pressure on the melting point of monoclinic sulphur. The two – phase equilibrium (SM – SL) along the curve CE is univarient. As the melting point of monoclinic sulphur is accompanied by a slight increase of volume, it follows from Clausius – Clapeyron equation that the melting point will rise slightly by the increase of pressure. The curve CE, therefore, slops slightly away from the pressure axis. As the slop of this curve is much less than that of the curve BE. The two curves meet at the point E. Thus, E is another triple point where three phases, viz., rhombic sulphur monoclinic sulphur and liquid sulphur (SR – SM – SL) are in equilibrium and the system is non – variant. At E, the temperature is 151°C and the pressure is 1290 atm.

Fusion curve of rhombic sulphur, represented by EG curve. Here, the two phase (S_R – S_L) equilibrium is also monovarient as the number of phases is 2.

Metastable equilibria indicated by solid line BF, EF, CF are metastable curve thus, here F represents melting point of the metastable rhombic sulphur. F, is the another triple point where the three phases viz. SR – SL – SV, coexist in metastable equilibrium with liquid.

It should be noted that the variation of vapour pressure of all phases of sulphur with temperature always can be studied with the help of **Clausius – Clapeyron equation**. The BE curve, slops away from the pressure axis because, dp/dt have positive sign in Clausius – Clapeyron equation due to lesser density (1.95 g/cm^3) of monoclinic sulphur than rhombic sulphur (2.05 g/cm^3) and V_B is larger than V_A

$$\frac{dp}{dT} = \frac{\Delta_x H}{T(V_B - V_A)}$$

5.7 PHASE EQUILIBRIUM OF TWO COMPONENT SYSTEM

Broadly, there are three types of two-component system involving solid-liquid equilibria.

Type I. Those in which the two components do not react with each other but simply mix into each other in the molten slate or in the solution. Examples of such system are lead-silver system and KI-H_2O system.

Type II. Those in which the components react to form a compound with congruent melting point. These are those system in which the two pure components react to form a compound which is stable up to its melting point At the melting point, it melts to give a liquid of the same

composition as that of the solid compound. The compound formed is then said to have a congruent melting point.

For example in $FeCl_3$-H_2O system, each hydrate formed is stable up to the melting point and possesses a congruent melting point.

Type III. Those in which the components react to form a compound with incongruent melting point. These are those two-compound formed does not remain stable up to the melting point. On heating, it starts decomposing before the melting point to give a new solid phase and a solution with composition different from that of the solid phase. When this happens, the compound is said to undergo a transition or peritectic(reaction and is said to have incongruent melting point. In general, a peritectic reaction may be represented by the equation

$C_2 = C_1$+ solution, molten),

C_2 represents is the compound formed as a result of reaction between the two pure components' and (C_1 is the new compound (or a pure consitituent) formed as a result of decomposition of compound (C_2 below its melting point. An example of this type of system is Na_2SO_4-H_2O system in which the hydrates formed undergo peritectic reaction.

5.7.1 Phase diagram of Bismuth-Cadmium (Bi-Cd) system:

This is an example of a two component system which forms a simple eutectic. The various phases that may be present are (I) solid bismuth (ii) solid cadmium (iii) solution of bismuth in cadmium or vice versa in the molten stale (iv) vapour.
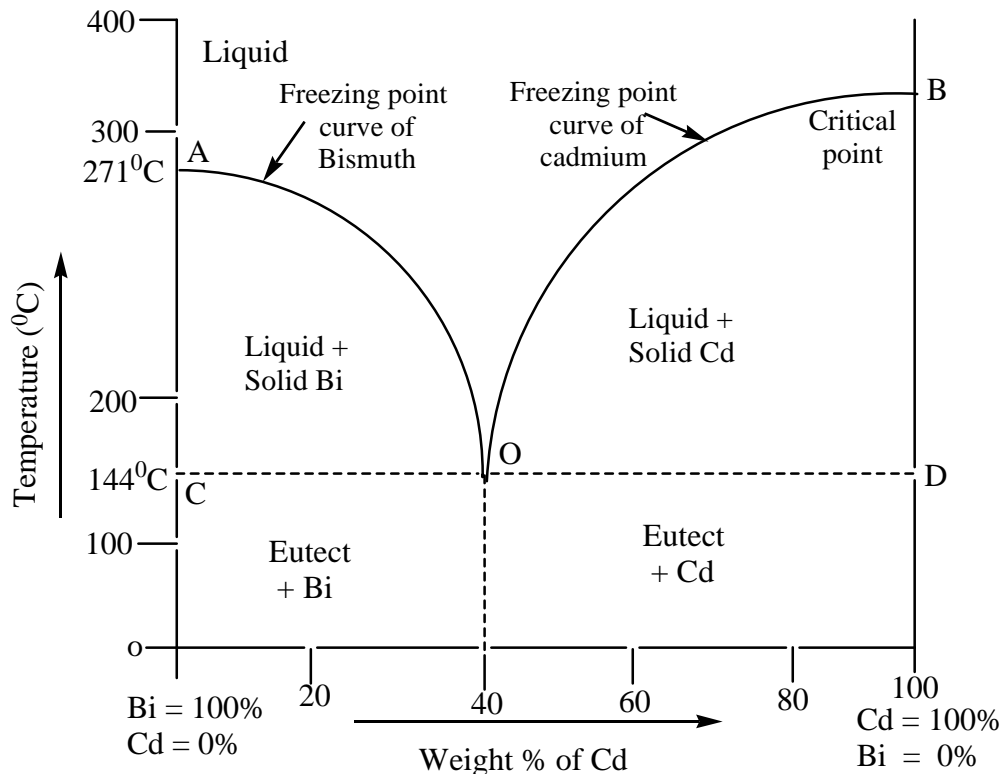
Fig. Phase diagram Bi-Cd system curves

Fig 5.4

Curve AO. It represents the freezing point curve of bismuth to which different amounts of cadmium are added. The point A represents the melting point, or freezing point of pure bismuth (271^0C). We find that the melting point (or) free/mi point) of bismuth is lowered gradually by addition of cadmium into it. The added cadmium goes into the solution and the separation of bismuth occurs till the point) is reach. At this point, no more cadmium goes into the solution as the solution becomes saturated with cadmium and hence the melting point of bismuth does not fall further. Thus the point O represents the composition with lowest melting (point 144^0C). Point O represents the eutectic po9int. Along the curve AO, two phases in equilibrium are solid bismuth and liquid melt (neglecting the vapour phase). Therefore the system is univariant as shown below.

Curve BO. This is the freezing point curve of cadmium to which different amounts of bismuth are added. The point B represent the melting point or freezing point of pure cadmium (32 1 V) We find that melting point of cadmium decreases as more and more of bismuth is added into it the added bismuth goes into the solution and the separation of solid cadmium takes place. This

continues till the point O is reached. At this point no more bismuth goes into the solution and the solution is said to have become saturated with bismuth.

Hence, the melting point does not fall any longer.

Along the curve two Phases solid cadmium and liquid melt are in equilibrium

Therefore,

$F=C-P+1=2+1=1$ i.e., the system is univariant.

it may be noted that the point -, on me curves AO and BO represent the initial freezing points while the points on the line CD represent the final freezing points. It may also be noted that the curve AO is not only freezing point curve of bismuth but may also be considered as solubility curve of bismuth because the points on this curve represent the solubilities of bismuth in the molten cadmium at various temperatures Similarly, the curve BO may also be considered as the solubility curve of cadmium.

Eutectic Point O. This is the point where the two curves AO and BO meet. At this point solid bismuth and solid cadmium are in equilibrium with the melt, i.e, three phases are present Degree of freedom at the point O is zero.

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

The point O represents the lowest possible temperature (144^0C) below a liquid phase cannot exist and above which the liquid phase cannot be enriched in either component by treezing out the other component. Such a liquid mixture of two components which has the lowest freezing point compared to all other liquid mixtures is called emetic mixture. This mixture freezes out completely at constant as solid phases in the same proportion in which they were present in the liquid phase. The temperature corresponding point O is called I he cutectic temperature. This is always lower than the melting points of the either component. In this system, eutectic mixture (containing about 40% Cd and 60% Bi by mass) melts at 144^0C, which is lower than the melting point of bismuth (271^0C of cadmium (321^0C).

5.7.2 Pb-Ag System:

Pb-Ag system is a four phase and two component systems for which a complete phase diagram can be represented as:
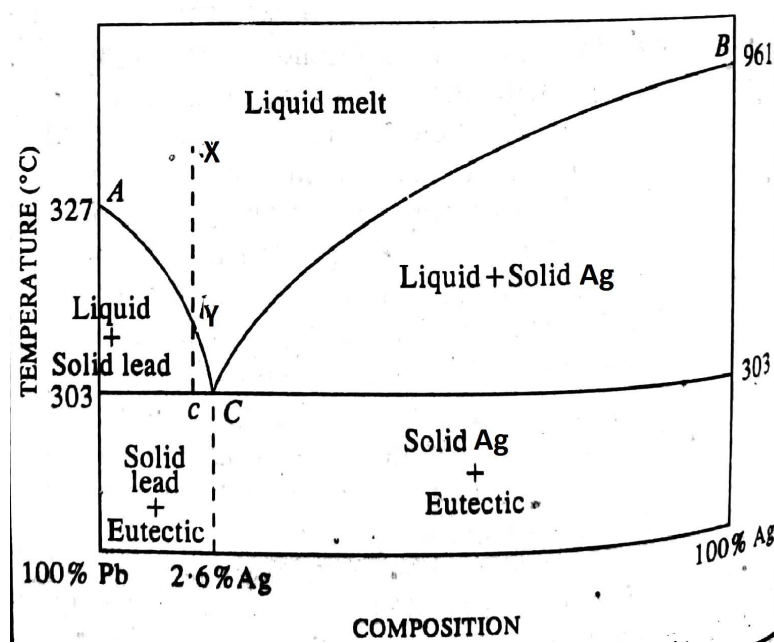
Fig.5.6 Phase diagram of Pb-Ag system

According to the above phase diagram the various regions, curves, eutectic point, eutectic T and eutectic composition in the phase diagrams of Pb-Ag system can be define d as:

Various regions: Different types of the regions present in the two component PB-Ag system are given as.

        a) Region above the ACB: Liquid solution of Pb and Ag

        b) Region within the ACD: Solid Pb and Solution of Ag in Pb

        c) Region within the BCD': solid Ag and the solution of Pb in Ag

Various curves:

1. Curve Ac indicates the freezing curve of Pb with the addition of Ag in which point A indicates the freezing point of pure Pb.

   In the curve Ac; C = 2, P = 2

   So according to reduced phase rule;

   F = C – P +1

   F = 2 -2 + 1

   F =

   i.e. System in the curve AC will be univarient.

2. Curve BC indicates the freezing curve of Ag with the addition of Pb, in which point B indicates the freezing point of pure Ag.

Eutactic point, Eutactic temperature and Eutactic composition: In the phase diagram of Pb-Ag system the melting point of AC and BCcurve is known as eutectic point. Temperature and composition corresponding to this eutectic point are known as eutectic temperature (303^0C) and eutectic composition (97.4% Pb + 2.6% Ag) for Pb-Ag system.

5.7.2.1 Pattinson's process for desilverisation of lead:

Galena (PbS. an ore of lead) is usually associated with silver. When galena is processed for the extraction of lead, some traces of silver pass into it, because silver is soluble in lead to some extent. The lead thus obtained is known as argentiferous lead the desilverisation of lead is carried out which can be easily understood from the phase diagram of lead-silver system, shown in Fig. 5.4.

The argentiferous lead containing small percentage of silver is first of all heated to a temperature well above its melting point so that the system consists only of liquid phase represented by the point x in Fig. 5.4. It is then allowed to cool gradually along the line xy without any change in concentration till the point y is reached. When this point is reached, lead starts separating and solution will contain progressively increasing amounts of silver. Further cooling shifts the system along the line yC. Lead continues to separate out. (Which can be removed with the help of ladles' perforated spoons) and the melt continues to be richer and richer in silver, till the point O is reached where an alloy containing about 2.4% of silver is obtained.

The above principle is employed in Pattinson's process which is used for increasing the relative proportions of silver in the alloy. The relative increase in the amount of solid lead that separates out and in the proportion of silver in the melt on cooling as shown in Figure.

5.8 SUMMARY

With the help of phase rule it is possible to predict qualitatively the effect of change of pressure, temperature and concentration on a heterogeneous system in equilibrium. In the phase diagram the various phases can be represented by area. One phase, by line two phases and by

point three phase in equilibrium. Metastable equilibrium, allotropy, enantiotropy, monotropy has been explained for equilibrium conditions of state of matter.

5.9 TERMINAL QUESTIONS:

A. Objective types questions:

1. The degree of freedom at a triple point unary diagram for water _____

(a) 0   (b) 1   (c) 2   (c) 3

2. Following is wrong about the phase diagram

(a) It gives information on transformation rate.

(b) Relative amount of different phases can be found under given equilibrium conditions.

(c) It indicates the temperature at which the different phases start to melt.

(d) Solid solubility limits are depicted by it.

3. Pick the odd one of the following:

(a) Isomorphous alloy   (b) Terminal Solid Solution

(c) Intermediate Solid Solution   (d) Compound

4. The boundary line between (Liquid + Solid) and (Solid) regions must be part of _____

(a) Solvus   (b) Solidus   (c) Liquidus   (d) Tie- Line

5. An invariant reaction that produces a solid up on cooling two liquids:

(a) Eutectic   (b) Peritectic   (c) Monotechtic   (d) Syntectic

6. A Liquid Phase produces two solid phases during _____ reaction up on cooling.

(a) Eutectic   (b) Eutectoid   (c) Peritectic   (d) Peritectoid

7. On heating one solid phase results in another solid phase plus one liquid phase during

----------- Reaction.

(a) Eutectic   (b) Peritectic   (c) Monotechtic   (d) Syntectic

8. In a one component system the maximum number of phases that can co-exists in

   Equilibrium is:

(a) 1   (b) 2   (c) 3   (d) 4

9. In terms of number of phases (P), components (C) and degrees of Freedom (F), the

   Phase rule is expressed as:

(a) $P + C = F + 2$ (b) $F = P + C – 2$

(c) $P + F = C + 2$ (d) $P - F = C + 2$

10. In the phase diagram of the benzene- naphthalene system, the point C is called the:

(a) Eutectic Point   (b) Congruent Point   (c) Triple Point   (d) Critical Point.

11. Lowest temperature is reached by using:

(a) $CaCl_2 2H_2O$ (b) Acetone with dry ice   (c) NH_4Cl (d) Ether + Dry Ice

12. A compound with an incongruent melting point decomposes on heating into:

(a) A liquid of the same composition as the solid.

(b) A new solid phase and a solution with a composition different from that of the solid

   Phase.

(c) A new and a solution with the same composition as that of the solid Phase.

(d) A solution of fixed composition.

B. Short Answer Questions:

1. Define the terms :- Phase, Components and degree of freedom

2. What do you understand by desilverization. (Pattinson's Process)

C. Long Answer Questions:

1. Discuss the phase diagram of water system

2. Discuss the phase diagram of sulpher system.

3. State the Phase rule and give its derivations.

5.11 NSWERS

1. (a)   2. (a)   3. (a) 4.(b) 5. (d) 6. (a) 7. (b) 8. (c) 9. (c) 10. (a) 11. (d) 12. (b)

Source of study material

9.   Essential of physical chemistry by Bahl, Bahl and Tuli.

10. Principles of physical chemistry By Puri, Sharma and Pathania.

11. Physical chemistry By   P.C. Rakshit.

12. Physical chemistry By Atkins.

UNIT 6: PHASE EQUILIBRIUM - II

6.13.1 Phenol- water system

6.13.2 Trimethylamine-water system

6.13.3 Nicotine- water system

6.14 Lower and upper consolute temperature

6.15 Effect of impurity on consolute temperature

6.16 Immiscible liquids, Steam distillation

6.17 Summary

6.18 Terminal Questions

6.19 Answer to SAQs

6.1 OBJECTIVES

After reading this unit you will be able to:

- Define Phase rule.

- Know congruent and incongruent melting point.

- Classify liquid- liquid mixture.

- Define the lower and upper consolute temperature.

- Explain the process of steam distillation.

- Define freezing mixture.

6.2 INTRODUCTION

Phase as we know is the homogenous part of a system which has same physical and chemical properties throughout the system. For example, mixture of gas consists of one phase. System on the other hand is the part of universe which is under consideration.

The present unit deals with the study of phase equilibrium that includes different topics like phase rule, congruent melting point, incongruent melting point, freezing mixture, liquid- liquid mixture, ideal liquid mixture, Henry's law, azeotropes, partially miscible liquids, lower consolute temperature, upper consulate temperature, immiscible liquids, steam distillation.

In order to understand the unit properly we will go through the above topic in detail along with suitable examples.

6.3 SOLID SOLUTION

Solid solution consists of a solute dissolved in a particular solvent forming a homogeneous solution. Here the crystal structure of the solvent does not change by the addition of the solute. For example metal alloys, moist solids. These solutions are used in industries. When these solutions attain unstability, the two phases (solute and solvent) separates out.

6.4 COMPOUND FORMATION WITH CONGRUENT MELTING POINT (Mg-Zn)

For two component system A and B, a compound AB is formed chemically. There are three phases, solid component A, solid component B and solid compound AB formed by combining A and B. As a result of melting, fourth phase i.e. liquid phase is formed. Congruent melting point is defined as a temperature when the composition of the liquid formed by melting of solid compound is same as the composition of the solid compound. At congruent melting point, system having two components gets reduced to one component as both the liquid and solid form of the compound AB have same composition. As the system is two components, we apply reduced phase rule for calculating the number of degree of freedom.

At congruent melting point: $F = C - P + 1 = 1 - 2 + 1 = 0$ (Non- variant)

Keeping magnesium (Mg) in place of A, Zinc (Zn) in place of B and compound $MgZn_2$ in place of AB, we obtain Mg- Zn system. Therefore, the system consists of four phases: solid Mg, solid Zn, solid $MgZn_2$ and liquid phase of $MgZn_2$. Figure 1 shows the phase diagram of Mg- Zn system which consists of area, curves and points.
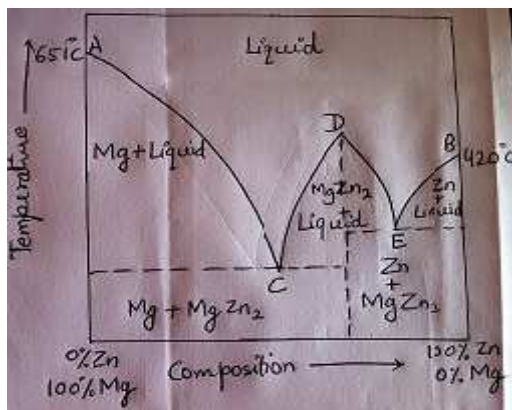
Figure 6.1. Phase diagram of Mg-Zn system

The figure shows that there are four curves: AC, CD, DE and EB. The curve AC represents the freezing point of Mg, curve CD represents the freezing point of intermetallic compound $MgZn_2$, curve DE represents the lowering of the melting point and curve EB represent the freezing point curve of Zn. Along the curve, two phases exist in equilibrium. Therefore applying reduced phase rule, we have: $F = C - P + 1 = 2 - 2 + 1 = 1$ (Monovariant). The area above the four curves represents only one phase i.e. liquid phase which consist of solution of Mg and Zn. Here the degree of freedom is two which is obtained by using reduced phase rule. There are three points in the phase diagram of Mg- Zn system i.e. point C, D and E. At point C, there are three phases in equilibrium: solid Mg, solid $MgZn_2$ and a liquid. Thus according to reduced phase rule, the number of degree of freedom is zero at the points. At point E, there are also three phases: solid Zn, solid $MgZn_2$ and a liquid phase. Here also the number of degree of freedom is zero. Point D represents a congruent melting point of the compound having two phases: one solid phase $MgZn_2$ and another liquid $MgZn_2$ having same composition.

6.5 INCONGURENT MELTING POINT (NaCl-H₂O), (FeCl₃- H₂O) AND (CuSo4- H2O) SYSTEM)

There are some compounds which on heating get decompose without melting. Therefore such compounds have different composition from that of the solid phase. Incongruent melting point also known as transition temperature of a compound is defined as the temperature at which the composition of a solid compound is different from the components formed by the decomposition of this solid compound. This decomposition results in the formation of another solid and a liquid which shows that there are three phases. The number of degree of freedom at incongruent melting point is equal to zero (non- variant). Now we will discuss two component system: $NaCl – H_2O$ system, $FeCl_3$- H_2O system and $CuSO_4$- H_2O system one by one.

6.5.1 NaCl – H₂O system:

This is a two component system having four phase: solid NaCl, solid H_2O, $NaCl.2H_2O$ and a liquid phase (solution). The phase diagram of $NaCl – H_2O$ system is given in Figure 2. The compound formed is $NaCl.2H_2O$ which dissociates to form another solid and a liquid.
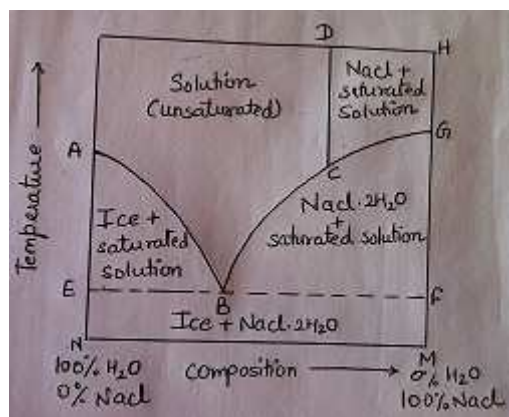
Figure 6.22. Phase diagram of NaCl – H₂O system

The phase diagram consists of curves, points and area. There are three curves represented by AB, BC and CD in the phase diagram. The curve AB represents the depression in freezing point of water which is due to the addition of sodium chloride (NaCl). As two phase are in equilibrium (ice + solution) along the curve, therefore number of degree of freedom is equal to one as calculated by using reduced rule ($F = C - P + 1 = 2 - 2 + 1 = 1$ (monovariant). The curve BC represents the solubility curve of hydrated NaCl i.e. $NaCl.2H_2O$. Along this curve, $NaCl.2H_2O$ and solution phase are in equilibrium. Therefore, the number of degree of freedom is one (monovariant). The third curve CD represents the equilibrium between solid NaCl and solution. Here also the degree of freedom is one. There are five area in the phase diagram A_1, A_2, A_3, A_4 and A_5. Figure 2 also shows that there are two points in the diagram, one point B and other point C. At point B, three phase exist in equilibrium (solution, ice and solid $NaCl.2H_2O$). Using reduced phase rule, the number of degree of freedom calculated is zero (non-variant). Point B is also known as eutectic point and the corresponding temperature is known as eutectic temperature. Point C represents incongruent meting point in which compound $NaCl.2H_2O$ decomposes to form NaCl and a liquid (saturated solution).

6.5.2 FeCl₃- H₂O system:

$FeCl_3$- H_2O system consists of two components $FeCl_3$ and H_2O which exist in vapour phase, ice, $Fe_2Cl_6.4H_2O$, $Fe_2Cl_6.5H_2O$, $Fe_2Cl_6.7H_2O$, $Fe_2Cl_6.12H_2O$. The phase diagram of $FeCl_3$- H_2O system consists of curves, points and areas as shown in Figure 3.
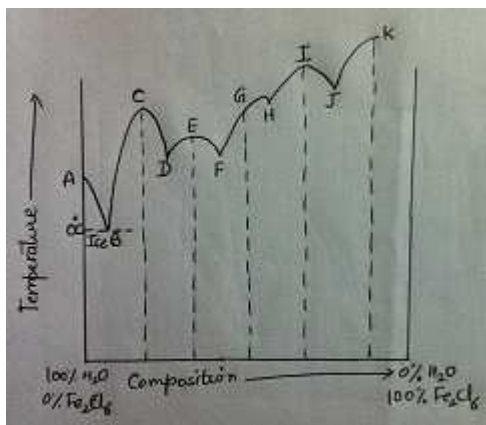
Figure 6.3. Phase diagram of FeCl₃- H₂O system

It is clear from phase diagram that FeCl$_3$- H$_2$O system consist of ten curves which are AB, BC, CD, DE, EF, FG, GH, HI, IJ and JK. Curve AB represents depression in freezing point of water on addition of FeCl$_3$. There are three phases (ice, vapour and solution) which are at equilibrium along the curve AB. The curve BC represents the solubility curve of Fe$_2$Cl$_6$.12H$_2$O along which three phase exist in equilibrium (vapour, saturated solution phase and Fe$_2$Cl$_6$.12H$_2$O). The curve CD represents the melting point curve of Fe$_2$Cl$_6$.12H$_2$O. The curve DE represents the solubility curve of Fe$_2$Cl$_6$.7H$_2$O while the curve EF represents the melting point curve of Fe$_2$Cl$_6$.7H$_2$O. The curve FG represents the solubility curve of Fe$_2$Cl$_6$.5H$_2$O while the curve GH represents the melting point curve of Fe$_2$Cl$_6$.5H$_2$O. The curve HI represents the solubility curve of Fe$_2$Cl$_6$.4H$_2$O while the curve IJ represents the melting point curve of Fe$_2$Cl$_6$.4H$_2$O. The last curve i.e. JK represents the solubility curve of anhydrous ferric chloride (Fe$_2$Cl$_6$).

There are nine points in the phase diagram of FeCl$_3$- H$_2$O system. These are point B, C, D, E, F, G, H, I and J. Point B, D, F, H and J are called eutectic points while the points C, E, G and I are called congruent melting point. At point B: ice, Fe$_2$Cl$_6$.12H$_2$O and solution phase exist in equilibrium. At point D: Fe$_2$Cl$_6$.12H$_2$O, Fe$_2$Cl$_6$.7H$_2$O and solution phase are in equilibrium. At point F: Fe$_2$Cl$_6$.7H$_2$O, Fe$_2$Cl$_6$.5H$_2$O and solution phase exist in equilibrium. At point H: Fe$_2$Cl$_6$.5H$_2$O, Fe$_2$Cl$_6$.4H$_2$O and solution phase exist in equilibrium while at point J: Fe$_2$Cl$_6$.4H$_2$O, Fe$_2$Cl$_6$ and solution exists in equilibrium. It is clear that at all the eutectic points, the degree of freedom is zero as the number of phase are three and component is two. At the congruent melting point, the solid phase (hydrate) and the liquid phase are in equilibrium having the same composition. The degree of freedom obtained by using reduced phase rule is zero.

6.5.3 CuSO₄- H₂O system:

CuSO₄- H₂O system is a two component system as it contains $CuSO_4$ and H_2O. The system consists of five phase: vapour, anhydrous $CuSO_4$, $CuSO_4.H_2O$, $CuSO_4.3H_2O$ and $CuSO_4.5H_2O$. Anhydrous means without water. Figure 4 represents the phase diagram of CuSO₄- H₂O system.
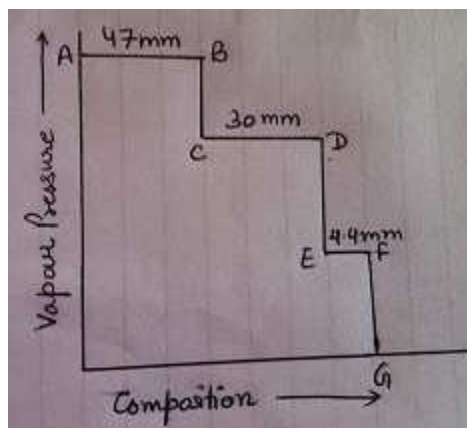

Figure 6.4 Phase diagram of CuSO₄- H₂O system

The phase diagram consists of curves: AB, BC, CD, DE, EF and FG. The curve AB represents the dehydration curve of $CuSO_4.5H_2O$ where it dissociates to form $CuSO_4.3H_2O$. Along the curve AB, three phases are in the equilibrium: $CuSO_4.5H_2O$, $CuSO_4.3H_2O$ and vapour phase. The curve BC represents the decrease in vapour pressure from 47 mm to 30 mm which is due to the conversion of $CuSO_4.5H_2O$ to $CuSO_4.3H_2O$. The curve CD represents the dehydration curve of $CuSO_4.3H_2O$ which is due to the formation of $CuSO_4.H_2O$. Along the curve CD, there are three phases in equilibrium: $CuSO_4.3H_2O$, $CuSO_4.H_2O$ and vapour. The curve DE represents the decrease in vapour pressure from 30 mm to 4.4 mm which is due to the conversion of $CuSO_4.3H_2O$ to $CuSO_4.H_2O$. The curve EF represents the dehydration curve of $CuSO_4.H_2O$ which results in the formation of anhydrous $CuSO_4$ at a particular pressure. Three phases exist in equilibrium along the curve EF: $CuSO_4.H_2O$, anhydrous $CuSO_4$ and vapour phase. The curve FG represents the decrease in vapour pressure resulting in the formation of anhydrous $CuSO_4$.

There are seven points in the phase diagram of CuSO₄- H₂O system: A, B, C, D, E, F and G. at point A, $CuSO_4.5H_2O$ is present in pure form. At point B, $CuSO_4.5H_2O$ get completely converted into $CuSO_4.3H_2O$. At point C, the dehydration of $CuSO_4.3H_2O$ starts. At point D, $CuSO_4.3H_2O$ get completely converted into $CuSO_4.H_2O$. At point E, the dehydration of

$CuSO_4.H_2O$ starts. At point F, $CuSO_4.H_2O$ get completely converted into $CuSO_4$. At point G, anhydrous $CuSO_4$ is present.

6.6 FREEZING MIXTURES

Freezing mixtures are defined as a mixture of salt and ice which decreases the temperature of the system. For example, mixture of sodium nitrate and ice, sodium chloride and ice, ammonium chloride and ice, ammonium nitrate and ice. Let us discuss how these mixtures lower the temperature of the system: When salt is added into ice, some of the salt get dissolve in water (formed by melting of ice) resulting in the formation of three phases: ice, salt and solution which are in contact with each other. At eutectic temperature, all three phase exist in equilibrium. The melting of ice and dissolution of salt require heat which results in the lowering of temperature.

6.6.1 Acetone-dry ice:

Acetone-dry ice constitutes a freezing mixture. Dry ice as we know is solid CO_2. This mixture is commonly used in the laboratory for lowering the temperature of the system. In a sealed container, when dry ice is added to the acetone, dry ice undergoes the process of sublimation (conversion of solid into vapour) causing intense lowering of temperature by taking heat from acetone. The freezing point of acetone is $-95\ ^oC$. By adding large amount of dry ice we can attain the freezing point of acetone. Cooling bath used in the laboratory also consist of a mixture of acetone and dry ice.

6.6.2 Liquid- liquid mixtures:

Liquid- liquid mixtures are also called by name solution of liquid in liquid. Solution as we know consist of a solute and a solvent. In liquid- liquid mixture, solute and solvent both are in liquid phase and are volatile in nature. The liquid- liquid mixture depends on the type of intermolecular forces and the nature of these forces between them. The properties of these mixtures depend upon the vapour pressure, viscosity, refractive index, surface tension etc. Depending upon the miscibility of two liquids, these mixtures are classified into three types:

6.6.2.1 Immiscible liquid- liquid mixture:

In these mixtures, both the liquids are insoluble in each other forming a layer between them. These liquid mixture do not interfere the properties of the individual liquid. For example, benzene in water, kerosene in water, oil in water.

6.6.2.2 Partially miscible mixture:

In these liquid mixtures, both the liquids are soluble to some extent or to a limited ratio resulting in the formation of two layers. With increase in temperature, the miscibility of these liquid mixture increases. For example, nicotine- water system, phenol- water system, triethylamine- water system.

6.6.2.3 Completely miscible mixture:

In these liquid mixtures, two liquids are completely soluble in each other at all ratio. For example, ethanol- water system, benzene- acetone system. These mixtures are classified into two types: ideal liquid mixture or ideal solution and non-ideal liquid mixture or non- ideal solution.

6.7 IDEAL LIQUID MIXTURES

These mixtures are also known as ideal solutions. In ideal solution, each component obeys Raoult's law at all temperature and concentration. For an ideal solution, enthalpy of mixing is zero ($\Delta H_{mix} = 0$) and volume of mixing is also zero ($\Delta V_{mix} = 0$). It means that final volume of the solution is equal to the sum of volume of two liquid being mixed. In ideal solution, the interaction between A-B is same as the interaction between A-A and B-B which are the constituent. The partial molar volume of a constituent in an ideal solution is equal to the molar volume of the constituent when present in the pure form. For example, n-hexane and n-heptane, benzene and toluene, carbon tetrachloride and chloroform, n-butyl chloride and n-butyl bromide.

6.8 RAOULT'S LAW

According to Raoult's law: At any temperature, the partial pressure of a component (volatile liquid) of a solution is equal to the vapour pressure of the pure component multiplied by the mole fraction of that particular component present in the mixture. Consider a binary mixture

containing two volatile liquid A and B. Let x_A and x_B are the mole fraction of two liquid A and B while P_A and P_B are the partial pressure of two liquid A and B. Hence according to Raoult's law:

$$P_A = x_A \, P_A^o \quad \text{and} \quad P_B = x_B \, P_B^o$$

Where P_A^o and P_B^o are the vapour pressure of the pure liquid A and B respectively. A solution is said to be ideal, if all the constituent of a mixture obeys Raoult's law at all temperature and concentration. Figure 5 represents the vapour pressure curve for an ideal solution.
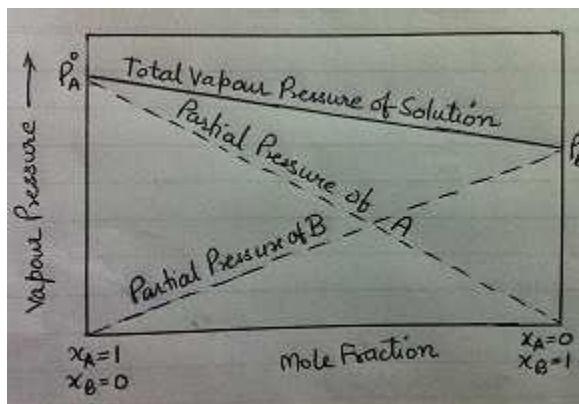
Figure 6.5 Vapour pressure curve for an ideal solution

When the constituent of a mixture affect the intermolecular forces or when there is a formation of a compound by the interaction of the components, Raoult's law is not applicable. Vapour pressure of a liquid is defined as the pressure exerted by the vapour in equilibrium with a liquid in a closed container a particular temperature. Let us calculate the vapour pressure of an ideal solution. Total vapour pressure of a solution (P) is equal to the sum of the partial pressure of two liquid A (P_A) and B (P_B) respectively.

$$P = P_A + P_B = \ x_A \, P_A^o \ + x_B \, P_B^o$$

6.9 HENRY'S LAW

Henry's law is applicable for a solution of a gas in a liquid. This law is given by William Henry. According to this law: At a particular temperature the mass of a gas (m) dissolved in definite amount of a solvent is directly proportional to the pressure of the gas (P) which is in equilibrium with the solution. Accordingly:

$$m = k \, P$$

Where k is proportionality constant or Henry's law constant. The value of k depends upon the nature of the gas and the solvent. Figure 6 shows the validity of Henry's law.
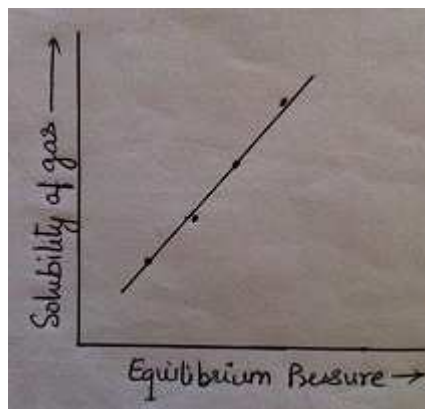
Figure 6.6 Validity of Henry's law

Henry's law is not applicable under the conditions given: Firstly, when the solubility of a gas in a particular solvent is low. Secondly, when a gas undergoes association or dissociation in the solvent. Thirdly, when pressure is very large and fourthly, when temperature is very low or very high.

6.10 NON- IDEAL SOLUTION

Non- ideal solutions are also known as non- ideal liquid mixtures or real solutions. If a solution don not obey Raoult's law over the entire range of concentration and temperature, the solution is said to be non- ideal solution. The vapour pressures of these solutions are higher or lower than the pressure obtained by using Raoult's law. Here the enthalpy of mixing and volume of mixing is not equal to zero. In these solutions, the force between A-B is different from A-A and B-B (individual components). Non- ideal solutions are classified into two types: Non- ideal solution showing positive deviation (vapour pressure obtained is higher than calculated using Raoult's law) and non- ideal solution showing negative deviation (vapour pressure obtained is lower than calculated using Raoult's law).

6.10.1 Non- ideal solution showing positive deviation:

In the solution of component A and B, the interaction between A-B is weaker than A-A and B-B interaction. Hence the vapour pressure of the solution is higher than the pressure predicted by Raoult. The enthalpy of mixing is positive. For example, ethanol and hexane, acetone and carbon disulphide, carbon tetrachloride and benzene, carbon tetrachloride and toluene. Figure 7 represents the curve showing positive deviation.
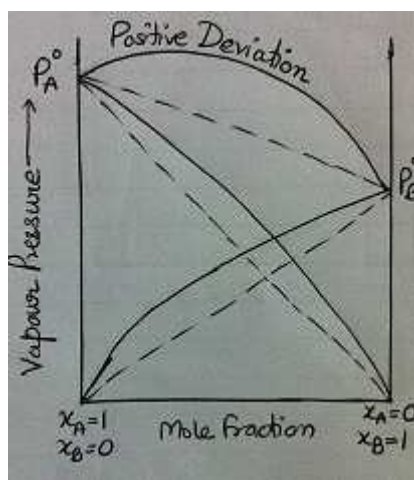
Figure 6.7 Non- ideal solutions showing positive deviation

6.10.2 Non- ideal solution showing negative deviation:

In the solution of component A and B, the interaction between A-B is stronger than A-A and B-B interaction. Here the vapour pressure of a solution is lower than the pressure predicted by Raoult. The enthalpy of mixing is negative. For example, acetone and water, phenol and aniline, chloroform and benzene, acetic acid and pyridine. Figure 8 represents the curve showing negative deviation.
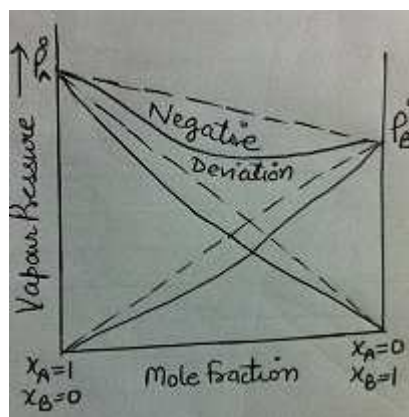
Figure 6.8 Non- ideal solutions showing positive deviation

6.11 AZEOTROPES (HCl-H₂O) (MAXIMUM BOILING AZEOTROPES)

Azeotropes are also known as constant boiling mixtures. It is defined as mixtures which have same composition both in solution phase as well as in vapour phase. It is difficult to separate the components of these mixtures by fractional distillation. Azeotropes have a characteristic boiling point which is either lower (negative deviation) or higher (positive deviation) than any of its constituents. Azeotropes having positive deviation are called minimum boiling azeotropes. For example, nitric acid and water. Azeotropes having negative deviation are called maximum boiling azeotropes. For example, ethanol and water.

Let us discuss HCl- H_2O system. It is a two component mixture. It possess maximum boiling point which shows that the system have low volatility. Figure 9 represents the boiling temperature versus composition curve of HCl- H_2O system.
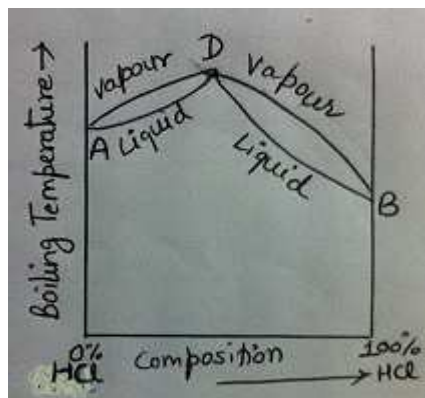
Figure 6.9 Boiling temperature versus composition curve of HCl- H_2O system

We know that pure water boils at 100°C and the boiling point of HCl is −85°C. Their mixture that constitutes the azeotrope boils at 108.5°C and at 1atm pressure contains 20.24% of HCl shown by point D. If a solution contains less than 20.24% of HCl undergoes distillation, the water constitute the distillate. This is shown by AD in the Figure 9. In this case, we are unable to recover the pure HCl as the residue left contain a mixture of the same composition (20.24% of HCl solution in water). If a solution contains more than 20.24% of HCl undergoes distillation as shown by BD, the pure HCl constitute the filtrate. In this case, we are able to recover the pure HCl as the residue having the same composition.

6.12 ETHANOL- WATER SYSTEM (MINIMUM BOILING AZEOTROPES)

This is a two- component system in which one component is ethanol and other is water. The azeotropic mixture of ethanol and water boils at 78.13°C and at one atmospheric pressure shown by point C. The mixture contains 95.6 % of ethanolic solution in water. Figure 10 represents the boiling temperature versus composition curve of C_2H_5OH- H_2O system.
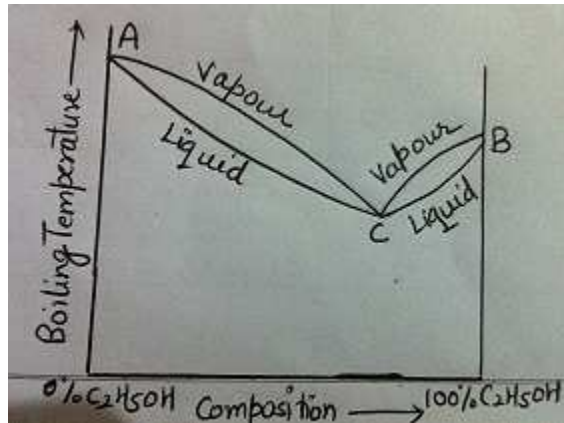
Figure 6.10 Boiling temperature versus composition curve of C₂H₅OH- H₂O system

If a solution having composition between pure water and 95.6 % ethanol undergoes distillation as shown in Figure 10 by AC, ethanol (95.6 %) constitute the distillate while the pure water constitute the residue. In second case, if the solution having composition between pure ethanol and 95.6 % ethanol undergoes distillation as shown in Figure 10 by BC, ethanol (95.6 %) and pure ethanol get separated.

6.13 PARTIALLY MISCIBLE LIQUIDS

As discussed earlier, these are the liquid mixture forming two layers which are soluble in each other to some extent. The miscibility of these liquid mixtures depends on temperature. At a particular temperature, two partially miscible liquid mixtures become completely miscible. This temperature is known as critical solution temperature or consolute temperature. For example, phenol- water system, triethylamine- water system and nicotine-water system. Let us discuss these systems one by one:

6.13.1 Phenol –water system:

When phenol mixed with water, there is a formation of two layers as these liquids are partially miscible. Figure 11 shows the variation of temperature with phenol composition. It is clear that with increase in temperature, the miscibility of two liquid increases. At 65.8 ^{o}C, two liquids (phenol and water) get completely miscible and the corresponding temperature is known as critical solution temperature. Critical solution temperature is a characteristic property of a particular system. This system possesses upper critical solution temperature.
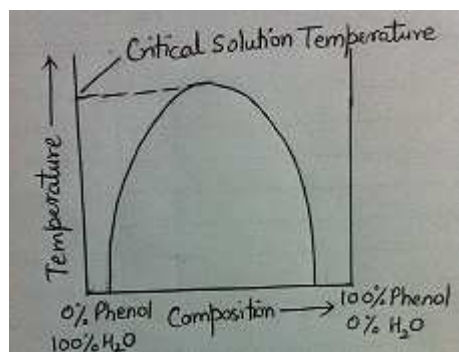
Figure 6.11 Phenol –water system

6.14.2 Triethylamine-water system:

In this system, two liquids which are taken are trimethylamine and water. Both the liquids are allowed to mix resulting in the formation of two layers. The critical solution temperature is below 18.5 ^{o}C and above this temperature, these two liquids becomes partially miscible as shown in Figure 12. These systems possess lower critical solution temperature.
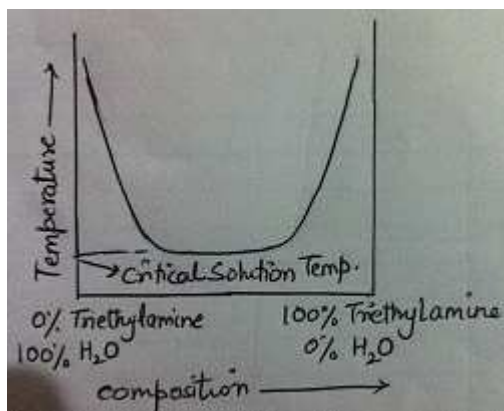
Figure 6.12 Triethylamine-water system

6.13.3 Nicotine- water system:

Here the two liquids taken are nicotine and water which are partially soluble. For this system there are two temperatures at which these liquid mixtures get completely miscible. These two temperatures are $60.8^{o}C$ (lower critical temperature) and $208^{o}C$ (upper critical temperature). It is clear that when temperature range is between $60.8\ ^{o}C$ to $208\ ^{o}C$, the two liquids become partially miscible as shown in Figure 13.
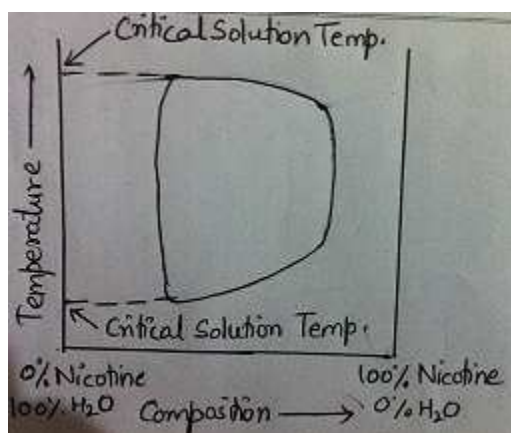
Figure 6.13 Nicotine- water system

6.14 LOWER AND UPPER CONSOLUTE TEMPERATUTE

As we have discussed earlier about the consolute or critical solution temperature, it is defined as a temperature at which two partially miscible liquid becomes completely miscible.

There are two consolute temperature: one is lower consolute temperature and the other is upper consolute temperature. In case of phenol- water system, there is upper consolute temperature which is 65.8 $^\circ$C, above which two liquids becomes completely miscible. The lower consolute temperature is possessed by trimethylamine- water system.

6.15 EFFECT OF IMPURITY ON CONSOLUTE TEMPERATURE

We know that consolute temperature is one of the characteristic properties of a system and is affected by the presence of small amount of impurities. In case first, if impurity is soluble in any one of the liquid, it will affect the miscibility (decreases) thereby raising the upper consolute temperature and decreasing the lower consolute temperature. For example, the presence of sodium chloride as impurity in phenol- water system raises the upper consolute temperature. In case second, if the impurity is soluble in both the liquid, the miscibility of two liquid increases thereby decreasing the upper consolute temperature and increasing the lower consolute temperature. For example, the presence of sodium salt (soap) in phenol- water system lowers the upper consolute temperature.

6.16 IMMISCIBLE LIQUIDS, STEAM DISTILLATION

Immiscible liquids as we have discussed earlier are not soluble in each other. For example, kerosene in water, oil in water. Distillation is a process that involves evaporation followed with condensation. In steam distillation, steam is passed into a round bottom flask containing the impure organic liquid. Through steam distillation, we purify the given organic liquid which is immiscible in water on the basis of their volatility. Figure 14 shows the process of steam distillation.
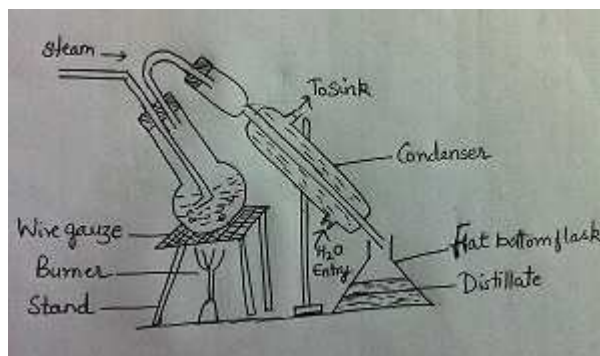
Figure 6.14 Steam distill

The Figure 14 consist of a condenser, adapter, flat bottom flask and round bottom flask. In round bottom flask, impure organic liquid containing water having non-volatile impurities is placed. Our aim is to remove the impurity and purify the organic liquid. Allow the steam to pass through the round bottom flask. Now using a burner, heat the flask which leads to the formation of vapour. The vapour along with steam passes through the condenser. Condenser as we know is an apparatus used for converting vapour phase into liquid phase. The distillate (liquid produced after the process of distillation) is collected in a flat bottom flask. In the flat bottom flask, the formation of two layers takes place. One layer is of pure organic liquid and another layer is of water. Then by using separating funnel, we can separate the two liquid. In this way, we purify the organic liquid. The process of steam distillation is used for the purification of phenylamine i.e. aniline and for calculating the approximate weight of an organic liquid.

6.17 SUMMARY

In this unit, we have discussed about the concept of phase, component, degree of freedom, congruent melting point, incongruent melting point, freezing mixtures, miscibility. We are able to know about the types of solution which are classified on the basis of miscibility and the process of steam distillation used for the purification of an impure organic liquid.

- **Congruent melting point** - Temperature when the composition of the liquid formed by melting of solid compound is same as the composition of the solid compound.

- **Incongruent melting point -** Temperature at which the composition of a solid compound is different from the components formed by the decomposition of this solid compound.

- **Azeotropes** - Mixture having same composition both in solution phase as well as in vapour phase.

- **Immiscible liquid mixture** – Liquid mixture not soluble in each other.

- **Consolute temperature** - Temperature at which two partially miscible liquid becomes completely miscible.

- **Partially miscible liquids** – Liquid mixture soluble to some extent.

- **Distillation** – Process involving evaporation followed with condensation.

6.18 TERMINAL QUESTIONS

A. Objectives Type Questions:

1. Phenol- water system consist a liquid mixture which are ………. miscible.

2. Consolute temperature is also known as ………. temperature.

3. Triethylamine-water system contain ………. consolute temperature.

4. Addition of NaCl in phenol- water system ………. the upper consolute temperature.

5. Steam distillation is used for the purification of ………. liquid.

6. Azeotropic mixture is also known as ………. mixture.

7. ………. law gives the relationship of solubility of a gas with pressure.

8. Ideal solution obeys ………. law at all range of temperature and concentration.

9. Non- ideal solutions are also known as ………. solution.

10. Kerosene in water consists of a system which is ………..

11. Water consists of ………. phases.

12. Phase rule for one –component system is given by ……….

13. Phase rule for two-component system is given by ………..

14. Chloroform and benzene constitute a system showing ………. deviation.

15. Ethanol and hexane constitute a system showing ………. deviation.

B. Short Answer Type Questions:

1. Explain in detail about the liquid- liquid mixture.

2. Explain the concept of congruent and incongruent melting point by giving suitable example of each.

3. What are Azetropes

C. Long Answer Type Questions:

1. State and explain the Rault's & Henery Law and also discuss the importence of these laws.

2. Write an example of partialy miribleliquid mixture.

3. Draw & discuss the phase diagram of Mg-Zn system.

4. Discuss the NaCl-H_2O System having incongruent melting point.

6.19 ANSWER

Fill in the blanks:

1. Partially; 2. Critical solution; 3. Lower; 4. Raises; 5. Organic; 6. Constant boiling; 7. Henry's; 8. Raoult's; 9. Real; 10. Immiscible; 11. Three; 12. F = C – P + 2; 13. F = C – P + 1; 14. Negative; 15. Positive.

Source of study material:

Bahl, A., Bahl, B. S., Tuli, G. D. (2014), Essentials of Physical Chemistry, S. Chand & Company Pvt. Ltd., New Delhi.

Puri, B. R., Sharma, L. R., Pathania, M. S (2012), Principles of Physical Chemistry, Vishal Publishing Co., Jalandhar, India.

UNIT -7 SURFACE CHEMISTRY

7.1 OBJECTIVES

After studying this Unit, you will be able to:

- Describe interfacial phenomenon and its significance;

- Define adsorption and classify it into physical and chemical adsorption;

- Explain mechanism of adsorption;

- Explain adsorption results on the basis of Freundlich adsorption isotherms and Langmuir's absorption isotherm;

- Explain Charge on the colloidal particle and size of the colloidal particle

- Explain Perrin's method of determination of the Avogadro's number

7.2 INTRODUCTION

Surface chemistry is the branch of Physical Chemistry that occurs at the surfaces or interfaces. The interface or surface is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas. Due to complete miscibility, there is no interface between the gases. The bulk phases that we come across in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends on the size of the particles of bulk phases. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallization occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

7.3 SOME COMMON TERMS USED IN SURFACE CHEMISTRY

a) **Adsorption:** As like to the liquid surface, there occur certain unbalance residual forces at the surface molecules of the solid substances. Thus the tendency of the surface molecules of the solid substances to attract the molecules of the other substances at the surface to minimize the unbalanced residual forces is known as adsorption phenomena. Example : When the gases like NH_3, Cl_2, SO_2 etc. comes in the contact of charcoal then there occurs the adsorption of the gases at the charcoal surface.

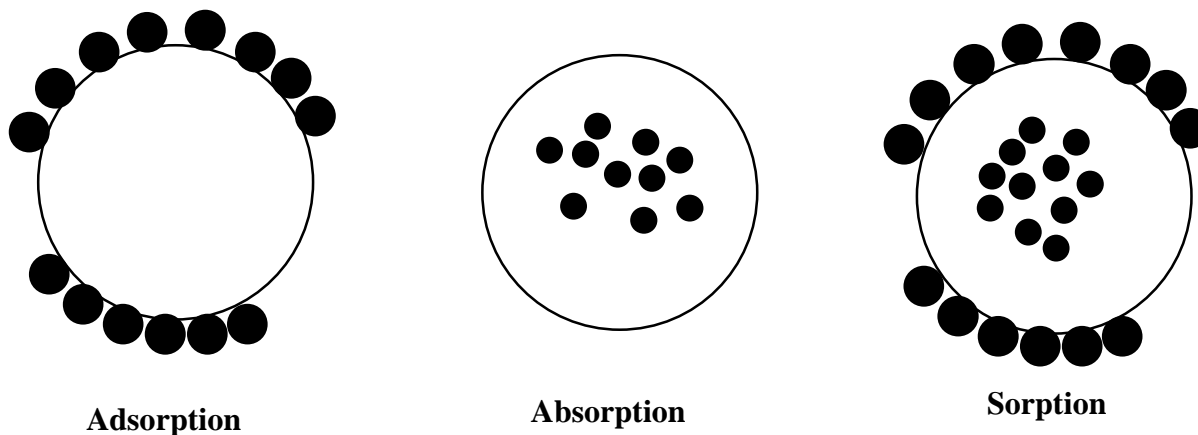In the adsorption phenomena two types of the species are involved:

a. **Adsorbent:** That substance which attracts the molecules of the other substance at its own surface will be called as adsorbent.

b. Generally solid substance can be used as a adsorbent in the adsorption phenomena. **Adsorbate:** That substances of which molecule are adsorbed at the surface of the adsorbent will be called as adsorbate.

Mostly gaseous molecule can behave as an adsorbate in the adsorption phenomena.

b) **Absorption:** The process of attracting the molecules of the other substance in the inner bulk is known as absorption phenomena. Example: When the NH_3ngas comes in the contact of H_2O then the NH_3 is absorbed by the H_2O to form the NH_4OH.

A. Sorption: When both the adsorption and absorption phenomena take place simultaneously, than such type of the process is known as sorption.

Representation of the adsorption, absorption and sorption process can be given as:

      Adsorption   **Absorption**   **Sorption**

7.4 TYPES OF ADSORPTION

Depending on the force of attraction between the adsorbate and adsorbent surface the adsorption can be divided in to two different types, which are given below:

1. **Physical adsorption:** Such type of the adsorption phenomena in which there occur a weak Van der Waal attraction force between adsorbate and adsorbent surface is known as physical adsorption.

2. **Chemical adsorption:** Such type of the adsorption phenomena in which there occur a strong chemical bonding between the adsorbate and adsorbent surface is known as chemical adsorption.

7.5 DIFFERENCE BETWEEN THE PHYSICAL AND CHEMICAL ADSORPTION

| Properties	Physical adsorption	Chemical adsorption
Specificity	Physical adsorption does not having the specificity	Chemical adsorption has specificity

|		
Force of attraction	In the physical adsorption there occur weak Vander waal force of attraction between the adsorbate and adsorbent.	In the chemical adsorption there occur strong chemical bonding between the adsorbate and adsorbent.
Enthalpy of adsorption	In the physical adsorption there occur very low enthalpy of adsorption(4-40KJ/mol)	In the chemical adsorption there occurs very high enthalpy of adsorption (40-400KJ/mol).
Activation energy	Physical adsorption required negiliziable activation energy value.	Chemical adsorption requires certain activation energy value.
Reversibility	Due to the weak Van der waal force of attraction between the adsorbate and adsorbent, the physical adsorption having reversible nature.	Due to the stronger chemical bonding between the adsorbate and adsorbent the chemical adsorption having irreversible nature.
Effect of temperature	With the increase in the temperature, the extent of physical adsorption is decreases.	With the increase in the temperature, the extent of chemical adsorption is initially increase and finally decreases.

7.6 ADSORPTION ISOBAR

At a constant pressure the graph plotted between the x/m (extent of adsorption) and temperature T is known as adsorption isobar. For the physical and chemical adsorption, the adsorption isobar can be represented as:
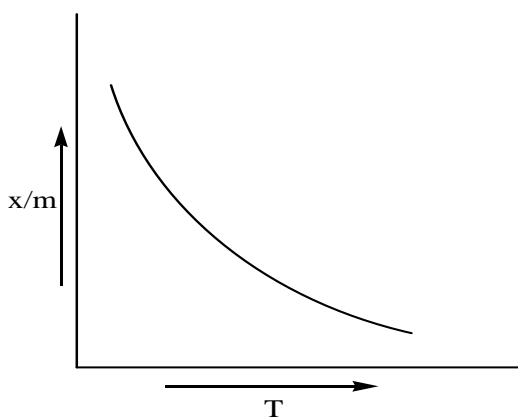
Adsorption isobar in physical adsorption
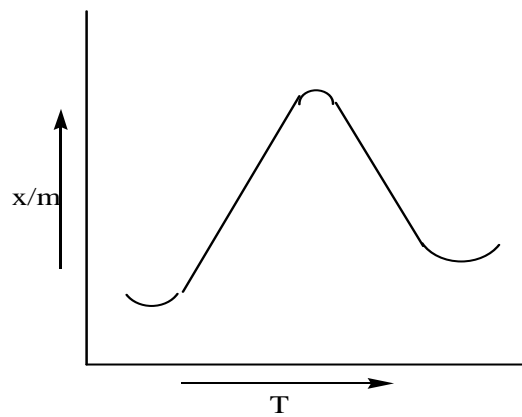
Adsorption isobar in physical adsorption

Where χ = Amount of the adsorbate at the adsorbent or m = Surface mass of the adsorbent.

Explanation: Physical adsorption require negligible amount of the activation energy due to which the physical adsorption can occur at the complete adsorbent surface at the very low temperature without providing the energy and with the increase in the in the temperature there occur the desorption by which the value of x as well as x/m will be decreases with the increase in the Temperature. While on the other hand chemical adsorption require a certain amount of activation energy due to which when the temperature increases then the increased temperature can provide the required activation by which the chemical adsorption is increases with the increase in the temperature but after a certain time interval when the complete adsorbent surface is adsorbed then the increase temperature can provide a certain amount of energy to cause the desorption by which the chemical adsorption is decreases.

7.7 ADSORPTION ISOTHERM

At the constant temperature the graph plotted between the extents of adsorption (x/m) and pressure (P) is known as adsorption isotherm.

There are some different types of the adsorption isotherm which can be defined as:

7.7.1 Freundlich and Langmuir adsorption isotherm:

A. Freundlich adsorption isotherm: In 1909 Freundlich has been proposed an empirical equation to define the effect of pressure on the adsorption of gases molecules at the solid surface, which is known as Freundlich absorption isotherm.

According to the Freundlich adsorption isotherm equation;

$$\frac{x}{m} \propto P^{\frac{1}{n}} \quad \text{or} \quad \frac{x}{m} \propto K^{\frac{1}{n}}$$

x/m = Extent of adsorption, P = Pressure, n = integer

Where K, n = constant variable

Test of the Freundlich absorption isotherm: According to the Freundlich absorption isotherm;

$$\frac{x}{m} \propto K^{\frac{1}{n}} \dots\dots\dots\dots \quad (1)$$

Taking the Log of the this equation

$$\ln\frac{x}{m} = \ln K \ P^{1/n}$$

$$\ln\frac{x}{m} = \ln K + \ln \ P^{1/n}$$

$$ln\frac{x}{n} = \ln K + \frac{1}{n}\ln P$$

<div align="center">Or</div>

$$\ln\frac{x}{m} = \frac{1}{n}\ln P + lnK \ \dots\dots\dots\dots\dots\dots \quad (2)$$

Compare equation number (2) with state line equation

$$Y \ = \ m \ x \ + \ C$$

Then,
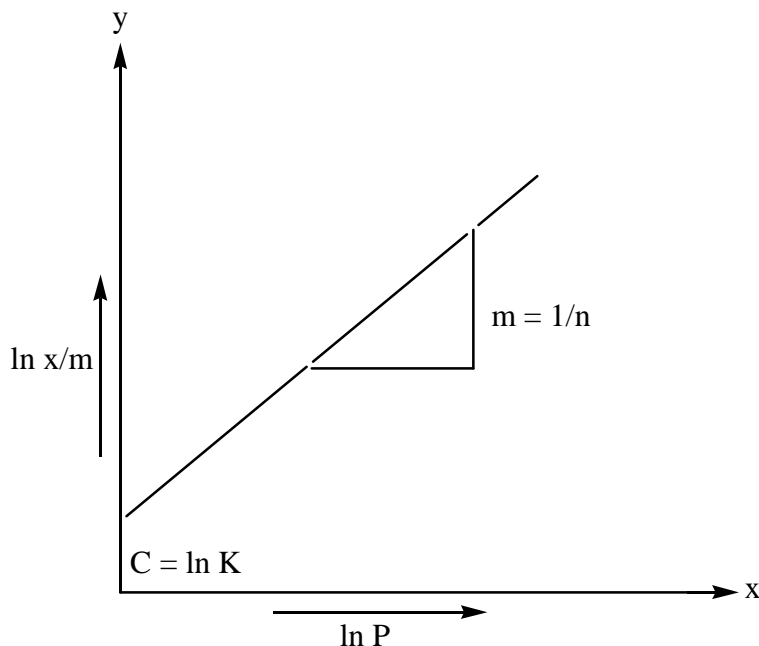
Fig. Freundlich absorption isotherm

Fig 7.1

Limitations of Freundlich adsorption isotherm:

1) Limitations of Freundlich adsorption isotherm equation is an empirical equation which does not having the mathematical proof.

2) Limitations of Freundlich adsorption isotherm equation cannot completely applicable at very low or high pressure.

Langmuir adsorption isotherm:

After the failure of Langmuir adsorption isotherm equation Langmiur has been proposed isotherms which define the adsorption of the gases molecule at the solid surface which is known as Langmuir adsorption isotherm.

Some of the postulates related with the Langmuir adsorption isotherm are given below.

1) According to the Langmuir when the gases molecule comes in the contact of solid surface then initially there occurs the formation of unimolecular layer at the solid surface. Bimolecular or multimolecular layer can also be formed at the solid surface by the Vander Waal attraction force but Langmiur does not consider the formation of bimolecular or multimolecular layer.

2) According to the langmiur when the gases molecules comes in the contact of solid surface then two types of the opposing process can occur at the solid surface which are known as

adsorption (condensation) and desorption (evaporation). Initially rate of the condensation being very high and rate of vaporization being very low but with the passes of time rate of condensation being decreases and rate of evaporation is increases, after a certain time interval both become equal to each other, this condition is known as adsorption equilibria.

Thus at the adsorption equilibria

$$\textit{Rate of condensation} \quad = \quad \textit{Rate of evoporation}$$

Derivation:

Suppose total surface area of adsorbent $= 1 \text{ cm}^2$

Surface area already covered $= \theta \text{ cm}^2$

Remaining surface area for adsorption $= (1-\theta) \text{ cm}^2$

Number of gases molecules striking at the surface $= n$

Fraction of the molecules adsorbed at the surface $= \alpha$

No. of adsorbing molecule $= n\,\alpha$

Then,

Rate of condensation $= (1-\theta)\, n\, \alpha$

Rate of evaporation $\propto \theta$

$$= K\,\theta$$

At adsorption equilibria,

Rate of condensation = Rate of evaporation

$(1-\theta)\, n\, \alpha = K\theta$

$n\alpha - n\,\alpha\,\theta = K\theta$

$n\alpha = K\theta + n\alpha\theta$

$n\alpha = \theta(K + n\alpha)$

$\theta = n\alpha / K + n\alpha$

$\dfrac{1}{\theta} = K + n\alpha / n\alpha$

$\dfrac{1}{\theta} = \dfrac{k}{n\alpha} + 1$

Since according to postulates of kinetic gas theory;

$n \propto P$

$n = \beta P$

so

$$\frac{1}{\theta} = \frac{K}{\alpha \beta P} + 1$$

$$\frac{K}{\alpha \beta} = \frac{1}{K'}$$

Then,

$$\frac{K}{\theta} = \frac{1 + K'P}{K'P}$$

$$\theta = \frac{K'P}{1 + K'P} \quad \ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

According to Langmiur,

$$\frac{x}{m} \propto \theta$$

$$\frac{x}{m} = K_2 \, \theta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

Putting θ from equation (1) to (2)

$$\frac{K}{m} = \frac{K_2 K'P}{1 + K'P} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots ..(3)$$

Case I: If P = very high

Then K'P>>> 1 or 1+K'P ~K'P

So $\frac{x}{m} = K_2 \ (Constant)$

Case II: If P = very low

1>>> K'P

Or 1+K'P ~1

so $\frac{x}{m} = K_2 K'P/1$

or $\frac{x}{m} \propto P$

Case III: At the average pressure range,

Langmiur adsorption isotherm equation behaves as like to Freundlich adsorption isotherm i.e.

$$\frac{x}{m} \propto P^{1/n}$$

According to Langmiue diagrammatic representation of all the above three different cases can be given as:
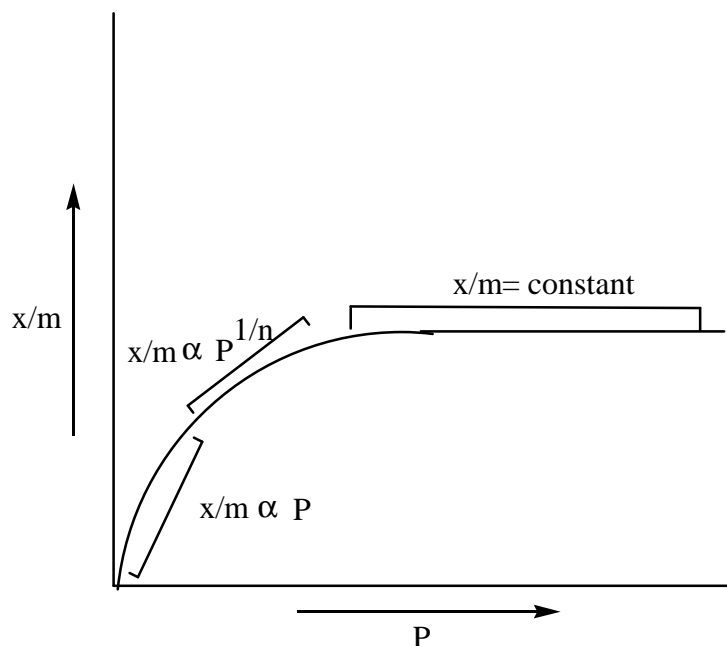
Fig. Langmiur adsorption isotherm

Fig. 7.2

7.8 CHARGES ON THE COLLOIDAL PARTICLES

The particles of a colloidal solution possess a definite electrical charge, either positive or negative. Due to the presence of the same charge, they repel each other and do not combine to form larger particles. This keeps them dispersed in the medium, and hence, a colloidal solution is stable.

Based on the nature of the charge on the colloidal particles, colloidal solutions are classified as positively charged or negatively charged sols.

Hydrated metallic oxides, like $Al_2O_3.xH_2O$, $Fe_2O_3.xH_2O$ and $Cr_2O_3.xH_2O$, and basic dyes like methylene blue, form positively charged sols.

Starch solution, metal sols like copper sol and gold sol, metal sulphide sols and acid dyes like Congo red, are examples of negatively charged sols.

A list of some common sols with the nature of charge on their particles is given below:

Positively charged sols	Negatively charged sols
Hydrates of metallic oxides, e.g., $Al_2O_3.xH_2O$, $CrO_3.xH_2O$ and $Fe_2O_3.xH_2O$, etc.	Metals, e.g., copper, silver, gold sols.
Hemoglobin (blood)	Acid dye stuffs, e.g., eosin, congo red sols.
Oxides, e.g., TiO_2 sol.	Sols of starch, gum, gelatin, clay, charcoal, etc.

The electrical charge on colloidal particles may be due to several reasons. These include electron capture by the colloidal particles during electro-dispersion of metals, preferential adsorption of ions from the solution, and the formation of an electrical double layer.
The combination of two layers of opposite charges around a colloidal particle is called the "Helmholtz electrical double layer."

The presence of equal or similar charges on colloidal particles is highly responsible in providing stability to the colloidal solution, because the repulsive forces between charged particles having same charge prevent them from aggregating when they come closer to one another.

7.9 SIZE OF THE COLLOIDAL PARTICLES

A colloidal dispersion comprises a collection of small particles, droplets, or bubbles of one phase, having at least one dimension between about 1 and 1000 nm, and dispersed in a second phase. Either or both phases may be in gas, liquid, solid or supercritical phase states.

Simple colloidal dispersions are two-phase systems, comprising a dispersed phase of small particles, droplets or bubbles, and a dispersion medium (or dispersing phase) surrounding them. Although the classical definition of colloidal species (droplets, bubbles, or particles)

specifies sizes of between one nanometer and one micrometer, in dealing with practical applications the upper size limit is frequently extended to tens or even hundreds of micrometers. For example, the principles of colloid science can be usefully applied to emulsions whose droplets exceed the 1 mm size limit by several orders of magnitude. At the other extreme, the field of nano- technology is pushing the lower size limit for organized structures below 1 nm. To give some idea of the sizes involved here, the diameter of a human blood cell is about 7500 nm (7.5 mm) that of an individual hemoglobin molecule is about 2.8 nm, while that of an oxygen molecule is about 0.16 nm.

7.10 PERRIN'S METHOD OF DETERMINATION OF THE AVOGADRO'S NUMBER

According to the Perrin's method when the substance is dissolved in the medium like H_2O then molecules of the substance in the medium can behave as a gas molecule and concentration of the molecules at the lower level in the medium being higher than the concentration in the upper level due to the gravitational force.

The value of potential energy for the molecule at the two different height as well as potential energy difference between these two levels can be given as:

$E_1 = mgh_1$

$E_2 = mgh_2$

$E = mg (h_2-h_1)$

For N_A number of molecules,

$$E = N_A \, mg \, (h_2-h_1) \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

According to Boltzmann vertical distribution law,

$$\frac{n2}{n1} = e^{-E/RT} \ \ldots\ldots\ldots\ldots\ldots(2)$$

Taking log of this equation

$$log_e \frac{n2}{n1} = log_e \, e^{-E/RT}$$

$$log_e \frac{n2}{n1} = -\frac{E}{RT} \ldots\ldots\ldots\ldots\ldots(3)$$

Putting E from equation (1) to (2)

$$log_e \frac{n2}{n1} = -NAmg \frac{h2-h1}{RT}$$

If the density of medium and species are e and e' respectively,

Then,

$$log_e \frac{n2}{n1} = NAmg \frac{h2-h1}{RT}\left(1-\frac{e}{e'}\right)$$

$$ln \frac{n2}{n1} = NAmg \frac{h2-h1}{RT}(e-e'/e')$$

Since m/e'= V

$$ln \frac{n2}{n1} = NAmg \frac{h2-h1}{RT}(e-e')$$

Or

$$\frac{RT}{NA} ln \frac{n2}{n1} = Vg \frac{h2-h1}{RT}(e'-e)\ldots\ldots\ldots(4)$$

If all the variables being given than the value of N_A can be calculated by the above equation and its value comes approx equal to the 6.023×10^{23} and known as Avogadro number.

7.11 SUMMARY

Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a solid resulting into a higher concentration on the surface than in the bulk. The substance adsorbed is called as adsorbate and the substance on which adsorption takes place is called adsorbent. In Physical Adsorption (physisorption), adsorbate is attracting to the adsorbent by weak force (Van der Waals forces), and in chemical Adsorption (chemisorptions), adsorbate is attracting to the adsorbent by strong chemical bond (like covalent bond, ionic bond etc.). Almost all solids substance adsorbs gases. The extent of adsorption of a gas on a solid depends upon nature of gas, nature of solid, surface area of the solid, pressure of gas and temperature of gas. The relationship between the extent of adsorption (x/m) and pressure of the gas at constant temperature is known as adsorption isotherm.

In this Chapter we talk about the phenomenon of Adsorption and its type i.e. Physisorption and Chemisorption. The factors on which the extent of adsorption of a gas on a solid are also given. Freundulich and Langmiur Adsorption Isotherm is also discussed under these factors.

7.10 TERMINAL QUESTIONS

A. Objective type Questions:

1. At the equilibrium position in the process of adsorption _____.

    (i) $\Delta H > 0$

    (ii) $\Delta H = T\Delta S$

    (iii) $\Delta H > T\Delta S$

    (iv) $\Delta H < T\Delta S$

2. The term 'Sorption' stands for

    (i) Absorption

    (ii) Adsorption

    (iii) Both adsorption and Absorption

    (iv) Desorption

3. Extent of physisorption of a gas increases with _____.

    (i) Increase in temperature.

    (ii) Decrease in temperature.

    (iii) Decrease in surface area of adsorbent.

    (iv) Decrease in strength of Van der Waals forces.

4. Which one of the following is **not** applicable to the phenomenon of adsorption?

    (i) $\Delta H > 0$

    (ii) $\Delta G < 0$

    (iii) $\Delta S < 0$

    (iv) $\Delta H < 0$

5. Which of the following is **not** a favorable condition for physical adsorption?

    (i) High pressure

    (ii) Negative ΔH

    (iii) Higher critical temperature of adsorbate

(iv) High temperature

6. Physical adsorption of a gaseous species may change to chemical adsorption with _____

> (i) Decrease in temperature

> (ii) Increase in temperature

> (iii) Increase in surface area of adsorbent

> (iv) Decrease in surface area of adsorbent

7. In physisorption adsorbent does not show specificity for any particular gas because ____

> (i) Involved van der Waals forces are universal.

> (ii) Gases involved behave like ideal gases.

> (iii) Enthalpy of adsorption is low.

> (iv) It is a reversible process.

8. Which of the following is an example of absorption?

> (i) Water on silica gel

> (ii) Water on calcium chloride

> (iii) Hydrogen on finely divided nickel

> (iv) Oxygen on metal surface

9. On the basis of data given below predict which of the following gases shows least adsorption on a definite amount of charcoal?

Gas	CO_2	SO_2	CH_4	H_2
Critical temp./K	304	630	190	33

> (i) CO_2

> (ii) SO_2

> (iii) CH_4

> (iv) H_2

10. For Freundilich isotherm a graph of log x/m is plotted against log P. The slope of the line and its y-axis intercept, respectively corresponds to

> (i) 1/n, k

> (ii) log 1/n, k

> (iii) 1/n, log k

> (iv) log 1/n, log k

B. Short Answer Type Questions:

1) Write any two characteristics of Chemisorption.

2) Why does physisorption decrease with the increase of temperature?

3) Why are powdered substances more effective adsorbents than theircrystalline forms?

4) Distinguish between the meaning of the terms adsorption and absorption. Give one example of each.

5) What is the difference between physisorption and chemisorption?

6) Give reason why a finely divided substance is more effective as an adsorbent.

7) What is an adsorption isotherm? Describe Freundlich adsorption isotherm.

8) Why is adsorption always exothermic?

9) Discuss the effect of pressure and temperature on the adsorption of gases on solids.

10) What is adsorption?

11) What is desorption?

12) What are adsorbate and adsorbent? Give an example.

13) Give two examples for adsorption.

14) Give differences between adsorption and absorption.

15) What is the effect of temperature on physical and chemical adsorption?

16) Mention any two applications of adsorption.

17) What happens to ΔH, ΔS and ΔG during the process of adsorption?

18) Write any three differences between two types of adsorption of gases on solids.

19) What are the applications of adsorption in chemical analysis?

C. Long Answer Type Questions:

1. Define the term with examples- a. Adsorption, Absorption and Sorption.

2. Discuss briefly Langmuir's adsorption isotherm

3. What is the difference between physical adsorption and chemical adsorption?

4. Discuss in detail Perrin's method for the determination the size of colloidal particles.

5. Derive the expression for Freundlich adsorption isotherm

7.13 ANSWER

1. ii, 2. iii, 3. ii, 4. i, 5. iv, 6. ii, 7. i, 8. ii, 9. iv 10. ii

Source of study material

13. Essential of physical chemistry by Bahl, Bahl and Tuli.

14. Principles of physical chemistry By Puri, Sharma and Pathania.

15. Physical chemistry By   P.C. Rakshit.

16. Physical chemistry By Atkins.

UNIT -8 ELECTROCHEMISTRY-I

CONTENTS:

8.1 OBJECTIVES

Most chemical reactions occur in solution. The study of such solutions constitutes one of the most important branches of physical chemistry. If we analyze the solubility of solutes in various solvents, we find that the polar solutes are more soluble in polar solvents whereas non polar solutes are soluble in non polar solvents. The general principle of solubility is like dissolves like. We see sodium chloride is soluble in water but it is insoluble in carbondisulphide or carbontetrachloride. The compounds which conduct electricity when dissolved in water or in the molten state are called electrolytes. Sodium chloride, copper sulphate etc are example of electrolytes. The substances which do not conduct electricity under these conditions are called non electrolytes.

8.2 INTRODUCTION

Substances like mica, wax, glass ebonite etc. strongly resist the flow of electricity and practically do not allow any current to flow through them. These substances are called non-conductors. On the other hand there are substances such as copper, silver, mercury, water solutions of salts acids etc. through which electric current can easily pass; these are called conductors. The conductors are broadly classified into two categories: (i) electric conductors or metallic conductors and (ii) electrolytic conductors or electrolytes.

Electronic conductors are included the metals, alloys, graphite etc. in which the electricity is carried exclusively by the transport of electrons. The electrons flow from a higher negative potential to a lower one; there is no transport of matter during the passage of electricity.

In electrolytes the flow of current is accompanied with actual transfer or migration of matter. Such transfer of matter leads to the decomposition of matter at the points where electricity enters or leaves the electrolyte and in the process helps in the transfer of electrons.

The electrolytes are solutions of salts, acids, bases usually in water. The conducting capacity of different electrolytes is different.

The word electrolysis can be split and resulting word –electro (meaning-electricity i.e. flow of electrons and lysis (meaning – pertaining to) explain the word completely.

8.3 ELECTRICAL TRANSPORT:

8.3.1 Conduction in metal and in electrolyte solution:

Metal in general allow an electric current to pass through and are called conductors of electricity. The phenomenon of an electrolyte by passing electric current through its solution is termed electrolysis. The process of electrolysis is carried in an apparatus called the electrolytic cell. The cell contains water-solution of an electrolyte in which dip two metallic rods, Electrodes. These rods are connected to the two terminals of a battery which is source of electricity. The electrode connected to the positive terminal of the battery attracts the negative ions (anions) and is called anode. The other electrode connected to the negative end of the battery attracts the positive ions (cations) and is called cathode.

### 8.3.1.1 Mechanism of electrolysis:

The process of electrolysis actually taking place is shown in fig 8.1. The cations migrate to the cathode and form a neutral atom by accepting electrons from.
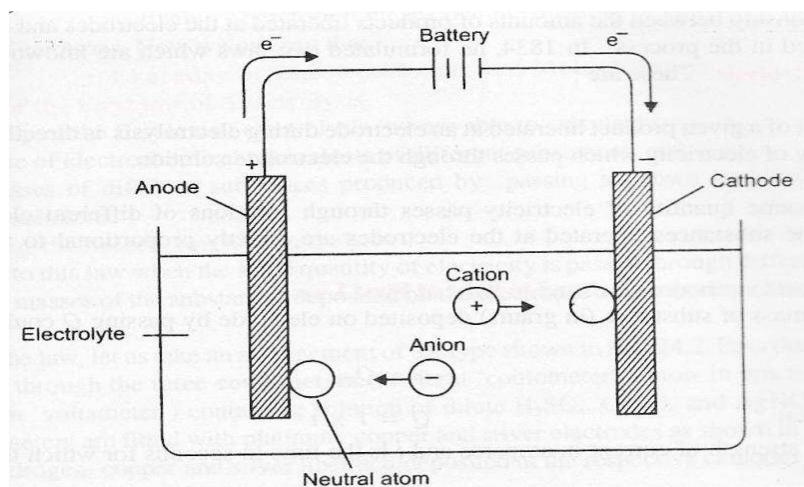
Fig 8.1 The mechanism of electrolysis

The anions migrate to the anode and yield a neutral particle by transfer of electrons to it. As a result of the loss of electrons by anions and gain of electrons by cations at their respective electrodes, chemical reaction takes place.

Let us consider the electrolysis of hydrochloric acid. In solution hydrochloric acid is ionised.

$$HCl \longrightarrow H^+ + Cl^-$$
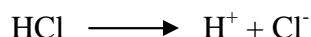
In the electrolytic cell Cl^- ions will move towards the anode and the H^+ ions will move toward the cathode. At the electrode, the following reaction will take place.

At cathode:

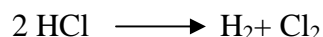$$H^+ + e^- \longrightarrow H \text{ (reduction)}$$

You see each hydrogen ion picks up an electron from the cathode to become a hydrogen atom. Paris of hydrogen then unite to form a molecule of hydrogen gas H_2.

At anode

$$Cl^- \longrightarrow Cl + e^- \text{ (oxidation)}$$

After the chloride ion loses its electron to the anode, pairs of chlorine atoms unite to form chlorine gas, Cl_2.

The net effect of the process is the decomposition of HCl into hydrogen and chlorine gases. The overall reaction is

$$2\ HCl \longrightarrow H_2 + Cl_2$$

	Cathode	Anode
Ions attracted	Cations	Anions
Direction of electron	Into cell	Out of cell
Movement		
Half reaction	Reduction	Oxidation
Sign	-ve; since it is attached	+ve; since it is attached
	to the –ve end of battery	to the +ve end of battery

Table 8.1 Description of the cell

Electrolytes obey Ohm's law, to the same extent as the metallic conductors. According to this law the current I flowing through a conductor is given by the relation I=E/R, where E is the

electromotive force i.e., the difference of potential at the two ends of the conductor, and R is resistance

$$I = E/R$$

Electric units:

There are a few electrical units which you should understand before taking up the study of quantitative aspects of electrolysis. These are:

Amperes: Current strength is generally expressed in amperes. The ampere is defined as the current which deposits 0.00118 gram of silver per second from a 15 per cent solution of silver nitrate in a coulometer. Or we can say an ampere is a current of one coulomb per second.

Coulomb: The quantity of electricity passing through a conductor is the product of current strength and time and is generally expressed in coulombs. A coulomb is a unit quantity of electricity. It is the amount of electricity which will deposit 0.001118 gram of silver from 15 per cent solution of silver nitrate in a coulometer.

Ohm: The unit of electrical resistance is ohm. It is the resistance offered at 0^0C to a current by a column of mercury 106.3 centimeter long of about one square millimeter cross-sectional area and weighing 14.454521 grams.

Volt: A volt is a unit of electromotive force. It is the difference in electrical potential required to send a current of one ampere through a resistance of one ohm.

Faraday's law of electrolysis:

Faraday discovered that there exists a definite relationship between the amounts of products liberated at the electrodes and the quantity of electricity used in the process. He formulated two laws in 1834, which are known as Faraday's law of electrolysis. The laws are as follows

Faraday's first law of electrolysis:

The amount of a given product liberated at an electrode during electrolysis is directly proportioned to the quantity of electricity which passes through the electrolytic solution.

Faraday's second law of electrolysis:

When the same amount of electricity passes through solutions of different electrolytes, the amount of substance liberated at the electrodes are directly proportional to their chemical equivalents.

These two laws have been shown to hold very rigidly provided the passage of electricity takes place entirely by electrolytic conduction. It applies to molten electrolytes as well as to solution of electrolytes and is independent of temperature, pressure or nature of solvent.

If m is the mass of substance deposited on electrode by passing Q coulombs of electricity, then

$$m \propto Q$$

But Q=Ixt

Where I is the strength of current in amperes and t is time in seconds for which current has been passed.

Therefore,   m $\propto$ Ixt

or   m= zxIxt

Here z is constant known as electrochemical equivalent of the electrolyte. If I=1 ampere and t=1 second then

m=z

from this it follows that, electrochemical equivalent is amount of substance deposited by one ampere current passing for one second (i.e., one coulomb)

It has been found that the quantity of electricity required to liberate one gram equivalent of substance is 96,500 coulombs. This quantity is known as Faraday and is denoted by the symbol F.

It is clear that the quantity of electricity to deposit one mole of substance is given by the expression,
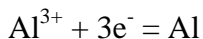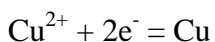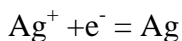
Quantity of electricity= nxF

Where n is the valence of the ion. Thus the quantity of electricity required to discharge.

one mole of Ag^+ $= 1xF = 1F$

one mole of $Cu^{2+} = 2xF = 2F$

one mole of $Al^{3+} = 3xF = 3F$

We can represent the reaction on the cathode as:

$Ag^+ +e^- = Ag$

$Cu^{2+} + 2e^- = Cu$

$Al^{3+} + 3e^- = Al$

It is clear that the moles of electrons required to discharge one mole of ions Ag^+, Cu^{2+} and Al^{3+} is one, two and three respectively. It means that the quantity of electricity in one Faraday is one mole of electrons. Now we can say

1 Faraday = 96500 coulombs= 1 mole electrons

Verification of the second law of electrolysis:

Faraday's second law states that when same quantity of electricity is passed through different electrolyte solutions, the masses of the substances deposited on the electrodes are proportional to their chemical equivalents.

To verify this law, let us take the arrangement of the type shown in fig. 8.2. Now pass the same amount of electricity through the three coulometers containing solutions of dilute sulphuric acid (H_2SO_4), copper sulphate ($CuSO_4$) and silver nitrate ($AgNO_3$) respectively. These coulometers are fitted with platinum, copper and silver
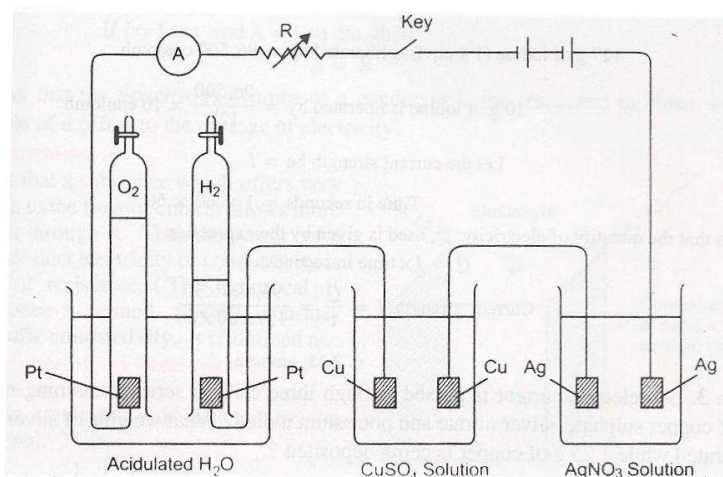
Fig. 8.2 Verification of Faraday's second law of electrolysis

electrodes as shown in fig. 8.2. The masses of hydrogen, copper and silver liberated/ deposited at the respective cathodes are in the ratio of their equivalent weights. That is

$$\frac{\text{mass of hydrogen liberated}}{\text{mass of copper deposited}} = \frac{\text{equivalent weight of hydrogen}}{\text{equivalent weight of copper}}$$

and

$$\frac{\text{mass of copper deposited}}{\text{mass of silver deposited}} = \frac{\text{equivalent weight of copper}}{\text{equivalent weight of silver}}$$

From this experiment, we can calculate the mass of hydrogen, copper and silver liberated at their respective cathodes by one coulomb of electricity. We find these are always

Hydrogen   = 0.00001036 g

Copper   = 31.78x0.00001036 = 0.0003292 g

Silver = 107.88x0.00001036   = 0.001118 g

Since the equivalent weights of hydrogen, copper and silver are 1. 31.78 and 107.88 g respectively, it follows that the electrochemical equivalents are proportional to chemical equivalents (or equivalent weights).

Faraday's second law of electrolysis helps to calculate equivalent weights of metals, the unit of electrical charge and the Avogadro number.

Examples:

(i) 0.1978 g of copper is deposited by a current of 0.2 ampere in 50 minutes. What is the electrochemical equivalent of copper?

Solution: Given t= 50x60 = 3000 seconds, I= 0.2 amperes, quantity of electricity used Q= Ixt = 3000x0.2 = 600 coulombs

Amount of copper deposited by 600 coulombs   = 0.1978 g

Amount of copper deposited by one coulombs   = 0.1978/600

                                                   = 0.0003296 g

This is chemical equivalent of copper

(ii) Calculate the current strength in amperes required to liberate 10 g iodine from potassium iodide solution in one hour. Equivalent weight of iodine in 127.

Solution:

$$127 \text{ g of iodine is liberated by} \qquad 96500 \text{ coulombs}$$

$$1 \text{ g of iodine will be liberated by} \qquad \frac{96500}{127} \text{ coulomb}$$

$$10 \text{ g of iodine will be liberated by} \qquad \frac{96500}{127} \times 10 \text{ coulombs}$$

Let the current strength be I

Time in seconds = 60x60 seconds

The quantity of electricity is given by Q=Ixt

I= Q/t = 96500x10

                    127x60x60

                    = 2.11 amperes

8.3.2 Electrolytic conduction:

From the above discussion it is clear that the flow of electricity through solutions of electrolytes is due to the migration of ions when potential difference is applied between the two electrodes. The power of electrolytes to conduct electrical currents is formed conductivity or conductance. It is defined as the reciprocal of resistance (R) of solution. Like metallic conductors, electrolytes obey Ohm's law. According to this law the current I flowing through a metallic conductor is given by the relation.

I= E/R

Where E is the potential difference at two ends (in volts); and R is the resistance measured in ohms (or Ω). The resitance R of a conductor is directly proportional to the length l and inversely proportional to the area of cross-section, A. That is

R $\propto \frac{l}{A}$

or R= $\rho \frac{l}{A}$ ………………………(8.1)

where ρ "rho" is a constant of proportionality and is called resistivity or specific resistance. Its value depends upon the material of the conductor. From (8.1) we can write

$$\rho = Rx\frac{A}{\rho}$$

If $\rho = 1\ cm\ and\ A = 1\ sq.cm,\ then$

ρ=R

It means that the specific resistance of a conductor is the resistance in ohms which one centimeter cube of it offers to the passage of electricity. The reciprocal of specific resistance, i.e., 1/ ρ is called specific conductance.

Specific conductance:

It is evident that a substance which offers very little resistance to the flow of current allows more current to pass through it. Thus the power of a substance to conduct electricity is the

converse of resistance. The reciprocal of specific resistance is termed specific conductance or specific conductivity. Hence,

The conductance of one centimeter cube (cc) of a solution of electrolyte is specific conductance (fig. 8.9). It is denoted by the symbol κ (kappa). Thus
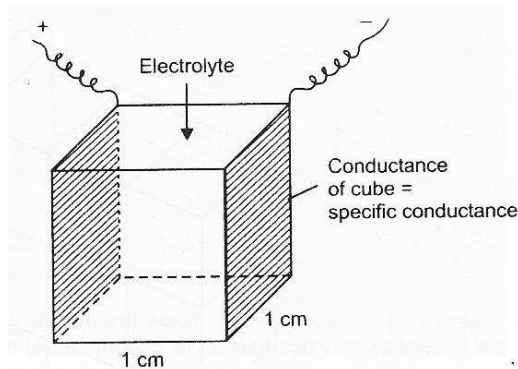

Fig. 8.3 specific conductance

$$\kappa = \frac{1}{\rho} = \frac{1}{R} x \frac{l}{A}$$

Unit of specific conductance:

Specific conductance is generally expressed in reciprocal ohms (r.o.) or mhos or ohm^{-1}. Its unit can be derived as follows:

$$= \frac{1}{A} \cdot \frac{R}{R} = \frac{1}{cm^2} x \frac{cm}{ohm}$$
$$= ohm^{-1} cm^{-1}$$

The internationally recommended unit for ohm^{-1}(or mho) is Siemens. When s is used the conductance is expressed as s cm^{-1}. The Siemens unit is named after Sir Willian Siemens, who was a noted electrical engineer.

The specific conductance increases with: (i) ionic concentration, and (ii) speeds of the ions concerned.

In measuring the specific conductance of aqueous solution of an electrolyte, the volume of water in which certain amount of water electrolyte is dissolved is always measured in cubic

centimeters and is known as dilution. If the volume of the solution is vcc, the specific conductance of the solution is written as κv.
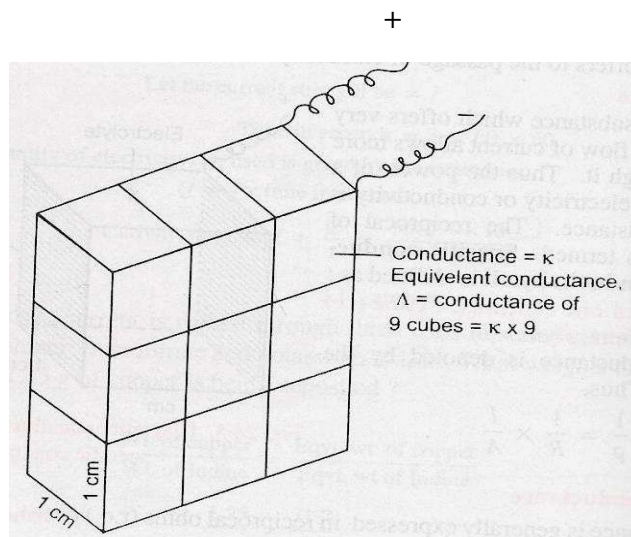
Equivalent conductance:

Specific conductance, although a suitable property for characterizing metallic conductance, is not so for characterizing electrolytic conductance where the value, amongst other things, depends upon the concentration of the solution of the electrolyte as well. While measuring conductance of electrolytes in solutions, another quantity of much greater significance, known as equivalent conductance, is frequently used.

Equivalent conductivity is the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by Λ. It is equal to the product of the specific conductance, κ and the volume V in cc containing one gram-equivalent of the electrolyte at the dilution V.

Thus $\Lambda = \kappa.V$

This is shown in fig 8.4. A solution having one gram-equivalent water between electrode placed 1 cm apart has $\Lambda = \kappa \times 9$

Fig 8.4 solution of 1 g-equivalent dissolved in 9cc of the electrolyte dissolved in, say, 9cc water be placed between two electrodes. 1 cm. apart.

The solution could be considered as consisting of nine cubes, each of which has a conductance κ (specific conductance). Thus the total conductance of the solution will be 9 x κ. Similarly, Vcc of solution will form V cubes and the total conductance will be κ xV.

If an electrolyte solution contains N gram equivalents in 1000cc of the solution, the volume of the solution containing 1 gram-equivalent will be 1000/N. Hence

$$\Lambda = \frac{\kappa \, 1000}{N}$$

The unit of equivalent conductance may be deduced as follows

$$\Lambda = \kappa x V$$

$$= \frac{1}{R} \cdot \frac{l}{A} \; x \; V$$

$$= \frac{1}{ohm} x \frac{cm}{cm_2} x \frac{cm_3}{eqvt}$$

$$= ohm^{-1} \; cm^2 \; eqvt.$$

Molar conductance:

Some times molar conductance is helpful in comparing conductances of electrolytes. It is defined as:

The conductance of all ions produced by one mole (one gram-molecular weight) of an electrolyte when dissolved in a certain volume Vcc is known as molecular conductance. It is denoted by μ, the value of molecular conductance is obtained by multiplying the specific conductance, κ by the volume in κ containing one mole of electrolyte.

Molar conductance $\mu = \kappa x V$. Here V is the volume of the solution in cc which contains one mole of the electrolyte.

Since $\kappa = \frac{1}{R} x \frac{l}{A}$

$$\mu = \frac{1}{R} x \frac{l}{A} x \; V$$

$$= \frac{1}{ohm} x \frac{cm}{cm2} x \frac{cm3}{mol}$$

$$= ohm^{-1} \; cm^2 \; mol^{-1}$$

Effect of dilution on specific conductance, equivalent conductance and molecular conductance:

Specific conductance is the conductance of one centimeter cube of a solution of an electrolyte. If we dilute the solution the specific conductance decreases. On diluting the solution the concentration of ions per cc decreases. Hence the specific conductance decreases. But the equivalent conductance and molar conductance increases with dilution. This is because equivalent conductance and molar conductance are the product of specific conductance and the volume of the solution containing one gram-equivalent or one mole of the electrolyte respectively. With dilution specific conductance decreases while volume increases. The increase in the second factor is much more than the decrease in the first factor. Also on dilution more and more electrolyte dissociates into ions and hence equivalent conductance and molecular conductance increases.

Volume, V in cc containing 1 g mol	Specific conductance, $ohm^{-1} cm^2 eqvt^{-1}$	Molar conductance $ohm^{-1} cm^2 mol^{-1}$
1,000	0.0744	74.4
5,000	0.01760	88.2
20,000	0.0479	95.9
500,000	0.000213	106.7
1,000,000	0.0001078	107.3
2,000,000	0.0000542	108.5
5,000,000	0.0000218	109.2
10,000,000	0.00001097	109.7

Table 8.2 specific and molar conductance of NaCl solution at 18^0C Strong and weak electrolytes:

Strong and weak electrolytes:

There are two classes of electrolytes, depending upon their ionisation

(i) Strong electrolytes

(ii) Weak electrolytes

Strong electrolytes:

A strong electrolyte is a substance that gives a solution in which almost all the molecules are ionized. Strong electrolytes have a high value of equivalent conductance even at low concentration. HCl, H_2SO_4, HNO_3, $HClO_4$, HI, HB_r, NaOH, KOH, Ca (OH) $_2$, Mg (OH)$_2$ and almost all salts are examples of some strong electrolytes.

Weak electrolytes:

A weak electrolyte is a substance that gives a solution in which only a small proportion of the solute molecules are ionized. Such solution is called a weak electrolytic solution. That has low value of equivalent conductance.

All organic acids such as acetic acid, oxalic acid; most organic bases and a few salts such as mercury chloride and lead acetate are some examples of weak electrolytes.

8.3.3 Measurement of electrolytic conductance:

As you know that conductance is the reciprocal of resistance, hence it can be determined by measuring the resistance of the electrolytic solution. This can be measured with the help of a Wheatstone bridge. The solution whose conductance is to be determined is placed in a special type of cell known as the conductivity cell.

Conductivity cell and cell constant:

The vessel in which the measurement of conductivity of solution is to be made is known as conductivity cell. They are of various shapes and sizes depending upon the nature of the solution taken. A simple type of conductance cell used in the laboratory is shown in fig 8.5. The electrodes fitted in the cell are made of platinum plates coated with platinum black. These are welded to platinum wires fused in two thin glass tubes. The contact with copper wires of the circuit is made by dipping them in mercury contained in the tube.
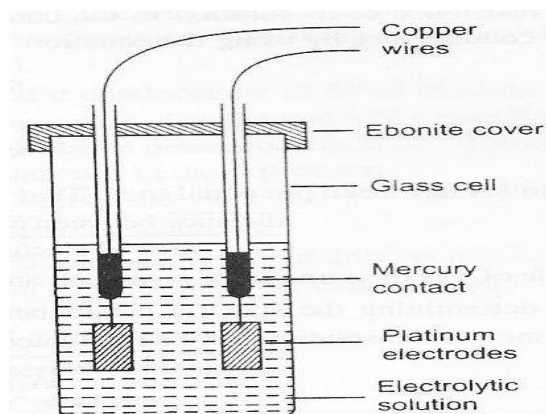

Fig 8.5 conductivity cell

The arrangement commonly used for the measurement of resistance of the conductivity cell is shown in fig 8.6. When a direct current is passed through a solution, the following two difficulties arise:

(i)   The electrodes are polarized i.e. the product of the electrolysis accumulate on them.

(ii)   The passage of current involves the decomposition of a portion of the solute so the concentration of this substance changes during passage electric current.

In order to remove these difficulties, we use alternating current in place of direct current. In this case galvanometer is replaced by head-phone. AB is a mangnin wire tightly stretched over a meter rule graduated in millimeters. A sliding contact G moves along this wire. R is resistance box. S is induction coil from which alternating current is led as shown in the fig 8.6. A conductivity cell containing the experimental electrolyte is attached in the bridge as shown.
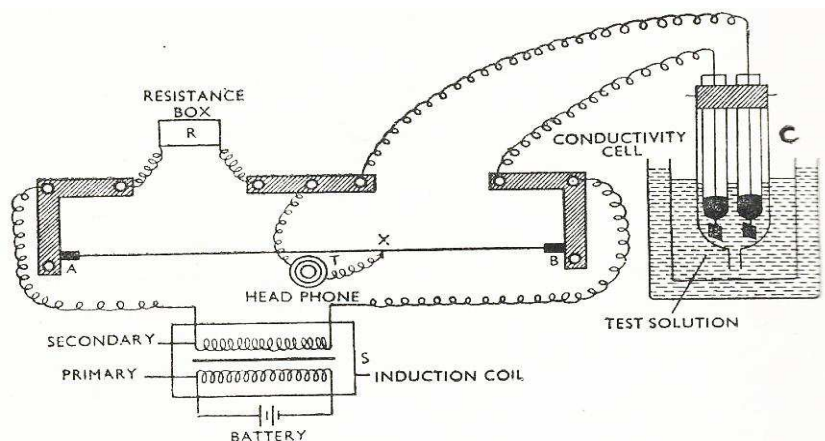
Fig 8.6 Apparatus for measuring conductivity

The sliding contact is moved slowly along the wire AB, till a point x is reached at which the potential becomes equal to that of R. under such condition, no current will flow through the head-phone and it will be silent. At all other points, a buzzing sound can be heard in the head-phone. In actual practice, it is not usually possible to obtain complete silence in the head-phone, so the point of minimum sound is taken as the null point of the experiment. When this occurs we have

$$\frac{resistance\ of\ C}{Resistance\ of\ R} = \frac{resistance\ of\ BX}{resistance\ of\ AX} = \frac{length\ BX}{length\ AX}$$

or Resistance of c = $\dfrac{length\ of\ BX}{length\ of\ AX}$ x resistance of R

The resistance of a solution in the conductivity cell as measured above can be converted to specific conductance by using the equation

$$K = \frac{1}{R} \cdot \frac{l}{A}$$

$$= \frac{1}{R} \cdot x$$

The ratio $\dfrac{l}{A}$ has been put equal to x, that is,

$$\frac{distance\ between\ the\ electrodes}{area\ of\ the\ electrodes} = x\ (cell\ constant)$$

The value of x is the same for a given cell and is called the cell constant.

After determining the specific conductance, κ the equivalent conductance, Λ and the molar conductance μ of the solution can be calculated by using the expression

$$\Lambda = \frac{\kappa \times 1000}{N}$$

and $\quad \mu = \dfrac{\kappa \times 1000}{M}$

where N is the gram-equivalent and M is the gram-mole do the electrolyte.

Determination of cell constant:

The exact value of cell constant (l/A) can be determined by measuring the distance between the electrodes (l) and the area of cross section (A). Actual measurement of these dimensions is very difficult. Therefore an indirect method is employed to determine the value of cell constant.

We know that:

Specific conductance $\kappa = \dfrac{1}{R} x \dfrac{l}{A}$

κ = observed conductance x cell constant

Hence cell constant = $= \dfrac{specific\ conductance}{observed\ conductance}$

To determine the cell constant, a standard solution of KCl whose specific conductance at a given temperature is known, is used. Then a solution of KCl of the same strength is prepared and its conductance determined experimentally at the same temperature. Substituting the two value in the above expression, the cell constant can be calculated.

Examples:

(i) Specific conductance of a decimolar solution of potassium chloride at 18^0C is 1.12 mho. The resistance of a conductivity cell containing the solution at 18^0C was found to be 55 ohm. Calculate the cell constant.

Solution:

R= 55 ohm, conductivity= 1/55 mho, κ=1.12 mho

Cell constant $= = \dfrac{1.12}{1/55} = 61.6$

(ii) The resistance of a decinormal solution of a salt-occupying a volume between two platinum electrodes 1.80 cm apart and 5.4 om^2 in area was found to be 320 ohms. Calculate the equivalent conductance of the solution.

Solution:

Given l=1.80 cm and A=5.4 cm^2

Hence cell constant $\kappa = \dfrac{l}{a} = \dfrac{1.80}{5.4} = \dfrac{1}{3}$

Observed conductance $= \dfrac{1}{32}$ mhos

Since the solution is $\dfrac{N}{10}$,   V= 10,000 ml

Specific conductance $= \kappa$ x observed conductance

$$= \dfrac{1}{3} x \dfrac{1}{32} = \dfrac{1}{96} \text{ mhos}$$

$\Lambda = \kappa$ x V $= \dfrac{1}{96}$ x 10,000 = 104.1 mhos cm^2 equiv^{-1}

8.4 ARRHENIUS THEORY OF IONIZATION

Arrhenius studies the conduction of current through water solutions of electrolytes. He came to believe that the conductivity of solutions was due to the presence of ions. In 1884 he put forward his theory of ionization. Arrhenius theory of ionization may be stated as:

(i)   When dissolved in water neutral electrolyte molecules are split up into two types of charged particles. These particles are called ions and the process was termed ionization.

The positively charged particles are called cations and the negatively charged ions were called anions.

The theory in modern form assumes that the ions are already present in the solid electrolyte and these are held together by electrostatic forces. When placed in water these neutral molecules to form separate anions and cations. Thus,

$$AB \longrightarrow A^+ + B^- \text{ old view}$$

$$A^+B^- \longrightarrow A^+ + B^- \qquad \text{modern view}$$
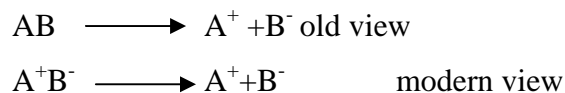
(ii)   The ions present in the solution constantly unite to form neutral molecules. Thus there is state of equilibrium between the undisassociated molecules and the ions

$$AB \rightleftharpoons A^+ + B^-$$

Applying to law of Mass Action to the ionic equilibrium we have,

$$\frac{[A^+][B^-]}{[AB]} = K$$

Where K is called the dissociation constant

(iii)   These charged particles are free to move through the solution to the oppositely charged electrode. This movement of ions constitutes the electric current through electrolytes. This explains the conductivity of electrolytes as well as the phenomenon of electrolysis.

(iv)   The conductivity of an electrolyte solution depends on the number of ions present in the solution. Thus the degree of dissociation of an electrolyte determines whether it is a strong electrolyte or a weak electrolyte.

Migration of ions:

We know that electrolyte dissociate in solution to form two types of ions namely cations (positive ions) and anions (negative ions).

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$
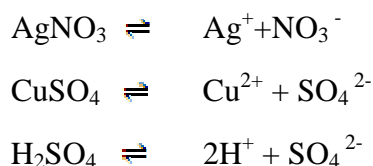
As the current is passed between the electrodes of the electrolytic cell, the ions migrate to the oppositely charged electrode. Thus in the electrolytic solution of $AgNO_3$, the cations (Ag^+) will move to the cathode and anions (NO_3^-) will move to anode.
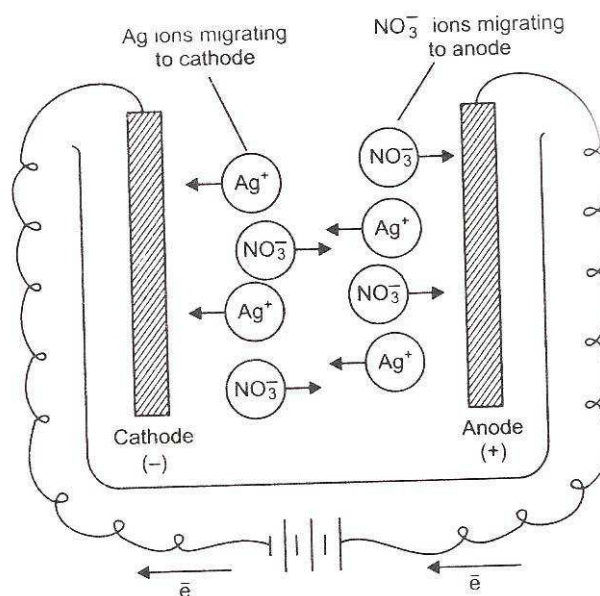
Fig 8.7 Migration of ions to opposite electrodes

The migration of ions ions through the electrolytic solution can be demonstrated the above experiment, fig 8.7.

Relative speed of ions:

From the above discussion it should be clear to you that the ions move to the oppositely charged electrode under the influence of the electric current. But the speed of the cations and anions are not necessarily the same. However, the speed of a cation moving away from the anode will be proportional to the fall of concentration of these ions at the anode. Similarly, the speed of an anion moving away from cathode will be proportional to the fall of concentration of anions around the cathode. Hittorf studied such changes experimentally and gave a general rule known as Hittorf's rule. It stated that:

The loss of concentration around any electrode is proportional to the speed of the ion moving away from it.

Studying electrolysis it is found that ions are always discharged in equivalent amount on the opposite electrodes. It is really due to the difference in the speeds of anions and cations that the changes in concentration around electrodes are caused. We also conclude that the loss in concentration around any electrode is proportional to the speed of the ion moving away from it. This is known as Hittorf's rule. Thus:

Fall in concentration around anode α speed of cation $v+$ and fall in concentration around cathode speed of anion $v-$.

Here $v+$ and $v-$ is the speed of cations and anions respectively. In deriving the above relation, an important assumption has been made, namely the discharged ions do not react with the material of the electrodes. In many cases they combine with the material of the electrodes rather and depositing on it. This results in an increase in concentration around such an electrode instead of decrease.

Migration speed of Ag^+ and NO_3^- ions:

Let us study the electrolysis of a solution of silver nitrate in cell using silver nitrate in a cell using silver electrodes. We find that instead of fall of concentration of silver nitrate around anode, it increases. This is due to fact that every NO_3^- ion that arrives at the anode dissolves from it one Ag^+ ion to form $AgNO_3$. If the electrodes were of platinum, the state of affairs would have been according to Hittorf's rule. With silver electrodes, however, we have the condition shown if fig 8.8
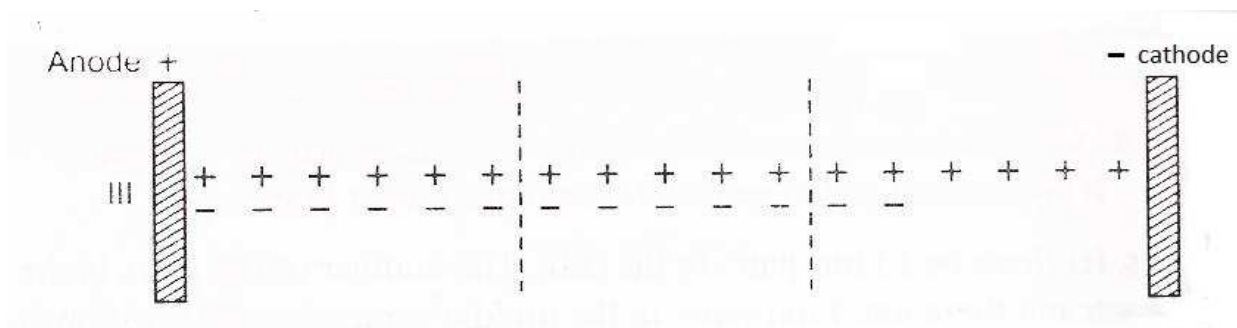
Fig 8.8 with silver electrodes concentration around the cathode falls while it increases around the anode.

8.5 TRANSPORT NUMBER

8.5.1 Definition:

From the above discussion of the Hittorf's theoretical device as discussed above, it is evident that the number of ions discharged at each electrode depends upon the sum of the speeds or nobilities of the two ions.

Since according to Faraday's first law of electrolysis the number of ions discharged at an electrode is proportional to the total quantity of electricity passed through the solution, hence it follows that the quantity of electricity carried by a particular ions is proportional to the mobility of that particular ion. The fraction of the total current carried by the cation or anion is termed its transport number or Hittorf's number.

The transport number of cation $t_+ = \dfrac{v_+}{v_+ + v_-}$

The transport number of anion $t_- = \dfrac{v_-}{v_+ + v_-}$

or $\dfrac{t_+}{t_-} = \dfrac{v_+}{v_-}$ and $t_+ + t_- = 1$

if the ratio $\dfrac{v_+}{v_-}$ is denoted by r we have, and

$\qquad r = \dfrac{t_+}{t_-} = \dfrac{t_+}{1 - t_+}$

and $t_- = \dfrac{1}{1 + r}$

8.5.2 Determination of transport number:

There are two methods for determination of transport number of an ion

  (i) Hittorf's method

  (ii) Moving boundary method.

(i) Hittorf's method:

This method is based on the concentration changes observed in the vicinity of the electrodes. According to Hittorf's rule, the loss of concentration around any electrode is proportional to the speed of the ion moving away from it. The apparatus used in this method consists of two vertical glass tubes joined together through a U-tube in the middle. All the three tubes are provided with stopcocks at the bottom. The U-tube is also provided with the stopcocks at the top of the two limbs fig 8.9. By closing these stopcocks, the communication between the solution in the cathode and anode limb can be stopped. The silver anode is sealed in a glass-tube and the cathode is a piece of freshly silvered foil. The apparatus is filled with a solution of silver nitrate and a steady current of about 0.01 ampere is passed for two to three hours. It is an

important precaution and the current is passed only for a short time so that too large a change in connection does not take place. The apparatus is connected with a silver or copper voltmeter (coulometer) as shown in the fig 8.9. This shows the circuit of the experiment.
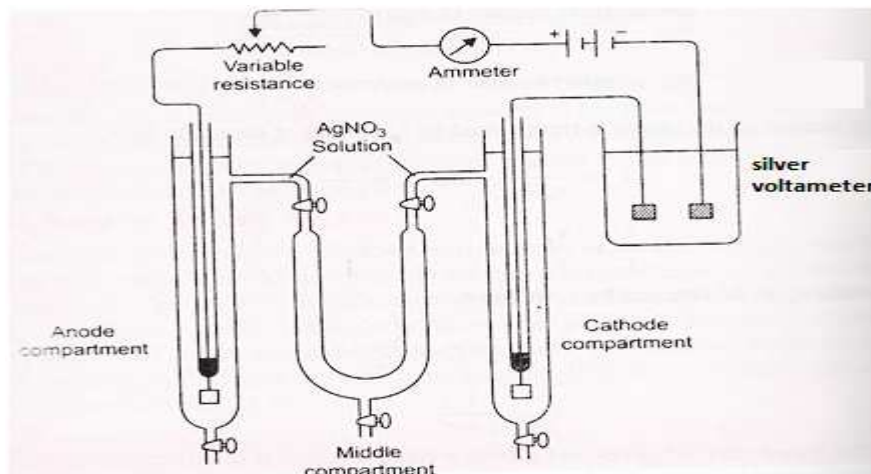
Fig 8.9 Hittorf's apparatus for determining transport number

When the current has been passed for about three hours, the stopcocks at the top of the U-tube are closed. The whole of the liquid in the anode compartment is carefully drained into a weighing flask and its weight determined. Its silver content is determined by titrating against a standard solution of potassium thiocynate. The weight of silver deposited in the silver coulometer is also noted if a copper coulometer is used in place of silver coulometer. The weight of silver equivalent to the copper deposited is calculated by multiplying it with 108/31.5. There should be no change in the concentration of the solution in the U-tube if the experiment has been successfully performed.

If the above experiment has been performed by using silver electrode, in this case nitrate ions attack the silver anode. Consequently there is increase in concentration of Ag^+ ions rather than decrease. The same experiment can be performed by using platinum electrodes to avoid the attack of ions on the anode.

Calculations:

Two different cases may arise:

Case I: When electrodes are un-attackable (Pt electrodes are used) after passing electric current;

Let weight of anodic solution taken out =a g

Weight of $AgNO_3$ present in it by titration = b g

Weight of water = (a-b) g

Before passing electric current:

Let weight of $AgNO_3$, in (a-b) g of water before passing the electric current be = c g

Hence fall in concentration

=(c-b) g of $AgNO_3$

$= \frac{c-b}{170}$ g eqvt of $AgNO_3$

$= \frac{c-b}{170}$ g equivalent of Ag = d (say)

Let the silver deposited in the silver voltameter be

$= w_1$ g

$= \frac{w_1}{108}$ g eqvt of Ag

= W g eqvt of Ag (say)

Transport number of Ag^+ (Ag+) $= \frac{\text{Fall in concentration around anode in g eqvt}}{\text{Amt of Ag deposited in g eqvt}} = \frac{d}{w}$

And transport number of NO_3^- ion (t NO_3) $= 1 - \frac{d}{w}$

Case II: When electrodes are attackable (Ag electrodes are used)

increase in concentration of anodie solution = (b-c) g of $AgNO_3$

$= \frac{b-c}{170} \times 108$ g of Ag

$= \frac{b-c}{170}$ g eqvt of Ag

= e say

If no Ag^+ ions had migrated from the anode, the increase in concentration of Ag^+ ions would have been equal to w

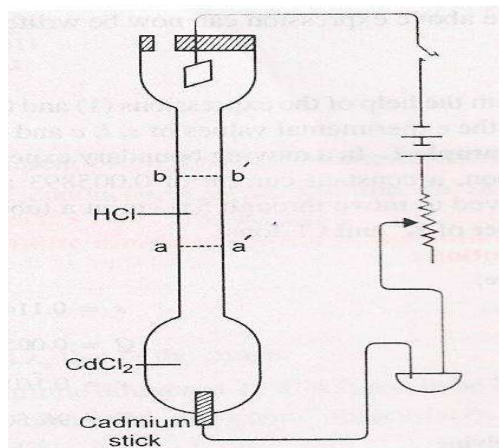Hence fall of concentration due to migration of Ag^+ ions=w-e

Hence transport number of Ag^+ ion (t$_{Ag+}$) $= \frac{w-e}{w}$

And transport number of NO_3^- ion (1- $\frac{w-e}{w}$)

(ii) Moving boundary method:

The moving boundary method is based on the direct observation of migration of ions in an electric field. This method is very accurate and has been used in recent years for precision measurement

Fig 8.10 The moving boundary method for determination of transport number

The apparatus used consists of a long vertical tube fitted with two electrodes at the two ends, as shown in fig 8.10. The tube is filled with a solution of cadmium chloride ($CdCl_2$) at the lower end and hydrochloric acid at the upper end in a way that there is a sharp boundary between the two. Here we have to determine the transport number of H^+ ions, hence HCl solution is taken. The selection of indicator electrolyte is chosen in such a way (in this case $CdCl_2$) that cation should not move faster than the cation whose transport number is to be determined.

The platinum cathode dipped in HCl solution is inserted at the top and the anode (cadmium stick) is introduced at the bottom.

On passing electric current through the apparatus, hydrogen gas is evolved at the cathode and H^+ ions move toward the cathode. The H^+ ions are replaced by Cd^{2+} ions and hence the boundary line moves in the upward direction. By noting the length through which the boundary moves and the quantity of electricity passed through the cell the transport number of H^+ ion can be calculated.

In general, if transport number of cation A^+ is to be determined, the electrolyte AX solution taken in the upper part of the apparatus and a layer of another electrolyte BX (known as indicator electrolyte) is selected so that the velocity of B^+ ion is less than A^+ ion. In such a case, the solution is described in fig 8.11.
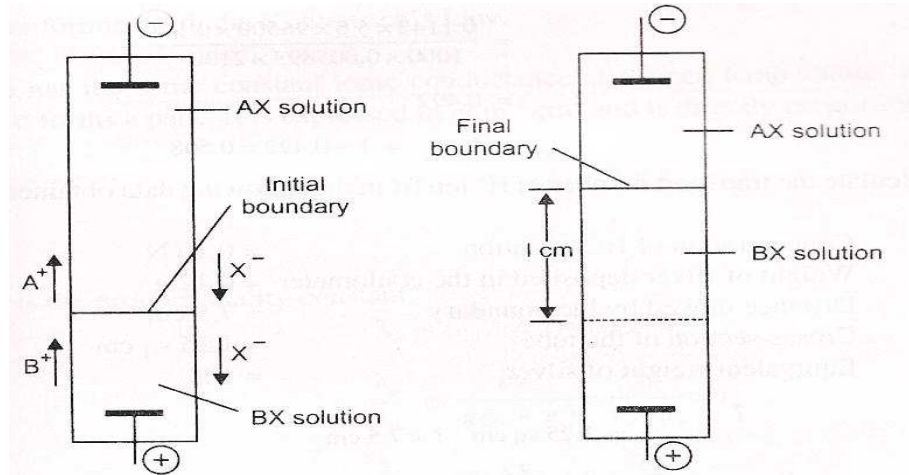
Fig 8.11 Moving boundary experiment for determining the transport number of A^+ ion.

Calculation:

Let c be the original concentration of A^+ ion in gram-equivalents per ml of the solution. If the distance through which the boundary moved $= 1$ cm, the area of cross-section of the tube= s sq cm.

Then the number of equivalents of A^+ moving upward $= s \times l \times c$

Let the number of faradays of current passed $= n$

The fraction of current carried by A^+ ions $= n \times t_{A+}$

Here $n \times t_{A+} = s \times l \times c$

and $t_{A+} = (s \times l \times c \times F)/Q$

Where n=Q/F, Q being the quantity of current passed and F stands for Faraday (=96500 coulombs)

Example:

Calculate the transport number of H^+ and Cl^- ions from the following data obtained by moving boundary method:

Concentration of HCl solution $= 0.10$N

Weight of silver deposited in the coulometer $= 0.12$g

Distance moved by the boundary $=7.5$ cm

Cross-section of the tube   = 1.25 sq cm

Equivalent weight of silver   = 108

Solution:

s   = 1.25 sq cm, l=7.5 cm

c   = 0.1 g eqvt/litre

= 0.1/1000 g eqvt/ml

108 g silver   = 1 Faraday

0.12 g silver $= \frac{.12}{108} = .00111$

Now t_{H^+} = s $\times$ l $\times$ c/n = 1.25x7.5x0.1/1000x0.0011

= 0.852

And transport number of Cl⁻ =1-0.852

= 0.148

8.6 KOHLRAUSH'S LAW

From the study of the equivalent conductance of electrolytes at infinite dilution Kohlrausch's discovered an interesting relationship between conductivity and transport number. At 25^0 the value of equivalent conductivity at infinite dilution λ_∞ for some electrolytes are given below:

Electrolyte	λ_∞ 25°C	Difference	Electrolyte	λ_∞ 25°C	Difference
NaBr NaCl	128·51 126·45	2·06	KBr NaBr	151·92 128·51	23·41
KBr KCl	151·92 149·86	2·06	KCl NaCl	149·86 126·45	23·41
LiBr LiCl	117·09 115·03	2·06	KNO₃ NaNO₃	144·96 121·55	23·41
NH₄Br NH₄Cl	151 80 149·74	2·06	KOH NaOH	271·52 248·11	23·41

Table 8.3 Equivalent conductivity at infinite dilution of some electrolytes

It is clear from the above table that when the bromine ion is replaced by chloride ion, a constant difference of 2.06 is produced in the value of the conductivity at infinite dilution. Similarly when potassium ion is replaced by sodium ion a difference of 23.41 is observed, anion remaining the same. In other words, each ion makes a certain definite contribution to the conductivity of solution. Hence in 1875, Kohlrausch's enunciated a law, known as Kohlrausch's law. It states that:

The equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductance of the component ions.

Mathematically the law may be expressed

$$\lambda_\infty = \lambda^0_a + \lambda^0_c$$

The values of λ^0_a and λ^0_c are called the ionic conductance of the anion and cation respectively at infinite dilution.

8.6.1 Application of Kohlaruch's law:

(i) Calculation of molar ionic conductance:

For each ion, the ionic conductance possesses a constant value at a fixed temperature and is the same no matter of which electrolyte it forms a part. It is directly proportional to the speed of the ions.

$$\lambda_a \, \alpha \, u_- \qquad \text{or} \, \lambda_a = ku_-$$

$$\lambda_c \, \alpha \, u_+ \qquad \text{or} \, \lambda_c = ku_+$$

Where k is the proportionality constant

Also λ_∞ α $(\lambda_a + \lambda_c)$ $= k(u_- + u_+)$

$$\frac{\lambda_a}{\lambda_\infty} = \frac{u_-}{u_- + u_-} = t_-$$

And $\frac{\lambda_c}{\lambda_\infty} = \frac{u_+}{u \pm u} = t_+$

Also $\frac{\lambda_a}{\lambda_c} = \frac{t_-}{t_+} = \frac{t_-}{1 - t_-}$

Hence from experimental values of transport number of the ions we can determine ionic conductance.

8.6.1.1 Ionic conductance of weak electrolytes:

Weak electrolytes do not ionize to a sufficient extent in solution and are far from being completely ionized even at very great dilution. The experimental value of $\lambda\infty$ in such cases is, therefore not possible. However it can be calculated with the help of Kohlraushs law.

$$\frac{\lambda a}{\lambda c} = \frac{t_-}{1-t_-}$$

$$\lambda_a - \lambda_a t_- = t_- \ \lambda_c$$

$$\lambda_a = t_-(\lambda_a + \lambda_c)$$

$$= t_- \lambda\infty$$

Thus the ionic conductance of an ion is obtained by multiplying the equivalent conductance at infinite dilution of any strong electrolyte containing that ion by its transport number.

In this manner, the ionic nobilities of the two ions present in the weak electrolyte can be calculated. Thus we can get the equivalent conductance of the electrolyteat infinite dilution by adding up two values also we can apply indirect method for evolution of equivalent conductance of week electrolyte.

Suppose equivalent conductance of acetic acid is to be determined at infinite dilution. For this we should know the equivalent conductance at infinite dilution of hydrochloric acid solution acetate and sodium chloride all strong electrolytes as shown below:

$$\lambda_{CH3COOH} = \lambda \ CH_3COO^- + \lambda_{H+}$$

$$= (\lambda_{HCl} + \lambda \ _{CH3COONa}) - \lambda_{Nacl}$$

The molar conductance at infinite dilution of a sparingly soluble substance, like silver chloride can also be obtained from similar considerations. Thus:

$$\lambda_{AgCl} = \lambda_{NH4Cl} + \lambda_{AgNO3} - \lambda_{NH4NO3}$$

8.6.1.2 Calculation of the solubility of sparingly soluble salts:

Substances like $PbSO_4$ or AgCl which are ordinarily called insoluble possess a definite value of solubility in water. This can be determined from conductance measurement of their saturated solution. Since a very small amount of solute is present it must be completely dissociated into ions even in a saturated solutions so that the equivalent conductance at infinite dilution. This accordingly to Kohlrausch`s law is sum of the ionic conductance.

So $\kappa v = \lambda \infty = \lambda_a + \lambda_c$

Knowing κ and $\lambda \infty$, we can be found out which is the volume in ml containing one g-equivalent of the electrolyte.

Example: The specific conductance of saturated solution of silver chloride at $18^0 c$ is 1.24×10^{-6} mhos after substracting that of water. The mobilities of Ag^+ and Cl^- ions at this temperature are 53.8 and 65.3 respectively, calculate the solubility of silver chloride in grams per liter.

Solutions:

Given $\kappa = 1.24 \times 10^{-6}$ mhos

$\lambda \infty = \lambda_{Ag+} + \lambda_{Cl-} = 53.8 + 65.3 = 119.1$

$\lambda \infty = \kappa . V$

$V = \dfrac{\lambda \infty}{\kappa} = \dfrac{119.1}{1.24 \times 10}$ ml

Hence $\dfrac{119.1}{1.24 \times 10}$ ml contains AgCl $= 1$ g equivalent $= 143.5$

1000ml contains AgCl $= \dfrac{143.5 \times 1.24}{119.1} \times 10^{-6} \times 1000$

$= 1.494 \times 10^{-3}$ g

8.6.1.3 Calculation of degree of dissociation or conductivity ratio:

The apparent degree of dissociation α of an electrolyte at the dilution v is given $\alpha = \lambda_v / \lambda \infty$ where λ_v is the equivalent conductance of the electrolyte at the dilution v and $\lambda \infty$ is the equivalent conductance at infinite dilution and this accordingly to kohlrausch is the sum of λ_a and λ_c.

8.7 CONDUCTOMETRIC TITRATIONS

Titrations in which conductance measurements are made in determining the end point are called conductometric titrations. These are acid-alkali reactions, precipitating reactions some displacement reactions. In these measurements the titrant is added from a burette into a measured volume of the solution to be titrated which is taken in a conductance cell and the conductance readings corresponding to the various additions are plotted against the volumes of titratent. This

way two linear curves are obtained, the point of intersection of which is the end point. The shape of curves obtained in certain types of titration is discussed below.

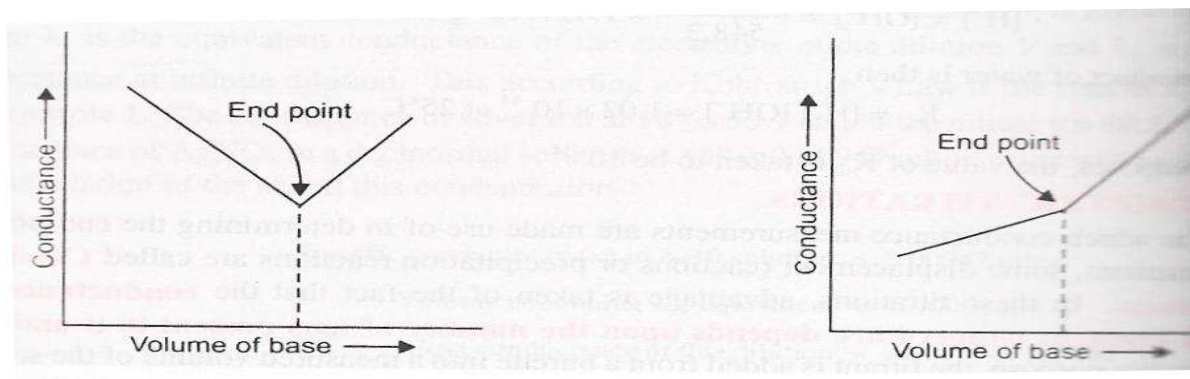## 8.7.1 Titration of strong acid against a strong base:

Let us consider, for example, the titration of strong acid (HCl) with a strong base (NaOH). Take 20 ml of acid solution in the conducting cell placed in a constant temperature bath and determine its conductance. Now add 1ml of sodium hydroxide solution from the burette at a time. As the alkali is added gradually, the hydrogen ions are replaced by slow moving sodium ions as represented below,

$$H^+(aq) + Cl^-(aq) + [\, Na^+(aq) + OH^-(aq)\,] \rightarrow Na^+(aq) + Cl^-(aq) + H_2O\,(l)$$
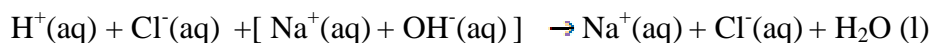
Hence on continued addition of sodium hydroxide, the conductance will go on decreasing until the acid has been completely neutralized, any further addition of alkali will result in introducing fast moving hydroxyl ion, the conductance therefore, after reaching a certain minimum value will begin to increase, on plotting conductance against the volume of alkali added, the point of minimum conductance, therefore concides with the end- point of the titration fig.8.12

8.7.2 Titration of weak acid against a strong alkali:

When a weak acid is titrated against a strong alkali we get a curve of the type Fig.8.13 (CH_3COOH /NaOH). The initial conductance of the solution is low because of the weak acid. On addition of alkali, highly ionized sodium acetate is formed.

Fig. 8.12 Conducometric titration curve   *Fig. 8. 13 Curve for titration of weak acid*

strong acid and strong base   *against a strong bas*

The acetate ions at first tend to suppress the ionization of acetic acid still further due to common ion effect, but after a while the conductance begin to increase because the conducting power of highly ionized salt exceeds that of the weak acid.

$CH_3COOH + Na^+ + OH^- \rightarrow CH_3OO^- + Na^+ + H_2O$ **(Feebly ionized)**
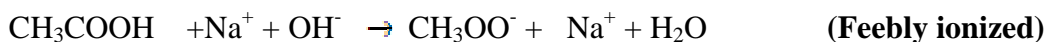
Immediately after the end point, further addition of sodium hydroxide introduces the fast moving hydroxyl ion. Thus the conductance value shows a sharp increase

The point of intersection of the two curves gives the end point fig.8.13

8.7.3 Titration of a strong acid against a weak base:

The curve obtained for the titration of a strong acid against a weak base (HCl /NH₄OH) is shown in Fig 8. 14. In this case the conductance of the solution first decreases due to the fixing up of fast moving H^+ ion and their replacement by slow moving NH_4^+ ions.
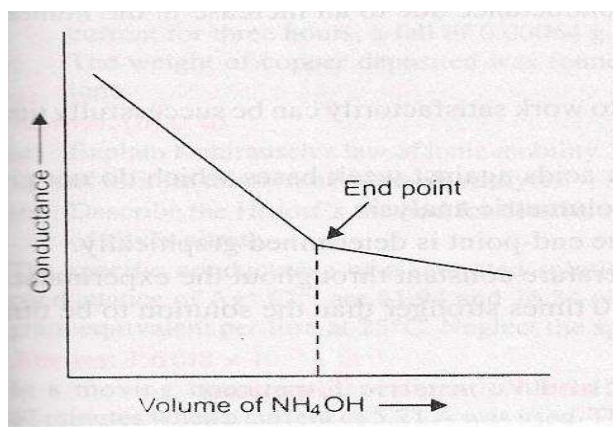
Fog 8.14 Titration curve of strong acid against weak base

After the end-point has been reached, the addition of ammonium hydroxide will not cause any appreciable change in conductance value as it is a weak electrolyte and its conductance is very small, compared to that of acid or its salt, the slope of the curve is as shown in fig.8.14.

8.7.4   Titration of weak acid and weak base:

Suppose we have to study titration of weak acid (CH_3COOH) against weak base (NH_4OH). The complete titration curve is shown in fig.8.15. The initial conductance of the solution in this case is low due to the poor dissociation of the weak acid. But it starts increasing as the salt CH_3COONH_4 is formed. After the equivalence point, the conductivity remains almost constant because the free base NH_4OH is a weak electrolyte, the end point is quite sharp.
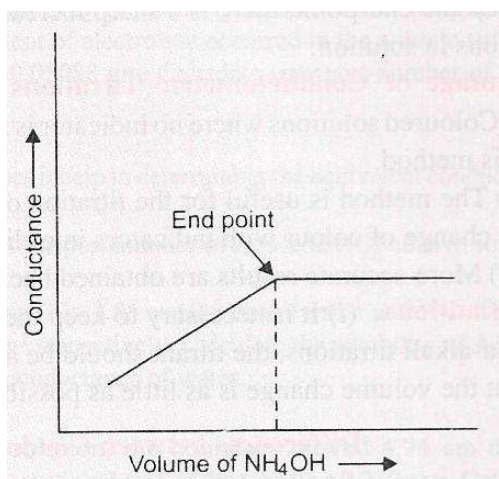

Fig 8.15 Titration curve of weak acid and weak base

8.7.5   Precipitation Titrations:

The end point in precipitation reactions can be accurately determined by conductometric titration. In the titration of potassium chloride against silver nitrate, for example, the change in conductance on the addition of silver nitrate is not much since the mobility of potassium ion and the silver ion is of the same order. Thus the curve is nearly horizontal fig.8.16
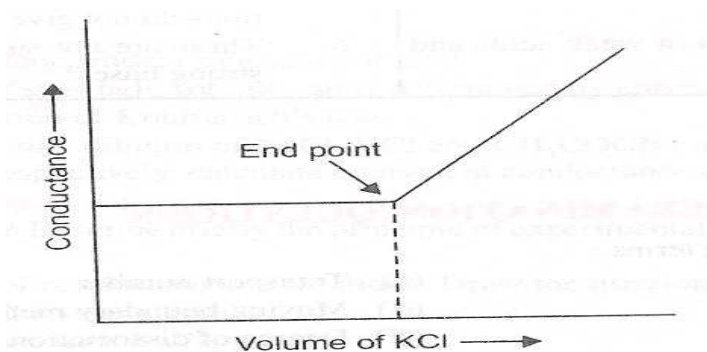

Fig 8.16 Curve for titration of KCl against AgNO₃

$Ag^+ + NO^-3 + K^+ + Cl^- \rightarrow K^+ + NO_3^- + AgCl$ (ppt)

After the end point, there is sharp increase in conductance due to increase in the number of free ions in solution.

For better results the titrations should be about 10 times stronger than the solution to be titrated, so that the volume change is as little as possible.

8.7.6 Applications of conductometric titrations:

There are several advantages of conductrometric titrations over ordinary volumetric titrations.

(i) Colored solutions where no indicator is found to work satisfactorily can be successfully titrated by this method.

(ii) The method is useful for the titration of weak acids against weak bases which do not give a sharp change of colour with indication in ordinary volumetric analysis.

   (iii) More accurate result are obtained because the end point is determined graphically

Differences between conductometric and volumetric titration.

Conductometric Titrations		Volumetric Titrations	
1.	Conductance measurements are done to check end points.	1.	Volume measurements are done to check end points.
2.	Titrations can be carried out even with coloured solution.	2.	These titrations fail in coloured solutions as suitable indicators are not available some times.
3.	Accurate results are obtained.	3.	Results are not so accurate
4.	End point in determined graphically.	4.	End point is determined by change in colour of indicator.
5.	In case of polybasic acids conductometric titrations can be used.	5.	In case of polybasic acids volumetric titrations do not give correct end points.
6.	These are successful even in weak acids and strong bases.	6.	These are not successful in weak acids and strong bases.

8.8 OSTWALD'S DILUTION LAW

According to Arrhenius theory of electrolyte dissociation, the molecule in an electrolyte in aqueous solution undergo spontaneous dissociation into positive and negative ions and that there is a dynamic equilibrium between ions and undissociated molecules. Ostwald noted that law of mass action can be applied to the ionic equilibrium in the case of chemical equilibrium in such systems.

Let us consider a electrolyte AB which dissociates in solution to form A^+ ion and B^- ions.

$$AB \rightleftharpoons A^+ + B^-$$

Let c be the concentration of the electrolyte per liter and α be the degree of dissociation, i.e., the fraction of total concentration of the electrolyte which exists in dissociated state. Then the concentration terms at equilibrium may be written as:

Initial state   c   o   o

$$AB \rightleftharpoons A^+ + B^-$$

Equilibrium concentration   c (1-α)   cα   cα

Applying law of mass action:

Rate of dissociation = $K_1 c (1-\alpha)$

Rate of combination = $K_2 c\alpha \times c\alpha$

Or $\quad \dfrac{c\alpha \times c\alpha}{c(1-\alpha)} = \dfrac{K_1}{K_2} = K$

0r $\qquad k = \dfrac{\alpha^2}{1-\alpha} c \quad$ mol liter^{-1} ……………….(1)

Equation (1) is mathematical representation of Ostwald`s dilution law. The constant K is called the dissociation constant or ionization constant. It is a constant value at constant temperature.

If one mole of electrolyte is dissolve in V liter of solution, then

$$c = \dfrac{1}{V}$$

Here V is known as dilution of the solution. Then equation (1) can be written as:

$$K = \dfrac{\alpha^2}{(1-\alpha)v} \qquad \text{……………………..(2)}$$

For weak electrolytes, the value of α is very small as compared to 1, so in most of the calculations we can take $1-\alpha \cong 1$. Thus Oswald`s dilution formula can be expressed as

$$K = \dfrac{\alpha^2}{v} \qquad \text{……………………………..(3)}$$

This law can be verified by determining the value of α and v. the value of α can be determined from conductivity measurements. $\alpha = \lambda_V/\lambda\infty$, λ_V and $\lambda\infty$ are the equivalent conductance at the dilution v and infinite dilution. their values are found from Kohraush`s law. The value of α at various dilution thus determined are inserted in the expression

K = $\dfrac{\alpha^2}{(1-\alpha)v}$ if K comes out to be constant, the Ostwald`s law stands verified.

However, the law failed completely when applied to strong electrolytes. The value of K far from remaining constant rapidly falls with dilution.

8.8.1 Factor that explain the failure of Ostwald`s law in case of strong electrolytes:

(i) The Oswald`s law is based on Arrhenius theory, which assumes that only a fraction of the electrolyte is dissociated at ordinary dilution and complete dissociation occurs only at infinite dilution. This is true for weak electrolytes. Strong electrolytes are almost completely ionized at all dilutions. The value of λ_v/λ_∞, does not give the accurate value of α. In this case it is only a conductivity ratio.

(ii) Ostwald`s law is derived on the assumption that the law of mass action holds for ionic equlibria as well. But the concentration of ions is very high; the presence of charge affects the equilibrium. Thus the law of mass action cannot be applied in simple form.

(iii) The ions obtained by dissociation may get hydrated and may affect the concentration terms.

8.9 THEORY OF STRONG ELECTROLYTES

A number of theories have put forward by different workers in order to explain the high conductance of strong electrolytes. In 1923 Debye and Huckle put forward their well known theory of strong electrolytes in which account is taken of the electrostatic force between the ions. A brief outline of the main ideas of the theory is given below,

(i) The strong electrolytes are completely ionized at all dilutions. The present position as it has ensured from the Raman spectra, X ray analysis of crystals, distribution coefficients and vapour pressures is that there is a very small amount of unionized substance also present and that instead of saying completely ionized we should say almost completely ionized.

(ii) The oppositely charged ions attracts each other, it suggest that anions and cations are not uniformly distributed in the solution of an electrolyte but that the cations tends to found in the vicinity of anions and vice- versa Fig 8.17 though the solution is on the whole

neutral, there is vicinity of any ion of predominance of ions of oppositely charge which we called counter ions.
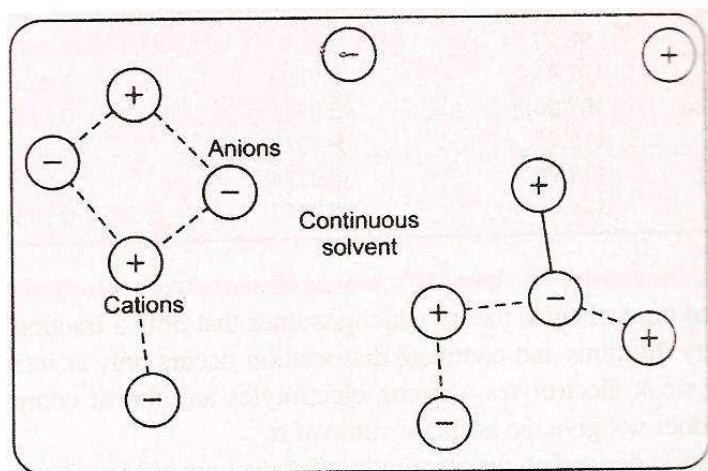

*Fig 8.17 Charge distribution in ionic solutions of strong electrolytes*

The ions are all the time on the move in all directions but on the average, more counter ions than like ions pass by any given ion. This spherical haze of opposite charge is called ionic atmosphere.

(i) Decrease in equivalent conductivity with increasing concentration is due to fall in mobilities of the ions due to greater interionic effect and vice-versa.

(ii) The ratio λ_v/λ_∞ does not correctly give the degree of dissociation α for strong electrolytes but only conductance coefficient f_c.

(iii) In spite of complete ionization the value of λ_v is much than λ_∞ because of the two effects, namely electroforetic effect and relaxation effect.

(a) Asymmetry or relaxation effect :

Suppose there is a central negative ion fig 8.18. This is surrounded by a number of positively charged ions which form its ionic atmosphere. This ionic atmosphere is symmetrically situated in the absence of any electrical field. When electrical field is applied, the negative ion moves towards the anode and the positive ionic atmosphere toward cathode. This leaves a large numbers of positive ions behind it than there are at front of the negative ion with the result that the symmetry of the atmosphere about the central ion is distorted.
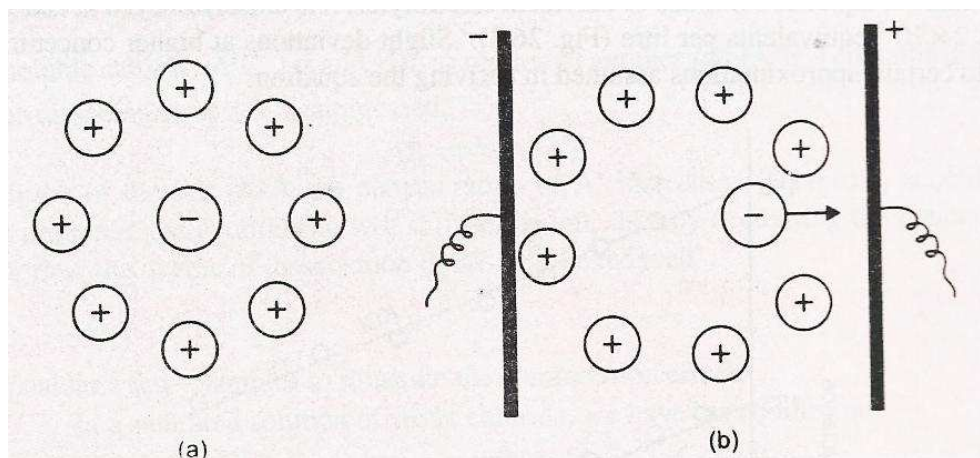
Fig 8.18   symmetric and asymmetric ionic atmospheres

Initially the force of attraction exerted by the ionic atmosphere on the central ion was uniform. It becomes greater now behind the ion than in front. As a result of this the negative ion experiences a force which tends to drag it backward and this slows down its movement in the forward direction. This behavior is known as asymmetry effect. It may be said that the negative ion which leaves the ionic atmosphere of positive ions behind to die away would built a new ionic atmosphere and the symmetry would be corrected. If this process of building up and dying away were instantaneous there would be no cause of symmetry and the atmosphere would always be symmetrically placed about the ions. But the formation of the new ionic atmosphere does not take place at the same rate at which the old one decays and the latter lags behind or take more time known as relaxation time. For this reason asymmetry effect is relaxation effect.

 Electrophoretic effect:

Another factor which acts as a drag tends to retard the motion of the ion is the tendency of the applied field to move the ionic atmosphere (to which the solvent molecules are attached) in a direction opposite to that in which the central ion associated with solvent molecules is moving. Thus the central negative ion moving towards the anode has to make its way through the ionic atmosphere with its associated solvent molecule which is moving in the opposite direction i.e. , towards cathode. This causes a retarding influence on the movements of the ion. This effect is called electrophoretic effect.

Both the above causes reduce the velocity of the ion and operate in solutions of strong electrolytes with the result that a value of equivalent conductance (λ_v) lower than the value at

infinite dilution $(\lambda\infty)$ obtained. At infinite dilution since the electrical effects are practically absent the two values tend to approach each other.

8.9.1 Debye- Huckel –Onsager conductance equation:

In 1926, Debye- Huckel and Onsager worked out mathematically the magnitude of asymmetry and electrphoretic effects in term of such factors as valency of ion concentration and dielectric constant and viscosity of the medium. For univalent electrolytes such as, KCl, which furnish two univalent ions, the following equation was derived.

$$\lambda_v = \lambda\infty \; -(\; A+B \; \lambda\infty)\sqrt{c}$$

Where A and B are constants and c is concentration in gm-equivalent per litre. These constants depend only on the nature of the solvent and the temperature and are given by the relationship.

$$A = \frac{82.4}{(DT)^{1/2}\eta} \quad \text{and} \quad B = \frac{8.20 \times 10^5}{(DT)^{3/2}}$$

Where D and η are the dielectric constant and coefficient of viscosity of the medium respectively at the absolute temperature T.

8.10 SUMMARY

In electrolysis, the flow of current is accompanied with actual transfer or migration of matter. You have studied in this unit that such transfer of matter leads to the decomposition of matter at the point where electricity enters or leaves the electrolyte and in the process helps in transfer of electrons. The topics, transport number, its determination, Arrhenius theory of electrolytic dissociation. Ostwald`s law and theory of strong electrolyte have been discussed in detail. The most important aspect of this unit is conductrometric titrations. The conductrometric method is particularly suitable as such titrations coloured solutions and precipitation reaction do not give a sharp end point. In order to get accurate result, the volume change during titration should be as little as possible. The titraint should, therefore, be ten times as strong as the solution in conductance cell in order to keep the volume change small.

8.11 TERMINAL QUESTION

A. Objective type questions:

Q.1. The units of specific conductance are:

   (a) ohm cm   (b) ohm cm^{-1} (c) ohm^{-1} (d) ohm^{-1} cm^{-1}

Q.2. The distance between two electrodes of a cell is 3.0 cm and area of each electrode is 6.0 cm^2, the cell constant is

   (a) 2.0   (b) 1.0   (c)   0.5   (d) 18

Q.3. When a strong acid is titrated against a strong base the end point is the

     Point of:

   (a) Zero conductance   (b)   maximum conductance

   (c) Minimum conductance   (d)   none of these

Q 4. The sum of the transport number of anion and cation is equal to:

        (a) 1   (b) 0   (c) 0.5   (d) ∞

Q.5. The fraction of total current carried by the cation or anion is termed as:

        (a) Fractional number   (b) transport number

        (c) Speed number   (d) carrier number

B. Short Answer type questions:

Q.6 Define the terms:

        (a)   Electrolysis

        (b) Specific conductance

        (c)   Transport number

        (d) Equivalent conductivity

Q.7 Define and explain the following terms:

        (a)   Degree of dissociation   (b)   Kohlrausch law

        (c)   Arrhenius theory   (d)   Precipitation titrations

C. Long answer type questions:

Q. 8 What is the Ostwald's dilution law? How it is verified? What are its limitations?

Q. 9 (a) State and explain Faraday`s law of electrolysis

(b) On dilution, specific conductance of an electrolyte decreases and equivalent conductance increases. Discuss

Q.10 State and explain Kohlrauschs`s law of independent migration of ions. How does it help in determining the equivalent conductivity at infinite dilution of weak electrolytes?

8.12. ANSWERS

1. (d) 2. (c) 3. (c) 4. (a) 5 (b)

Source of study material

(i) Essential of physical chemistry by Bahl, Bahl and Tuli.

(ii) Principles of physical chemistry By Puri, Sharma and Pathania.

(iii)Physical chemistry By   P.C. Rakshit.

(iv)Physical chemistry By Atkins.

UNIT -9 ELECTROCHEMISTRY- II

CONTENTS:

9.1 OBJECTIVE

In the previous unit much has been discussed about electrolysis, electrical transport, conduction, Ohm's law factors affecting electrolysis, electrolytic dissociation, Arrhenius theory

of electrolyte dissociation, transport number, determination of transport number by different methods, Conductance etc.

Ostwald's dilution law, its failure in case of strong electrolytes and theory of strong electrolytes has been discussed in detail. Much emphasis has been given to Kohlrausch's law and its applications, particularly the conductometric titration.

9.2   INTRODUCTION

Electrochemistry is the branch of physical chemistry that studies the relationship between electricity, as a measurable and quantitative phenomenon, and identifiable chemical change, with either electricity considered an outcome of a particular chemical change or vice-versa. These reactions involve electric charges moving between electrodes and an electrolyte (or ionic species in a solution). Thus electrochemistry deals with the interaction between electrical energy and chemical change.

When a chemical reaction is caused by an externally supplied current, as in electrolysis, or if an electric current is produced by a spontaneous chemical reaction as in a battery, it is called an electrochemical reaction. Chemical reactions where electrons are transferred directly between molecules and/or atoms are called oxidation-reduction or (redox) reactions. In general, electrochemistry describes the overall reactions when individual redox reactions are separate but connected by an external electric circuit and an intervening electrolyte.

9.3 TYPES OF CELLS

In these unit different aspects of cells, their functioning, types of cells, electrode reactions, EMF of a cell and free energy change will be discussed.

9.3.1 Galvanic cell:

A galvanic cell is a device in which the free energy of a chemical process is converted into electrical energy. Usually such a cell consists of two electrodes immersed in one or more suitable electrolytes. When the electrodes are connected externally by a metallic conductor, current flows from one electrode to another and inside the cell chemical change occur at the

surface of electrodes. On joining the electrodes externally oxidation occurs at one electrode and reduction at the other electrode. The electrode at which oxidation occurs is called a negative electrode or cathode while the electrode at which reduction occurs is called positive electrode or anode. The reason for this nomenclature is that oxidation is accompanied by liberation of electrons which are given up to the electrode at which oxidation occurs. The electrode, thus acquires a negative charge. Reduction, on the other hand, is accompanied by consumption or elimination of electrons from the electrode which thereby acquires a positive charge.

9.3.2 Electrochemical cell:

Consider for example a copper rod dipping in a solution of copper sulphate and a zinc rod dipping in a solution of zinc sulphate. The two metal rods are connected by a metallic conductor.

When a bar of zinc is dipped in a solution of copper sulphate, copper metal is deposited on the bar fig 9.1. The net reaction is

$$Zn + Cu^{2+} \longrightarrow Zn^{++} + Cu$$
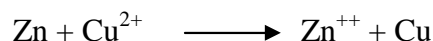
This is a redox reaction and the two half reactions are

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

In this change, Zn is oxidised to give Zn^{2+} and copper is reduced to Cu atoms. The electrons released in the first half-reaction are used up by the second half-reaction. Both the half-reaction occur on the zinc bar itself and there is not net charge.

Now let the two half reactions occur in separate compartments which are connected by a wire fig 9.2. The electrons produced in the left compartment flow through the wire to the other compartment. However, the current will flow for an instant and then stop. The current stops flowing because of the charge build on the two compartments. The electrons leave the left compartment and would become positively charged. The right compartment receives electrons and become negatively charged. Both these factors oppose the flow of electrons (electrical current) which eventually stops.
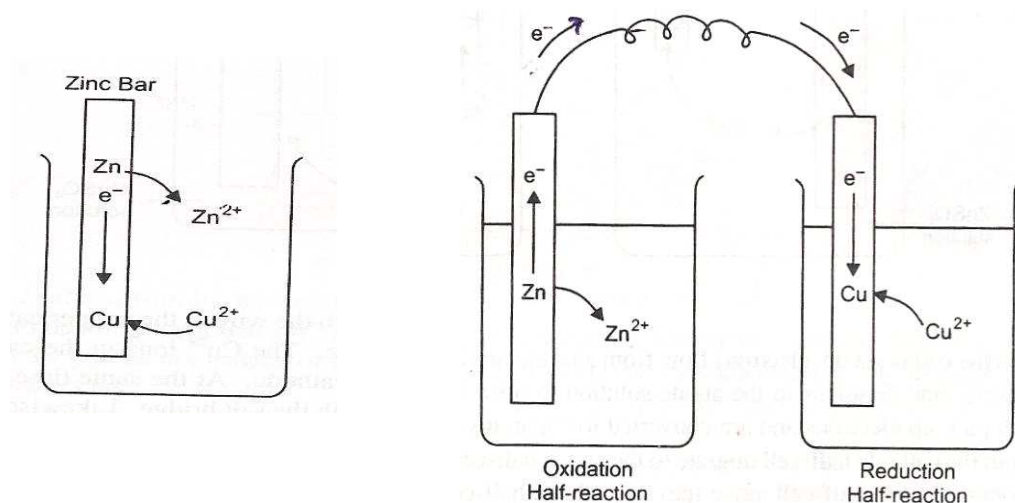
Fig 9.1 Redox reaction taking Place at zinc electrode Fig 9.2 Separate cell reactions cause flow of current

9.3.3 Voltaic cell:

A voltaic cell also known as galvanic cell is one in which electrical current is generated by a spontaneous redox reaction, a simple voltaic cell is shown in fig 9.3.

A bar of zinc metal (anode) is placed in zinc sulphate solution in the left container. A bar of copper (cathode) is immersed in copper sulphate solution in the right container. The zinc and copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution in agar-agar jelly interconnects the solution in the anode compartment and the cathode compartment.
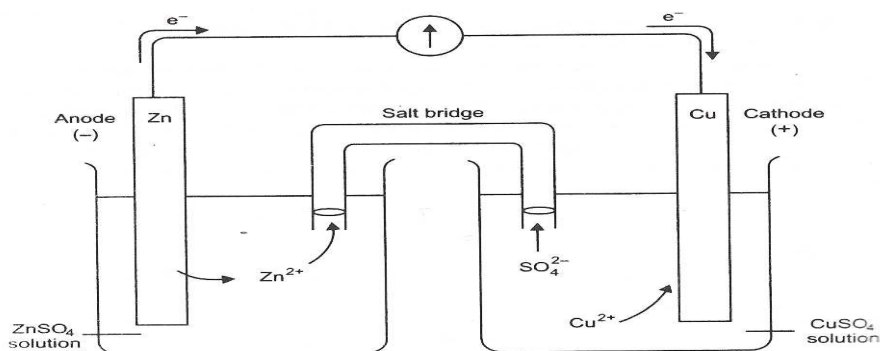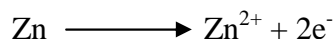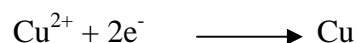

Fig 9.3 A simple voltic cell

The oxidation half-reaction occurs in the anode compartment.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

The reduction half-reaction takes place in the cathode compartment.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Net reaction in the cell is

$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$$
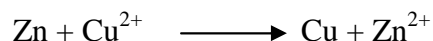
When the cell is set up, electrons flow from the zinc electrode through the wire to the copper electrode. As a result, zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the cathode half cell pick up electrons and are converted to Cu atoms on the cathode. At the same time SO_4^{2-} ions from the cathode half cell migrate to the anode half-cell through the salt bridge. Likewise Zn^{2+} ions from the anode half-cell move into the cathode half-cell. The flow of ions from one half-cell to the other completes the electrical circuit which ensures continuous supply of current. The cell will operate till either the zinc metal or copper ions are completely used up.

The cell is represented as

$$Cu/Cu^{2+}/Zn/Zn^{2+}$$
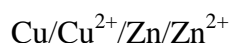
9.4 TYPES OF REVERSIBLE ELECTRODES

For thermodynamic treatment of galvanic cells it is essential that these cells operate in a thermodynamically reversible manner. In order to find out if a given cell is reversible or not, it is connected to an external source of EMF acting in the opposite direction. The cell will be reversible if it satisfies the following conditions:

   (i) If the opposing EMF is exactly equal to that of the cell itself, no current is given out by the cell and no chemical reaction takes place in the cell.

   (ii) If the opposing EMF is infinitesimally smaller than that of the cell itself, an extremely small current is given out by the cell and a correspondingly small amount of the chemical reaction takes place in the cell.

   (iii) If the opposing EMF is infinitesimally greater than that of the cell itself, an extremely small current flow through the cell in the opposite direction and a small amount of the chemical reaction also takes place in the reverse direction.

Some common types of reversible electrodes are given below:-

9.4.1 Gas electrode:

Hydrogen electrode:

Hydrogen gas bubbling at one atmosphere pressure in a solution of hydrochloric acid constitute hydrogen electrode fig 9.4. It is represented as:
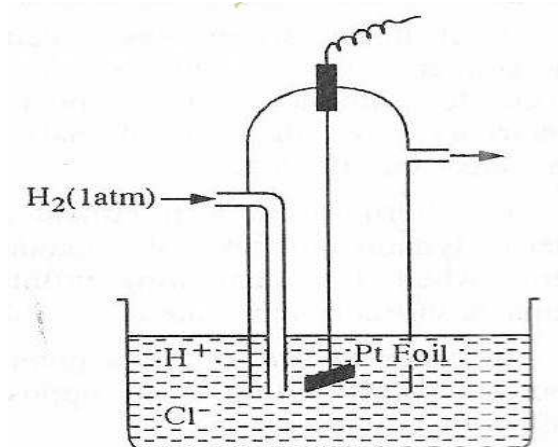

Fig 9.4 Hydrogen electrode

Pt/H$_2$ (1 atm.)/H$^+$ (a=1)   or Pt; H$_2$(g), H$^+$.

On account of hydrogen being a gas, a special device is made in order to make the potential difference between the gas and the solution measurable. This device consists in placing a small strip of platinized platinum foil such that it is half immersed in the solution and half surrounded by the gas. The finally divided platinum on platinum foil absorbs hydrogen and in that condition behaves as if, it was a solid electrode of the gas. It freely permits the change from the gaseous state to the ionic state and vice versa.

9.4.2 Metal-metal ion electrode:

An electrode of this type consists of metal rod dipping in a solution containing its own ions. For example zinc rod dipping in zinc sulphate solution or copper rod dipping in copper sulphate solution as you have studied in 9.3 above

The electrode reaction may represented in general as

$$M^+ (aq) + e- \longrightarrow M(s)$$
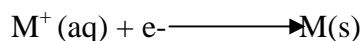
If the metal rod behaves as positive electrode (i.e., the reaction at the electrode involves reduction), the equilibrium will shift towards the right. The concentration of M^+ ions in solution will, therefore, decrease.

If on the other hand, the metal rod behaves as negative electrode (i.e., the electrode reaction involves oxidation), the above equilibrium shifts towards the left. The concentration of the M^+ ion in the solution will therefore, increase fig 9.4.

9.4.3 Metal-insoluble metal salt electrodes:

This electrode consists of a metal and a sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion. An important electrode of this type is the calomel electrode.

Calomel electrode consists of mercury, solid mercurous chloride and a solution of potassium chloride. The electrode is represented as Hg, Hg_2Cl_2 (5); KCl (solution)
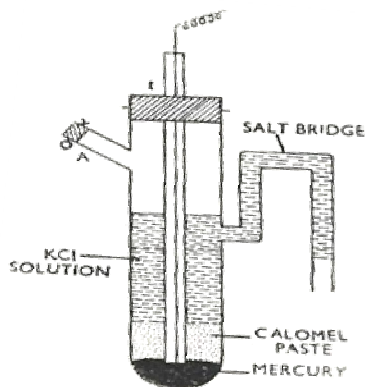
Fig 9.5 The calomel electrode

It can be easily setup in the laboratory as follows:

Mercury of high grade purity is placed at the bottom of a glass tube having a side tube on each side; it is known as calomel vessel fig 9.5. Mercury is covered by a paste of mercurous chloride (calomal), as shown. A solution of potassium chloride is introduced above the paste through the side tube. The concentration of the solution is either decinormal, normal or else the solution is fully saturated. A tube t containing mercury and with fused in platinum wire at its

lower end to serve as contact with the mercury of the electrode is then introduced. The tube should contain sufficient mercury to sink the platinum contact to rest on the base of the tube. The side tube is filled with a jelly of agar-agar and KCl. This tube is connected with the help of this tube through a salt bridge with the other electrode, the potential of which is to be determined.

9.4.4 Oxidation-reduction electrodes:

The term, oxidation-reduction electrode is used for those electrodes in which the potential is developed from the presence of ions of the same substance in two different valance (i.e., oxidation) states. Such an electrode is setup by inserting an unattackable metal such as platinum on an appropriate solution. Thus, when a platinum wire is inserted in a solution containing Fe^{2+} and Fe^{3+} ions it is found that the wire acquires potential. The potential at the electrode arises from the tendency of the ions in one oxidation state to change into the more stable oxidation state.

The electrode reaction may be represented as follows:

$$Fe^{3+} (aq) + e^- \rightleftharpoons F_e^{2+} (aq)$$
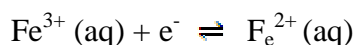
The function of the platinum wire is to pick up the electrons and to provide electrical contact to the electrode.

Another important type of oxidation reduction is quinhydron electrode. This electrode consists of a platinum wire placed in a solution containing hydroquinone (QH_2) and quinone (Q) in equimolar amount. The electrode reaction in this case is represented as follows

This electrode which may be represented as:
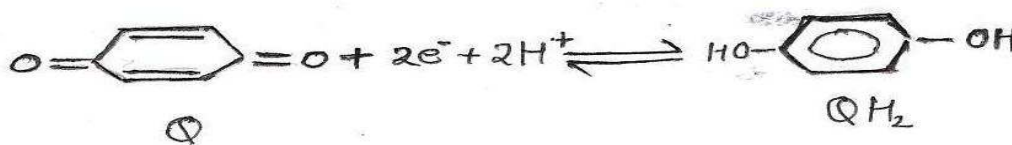
Pt, Q, QH_2; H^+ (aq), is reversible with respect to H^+ ions.

9.5 CELL REACTIONS
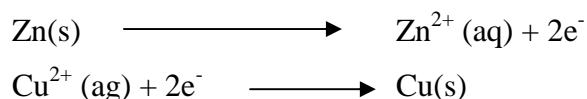
The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half reactions taking place in the anode and cathode compartments. The net chemical change obtained by adding the two half reactions is called the cell reaction. Thus, a simple voltaic cell, we have

(a) Half reactions:

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

(b) Cell reaction by adding up the half reactions:

$$Zn (s) + Cu^{2+} (aq) \longrightarrow Zn^2 (aq) + Cu(s)$$
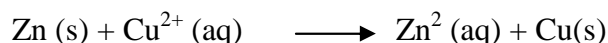
In Zn-Cu voltaic cell, electrons are released at the anode and it becomes negatively charged. The negative electrode pushes electrons through the external circuit by electric repulsions. The copper electrode gets positive charge due to the discharge of Cu^{2+} ions on it. Thus electrons from the outer circuit are attracted into this electrode. The flow of current through is determined by the 'push' of electrons at the anode and the 'attraction' of electrons at the cathode. These two forces constitute the driving force or electrical pressure that sends electrons through the circuit. This driving force is called the electromotive force (e.m.f.) or cell potential.

The e.m.f. or cell potential is measured in units of volts (V) and is also referred as cell voltage.

9.5.1 Cell diagram or representation of a cell:

A cell diagram is a depiction of an electrochemical cell. For this purpose, we will consider that a cell consists of two half cells. Each half-cell is again made of metal electrode in contact with metal ions in solution.

In 1953 **IUPAC (International Union of Pure and Applied Chemistry)** recommended the following conventions for writing cell diagrams. Let us illustrate these with reference to zinc-copper cell.

(i) A single vertical line:

In this representation (/) represents a phase boundary between metal electrode and ion solution. These the two half cells in a voltaic cell are indicated as

Zn / Zn^{2+} Cu^{2+} / Cu phase boundary

Anode half cell   Cathode half cell
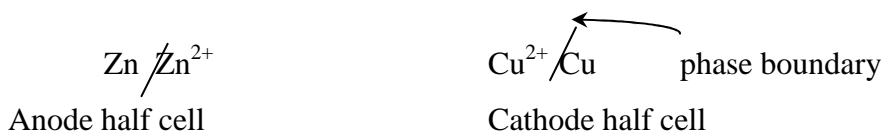
      It may be noted that the metal electrode in anode half-cell is on the left, while in cathode half cell it is on the right of the metal ion.

**(ii) A double vertical line:**

      The double vertical line represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.

(iii) Anode half cell is written on the left and cathode half cell on the right.

(iv) In the complete cell diagram, the two half cells are separated by a double vertical line (salt bridge) in between. The zinc-copper cell can now be written as

Zn/Zn^{2+} $\|$ Cu^{2+}/Cu salt bridge

Anode half cell   cathode half cell
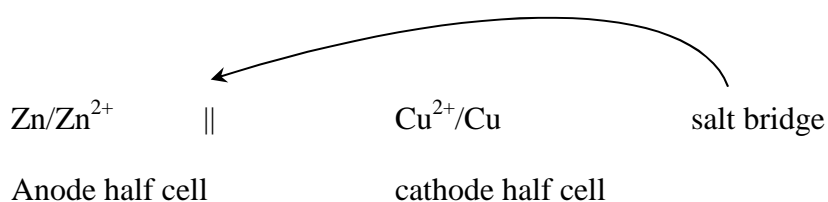
(v) The symbol of an inert electrode like platinum electrode is often enclosed in a bracket. For example:

$Mg/Mg^{2+} \| H^{+}/H_2$ (Pt)   inert electrode
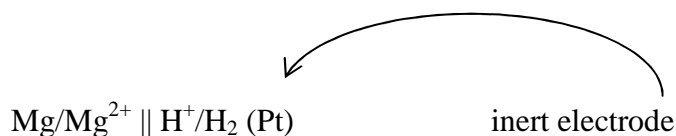
9.5.2 Convention regarding sign of e.m.f. value:

      The magnitude of e.m.f. of a cell reflects the tendency of electrons to flow externally from one electrode to another. The electrons are transported through the cell solution by ions present and pass from the positive electrode (Cu in case of Daniel cell) to the negative electrode. This corresponds to a clockwise flow of electrons through the external circuit. Thus the e.m.f. of the cell is given the +ve sign. If the e.m.f. acts in the opposite direction through the cell circuit it

is quoted as –ve value. For, Daniell cell has an emf of 1.1V and the coper electrode is positive. This can be expressed in two ways:

Zn /ZnSO$_4$ || CuSO$_4$ |Cu   E=1.1V

Cu/CuSO$_4$ || ZnSO$_4$/Zn   E=-1.1V
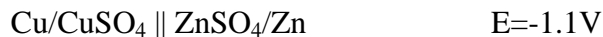
The negative sign indicates that the cell is not feasible in the given direction. The reaction will take place in the reverse direction.

9.5.3 Calculating the emf of a cell:

The e.m.f. of a cell calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula

$$E_{cell} = E_{cathode} - E_{anode}$$
$$= E_R - E_L$$

Where E_R and E_L are the reduction potentials of the right-hand and left-hand electrodes respectively. It may be noted that the absolute values of these reduction potentials cannot be determined. These are found by connecting the half cell with a standard electrode whose reduction potential is known.

9.6   SINGLE ELECTRODE POTENTIAL:

As you have studied that each galvanic cell is made up of two electrodes. At one electrode oxidation takes place, i.e., electrons are evolved. At the other electrode reduction takes place, i.e., electrons are taken up.

The tendency of an electrode to lose or gain electron when it is in contact with its own ions in solution, is called electrode potential. Since tendency to gain electrons means also the tendency to get reduced. This tendency is called reduction potential. Similarly, the tendency to lose electrons means the tendency to get oxidized. Hence this tendency is called oxidation potential. Oxidation potential is reverse of reduction potential. Thus, if the reduction potential of electrode under given conditions is 1.5 volts, then its oxidation potential is taken as -1.5 volts and vice-versa.

It is not possible to determine experimentally the potential of a single electrode (i.e., of a half cell). It is the difference of potential between two electrodes that we can measure by combining them to give a complete cell. By arbitrarily fixing potential of one electrode as zero (just as freezing point of water at atmospheric pressure is arbitrarily fixed as zero on the temperature scale), it is possible to assign numerical values to potentials of the various other electrodes.

9.7 STANDARD HYDROGEN ELECTRODE

The potential of a reversible hydrogen electrode in which the gas at one atmospheric pressure is bubbled through a solution of hydrogen ions of unit activity (or, to be approximate, 1M concentration) has been fixed as zero. This electrode is known as standard hydrogen electrode (fig 9.6) and is represented
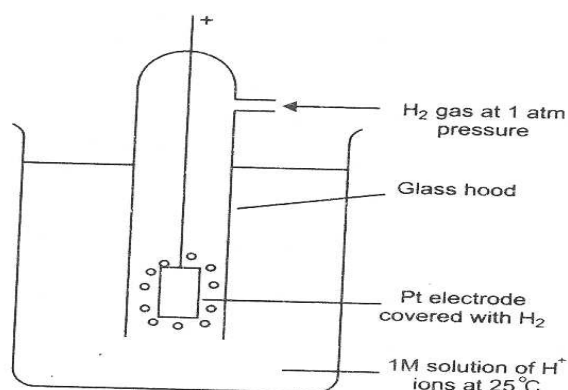
Fig 9.6 Standard hydrogen electrode

as: Pt; H_2(g) (1atm), H^+(aq) (c=1M)

All other single electrode potentials measured with respect to standard hydrogen electrode are referred to as potentials on the hydrogen scale.

If it is required to find the electrode potential of, say, zinc electrode dipping in a solution of zinc sulphate (i.e., Zn, Zn^{2+} electrode), all that is needed is to combine it with the hydrogen electrode so as to have a complete cell represented as:

Zn, Zn^{2+} (aq)/H_2 (g) (1 atm); H^+(aq) (C=1M) ; Pt
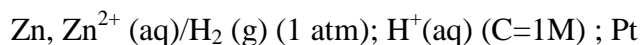
The e.m.f. of the cell determined potentiometrically, is then equal to potential of the zinc electrode (on the hydrogen scale) since potential of the standard hydrogen electrode is taken as zero.

In this case, reduction occurs at the hydrogen electrode and oxidation takes place at the zinc electrode shown below:

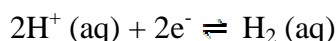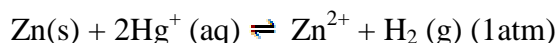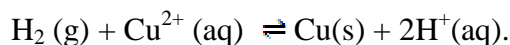Hydrogen electrode:

$$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (aq)$$

Zinc electrode:

$$Zn(s) \rightleftharpoons Zn^{2+} + 2e^-$$

∴ The net reaction is

$$Zn(s) + 2Hg^+ (aq) \rightleftharpoons Zn^{2+} + H_2 (g) (1atm)$$

If copper electrode is connected with the hydrogen electrode the oxidation takes place at the hydrogen electrode and reduction occurs at the copper electrode. The net reaction is then

$$H_2 (g) + Cu^{2+} (aq) \rightleftharpoons Cu(s) + 2H^+(aq).$$

9.8 SECONDARY REFERENCE ELECTRODE; CALOMEL ELECTRODE

It is not convenient to use the standard hydrogen electrode (SHE) as the reference electrode. This is because it is difficult to maintain the activity of H^+ions
In the solution at unity and to keep the pressure of the gas uniformly at one atmosphere, a far better reference electrode is calomel electrodes which have been described in fig 9.5 of this unit. It can be set up conveniently and can be used for a long with any subsequent attention. The potential of the calomel electrode, on hydrogen scale, has been measured carefully by connecting it with a standard hydrogen electrode. The potential of the electrode depends upon the concentration of KCl solution in the calomel vessel. The value of 0.1M KCl, 1.0 M KCL and a standard solution of KCl are 0.3335 volt, 0.2810 volt and 0.2422 volt, respectively, at 25^0 C. The

calomel electrode with saturated solution is most commonly used and is referred as standard calomel electrode (SCE).
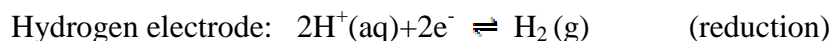
9.9 SIGN OF ELECTRODE POTENTIAL

According to the latest convention adopted by IUPAC (**International Union Of Pure And Applied Chemistry)**, the electrode potential is given a positive sign if the electrode reaction involves reduction when connected to the standard hydrogen electrode reaction involves oxidation when connected to the standard hydrogen electrode whose potential is taken arbitrarily as zero.

Thus with copper electrode (copper rod dipped in a solution of copper salt) is connected with a standard hydrogen electrode, reduction takes place at the copper electrode. The electrode reactions are as follows:

Copper electrode $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(S)$ (reduction)

Hydrogen electrode $H_2(g) \rightleftharpoons 2H^+ + 2e^-$ (oxidation)
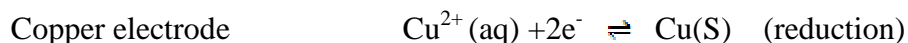
Hence the potential of copper electrode is taken as positive. Thus $E_{(Cu^{2+}, Cu)}$ is positive.

If zinc electrode is connected with the standard hydrogen electrode, oxidation takes place at the zinc electrode. The electrode reaction are shown as follows,

 Zinc electrode: $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$ (oxidation)

Hydrogen electrode: $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ (reduction)

Hence, the potential of zinc electrodeis taken as negative. Thus $E_{(Zn^{2+}, Zn)}$ is negative.

9.10 NERST EQUATION: EFFECT OF ELECTROLYTE CONCENTRATION ON ELECTRODE POTENTIAL

Suppose the reaction occurring in a galvanic cell is represented as:

$aA + bB \rightleftharpoons cC + dD$

Suppose in a particular cell reaction, n is the number of electrons liberated at one electrode (or taken up at the other electrode) then evidently, n faradays (nF) of electricity will be generated in

the complete cell reaction. If, for the sake of simplicity, the emf of the cell is denoted by E, then, electrical energy produced by the cell $= nFE$ Hence $-\Delta G = nFE$

Then from Van`t Hoff isotherm we know that the thermodynamic potential change would be

$$\Delta G = \Delta G^0 + RT \ln K$$

Since $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$

The other equation becomes

$$E = E^0 - \frac{RT}{nF} \ln K$$

Where, $E^0 =$ standard electrode potential

                    $R =$ gas constant,

                    $T =$ absolute temperature,

                    $n =$ number of electrons transported in the half reaction,

                    $F =$ faraday of electricity,

                    $K =$ equilibrium constant,

For oxidation hall- cell reaction when metal electrode M gives M^{2+} ions:

$$M \longrightarrow M^{2+} + 2e^-$$

$$E = E^0 - \frac{RT}{2F} \ln \left(\frac{M}{M^{2+}}\right) \quad \text{For solids } M = 1$$

Then $E = E^0 + \frac{RT}{2F} \ln(M^{2+})$ …………..……………….(1)

This equation (1), which gives the effect of concentration of M^{2+} ion on the potential of M^{2+}, M electrode and is known as Nernst equation.

In the case of hydrogen electrode, the equation is represented as:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$
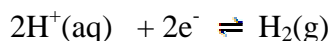
Hence $E = E^0 + \frac{RT}{F} \ln [H^+]$ …………………………………(2)

Because activity of H_2 gas at one atmosphere pressure is taken as unity. Here E^0 for hydrogen electrode is arbitrarily taken as zero, we have

$$E = \frac{RT}{F}\ln(H^+) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3)$$

In the case of Fe^{3+}, Fe^{2+} electrode, the equilibrium is represented as

$$Fe^{3+}(aq) + \rightleftharpoons Fe^{2+}(aq)$$

Here $\quad E = E^0 - \frac{RT}{F}\ln\left[\frac{Fe^{2+}}{Fe^{3+}}\right]$

$$= E^0 - \frac{RT}{F}\ln\left[\frac{Fe^{3+}}{Fe^{2+}}\right]$$

It follows from the above discussion that if we write the electrode reaction, in general as:

Oxidized state + ne⁻ $\rightleftharpoons$ reduced state

$$E = E^0 - \frac{RT}{F}\ln\left[\frac{reduced\ state}{oxidised\ state}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4)$$

9.11 STANDARD ELECTRODE POTENTIAL

That the potential of an electrode at a given temperature we have discussed above, depends upon the concentration of the ion in the surrounding solution, if the concentration of the ions is unity and temperature 25^0C, the potential of the electrode is termed as the standard electrode potential.

The standard electrode potential of a number of electrodes is given in the table 9.1. These values are said to be on hydrogen scale since in these determinations the potential of a standard hydrogen electrode used as a reference electrode, has been taken as zero. The values of standard electrode potentials arranged in a decreasing order constitute what is called the electrochemical series.

Table 9.1 electrochemical series, standard electrodes potential at 25^0C.

Reduction Half-reaction	$E°$ (V)
$F_2 + 2e^- \longrightarrow 2F^-$	2.87
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.78
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	1.69
$Au^{3+} + 3e^- \longrightarrow Au$	1.50
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.36
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
$2H^+ + 2e \longrightarrow H_2$	**0.00**
$Sn^{2+} + 2e^- \longrightarrow Sn$	-0.14
$Cd^{2+} + 2e^- \longrightarrow Cd$	-0.40
$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76
$H_2 + 2e^- \longrightarrow 2H^-$	-2.23
$Mg^{2+} + 2e^- \longrightarrow Mg$	-2.37
$Na^+ + e^- \longrightarrow Na$	-2.71
$Li^+ + e^- \longrightarrow Li$	-3.05

This table includes a large variety of electrodes (half-cell) along with their electrode reaction and standard electrode potential. The higher its positive value the greater is the tendency of the oxidized form to get reduced by accepting electrons. And, conversely, the greater the negative value, the greater is the tendency of the reduced form to get oxidized by donating electrons.

Now any two suitable half- cells can be combined to form a galvanic cell. The emf of the cell and the feasible cell reaction can be easily determined with the help of the information given in this table. For this the following rules have been suggested:

Representation of cell. The electrode on the right is written in the order : ion, electrode (e.g., Cu^{++},Cu) and the electrode on the left is written in the order :electrode, ion, (e.g., Zn, Zn^{2+}). In the galvanic cell formed by the combination of two electrodes, oxidation occurs at the left hand

electrode and reduction at the right hand electrode so that the electric current (electrons) in the external circuit flow from the left hand electrode (L.H.E.)to the right hand electrode (R.H.E.).
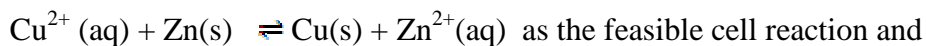
Determination of cell the potential and the emf of the cell reaction:

According to the latest convention, both the half reactions are written as reduction reaction along with their standard electrode potentials in the form of chemical equations. After balancing the number of electrons if necessary, the half-cell reaction equation with a lower electrode potential is subtracted forms the one with a higher electrode potential. The result gives the cell potential as well as the feasible cell reaction.

The two half cell reaction in Daniell Cell are written as,

(i) Cu^{2+} (as) + $2e^-$ $\rightleftharpoons$ Cu(s): $E^0 =$ +0.34 V

(ii) Zn^{2+} (aq) + $2e^-$ $\rightleftharpoons$ zn(s): $E^0 =$ -0.76

Substracting eq. (ii) from eq. (i) we get

Cu^{2+} (aq) + Zn(s) $\rightleftharpoons$ Cu(s) + Zn^{2+}(aq) as the feasible cell reaction and

0.34 – (-0.76) =1.10 Vas cell potential.

9.12 SUMMARY

In this unit the functioning of the cells have been discussed in detail. The voltaic cell also known as galvanic cell is one in which electrical current is generated by a spontaneous redox reaction. Different types of reversible electrodes and their functioning the functioning of hydrogen electrode and calomel electrode have been discussed in detail. Different cell reaction has also been discussed.

9.13 TERMINAL QUESTIONS

A. Multiple choice /objective type questions:

Q.1   For the half cell reaction O_2 (g) +$2H_2O$ (l) +$4e^-$ $\rightarrow$$4OH^-$(aq) -$\Delta G^0/FE^0$ is equal to

(a) 1,   (b) 2   (c) 3   (d) 4

Q.2   In any electrochemical cell, the cathode is always…….

(a) A non metal   (b) attached to battery (c) the electrode at which some   species gain electron (d) the electrode at which some species lose electron.

Q.3   The site of oxidation in an electrochemical cell is

(a) The anode   (b)   the cathode   (c)   the electrode   (d) the salt bridge

B. Short answers type questions:

Q.4   Define electrochemical cell.

Q.5   What do you mean by electrode potential.

Q.6   Write a short note on redox reactions.

C. Long answer type questions:

Q.7   Describe the construction and working of calomel electrode.

Q.8.   Explain the term electrode potential. Derive Nernst equation for describing the effect of concentration of electrolyte on electrode potential. What is meant by standard electrode potential?

9.14 ANSWERS

1. (d)   2. (c) 3. (a)

Source of study material

1.   Essential of physical chemistry by Bahl, Bahl and Tuli.
2.   Principles of physical chemistry By Puri, Sharma and Pathania.
3.   Physical chemistry By   P.C. Rakshit.
4.   Physical chemistry By Atkins.

UNIT-10 ELECTROLYTIC AND GALVANIC CELLS

CONTENTS:

10.1 OBJECTIVES

In unit 9 you have studied some basics of cells, electrodes, functioning of electrodes, various electrode reactions, primary and secondary reference electrodes, electrochemical series and its significance.

10.2 INTRODUCTION

In a Daniell cell a zinc rod is immersed in a $ZnSO_4$ solution and a copper rod in a copper sulphate solution. The two solutions are kept separated by a porous partition. This porous partition allows current to pass through but prevents mass diffusion. Zinc and copper rods are two electrodes. When these are connected externally by a metallic wire, current flows in the circuit. Copper is said to be the positive pole and zinc the negative.

In this unit you will study reversible and irreversible cells, measurement of cell emf, over voltage, calculation of some thermodynamic parameters and some other related topics.

10.3 REVERSIBLE AND IRREVERSIBLE CELLS

The electrochemical cells may be reversible or irreversible. In a reversible cell it is implied that the chemical reaction occurring in the cell may proceed in either direction depending upon the direction of flow of current. If we apply an emf from an external source so as to cause a current to flow in the opposite direction the chemical action is reversed. The driving and opposing forces may be only infinitesimally different. When these requirements are satisfied the cell is reversible. When the chemical reaction cannot be reversed by the application of external e.m.f., the cell is irreversible.

The Daniell cell is an example of a reversible cell. When 2 coulombs of electricity produced, 65/96500 gm of zinc goes into the solution at the anode and 63.5/96500 gm of copper is deposited at the cathode. Now if an external e.m.f. is applied such that 2 coulombs of electricity are passed in the opposite direction, the cell will return to original state, i.e., the quantity of zinc as dissolved earlier will be deposited at the anode and the previous quantity of copper will be dissolved at the cathode. The cell is thus reversible.

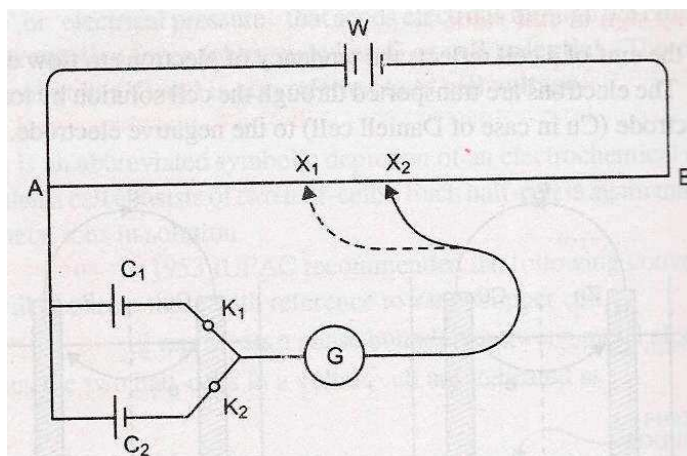Now let us consider the following cell:

Zn /H$_2$SO$_4$/Cu

In this cell one Faraday of electricity is produced, when one gm equivalent zinc goes into the solution and one gm-equivalent hydrogen is liberated at the cathode (Cu). If one faraday of electricity is passed through the cell in opposite direction one gm-equivalent of copper goes into the solution and one gm-equivalent of hydrogen is liberated at the zinc electrode. The original state is not reproduced; the reaction is also not reversed. This is an irreversible cell.

In a cell there are two electrodes. Each of the electrodes in contact with its ionic solution is called a single electrode or half cell. In a reversible cell each half cell is also reversible. Thus in Daniell cell the anode zinc (Zn/Zn^{++}) in contact with zinc ions is a reversible half cell; and copper (Cu/Cu^{++}) in contact with copper ions is other reversible half cell.

10.4 DETERMINATION OF CELL e.m.f.

The e.m.f. of an unknown cell can be measured with the help of a potentiometer fig 10.1. It consists of a wire AB which is about a meter long. The

Fig 10.1 Measurement of emf of a cell

two ends of this wire are connected to a working battery W. A standard cell C$_1$ (a cell of known e.m.f.) is connected to the end A. At the other end, the cell C$_1$ is connected to a galvanometer through a key K$_1$. The galvanometer is then joined to a sliding contact that moves on the wire AB. The cell C$_2$ whose e.m.f. is to be measured is similarly connected to the key K$_2$, the galvanometer and then the sliding contact. By using the key K$_1$ the cell C$_1$ is put into the circuit

and the contact is moved to and fro along AB. When no current flows through the galvanometer, the point of contact X_1 is recorded. Then by using the key K_2, the cell C_2 is put into the circuit and the procedure is repeated to find the corresponding point X_2. The e.m.f. of the cell C_2 is calculated by using the following equation:

$$\frac{emf \ of \ C_2}{emf \ of \ C_2} = \frac{distance \ AX_2}{distance \ AX_2}$$

Cell e.m.f. can also be measured electronic voltmeters of digital type.

10.5 DETERMINATION OF ΔG, ΔH, ΔS AND K OF A CELL REACTION

Suppose in a particular reaction, n is the number of electrons liberated at one electrode, then, evidently, n faradays (nF) of electricity will be generated in the complete cell reaction. If, for the sake of simplicity, the e.m.f. of the cell is denoted by E then:

Electrical energy produced by the cell = nFE

Hence $-\Delta G$ = nFE, …..…….(1)   (ΔG=free energy change)

From Gibbs-Helmholtz equation, decrease in free energy, -ΔG, of a cell reaction at constant pressure, would be given by the expression

$$-\Delta G = -\Delta H - T \left(\frac{\partial \Delta G}{\partial T} \right)_p \ldots\ldots\ldots\ldots..(2)$$

Where $= -\Delta H$ is the decrease in enthalpy of the cell reaction at constant pressure. Substituting the value of ΔG from equation (1).

we have $nFE = -\Delta H - T \left[\frac{\partial}{\partial T} (-nFE) \right]_p$

$$= = -\Delta H - nFT \left(\frac{\partial E}{\partial T} \right)_p \qquad \ldots\ldots\ldots\ldots.(3)$$

This equation means, whether electrical energy, viz. nFE is equal to or less than the enthalpy of the reaction (ΔH) depends upon the sign of $\left(\frac{\partial E}{\partial T} \right)_p$, i.e., upon the sign of the temperature coefficient of the e.m.f. of the cell. If it is zero, the electrical energy will be equal to the enthalpy

of the cell reaction. If it is positive, i.e., if the e.m.f. of the cell increases with rise in temperature, the electrical energy will be greater than the enthalpy of the cell reaction. The additional energy will be supplied to the cell by the surroundings and if that is not possible, the temperature of the cell will fall during the working. If $\left(\frac{\partial E}{\partial T}\right)_P$ is negative, the electrical energy will be smaller than the enthalpy of the cell reaction. The difference between the two values will be given out as heat to the surroundings and if that is not possible, the temperature of the cell will rise during the operation. In the case of Daniell cell $\left(\frac{\partial E}{\partial T}\right)_P$ is very small. Therefore the electrical energy is very close to the enthalpy of the cell reaction.

If the heat of reaction (or free energy change) and the temperature coefficient of a cell are known, we can calculate the e.m.f., E, of the cell. For example, in the case of Daniell cell $\left(\frac{\partial E}{\partial T}\right)_P$ is nearly zero, n=2 and ΔH=-50.100 cals.

Since 1 cals. =4.185 volt coulomb

$$E = -\frac{\Delta H}{nF} = -\frac{4.185 \times (-50.100)}{2 \times 96500}$$

$$= 1.09 \text{ V}$$

Thus the e.m.f. of the Daniell cell is 1.09 volts. Conversely, if the e.m.f. of the reversible cell and its temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_P$ are known, ΔH (orΔG) can be calculated. The heats of reaction calculated from the e.m.f. measurements are nearly the same as derived from thermal experiments.

The entropy change related to the enthalpy change and free energy by the well known thermodynamic expression.

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

Hence $-\Delta S= (\Delta G - \Delta H)/T$ …………..(4)

Example:

The emf of the cell Cd, $CdCl_2$ 5/2 H_2O (saturated) // AgCl(s), Ag in which the reaction is

Cd(s) + 2AgCl(s) + aq $\rightleftharpoons$ $CdCl_2$ 5/2H_2O (sat) + 2 Ag(s) is 0.6753 volt at 25^0C and 0.6915 volt

at 0^0C. Calculate the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of

the cell reaction at 25^0C.

Solution: (i) Free energy change (ΔG)

The cell reaction requires 2 faradays of electricity for its completion i.e., n=2

Now ΔG = -nFE

      = -2x96500 C mol^{-1}x0.06753 volts

      = -130332.9 joule   (as volt x coulomb=joule)

      = -130.33 KJ

(ii) Enthalpy change:

The e.m.f. of the cell is given by

$$E = -\frac{\Delta H}{2F} + T(\frac{\partial E}{\partial T})_P$$

In this case, the e.m.f. decreases with increase of temperature i.e., $(\frac{\partial E}{\partial T})_P$ is negative. Thus $(\frac{\partial E}{\partial T})_P =$

$-(\frac{0.6915v - 0.6753v}{25.R})$

      = -0.00065vk^{-1} at atmospheric pressure

$\therefore$ 0.6753V = $\frac{\Delta H}{2x96500C\,mol^{-1}}$ + 298 (-0.00065VK^{-1})

      = -167717 joule

      = -167.72 KJ

(iii) Entropy change:

$$-\Delta S = \frac{\Delta G - \Delta H}{T}$$

$$= -\frac{-130.33 - (-167.72}{298K}$$

$$= 0.1238 \text{ KJ K}^{-1}$$

$$= 123.8 \text{ KJ}^{-1}$$

10.5.1 Electromotive force and equilibrium constant of a cell reaction:

Suppose the reaction occurring in a reversible cell is represented by the general equation.

$$A+B \rightleftharpoons C+D$$

The decrease in free energy, $-\Delta G$ accompanying the process is given by the well known thermodynamic equation.

$$-\Delta G = -\Delta G^0 - RT\ln Q \qquad \text{………………..} (5)$$

Where $-\Delta G^0$ is the decrease in free energy accompanying the same process when all the reactants and products are in their standard states of unit activity and Q stands for the reaction quotient of the activities of the products and of the reactants at any given state of the reaction, that is

$$Q = (a_c a_D)/(a_A a_B)$$

If E is the emf of the cell in volts and the cell reaction involves the passage of n faradays, i.e., nF coulombs, the electrical energy produced by the cell is n FE volt coulombs i.e., joules.

So $nFE = -\Delta G^0 - RT\ln Q \qquad \text{…..………} (6)$

From van't Hoff's isotherm we know

$$-\Delta G^0 = -RT\ln K \qquad \text{………………..} (7)$$

Where K is equilibrium constant for the reaction. Substituting in equation (6)

We get-

$$nFE = RT\ln K - RT\ln Q \qquad \text{………….} (8)$$

substituting the value of Q we get,

$$nFE = RT\ln K - RT\ln(a_C a_D)/a_A a_B) \qquad \text{…….} (9)$$

---

or $\quad E = \frac{RT}{nF} lnK - \frac{RT}{nF} ln$ $(a_C a_D)/a_A a_B$

$$= \frac{2.303RT}{nF} logK - \frac{2.303RT}{nF} log \left(\frac{a_C a_D}{a_A a_B}\right) \quad ....(10)$$

Knowing the emf of the cell, temperature of the cell reaction and the concentration of reactants and products of the cell reaction we can calculate the equilibrium constant of the cell reaction.

10.6 POLARIZATION

In a cell at equilibrium, for each ionic species, the rate of electron transfer across an electrode in the cathodic direction is exactly balanced by an equal rate of electron transfer in the anodic direction, so that the current density, ; (current per unit area) is

$\quad i_c = i_a = i_o$

The equilibrium difference in electric potential is determined by this condition. When an electrochemical cell is operating under non-equilibrium conditions $i_c \neq i_a$ and these is net current density $i = i_c - i_a$. The electric potential difference between the terminals of the cell departs.

In a voltic cell electric energy is produced at the cost of chemical reactions. From thermodynamics considerations we know that the amount of electrical energy produced under reversible conditions is equal to the free energy decrease. But if the electrode processes are irreversible, the electrical energy output will be less than the decrease in free energy; a portion of the free energy will be dissipated as heat.

The opposite non-spontaneous process, namely the chemical reaction at the cost of electric energy, can be affected by passing electricity under a suitable applied potential through a cell where the same chemical transformation could occur. This is electrolysis and would increase the free energy. Under reversible conditions, the free energy changes, though opposite in sign, would be equal in magnitude in the two opposite transformations.

But in most of our practical applications, which are generally rapid, the condition of reversibility are not observed. The energy required to carry out the chemical reaction is that necessary for the thermodynamically reversible change plus an extra amount to compensate for

the irreversibility. It is thus easily realized that under irreversible conditions, the applied potential needed for electrolysis would be greater than the reversible e.m.f. of the corresponding voltaic cell. The extra voltage required over the theoretical value for electrolysis is called polarization voltage, this phenomenon is known as polarization and the cell is said to be polarized.

From the equilibrium value $\Delta\emptyset = E$, the e.m.f. If the cell is converting chemical energy into electrical energy, $\Delta\emptyset < E$. If the cell is using an extra source of electric energy to carry out a chemical reaction, $\Delta\emptyset > E$. The actual value of $\Delta\emptyset$ depends on the current density I at the electrodes. The differences,

$\Delta\emptyset_i - \Delta\emptyset_{(o)} = \eta$ is called polarization.

10.7 OVER VOLTAGE OR OVER POTENTIAL

In an electrolytic cell the discharge of an ion on the cathode would occur at the standard half-cell reaction potential as indicated in table 9.1. Thus the H^+ ions will discharge at the cathode at $E^0 = 0.00V$. It has been experimentally found to be nearly true using platinum black (i.e., finally divided platinum) as the cathode. However with other metal electrodes, for example, mercury and zinc, the voltage needed for the discharge of H^+ ions (evolution of H_2) is considerably higher than 0.00V. This difference between the observed voltage (E) and the standard half-reaction voltage (E^0) is called the hydrogen over voltage.

Over voltage of an electrochemical reaction may be defined as the difference between the potential of an electrode, (a) at which the reaction is actually taking place and another electrode, (b) which is at equilibrium potential for the same reaction.

With platinum and lead electrodes we require a current of 1.7 and 2.2 volt respectively for the electrolysis of H_2SO_4 against a theoretical value of 2.3 volt. This is explained by the fact that the passage of small current is accompanied by a relative large polarisation which depends on the nature of electrode. So over voltage may also be defined as the diference between the potential of an electrode when gas evolution is actually observed and the theoretical reversible value for the same solution.

10.7.1 Hydrogen overvoltage:

At a platinised platinum electrode, H_2 is liberated practically at the reversibly hydrogen potential of the solution. With other electrodes, a more negative potential is required to secure its liberation. The hydrogen overvoltage may be defined as, the difference between the potential of an electrode at which hydrogen gas is actually evolved and the potential of reversible hydrogen electrode with reference to the same solution.

Over voltage is a polarization potential associated with the process occurring at the electrode surface. This effect is particularly important when the product of electrolysis is a gaseous one. An irreversibility is introduced in the process at the electrode due to slowness at some stage. Usually two or three stages are involved in the discharge of the product on the electrode. First the ions are deposited on the electrode and neutralized; the neutral atoms are then deposited or rendered into molecules, if polyatomic; and finally the molecules escape if gases in the form of bubbles. The liberation of hydrogen at the smooth Pt-cathode can be explained as follows:

The steps associated with H_2^- evolution are

(a) $H^+ + e^- \rightleftharpoons \quad H$ atom

(b) $2H \quad \rightleftharpoons \quad H_2$ (adsorbed)

(c) H_2(adsorbed) $\rightleftharpoons H_2$ gas

The processes at (a) and (c) are quite rapid and these equilibria are easily attained. But for the process at (b), the formation of hydrogen molecule from atomic hydrogen is a slow process and consequent equilibrium is only arrived at with difficulty. For given H^+ ion concentration in the solution, the electrode potential will be determined by H^+ ion concentration and hence by atomic hydrogen on the electrode. The atomic hydrogen concentration is again dependent on gaseous hydrogen molecules. As equilibrium (b) is not readily attained, the electrode cannot act as reversible H_2- electrode. Because of the slowness of the reaction $2H \longrightarrow H_2$, a relatively high concentration of atomic hydrogen on the electrode is necessary before the rate of reaction $2H \rightarrow H_2$ would equal the rate at which H^+ ions are discharged by process (a). This high concentration of atomic hydrogen is much greater than required by equilibrium envisaged in process (a). The result is that due to high concentration of atomic hydrogen, and hence H^+ ions, the electrode

potential is much greater than that of the reversible hydrogen electrode. This excess of e.m.f. is the overvoltage of hydrogen on that electrode. If the electrode be such which catalyze the process (b), i.e., the hydrogen atom are catalyzed to form H_2-molecules then the overvoltage can be considerably reduced. In fact if platinized platinum be used the overvoltage is practically absent.

The overvoltage at cathode or anode depends on the following:

(i) The nature and physical state of the electrode employed
(ii) The physical state of the substance deposited. If it is a metal, overvoltage is usually small but for a gas the overvoltage is higher.
(iii)The current density employed and the temperature.

The values for hydrogen overvoltage on some metals are listed in table 10.1. In general the additional potential, over and above the electrode potential, this is needed to secure the evolution of the gas.

Cathode	Overvoltage
Mercury	0.78V
Zinc	0.70V
Copper	0.23V
Silver	0.15V
Platinum black	0.00V

Table 10.1 Hydrogen over voltage on some metal cathodes in dilute H_2SO_4

10.8 CONCENTRATION CELL WITH AND WITHOUT TRANSPORT

10.8.1 Concentration cells:

In the case of galvanic cells, the electrical energy arises from the chemical reactions which take place in the cells. There is another category of cells in which e.m.f. arises not due to

chemical reaction but due to transfer of matter from one half-cell to other because of difference in the concentration of the species involved. These are called concentration cells.
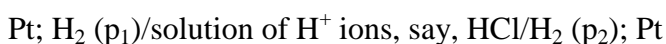
Concentration cells are of two types:

1. Electrode-concentration cells and
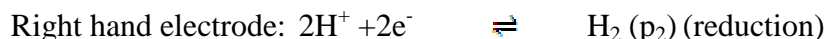2. Electrolyte-concentration cells.

10.8.2 Electrode concentration cells:

In these cells, two like electrodes at different concentrations are dipping in the same solution. Two hydrogen electrodes at unequal gas pressure immersed in the same solution of hydrogen ions constitute an electrode-concentration cell.

This may be represented as follows:

Pt; H_2 (p_1)/solution of H^+ ions, say, HCl/H_2 (p_2); Pt

The reactions occurring are:

Right hand electrode: $2H^+ + 2e^-$ $\rightleftharpoons$ H_2 (p_2) (reduction)

Left hand electrode H_2 (p_1) $\rightleftharpoons 2H^+ + 2e^-$ (oxidation)

Overall reaction H_2 (p_1) $\rightleftharpoons$ H_2 (p_2)

This reaction is evidently independent of the concentration of electrolyte.

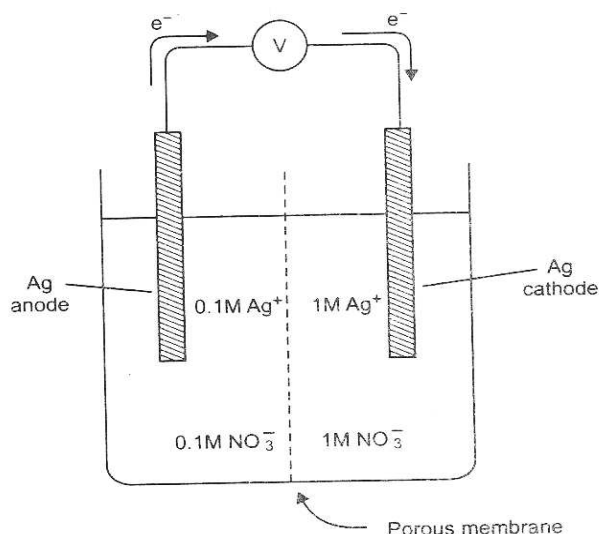## 10.8.3   Electrolyte concentration cells:

In these cells, the two electrodes of the same metal are dipping in solutions of metal ions at different concentrations. Hence concentration cell may be defined as "a cell in which emf arises as a result of different concentrations of the same electrolyte in the component of half cells". One such cell is represented below fig 10.2.

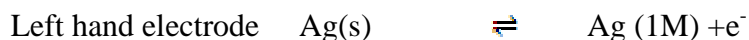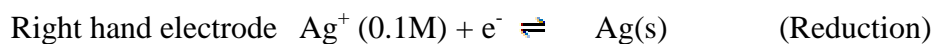$$Ag/Ag^+ \ (1M) \ || \ (0.1M) \ Ag^+/Ag$$

A typical concentration cell is shown in fig 10.2. It consists of two silver electrodes, one immersed in 0.1M silver nitrate solution and the other in 1M solution of same electrolyte. The two solutions are in contact through a membrane (or a salt bridge). When the electrodes are

connected by a wire, it is found experimentally that electrons flow from the electrode in more dilute solution (0.1M) to that in the more concentrated (1M) solution.

Fig 10.2 A concentration cell

The reactions occurring are

Right hand electrode $Ag^+ (0.1M) + e^- \rightleftharpoons$ $Ag(s)$ (Reduction)

Left hand electrode $Ag(s)$ $\rightleftharpoons$ $Ag (1M) + e^-$

Overall reaction is $Ag^+ (0.1M)$ $\rightleftharpoons$ $Ag^+ (1M)$

Thus in a bid to equalise concentration of Ag^+ ions in the two compartments the cell will develop e.m.f. to cause transfer of electrons. Eventually, the solutions in two compartments will have equal Ag^+ ion concentration and there will be no e.m.f. recorded.

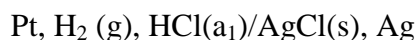## 10.8.4 Types of concentration cells:

Electrolyte-concentration cells in which solutions of the same electrolyte of different concentration are used are of two types. In one of the types, the two electrolytic solutions are not in direct contact with each other and the transfer of ions from one solution to the other does not take place directly. These are called concentration cells without transference. The two solutions are separated from each other by means of a salt bridge or by any other means. In the second type, the two solutions are in direct contact with each other. The transference of ions from one

solution to the other takes place directly. Such cells are called concentration cells with transference.

10.8.5   Concentration cell without transference:

When two concentration cells in which two solutions are separated from each other through a salt bridge we get concentration cell without transference. Some other means may also be employed to keep the solutions apart and bring out the transference of ions indirectly.

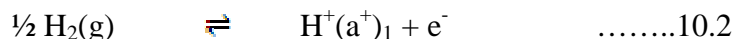Let us consider a simple electrochemical cell such as:

Pt, H_2 (g), $HCl(a_1)$/AgCl(s), Ag

Let the activity of H^+ ions in the solution be (a^+), and that of Cl^- ions (a^-). Since reduction takes place on the right hand electrode and oxidation on the left hand electrode. The two half-cell reactions will be as follows:
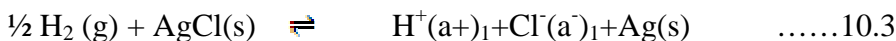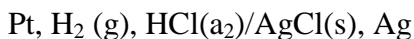
Reduction half-cell reaction:

$$AgCl + e^- \rightleftharpoons Cl^-(a_-)_1 + Ag(s) \quad \text{.......10.1}$$

Oxidation half reaction

$$\frac{1}{2} H_2(g) \rightleftharpoons H^+(a^+)_1 + e^- \quad \text{........10.2}$$
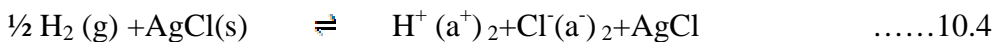
The net reaction taking place in the cell for one faraday of electricity is obtained by adding equations (10.1) and (10.2). Thus

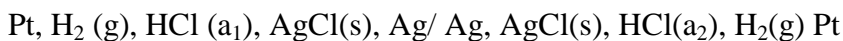$$\frac{1}{2} H_2 (g) + AgCl(s) \rightleftharpoons H^+(a+)_1 + Cl^-(a^-)_1 + Ag(s) \quad \text{......10.3}$$

Now consider the same cell with difference that the activity of HCl solution is now a_2:

Pt, H_2 (g), $HCl(a_2)$/AgCl(s), Ag

The net reaction by passing one faraday of electricity will be now as follows:

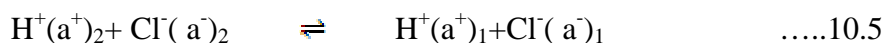$$\frac{1}{2} H_2 (g) + AgCl(s) \rightleftharpoons H^+ (a^+)_2 + Cl^-(a^-)_2 + AgCl \quad \text{......10.4}$$

Now consider the situation when the two cells are connected to each other in such a way that they send current in opposite direction. Thus:

Pt, H_2 (g), HCl (a_1), AgCl(s), Ag/ Ag, AgCl(s), $HCl(a_2)$, H_2(g) Pt

  1 atm   1 atm

The overall reaction of the combined cell for the passage of one faraday of electricity will be obtained by subtracting equation (10.4) from equation (10.3) i.e.,
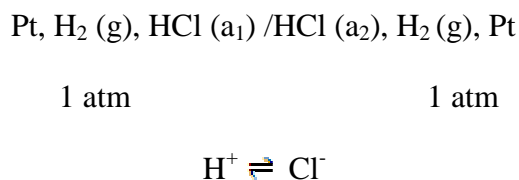
$$H^+(a^+)_2 + Cl^-(a^-)_2 \rightleftharpoons H^+(a^+)_1 + Cl^-(a^-)_1 \qquad .....10.5$$

Thus, for the flow of one faraday of electricity, the overall reaction is the transfer of one mole of each of H^+ and Cl^- ions or one mole of HCl from solution of activity a_2 to that of activity a_1. Since the two solutions are not in direct-contact with each other, it is concentration cell without transference.

Hence emf of such a cell would be given by $E_{w.o.t.} = \frac{RT}{F} \ln \frac{(a^+)_2}{(a^+)_1}$

10.8.6 Concentration cell with transference:

Let us consider a concentration cell formed by combining two hydrogen electrodes in contact with HCl solution of different concentrations. The two solutions are in contact with each other, as shown:

Pt, H_2 (g), HCl (a_1) /HCl (a_2), H_2 (g), Pt

    1 atm   1 atm
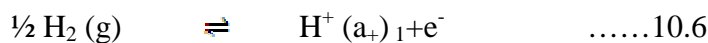
            $H^+ \rightleftharpoons Cl^-$

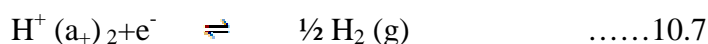The reaction on the left involves oxidation and on the right involves reduction.

The following changes are involved for the passage of one faraday of electricity:

Faraday of electricity:

Left hand electricity:

$$\tfrac{1}{2} H_2 \text{ (g)} \rightleftharpoons H^+ (a_+)_1 + e^- \qquad ......10.6$$

Right hand electrode:

$$H^+ (a_+)_2 + e^- \rightleftharpoons \tfrac{1}{2} H_2 \text{ (g)} \qquad ......10.7$$

Thus H^+ ions are generated at the left hand electrode and consumed at the right hand electrode as the current flows. Since the solutions are in direct contact with each other, the ions are free to move from one solution to the other when current flows through the cell. In this case, evidently, H^+ moves from the solution on the left hand side to that on the right hand side. Since anions move in direction opposite to that in which cations move, Cl^- ions migrate from right to left, as shown in the cell above.

Knowing the activity of the uni-univalent electrolyte, the emf of the cell can be calculated as;

$$E_{wt} = t_- \frac{RT}{F} \ln \frac{a_2}{a_1}$$

This equation is used for calculating activity of an electrolyte at a given concentration from the experimental value of E_{wt}. One of the solutions used should be known activity.

10.9 LIQUID JUNCTION POTENTIAL

In chemical cells of the type,

Zn /ZnSO$_4$ soln / CuSO$_4$ soln / Cu,

Zn /ZnSO$_4$ soln /0.1NKCl/H$_g$Cl$_2$(s)/ Hg,

Cd /CdSO$_4$ soln / Fe^{2+}-Fe^{3+} (Pt), etc

Two different solutions are in contact. There indeed is a junction of the two solutions from the two half-cells. The ions present on either side of the junction have a tendency to diffuse into the other side. The speeds of the different ions of the two electrolytes, even those of cations and anions of the same electrolyte, are different. The result is that the faster ion moves across the boundary ahead of the slower. So one side of the boundary becomes positively charged and the other negatively. That is, an electrical double layer is formed at the junction of the two liquids. The attraction between the two opposite charges prevents any appreciable separation of anions from cations. At the junction of two electrolytes there exists a potential difference, called liquid junction potential (ξ). Its magnitude depends upon the relative velocities of migration of ions. Even if the same electrolyte be present in the two half-cells at different concentrations, the junction potential will arise due to difference in the speeds of anions and cations.

10.10 APPLICATION OF CONCENTRATION CELLS:

The e.m.f. measurement finds a number of applications. Some of these applications are given below:

10.10.1 Determination of transport number:

The e.m.f. of a concentration cell with transference is represented by $E_{w.t}$, in which the end electrodes are reversible with respect to cation, is given by the equation.

$E_{w.t.} = t_{-}(RT/F)\ln(a_2/a_1)$ …….……..10.8

The e.m.f. of the same cell with the same solution but without transference, denoted by $E_{w.o.t.}$ is given by

$E_{w.o.t.} = RT/F \ln(a_2/a_1)$ ………..…10.9

Thus the, ratio of the e.m.f of the two concentration cells, one with transference and one without transference, gives transport number of the anion, if the electrode are reversible with respect to the cation.
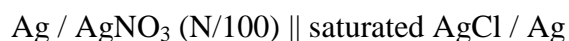
If the electrodes are reversible with respect to the anion, then the ratio of the two e.m.f. will give the transport number of the cation of the electrolyte.

10.10.2 Determination of solubility of sparingly soluble salts:

The ionic concentration of a solution can be calculated from the e.m.f. of a concentration cell. In case of a sparingly soluble salt, the salt can be supposed to be completely ionized even in saturated solution. Hence the ionic concentration is proportional to the solubility of the salt.

Suppose we want to find the solubility of silver chloride.

This can be done by measuring the e.m.f., E of the cell;

Ag / AgNO$_3$ (N/100) || saturated AgCl / Ag

The e.m.f. of the cell at 25^0 is given by the relation

$$E = \frac{0.0591}{n} \log C_2/C_1$$

Here, n, the valence of Ag^+ ion is 1 and the concentration of Ag^+ in N/100 $AgNO_3$ solution is 0.01 gm ion per liter.

Hence $E = \frac{0.0591}{1} \log \frac{0.01}{C_1}$

From this expression, the concentration of AgCl in gm ions per liter can be calculated. Multiplying this by 143.5, the molecular weight of AgCl, we get the solubility of silver chloride in gms per liter.

10.10.3 Determination of valence of ions:

Valence of ion can be determined from e.m.f. measurement. The valence of mercurous ion was in doubt for a long time. It was finally established by determining the emf of a concentration cell of the type given below:

Mercury, mercurous nitrate solution (C1) ‖ Mercuruous nitrate solution (C_2)/Mercury. The salt bridge represented by the two vertical lines connecting the two solutions contains saturated solution of ammonium nitrate.

The e.m.f. of the cell, E assuming the activity coefficients to be equal to unity is given by the expression

$$E = (RT/nF) \ln (c_2/c_1)$$

Where n is the valence of mercous ion and c_2 is greater than c_1,

Thus, $E = \frac{0.0591}{n} \log \frac{c_2}{c_1}$ (at 25^0C)

It was found that when $C_2/C_1 = 10$, the emf was 0.0295 volt. Therefore, the valency of mercurous ion is 2 and it should be represented as Hg_2^{2+}.

10.10.4   Determination of activity coefficient of electrolytes:

Activity coefficient of electrolytes can be determined by e.m.f. measurements. Suppose we want to determine the activity coefficient of hydrochloric acid. Consider a cell without liquid junction containing HCl. The two electrodes are so chosen that one is reversible with respect to the cation of the electrolyte (in this case, H^+ ion) and other is reversible with respect to the anion

(i.e., Cl⁻ ion). Evidently, the first electrode is hydrogen electrode and the other can be the silver-chloride electrode. Accordingly, the cell arrangement is as follows:

$$\text{Pt; } H_2 \text{ (g) (1atm) / HCl (m) / AgCl (s), Ag(s)}$$

Where m is the molality of HCl solution.

The cell reaction is

$$\tfrac{1}{2} H_2 \text{ (g)} + AgCl(s) \rightleftharpoons Ag(s) + H^+(m) + Cl^-(m)$$

Then e.m.f. of the cell at 25^0C is given by

$$E = E^0 - 0.0591 \log\left(a_{H^+} + a_{Cl^-}\right) / (a_{H_2})^{1/2} \qquad \text{...........10.10}$$

Because the activity of Ag(s), AgCl(s) and H_2 gas at one atmosphere pressure is taken as unity.

$$E = E^0 - 0.0591 \log a_{H^+} a_{Cl^-} \qquad \text{...........10.11}$$

As we know

$$a_{H^+} + a_{cl^-} = (a\pm)^2 = (\gamma m)^2 = \left(\gamma_\pm\right)^2 m^2$$

Where $\left(\gamma_\pm\right.$ and m are the mean ionic activity coefficient and the molality of HCl

Respectively. Hence from equation 10.11 we get

$$E = E^0 - 0.0591 \log \gamma_\pm^2 m^2 \qquad \text{..............10.12}$$

$$E = E^0 - 0.0591 \log s \, \gamma_\pm^2 - 0.1182 \log m \qquad \text{...........10.13}$$

Rearranging,

$$E + 0.1182 \log m = E^0 - 0.1182 \log \gamma_\pm \qquad \text{......10.14}$$

The two unknown E^0 and $\gamma_\pm$ in equation (10.14) can be determined by measuring EMF of the cell over various concentrations of HCl, including dilute concentrations. At in finite dilution, m=0 gives E^0 as the y intercept. Knowing the value of E^0, the mean ionic activity coefficient $\gamma_\pm$ of HCl at any other concentration can be determined from emf data of the cell at that concentration.

10.11 SUMMARY

In this unit you have studied various aspects of reversible cells and irreversible cells, determination of e.m.f. of cells, polarization over voltage, liquid junction potential and concentration cells with and without transport.

The applications of e.m.f. measurement has been described in detail, namely the valence of ions, determination of solubility of sparingly soluble salt, activity coefficients and some other uses.
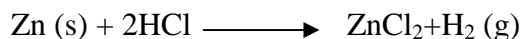
10.12 TERMINAL QUESTIONS:

A. Multiple choice/Objective type questions:

Q.1   In the reaction:

$$Zn\ (s) + 2HCl \longrightarrow ZnCl_2 + H_2\ (g)$$

   (a) Zinc is oxidized   (b) the oxidation number of chlorine remains unchanged

   (c) The oxidation number of hydrogen changes from +1 to 0 (d) All are correct

Q.2 The site of oxidation in an electrochemical cell is:

   (a) The cathode   (b) the anode   (c) the electrode   (d) the salt bridge

Q.3 Electrolytic cells are electrochemical cells in which ………….reactions are forced to occur by the input of electrical energy.

   (a) Sponteneous (b) non-sponteneous   (c) exothermic   (d) endothermic

B. Short answers type questions:

Q.4   Write a note on liquid junction potential.

Q.5   What are concentration cells?

Q.6   Write a note on over voltage.

C. Long answer type questions:

Q. 7 (a) what are reversible and irreversible cells? How e.m.f. of a cell is determined?

(b) Write a note on liquid junction potential? How it is eliminated.

Q. 8 (a) Discuss the functioning of concentration cell with transport and concentration cell with transport.

(b) Describe applications of e.m.f. measurements.

10.13 ANSWERS

1. (d) 2. (b) 3. (b)

Source of study material

1. Essential of physical chemistry by Bahl, Bahl and Tuli.
2. Principles of physical chemistry By Puri, Sharma and Pathania.
3. Physical chemistry By   P.C. Rakshit.
4. Physical chemistry By Atkins.