**MSCCH-503**

M. Sc. I Semester

PHYSICAL CHEMISTRY-I
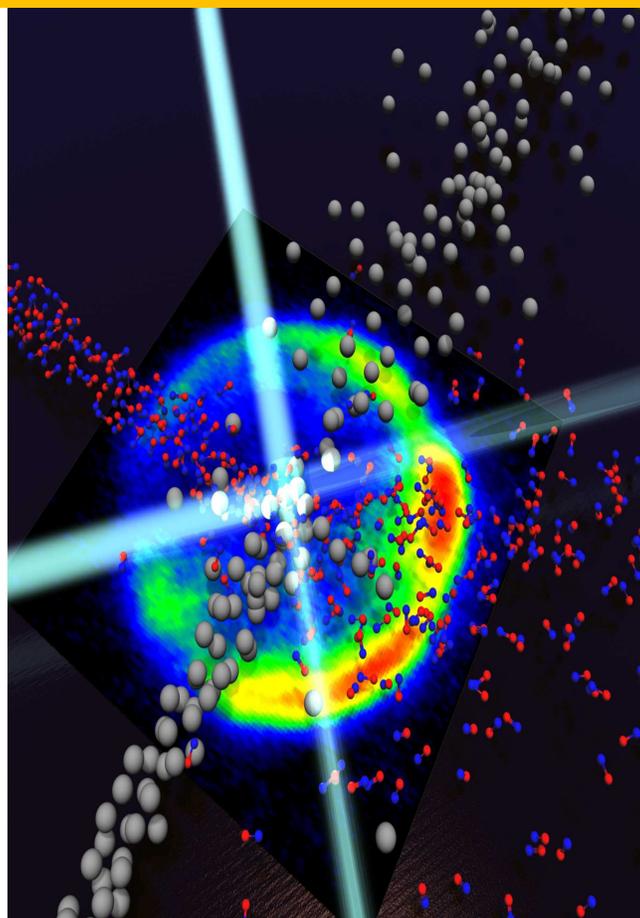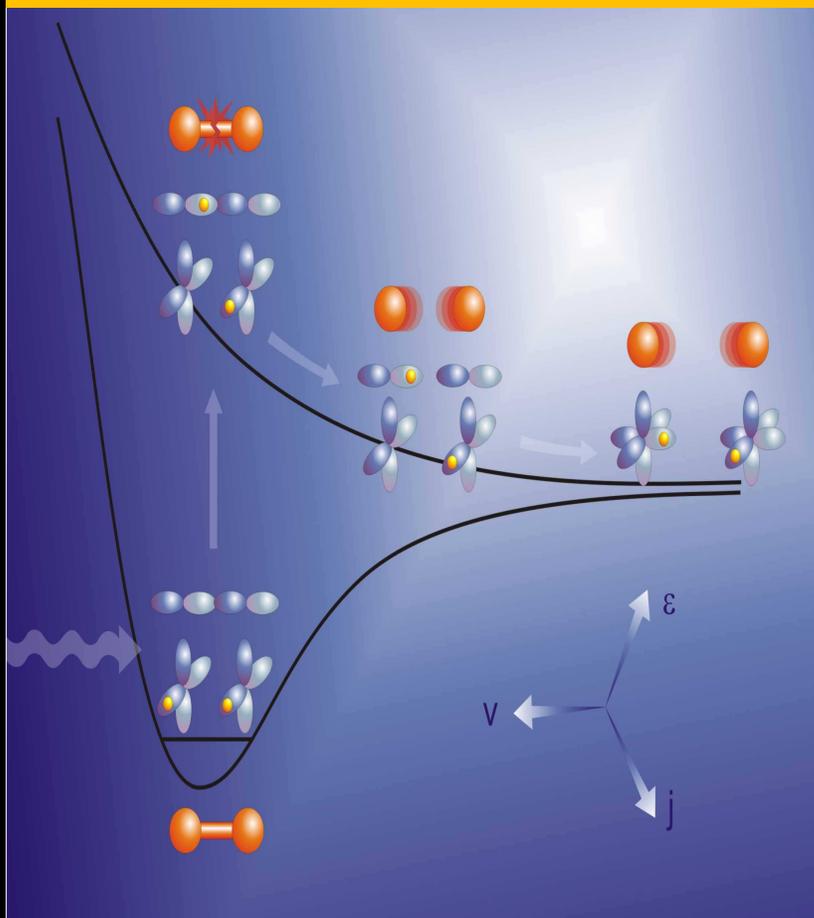
SCHOOL OF SCIENCES

DEPARTMENT OF CHEMISTRY

UTTARAKHAND OPEN UNIVERSITY

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1.1 *INTRODUCTION*

Thermodynamics is the branch of chemistry that deals with energy transformation in all type of physical chemical and biological processes. Thermodynamics leads with three fundamental laws which are purely based on human experiences. These are the first, second and third law of thermodynamics. These laws provide numerical approach of prediction of spontaneity and feasibility of various   processes under prescribed set of conditions. Thermodynamic principles allow deriving most of the important laws of the physical chemistry such as *vant* Hoff's law, phase rule and distribution law.

Thermodynamics is applicable to the microscopic system consisting of matter in bulk and not to microscopic systems of individual atoms or molecules. It does not bother about the time factor. That means it does not tell anything regarding the rate of a physical change or a chemical reaction. It is concerned only with initial and final states of the system. Thermodynamic principles correlate different observable properties of system without providing their magnitudes.

A thermodynamic system is said to be in a certain state when all its properties are fixed. The fundamental properties which determine state of a system are Pressure (P), temperature (T), volume (V), mass and composition. Change in magnitude of such properties alters the state of system. For such reasons, these parameters are regarded as state variables or state functions for a system. A change in system from the initial state to final state will accompanied by a change in state variables. However, it is not necessary that all the state variables under specified set of conditions may completely define a system. The relation among state variables is defined as equation of state. For an ideal gaseous system, the equation of state PV =nRT, where R=gas constant may be isolated through implication of the fundamental approach based on Boyles and Charles laws.

Binary relation of state variables under specified set of conditions liberates thermodynamic properties of a system. Such thermodynamic properties are internal energy (E) enthalpy (H), entropy (S), Gibbs free energy (G), Helmholtz function(A), chemical potential (μ), heat capacity etc. For example, at fixed mass of an ideal gas, at constant volume, H =f(T,P).Similarly other thermodynamic properties such as internal energy and entropy may be defined as E=f(T,V) and S=f(E,V) respectively.

1.2 REVERSIBLE AND IRREVERSIBLE PROCESS

1.2.1 Reversible process:

Reversible processes proceed from the initial to the final state of a system through an infinite series of infinitesimally small stages. At each of stages, the system remains in the state of equilibrium.

1.2.2 Irreversible process:

An irreversible process proceeds when system goes from initial to final state in a single step in such a way that it cannot be reversed.

In this process the system remain in the state of equilibrium at initial and final stages, however, such equilibrium conditions are not well maintained the intermediate stages.

Let us consider specific quantity of a gas in a cylinder with a weightless and frictionless piston. The expansion of the gas can be carried out by two methods as shown in fig.1.1. Let the pressure applied on the piston be P which equal to the external pressure of the gas. Since the external and internal pressure are exactly
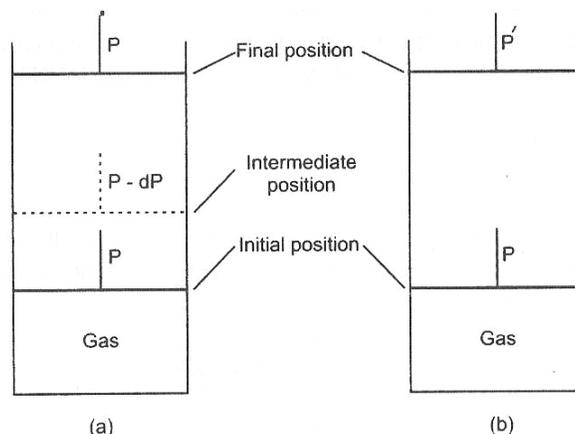
Fig.1.1 Work in reversible (a) and irreversible process (b)

Counter balanced, the piston remains stationary and there is no change in the volume of the gas. Now suppose the pressure on the piston is decreased by an infinitesimal amount dP, thus the external pressure on the piston being P-dP, the piston moves up and the gas will expend by an infinitesimal small amount. The gas will therefore be expended infinitely slowly (reversible process). At all stages in the expansion of the gas, dP being negligibly small the

gas is maintained in a state of equilibrium throughout. If at any point of the process the pressure is increased by dP, the gas would contract reversibly fig.1.1 (a).

Now on the after hand, the expansion is irreversible, if the pressure on the piston falls suddenly, it moves upward rapidly in a single operation fig.1.1 (b).the gas is in equilibrium state in the initial and final stages only, the expansion of the gas, in this case, takes place in an irreversible manner.

1.3 THERMODYNAMIC WORK

Reversible and irreversible work:

Thermodynamic work, often called as P-V work is the work done in expansion (or compression) of a gas. Let us consider a gas contained in a cylinder fitted with a frictionless piston. Pressure (P, which is force per unit area) of the gas, exert a force on the piston fig.1.2. This can be balanced by applying an equal but opposite pressure from out- side on the piston. Let it be designated as P_{ext}. It is a external pressure which is used in evaluating work. This is true whether it is expansion or contraction.
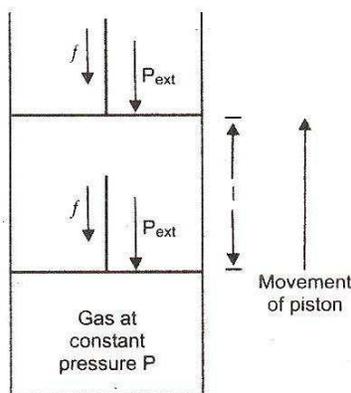
Fig.1.2 Pressure volume work of a system

If the gas expands at constant pressure, the piston will move to a distance l. Since,

Work = force $\times$ distance

$$= f \times l \qquad \dots\dots\dots\dots 1.1$$

and pressure is force per unit area

$$\frac{f}{A} = P_{ext}$$

$$\text{or } f = P_{ext} \times A \qquad \dots\dots\dots\dots 1.2$$

Here A is the cross- section area of the piston.

From equation 1.1and 1.2 we have

Work = ω=P_{ext} . A.l

     = P_{ext} . ΔV ..……..………1.3

Work is done at the expense of internal energy, hence the internal energy decreases and work done bears a negative sign. Work may be expressed in dynes-centimeter, ergs, joules. PV work as well be expressed as the product of pressure and volume units e.g., litre / atmospheres.

If the initial volume is $V_1$and final volume is V_2 then work in this case will be

W= -P_{ex} (V_2 –V_1)

     It is to be noticed that the work done by the system is not a state function, it depends upon the path of transformation. In the case just cited above pressure the piston is decreased as volume changes from initial volumeV_1 to final volume V_2, this is irreversible work.

Consider a system in which an ideal gas is confined in a cylinder with a frictionless piston fig.1.3.
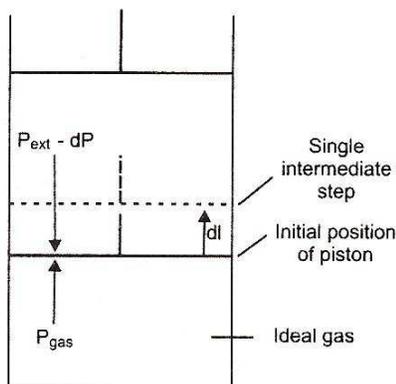
Fig.1.3 Isothermal reversible expansion work

Suppose it expands reversibly from $V_1$to V_2 at a constant temperature. The pressure of the gas is successively reduced from $P_1$to P_2. Let us reduce the pressure P_1 by an infinitesimal amount Δp, i.e., let the pressure be P_1-Δp and the volume increases be Δv, then the work done by the system would be (P_1 -Δp) Δv ≈$P_1\Delta v$,

As Δp is very small, Δv will also be very small, and the multiplication of these two will be very small quantity and can be neglected. Then the new pressure is again reduced infinitesimally and a little more expansion involving again P Δv work would be available. In this way by infinitely large number of successive steps we can expend the gas from volume V_1 to V_2. Let the equilibrium pressure attained by the gas, when the volume becomes V_2 be P_2. The total work done by the gas during expansion would be summation of all these minute quantities, i.e.,

$$W = \int_{V_1}^{V_2} (P - dP)dV$$

$$\approx \int_{V_1}^{V_2} P\, dV \qquad \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.4$$

Here $dP.dv$ will be very small quantity and can be neglected. We must remember that P has also been changing during the expansion continuously. If the system contains n gm.moles of the gas and the gas be supposed ideal one, then

$$W = \int_{v_1}^{v_2} \frac{nRT}{V} = nRT \ln \frac{V_2}{V_1}$$

For one mole of an ideal gas the expression work will be

$$W = RT \ln \frac{V_2}{V_1} \qquad \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.5$$

$$as \; \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$W = RT \ln \frac{P_1}{P_2} \qquad \qquad \ldots\ldots\ldots\ldots\ldots\ldots 1.6$$

Since the change has been carried out in successive stages of infinitesimal amount and therefore it is reversible process. The work in the isothermal reversible expansion of one mole is

$$W = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots 1.7$$

This work is the product of force and displacement. The displacement in this case is specified, namely $(V_2 - V_1)$. Hence greater the magnitude of the force or pressure, the greater

would be magnitude of the work. If the pressure over the piston were made greater than (P_1 - Δp) there obviously would be no expansion.

Therefore if we want to have expansion as desired, (P_1 - Δp) is the maximum that could be applied. So the work obtained in the equation (1.7) is the maximum. That could be applied. If the pressure over the piston were made appreciably less, instead of infinitesimally smaller than the gas pressure, the work would be evidently less than obtained above and the process also would be more irreversible. Hence we conclude that the work in the reversible process is the maximum and is greater than that in the irreversible process.

It can be proved in the following manner.

For this we carry out the expansion of the same gas in two ways. Firstly, we change the volume as before until the pressure is P_2, the process is reversible work.

$$W_r = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2} \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots 1.7$$

Secondly, we reduce the pressure over the piston at once to P_2, which would be equilibrium pressure of the gas when the volume is V_2, then the gas would immediately expands against a constant pressure P_2 the process is irreversible work is

$$W_{ir} = P_2 (V_2 - V_1) \qquad = P_2 \left(\frac{RT}{P_2} - \frac{RT}{P_1} \right)$$

$$= RT \left(1 - \frac{P_2}{P_1} \right)$$

$$W_r - W_{ir} = RT \ln \frac{P_1}{P_2} - RT \left(1 - \frac{P_2}{P_1} \right)$$

$$= RT \left(\frac{P_1 - P_2}{P_2} \right) - RT \left(\frac{P_1 - P_2}{P_1} \right)$$

$$= RT (P_1 - P_2) \left(\frac{1}{P_2} - \frac{1}{P_1} \right)$$

$$= RT (P_1 - P_2) \left(\frac{P_1 - P_2}{P_1 P_2} \right)$$

$$= RT \frac{(P_1 - P_2)^2}{P_1 P_2} \qquad \dots\dots\dots\dots\dots 1.8$$

This is positive quantity whatever be the value of P_1 and P_2,

i.e. $W_r > W_{ir}$

1.4   WORK IN REVERSIBLE CYCLE PROCESS

We know that when gas has expanded to volume V_2 the gas pressure has come down to P_2. If the pressure is increased by infinitesimal amounts in successive stages the volume becomes V_1 and therefore, pressureP_1. The work done in the system will be

$$W^` = \sum P_2 . \Delta V = \int_{V_2}^{V_1} P dV$$

$$= RT \ln \frac{V_1}{V_2} = - RT \ln \frac{V_2}{V_1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots 1.9$$

Here the work term becomes the same with reversal of sign. Thus if the complete reversible cycle of expansion and contraction is carried out at constant temperature then the net work would be zero.

$$\sum W = W + W^` = RT \ln \frac{V_2}{V_1} - RT \ln \frac{V_2}{V_1} = 0$$

Or in an isothermal reversible cyclic process,

$$\oint dw = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots 1.10$$

1.5   FIRST LAW OF THERMODYNAMICS

All class of physical, chemical or biological transformations into one another are assumed to facilitate at the cost of conservation of energy and matter. The transformations and conservation of energy during processes are studied under the first law of thermodynamics. According to this law, the energy transformations in all the processes are purely conservative and proceed without any creation or loss of energy. Such kind of statements however doesn't hold when Einstein's relation inter-conversions of energy and matter are considered as below:

$$E = mc^2 \qquad \ldots\ldots\ldots\ldots\ldots..1.11$$

Where E is energy associated with matter of mass 'm' and 'c' is the velocity of light in vacuum, a constant. In our present discussion, we shall have no occasion to consider this inter conversion of energy and matter and we shall take the first law to be strictly true.

1.6   INTERNAL ENERGY

Thermodynamically, internal energy of a system of a fixed mass is the unique function of temperature and volume as expressed   below:

$$E = f(V, T)$$

Any change in internal energy, may be expressed through following exact differential:

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

The internal energy of a system is determined by the state of a system and is dependent of the path by which it is obtained. Hence the internal energy of a system is a state function.

1.7   MATHEMATICAL FORMULATION OF FIRST LAW OF THERMODYNAMICS

Suppose a system is in state A having energy E_A and undergoes a change to another state B with energy E_B . During this change, absorption of a small quantity of heat q at stage A , will impart net amount of energy to system as E_A+q. This will allow the system to perform   work, with final energy of E_B+w. From the law of conservation of energy this follows that:

$$E_A+q = E_B+w$$

$$E_B - E_A = q - w$$

or $\Delta E = q-w$ …………………1.12

For small changes

$$dE = \delta q - \delta w$$

Here E is state function hence its change is dE and q and w are not state functions, they depend upon the path, hence, δq and δw.

1.8   ENTHALPY

Suppose the change of state of a system is brought at constant pressure P. In that case there will be change of volume from V_A to V_B. Under such conditions,   system may execute the work done (w) as below:

w = -P (V$_B$ – V$_A$)   …………………1.13

Substituting the value of work from 1.13 to 1.2 will result

Δ E = q – P (V$_B$ –V$_A$)

E$_B$-E$_A$ = q –P (V$_B$ – V$_A$)

Rearranging above expression will result

(E$_B$+PV$_B$) – (E$_A$+ PV$_A$) = q   …..…………….1.14

The quantity E + PV is known as total energy stored and thermodynamically termed as enthalpy (H) of the system

H = E + PV   ..………………1.15

In this equation E, P and V are all state functions, thus H, the value of which depends upon the value of E, P and V must also be the function of state. Hence the value is independent of the path by which the state of the system is changed.

From equation 1.14 and 1.15 are have

H$_B$-H$_A$ = ΔH   …………………1.16

Since H$_A$ and H$_A$ are definite quantities, it is evident that ΔH, like ΔE is a definite quantity depending upon initial and final states. We can write

ΔH = ΔE + PΔV   …………………1.17

Here ΔV is increase in the volume under gone by the system.

For a fixed mass of system H=f(T,P), that represents the following exact differential

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

1.9   CALCULATION OF C$_P$-C$_V$ THERMODYNAMICALLY

Heat capacity is defined as the quantity of heat required to raise the temperature of the system from the lower to the higher temperature divided by the temperature difference. If q

calories are the heat absorbed by mass m and the temperature rises from T_1 to T_2, the heat capacity is given by the expression

$$c = \frac{q}{m(T_2 - T_1)}$$ ………………..1.18

For unit mass say restricted to 1 gm, heat capacity is called the specific heat of the system. However, if mass of the system is one mole, then the heat capacity is called molar heat capacity (C). Heat capacity varies with temperature; hence the true molar heat capacity is defined by the equation

$$C = \frac{dq}{dT}$$ ………………..1.19

Molar heat capacity is defined as the amount of heat required to raise the temperature of one mole of substance or system by 1K.

Since heat is not the state function, it is necessary to fix either of a thermodynamic variable such as P or V at which the temperature of system is raised by one degree. This generates two different kinds of the heat capacities. First kind of heat capacity is defined as "heat capacity at constant volume (C_v)" and another one is the "heat capacity at constant pressure (C_p)".

From first law of thermodynamics we know

$$dq = dE + PdV$$

Hence $$\frac{dq}{dT} = \frac{dE}{dT} + \frac{PdV}{dT}$$ ………………….1.20

at constant volume dV= 0 hence $(\frac{dq}{dT})_v = (\frac{dE}{dT})_V$

$$C_v = (\frac{\partial E}{\partial T})_V$$ ………………….1.21

From equation 1.20

$$C_v = \frac{\partial E}{\partial T} + P(\frac{\partial V}{\partial T})_P$$ ………………….1.22

and $$H = E + PV$$

Hence $$(\frac{dH}{dT})_P = (\frac{\partial E}{\partial T})_P + P(\frac{\partial V}{\partial T})_P$$ ………………….1.23

Comparing 1.22 and 1.23

$$C_P = (\frac{\partial H}{\partial T})_P$$

Now $C_p - C_v = (\frac{\partial H}{\partial T})_P - (\frac{\partial E}{\partial T})_V$

Since H = E+ PV

$$C_p - C_v = (\frac{\partial E}{\partial T})_P + P(\frac{\partial V}{\partial T})_P - (\frac{\partial E}{\partial T})_V \qquad \text{...................1.24}$$

We know E = f (V, T)

$$dE = (\frac{\partial E}{\partial T})_V \, dT + (\frac{\partial E}{\partial V})_T \, dV$$

Dividing both sides by dT and keeping pressure constant

$$(\frac{dE}{dT})_P = (\frac{\partial E}{\partial T})_V + (\frac{\partial E}{\partial V})_T (\frac{\partial V}{\partial T})_P \qquad \text{...................1.25}$$

Putting this value of $(\frac{dE}{dT})_P$ in equation 1.24

$$C_p - C_v = (\frac{\partial E}{\partial T})_V + (\frac{\partial E}{\partial V})_T (\frac{\partial V}{\partial T})_P + P(\frac{\partial V}{\partial T})_P - (\frac{\partial E}{\partial T})_V$$

$$= (\frac{\partial V}{\partial T})_P \{(\frac{\partial E}{\partial V})+P\}$$

For an ideal gas $(\frac{\partial E}{\partial V})_T = 0$

Hence $C_p - C_v = P(\frac{\partial V}{\partial T})_P = P. \frac{R}{P}$

Since PV=RT and $(\frac{\partial V}{\partial T})_P = \frac{R}{P}$

$$C_p - C_v = R \qquad \text{....................1.26}$$

1.10 JOULE'S LAW

Joule carried out experiments to find out change in internal energy of a gas. The arrangement for the experiment is shown in fig. 1.4

Let us consider two containers A and B connected by a stop cock at the middle and placed in a water bath. The temperature of the bath was noted. The stop cock was then opened and the temperature was again recorded. No temperature change was found. Since ideal gas expends against vacuum without work and does not exchange heat with the surroundings that keeps the temperature of water bath to be constant. Thus from the first law of thermodynamics.
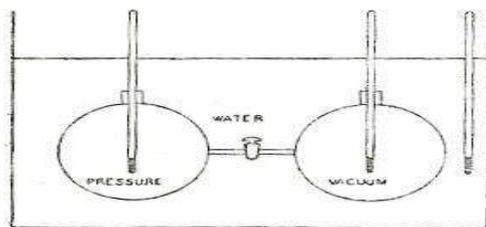
Fig.1.4 Joule's Experiment

$$dq = dE + d\omega$$

or $dE = dq - d\omega = 0$ both dq=0 and dw=0,

hence dE=0

but $dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_v dT$

Since dT = 0

$dE = \left(\frac{\partial E}{\partial V}\right)_T dV = 0$

as $dV \neq 0$ since the gas which was occupying one container, now occupies both the containers

Hence $\left(\frac{\partial E}{\partial V}\right)_T = 0$ ………………….1.27

We can write $\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$

Since $\left(\frac{\partial P}{\partial V}\right)_T \neq 0$ so $\left(\frac{\partial E}{\partial P}\right)_T = 0$ ..…………………1.28

We know H = E + PV

$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial E}{\partial T}\right)_T + \left(\frac{\partial(PV)}{\partial T}\right)$

$\left(\frac{\partial H}{\partial P}\right)_T = 0$ ………………….1.29

1.11 JOULE THOMSON EFFECT

The phenomenon of producing lower temperature when a polar gas is made to expend adiabatically from the region of high pressure into a region of low pressure is known as Joule Thomson effect. Non polar gases such as Hydrogen and Helium are warmed up under similar circumstances. The temperature below which a gas becomes cooler on expansion is known as the inversion temperature.

Experimental Details:

The experiment performed by Joule and Thomson to measure the temperature change on expansion of a real gas is illustrated in fig 1.5
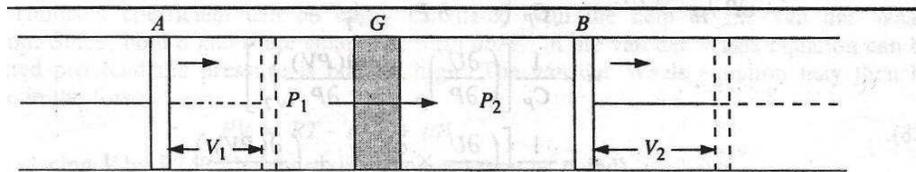
Fig.1.5 porous plug experiment

A tube of non conducting material filled with a porous plug in the middle and two frictionless piston A and B on the side is taken. Let a volume of V_1 of a gas at pressure P_1 be forced through the porous plug by the slow movement of piston A. the gas on right hand chamber is allowed to expand to volume V_2 and pressure P_2 by moving the piston B outward. The change in temperature is found by taking reading on the two thermometers.

Work done on the gas   = P_1V_1

Work done by the gas   = P_2V_2

Net work done by the gas = $P_2V_2-P_1V_1$

Since the expansion of the gas is done adiabatically, the system is not in a position to absorb heat from the surroundings. The system thus does work at the expense of the internal energy. Hence the internal energy decreases from E_1 to E_2

$P_2V_2 - P_1V_1 = E_1-E_2$

or $P_2V_2 +E_2 = P_1V_1+ E_1$

or $H_2 = H_1$ ………………1.30

or $\Delta H =0$

This reveals that Joule-Thomson expansion of a gas takes place at constant enthalpy. Hence this kind of expansion is also called isoenthalpic.

The rate of change in temperature with pressure when enthalpy remains constant is called Joule-Thomson coefficient.

$$\mu_{J.T.} = \left(\frac{\partial T}{\partial P}\right)_H$$ ………………..1.31

Since such flow through porous plug, usually the gas runs into lower pressure, i.e., dp is negative. Hence μ will be positive if dT is also negative, i.e., if temperature falls. Except

Hydrogen and Helium at ordinary temperature almost all gases cool down in passing through porous plug. For Hydrogen and Helium $\mu < 0$.

We know

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

in the above experiment dH =0

so $$\left(\frac{\partial H}{\partial T}\right)_P dT = -\left(\frac{\partial H}{\partial P}\right)_T dP$$

or $$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_P$$

$$= -\frac{1}{C_P}\left(\left(\frac{\partial H}{\partial P}\right)_T\right) \qquad \dots\dots\dots\dots.1.32$$

$$\mu_{J.T.} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

1.12 JOULE-THOMSON COEFFICIENT IN IDEAL GAS

We know H=E+PV, so equation 1.32 can be Written as

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu_{J.T.} = -\frac{1}{C_P}\left\{\frac{\partial}{\partial P}(E+PV)\right\}$$

$$= -\frac{1}{C_P}\left\{\left(\frac{\partial E}{\partial P}\right)_T + \frac{\partial}{\partial P}(PV)_T\right\}$$

$$= -\frac{1}{C_P}\left\{\left(\frac{\partial E}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T + \frac{\partial}{\partial P}(PV)_T\right\} \qquad \dots\dots\dots\dots1.33$$

In this equation $\left(\frac{\partial E}{\partial V}\right)_T$ of a gas is usually positive quantity, while $\left(\frac{\partial V}{\partial T}\right)_T$ for any gas is always a negative quantity. As a result the first term is always positive. The magnitude of second term $\left\{\frac{\partial}{\partial P}(PV)\right\}_T$ may be negative or positive. At low temperature the value of this term is negative under these conditions both the term are positive, μ has positive value. That means cooling will take place.

For ideal gases PV is constant and first term is zero hence the μ =0.

1.13 JOULE-THOMSON COEFFICIENT FOR A REAL GAS

Joule-Thomson coefficient for a real gas can be calculated with the help of *van der Waals* equation. Since, both a and b are small, the term ab/V^2 in the equation can be neglected provided pressure is not too high. The Von der Waal equation can be written as

$$PV = RT - \frac{a}{V} + bP \qquad \ldots\ldots\ldots\ldots 1.34$$

Replacing V by $\frac{RT}{P}$ we have

$$PV = RT - \frac{aP}{RT} + bP$$

$$V = \frac{RT}{P} - \frac{a}{RT} + b \qquad \ldots\ldots\ldots\ldots 1.35$$

Differentiating the equation with respect to temperature at constant pressure, we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2} \qquad \ldots\ldots\ldots\ldots 1.36$$

Rearranging equation 1.34, we have

$$RT = P(V - b) + aP/RT$$

Dividing both sides by PT we get

$$\frac{R}{P} = \frac{V-b}{T} + \frac{a}{RT^2} \qquad \ldots\ldots\ldots\ldots 1.37$$

Substituting the value of R/P from equation 1.36 in equation 1.35 we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{a}{RT^2} + \frac{a}{RT^2}$$

$$= \frac{V}{T} - \frac{b}{T} + \frac{2a}{RT^2}$$

$$T\left(\left(\frac{\partial V}{\partial T}\right)_P = V + \frac{2a}{RT} - b\right.$$

$$T\left(\left(\frac{\partial V}{\partial T}\right)_P - V = \left(\frac{2a}{RT} - b\right)\right.$$

The well known thermodynamic relation is:

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \frac{\partial H}{\partial P} \qquad \ldots\ldots\ldots\ldots 1.38$$

From equation 1.38, equation 1.31 becomes

$$-\left(\frac{\partial H}{\partial P}\right)_H = \frac{2a}{RT} - b \qquad \ldots\ldots\ldots\ldots 1.39$$

From equation 1.37 and equation 1.39 we get

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{c_P}\left[\frac{2a}{RT} - b\right] \qquad \ldots\ldots\ldots\ldots 1.40$$

From this equation it is clear that Joule – Thomson coefficient is positive as long as $\frac{2a}{RT}$ is greater than b. This is the case when temperature is low. At high temperature $\frac{2a}{RT} < b$ hence μ is negative. Since a, b and R are constant, it is evident that the magnitude and sign of Joule Thomson coefficient depends only upon the temperature at which the gas is allowed to expand.

The temperature at which the Joule – Thomson coefficient changes sign is known as the **inversion temperature** (T_i) At this temperature $\mu_{\text{J.T.}}$ is zero so that

$$\frac{2a}{RT_i} = b \quad \text{or } T_i = \frac{2a}{Rb}$$ …………………..1.41

Here T_i represents inversion temperature. This inversion temperature depends upon the *van der Waals* constant a and b of the gas.

1.14 SECOND LAW OF THERMODYNAMICS

Foundation of the second law of thermodynamics was laid by German scientist Rudolf Clausius in 1850 though examining the relation between heat transfer and work. First law of thermodynamics although states the rule of conservation of energy but doesn't intimate about the direction through which the process is going on. Realizing directional nature of the process, Clausius proposed that:

"Heat always flows spontaneously from hotter to colder region, and never the reverse, unless external work is performed on the system".

Heat cannot spontaneously flow from cold regions to hot regions without external work being performed on the system, which is evident from ordinary experience of refrigeration, for example. In a refrigerator, heat flows from cold to hot, but only when forced by an external agent, the refrigeration system.

In another approach, Lord Kelvin proposed that:

"It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects".

Just like first law, the second law of thermodynamics is also truly a law of experience gathered from observations of nature. Any such experience which would determine the criteria for the direction for the occurrence of a change will be the basis of second law.

1.15 CYCLIC PROCESS

Cyclic process represents revival of original state of a system after completing a series of changes. An isothermal cycle is one that complete at constant temperature. At the same time if changes are carried out reversibly it is called reversible cycle. Although the reversible cyclic processes are purely theoretical and imaginary, the concept to demonstrate maximum conversion of heat into work.

Efficiency of a machine or engine is defined as the fraction of heat absorbed by a machine or engine which it can convert into work.

$$\eta = \frac{Q_2 - Q_1}{Q_2} = \frac{W}{Q_2} = \frac{T_2 - T_1}{T_2} \qquad \ldots\ldots\ldots\ldots\ldots 1.42$$

Where Q_1 is heat absorbed at temperature T_1 and Q_2 the heat rejected at temperature T_2.

1.16 ENTROPY: NATURE OF DQ AND DQ/T

Rudolf Clausius in the early 1850s observed that irreversible process proceed with dissipation of small amount of heat energy δQ across the system boundary. Clausius has coined the term entropy (S) to explain such loss of energy during irreversible processes. Entropy is a state function; it depends only on the state of a system and not on the past history. Presently, entropy is recognized as a thermodynamic quantity representing the unavailability of a system's thermal energy for conversion into mechanical work, often interpreted as the degree of disorder or randomness in the system. Thermodynamically, for a fixed mass of system, entropy is expressed as S=f(E,V) for that the exact differential is expressed as:

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

The amount of heat absorbed or evolved in a process carried out reversibly at temperature T may be evaluated through application of Carnot cycle.

Suppose a system changes from one to another state, the heat dq is either absorbed or evolved. The value of dq depends upon path of transformation and hence it is not a perfect differential. From Carnot cycle we know the efficiency of an engine is given by the relation

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

or $\quad \frac{q_1}{T_1} = \frac{q_2}{T_2}$ $\ldots\ldots\ldots\ldots\ldots 1.43$

The above equation may be written in general form as $\frac{q_{rev}}{T_1} = constant$

Where q_{rev} is the amount of heat absorbed or evolved in a process carried out reversibly at temperature T. The term q_{rev}/T denotes a definite quantity or a state function, called entropy change of the system.

If we assign positive sign to the heat absorbed (q_2) and negative sign to heat given out q_1 the equation 1.43 can be written as

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

or $\quad \dfrac{q_2}{T_2} + \dfrac{q_1}{T_1} = 0 \qquad\qquad$ ....…………..1.44

Fig. 1.6 demonstrates a reversible cycle ABA to be made up of large number of Carnot cycles and adiabatic curves under isothermal conditions.
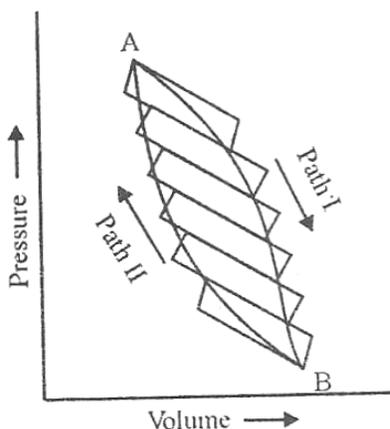
Fig 1.6 Entropy change in a cyclic process

The lines slanting horizontally stand for adiabatics and those slanting vertically stand for isothermals. Starting from A and going along the Carnot cycles successively, the whole of cycle ABA can be covered. Now the cycle ABA which is reversible one, consists of a series of Carnot cycles for each of which the following expression will hold good.

$$\sum \frac{dq_{rev}}{T} = 0 \qquad\qquad$$ …………….1.45

The cycle ABA can be regarded as comprising of two paths, i.e., from A to B and back from B to A, thus

$$\sum \frac{dq_{rev}}{T} = \int_A^B \frac{dq}{T}\,(path\ I)\ + \int_B^A \frac{dq}{T}\,(path\ II) = 0 \quad$$ …….1.46

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

Thus it is clear that

$\int_A^B \frac{dq}{T}$ (path I) $= \int_B^A \frac{dq}{T}$ (path II)

or $\int_A^B \frac{dq}{T}$ (path I) $= \int_A^B \frac{dq}{T}$ (path II)   ....……1.47

From equation 1.47 it is clear that $\int_A^B \frac{dq}{T}$ is a definite quantity independent of path taken for the change and depends only on initial state and final state. In other words it is a perfect differential. The function $\int \frac{dq}{T}$ is called entropy and is denoted by symbol S first proposed by Clausius (1854). If SB be entropy in state B and S_A entropy in state A then change in entropy ΔS is given as

$$\Delta S = S_B - S_A = \int_A^B \frac{dq_{rev}}{T}$$ ………………..1.48

Generally the equation is written as

$$ds = \frac{dq}{T}$$

For a very small change $ds = \frac{dq_{rev}}{T}$

It is not easy to define the actual entropy of a system. However it is easier to define change of entropy during a change. It is clear from equation 1.48 that when heat is absorbed by the system dq is positive. T is always positive. Thus ΔS is positive. That means entropy of the system increases by the absorption of heat. Hence, evolution of heat by the system means entropy decreases.

Since the entropy change is expressed as heat absorbed or evolved per unit temperature, entropy data are numerically expressed in terms of joules per degree per mole (JK^{-1}). This is known as entropy unit, e.u.

In isothermal reversible expansion of an ideal gas, there will be no change in internal energy dE=0. In that case from first law

$$\Delta E = dq - \omega$$

or $dq = \omega$

If the gas is expanding from volume V_1 to V_2 for n moles

$$dq = \omega = nRT \ln \frac{V_2}{V_1}$$

$$\Delta S = nR \ln \frac{V_2}{V_1}$$ 1.49

Entropy of one mole of a substance in pure state at 25^0C and one atmospheric pressure is defined as standard entropy of that substance and is denoted by S^0: During the reaction, each reactant and each product are in their standard state. Under such conditions; the overall entropy change may be evaluated as:

$$\Delta S^\circ = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$

1.17 PHYSICAL SIGNIFICANCE OF ENTROPY

When a system is left to itself it will gradually pass into a state of equilibrium. This is common experience. The state of equilibrium means a state of maximum disorder or chaos. If we let loose a quantity of yellowish green chlorine gas at corner of the floor of the room, the gas would spread in all directions until it would be most chaotically distributed into the entire room and the equilibrium will be reached. If we arrange a number of red and black balls in a tray in a particular pattern and then shake the tray, the balls will be mixed up in the most disordered fashion. These are all natural processes and we never find the opposite to happen in nature. These processes are irreversible and thus lead to entropy increase. The more the system reaches equilibrium, the greater is the disorder and irreversibility, and when the equilibrium is reached, it has the maximum disorder. Hence the entropy also goes on increasing and reaches its maximum at the equilibrium state. In other words, entropy is the measure of the disorder of the system.

Now if we attempt to bring order to system entropy decreases. Suppose we have a gas in equilibrium confined in a cylinder with a piston. The piston is now some what raised upwards increasing the volume slightly. All the molecules, in whatever direction those might be moving, are subjected now to a tendency of motion in the direction of piston. This is indirectly an attempt to bring some order. In consequences, the gas is cooled and the entropy decreases. So in the crystalline state of pure substances the entropy becomes the least as there is perfect order or least chaos.

1.18 ENTROPY OF A PERFECT GAS

From first law of thermodynamics, it is possible to express entropy of a perfect gas.

We know,

dq=dE+PdV

Dividing both the sides by T, we get

$$\frac{dq}{T} = \frac{dE}{T} + \frac{P}{T}dV$$

$$dS = C_v\frac{dT}{T} + R\frac{dV}{V} \quad \text{(for one gm. mol)}$$

or $dS = CvlnT + RdlnV$ ………….1.50

on integrating $S = C_v lnT + RlnV + S_0$ …….……1.51

S_0 is constant of integration.

rearranging (putting $CP - R = c_v$) we get

$S = C_p lnT - RlnP + S`0$ …………..1.52

1.19 CHANGE OF ENTROPY WITH TEMPERATURE

We know

$dq = C_v dT + PdV$

$TdS = C_v dT + PdV$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \text{or} \quad \Delta S = \int_{T_1}^{T_2} \frac{C_v dT}{T}$$ ……………..1.53

Since $H = E + PV$

$dH = dE + PdV + VdP$

$= dq + VdP$

$= TdS + VdP$

$TdS = dH - VdP = C_p dT - VdP$

$$\left(\frac{\partial S}{\partial T}\right)_P - \frac{C_P}{T} \quad \text{or} \quad \Delta S = \int_{T_1}^{T_2} \frac{C_P dT}{T} \qquad \qquad \dots\dots\dots\dots\dots 1.54$$

1.20 ENTROPY OF MIXING

When two or more gases are brought in contact, they immediately diffuse into one another and mix up irreversible. Such a spontaneous process would lead to increase in entropy. If the gases are ideal we can drive the relation for mixing.

Let one mole of gas A and one mole of gas B are mixed together at constant temperature T and pressure P. Before mixing the entropies are

$$S_A = C_{P_A} \ln T - R \ln P + S_{0A}$$

$$S_B = C_{P_B} \ln T \quad R \ln P \mid S_{0B}$$

After mixing, the final pressure remaining constant, the partial pressures of A and B may be denoted by P_A and P_B such that $P = P_A + P_B$ the entropies of two gases in the mixture are

$$C_{A_m} = C_{P_A} \ln T - R \ln P_A + S_{0A}$$

$$C_{B_m} = C_{P_B} \ln T \quad R \ln P_B \mid S_{0B}$$

Total entropy change is given as

$$\Delta S_m = \left(S_{A_m} + S_{B_m}\right) - \left(S_A + S_B\right)$$

$$= -R \ln \frac{P_A}{P} - R \ln \frac{P_B}{P} \qquad \qquad \dots\dots\dots\dots 1.55$$

Since $\ln P_A/P$ or $\ln P_B/P$ is negative quantity

Hence, $\Delta S_m = +ve$, that means mixing of two or more gases is a irreversible process.

1.21 WORK FUNCTION OR HELMHOLTZ FREE ENERGY A AND GIBBS FREE ENERGY OR GIBBS POTENTIAL G

Till now we have studied only three thermodynamic functions, viz. the internal energy (E), enthalpy (H) and entropy (S). In addition to these three thermodynamic functions there are two additional thermodynamic functions which also depend only on initial and final states of system. These functions are work function and free energy functions represented by A and G respectively. These functions are such that they utilize entropy in their derivation. With these functions the entropy change can be determined more conveniently.

$$A = E - TS$$ ………………………1.56

$$G = H - TS$$ …………………...1.57

We know E, H and S depend on the state of the system, it is clear that both A and G also depend upon the state only. The exact nature of these functions will be clear from the following discussion.

Let us consider that a thermodynamic system changes from initial state to final state at constant temperature. Let A_1, E_1 and S_1 be the work function, internal energy and entropy in the initial state and A_2, E_2 and S_2 are the values of these functions in the final state respectively then,

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

Subtracting second equation from first equation

We get $$A_2 - A_1 = E_2 - E_1 - TS_2 + TS_1$$

or $$\Delta A = \Delta E - T\Delta S$$ …………..………1.58

From first law of thermodynamics and from entropy equation

$$\Delta A = \Delta E - q$$

or $$-w = \Delta E - q$$

$$-\Delta A - w$$ …....…………….1.59

i.e. decrease in work function A in any process at constant temperature gives that maximum work that can be obtained from the system during the change this function, A is therefore termed as work function this is also referred as Helmholtz free energy or Helmholtz function. Similarly, from free energy function we get

$$\Delta G = \Delta H - T\Delta S$$
$$= \Delta E + P\Delta V - T\Delta S$$
$$= \Delta A + P\Delta V$$
$$= -w + P\Delta V$$

or $\quad -\Delta G = w - P\Delta V$

In this equation PV signifies the work done against pressure. Hence $-\Delta G$ gives the maximum work obtainable from the system other than pressure volume work. This is known as **net work**.

1.22 CHANGE IN A AND G WITH THE PARAMETERS OF THE SYSTEM

If a closed system undergoes a change, the only work involved being mechanical against the pressure, the infinitesimal reversible changes of A and G. would be

$$dA = dE - TdS - SdT$$
$$= -PdV - SdT \qquad \ldots\ldots\ldots\ldots1.60$$

and $\quad dG = dH - TdS - SdT$

$$dE = PdV + VdP - TdS - SdT$$
$$= TdS - PdV + PdV - TdS - SdT + VdP$$
$$= VdP - SdT \qquad \ldots\ldots\ldots\ldots..1.61$$

From equation 1.60

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \ldots\ldots\ldots\ldots1.62$$

And from equation 1.61

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \ldots\ldots\ldots\ldots1.63$$

From equation 1.62 and 1.63 different forms of Gibbs Helmholtz equation can be derived by substituting these values of in their respective equations of work function and Gibbs free energy.

$$A = E + T\left(\frac{\partial A}{\partial T}\right)_V$$

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P$$

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

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

1.23 MAXWELL'S RELATIONS

We know E is internal energy, $H = E + PV$,

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

$$dE = \delta q - w = TdS - PdV \qquad \text{.........1.64}$$

$$dH = dE + PdV + VdP = TdS + VdP \qquad \text{..........1.65}$$

$$dA = dE - TdS - SdT = -PdV - SdT \qquad \text{...........1.66}$$

$$dG = dH - TdS - SdT = VdP - SdT \qquad \text{...........1.67}$$

From equation 1.64

$$\left(\frac{\partial E}{\partial S}\right)_V = T \qquad \text{and} \qquad \left(\frac{\partial E}{\partial V}\right)_S = -P$$

$$\frac{\partial^2 E}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S \qquad \text{and} \qquad \frac{\partial^2 E}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V$$

So $\qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

Similarly $\qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad \text{............1.68}$$

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

These are four Maxwells relations. The last two relations give us the isothermal dependence of entropy on volume and pressure.

SOURCE OF STUDY MATERIAL

1. Thermodynamics   : By P.C. Rakshit

2. Advanced Physical Chemistry   : By J.N. Gurtu & A. Gurtu

3. Principles of Physical Chemistry   : By Puri, Sharma & Pathania

4. Essentials of Physical Chemistry   : By B.S. Bahl, Arun Bahl, G.D. Tuli

5. Physical Chemistry   : By Walter J. Moore

UNIT –2 CLASSICAL THERMODYNAMICS-II

CONTENTS

2.1   INTRODUCTION

This unit deals with thermodynamics of open system, phase equilibria,   fugacity and derivation of law of mass action.

2.2   PARTIAL   MOLAR   QUANTITIES/   CHEMICAL POTENTIAL

Internal energy (E), enthalpy (H), work function A, Gibbs free energy G, and entropy (S) are all extensive properties. The value of these thermodynamic properties varies with energy and matter content of the system. This is quite possible that the system may exclusively exchange energy with surroundings, keeping material content to be constant. This

class of system is defined as closed system. Thermodynamically, a closed system is defined as:

$$X=f(P,T) \qquad\qquad dV=0$$

$Y=f(P,V) \qquad\qquad dT=0$

$Z=f(T,V) \qquad\qquad dP=0$

However, if a system is capable to exchange the energy and matter with surroundings, this is called open system. This class of system is defined as open system. Thermodynamically, an open system is defined as:

$$X=f(P,T,n_1,n_2,\text{--------}) \qquad\qquad dV=0$$

$Y=f(P,V,,n_1,n_2,\text{--------}) \qquad\qquad dT=0$

$Z=f(T,V,n_1,n_2,\text{--------}) \qquad\qquad dP=0$

Where, n_1, n_2 etc, are the quantities (g mol) of 1st, 2nd and onwards components of the system.

In order to ascertain the effect of change in X with reference to mass and thermodynamic variables, let us consider any one class of the class of an open system

$X=f(P,T,n_1,n_2,\text{--------}) \qquad\qquad dV=0$

For small change in temperature pressure and number of moles of components, the change in thermodynamic property of an open system is represented as,

$$dX = \left(\frac{\partial x}{\partial T}\right)_{P,n_1,n_2\ldots} dT + \left(\frac{\partial X}{\partial P}\right)_{T,n1,n_2\ldots} dP + \left(\frac{\partial X}{\partial n_1}\right)_{T,P,n_2,n_3\ldots} dn_1 + \cdots \ldots\ldots\ldots$$

The term $\left(\frac{\partial X}{\partial n_1}\right)_{T,P,n_2,n_3\ldots}$ is called partial molar property for the first component. This is more often represented as $\bar{X}_1$ which denotes the rate of change of X on addition of one mole of the first component keeping other variables unchanged.

For change in the mass of system, at constant temperature and pressure, we have

$$dX_{T,P}=\bar{X}_1 dn_1+\bar{X}_2 dn_2+\bar{X}_3 dn_3 \qquad\qquad \ldots\ldots\ldots\ldots.2.2$$

It may be noted that X stands for any extensive property.

Thus for i^{th} component in a system,

Partial molar internal energy $= \left(\frac{\partial E}{\partial n_i}\right)_{T,P,n_1,n_2\ldots} = \bar{E}_i$

Partial molar enthalpy $= \left(\dfrac{\partial H}{\partial n_i}\right)_{T,P,n_1,n_2\ldots} = \bar{H}_i$

Partial molar volume $= \left(\dfrac{\partial V}{\partial n_i}\right)_{T,P,n_1,n_2\ldots} = V_i$

So partial molar volume of 1st component-

$$\left(\dfrac{\partial V}{\partial n_1}\right)_{T,P,n_2,n_3\ldots} = V_i \qquad\qquad \ldots\ldots\ldots\ldots\ldots\ldots..2.3$$

The most important partial molar property is partial molar free energy.

The change in the thermodynamic potential (Gibbs potential G) at a constant temperature and pressure can be expressed as

$$(dG)_{TP} = \left(\dfrac{\partial G}{\partial n_1}\right)_{TPn_2 n_3\ldots} dn_1 + \left(\dfrac{\partial G}{\partial n_2}\right)_{TPn_1 n_3\ldots} dn_2$$

$$= G_1\,dn_1 + G_2\,dn_2 + G_3\,dn_3 \ldots\ldots \qquad\qquad \ldots\ldots\ldots\ldots.2.4$$

The partial molar free energy is given by $\bar{G}_i = \left(\dfrac{\partial G}{\partial ni}\right)_{TPn_1 n_2\ldots}$

J.W. Gibbs proposed that for i^{th} component of an open system, chemical potential is represented as μ_i .

Hence $\left(\dfrac{\partial G}{\partial ni}\right)_{TPn_1,n_2\ldots} = \bar{G}_i = \mu_i$ $\ldots..\ldots\ldots\ldots\ldots.2.5$

That means equation 2.4 can be written as

$$dG_{TP} = \mu_1 dn_1 + \mu_2 dn_2 + \qquad\qquad \ldots..\ldots\ldots\ldots\ldots.2.6$$

It must be noted that μ_i is independent of the mass of system but not independent of composition of the system.

2.3 GIBBS DUHEM EQUATIONS

Suppose at constant temperature and pressure, all the molar concentration of components are increased in the same proportion of their initial amounts. This implies to increase of first

component as $n_1 \Delta x$, of the second component as $n_2 \Delta x$, etc. For i^{th} component, similarly increase will be expressed as $n_i \Delta x$. Hence

$$dn_1 = n_1 \Delta x, \; dn_2 = n_2 \Delta x \; dn_i = n_i \Delta x$$

Since G is an extensive property, the increase, $\Delta G = G \Delta x$ from equation 2.5

$$dG = \mu_1 n_1 \Delta x + \mu_2 n_2 \Delta x + \ldots\ldots\ldots$$

$$G \Delta x = \mu_1 n_1 \Delta x + \mu_2 n_2 \Delta x \ldots\ldots\ldots$$

or $G = \mu_1 n_1 + \mu_2 n_2 + \ldots\ldots$ ....…………..…2.7

Total differential of G of equation 2.6 is written as

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \ldots\ldots$$

$$= (\mu_1 dn_1 + \mu_2 dn_2 + \ldots\ldots\ldots) + n_1 d\mu_1 + n_2 d\mu_2 + \ldots\ldots.) \ldots..2.8$$

Subtracting equation 2.6 from eqn. 2.8 we get

$$n_1 d\mu_1 + n_2 d\mu_2 + \ldots\ldots\ldots\ldots = 0 \qquad\qquad \ldots\ldots\ldots..2.9$$

Thus we have three useful relations for chemical potential with the composition of the system.

(i) $G = \mu_1 n_1 + \mu_2 n_2 + \ldots\ldots\ldots\ldots\ldots = 0$

(ii) $dG = \mu_1 dn_1 + \mu_2 dn_2 + \ldots\ldots\ldots = \Sigma \mu dn \qquad \ldots\ldots 2.10$

(iii) $O = n_1 d\mu_1 + n_2 d\mu_2 + \ldots\ldots\ldots = \Sigma n d\mu \qquad \ldots\ldots\ldots.2.10$

These are commonly known as Gibbs Duhem relations.

Now consider a solution having two components in equilibrium with their vapours at constant temperature and pressure. If a binary system undergoes an infinitesimal change of the composition, Gibbs Duhem equation takes the form:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \qquad\qquad \ldots\ldots\ldots\ldots..2.11$$

Here n_1 and n_2 are number of moles of the two components and μ_1 and μ_2 are respective chemical potentials. Dividing the above equation by $n_1 + n_2$ we get

$$\frac{n_1}{n_1 + n_2} d\mu_1 + \frac{n_2}{n_1 + n_2} d\mu_2 = 0$$

or $\quad\quad\quad\quad x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad\quad$ ….....………2.12

Where x_1 is mole fraction of constituent 1 and x_2 mole fraction of constituent 2. We can write equation 2.12 in the following form

$$x_1\left(\frac{\partial \mu_1}{\partial x_2}\right)_{TP} dx_1 + x_2\left(\frac{\partial \mu_2}{\partial x_2}\right)_{TP} dx_2 = 0 \quad\quad ...…………….2.13$$

We know $\quad\quad x_1 + x_2 = 1$

$$dx_1 + dx_2 = 0 \quad \text{or} \quad dx_1 = - dx_2$$

Substituting the value of dx_1, in equation 2.13 we get

$$x_1\left(\frac{\partial \mu_1}{\partial x_2}\right)_{TP} - \left(\frac{\partial \mu_2}{\partial x_2}\right)_{TP} = 0$$

or $\quad\quad\quad \left(\frac{\partial \mu_1}{\partial \ln x_1}\right)_{TP} = \left(\frac{\partial \mu_2}{\partial \ln x_2}\right)_{TP} = 0 \quad\quad$ ……….....…2.14

This is alternative form of the Gibbs Duhem equation.

2.4 VARIATION OF CHEMICAL POTENTIAL

2.4.1 Variation with Temperature:

We know chemical potential by definition is give by

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{TPn_2 n_3...} = \overline{G_i} \quad\quad\quad ……….……. 2.15$$

Differentiating this equation with respect to temperature at constant pressure we get

$$\left(\frac{\partial \mu i}{\partial T}\right)_{Pn_2 n_3...} = \left(\frac{\partial^2 G}{\partial T \partial n i}\right) \quad\quad\quad …..………….2.16$$

We know $\quad\quad \left(\frac{\partial G}{\partial T}\right)_{Pn_2 n_3...} = S \quad\quad\quad …..………….2.17$

Hence differentiating this equation with respect to n_i at constant temperature and pressure we get

$$\left(\frac{\partial^2 G}{\partial n_i \partial T}\right) = \left(\frac{\partial S}{\partial n_i}\right)_{TPn_2 n_3 \dots}$$ ……………….2.18

Comparing equation 2.16 with 2.18 we get

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{Pn_2 n_3 \dots} = \left(\frac{\partial S}{\partial n_i}\right)_{TPn_2 n_3 \dots} = \bar{S}_i$$ ……………….2.19

This is partial molar entropy by definition. This equation gives variation of chemical potential of any constituent i with temperature.

2.4.2 Variation of Chemical Potential with Pressure:

We know $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{TPn_2 n_3 \dots} = \bar{G}_i$

Differentiating above equation with respect to pressure at constant temperature

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{Tn_2 n_3 \dots} = \left(\frac{\partial^2 G}{\partial P \partial n_i}\right)$$ ………………2.20

We know $\left(\frac{\partial G}{\partial P}\right)_{Tn_2 n_3 \dots} = V$

Differentiating above equation with respect to n_i at constant temperature and pressure we get

$$\left(\frac{\partial V}{\partial n_i}\right)_{TPn_2 n_3} = \left(\frac{\partial^2 G}{\partial n_i \partial P}\right) = \bar{V}_i$$ ………………..2.21

Now, suppose there is a system containing a mixture of ideal gases at constant temperature T, we get

n= $n_1+n_2+n_3 +$ ……………………..$n_i +$ ……..

and $V = (n_1 + n_2 + n_3 + \cdots \dots) \frac{RT}{V}$

Differentiating the above equation with respect to n_i (moles of compound i) at constant temperature and pressure (all n's remaining unchanged).

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P} = \frac{RT}{P}$$

or partial molar volume $\bar{V}_i = RT/P$

Substituting this value of partial molar volume in equation 2.21

We get $\left(\frac{\partial \mu_i}{\partial P}\right)_T = V_i$ —

or $d\mu_i = RT\, d\ln P$

But we know partial pressure of the component, $p_i = (n_i/n)\, P$

For a system n_i and n are fixed that is constant, hence

    $\partial \ln p_i = \partial \ln P$

so $d\mu_i = RT\, d\ln P_i$

or $\mu_i = RT \ln P_i + Z_i$ (Z_i being constant of integration)

If only a pure substance is present then $\mu = RT \ln P + Z$.

The constant Z depends on temperature and nature of gas. At standard state chemical potential is denoted by μ^0.

Then $\mu_i = RT\ln + Z_i$ or $Z_i = \mu_{i\,(P)}^0$ …..………..2.22

    $\therefore \mu_i = RT \ln P_i + \mu_{i\,(P)}^i$

This is the relation connecting chemical potential with pressure of a component in an ideal gas mixture.

We know $P_i = C_i RT$ where C_i molar concentration of component is i.

Hence $\mu_i = RT \ln C_i RT + \mu_{i\,(P)}^0$

        $- RT \ln C_i + \mu_{i\,(C)}^0$

Also we know $p_i = N_i P$ N_i being the mole fraction of the component $i = \frac{n_i}{n}$

    $\mu_i = RT \ln N_i P + \mu_{i\,(P)}$

        $= RT \ln N_i + \mu_{i\,(N)}$

Thus we have

$$\mu_i = \mu_{i(P)} + RT \ln p_i$$
$$\mu_i = \mu_{i(C)} + RT \ln C_i$$
$$\mu_i = \mu_{i(N)} + RT \ln N_i$$

..............2.23

Since all gas laws of ideal gases also extended to ideal solution, the equation 2.23 will hold true for ideal solutions also.

2.5 CLAPEYRON EQUATION

Consider two phases A and B in equilibrium of the same component with each other at constant temperature (T) and pressure (P). If the two phases are in equilibrium then free energy in both the phases should be same, i.e.,

$$G_A = G_B$$

Where G_A is free energy in phase A and G_B free energy in phase B. now temperature is raised to $T + dT$ and pressure is raised to P+dP then free energy in phase A will be $G_A + dG_A$ (suppose) and in phase B will be $G_B + dG_B$. Since the

system is in equilibrium, then $G_A + dG_B = G_B + dG_B$ 2.24

From equation 2.23 we have $dG_A = dG_B$ 2.25

We know $dG = VdP - SdT$

Hence

$$dG_A - V_A dP - S_A dT$$

and $$dG_B = V_B dP - S_B dT$$

Putting these values in equation 2.25

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

Rearranging the term we get

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

$$\frac{dP}{dT} = \frac{(S_B - S_A)}{V_B - V_A} = \frac{\Delta S}{V_B - V_A}$$

ΔS is change in entropy

We know from our earlier knowledge

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

At equilibrium $\Delta G = 0$, so $\Delta H = T\Delta S$

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

So we get $\frac{dP}{dT} = \Delta H / T(V_B - V_A)$ 2.26

In this equation ΔH is change in enthalpy taking place at temperature T. V_B and V_A are molar volumes of the component in B and A phases respectively and $\frac{dP}{dT}$ represents rate of change of temperature with pressure.

Equation 2.26 relates the change in equilibrium pressure with temperature T occurring in a system having two phases of the same component. This equation is named as Clapeyron's equation.

For solid liquid equilibria, ΔH represents molar heat of fusion, V_B represents molar volume in liquid phase and V_A represents molar volume in solid phase. The equation is helpful in determining effect of pressure on boiling point.

For liquid vapour equilibria, ΔH represents molar heat of vaporisaton, V_B represents molar volume in vapour phase and V_A represents molar volume in liquid phase, T represents boiling point of the liquid. For such equilibria clapeyron equation can be written as

$$\frac{dP}{dT} = \frac{\Delta H_V}{T(V_V - V_L)}$$ 2.27

Since $(V_V - V_L) = +ve$ quantity (since volume in vapour phase is always greater than volume in liquid phase) hence boiling point increases with pressure.

2.6 CLASIUS CLAPEYRON EQUATION

In equation 2.27, since volume in vapour phase is much greater than volume in liquid phase; $(V_V \gg V_L)$ hence. $V_V - V_L \approx V_V$. Substituting $V_V - V_L$ with V_V, the equation 2.27 is reduced as

$$\frac{dP}{dT} = \frac{\Delta H_V}{T V_V}$$

Assuming that the system behaves ideally, the above equation may modified through substituting $V_V = \frac{RT}{P}$

$$\frac{dP}{dT} = \frac{\Delta H_V}{RT^2} \cdot P \quad \text{or} \quad \frac{dP}{P} = \frac{\Delta H_V}{RT^2}$$

or $\quad \dfrac{d\ln P}{dT} = \dfrac{\Delta H_V}{RT^2}$ …………….. 2.28

This is is Clausins Clapeyron equation

On integrating this equation between limits P_2 at T_2 and P_1 at T_1

we get

$$\int_{P_1}^{P_2} d\ln P - \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT$$

$$\ln \frac{p_2}{p_1} = \frac{\Delta H}{R} \left| -\frac{1}{T} \right|_{T_1}^{T_2}$$

$$= \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

The above equation is defined as Clausius Clapeyron equation. This equation has following applications

1. In determining heat of vaporization
2. In determining effect of pressure on boiling point
3. In studying thermodynamics of elevation in boiling point
4. In studying thermodynamics of depression in freezing point.

2.7 FUGACITY

The actual behavior of real gases is different from behavior of idea gases. Lewis introduced concept of fugacity for representing actual behavior of real gases. The fugacity, in substituting for pressure, will include in it the imperfections of the real gases and yet retaining the form of equation. Thus, fugacity is a sort of fictitious pressure "which is used to order to retain for real gases simple forms of equations which is used for ideal gases only."

For ideal gases $G = G^0 + RT\ln P$ or $\mu = \mu^0 + RT\ln P$

For real gases $G = G^0 + RT\ln f$ or $\mu = \mu^0 + RT\ln f$ 2.29

Equation 2.29 evidently, gives the free energy of real gases at temperature T and pressure P at which fugacity can be taken as f.

so for real gases $(dG)_T = nRT(\ln f)$ (for n moles) 2.30

Integrating the equation 2.30 for fugacities f_1 and f_2 at constant temperature T gives

$$\Delta G - nRT\ln\left(\frac{f_2}{f_1}\right)$$ 2.31

If P is actual pressure, the ratio $\frac{f}{P}$ approaches to unity, when P approaches to zero, in that case a real gas approaches to ideal behavior. The fugacity can be defined as

$$\lim_{P \longmapsto 0} f/p = 1$$

At low pressure fugacity is equal to pressure. But at high pressure the two terms differ materially.

Now $\qquad G = G^0 + RT\ln f$

Differentiating this equation will respect to pressure at constant temperature and constant number of moles of the various constituents. i.e., in a closed system, we get.

$$\left(\frac{\partial G}{\partial T}\right)_T = RT\frac{\partial}{\partial P}(\ln f) \qquad\qquad \text{(As } G^0 \text{ is constant quantity)}$$

As $\left(\frac{\partial G}{\partial T}\right)_T = V$ $\qquad$ we have $\frac{\partial}{\partial P}(\ln f) = \frac{V}{RT}$ 2.32

At a definite temperature equation 2.32 can be written as

$$RT\ln f = Vd^P$$ 2.33

The departure from ideal behavior can be written as

$$\propto = V_i - V$$

$$= \frac{RT}{P} - V \qquad \text{for an ideal gas } V = \frac{RT}{P}, \text{ V is volume of real gas}$$

$$\propto dP = \frac{RT}{P} dP - V dP$$

From equation 2.32 the above equation can be written as

$$RT\, d\ln f = RT\, d\ln P - \propto dP$$

$$RT\, d\ln \frac{f}{P} = -\propto dP$$

Integration this equation between pressure 0 and P we get

$$\ln \frac{f}{P} = -\frac{1}{RT} \int_0^P \propto dP \qquad\qquad\qquad \dots\dots\dots 2.34$$

$$\log f = \log P - \int_0^P \frac{\propto}{RT} dP \qquad\qquad \dots\dots\dots 2.35$$

The value of the integral of equation 2.35 can be evaluated experimentally:
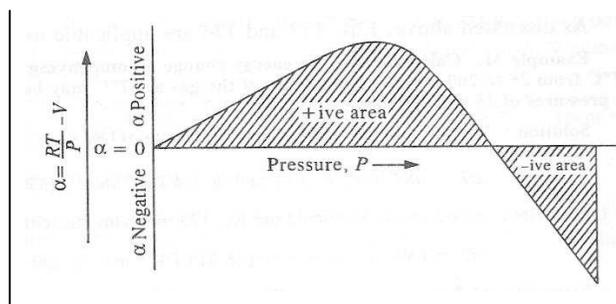
Fig. 2.1 Determination of fugacity

Now $\propto$ as given in the above equation can be determined at different pressures. These values are plotted against corresponding pressure as shown in fig. 2.1. The shaded area under the curve between pressure P=0 and any given pressure P, gives the value of the integral $\int_0^P \propto dP$. f (fugacity) can be evaluated at any given pressure P of the gas through substituting this value in equation 2.35,. Since departure from ideal behavior ($\propto$) can be both positive as well as negative. Thus, the fugacity of the gas can be less than the pressure or more than the pressure. It is clear from above figure the area and hence the value of f is positive at low pressure and more than P at high pressures.

2.8   PHYSICAL SIGNIFICANCE OF FUGACITY

If a system or a part of system be at higher temperature than that of its surroundings, then heat energy will escape from the former to latter. The higher the temperature the greater the tendency of the heat escapes. Let us consider a system consisting of liquid water in contact until its vapour. Water molecules in liquid phase will have a tendency to escape into vapour phase by evaporation while those in the vapour phase will have a tendency to escape into the liquid phase by condensation. At equilibrium the two escaping tendencies will be equal. It is accepted that each substance in a given state has a tendency to escape from that state. This escaping tendency was termed as fugacity by Lewis.

2.9 THERMODYNAMIC DERIVATION OF LAW OF MASS ACTION

van't Hoff deduced the law of mass action thermodynamically by using an equilibrium box in which all the systems were in equilibrium with each other at constant temperature.

This box is simply hypothetical and it has following properties

(a) The walls of the box are rigid having indefinite dimensions.

(b) The walls may be suitably made permeable to various components.

(c) The various components present are in equilibrium with each other.

(d) The working substances are ideal gases.

(e) The box is assumed to have large dimensions so that there is no change in concentration or pressure (partial) of any component, if a small amount of those is added or removed from it.

(f) The temperature of the box remains constant.

Now let us consider a chemical change at constant temperature

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

Consider two equilibrium boxes 1 and 2 in which components A,B,C and D are in equilibrium, Suppose P_A, P_B, P_C and P_D are partial pressures of the A, B, C and D and C_A, C_B, C_C, and C_D are the concentrations for box no. 1 similarly P_A', P_B', P_C' and P_D' are partial pressures of A, B, C and D and C_A', C_B', C_C', and C_D' are corresponding concentrations in the box no. 2.

(a) Let us calculate the work done in transferring one mole of A. By means of the piston moving outwards infinitesimally slowly, one mole of A is removed from box (1) so that the partial pressure of A (which is Pa) remains constant. The amount of work done is $P_A V_A$. Where V_A is the volume of one mole of A under pressure P_A.

(b) As the partial pressure is different in two boxes, that the removed gas from box(1) is changed isothermally and reversibly from P_A to P_A' by working the piston.

The amount work done is $RT \ln \dfrac{P_A}{P_A'}$

(c) The gas is now ready to be put in the box no. (2) by compressing the gas infinitesimally slowly by working the piston, so the partial pressure of A in the box (2) (which is P_A') remains constant. This will be put in box no. 2.

The work done in the process is $P_A' V_A'$ where V_A' is volume of one mole of A under a partial pressure of P_A'

Total work done in this process is

$$w_1 = P_A V_A + RT \ln \frac{P_A}{P_A'} - P_A' V_A'$$

$$= RT \ln \frac{P_A}{P_A'} \quad (\text{since } P_A V_A = P_A' V_A') \qquad \text{............... 2.36}$$

We know partial pressure is proportional to concentration

$$w_1 = RT \ln \frac{C_A}{C_A'} \qquad \text{................ 2.37}$$

Similarly one mole of B is transferred from box-1 to box-2, the work done will be

$$w_2 = RT \ln \frac{P_B}{P_B'} = RT \ln \frac{C_B}{C_B'} \qquad \text{...................2.38}$$

At the same time one mole of C and one mole of D are transferred from box(2) to box(1), they interact to produce A or B to maintain the equilibrium the work done will be

$$w_3 = RT \ln \frac{p'_C}{p_C} = RT \ln \frac{c'_C}{c_C} \qquad \ldots\ldots\ldots\ldots 2.39$$

$$w_4 = RT \ln \frac{p'_D}{p_D} = RT \ln \frac{c'_D}{c_D} \qquad \ldots\ldots\ldots\ldots 2.40$$

When one mole of C and one mole of D are transferred from box(2) to box(1) they interact to produce A and B to maintain the equilibrium.

For such an isothermal cyclic process total amount of work done is zero, as the system remains always in equilibrium.

Here $\quad w_1 + w_2 + w_3 + w_4 = 0$

$$RT \ln \frac{p_A}{p'_A} + RT \ln \frac{p_B}{p'_B} + RT \ln \frac{p'_C}{p_C} + RT \ln \frac{p'_D}{p_D} = 0$$

or $\quad \ln \frac{p_A}{p'_A} + \ln \frac{p_B}{p'_B} = \ln \frac{p'_C}{p'_C} + \ln \frac{p'_D}{p'_D}$

$$\ln \frac{p_A p_B}{p'_A p'_B} = \ln \frac{p_C p_D}{p'_C p'_D} \quad , \quad or \; \frac{p'_C p'_D}{p'_A p'_B} = \frac{p_C p_D}{p_A p_B} = K_p \qquad \ldots\ldots\ldots 2.41$$

Similarly $\dfrac{c_C c_D}{c_A c_B} = \dfrac{c'_C c'_D}{c'_A c'_B} = K_C \qquad \ldots\ldots\ldots\ldots 2.42$

Equation 2.41 and 2.42 are the two forms of law of mass action.

2.10 FREE ENERGY CHANGE (G) IN CHEMICAL REACTIONS

Suppose at a given temperature T and at a given set of arbitrarily chosen pressure (or concentration) one mole of A reacts with one mole of B yielding one mole of C and one mole of D, i.e.,

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

The change in free energy in a system due to chemical reaction at constant temperature and pressure would be

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

2.11 ACTIVITY CONCEPT

The chemical potential equation is

$$\mu_i = \mu_i + RT \ln f_i$$

Since the absolute value of chemical potential is not known, it is not possible to evaluate the value of μ_i of a substance. The function fugacity was introduced into the expression of the thermodynamic potential to cover the departure from ideal behavior of the system. Lewis introduced another function called activity or relative fugacity, denoted by 'a'. If f and f^0 denote the fugacities of a substance in a given state and in a standard state, arbitrarily chosen, then the activity 'a' is the ratio of two fugacities,

$$a = \frac{f}{f^0}$$ 2.43

It is obvious that in the standard state activity is $a^0 = \frac{f^0}{f^0} = 1$

From the above it is clear that activity of a substance in any given state is defined as the ratio of the fugacity of the substance in that state to the fugacity of same substance in standard state.

The difference between chemical potential of a substance in any state and that in the pure state is given by

$$\mu_i - \mu_i^0 = RT \ln\left(\frac{f_i}{f_i^0}\right)$$

$$= RT \ln a$$

So $$\mu_i = \mu_i^0 + RT \ln a$$ 2.44

Since activity is the ratio of fugacity, its numerical value will depend upon the standard state, which may be arbitrary fixed. Since, activity and the fugacity are numerically the same. For gases and vapours, at standard state, fugacity is unity. Thus a=f/f⁰=f/1=f

For an ideal gas fugacity and pressure are equal and the same is also true for other gases at low pressures. Hence in all such cases $a = f = P$

For pure liquids and solids activities in pure state under one atmospheric pressure are taken as unity at each temperature. But in solutions it is not always convenient to assume the pure state as the standard for unit activity. It is necessary to consider the activities of solutes and solvents separately.

Let us consider a reaction to take place in solution

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

The equilibrium constant for this reaction is written as

$$K = \frac{a_C a_D}{a_A a_D} \qquad \dots\dots\dots\dots\dots.2.45$$

Where a_A a_B, a_C and a_D represent the ideal concentrations in terms of molality (m) or activities of the respective constituents A, B, C and D. If 'a' represents the ideal concentration and 'c' or 'm' the real concentration, the ratio a/m is known as activity coefficient (γ). Activity coefficient is the measure of extent to which an ion or molecule departs from ideal behavior. The ionization of a uni-univalent electrolyte of type AB can be represented as

$$AB \rightleftharpoons A^+ + B^-$$
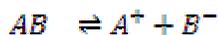
The equilibrium constant K is written as

$$K = \frac{a_+ a_-}{a_2}$$

where a_+ is the activity of cation (A^+), a_- the activity of anion (B^-) and a_2 is the activity of the undissociated electrolyte (AB).

The mean ionic activity of the two ions ($a\pm$) may be regarded as the geometric mean of the activities of the respective ions

$$a\pm = \sqrt{a_+ x a_-} = (ka_2)^{1/2}$$

The activity coefficient of cation is $\gamma_+ = \frac{a_+}{c_+}$ and that of anion is $\gamma_- = \frac{a_-}{c_-}$. The mean activity coefficient $(\gamma\pm)$ of the two ions is regarded as the geometric mean of the activity coefficients of the respective ions.

$$\gamma - \gamma\pm - \sqrt{\gamma_+ \gamma_-}$$

$$= \sqrt{\frac{a_+}{c_+} \cdot \frac{a_-}{c_-}}$$

$$= \frac{a\pm}{c\pm}$$

$$= \frac{\sqrt{ka^2}}{c}$$

Where $c\pm = c$

2.12 ACTIVITY COEFFICIENTS OF ELECTROLYTES

The concept of activity coefficient generally applicable to all cases. Because of the ionic dissociation in solution of electrolyte the expression require certain modification. At a given temperature under unit pressure the standard state of an ionic species is such that at infinite dilution, the activity becomes equal to its concentration. The concentration is generally expressed in molality or molarity. Then

$$a_+^0 = m_+^0 \qquad\qquad\qquad a_+^0 = c_+^0$$

Lt m $\longrightarrow$ 0   Lt c $\longrightarrow$ 0

$$a_-^0 = m_-^0 \qquad\qquad\qquad a_-^0 = c_-^0$$

 In molal units   in molar units

+ Sign refer to cations and – signs refer to anions. Now let us consider a simple case of uni-univalent electrolyte AB, which ionizes in solutions as:

$$AB \rightleftharpoons A^+ + B^-$$

Suppose μ_2, μ_+ and μ_- are the chemical potentials of the electrolyte molecule, cation and anion respectively. Then

$$\mu_2 = RT\ln a_2 + z_2^0$$

$$\mu_+ = RT\ln a_+ + z_+^0$$

$$\mu_- = RT\ln a_- + z_-^0$$

Where z^0 terms are constant, representing corresponding chemical potentials at the standard state.

Assuming the electrolyte dissociates completely, as in the case of strong electrolytes or solutions at infinite dilution, then

$$\mu_2 = \mu_+ + \mu_-$$

And also at standard state

$$\mu_2^0 = \mu_+^0 + \mu_-^0$$

i.e., $$z_2^0 = z_+^0 + z_-^0$$

we can write $RT\ln a_2 + z_2^0 = RT\ln a_+ + z_+^0 + RT\ln a_- + z_-^2$

or $a_2 = a_+ a_- = (a\pm)^2$

$a\pm$ is called mean ionic activity

Therefore $a\pm = a_2^{1/2}$

If we take a multivalent electrolyte in general, Av^+Bv^- which dissociate as

$$Av^+Bv^- = v^+A^+ + v^-B^-$$

Assuming complete dissociation

$$\mu_2 = v^+A^+ + v^-B^-$$

We can write

$$a_2 = a_+^{v^+} a_-^{v^-}$$

$$= a_\pm^v$$

or $a\pm = a_2^{1/v}$

This is mean ionic activity of a multivalent electrolyte.

2.13 *CHANGES IN GIBBS FREE ENERGY (G) IN CHEMICAL REACTIONS*

Let us consider a general reaction in which a mole of A are reacting with b moles of B to produce c moles of C and d moles of D at a given temperature T,

$$aA + bB \rightleftharpoons cC + dD$$

The change in thermodynamics potential (Gibbs potential) in the system due to the chemical reaction at constant temperature and pressure, is given by

$$\Delta G = G_{prc} - G_{rea}$$

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

Where μ is chemical potential

We know $\mu = RT\ln a + z$

We have

$$\Delta G = d(RT\ln a_D + Z_D) + c(RT\ln a_c + Z_c)$$

$$-a(RT\ln a_A + Z_A) - b(RT\ln a_B + Z_B)$$

$$= RT\ln(a_D^d a_C^c / a_A^a a_B^b) + dz_D + cz_c - az_A - bz_B$$

$$= RT\ln(a_D^d a_C^c / a_A^a a_B^b) + Z \qquad \ldots\ldots\ldots\ldots 2.46$$

where Z is a constant

In this expression a_A, a_B, a_C and a_D are the activities of the components in the arbiturary choosen conditions for the reaction.

It must be kept in mind that this relation is valid for any chosen state and therefore would also be valid it we start with components in the equilibrium state. Now, using o for denoting   equilibrium   conditions,

$$\Delta G_o = RT\ln\left(\frac{a_{oD}^d a_{oC}^c}{a_{oA}^a a_{oB}^b}\right) + Z$$

$$= RT\ln K_a + z$$

But at equilibrium $\Delta G_o = 0$

Then $Z = -RT \ln K_a$ 2.47

Then for any equilibrium reaction, the change in the thermodynamic potential would be

$$\Delta G = -RT \ln K_a + RT \ln (a_D^d a_C^c / a_A^a a_B^b)$$

$$= -RT \ln K_a + RT \sum v \ln a \qquad ....2.48$$

As this expression is derived at constant pressure this relation is commonly known as **van't Hoff's reaction isotherm.**

In terms of fugacity

$$\Delta G_f = -RT \ln K_f + RT \sum v \ln f$$

In terms of concentration

$$\Delta G_c = -RT \ln K_c + RT \sum v \ln c \qquad ....2.49$$

In terms of pressure

$$\Delta G_p = -RT \ln K \ln K_p + RT \sum v \ln P \qquad ....2.50$$

The importance of this reaction isotherm lies in the fact that can predict the feasibility of the reaction. It is well known fact that when a reaction precedes spontaneously, the Gibbs potential gradually diminishes until it becomes minimum at equilibrium. This means that for spontaneous reactions ΔG is negative. That is in equation 2.49. $\sum v \ln c$ should be less than $\ln k_c$. If the conditions are so chosen that $\sum v \ln c$ becomes greater than $\ln k_c$ then the reaction will not occur. If we reduce the concentrations (or pressures) of the products and increase those of reactants, then $\sum v \ln c$ would diminish and the possibility of the reaction in the desired direction improves. Thus we can determine the direction of a chemical change.

2.14 STANDARD VALUE OF GIBBS POTENTIAL

The value of change in Gibbs potential is given by the relation, as we have deduced above.

$$\Delta G = -RT \ln K_a + RT \sum v \ln a$$

If the reaction is carried out in such a condition that all the reactants and products are at unit activity, under these conditions the change in thermodynamics potential is called the standard change in Gibbs potential (G) and is denoted at ΔG°, so,

$$\Delta G^\circ = -RT \ln K_a$$

Because then $\sum v \ln a = 0$

Then the equation for Gibbs potential change is given by

$$\Delta G = \Delta G^\circ + RT \sum v \ln a \qquad\qquad ………….2.51$$

For ideally behaving systems the corresponding relations are,

$$\Delta G^\circ = -RT \ln K_c$$

and $\Delta G^\circ - -RT \ln K_p$

Then

$$\Delta G = \Delta G^\circ + RT \sum v \ln c$$

and $\quad \Delta G = \Delta G^\circ + RT \sum v \ln P$

2.15 VAN'T HOFFS EQUATION AND VAN'T HOFFS ISOCHORE

van't Hoff reaction isotherm is given by the relation

$$\Delta G = -RT \ln K_p + RT \sum v \ln P$$

Differentiating this equation with respect to temperature at constant pressure

$$\frac{\partial}{\partial T}(\Delta G) = -RT \frac{\partial}{\partial T}(\partial n K_p) - R \ln K_p + R \sum v \ln P + RT \frac{\partial}{\partial T} \sum v \ln P$$

We know $\sum v \ln P$ is a fixed quantity as pressure of the components is arbitrarily chosen, hence

$$\frac{\partial}{\partial T}\sum v \ln P = 0$$

Multiplying both the sides by T, we have

$$T\frac{\partial}{\partial T}(\Delta G) = -RT^2\frac{\partial}{\partial T}(\ln K_p) - RT \ln K_p + RT \sum v \ln P$$

$$= \Delta G - RT^2\frac{\partial}{\partial T}(\ln K_p)$$

Rearranging the term we have

$$RT^2\frac{\partial}{\partial T}(\ln K_p) = \Delta G - T\frac{\partial}{\partial T}(\Delta G)$$

From Gibbs- Helmholtz relation we know

$$\Delta G - T\frac{\partial}{\partial T}(\Delta G) = \Delta H$$

So $\qquad RT^2\frac{\partial}{\partial T}(\ln K_p) = \Delta H$

Hence $\frac{\partial}{\partial T}(\ln K_p) = \frac{\Delta H}{RT^2}$ ………….. 2.52

This equation is commonly known as van't Hoff equation.

We know,

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

$$\ln K_p = \ln K_c + \Delta n \ln (RT)$$

$$= \ln K_c + \Delta n \ln R + \Delta n \ln T$$

$$\frac{\partial}{\partial T}\ln K_p = \frac{\partial}{\partial T}\ln K_c + \frac{\Delta n}{T}$$

Substituting the this value in equation 2.52

We get

$$\frac{\partial}{\partial T}\ln K_c = \frac{\Delta H}{RT^2} - \frac{\Delta n}{T}$$

$$= \frac{\Delta H - \Delta nRT}{RT^2}$$

$$= \frac{\Delta E}{RT^2} \qquad\qquad …..……..2.53$$

In this expression ΔE is the energy change at constant volume, i.e., heat change at constant volume. This relation for the variation of equilibrium constant K_C with temperature at constant volume is commonly mentioned as van't Hoff isochore.

2.16 FEASIBILITY OF A REACTION

Free energy (G) and work function (A) are useful in determining feasibility of a reaction or its attainment of equilibrium. We know that entropy remains unchanged in reversible change, but irreversible changes are accompanied with increase in entropy, therefore

For reversible change $\qquad\qquad \Sigma\, dS = 0$

For Irreversble change $\qquad\qquad \Sigma\, dS > 0$

Now suppose there is a system with its surroundings. Let ds and ds` be the entropy-change in the system and surroundings respectively. Therefore

(i) For reversible change ds+ds`=0

(ii) For irreversible change ds+ds`>0

Combining the two change we may write

$$ds + ds` \gtreqless 0 \qquad\qquad ………….2.54$$

If we regard the change in the surrounding as reversible and suppose the surroundings supply heat dq reversibly, then $ds` = -\frac{dq}{T}$

If dE is internal energy increase of the system and w be the work done by the system, then from the first law,

$$ds` = -\frac{dE + w}{T}$$

Now $ds + ds' \geq 0$

Then $ds' - \frac{dE+w}{T} \geq 0$

Herein, symbols in this equation refer to the system only.

Hence,

(a) For a real process to occur in nature

$TdS - dE - w > 0$ …………2.55

(b) At an infinitesimal reversible change of system

$TdS - dE - w = 0$ …………2.56

This condition is valid once the system is at equilibrium. Now suppose the work is mechanical i.e., w=PdV, we can write the above equation in the following form

$$TdS - dE - PdV \geq 0 \qquad \text{……………2.57}$$

(i) If E and V are constant, then

$dS_{EV} \geq 0$

The inequality sign for real changes and the equality sign for condition of equilibrium. This means at equilibrium S becomes maximum and

$$dS_{EV} = 0 \qquad \text{……………2.58}$$

(ii) From the definition of work function

$A = E - TS$

$dA = dE - TdS - SdT$

Substituting this value of dA in eqn 2.57

We get,

$-dA - SdT - PdV \geq 0$

or $dA \leq -SdT - PdV$

In isothermal process, if system does not produce any work,

$$dA \leq 0$$ ……………..2.59

For real processes $dA < 0$ i.e. free energy diminishes. When equilibrium is attained free energy becomes minimum and $dA = 0$

(a) For equilibrium $dA_{T,V} = 0$

(b) For spontaneous change $dA_{T,V} < 0$

(iii) Gibbs free energy equation is

$$G = H - TS$$

$$dG - dH - TdS - SdT$$

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

Substituting this value of dG in equation 2.57

We get,

$$-dG + VdP - SdT \geq 0$$

or $$dG \leq VdP - SdT$$ ……………..2.60

In an isothermal process at constant pressure

$$dG \leq 0$$

For real process Gibbs free energy decreases $dG < 0$. When equilibrium attained, Gibbs free energy is minimum, $dG = 0$

For a process to occur spontaneously $dG_{TP} < 0$, in other words Gibbs free energy change (ΔG) should be negative. Every process tends to attain equilibrium, so G will diminish gradually and at equilibrium it will attain the minimum value, i.e., $dG_{TP} = 0$

∴ For a spontaneous process $dG_{TP} < 0$

and at equilibrium $$dG_{TP} = 0$$

The possibility of spontaneous occurrence of a chemical process is determined by ascertaining whether the Gibbs free energy change (ΔG) is negative for the change under the given conditions.

Since

$$\Delta G = \Delta H - T\Delta S, \qquad\qquad\qquad\qquad ....2.61$$

The Gibbs free energy change can be determined if we can find the change in enthalpy (ΔH) and the change in entropy (ΔS) for the reaction.

The enthalpy change (ΔH) is obtained from the measurement of the heat of reaction or it may be calculated from the bond energies in the molecules of reactants and products.

The entropy change (ΔS) is obtained from the individual entropies of reactants and products, or from other measurements such as e.m.f. etc. The entropy increases whenever as a result of the reaction the randomness increases. It is generally true that when a solid reactant gives gaseous products, the entropy increases, i.e., ΔS is positive. In gaseous reactions the sign of the entropy-change is determined from the number of product and reactant molecules. If the number of product molecules be larger, ΔS will be positive. All dissociation processes are attended with an increase in entropy.

The variation of entropy-change with temperature and variation of enthalpy-change with temperature are not very large. The approximate estimations, ΔH and ΔS may be determined at a convenient temperature may be used for reactions at other temperatures without an appreciable error. But the change in Gibbs free energy (ΔG) varies considerably with temperature.

From equation 2.60 it is clear that (i) the more negative ΔH is more negative ΔG and (ii) more positive ΔS the more negative is ΔG. This shows that the system at constant pressure and temperature would try to move to the state of maximum entropy and minimum enthalpy.

In processes where ΔH is negative and ΔS is positive, we have negative value of ΔG, such processes would occur spontaneously.

Example -1

$$N_2O \rightarrow N_2 + \frac{1}{2}O_2$$
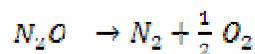
Here ΔH for the dissociation of N_2O is -2000 cal and ΔS is 18 cal/degree. Hence at 25^0C

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

$$\Delta G = -2000 - 298 x 18 = -25364 \, cal$$

The dissociation of N_2O would be spontaneous.

Example -2

$$C + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$
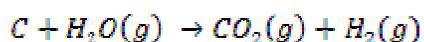
This reaction is endothermic. This reaction will proceed if $T\Delta S$ is positive and greater than ΔH. Here entropy increases, as reactant C has least disorder, $\Delta S = 32$ cal/degree. The enthalpy change was found to be +31400 cal.

Hence at 25^0C

$$\Delta G = 31400 - 32 x 298 = +21864$$

But if temperature is 1200^0K then

$$\Delta G = 31400 - 32 x 1200 = -7000$$

Therefore the reaction will not occur at 298^0K but will be spontaneous at 1200^0K.

This also shows the profound influence of temperature on ΔG.

TERMINAL QUESTION

Short Answer type questions

1. Describe energy of activation. How can energy of activation be determined?

2. Derive the relation $(\partial P/\partial T)_V = (\partial S/\partial V)_T$

3. Derive the law of mass action thermodynamically.

4. Derive the relation for entropy of a perfect gas.

5. At NTP, 2.8 litre of oxygen were mixed with 19.6 litre of hydrogen. calculate the

    entropy change.

6. Derive Gibbs-Deeham equation.

7. Define chemical potential. What is its physical significance?

8. Show that reversible work is always greater than irreversible work.

9. Establish for one mole of a perfect gas :

$$S = C_V \ln P + C_p \ln V + constant$$

10. Establish the relation : $RT \ln (f/p) = (V-V_i)dP$

Long answer type questions:

1. (a) Starting from the limitation of Gibbs-Helmholtz relation, discuss Nernst heat

    theorem. What are the limitations of Nernst heat theorem? Discuss third law of

    thermodynamics.

2. (a) Define fugacity. How can fugacity be determined in the laboratory?

    (b) Derive two important forms of Gibbs-Helmholtz relation.

3.   (a) Write a note on Maxwell-Boltzman statistics.

     (b) Discuss Duham-Murgules equation.

     (c) Write a note on chemical potential.

4. (a) Define partition function.

    (b) Derive the relation for internal energy, entropy, pressure and heat capacity in

    terms of partition function.

5.   (a) Discuss partition function and different types of energies

(b) Establish Debye's T^3 law for heat capacity of solids.

SOURCE OF STUDY MATERIAL

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1. Thermodynamics   : By P.C. Rakshit

2. Advanced Physical Chemistry   : By J.N. Gurtu & A. Gurtu

3. Principles of Physical Chemistry : By Puri, Sharma & Pathania

4. Essentials of Physical Chemistry : By B.S. Bahl, Arun Bahl, G.D. Tuli

5. Physical Chemistry   : By Walter J. Moore

UNIT-3 STATISTICAL THERMODYNAMICS

CONTENTS

3.1   INTRODUCTION

Statistical mechanics provides a link between quantum mechanics and classical thermodynamics. The classical thermodynamics is based on empirical laws in which variables, pressure temperature, energy are regarded as function of state. In the derivation of various relations of thermodynamic function, it is not necessary at any point to take account the constitution of the material system, i.e., the constitution of the material system ignored. The experimental observations support the laws; the drawback of the classical thermodynamics is that we cannot calculate the absolute value of the thermodynamic function of a substance directly. Classical Thermodynamics gives no indication as to the possible origin of the laws. In order to overcome, this new method of approach has been developed which is known as statistical thermodynamics.

In statistical thermodynamics the matter is pictured as composed of innumerable particles in motion. The physical behavior of the particles is governed by the laws of classical thermodynamics subject to quantum mechanical principles. Even in the smallest system, the number of particles is so large that it is impossible to follow the behavior of every individual

particle. Statistical methods are essentially employed to express the property of the system, particularly to find out what fractions of the molecules have a given energy.

Statistical mechanics can be applied easily to simple ideal systems such as monoatomic gases and diatomic gases. For applications to interacting systems such as liquids (where strong intermolecular forces exist), the details of the intermolecular potential energy, which is not accurately known, have also to be taken into account. That is why statistical mechanics of liquids is a difficult but fascinating subject. Gases under high pressure too are difficult to treat statistically since they deviate strongly from ideality. In recent years statistical methods have been applied successfully to simple liquids and dense gases. It is easier to find out the value of entropy, free energy, enthalpy, heat capacity etc. from spectroscopic data by using statistical method.

3.2 PROBABILITY

If we toss a coin, either head or tail will come up. We cannot predict whether head or tail will come up in a particular toss. But we can reasonably say that in any toss there is a fifty percent chance of the head being up. That is desired probability of the event is one in two. Let us take another case. If a single card is drawn out from a well-shuffled deck of cards, the probability or chance of drawing a heart is one in four, the probability of drawing a king is one in thirteen, and the probability of drawing a king of hearts is one in fifty two.

If there are n equally likely and mutually exclusive ways of occurrence of an event in a given set of conditions, then out of these n ways m are favorable to an event A, then the mathematical probability of A is m/n. We may define this in another way. If a occurrence succeeds in p ways and fails in q ways, all the ways being exclusive and equally likely, then the probability of the event succeeding is p/(p+q). For example if we want to hit in color out of the four colors, then we can hit at any particular color in one way, i.e., p=1, we may hit at any of the three color, i.e., equally likely cases of failure is 3, i.e., q=3. Hence the probability of succeeding is given by

$$\frac{p}{p+q} = \frac{1}{1+3} = \frac{1}{4}$$

Hence the probability of an event

$$= \frac{number\ of\ cases\ in\ which\ the\ event\ occurs}{total\ number\ of\ cases}$$

There are two simple theorem of probability:

(i) If several events occur exclusively, then the total probability of their occurrence is the sum of the probabilities of their separate occurances.

When two events occur and the probability of first event be w_1 and the second event w_2 then total probability of both first and second occurring is $w_1 + w_2$

Suppose we have two dice and they are tossed. We intend to find out the probability of obtaining a total of 8 points. There are only the following five different ways of securing 8 points.

| 1st die | 6 | 5 | 4 | 3 | 2 |
| 2nd die | 2 | 3 | 4 | 5 | 6 |

Now let us consider the first combination (6 and 2), there is only one way out of six in which six will come at the top of the first die, and also there is only one way for a two to come at the top of second die. Thus the probability of obtaining eight by first combination is thus $\frac{1}{6} x \frac{1}{6} = \frac{1}{36}$.

This is true for every other four remaining combinations. Hence the total probability of getting an eight is $\frac{5}{36}$.

(ii) The probability of the simultaneous occurrence of two events A and B, is given by the product of the probability of event A and the (conditional) probability of B, when the event A has occurred.

If w_A is the unconditional probability of A and w_B is probability of B when A has already occurred, then the probability of their simultaneous occurrence (w_{AB}) is given by

$$W_{AB} = w_A w_B$$

Suppose from a well shuffled deck of cards we intend to draw the king and queen of hearts. The probability of obtaining king of hearts by a single draw is 1/52. If the king of hearts has been received, the probability of securing the queen of hearts from the remaining is 1/51. The total probability of simultaneously obtaining the pair is $\frac{1}{52} x \frac{1}{51} = \frac{1}{2652}$.

Now let us discuss some other cases. Let us toss two different coins a large number of times and count the number in which

(i) The two tails fall uppermost t_1t_2

(ii) The two heads fall uppermost h_1h_2

(iii) Tail of first coin and head of second coin uppermost t_1h_2

(iv) Head of first coin and tail of second coin uppermost h_1t_2

Where t denotes tail and h denotes head and suffix 1 and 2 indicate the first and second coin.

Now there are two possible events for first coin and two possible events for second coin. Hence total possible events will be $(t_1+h_1)(t_2+h_2) = 2x2=4$. Obviously any one of the four cases can occur. The probability of each of the four equally like cases is ¼.

If we have four coins, the total possible cases by simultaneous toss of the four coins is $(t+h)^4 = 2^4 = 16$. There are, however, five possible combinations or states. These are
tttt, ttth, tthh, thhh, hhhh

Now we select any one of these combinations say tthh (two tails and two heads upwards)

tthh   thht   thth   htth   htht   hhtt

That is there are six ways in which two tails and two heads be upwards from 4 coins. For th^3 there are four possible ways to obtaining the same.

The total possible event is given by $(t+h)^4$.
Expending this binomially we get

$(t+h)^4 = t^4 + 4t^3h + 6t^2h^2 + 4th^3 + h^4$. In this equation the exponents of t and h indicate the number of tails and heads upwards in a given combination. If you examine the equation the coefficient of the term indicate the number of ways the particular combination would occur, the total is 2^4 or 16. Thus probability of t^2h^2 is $\frac{6}{24}$ or $6x2^{-4}$ This is mathematical probability of t^2h^2.

The same result can be obtained as follows. Total number of possible events is (t_1+h_1) (t_2+h_2) i.e. 4. The total permutation of these four is 4! But this number also includes the permutation of two events of first coin and two events of second coin for t^2h^2 which is 2! x 2!.

Hence the real number of micro states or possibilities of complextion would be $\frac{4!}{2!\times2!} = \frac{4\times3\times2}{2\times2} = 6.$ The same result we obtained above.

Now if number of individuals be n and these are accommodated in several houses or cells, such that n_1 are in cell 1, n_1 in cell 2 n_3 in cell 3 etc; the number of microstates for a given combination or macrostate is given by

$$p = \frac{n!}{n_1 \times n_2!...} = \frac{n!}{\pi n_i!}$$

Where π denotes product of terms following it. Again we have taken the case of coins. Suppose we have n identical coins tossed as described earlier. Following our usual method to all the n coins. The total number of cases or macrostate that can occur is given by $(t+h)^n=2^n$

The possible combinations or microstates are

t^n, $t^{n-1}h$, $t^{n-2}h^2$ …………$t^p t^q$ h^{n-1}, h^n

when p+q=n

The coefficient of the terms $t^p h^q$ in the binomial expansion of the above is

$$\frac{n!}{p!\times q!} = \frac{n!}{p!(n-p)!}$$

This is the total number of complexions or microstates that would arise when p coins have tails and q coins have heads upwards. This can be done ^nC_p ways.

The mathematical probability of the occurrence of $t^p h^q$ is therefore

$$W= {^nC_p}/2^n =\frac{n!}{p!(n-P)!} 2^{-n} \qquad\qquad …………….3.1$$

Plank introduced the term thermodynamic probability or statistical probability denoted by P to indicate the total number of possible complexions or microstate for any given combination.

Thus it is different from mathematical probability

Thermodynamic probability $= P = \frac{n!}{\pi n_i!}$

Mathematical probability $W = \frac{n!}{\pi n_i!} x \, C^{-n}$

Where each individual item of the system can give rise to c-cases.

It is clear from these two probabilities that because total number of possible cases (C^n) is constant, thermodynamic probability (W) is proportional to mathematical probability (P)

3.3   BOLTZMANN DISTRIBUTION

Let us consider a system of constant energy E, composed of n identical particles at temperature T which has the following characteristics.

(a) Particle do not attract or repel each other.

(b) Each particle is distinguishable from the other.

(c) No restriction on assigning various energy levels to the particles is being imposed.

All these assumptions lead to the classical Boltzmann distribution law. All the particles are not in the same energy level. Let there be n particles such that n, particles in energy level ϵ_1, n_2 particles in energy level ϵ_2 and so on. Irrespective of this distribution, total number of particles and energy of the system is constant i.e.,

$$n = \sum n_i \qquad \qquad \text{……………..3.2}$$

$$E = \sum n_i \, \epsilon_i \qquad \qquad \text{…………….. 3.3}$$

The allowed energy levels are fixed by quantum mechanical principles. As the occupation number n_1, n_2 etc in different energy levels change the distribution also changes there are obviously number of ways of distribution, similar to the arrangement of n boys in p rooms, so that n_1, in one room, n_2 boys in other room and so on. This number is given by

$$P = \frac{n!}{n_1! \, n_2! \cdots} \qquad \qquad \text{………………..3.4}$$

Thus the thermodynamic probability of a distribution is equal to number of ways of realizing the distribution. This equation is used to determine the probability for all distributions of all the molecules in a given molecular system in different energy levels at a constant total energy.

In equation 3.4, n is the total number of molecules and the summation is over all the energy levels. It is possible to realize a given energy level in more than one way i.e., more than one quantum has the same energy. When this happens, the total energy is said to be degenerate. Let g_i be the degeneracy (or multiplicity) of the energy level ϵ_i. This means if there is one particle in each energy level there are g_i ways of distributing. For two particles in

the ith level, there are g_i^2 possible distribution. Thus for n_i particles in i^{th} level, there are g_i^{ni} possible distribution. Hence the thermodynamic probability for the system of n particles is given by

$$P = n! \frac{\pi}{i} \frac{g_i^{ni}}{n_i!} x \; constant \qquad \ldots\ldots\ldots\ldots3.5$$

We know from Boltzmann equation

$$S = klnW \qquad or \quad klnP \qquad \ldots\ldots\ldots\ldots3.6$$

The probability must be maximum for an equilibrium state, so at equilibrium

$$S = kinP_{max}$$

We are thus interested in finding the distribution that will make W a maximum.

It is more convenient to maximize the logarithm of P. It is known from calculus that at the maximum the derivative of function vanishes.

Now we confine our investigation to a closed system of independent particles, it would meet the following two requirements:

(i) Total number of particles is constant i.e.

$$n = \Sigma n_i = constant \qquad \ldots\ldots\ldots\ldots3.7$$

(ii) Total energy, E of the system is constant i.e.,

$$E = \Sigma n_i \in_i = constant \qquad \ldots\ldots\ldots\ldots3.8$$

Since total number of particles is constant

$$dn = \Sigma \, dn_i = 0 \qquad \ldots\ldots\ldots\ldots3.9$$

and total energy is also constant

$$dE = \Sigma \in_i \, dn_i = 0 \qquad \ldots\ldots\ldots\ldots3.10$$

Taking logarithms of both the sides of equation 3.5 we have

$$lnP = ln \, n! + \overset{\Sigma}{_i} n_i \, ln \, g_i - \overset{\Sigma}{_i} n_i \, ln \, n_i + constant$$

Using Stirling's formula for factorials of large numbers:

$$ln \, x! = x \, ln \; x - x \qquad \ldots\ldots\ldots\ldots3.11$$

$$lnP = nln\ n - n + \sum n_i\ lng_i - \sum n_i\ ln\ n_i + \sum n_i + constant$$

$$= nln\ n - n + \sum n_i\ lng_i - \sum n_i\ ln\ n_i + n + constant$$

$$= nln\ n + \sum n_i\ lng_i - \sum n_i\ ln\ n_i + constant \qquad\qquad \dots\dots\dots\dots3.12$$

Differentiating equation 3.12 and keeping in mind n and g_i are constants

$$dlnP = \sum_i\ ln\ g_i\ dn_i - \sum ln\ n_i\ dn_i - n_i d\ ln\ n_i \qquad\qquad \dots\dots\dots\dots\dots3.13$$

As $\qquad \sum n_i\ dln\ n_i = \sum n_i \frac{dn_i}{n_i} = \sum \frac{dn_i}{i} = 0 \qquad\qquad \dots\dots\dots\dots3.14$

At equilibrium

$$dlnP = \sum_i n_i\ ln\ g_i\ dn_i - \sum_i n_i\ ln\ ni\ dn_i = 0 \qquad\qquad \dots\dots\dots\dots3.15$$

If the system were open then n_i would vary without restriction and the variation would be independent of one another. It would then be possible to solve the equation 2.15 by setting each of the coefficients of the dn_i terms equal to zero. But our system is closed one end since n is constant, the value of dnl are not independent of one another, as it is seen in equation no 3.14.

To solve the equation 3.15 we apply the Lagrange's method of undetermined multipliers. We can write equation 3.15 in the following form

$$\sum ln\frac{g_i}{n_i}dn_i = 0 \qquad\qquad \dots\dots\dots\dots\dots3.16$$

Now multiply 3.9 by α and 3.10 by β and subtract the addition from equation 3.16

$$\sum(ln\frac{g_i}{n_i} - \alpha - \beta \in_i)dn_i = 0 \qquad\qquad \dots\dots\dots\dots\dots3.17$$

The variable dn_1, dn_2 etc is independent of each other, so that the equation 3.17 to hold each term in the summation must be zero.

$$ln\frac{g_i}{n_i} - (\alpha - \beta \in_i = 0$$

$$ln\frac{g_i}{n_i} = (\alpha + \beta \in_i = 0$$

$$ln\frac{g_i}{n_i} = -(\alpha + \beta \in_i$$

$$n_i = g_i \, e^{-(\alpha + \beta \varepsilon_i)}$$ …..…………….3.18

Now $$\sum n_i = \sum g_i e^{-\alpha} \, e^{-\varepsilon_i/kT}$$

or $$n = \sum g_i e^{-\alpha} \, e^{-\varepsilon_i/kT}$$ …………….. 3.19

$$n = \sum g_i e^{-\alpha} \, e^{-\varepsilon_i/kT}$$ ……………….3.20

Dividing equation 3.18 by equation 3.20 we get

$$\frac{n_i}{n} = \frac{g_i e^{-\alpha} \, e^{-\varepsilon_i/kT}}{\sum g_i e^{-\alpha} \, e^{-\varepsilon_i/kT}}$$

$$\frac{n_i}{n} = g_i \, \frac{e^{-\varepsilon_i/kT}}{\sum g_i \, e^{-\frac{\varepsilon_i}{kT}}}$$ ……………….3.21

This is general form of Boltzmann distribution law

3.4 PARTITION FUNCTION

The denominator in the equation 3.21, $\sum e^{-\varepsilon_i/kT}$ is sum of the factor $e^{-\varepsilon_i/kT}$ over all energy levels. It is called partition function and is represented by f.

$$f = \sum g_i e^{-\varepsilon_i/kT}$$

Then Boltzmann distribution law can be written as.

$$n_i = \frac{n}{f} g_i \, e^{-\varepsilon_i/kT}$$ …..…………3.22

Qualitatively speaking, the partition function is a measure of available energy levels and it indicates how the particles are distributed among the various energy states.

3.5 PARTITION FUNCTION AND THERMODYNAMIC FUNCTIONS

3.5.1 Internal energy

The internal energy E of a system of n particles is given by the equation

$$E = \sum n_i \in_i$$

$$= \sum \in_i \frac{n}{f} e^{-\epsilon_i/kT}$$

$$= \frac{n}{f} \sum \in_i e^{-\epsilon_i/kT} \quad \text{(substituting g=1)}$$

but $\qquad f = \sum e^{-\epsilon_i/kT}$

$$\frac{df}{dT} = \frac{1}{kT^2} \sum e^{-\epsilon_i/kT}$$

So $\qquad kT^2 \frac{\partial f}{\partial T} = \sum \in_i e^{-\epsilon_i/kT}$

Hence $\quad E = \frac{n}{f} \sum \epsilon_i e^{-\epsilon_i/kT} = \frac{nkT^2}{f} \frac{df}{dT}$ 3.23

For a gm mole

$$E = NkT^2 \frac{d\ln f}{dT} \qquad\qquad ....3.23 \text{ (a)}$$

The average energy of each molecule

$$\in = kT^2 \frac{d\ln f}{dT} \qquad\qquad ....3.24$$

3.5.2 Entropy:

The relation between entropy and probability W is given by the relation.

$$S = k\ln W \qquad\qquad ......…......3.25$$

We know W is proportional to the thermodynamics probability (P)

$$S - B = k \ln P \quad \text{(B is a constant)}$$

$$(S\text{-}B)/k = n \ln n - \sum ni \, (\ln n - \ln f - \beta \in_i)$$

$$= n\ln n - \ln n \sum n_i + \ln f \sum n_i + \beta \sum n_i \in_i$$

$$= n\ln n - n\ln n + n \ln f + \beta E$$

Since $\qquad\qquad \sum n_i \ \epsilon_i = E$

$$S - B = kn \ \ln f + k\beta E \qquad\qquad ....3.26$$

From Plank's arbitrary assumption $B = 0$ and $\beta = \frac{1}{kT}$

$$S = n \ k \ln f + nkT\frac{d\ln f}{dT}$$ Similarly, Pressure P, Gibbs free energy G, work

function A, heat capacity C_v, enthalpy H can be represented in terms of partition function.

3.6   *THE THIRD LAW OF THERMODYNAMICS*

Statistical formulation of third law can be made in the following way. We know.

$$S_T - S_0 = \int_0^T \frac{c_p}{T} dT \qquad\qquad ....3.27$$

At very low pressure $C_p \approx C_v$.

Hence $\qquad\qquad S_T - S_0 = \int_0^T \frac{c_v}{T} dT$

and $\qquad\qquad C_v = \left(\frac{dE}{dT}\right)_V$

so $\qquad S_T - S_0 = \int_0^T \frac{1}{T} \left(\frac{dE}{dT}\right)_V dT$

$$= \int_0^T \frac{1}{T}\frac{d}{dT}\left(kT^2\frac{\partial \ln z}{dT}\right)_V dT$$

Hence Z is molar partition function

$$= kT\left(\frac{d\ln Z}{dT}\right)_V + k\int_0^T \left(\frac{d\ln Z}{dT}\right)_V dT$$

(by differentiating partially)

$$= \frac{E}{T} + k\ln(Z)_T - k\ln(Z)_0$$

Equating temperature independent terms we get

$$S_0 = k \ln 2_0 = k \ln (f^N)_0$$

$$= R \, ln(f)_0$$

$$= R \, ln(g_0 e^0)$$

$$= R \ln g_0$$

Here g_0 is statistical weight factor of the lowest energy state. For a perfect crystal at 0^0 K there is only one arrangement, which means $g_0 = 1$. Hence the entropy $S_0 = 0$ which is third law

Now $\quad\quad S_T = \frac{E}{T} + R \, lnf_T$ ………3.28

In general we can write

$$S = \frac{E}{T} + R \, ln \, f$$ ………….3.29

This is the expression for entropy at any temperature T.

3.7   BOSE – EINSTEIN STATISTICS

In classical distribution of particles are distinguished from one another. If two particles interchange their positions (or energy states) a new complexion would occur. But in Bose – Einstein statics we start will identical particles which are indistinguishable. Therefore the interchange of two particles between two energy states will not give rise to new complexion or micro-state.

For example, suppose then are four particles distributed between two cells, say x and y, three in x cell and one in Y cell. Then would give rise to four complexions if

cell x	Abc	abd	acd	bcd	aaa
cell y	d	c	b	a	a

Boltzmann   Bose Einstein

They are distinguishable (Boltzmann) and only one complexion, if indistinguishable (Bose Einstein)

Suppose there are n indistinguishable particles. Consider n_i with energy E_i with degeneracy g_i. These n_i particles have to be distributed among g_i states, we shall need $g_i - 1$ partitions to place the n_i particles in p_i sections, each section corresponding to an energy state. It means g_i is the degeneracy of the level. The problem is to distribute n_i particles into g_i sections without any restrictions. The permutation of ni particles and $gi - 1$ partitions simultaneously is given by $n_i + g_i - 1)!$. But this includes the permutations of n_i particles and $g_i - 1)$ partions amongst themselves also, as both these groups are internally indistinguishable.

Hence the actual number in which ni particles may be allocated in gi states is given by.

$$\frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}$$

The thermodynamic probability is then given by.

$$P = II \ \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!} \qquad\qquad \ldots\ldots\ldots\ldots.3.30$$

Using sterling's formula and neglecting unity as compared to g_i (since g_i is very large) we get

$$\ln P = \sum[(n_i + g_i)\ln(n_i + g_i) - (n_i + g_i) - n_i \ln n_i + n_i - g_i \ln g_i + g_i]$$

$$= \sum[n_i \ln\left(1 + \frac{g_i}{n_i}\right) + g_i \ln\left(1 + \frac{n_i}{g_i}\right)]$$

hence $\ d\ln P = \sum \ln\left(1 + \frac{g_i}{n_i}\right) dn_i + n_i \frac{n_i}{g_i+n_i}\left(-\frac{g_i}{n_i^2}\right) + g_i \frac{1}{g_i} \frac{g_i}{n_i+g_i} \ dn_i]$

$$d\ln P = \sum \ln\left(1 + \frac{g_i}{n_i}\right) dn_i$$

As at the maximum $d\ln P = 0$

We have $\qquad \sum \ln\left(1 + \frac{g_i}{n_i}\right) dn_i = 0 \qquad\qquad \ldots\ldots\ldots\ldots.3.31$

As deduced in Boltzmann law, we have

$$\sum dn_i = 0 \qquad\qquad\qquad \text{………….…..3.32}$$

$$\sum \in_i dn_i = 0 \qquad\qquad\qquad \text{……….…..3.33}$$

Multiplying eqn. 2.32 by α and eqn. 2.33 by β and substract eqn. 2.31 from their sum we get

$$\sum \left[\alpha + \beta \in_i - \ln\left(1 + \tfrac{g_i}{n_i}\right) \right] dn_i = 0$$

Since $dn_i \neq 0$ we have

$$\ln\left(1 + \tfrac{g_i}{n_i}\right) = \alpha + \beta \in_i$$

$$1 + \tfrac{g_i}{n_i} = e^{\alpha + \beta \in_i}$$

$$ni = \frac{g_i}{e^{\alpha} e^{\beta \in_i} - 1} \qquad\qquad \text{……………3.34}$$

Equation 2.34 is Bose – Einstein distribution law.

3.8 FERMI – DIRAC STATICS

In classical statics or in Bose-Einstein statistics there was no restriction to the number of particle present in any energy state. On applying this concept to particles like electrons the Pauli's exclusion principle is invoked. Pauli's exclusion principal says that two particles in an atom cannot be in the same energy level. It means that not move than one particle can be assigned to a particular energy state.

Suppose there be n_i particles of energy E_i in which there are gi energy states. If all the particles are assumed to be identical and that only particles can be identical and that number of ways ni particles can be distributed among gi states in that group can be written as

$$\frac{g_i!}{n_i!(g_i - n_i)!}$$

The thermodynamics probability is given by after considering all the groups in the macrostate.

$$P = II \frac{g_i!}{n_i!(g_i - n_i)!}$$

Hence, $\quad \ln P = \sum \ln g_i! - \ln n_i! - \ln(g_i - n_i)!$

$$= \sum [g_i \ln g_i - n_i \ln n_i - (g_i - n_i)\ln(g_i - n_i)]$$

Since g_i is constant

$$d\ln P = \sum \ln \frac{g_i - n_i}{n_i}) dn_i$$

At the maximum $\quad d\ln P = 0$

$$\sum \frac{\ln(g_i - n_i)}{n_i} dn_i = 0$$

or $\qquad\qquad\qquad \sum \ln \left(\frac{g_i}{n_i} - 1\right) dn_i = 0 \qquad\qquad\qquad\qquad$ ………..…..3.35

From the derivation of Boltzmann distribution law we know

$$\sum dn_i = 0 \qquad\qquad\qquad\qquad$$ …………….…..3.36

$$\sum \in_i dn_i = 0 \qquad\qquad\qquad\qquad$$ ………….…..3.37

Multiplying eqn. 3.36 by α, 3.37 by β and substracting eqn. 3.35 we get

$$\sum \left[\alpha + \beta \in_i - \ln \left(\frac{g_i}{n_i}\right)\right] dn_i = 0$$

Since $dn_i \neq 0$ and α and β are arbitrary constants, the terms with in each of the parantheses would equate to zero.

so, $\quad \alpha + \beta \in_i - \ln \left(\frac{g_i}{n_i} - 1\right) = 0$

$$\ln \frac{g_i}{n_i} - 1 = \alpha + \beta \in_i$$

$$\frac{g_i}{n_i} - 1 = e^{\alpha + \beta \in_i}$$

or $\qquad n_i = \frac{g_i}{e^{\alpha + \beta \in_i} + 1} \qquad\qquad\qquad\qquad$ ……………..3.38

Equation 2.39 gives Fermi-Dirac distribution law. Non α or ϵ_i is large, both Bose-Einstein and Fermi-Dirac distribution are rendered into the form

$$n_i = g_i \, e^{-\alpha} e^{-\beta \epsilon_i}$$

This is same as Boltzmann distribution law.

3.9 MOLAR PARTITION FUNCTION:

In the above discussion we have considered systems in which there are n distinguishable particles distributed in different energy levels and f represents the molecular partition function. But we have to deal with large scale systems, in which quantities are taken in gm-moles.

Let us take a system which may be supposed to be constituted a large numbers of smaller ones each with a gm-mole of the substance. That is, the individual unit here is not a molecule but a mole. Let the energy levels allowed for the whole system (each one mole) be E_1, E_2...... and let there be x such systems in all. In each of these systems there are, of course N, Avogadro number of molecules. Then, the average energy E, of each such unit is

$$E = \frac{\sum x_i E_i}{\sum x_i}$$

If Z is partition function of these systems, then

$$Z = \sum e -\frac{E_i}{kT}$$

Now applying the same procedure in equation 3.24 the energy of the system will be

$$E = kT^2 \left(\frac{d\ln z}{dT}\right) \qquad \qquad ....3.39$$

From equation 2.23 (a) we have energy of one mole is

$$E = NkT^2 \left(\frac{d\ln f}{dT}\right)$$

$$= kT^2 \left(\frac{d\ln f^N}{dT}\right)$$

This is the relation we have in equation 3.39. Hence

$$Z = f^N$$

The entropy then can be written as

$$S = NkT\frac{d\ln f^N}{dT} + k\ln f^N$$

$$= NkT\frac{d\ln f}{dT} + Nk\ln f$$

This equation is useful for calculating entropy of the system, provided partition function is known.

3.10 TERMINAL QUESTIONS

1. Define probability?
2. Derive Boltzmann Distribution equation.
3. What is Partition function.
4. Give the relation between partition function and thermodynamic functions.
5. Define the third law of Thermodynamics.
6. Define Bose-Einstein statistics.
7. Define Fermi – Dirac statics.
8. What is molar partition function?
9. Derive third law of Thermodynamics.

SOURCE OF STUDY MATERIAL

1. Thermodynamics   : By P.C. Rakshit

2. Advanced Physical Chemistry   : By J.N. Gurtu & A. Gurtu

3. Principles of Physical Chemistry   : By Puri, Sharma & Pathania

4. Essentials of Physical Chemistry   : By B.S. Bahl, Arun Bahl, G.D. Tuli

5. Physical Chemistry   : By Walter J. Moore

UNIT: 4 APPLICATIONS OF STATISTICAL THERMODYNAMICS

CONTENTS

4.0 INTRODUCTION

Statistical thermodynamics analysis is facilitated through the use of the partition function. This is great analytical tool. It is a fact that most often the molecules are associated with energy of different types. In expressing the partition functions, all these forms of energy must be taken into account.

4.1 VARIOUS TYPES OF PARTITION FUNCTIONS

Let us take a system containing n molecules of identical physical nature with different forms of energies. Such energies may include translational, rotational, vibrational etc. Let the different types of energy be label t, r, v……….

The allowed energy-levels of the t types are $\epsilon_{t_1}, \epsilon_{t_2}, \epsilon_{t_3}$ …….., for r type are $\epsilon_{r_1}, \epsilon_{r_2}, \epsilon_{r_3}$ ………., and so on for other types.

The Boltzmann distribution will be represented by.

$$n_i^t = \frac{n}{f_t} \, e^{\frac{-\epsilon_{t1}}{kT}}$$

$$n_i^r = \frac{n}{f_r} \, e^{\frac{-\epsilon_{r1}}{kT}}$$

$$n_i^v = \frac{n}{f_v} \, e^{\frac{-\epsilon_{v1}}{kT}}$$

Where f_f, f_r, f_v …. etc. are partition functions appropriate to t, v, and r types of energy.

The total energy E of the system is

$$E = \sum \epsilon \, t_1 n_i^t + \sum \epsilon_{r_1} \, n_i^r + \sum \epsilon_{vl} \, n_i^v \qquad \text{…………..}$$

$$= NkT^2 \frac{d}{dT} \ln f_t + NkT^2 \frac{d}{dT} \ln f_r + NkT^2 \frac{d}{dT} \ln f_v \qquad \text{……….}$$

$$= NkT^2 \frac{d}{dT} \ln (f_t, f_r, f_v \text{………}) \qquad \text{………….4.1}$$

If f is the net molecular partition function, when every molecules is capable of freely taking any number of types of energy, we can write

$$E = NkT^2 \frac{d}{dt} \ln f \qquad\qquad ....4.2$$

Comparing equation 4.1 and equation 4.2 we have

$$f = f_t, f_r, f_v .... \qquad\qquad ....4.3$$

Now we can state that net partition function is the product of the separate partition functions in respect of different types of energy independently associated with the molecules.

4.2   PARTITION FUNCTION FOR TRANSLATIONAL ENERGY

Let us consider motion of the particle along x- direction. The molecular partition function due to translation in that direction is given by.

$$f_{t(x)} = \sum g_t e^{\frac{-\epsilon_t}{kT}} \qquad\qquad ....4.4$$

Here g_t is statistical weight factor which is unity in this case for each translational level and ϵ_t is the translation energy of molecule in x-direction.

$$\text{So} \quad f_{t(x)} = \sum e^{\frac{-\epsilon_t}{kT}}$$

The translational energy is also quantized, though the differences in energy levels are quite small. The particle would exhibit periodicity in translational motion only due to impacts on the walls of the container. Consider a cube having length l. The molecules moving along x-direction will repeat its motion each time it complete a path 2l. If λ is the wavelength associated with the matter wave, we have

$$n\lambda = 2l$$

Where n is an integer. The translational energy (ϵ_x) along the x - axis is given by

$$\epsilon_x = \frac{1}{2}mc_x^2$$

$$= \frac{1}{2m}. p_x^2$$

Here c_x is velocity and p_x is momentum associated with the moving particle.

According to de Broglie, there is associated with any particle of mass m moving with a velocity c_x in a single direction, a wavelength λ.

Therefore $\dfrac{h}{\lambda} = p_x = mc_x$

Hence $\epsilon_x = \dfrac{1}{2m}\left(\dfrac{h}{\lambda}\right)^2$

$$= \dfrac{1}{2m}\left(\dfrac{hn}{2l}\right)^2$$

$$= \dfrac{n^2 h^2}{8l^2 m} \qquad\qquad \dots\dots\dots\dots 4.5$$

Substituting the value of ϵ_x in equation 4.4

We get

$$f_{t(x)} = \sum \overline{e} \;\; \dfrac{\epsilon_x}{kT}$$

$$= \sum e^{\dfrac{n^2 h^2}{8l^2 m}}{kT} \qquad\qquad \dots\dots\dots\dots 4.6$$

Since energy levels are very close, the variation of energy may be taken to be continuous and hence the summation may be replaced by integration.

$$f_{t(x)} = \int_0^\infty e^{-\left(\frac{n^2 h^2}{8l^2 mkT}\right)} \, dn$$

Put $\dfrac{n^2 h^2}{8l^2 m} = a^2$

$nh - al(8mkT)^{\frac{1}{2}}$

$n = \dfrac{al}{n}(8mkT)^{\frac{1}{2}}$

$$dn = \frac{l}{h}(8mkT)^{\frac{1}{2}}da$$

$$f_{t(x)} = \frac{(8mkT)^{\frac{1}{2}}}{h}l\int_0^\infty e^{-a^2}da$$

The value of $\int_0^\infty e^{-a^2}da = \sqrt{\frac{\pi}{4}}$

So $f_{t(x)} = \frac{(2\pi mkT)^{\frac{1}{2}}}{h}l$ 4.7

If we consider the translational motion in all the three directions (x, y and z), the molecular partition function for translation would be

$$f_t = f_{t(x)}f_{t(y)}f_{t(z)}$$

$$= \frac{(2\pi mkT)^{\frac{1}{2}}}{h}l \cdot \frac{(2\pi mkT)^{\frac{1}{2}}}{h}l \cdot \frac{(2\pi mkT)^{\frac{1}{2}}}{h}l$$

$$= \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \cdot l^3$$

Since $l^3 = V$, volume of the cube

$$f_t = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}V$$ 4.8

In case of monoatomic gas, the molar partition function is

$$Z = \frac{f^N}{N!} = \frac{1}{N!}\left[\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}V\right]^N$$

From Stirling's formula $N! = \left(\frac{N}{e}\right)^N$

So, $Z = \left(\frac{e}{N}\right)^N\left[\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}V\right]^N$

$$= \left[\frac{(2\pi mkT)^{\frac{3}{2}}}{Nh^3}V_e\right]^N$$

$$lnz = Nln\ \frac{(2\pi mkT)^{\frac{3}{2}}}{Nh^3}V_e \qquad \dots\dots\dots\dots 4.9$$

4.3   INTERNAL ENERGY OF A MONOATOMIC GAS

Internal energy of a monoatomic gas can be obtained by making use of equation 4.9. In the case of monoatomic gas, rotational and vibrational energies are absent and volume V is constant.

We have from equation 4.8

$$f_t - \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}.V_\square$$

Taking log of both sides of equation, we get

$$log_{f_t} = log\left[\frac{(2\pi mkT)^{\frac{3}{2}}}{Nh^3}.V_\square\right]$$

$$= logT^{\frac{3}{2}} + log\left[\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}.V_\square\right]$$

$$\frac{d}{dT}logf_t = \frac{d}{dT}\left(\frac{3}{2}logT\right)$$

$$= \frac{3}{2}T \qquad \dots\dots\dots\dots 4.10$$

Now $\quad E =, kT - 2.\left(\frac{dlnz^\square}{dT}\right)$

$$= NkT^2\frac{dnlf_t}{dT}$$

$$= RT^2.\frac{dlnf_t}{dT}$$

$$= RT^2 \cdot \frac{3}{2T}$$

$$= \frac{3}{2} RT$$

4.4   SACKUR TETRODE EQUATION

This equation evaluates the entropy of monoatomic gas

The translational entropy from entropy equation is $S = \frac{E}{T} + k \ln z$

$$= \frac{3}{2} R + \frac{\left(Nk \ln (2\pi m KT)^{\frac{3}{2}}\right)}{Nh^3} \cdot Ve$$

$$= \frac{3}{2} R + R \ln \frac{(2\pi mkT)^{\frac{3}{2}}}{Nh^3} \cdot Ve$$

$$= R \ln \frac{(2\pi mkT)^{\frac{3}{2}}}{Nh^3} \cdot Ve^{\frac{5}{2}}$$

Since $\qquad PV = RT$, we have $V = \frac{RT}{P}$

$$S = R \ln \frac{(2\pi mkT)^{\frac{3}{2}}}{Nh^3} \cdot \frac{RT}{P} e^{\frac{5}{2}}$$

$$= R \ln \frac{(2\pi mkT)^{\frac{3}{2}} \cdot T^{\frac{5}{2}} e^{\frac{5}{2}} \cdot R}{Nh^3 \cdot P} \cdot Ve^{\frac{5}{2}}$$

$$= R \ln \frac{(2\pi M)^{\frac{3}{2}} (ek) \left(k^{\frac{5}{2}} T^{\frac{5}{2}} \right)}{N^{\frac{3}{2}} h^3 \cdot P}$$

or
$$S = \frac{R \ln (2\pi)^{\frac{3}{2}} (ek)^{\frac{5}{2}}}{N^{\frac{3}{2}} h^3} + \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R \ln P \qquad \ldots\ldots\ldots\ldots 4.11$$

The equation 4.11 is known as Sackur Tetrode equation.

4.5   PARTITION FUNCTION FOR DIATOMIC GAS MOLECULES

4.5.1   Rotational Partition Function

The rotational energy ϵ_r for diatomic molecules considered as rigid rotator is given by

$$\epsilon_r = \frac{j(j+1)h^2}{8\pi^2}I$$

for j^{th} quantum level – here

$$I = \mu r^2$$ = moment of inertia

The partition function for rotational energy of a diatomic molecule is given by

$$f_r = \sum g_r\, e^{\frac{-\epsilon_r}{kT}}$$

As axis of rotation is defined by two coordinates, which means that there are two rotational degree of freedom. Each quantum level of rotational will bring in two possible modes of distribution of rotational energy. Thus the statistical weight factor (g_r) in the rotational level j is given by (2j+1). Hence the rotational partition function can be written as

$$f_r = \sum g_r\, e^{\frac{-\epsilon_r}{kT}}$$

$$= \sum (2j+1)\, e^{-\frac{j(j+1)h^2}{8\pi^2 IkT}}$$

…………………4.12

As the magnitude of I is comparatively large and the rotational levels are close we may write equation 4.12 in the following form

$$f_r = \int_0^\infty (2j+1)\, e^{-\frac{j(j+1)h^2}{8\pi IkT}}$$

$$= \int_0^\infty (2j+1)\, e^{-\beta j(j+1)}\, dj$$

……………..4.13

Where $\beta = \dfrac{h^2}{8\pi^2 IkT}$

Now suppose $j(j+1) = G$

Then $dG = 2(j+1)dj$

Then the equation 4.13 may be written as

$$f_r = \int_0^\infty e^{-\beta G} dG$$

$$= \frac{1}{\beta} = \frac{8\pi^2 IKT}{h^2} \qquad \qquad \ldots\ldots\ldots..4.14$$

This value of f_r is valid for hetero nuclear molecules like HCl, NO etc. For homo nuclear molecules like $O^{16}\,O^{16}$, $N^{14}\,N^{14}$ etc where the molecules when reversed becomes indistinguishable from initial state; in that case the partition function is to be divided by the number of symmetry 2. That is

$$f_r = \frac{8\pi I k T}{2h^2} \qquad \qquad \ldots\ldots\ldots..4.15$$

That means when symmetry is σ the partition function is given by

$$f_r = \frac{8\pi I k T}{\sigma h^2} \qquad \qquad \ldots\ldots\ldots\ldots..4.16$$

Now the rotational energy of a mole of a diatomic gas is given by the relation

$$Er = NkT^2 \frac{d\ln f_r}{dT}$$

$$= NkT^2 \frac{d}{dT} \frac{8\pi^2 IkT}{6h^2}$$

$$= NkT$$

$$= RT \qquad \qquad \ldots\ldots\ldots\ldots.4.17$$

4.5.2 Vibrational Partition Function

The partition function for vibrational energy of a diatomic molecule is given by

$$f_v = \sum g_v \, e^{-\frac{E_v}{kT}}$$

Where g_v is statistical weight factor which is unity for vibration levels.

$$f_v = \sum e^{-\frac{E_v}{kT}}$$

Hence   ………………………4.18

The vibrational energy of diatomic molecule is given by

$$E_v = \left(n + \frac{1}{2}h\nu\right)$$

In this expression ν is fundamental frequency of vibration and n is an integer 0, 1, 2….. etc.

Now the vibrational partition function may be written as

$$f_v = \sum_0^m e^{-\frac{\left(n+\frac{1}{2}\right)h\nu}{kT}}$$

$$= e^{(-1/2 \; h\nu/kT)}(1 + e^{(-h\nu/kT} \; | \; e^{(-2h\nu/kT)}) |$$

……)

$$= e^{-\frac{1 h\nu}{2kT}}\left(1 - e^{-\frac{h\nu}{kT}}\right)^{-1} \qquad \text{……………….4.19}$$

In this expression the quantity $\frac{1}{2}\frac{h\nu}{kT}$ is very small and as a first approximation,

$$f_v = \left(1 - e^{-\frac{h\nu}{kT}}\right)^{-1} \qquad \text{……………….4.20}$$

4.6   *ELECTRONIC PARTITION FUNCTION*

Many monoatomic as well as polyatomic molecules have multiple electronic ground states. In other words, in their normal states there are two or more electronic levels with energies so close together that they may be considered as a single level with a statistical

weight factor greater than unity. In addition to this, there may be some excited electronic states whose energy may be considerably greater than that of the ground states. As we increase the temperature, such excited states become more and more occupied. Hence electronic partition function is greater than unity and varies with temperature. The statistical weight factor for each electronic level, normal or excited is equal to (2j+1), where j is the resultant quantum number of the atom in the given state.

Now electronic partition function

$$f_e = \sum (2j+1)e^{\frac{-\epsilon_e}{kT}}$$

Here ϵ_e is the energy of the electronic state is excess of the lowest state i.e., ground state. In the ground state $\epsilon_e = 0$ therefore $\dfrac{e^{-\epsilon_0}}{kT}$ become unity.

4.7 EQUIPARTITION OF ENERGY

According to law of equipartition of energy, the total energy of a molecule is divided equally amongst the various degrees of freedom of the molecule, for each degree of freedom of the molecule, for each for each $\frac{1}{2}kT$ per molecule or $\frac{1}{2}RT$ per mole.

The different kinds of energy possessed by a molecule are usually expressible in squared terms for each degree of freedom. Thus the kinetic energy is of the form $\frac{1}{2}mc^2$, rotational energy, $\frac{1}{2}Iw^2$, vibrational energy $\frac{1}{2}kx^2 + \frac{1}{2}mx^2$ and so on. Let there be r terms, associated with the energy of a molecule.

Then total energy E of the molecule is given as

$$\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3 \ \ldots\ldots \epsilon_r$$

$$= b_1 x_1^2 + b_2 x_2^2 + b_3 x_3^2 \ \ldots\ldots\ldots\ldots + b_r x_r^2$$

The partition function of the molecule,

$$f = f_1 f_2 f_3 \ \ldots\ldots\ldots f_r$$

$$= \int_0^\infty e^{-\beta b_1 x_1^2} dx_1 \int_0^\infty e^{-\beta b_2 x_2^2} dx_2 \quad \ldots\ldots$$

Put $\qquad \beta x_1^2 = Y_1^2$

$$\beta^{\frac{1}{2}} dx_1 - dy_1$$

$$dx_1 = \frac{dy_1}{\beta^{\frac{1}{2}}}$$

or

putting the value dx_1, dx_2 etc…. in the above equation

we have

$$f = \int_0^w e^{-\beta b_1 x_1^2} dx_1 = \frac{\int_0^\infty e^{-b_1 y_1^2}}{\beta^{\frac{1}{2}}} dy_1$$

$$= \beta^{-\frac{1}{2}} \int_0^\infty e^{-b_1 y_1^2} dy_1$$

$$= \beta^{-\frac{1}{2}} . Q_1$$

Hence $f = \beta^{-\frac{1}{2}} . Q_1 . \beta^{-\frac{1}{2}} . Q_2 \ldots\ldots$

$$= \beta^{-\frac{1}{2}} . [(Q]_{,1} Q_{,2} Q_{,3} \quad \ldots\ldots)$$

$$= \beta^{-\frac{1}{2}} . Q \qquad\qquad\qquad\qquad \ldots\ldots\ldots\ldots4.21$$

Where $Q = [(Q]_{,1} Q_{,2} Q_{,3} \ldots\ldots)$

It is to be remembered that Q_1, Q_2, Q_3 etc and hence Q would not contain β .

We know $\qquad \in = \dfrac{E}{N}$

$$= kT^2 \frac{d\ln f}{dT}$$

$$= -\frac{d\ln f}{d\left(\frac{1}{kT}\right)}$$

$$= -\frac{\partial}{\partial\beta}\ln f$$

Hence $\quad C = -\partial/\partial\beta \left(\ln \beta^{r}(1/2) Q\right)$

$$= \frac{\partial}{\partial\beta\left(\frac{r}{2}\ln\beta - \ln Q\right)}$$

$$= \frac{r}{2\beta}$$

$$= \frac{r}{2}kT \qquad\qquad\qquad\qquad \ldots\ldots\ldots\ldots\ldots\ldots.4.22$$

Equation 4.22 means that if the energy would be expressed as sum of r squared terms, the average energy e is r x $\frac{1}{2}kT$. Hence for each degree of freedom (square term) the energy is $\frac{1}{2}kT.$ This is principle of equipartition of energy.

But in some instances such conditions are not fulfilled. In the case of a gas in a gravitational field. In this case the energy is not a square term but mgh, the mean gravitational potential energy is not $\frac{1}{2}kT$. Similarly in these cases where energy taken up is quantised, the energy associated with them is not a linear function of temperature.

In the case of crystals, say of metals, the atoms have only vibration motion. The vibration may occur in three directions and each mode has two degree of freedom. Hence

$$\in = \frac{1}{2}kT \quad \text{x 3 x 2=3kT}$$

or $\qquad\qquad E = 3RT \approx 6 \ cal \qquad\qquad\qquad \ldots\ldots\ldots\ldots.4.23$

This is known as Dulong-Petit's law. Equation 4.23 means heat capacity should be independent of temperature. But considerable variation with temperature has been noticed. That is, the principle of equipartition of energy has failed.

4.8   RELATION BETWEEN PARTITION FUNCTION AND THERMODYNAMIC FUNCTIONS

4.8.1 Partition Function and Internal Energy

The internal energy of a system of n molecules is given by

$$E = n_0 \, \epsilon_0 + n_1 \, \epsilon_1 + n_2 \, \epsilon_2 \quad \ldots\ldots$$

$$= \sum n_i \, \epsilon_i$$

$$= \sum \epsilon_i \left(\frac{n}{f} \, e^{\frac{-\epsilon_i}{kT}} \right)$$

$$= \frac{n}{f} \sum E_i \, e^{\frac{-\epsilon_i}{kT}} \qquad\qquad\qquad\ldots\ldots\ldots\ldots\ldots 4.24$$

But we know

$$f = \sum e^{\frac{-\epsilon_i}{kT}}$$

Hence

$$\frac{df}{dT} - \frac{1}{kT^2} \sum e^{\frac{-\epsilon_i}{kT}}$$

So

$$kT^2 \frac{df}{dT} = \sum e^{\frac{-\epsilon_i}{kT}} \qquad\qquad\qquad \ldots\ldots\ldots\ldots\ldots 4.25$$

From equation 4.25 equation 4.24 becomes

$$E = \frac{nkT^2}{f} \frac{df}{dT}$$

$$= nkT^2 \frac{d\ln f}{dT} \qquad\qquad\qquad\qquad \ldots\ldots\ldots\ldots 4.26$$

For one mole, n may be replaced by Avogadro's number N. hence

$$E = NkT^2 \frac{d\ln f}{dT}$$

$$= RT^2 \frac{d\ln f}{dT} \qquad\qquad \ldots\ldots\ldots\ldots\ldots\ldots 4.27$$

The average energy of each molecule is then written as

$$\in = kT^2 \frac{d\ln f}{dT} \qquad\qquad \ldots\ldots\ldots\ldots\ldots 4.28$$

4.8.2 Partition Function and Entropy

The entropy equation is terms of partition function can be derived as follows.

The Boltzmann distribution law may be written as

$$n_i = \frac{n}{f} e^{-\beta \in_i}$$

Then $\qquad\qquad \ln n_i = \ln n - \ln f - \beta \in_i \qquad\qquad \ldots\ldots\ldots\ldots 4.29$

Now the relation between entropy and probability is

$$S = k\ln W \qquad \text{(W=mathematical probability)}$$

We know thermodynamic probability (W is proportional to mathematical probability (P).

$$S - B - k\ln P \qquad \text{(where B is constant)}$$

Since $\qquad\qquad \ln P - n\ln n - \sum n_i \ln n_i \qquad\qquad \ldots\ldots\ldots\ldots 4.30$

$$\frac{S-B}{k} = n\ln n - \sum n_i \ln n_i$$

Substituting the value of n_i from equation 4.29,

We have

$$(S - B)/k = n\ln[\![n -]\!] \Sigma\overline{\equiv}n_i i\, (\ln n - \ln f - \beta \in_i i$$

As

$$\sum n_i \, \epsilon_i = E$$

$$\frac{S-B}{k} = n \ln n - n \ln n + n \ln f + \beta E$$

$$\frac{S-B}{k} = n \ln f + \beta E$$

$$S - B = kn \ln f + k\beta E \qquad\qquad \dots\dots\dots\dots 4.31$$

Differentiating equation 4.31 at constant volume

We get

$$\left(\frac{dS}{dE}\right)_V = \frac{nk}{f}\left(\frac{df}{d\beta}\right)_V \left(\frac{d\beta}{dE}\right)_V + k\beta + kE\left(\frac{d\beta}{dE}\right)_V$$

Since

$$f = \sum e^{-\beta t_i}$$

$$\frac{df}{d\beta} = -\sum \epsilon_i \, e^{-\beta \epsilon_i}$$

$$= -\frac{E}{n}f$$

∴

$$\left(\frac{dS}{dE}\right)_V = -\frac{nk}{f}\left(\frac{Ef}{n}\right)\left(\frac{d\beta}{df}\right)_V + k\beta + kE\left(\frac{d\beta}{dE}\right)_V$$

or

$$\left(\frac{dS}{dE}\right)_V - k\beta$$

From first and second law of thermodynamics

We have $dE + PdV = TdS$

$$\left(\frac{dS}{dE}\right)_V = \frac{1}{T}$$

Hence $\quad k\beta = \dfrac{1}{T}$

So $\quad \beta = \dfrac{1}{kT}$ ………………..4.32

So partition function can be written as

$$f = \sum e^{\frac{-\epsilon_i}{kT}}$$

And $\quad n_i = \dfrac{n}{f} e^{\frac{-\epsilon_i}{kT}}$

Now from equation 4.31

$$S - B = kn\ln f + k\beta E$$

$$= kn\,\ln f + \dfrac{E}{T} \quad ; \text{As } \beta = \dfrac{1}{kT} \qquad \text{………………..4.33}$$

Substituting the value of E we get

$$S = kn\,\ln f + nkT d\,\dfrac{\ln f}{dT}$$

4.8.3 Partition Function and Work Function (A)

We know that work function is defined as

$$A = E - TS$$

By substituting the value of E and S

From above we get

$$A = E - T\left[k\ln f + nkT\dfrac{d\ln f}{dT}\right]$$

$$= E - nkT\ln f - nkT^2\dfrac{d\ln f}{dT}$$

$$= -nkT lnf \quad \text{Since} \quad E = nkT^2 \frac{dlnf}{dT} \qquad \text{................4.34}$$

4.8.4 Partition Function and Pressure:

$$dA = -PdV - SdT$$

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

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

Since $A = -nkT lnf$

$$\left(\frac{\partial A}{\partial f}\right) = -\frac{nkT}{f}$$

So $\quad P = \frac{nkT}{f}\left(\frac{\partial f}{\partial V}\right)$

$$= nkT\left(\frac{\partial lnf}{\partial V}\right)_T \qquad \text{...................4.35}$$

4.8.5 Gibbs Function and Partition Function

We know $G = H - TS$

$$= E + PV - TS$$

$$= A + PV$$

$$= -nkT lnf + nkT\left(\frac{\partial lnf}{\partial V}\right)_T .V$$

$$= -nkT\left[lnf - \left(\frac{\partial lnf}{\partial lnV}\right)_T\right]$$

4.8.6 Enthalpy and Partition Function

By definition $H = E = PV$

$$= nkT^2 \frac{\partial lnf}{\partial T} + nkT \left(\frac{\partial lnf}{\partial lnV}\right)_T .V$$

$$= nkT \left[\frac{\partial lnf}{\partial lnT} - \left(\frac{\partial lnf}{\partial lnV}\right)_T\right]$$

...............4.36

4.8.7 Heat capacity (C_v) and Partition Function

By definition $$C_v = \left(\frac{dE}{dT}\right)_V$$

Substituting the value of E in this expresstion

$$C_v = nk \frac{d}{dT}\left(\frac{T^2 dlnf}{dT}\right)$$

.…..…………4.37

4.8.8 Equilibrium Constant and Partition Function

The equilibrium constant of a chemical change can also be evaluated from the partition function of the reactants and products.

We know from Gibbs potential

$$G = H - TS$$

$$= E + PV - TS$$

$$= A + PV$$

(As $E - TS = A$, the work function)

So $G = A + RT$

$PV = RT$ for a perfect gas

From our earlier discussion we know

$A = -kT lnZ$ …from equation   .……………4.38

Hence $G = -kT lnZ + RT$

$$= -kTln\frac{fN}{N!} + RT$$

$$= -RTln\frac{fe}{N} + RT$$

Since
$$N! = \frac{N}{e}$$

Hence
$$G = -RTln\frac{f}{N} - RTlne + RT$$

$$= -RTln\frac{f}{N} \qquad\qquad \ldots\ldots\ldots\ldots\ldots 4.39$$

Now total energy of a molecule can be written as

$$\epsilon = \epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e + \epsilon_0$$

In this expression ϵ_t is translational energy, ϵ_r is rotational energy, ϵ_v vibrational energy, ϵ_e electronic energy and ϵ_0 is zero energy i.e., the energy possessed by the molecule at the ground state at $T = 0K$. Usually the zero of energy to which all other energies are referred is the energy of dissociated atoms infinite distance apart, at 0K. The molecule at 0K would possess some energy which is zero-energy, ϵ_0.

Now molecular partition function of a gas is given by

$$f^0 = f_t{}^0 \times f_r{}^0 \times f_v{}^0 \times f_e{}^0 \times e^{\frac{-\epsilon_0}{kT}}$$

$$= \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} V \times f_{int}{}^0 \times \phi_0$$

Where $\phi_0 = e^{\frac{-\epsilon_0}{kT}}$ and $f_{int}{}^0 = f_r{}^0 f_v{}^0 f_e{}^0$

Putting $\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \times f_{int}{}^0 = f$

We get

$$= f \cdot V \phi_0$$

Substitute this value of partition function in equation 4.39,

$$G = -RT \ln \left(\frac{f \cdot V \phi_0}{N} \right)$$

$$\ldots\ldots\ldots\ldots\ldots 4.40$$

Put $V = \dfrac{RT}{P}$ and at standard state, where $P = 1$ the value of G will be G^o we have the expression

$$G^o = -RT \ln \left(\frac{f \cdot RT \, \phi_0}{N} \right)$$

$$= -RT \ln (f \cdot kT \, \phi_o) \qquad \ldots\ldots\ldots\ldots 4.41$$

Now let us consider a general gaseous equation in which a moles of A and b moles of B reacting to give c moles of C and d moles of D, we have,

$$aA + bB \rightleftharpoons \text{cC+dD}$$

In this equilibrium

$$\Delta G^o = c G_C^o + d G_D^o - a G_A^o - b G_B^o$$

Substituting the value of G_A^o, G_B^o, G_C^o, and G_D^o

As described in equation 3.40, we get

$$\Delta G = -RT \ln \left[\frac{f_C^{\cdot c} \times f_D^{\cdot d}}{f_A^{\cdot a} \times f_B^{\cdot b}} \right] (kT)^{\Delta n} [\phi_{\downarrow o}]^{\Delta n}]$$

$$\ldots\ldots\ldots\ldots 4.42$$

Here $\quad \Delta n = (c + d) - (a + b)$

and $\quad \phi_o^{\Delta n} = \dfrac{\phi_{OC}^c \times f_{OD}^d}{f_{OA}^a \times f_{OB}^b}$

but we know

$$\Delta G^0 = -RTlnkP \qquad \qquad \text{………….....4.43}$$

Hence equilibrium constant K_P is given by the relation

$$K_P = \frac{f_C^{\cdot C} \times f_D^{\cdot d}}{f_A^{\cdot a} \times f_B^{\cdot b}} \times e^{\frac{\Delta E_0}{RT}} (kT)^{\Delta n} \qquad \qquad \text{……………4.44}$$

4.9   HEAT CAPACITY OF SOLIDS

We have discussed above that if the energy could be expressed as sum of r squared terms, the average energy E is rx1/2KT. Hence, for each degree of freedom the energy is ½ KT. This is law of equilibrium of energy.

But in some instances such conditions are not fulfilled. For example in the case of gas in gravitational field, where potential energy is not a squared term but mgh, the mean gravitational potential energy is not ½ KT. Similarly, in these cases where energy taken up is quantized, the energy associated with them is not linear function of temperature.

We have seen in our earlier discussions that in crystals, the atoms have only vibratory motion. In that case vibration may occur in three directions and each mode has two degree of freedom.

Hence $$\epsilon = \frac{1}{2}KT \times 3 \times 2 = 3KT$$

or $$E = 3RT$$

$$\approx 6\ cal$$

The above equation indicates that heat capacity is independent of temperature. However, considerable variation in heat capacity of solids with temperature has been noticed, that reveals the failure of the principle of equilibrium of energy.

4.10   QUANTUM THEORY OF HEAT CAPACITY OF SOLIDS

The atoms in the crystalline solids are arranged in one set pattern and have only vibratory motion, the electronic levels are assumed to be excited. For each atom, there are three vibrational degrees of freedom, therefore, for one mole of crystal of V atoms i.e., one

gm. Mole, there are $3N$ degrees of freedom. The vibrational motion is considered harmonic, so that an oscillating atom at the nth level will have the energy,

$$\epsilon = \left(n + \frac{1}{2}\right)h\upsilon$$

Where υ is the fundamental frequency? Einstein (1907) proposed the quantum treatment of the specific heat of solids. He considered that N atoms of the crystal were all independently vibrating with common frequency υ. Then the partition function for the whole crystal is given by,

$$f^N = \sum \left[\left[e^{-\frac{\left(n+\frac{1}{2}\right)h\upsilon}{kT}}\right]\right]^{3N}$$

$$= \left[e^{-\frac{\frac{1}{2}h\upsilon}{kT}}\left(1 - \left[\left(e^{-\frac{h\upsilon}{kT}}\right)\right]^{-1}\right)\right]^{3N}$$

Taking log of both the sides we get,

$$Nlnf = -\frac{3}{2}\frac{Nh\upsilon}{kT} - 3Rln\left(1 - e^{-\frac{h\upsilon}{kT}}\right)$$

$$lnf = -\frac{3}{2}\frac{h\upsilon}{kT} - 3\ln\left(1 - e^{-\frac{h\upsilon}{kT}}\right) \qquad\qquad \dots\dots\dots\dots 4.45$$

We have earlier calculated the vibrational energy of a mole of diatomic gas equal to

$$E_\upsilon = \frac{3Nh\upsilon}{2} + 3Nh\upsilon\frac{e^{-\frac{h\upsilon}{kT}}}{1 - e^{-\frac{h\upsilon}{kT}}}$$

$$E = \frac{3}{2}Nh\upsilon + 3N\frac{h\upsilon}{\left(e^{\frac{h\upsilon}{kT}}\right)} \qquad\qquad \dots\dots\dots\dots 4.46$$

Then the heat capacity is given by

$$Cv = \left(\frac{\partial E}{\partial T}\right)$$

$$= 3NK \left(\frac{hv}{kT}\right)^2 \frac{\frac{e^{hv}}{kT}}{\frac{(e)^{hv}}{[kT-1)}^2}$$ 4.47

This is known as Einstein's equation. At fairly high temperature, it is clear from the above equation that Cv=3R, which is classical result of Dulong and Petit's. This led Debye to produce certain modifications in the assumptions of Einstein.

Debye suggested that all the atoms were not oscillating with the same frequency as suggested by Einstein. He pointed out that the atoms were vibrating with a spectrum of modes of vibrations ranging from v_0 (frequency at ground state) to some maximum frequency v_m. The difference between v_0 and v_m is so large that it may assume that v_0 is practically zero. The modes of vibrations are limited in number.

The modes of vibration of a radiation between v and v + in volume V is given by

$$dn = \frac{4\pi V}{C^3} v^2 dv$$

Here C is average velocity of elastic waves in the crystal. The total modes of vibration in the crystal is 3N. Hence,

The total modes of vibration in the crystal are then

$$\int_0^{v_m} \frac{12\pi V}{C^3} v^2 dv = 3N$$

or $$v_m^3 = \frac{3}{4\pi} \frac{Nc^3}{V}$$

Then $$\frac{V}{C^3} = \frac{3N}{4\pi v_m^3}$$ 4.48

We have therefore

$$\phi_v = 12\pi \frac{3N}{4\pi v_m^3} \cdot v^2 = \frac{9N}{v_m^3} v^2$$

$$\ldots\ldots\ldots\ldots\ldots 4.49$$

The vibrational partition function is given by

$$f = e^{-\frac{1}{2}\frac{hv}{kT}} \left(1 - e^{-\frac{hv}{kT}}\right)^{-1}$$

$$\log f = -\frac{1}{2}\frac{hv}{kT} - \ln\left(1 - e^{-\frac{hv}{kT}}\right)$$

The parittion function of the whole crystal may be obtained by attaching to each frequency the partition function of the single oscillation i.e.,

$$N\ln f = \int_0^{vm} [\phi(v) \left[-\frac{1}{2}\frac{hv}{kT} - \ln\left(1 - e^{-\frac{hv}{kT}}\right]\right]dv$$

$$= \frac{N}{v_m^3} \int_0^{vm} \left[-\frac{1}{2}\frac{hv}{kT} - \ln\left(1 - e^{-\frac{hv}{kT}}\right)\right]v^2 dv$$

$$= -\frac{9Nhv_m}{8\ kT} - 3N\ln\left(1 - e^{-\frac{hv}{kT}}\right) + \frac{3N}{v_m^3}\int_0^{v_m} \frac{\frac{hv}{kT} e^{-\frac{hv}{kT}}}{1 - e^{-\frac{hv}{kT}}}\ dv$$

$$\ldots\ldots\ldots 4.50$$

At very low temperature the second term is very small and can be neglected. We have then

$$N\ln f = \frac{9Nhv_m}{8\ kT} + 3N\left(\frac{kT}{hv_m}\right)^3 \int \frac{x^3}{e^{x}-1}dx$$

$$-\frac{9Nhv_m}{8\ kT} + 3N\left(\frac{kT}{hm}\right)^3 \frac{\pi^4}{15}$$

$$\ldots\ldots\ldots\ldots 4.51$$

Now $$E = nkT^2 \frac{d\ln f}{dT}$$

$$\ldots\ldots\ldots\ldots 4.52$$

Substituting the value from above in the energy equation we get

$$E = \frac{9}{8}Nhv_m + \frac{3\pi^4}{5}Nk\left(\frac{k}{hv_m}\right)^3 T^4$$

The heat capacity is then given by

$$C_v = \left(\frac{dE}{\partial T}\right) = \frac{12\pi^4}{5} Nk \left(\frac{k}{h\nu_m}\right) T^3 \qquad \text{..............4.53}$$

Equation 4.53 is known as Debye's specific heat relation at low temperature. Expressing $\frac{h\nu_m}{k} = \theta$, the above equation becomes

$$C_v = \frac{12\pi^4}{5} R \frac{T^3}{\theta^3} \qquad \text{..............4.54}$$

Since for a given substance the value of θ is constant, hence C_v varies with T^3 at low temperature. This law is known as Debye's T^3 law.

4.11   RESIDUAL ENTROPY

Entropies calculated using third law of thermodynamics are called thermal entropy. However statistical entropies are more rigorous. It is found that the thermal entropies are smaller than the statistical entropies and deviate ranging from 3.1 to 4.83 JK^{-1} mol^{-1}. We thus conclude that entropies of substance (such as H_2, D_2, NO, N_2O, H_2O etc.) are not zero at 0K in accordance to third law, but finite. These entropies are called residual entropies.

We know that   S=klnW=kln1=0 which is true according to third law of thermodynamics. The occurrence of residual entropy at 0K in the substances as mentioned above, suggests that the lowest energy level in these systems is degenerate. This approach has been used to explain the residual entropy. The existence of residual entropy is a crystal at 0K is presumably due to the alternative arrangements of molecules in the solid. Such arrangements are shown in fig. 4.1 for CO and N_2O :

CO	CO	CO	CO		CO	CO	OC	OC
CO	CO	CO	CO		CO	OC	OC	CO
NNO	NNO	NNO	NNO		NNO	NNO	ONN	ONN
NNO	NNO	NNO	NNO		NNO	ONN	ONN	NNO
	(a)					(b)		

Fig. 4.1 Alternative molecular arrangements (a) perfect crystal (b) actual crystal

Since both the arrangements are equally likely. From Boltzmann entropy equation,

S=klnW

But W=2^N (N is Avogadro's number)

We get

S=kln2^N

=Nkln2

=Rln2

=(8.314JK^{-1} mol^{-1}) (2.303) (0.3010)

=5.76K^{-1} mol^{-1}.

As the residual entropies are found experimentally to be less than this value, it is evident that the two alternative orientations of CO and N_2O molecules in the solid state at 0K are not completely random.

The occurrence of residual entropy in ice is also attributed to the molecular disorder at 0K. In ice crystal, each ice molecule is tetrahedrally coordinated to four other water molecules by hydrogen bonds. This enables that crystal to exist in many configurations at 0K. For H_2 and D_2 the thermal entropies at 0K are less than the corresponding statistical entropies. The calculation of the statistical entropy assumes that there exists equilibrium between ortho H_2 and para H_2 at all temperatures. The ΔS_{mix} of ortho H_2 and para H_2 is found to be 18.37 JK^{-1} mol^{-1} in the vicinity of 0K. when this value is added to the thermal entropy (calculated from heat capacity measurements), the agreement with the statistical entropy is very good.

4.12 TERMINAL QUESTIONS

1. Define various types of partition functions.
2. Give partition function for translational energy.
3. Give Sackur Tetrode Equation

4. Define partition function for diatomic gas molecules.

5. Give relation between partition function and thermodynamic functions.

6. Explain quantum theory of heat capacity of solids.

SOURCE OF STUDY MATERIAL

1. Thermodynamics   : By P.C. Rakshit

2. Advanced Physical Chemistry   : By J.N. Gurtu & A. Gurtu

3. Principles of Physical Chemistry   : By Puri, Sharma & Pathania

4. Essentials of Physical Chemistry   : By B.S. Bahl, Arun Bahl, G.D. Tuli

5. Physical Chemistry   : By Walter J. Moore

UNIT 5: THEORIES OF REACTION RATE

CONTENTS

5.1 OBJECTIVES

After reading this unit, you will be able to:

- Define rate of reaction.
- Explain collision theory of reaction rate along with its limitations.
- Describe the transition state theory that includes both its thermodynamical and statistical formulation.
- Write Lindemann's mechanism of unimolecular reaction.
- Give the concept of Hinshelwood's treatment of the unimolecular reactions.
- Write short on potential energy surface.

5.2 INTRODUCTION

The present unit deals with theories of reaction rate that includes different theories like collision theory, transition sate theory and theories of unimolecular reactions. Unimolecular theories include Lindemann's theory, Hinshelwood's theory and RRKM theory. In addition to these theories of reaction rate, we will discuss about potential energy surface.

5.3 THEORIES OF RATE OF REACTION

Rate of reaction is also known as reaction rate. It is defined as the rate of change of concentration of reactants or products per unit time. As the reaction proceeds, the concentration of reactant decreases while the concentration of the products increases. Therefore the rate of reaction for a general reaction is given by:

$$A \longrightarrow B$$

$$r = - d\,[A]/dt = + d[B]/dt$$

where (–) sign shows decrease in concentration of reactant A while the (+) sign shows increase in the concentration of product B, infinitesimally small change in concentration is represented by d. The rate of reaction is expressed in mole litre^{-1} time^{-1}. Generally the time taken is in seconds hence the rate is expressed in mol l^{-1} s^{-1}. According to rate law, rate of reaction is directly proportional to the concentration of the reactants, raised to some power. For a general reaction:

$$A \longrightarrow B$$

$$r = k\,[A]$$

where k = proportionality constant = rate constant or velocity constant of a reaction

The concentration terms in the rate law expression are raised to some power, this power is known as order of reaction. This is the basic idea of chemical kinetics. Now let us discuss different theories of reaction rate

5.3.1 Collision theory of reaction rate

The collision theory of reaction rate is developed by Arrhenius and van't Hoff. According to collision theory of reaction rate, reactant molecules must collide with each other that result in a chemical reaction. There are two theories of collision: one is classical collision theory while the other is modern collision theory. Let us discuss these theories one by one:

5. 3.1.1 Classical collision theory

According to classical collision theory, gaseous reactant molecules collide with each other that result in a chemical reaction and the rate of this reaction is directly proportional to the number of colliding reactant molecules. Let us consider a reaction in which reactant X and Y reacts or collides to form product XY. Therefore according to classical collision theory:

$$X + Y \qquad XY \qquad\qquad \longrightarrow$$
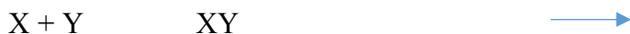
Rate of reaction is proportional to [X] [Y]

Where [X] and [Y] is the concentration of reactant X and Y. Let us consider a collision between two gas molecules C and D. The number of collision occurring between two gas molecules per second per centimeter cube is given by Z which is known as collision number. Z for bimolecular collision is given by Z_{CD}:

$$Z_{CD} = n_C\, n_D\, (d_{CD})^2\, (8\Pi RT/\mu)^{1/2} \quad \ldots\ldots\ldots\ldots \text{(1)}$$

Where n_C is the number of gaseous molecule (C), n_D is the number of gaseous molecule (D), d_{CD} is the average collision diameter, R is gas constant, T is absolute temperature (in Kelvin) and μ is reduced mass. The average collision diameter (d_{CD}) is given by $(d_C + d_D)/2$ while the reduced mass μ is given by $m_C\, m_D/\, m_C + m_D$, where m_C is molecular mass of gas C and m_D is molecular mass of gas D. Hence collision number Z can be written as:

$$Z_{CD} = n_C \, n_D \, \{(d_C + d_D)/2\}^2 \, \{8\Pi RT \, (m_{C} + m_D) / m_C \, m_D\}^{1/2} \ldots\ldots\ldots (2)$$

On applying chemical kinetics to bimolecular collision among gaseous molecule C and D, rate constant (k) expression is given by:

$$k = Z \, e^{-E/RT} \quad \ldots\ldots\ldots.. (3)$$

In order to check the validity of equation 3, reaction between hydrogen (H_2) and iodine (I_2) is taken into consideration. It has been observed that at 556K, the rate constant which is obtained experimentally is 3.7×10^{-7}. The value of rate constant using equation 3 is calculated and is equal to 5.5×10^{-7}. The value of rate constant thus obtained is in good agreement with the experimental value that proves the validity of the rate constant expression for bimolecular collision between hydrogen and iodine. Similar agreement has also been observed in case of reaction or collision between nitrogen and oxygen.

But in certain reactions like polymerization of 1,3-butadiene, polymerization of two molecules of ethylene, it was found that the experimental rate constant is less than that obtained from equation 3. Similarly there are certain reactions in which experimental rate constant is much higher than obtained from equation 3 like in case of chain reactions. As it is clear from above that rate constant given in equation 3 is not applicable to all reactions but applicable only to simple gaseous reactions. Hence the classical collision theory needs modifications and a collision theory known as modified collision theory is proposed.

5.3.1.2 Modified collision theory

Simple collision theory was modified by Arrhenius and a modified collision theory was proposed. The theory considers several points:

* All collisions among the molecules are not responsible for causing a chemical reaction. Only those collisions are effective (workable) which possess a minimum amount of energy known as activation energy for a chemical reaction to occur. It has been observed that when the colliding molecule possess energy equal to or greater than activation energy then only the chemical reaction takes place otherwise not . It means that when energy of colliding molecules is lower than the activation energy then no chemical reaction takes place. Therefore in the rate expression for bimolecular collision (equation 3), a new term called steric factor or probability factor is introduced. Therefore equation 3 is written as:

$$k = PZ\ e^{-E/RT} \quad \ldots\ldots\ldots\ (4)$$

where P is the probability factor or steric factor having value from 1 to 10^{-8}. It has been found that probability factor is related to entropy change by the expression:

$$P_1/P_2 = e^{\Delta S/R} \quad \ldots\ldots\ldots\ (5)$$

Where P_1 is probability factor for forward reaction and P_2 is probability factor for backward reaction (condition is that the reaction is reversible).

- The colliding molecules should must possess a proper orientation required for the reaction to occur. In simple words, we can say that only effective collision (collision having correct orientation) leads to a chemical reaction. The proper orientation means that there must be direct contact among the atoms which are involved in bond breaking and bond forming. This will become more clear by Figure 1 given below:
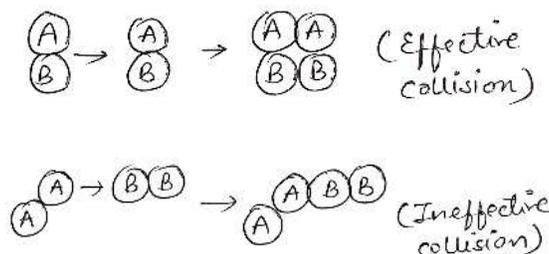
Figure 1. Diagram showing effective and ineffective collision

- In case of collision between same molecules, pre-exponential factor A is given by expression:

$$A = (3.89 \times 10^{29})\ P\ d^2\ (T/M)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ (6)$$

Where T is absolute temperature, M is molar mass (gram per mole), P is probability factor and d is average collision diameter. Similarly for different molecules undergoing collision, d is replaced by d_{12} which is given by $(d_1 + d_2)/2$ while M is replaced by M_1M_2/M_1+M_2. For this A is given by:

$$A = (2.75 \times 10^{29})\ P\ (d_{12})^2\ (T/\mu)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ (7)$$

Therefore it is finally concluded that only those collisions are effective (leads to a chemical reaction) in which colliding molecules must possess proper orientation and energy.

5.3.1.3 Limitations of collision theory

Though the theory is applicable in case of simple gas molecule but it suffers certain limitations:

- Classical collision theory do not consider the internal motion of the molecules taking part in a collision which leads to a chemical reaction.
- In order to relate the probability factor with the properties of the colliding reactant molecules, several attempts were made but satisfactory results were not obtained.
- As modified collision consider the concept of classical collision theory which is based on classical mechanics that require modifications.
- Only kinetic energy of the reactant molecules is considered not the vibrational or rotational energy. The reason of not taking this energy is not clear.

5.3.2 Transition sates theory or activated complex theory

Transition state theory (TST) is also known as activated complex theory (ACT) or absolute reaction rate theory. This theory was proposed by Pelzer and Minger but later on by Eyring, Evans and Polanyi. As by using this theory, we can find the absolute value of rate constant by using physical properties therefore the theory is also known by name absolute theory. This theory considers the quantum mechanics instead of classical mechanics. According to transition sate theory, collisions among the reactant molecules do not lead to chemical reaction but there is change in potential energy of the reactants as it changes when reactants approaches from infinite distance in order to react and then forms products. Reactants having sufficient energy from infinite distance approach each other and form an activated complex which further forms the products. The reaction is given below:

Reactants ↔ Activated complex → Products

For example, there are two reactants X_2 and Y_2, they reacts to form an activated complex which together forms products.

$$X_2 + Y_2 \rightleftharpoons (X_2Y_2)^* \longrightarrow 2XY \ (Products)$$
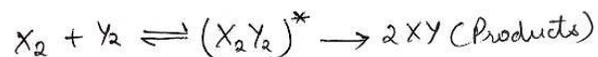
Activated complex is a special molecule that possesses highest energy or most unstable molecule that possesses three translational degree of freedom in which forth degree of freedom is along the reaction coordinate. It has transient existence. In activated complex, as the bond among the atoms are weak hence one vibrational degree of freedom is less than the normal molecule. This vibrational degree of freedom changes to translational degree of freedom hence possess forth degree of freedom (translational). On the basis of transition state theory, energy profile diagram is given in Figure 2.
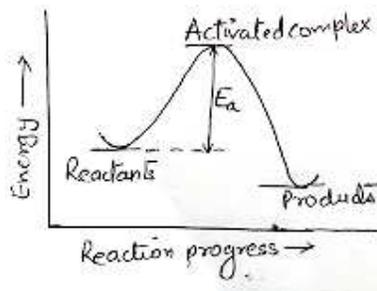
Figure 2. Energy profile diagram for exothermic reaction

It is clear from Figure 2 that energy of products is less than energy of the reactants, therefore $E_{products} - E_{reactants}$ is negative. This shows that change in energy is negative which indicates that during the formation of products, some energy is released (exothermic). Figure 2 also shows that activation energy (E_a) is the difference between the energy of the activated complex and energy of the reactants. Similarly for endothermic reaction, the energy profile diagram is given below in Figure 3.
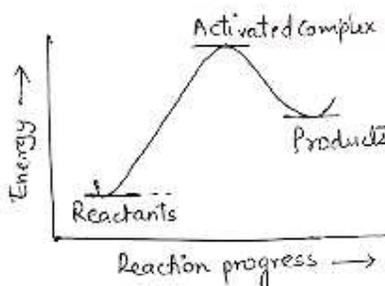
Figure 3. Energy profile diagram for endothermic reaction

Now we will study the formulation of activated complex theory in terms of statistical mechanism and thermodynamics. Let us discuss these formulations one by one.

5.3.2.1 Statistical mechanics formulation of activated complex theory

It is also known as statistical formulation of reaction rate. In order to show statistical formulation of reaction rate, the following mechanism is considered.

$$X_2 + Y_2 \rightleftharpoons (X_2Y_2)^* \longrightarrow 2XY \text{ (Products)}$$
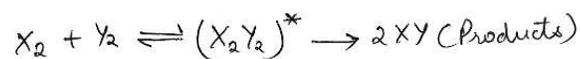
Where $X_2Y_2^*$ represents activated complex. It is clear from the above mechanism that rate of reaction (decomposition) is directly proportional to the concentration of the activated

complex [$X_2Y_2^*$]. The rate of decomposition of activated complex also depends upon the number of activated complex that cross the energy barrier per unit time. This is called frequency of crossing the energy barrier and is given by the ratio of average velocity of activated complex to the length (d) at the highest energy level (i.e. activated complex energy state). According to kinetic theory of gas, the average velocity (v_{avg}) is given by:

$$v_{avg} = (kT/ 2\Pi m)^{1/2} \ \text{....... (8)}$$

where k is Boltzmann constant, T is absolute temperature, m is the mass of the activated complex. Therefore frequency of crossing the energy barrier is given by: $(kT/ 2\Pi m)^{1/2} / d$

In addition to concentration of activated complex and frequency of crossing the energy barrier, the rate of reaction (decomposition) also depends upon the chance (probability) of crossing the energy barrier by the activated complex. The probability is shown by expression: $d (2\Pi mkT)^{1/2} /h$

Therefore on multiplying all these factors, rate of reaction (decomposition) is given by r_d:

$$r_d = [X_2Y_2^*] \times (kT/ 2\Pi m)^{1/2} / d \times d (2\Pi mkT)^{1/2} / h$$

$$r_d = (kT/h) \times [X_2Y_2^*]$$

Here kT/h refers to universal frequency. Now it is clear that activated complex is formed from reactants therefore rate of formation (r_f) is directly proportional to the concentration of the reactant X and Y. Therefore:

$$r_f = k_f [X] [Y]$$

As activated complex has transient existence or it is an intermediate therefore steady state approximation is applied. According to steady state approximation, the rate of formation and decomposition of an intermediate (in this case activated complex) is equal. Hence: $r_f = r_d$

$$k_f [X] [Y] = (kT/h) \times [X_2Y_2^*]$$

$$k_f = (kT/h) \times [X_2Y_2^*] / [X] [Y]$$

K* is equilibrium constant and is given by:

$$K^* = [X_2Y_2^*] / [X] [Y]$$

$$k_f = (kT/h) \times K^* \ \text{......... (9)}$$

On applying statistical mechanism: $K^* = (\theta^* / \theta_X \theta_Y) \times e^{-\Delta E_o / RT}$

Where θ^*, θ_X and θ_Y are the partition function of reactants X, Y and activated complex respectively. $-\Delta E_o$ is the change in energy (zero point). On putting the value of K^* in equation (9), we obtain:

$$k_f = (kT/h) \times (\theta^* / \theta_X \theta_Y) \times e^{-\Delta E_o / RT} \quad \text{....... (10)}$$

5.3.2.2 Thermodynamic formulation of activated complex theory

By using thermodynamics, we can express the rate constant of the reaction (mechanism) which is according to activated complex theory. This expression of rate constant containing thermodynamic functions is called thermodynamic formulation of reaction rate or activated complex theory. On considering the general mechanism:

$$X_2 + Y_2 \rightleftharpoons (X_2 Y_2)^* \longrightarrow 2XY \ (Products)$$

As discussed earlier that in statistical formulation of reaction rate, rate constant is given by:

$$k_f = (kT/h) \times K^* \quad \text{....... (11)}$$

According to second law of thermodynamics, $-\Delta G = RT \ln K$

Where T is absolute temperature and R is gas constant. On applying this reaction isotherm on first step of the mechanism given by activated complex theory we obtain:

$$-\Delta G^* = RT \ln K^* \quad \text{......... (12)}$$

From the definition of free energy, when there is change in the state of the system, change in free energy is given by relation: $\Delta G = \Delta H - T \Delta S$

Applying to activated complex theory at constant temperature: $\Delta G^* = \Delta H^* - T \Delta S^*$

On putting the value of ΔG^* in equation 12, we obtain: $-(\Delta H^* - T \Delta S^*) = RT \ln K^*$

$$\ln K^* = -(\Delta H^* - T \Delta S^*) / RT$$

$$K^* = e^{-(\Delta H^* - T \Delta S^*) / RT}$$

On putting the value of K^* in equation 11, we obtain: $k_f = (kT/h) \times e^{-(\Delta H^* - T \Delta S^*) / RT}$

$$k_f = (kT/h) \times e^{-\Delta H^* / RT} \times e^{\Delta S^* / R} \quad \text{......... (13)}$$

Equation 13 is known as Wyne- Jones and Eyring equation or simply Eyring equation. Equation 13 represents thermodynamic formulation of reaction rate in which rate expression contains thermodynamic functions. For gaseous reactions

$$\ln k_f = \ln kT/h - \Delta H^* / RT + \Delta S^* / R$$

On differentiating the above equation with respect to temperature, we obtain:

$$d\ln k_f/dT = \Delta H^* / RT^2 + 1/T$$

$$d\ln k_f/dT = (\Delta H^* + RT)/ RT^2 \dots\dots (14)$$

According to Arrhenius equation which shows the dependence of rate constant on temperature is given by expression: $k = A \, e^{-Ea/RT}$

On taking log and differentiating with respect to temperature, we obtain:

$$d\ln k_f/ dT = E_a / RT^2 \dots\dots.. (15)$$

On comparing equation 14 and 15, we obtain: $(\Delta H^* + RT)/ RT^2 = E_a / RT^2$

$$\Delta H^* = E_a - RT$$

On putting the value of ΔH^* in Eyring equation, we obtain: $k_f = (kT/h) \times e^{-(Ea-RT)/RT} \times e^{\Delta S^*/R}$

5.3.2.3 Comparison of activated complex theory and collision theory

From collision theory: $k_f = PZ \, e^{-E/RT}$

On putting the value of k_f in Eyring equation, we obtain:

$$Z \, e^{-E/RT} = (kT/h) \times e^{-\Delta H^*/RT} \times e^{\Delta S^*/R}$$

If ΔH^* is approximately equal to E, then $\Delta H^* \approx E$, therefore by replacing ΔH^* by E, we obtain:

$$PZ \, e^{-E/RT} = (kT/h) \times e^{-E/RT} \times e^{\Delta S^*/R}$$

$$PZ = (kT/h) \times e^{\Delta S^*/R}$$

$$P = (kT/hZ) \times e^{\Delta S^*/R}$$

The value of probability factor is found to be in between 10^{-5} to 10^{-10}. The value of P is less than the value obtained from collision theory which shows that reaction proceeds more

slowly on the basis of activated complex theory. ACT provides the physical significance of probability factor by relating it to entropy of activation ΔS^*.

It has been found that for reactions between simple molecules, both collision theory and activated complex theory give same results but when reaction occurs in between complex molecules, activated complex theory give satisfactory result while collision theory fails.

5.4 THEORY OF UNIMOLECULAR REACTIONS

Before coming to the theories of unimolecular reactions, let us discuss about the unimolecular reactions. Reactions in which one reactant molecule forms the activated complex or one reactant molecule forms the products. As the name indicate unimolecular which indicates one reactant molecule. Unimolecular reactions are classified into two types: elementary unimolecular reaction and free radical unimolecular reactions. Let us discuss these reactions one by one:

- Elementary unimolecular reactions: The reaction in which products are formed from reactants in a single step that involve a formation of an activated complex. For example, formation of propylene from cyclopropane.
- Free radical unimolecular reactions: In these reactions as the name suggests, free radicals are formed as an intermediate instead of single activated complex. Several decomposition reactions comes under this category.

Now coming to theories of unimolecular reactions. Various theories are there which explain the mechanism of unimolecular reactions which include Lindemann's theory, Hinshelwood theory and RRKM theory. We will now discuss all these mechanism or theories on by one:

5.4.1 Lindemann's theory

This theory was proposed by F.A Lindemann and subsequently supported by Christiansen According to Lindemann, the following mechanism is proposed for conversion of A into Products

(i) $A + A \longrightarrow A^* + A$ (Collisions causing activation of molecules): rate constant k_1

(ii) $A^* + A \longrightarrow A + A$ (Collisions causing deactivation of molecules): rate constant k_2

(iii) $A^* \longrightarrow$ Products (Formation of products or decomposition): rate constant k_3
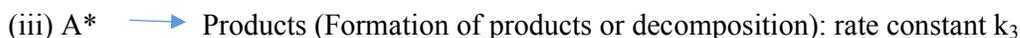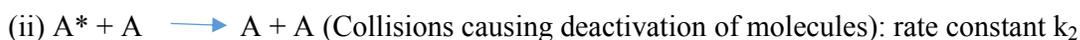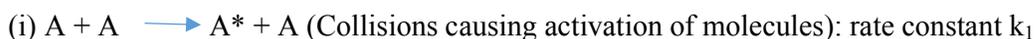
Here A is reactant molecule, A* is an energized or activated molecule having sufficient energy to form products but A* is not an activated complex. According to Lindemann's mechanism, reactant molecules collide with each other and form A* by the process known as activation which is shown by step one having rate constant k_1. The energized molecule has two possibility whether it forms products by the process of decomposition which is shown by step three having rate constant k_3 or may get deactivated to form back the reactant molecules which is shown by step two having rate constant k_2. As there is time gap between activation process and decomposition process therefore in this time gap, deactivation of energized molecules takes place. As A* is an intermediate therefore steady state approximation is applied to it.

$$\text{Rate of formation of A*} = d[A^*]/dt = k_1 [A]^2 - k_2 [A][A^*] - k_3 [A^*]$$

On applying steady state: $d[A^*]/dt = 0$

$$\text{Hence: } k_1 [A]^2 - k_2 [A][A^*] - k_3 [A^*] = 0$$

$$k_1 [A]^2 - k_2 [A][A^*] - k_3 [A^*] = 0$$

$$k_1 [A]^2 = k_2 [A][A^*] + k_3 [A^*]$$

$$k_1 [A]^2 = [A^*] (k_2 [A] + k_3)$$

$$[A^*] = k_1 [A]^2 / k_2 [A] + k_3$$

We know that rate of reaction is proportional to the concentration of the energized molecule as in this step formation of products takes place. Therefore:

$$r = k_3 [A^*]$$

On putting the value of $[A^*]$ from above expression we obtain: $r = k_3 k_1 [A]^2 / k_2 [A] + k_3$

For reactions taking place in gaseous phase, the concentration term is replaced by pressure terms. Hence: $r = k_3 k_1 P^2 / k_2 P + k_3$

Two case arises:

-          Case 1: At high pressure: $P \gg k_3$, therefore k_3 can be neglected.

$$r = k_3 k_1 P^2 / k_2 P$$

$$r = k_3 k_1 P / k_2$$

This expression shows that at high pressure, rate of reaction is directly proportional to pressure of a gas raised to power one or we can say it obeys first order kinetics.

- At low pressure: $P \ll k_3$, therefore $k_2 P$ can be neglected.

$$r = k_3 k_1 P^2 / k_3$$

This expression shows that at low pressure, rate of reaction is directly proportional to pressure of a gas raised to power two or we can say it obeys second order kinetics.

Though the theory given by Lindemann is quite satisfactory in explaining the mechanism of unimolecular reactions but there are some drawbacks:

- According to Lindmann, rate expression comes out to be: $r = k_3 k_1 P^2 / k_2 P + k_3$

If reaction obeys first order kinetics: $r = k [A]$

$$k [A] = k_3 k_1 [A]^2 / k_2 [A] + k_3$$

$$\text{On taking reciprocal: } 1/ k [A] = (k_2 [A] + k_3)/ k_3 k_1 [A]^2$$

$$1/ k = (k_2 [A] + k_3)/ k_3 k_1 [A]$$

$$1/ k = (k_2 [A] / k_3 k_1 [A]) + (k_3/ k_3 k_1 [A])$$

$$1/ k = (k_2 / k_3 k_1) + (1/ k_1 [A])$$

Graph is plotted between $1/ k$ versus $1/ [A]$, result straight line with slope $1/k_1$ and intercept $k_2 / k_3 k_1$. But instead of straight line there is deviation from it. Lindemann's drawback leads Hinshelwood to put forward his theory. Let us now discuss Hinshelwood's theory of unimolecular reactions.

5.4.2 Hinshelwood's theory

Hinshelwood on the basis of statistical mechanism determines the chance or probability of a reactant molecule to become active by collision. Hinshelwood provides an analytical formulation of Lindemann's theory. According to Hinshelwood, the probability of deactivation of energized molecule (A*) formed by collisions of reactant molecules (A) is equal to one. According to Hinshelwood, rate constant (k) is given by expression:

$$k = \{Z/(S-1)!\} \times (E/kT)^{S-1} e^{-E/kT}$$

where Z is collision number, S is number of vibrational degree of freedom the value of which is obtained by hit and trial method, k is Boltzmann constant , T is absolute temperature and E is energy of activation. For the molecule having one vibrational degree of freedom, the above expression of k reduced to:

$$k = Z \, e^{-E/kT}$$

It has been found that for large value of S, pre-exponential factor (A) depends strongly on the temperature. Though the theory is successful but there are certain limitations:

- The theory does not show the dependence of pressure on rate constant.
- From Lindemann's theory on which Hinshelwood theory is based, the variation of 1/ k versus 1/ [A] should be straight line but there are deviations in the curve which was not explained by Hinshelwood.

5.4.3 RRKM theory

RRKM theory of unimolecular reaction stands for Rice- Rampsberger- Kassel- Marcus theory. This is one of the most refined and successful theory of reaction rate. According to RRKM theory which on the basis of activated complex theory considered all vibration of energized molecule (A*) as vibrational frequency and all rotation of energized molecules as rotational constant. RRKM proposed the mechanism which is as follows:

(i) $A + A \longrightarrow A^* + A$ (Collisions causing activation of molecules): rate constant k_1

(ii) $A^* + A \longrightarrow A + A$ (Collisions causing deactivation of molecules): rate constant k_2

(iii) $A^* \longrightarrow A^{\#}$ (Conversion of energized molecule into activated molecule): rate constant k_3

(iii) $A^{\#} \longrightarrow$ Products (Formation of products or decomposition): rate constant k_4

Here A* is energized molecule and $A^{\#}$ is activated molecule. Activated molecule forms product and possess minimum amount of energy known as activation energy. According to RRKM theory:

$$dk_1/k_2 = N \, c(\varepsilon_c) \, e^{-\varepsilon_c/kT} \, d\varepsilon_c / f_c$$

Where $N \, c(\varepsilon_c)$ is the energy density of the degree of freedom that contribute to bond breaking, f_c is the partition function where c represents critical energy contribution and ε_c is critical energy of the activated complex which is more than zero point energy. The critical

energy ε_c is equal to the sum of energies of motion along the reaction coordinate and energy associated with vibrations and rotations. It has been found that at high pressure, RRKM theory give the same expression of rate constant as given by activated complex theory. Therefore we can say that at high pressure, RRKM theory get reduced to transition state theory or activated complex theory. At high pressure, thermal Boltzmann distribution is maintained at all energies. At high pressure, the expression for rate constant is:

$$k = (kT/h) \times (f^{\#}/f_A) \times e^{-E/kT}$$

where $f^{\#}$ represents partition function of activated complex and f_A represents partition function of reactants. This is all about the theories of reaction rate.

5.5 POTENTIAL ENERGY SURFACE

Potential energy surface is short is also known as PES. The concept of PES is applied to several branch of science that includes physics, chemistry. The properties of structure comprising of atoms are predicted by applying the concept of PES. This surface represents the energy of a system which is generally based on the position of the atoms. Energy profile diagram also refers to potential energy diagram or PES represents the variation of energy with reaction progress. In potential energy diagram or curve, there is a point at which potential energy is maximum along the reaction coordinate. This point is known as saddle point which corresponds to transition state. There are stationary points in the curve that represents stable chemical species or species with lowest energy. On the basis of bond length extension in the activated complex in comparison to bond length of the reactants or product, potential energy surface is classified into two types: attractive potential energy surface and repulsive potential energy surface. In order to define these types, let us take a general reaction: X + Y-Z $\longrightarrow$ X-Y + Z

 The bond length of newly formed bond (r_{XY}) is equal to the difference of the bond length of XY in the transition state ((r_{XY})* and bond length of XY in the product molecule (r^1_{XY}) i.e. $r_{XY} = r_{XY}* - r^1_{XY}$. In this reaction there is cleavage of Y-Z bond thus $r_{YZ} = r_{YZ}* - r^1_{YZ}$, where r^1_{YZ} refers to bond length of Y-Z bond of the reactants. Potential energy surface is said to be attractive when $r_{XY} > r_{YZ}$ for those reactions in which heat is evolved. Here transition state is achieved by bringing the reactants close to each other. For example, K and Br_2 to form KBr and Br. Potential energy surface is said to be repulsive when $r_{XY} < r_{YZ}$ for those reactions in which heat is evolved. Here transition state is achieved by the separation of the products. For

example, H and Cl_2 to form HCl and Cl. The potential energy diagram is given in Figure 4 in which AB represent lowest energy path. Point o gives the potential energy of these atoms X, Y and Z which are well separated from each other.
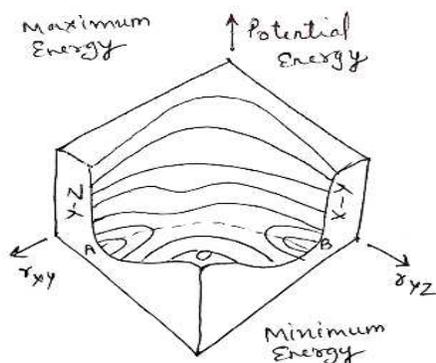

Figure 4. Potential energy surface for reaction X + Y-Z $\longrightarrow$ X-Y + Z

For the reaction in which energy is absorbed, the PES is said to be attractive when translational energy of the reactants is effective. The PES is said to be repulsive when vibrational excitation of the reactants is effective. The concept of PES is very useful in determining the geometry of a molecule and kinetics of a chemical reaction by considering the position of the atoms.

5.6 SUMMARY

In this unit we have discussed the theories of rate of reactions that includes collision theory and activated complex theory. Collision theory is discussed under two headings: classical collision theory and modern collision theory. In activated complex theory, we discussed its statistical and thermodynamical formulation of reaction rate. Then we move forward to unimolecular reactions where we studied about the theories of unimolecular reactions which include Lindemann's mechanism, Hinshelwood mechanism and RRKM mechanism. In addition to all these, we also studied about the potential energy surface that plays an important role in determining the molecular structure.

5.7 SELF-ASSESSMENT QUESTIONS (SAQ)

Fill in the blanks:

1. According to collision theory, the molecules must undergo ……….

2. Rate of reaction in a collision process is directly proportional to the ………. of the colliding reactant molecules.

3. The number of collision occurring among gas molecules (reactants) per second per centimeter cube is given by ………

4. The value of probability factor or steric factor obtained from collision theory varies from ……….

5. Classical collision theory is applied to ………. gas molecules.

6. Probability factor is related to ………. change of the reaction.

7. For effective collision, molecules must have proper ……….

8. ………. and ………. developed the collision theory of reaction rate.

9. According to ACT, reactants before forming the products forms an intermediate known as ……….

10. The energy of the activated complex is ………. in the energy profile diagram.

11. The statistical formulation of reaction rate is given by ……….

12. The thermodynamic formulation of reaction rate is given by ……….

13. Reaction isotherm is given by the expression ……….

14. ………. theory explain the physical significance of probability factor.

15. The value of steric factor obtained from activated complex theory is in the range ……….

16. According to Lindemann's hypothesis, at low pressure the unimolecular reaction obeys ………. order kinetics.

17. At high pressure, unimolecular reactions obeys ………. order kinetics according to Lindemann.

18. The most successful theory that explains the mechanism of unimolecular reaction is ………. theory.

19. A* represents ………. molecule.

20. According to Hinshelwood, A* forms ………. molecule.

5.8 GLOSSARY

- **Activated complex**: Unstable molecule having highest energy in the energy profile diagram.

- **Potential energy surface**: Surface associated with the position of atoms that represents the energy of the system.

- **Activation energy**: Minimum energy that the reactants molecules must have in order to form products.

- **Steady state approximation**: Rate of formation and rate of dissociation is same for the intermediate.

5.9 ANSWERS TO SAQ's

- Fill in the blanks:

1. Collision; 2. Concentration; 3. Collision number; 4. 1 to 10^{-8}; 5. Simple; 6. Entropy; 7. Orientation; 8. Arrhenius and van't Hoff; 9. Activated complex; 10. Maximum; 11. $k_f = (kT/h) \times (\theta^*/ \theta_X \theta_Y) \times e^{-\Delta E_o / RT}$; 12. $k_f = (kT/h) \times e^{-\Delta H^* / RT} \times e^{\Delta S^* / R}$; 13. $- \Delta G = RT \ln K$; 14. Activated complex theory; 15. 10^{-5} to 10^{-10}; 16. Second; 17. First; 18. RRKM; 19. Energized; 20. Activated molecule.

5.10 REFERENCES

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5.11 TERMINAL QUESTIONS

- Explain activated complex theory along with its statistical and thermodynamical formulation of reaction rate.

- Describe different theories of unimolecular reactions including Lindemann, Hinshelwood and RRKM theories.

UNIT 6: SOLUTION KINETICS

CONTENTS:

6.11 Answers to SAQ's

6.12 References

6.13 Terminal Questions

6.1 OBJECTIVES

After reading this unit, you will be able to:

- Define dielectric constant.
- Define ionic strength of a solution.
- Explain different factors that affect the rate of reaction occurring in solution.
- Explain the concept of primary and secondary salt effect.

6.2 INTRODUCTION

In the lower classes, we studied about the chemical kinetics which deals with the rate or speed with which chemical reaction takes place. For example, corrosion is a very slow process or have low rate of reaction. By using chemical kinetics, the mechanism of the chemical reaction can be determined. There are several factors that affect the rate of chemical reaction occurring in solution, gaseous phase or condensed phase. Solution as we know consist of a solute and a solvent. A solute is present in small amount while the solvent is present in large amount in the solution. For example, solution of sugar in water.

The present unit deals with the study of solution kinetics or the study of rate of rate with which solute reacts with the solvent or kinetics of reactions in solution. In this unit, we will discuss about different factors that affects the rate of reaction occurring in solution, the concept dielectric constant, ionic strength followed with primary and secondary salt effect.

The chapter is quite interesting as it deals with the interaction of solvent with the solute in solution thereby affecting the reaction rate. In order to understand the topic more clearly, we will go through the entire chapter in order to study the factors affecting the kinetics of reactions occurring in solution.

6.3 RATE OF REACTION

Rate of reaction is also known as reaction rate. It is defined as the rate of change of concentration of reactants or products per unit time. As the reaction proceeds, the concentration of reactant decreases while the concentration of the products increases. Therefore the rate of reaction for a general reaction is given by:

$$A \longrightarrow B$$

$$r = - d\,[A]/dt = + d[B]/dt$$

where (−) sign shows decrease in concentration of reactant A while the (+) sign shows increase in the concentration of product B, infinitesimally small change in concentration is represented by d. The rate of reaction is expressed in mole $litre^{-1}time^{-1}$. Generally the time taken is in seconds hence the rate is expressed in mol l^{-1} s^{-1}. According to rate law, rate of reaction is directly proportional to the concentration of the reactants, raised to some power. For a general reaction:

$$A \longrightarrow B$$

$$r = k\,[A]$$

where k = proportionality constant = rate constant or velocity constant of a reaction

The concentration terms in the rate law expression are raised to some power, this power is known as order of reaction. This is the basic idea of chemical kinetics. Now let us discuss the factors that affect the rate of reaction.

6.4 FACTORS AFFECTING REACTION RATE

There are several factors that affect the rate of reaction:

6.4.1Concentration of reactants: From rate law, it is clear that rate of reaction is directly proportional to the concentration of the reactants. Therefore more is the concentration of reactant more will be the rate of reaction as more is the collision among the reactants. According to collision theory, reaction occurs by the collision between the reactant molecules.

6.4.2 Temperature

We know that temperature is directly proportional to average kinetic energy. More is the kinetic energy, more is the speed of the reacting molecules and more is collision which thereby increases the rate of reaction. It has been observed that for every 10°C rise in temperature, the rate of reaction increases by a factor two or three. At two temperature that differ from each other by 10°C, the ratio of the rate constant of a reaction is called temperature coefficient of a reaction.The value of temperature coefficient is 2 or 3 as discussed above.

$$\text{Temperature coefficient} = k_{T+10} / k_T$$

Where k represents rate constant at two temperature that differ from each other by 10°C. During the decomposition of HI, the rate of reaction increases by a factor of 1.7 when temperature increases by 10°C.

6.4.3 Catalyst

These are certain substances that alter the rate of reaction. These substance generally increases the rate of reaction without being consumed in the reaction and are termed as catalyst. These substances remain unchanged in chemical composition and in amount at the end of the reaction. The addition of a catalyst in a reaction increases the rate by lowering the activation energy of the reaction due to which more number of reactant molecules cross the energy barrier and form the products as there is an energybarrier between the reactant and the product. Activation energy is the minimum amount of energy that the reactants molecules must possess in order to form products. It is represented by E_a. For example, in the decomposition of potassium chlorate, MnO_2 (Manganese dioxide) acts as a catalyst which speeds up the decomposition. The plot explaining the effect of catalyst on activation energy is given in Figure 1.
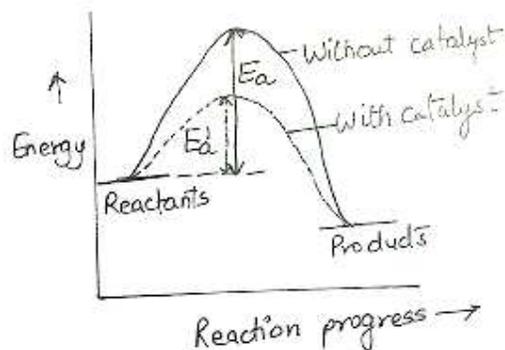
Figure 1. Effect of catalyst on activation energy

6.4.4 Intensity of light

There are certain reaction that takes place in presence of light. Such reactions are called photochemical reactions. In these reactions, photons are absorbed by the reactant molecules. Hence, more is the no. of photons (light radiations) provided to the reactant molecules, more is the energy to cross the energy barrier which results in the increase of reaction rate. For example, the rate of photosynthesis increases when more photons are provided to the reactant molecules or when day is sunny.

6.4.5 Surface area of the reactant

In case of heterogeneous reaction when reactants are not in same phase (like one reactant is in solid phase and the other one is in gas phase), larger is the surface area of the reactant, more will be the rate of reaction. This is because the reactions occur only at the surface of the reacting species. For example, the rate of reaction for a lump of a solid is less than the rate where it is present in powdered form as powder occupies more surface than the lump. The rate of homogeneous reaction (both phase are same) is more than the rate of heterogeneous reaction.

6.4.6 Nature of the reactants

Ionic compounds react with faster rate than the covalent compounds because the later require energy to break the bond. For example, when silver nitrate ($AgNO_3$) is added to sodium chloride solution (NaCl), silver chloride (AgCl) is formed as a precipitate immediately.

$$NaCl + AgNO_3AgCl \longrightarrow (precipitate) + NaNO_3$$

6.4.7 Pressure

If the reaction takes in gaseous phase, the increase in pressure increases the number of collision among the gaseous molecules, thereby increasing the rate of reaction. As in case of gaseous reaction, according to rate law, rate of reaction is directly proportional to the partial pressure of the reactant species.

6.4.8 Solvent effect

In case of solution, we consider the effect of solvent on rate of reaction. The viscosity and dielectric constant of a solvent affect the reaction rate. Before discussing its effect on reaction rate, let us have some common knowledge about the viscosity and dielectric constant. Viscosity of a liquid is defined as the resistance in the flow of liquid. Liquid consist of layers of molecules that are arranged one over the other. This exerts resistance in the flow of a liquid. Viscosity is inverse of fluidity. Fluidity is the ability of a liquid to flow. Viscosity is represented by η. The unit of viscosity is Poise (P). With increase in temperature, viscosity of liquid decreases. Dielectric constant of a solvent is defined as the capacity of the solvent to weaken the force of attraction (electrostatic) between ions (solute) and to separate them. Dielectric constant is represented by ε.Water which is regarded as a universal solvent has dielectric constant value equal to 79.8. Due to high value of dielectric constant, when solute is added into the water, the water weakened the force of attraction by which solute molecules are attached resulting in the free movement of ions (solute). Thus water is a strong dissociating solvent. In vacuum, the value of dielectric constant is one for all the solvents.

6.5 *FACTORS AFFECTING REACTION RATEIN SOLUTION*

As we have discussed above that dielectric constant and viscosity affect the reaction rate in solution. Each factor is discussed in detail below:

6.5.1 Effect of dielectric constant on rate of reaction

In order to show the effect of dielectric constant (ε) on rate of reaction, the theory of absolute reaction rate also known as transition state theory has been undertaken into consideration.According to this theory, ions undergoing the reaction in a medium of dielectric constant (ε) are considered as a sphere. Let us consider an ionic reaction involving ions A and B. Ionic reactions are those reactions that occurs in between the ions. Let r_A and$r_B$be the radius of two ions having charge $Z_A e$ and $Z_B e$ respectively. Initially these two ions A and B

are at an infinite distance. According to the activated complex theory, when these two ions are brought together in order to form the activated complex, the work done (W) is given by:

$$W = (Z_A e)(Z_B e) / \varepsilon\, d_{AB}$$

Where ε is dielectric constant of the solvent, d_{AB} is the distance between two ions in an activated complex.

$$W = Z_A Z_B e^2 / \varepsilon\, d_{AB}$$

If ions possess charges of same sign (both are either positive or both are negative), the work is positive. If ions possess charges of different sign (one ion is positive while the other ion is negative), the work is negative. This work is equal to electrostatic distribution. The free energy of activation (ΔG^*) per molecule is given by the sum of free energy that contribute to electrostatic distribution and non- electrostatic distribution (N.E.S.).

$$\Delta G^*/ N = \Delta G^*_{N.E.S.} / N + Z_A Z_B e^2 / \varepsilon\, d_{AB} \quad\ldots\ldots.. (1)$$

Where N is Avagadro's number. On multiplying equation 1 by N, we obtain:

$$\Delta G^* = \Delta G^*_{N.E.S.} + Z_A Z_B e^2 N / \varepsilon\, d_{AB} \quad\ldots\ldots (2)$$

From thermodynamics formulation of reaction rate (activated complex theory), rate constant is related to free energy of activation (ΔG^*) by the expression:

$$k = \frac{kT}{h} e^{-\Delta G^*/RT}$$

Where kT/h is universal frequency, k is Boltzmann constant, and T is absolute temperature while h is Planck's constant. On putting the value of ΔG^* in the above equation, we obtain:

$$k = \frac{kT}{h} e^{-(\Delta G^*_{N.E.S.} + Z_A Z_B e^2 N / \varepsilon\, d_{AB})/RT}$$

$$k = \frac{kT}{h} e^{-\Delta G^*_{N.E.S.}/RT} e^{-Z_A Z_B e^2 N / \varepsilon\, d_{AB} RT}$$

On taking natural log:

$$\ln k = \ln \frac{kT}{h} - \Delta G^*_{N.E.S.} / RT - Z_A Z_B e^2 N / \varepsilon\, d_{AB} RT$$

Keeping $\frac{kT}{h} - \Delta G^*_{N.E.S.} / RT = k_0 =$ another constant, we obtain:

$$\ln k = \ln k_0 - Z_A Z_B e^2 N / \varepsilon\, d_{AB} RT$$

When a graph is plotted between ln k versus $1/\varepsilon$, a straight line is obtained having slope $Z_A Z_B e^2 N / d_{AB} RT$ and intercept ln k_0 which is shown in Figure 2.
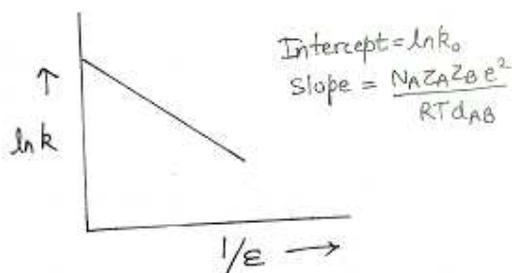

Figure 2. Variation of rate constant with dielectric constant

It is concluded that for an ionic reactions, with increase in dielectric constant of a solvent, rate constant increases thereby increasing the rate of reaction while with decrease in dielectric constant of the solvent, the rate of reaction decreases. This equation correlating rate constant with dielectric constant is valid for a large number of ionic reactions.

6.5.2 Effect of viscosity

In order to show the effect of viscosity on rate of reaction, let us consider to reactant molecules A and B having radii r_A and r_B respectively. The number of collision (encounters, υ) between A and B per cubic centimeter is given by equation given below. One thing to be noted here is that encounter word is used in place of collision. Collision word is used in case of gases while for liquids and solids, encounter is used because here the solute molecules get surrounded by the solvent molecules forming a cage.

$$\upsilon = 4\Pi\ (r_A + r_B)\ (D_A + D_B)\ n_A n_B\ cm^{-3}\ s^{-1} \ \ldots\ldots\ (1)$$

where D_A , D_B are their respective diffusion coefficient and n_A, n_B are the number of molecules per centimeter cube of A and B respectively. If each encounter leads to a chemical reaction then the number of encounter is equal to rate of reaction.

$$\upsilon/\ N = 4\Pi\ (r_A + r_B)\ (D_A + D_B)\ (n_A\ /N)(n_B\ /\ N) mol cm^{-3}\ s^{-1}$$

where N is Avogadro's number.

$$\upsilon = k_D n_A n_B /\ N \ \ldots\ldots.\ (2)$$

where k_D is diffusion- controlled rate constant. On putting the value of υ in equation 1.

$$k_D n_A n_B /\ N = 4\Pi\ (r_A + r_B)\ (D_A + D_B)\ n_A n_B$$

$$k_D / N = 4\Pi (r_A + r_B) (D_A + D_B)$$

$$k_D = 4\Pi N (r_A + r_B) (D_A + D_B) \text{ ……. (3)}$$

For spherical particles of a liquid, diffusion coefficient is related to radius (r) of the molecule and the coefficient of viscosity (η) by Stoke 's equation given below:

$$D = kT/ 6 \Pi \eta r$$

Where k is Boltzmann constant, T is absolute temperature. For reactant molecule A and B,

$$D_A = kT/ 6 \Pi \eta r_A; \quad D_B = kT/ 6 \Pi \eta r_B$$

On putting the value of D_A and D_B in equation 3, we obtain:

$$k_D = 4\Pi N (r_A + r_B) (kT/ 6 \Pi \eta r_A + kT/ 6 \Pi \eta r_B)$$

$$k_D = 4\Pi N (r_A + r_B) [kT/ 6 \Pi \eta (1/ r_A + 1/ r_B)]$$

$$k_D = 4\Pi N (r_A + r_B) [kT (r_A + r_B)/ 6 \Pi \eta r_A r_B]$$

$$k_D = 4\Pi N kT (r_A + r_B)^2 / 6 \Pi \eta r_A r_B$$

$$k_D = 2 R T (r_A + r_B)^2 / 3 \eta r_A r_B \qquad (k = R/ N)$$

If $r_A = r_B$: $k_D = 8 RT / 3\eta$ …….. (4)

Equation 4 is Debye- Smoluchowski equation. In this equation, diffusion -controlled rate constant is inversely proportional to coefficient of viscosity (η) of the solvent. This shows that more is the viscosity of the solvent; less will be the rate of reaction. Therefore, viscosity is inversely proportional to the rate of reaction.

6.6 IONIC STRENGTH

Ionic strength of a solution is defined as the measure of electrical intensity. This electrical intensity is due to the presence of ions in the solution. Ionic strength is represented by I. The expression of ionic strength for two ions in solution is given by:

$$I = \frac{1}{2} (m_1 Z_1^2 + m_2 Z_2^2)$$

Where m_1 ismolality of ion 1 in solution, m_2 is molality of ion 2 in solution, Z_1 is valency of ion 1, Z_2 is valency of ion 2. For example, in case of KCl (single electrolyte), there are two ions, K^+ and Cl^-. In case of solution containing different ions (i), I is written as:

$$I = \tfrac{1}{2} \sum m_i Z_i^2$$

6.7 SALT EFFECT

In case of salts, ions are formed. These ions exert force on each other. Ionic strength which has been discussed above affects the rate of reaction. This is studied under topic salt effect. The concept of salt effect was given by J. N. Bronsted and N. Bjerrum. Salt effects are classified into primary salt effect and secondary salt effect. Let us discuss these effects one by one:

6.7.1 Primary salt effect

This effect is seen in those reactions which do not involve catalyst. In case of primary salt effect, the ions that act as a reactant first combine to form activated complex. Some of the activated complex gives product while some of the activated complex becomes deactivated to give back the ions (reactants). This mechanism is according to activated complex theory. The reaction is shown below:

$$A^{Z_A} + B^{Z_B} \underset{k_1}{\overset{k}{\rightleftharpoons}} (AB^*)^{Z_A + Z_B} \xrightarrow{k_2} Products$$
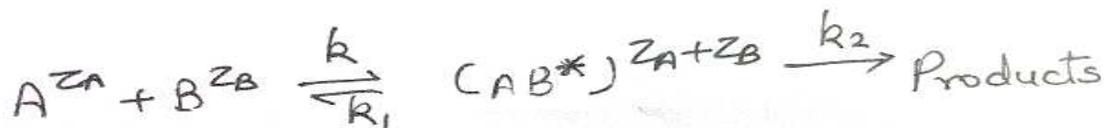
WhereA and B are the ions; Z_A and Z_B are their valencies respectively. AB is the activated complex having valency $Z_A + Z_B$. According to rate law, rate of reaction is proportional to the concentration of the activated complex.

r =k_2[AB*] ………. (1)

It is clear from the reaction that there is equilibrium between ions and activated complex. Therefore the equilibrium constant (K) is given by:

K = a*/ $a_A a_B$

Where a is the activity. We know that activity coefficient (ɣ) is equal to a/ c. Therefore:

a = ɣ c

$$K = ɣ^* [AB^*]/ ɣ_A [A] \, ɣ_B [B]$$

$$[AB^*] = K \, ɣ_A ɣ_B [A] [B] / ɣ^*$$

On putting the value of [AB*] in equation 1, we obtain:

$$r = k_2 \ K \ \gamma_A \gamma_B \ [A] \ [B] \ / \ \gamma^*$$

$$r = k' \ \gamma_A \gamma_B \ [A] \ [B] \ / \ \gamma^* \ \ldots \ldots (2)$$

where $k_2 \ K = k'$ = another constant. For the reaction in equilibrium: $r = k \ [A] \ [B]$

$$k = r \ / \ [A] \ [B]$$

Putting the value of r from equation 2 in above expression, we obtain:

$$k = k' \ \gamma_A \gamma_B \ [A] \ [B] \ / \ \gamma^* [A] \ [B]$$

$$k = k' \ \gamma_A \gamma_B \ / \ \gamma^*$$

On taking natural log: $\ln k = \ln k' + \ln \gamma_A \gamma_B \ / \ \gamma^*$

$$\ln k = \ln k' + \ln \gamma_A + \ln \gamma_B - \ln \gamma^* \ \ldots \ldots (3)$$

For the solution of electrolyte, according to Debye- Huckel limiting law: $\ln \gamma_i = - AZ_i^2 \ I^{1/2}$

Where I is the ionic strength of the solution, A is the constant for a particular solvent while Z_i is the valency of ith ion. Therefore:

$$\text{For ion A: } \ln \gamma_A = - AZ_A^2 \ I^{1/2}$$

$$\text{For ion B: } \ln \gamma_B = - AZ_B^2 \ I^{1/2}$$

$$\text{For activated complex: } \ln \gamma^* = - A \ (Z_A + Z_B)^2 \ I^{1/2}$$

Now putting the value of $\ln \gamma_A$, $\ln \gamma_B$ and $\ln \gamma^*$ in equation 3, we obtain:

$$\ln k = \ln k' - AZ_A^2 \ I^{1/2} - AZ_B^2 \ I^{1/2} - (- A \ (Z_A + Z_B)^2 \ I^{1/2})$$

$$\ln k = \ln k' - AZ_A^2 \ I^{1/2} - AZ_B^2 \ I^{1/2} + A \ (Z_A + Z_B)^2 \ I^{1/2}$$

$$\ln k = \ln k' - A \ I^{1/2} \ [Z_A^2 + Z_B^2 - (Z_A + Z_B)^2]$$

$$\ln k = \ln k' - A \ I^{1/2} \ [Z_A^2 + Z_B^2 - (Z_A^2 + Z_B^2 + 2 \ Z_A \ Z_B)]$$

$$\ln k = \ln k' - A \ I^{1/2} \ (Z_A^2 + Z_B^2 - Z_A^2 - Z_B^2 - 2 \ Z_A \ Z_B)$$

$$\ln k = \ln k' - A \ I^{1/2} \ (- 2 \ Z_A \ Z_B)$$

$$\ln k = \ln k' + 2 \ A \ I^{1/2} \ Z_A \ Z_B$$

In case of water as a solvent, constant A possesses value 0.509. On putting this value on above expression, we obtain:

$$\ln k = \ln k' + 2\,(0.509)\,I^{1/2}\;Z_A\,Z_B$$

$$\ln k = \ln k' + 1.018\,I^{1/2}\;Z_A\,Z_B \;\ldots\ldots\ldots\;(4)$$

Equation 4 shows that the rate constant or rate of reaction depends on the valencies of ions as well as the ionic strength (I) of the solution. This is primary salt effect and equation (4) is called Bronsted- Bjerrum equation. On the basis of chemical reaction involved, different case arises:

Case 1: If $Z_A\,Z_B$ = positive

It means that both the ions undergoing the chemical reaction possess either positive charge or negative chargethen only the product of $Z_A\,Z_B$ is positive. It is clear from Bronsted- Bjerrum equation that with increase in the ionic strength of the solution, rate constant increases thereby increasing the rate of reaction. For example:

$$S_2O_3^{2-} + I^- \longrightarrow \text{Products}$$

$$[Co\,(NH_3)_5Br]^{2+} + Hg^{2+} \longrightarrow \text{Products}$$
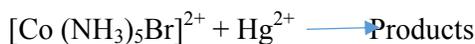
Case 2: If $Z_A\,Z_B$ = negative

It means that one of the reactant (ion) possess negative charge then only the product of $Z_A\,Z_B$ is negative.It is clear from Bronsted- Bjerrum equation that with increase in the ionic strength of the solution, rate constant decreases thereby decreasing the rate of reaction.For example:

$$H^+ + Br^{-1} \longrightarrow \text{Products}$$

Case 3: If $Z_A\,Z_B$ = zero

It means that one of the reactant is non- electrolyte. It is clear from Bronsted- Bjerrum equation that rate constant does not vary with ionic strength of the solution.For example:

$$ICH_2COOH + CNS^- \longrightarrow \text{Products}$$

All these three cases are represented in Figure 3.
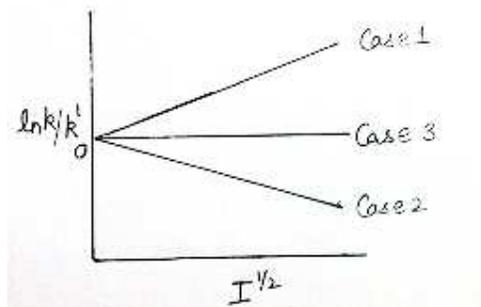
Figure 3. Variation of rate constant with ionic strength

6.7.2 Secondary salt effect

This effect is seen in those reactions that involve catalyst. In order to understand the secondary salt effect, there must be change in the concentration of the catalyst involved. This effect is shown by equation 5, given below:

$$\ln k = \ln k' + 1.018 \, I^{1/2}$$

This equation shows that rate constant does not depend on the valency but it only depends upon the ionic strength of the solution. With increase in the ionic strength of the solution, rate constant also increases thereby increasing the rate of reaction.

6.8 SUMMARY

In this unit, we have discussed about the kinetics that takes place in a solution. The topic consists of factors that affect the rate of reaction in solution that includes dielectric constant and viscosity. Further an idea of ionic strength is given which is then correlated with the rate constant which was explained under primary and secondary salt effect.

6.9 SELF- ASSESSMENT QUESTIONS (SAQ)

- Fill in the blanks:

1. With increase in concentration of the reactant, rate of reaction ……….

2. Temperature coefficient is defined as the ratio of two ………. that differ from each other by $10^{o}C$.

3. Catalyst ………. the rate of reaction by ………. the activation energy of the reaction.

4. The effect of pressure is considered, if the reaction occurs in ………. phase.

5. Dielectric constant is the property of a ……….

6. Rate of reaction ………. with increase in the dielectric constant of the solvent.

7. More is the viscosity of the solvent, ……. will be the rate of reaction.

8. Ionic strength of a solution is represented by ……….

9. Primary salt effect is seen in those reactions that involves ………. reactions.

10. In secondary salt effect,………. reactions are considered.

- Multiple choice questions:

1. When the product of valency of ions (Z_AZ_B) is positive then the rate of reaction increases due to:

a. Increase in ionic strength.

b. Decrease in ionic strength.

c. No effect

d. None of the above.

2. In Bronsted- Bjerrum equation, the value of constant A for water as a solvent is equal to:

a. 0.059

b. 0.509

c. 0.00509

d. 0.00

3. Bronsted- Bjerrum equation is written as:

a. $\ln k = \ln k' + 2\, A\, I^{1/2}\ (Z_A + Z_B)$

b. $\ln k = \ln k' + 2\, A\, I^{1/2}\ Z_A\, Z_B$

c. $\ln k = \ln k' - 2\, A\, I^{1/2}\ Z_A\, Z_B$

d. $\ln k = \ln k' - 2\, A\, I^{1/2}\ (Z_A + Z_B)$

4. Ionic strength of a solution containing two ion is given by formula:

a. $I = \frac{1}{2}\,(m_1Z_1^2 + m_2Z_2^2 + m_3Z_3^2)$

b. $I = \frac{1}{2} (m_1Z_1^2 + m_2Z_2^2)$

c. $I = \frac{1}{2} (m_1Z_1 + m_2Z_2)$

d. $I = 2 (m_1Z_1^2 + m_2Z_2^2)$

5. In Debye- Smoluchowski equation, the rate constant (k_D) is:

a. Directly proportional to viscosity.

b. Inversely proportional to viscosity.

c. Independent of viscosity.

d. Depend on second power of viscosity.

6. Stoke's equation is given by:

a. $D = kT/ 6 \Pi \eta r$

b. $D = kT\eta / 6 \Pi r$

c. $D = kT^2/ 6 \Pi \eta r$

d. $D = kT/ 6 \Pi \eta r^2$

7. Temperature coefficient is defined as the ratio of rate constant that differ from each other by:

a. $20^o C$

b. $10^o C$

c. $30^o C$

d. $05^o C$

8. Catalyst increases the rate of reaction by:

a. Increasing the activation energy.

b. Decreasing the activation energy.

c. Increasing the concentration of the reactants.

d. None of the above.

- Short answer type questions:

1. How temperature affect the rate of reaction?

2. Show the effect of catalyst on rate of reaction?

3. Solvent affects the rate of reaction. Explain how in brief?

4. Define dielectric constant of a solvent.

5. Write Debye- Smoluchowski equation.

6. Write Bronsted- Bjerrum equation.

7. Define viscosity of a solution.

8. Write short note on activated complex theory.

6.10 GLOSSARY

- **Dielectric constant** - Capacity of the solvent to weaken the force of attraction present in solute.
- **Viscosity**: Resistance in the flow of liquid.
- **Ionic strength**: Measure of electrical intensity.

6.11 ANSWERS TO SAQ's

- Fill in the blanks:

1. Increases; 2. Rate constant; 3. Increases, lowering; 4. Gas; 5. Solvent; 6. Increases; 7. Less, 8. I; 9. Non- catalytic; 10. Catalytic

- Multiple- choice questions

1. a. Increase in ionic strength; 2. b. 0.509; 3. b.ln k = ln k' +2 A $I^{1/2}$ Z_A Z_B; 4. b. I = ½ $(m_1Z_1^2 + m_2Z_2^2)$; 5. b. Inversely proportional to viscosity; 6. a. D = kT/ 6 Π ŋr; 7. b. 10^oC; 8. b. Decreasing the activation energy.

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6.13 TERMINAL QUESTIONS

- Describe in detail the various factors that affect the rate of reaction.
- Explain the effect of dielectric constant on the rate of reaction taking place in solution.
- Viscosity of a solvent affects the rate of reaction in solution. Explain.
- Explain in detail the primary and secondary salt effect.

UNIT-7 THE FAST REACTION KINETICS

CONTENTS:

7.1 OBJECTIVES

After reading this unit you will be able to:

- Know about the kinetics of fast reactions.

- Describe various methods of studying the rate of fast reactions that includes relaxation method, flow method and flash photolysis method.
- Write note on molecular reaction dynamics.
- Explain the kinetics of hydrogen-chlorine reaction and hydrogen-bromine reaction.
- Give the mechanism of pyrolysis of acetaldehyde that includes its kinetics also.
- Describe the kinetics of enzyme catalyzed reactions.

7.2 INTRODUCTION

In earlier chapters we have studied about chemical kinetics that deals with moderate reactions. Moderate reactions are those reactions that occur not very fast or not very slow like acid-catalyzed hydrolysis of esters. In fast reactions, reaction takes place so fast in such a short time (few second or less) than required to mix the reactants. For these reactions, rate is not obtained by conventional methods. Some other methods are used for determining the rate which are mentioned below in further topics.

The present unit deals with kinetics of fast reactions in which we will go through various methods for studying the rate of fast reactions that includes relaxation method, flow method and flash photolysis. In addition to these, we will have a general idea of molecular reaction dynamics. On moving forward, we will study about the kinetics of chain reactions that includes hydrogen- chlorine reaction, hydrogen – bromine reaction and pyrolysis of acetaldehyde. Finally we will conclude on the topic, kinetics of enzyme reactions.

The entire unit is quite interesting as after reading the unit we will be able to know how the rate of fast reactions are determined that takes place in few seconds. We will also came to know about the kinetics of reaction catalyzed by enzymes which are biological catalysts. Let us now discuss these topics one by one.

7.3 GENERAL IDEA OF KINETICS OF FAST REACTIONS

As we have discussed earlier that fast reactions takes place in few seconds or even less than this. Fast reactions are also known by name rapid reactions. For studying the rate of these reactions, conventional methods (common method) for determining rate are not applied. Methods used for determining the rate of fast reactions was given by Manfred Eigen (German chemist) which are as follows:

7.3.1 Relaxation method

Relaxation method is one of the methods for determining the rate of fast reactions that takes place in solution. Eigen and his coworkers put forward this method. In this method, there is a sudden change in some of the physical parameter of a system that is in equilibrium. This physical parameter includes temperature, pressure and electric field. Due to this change in the system there is change in state of a system or we can say that there is change in temperature, pressure or electric field. Relaxation is defined as a time required attaining the equilibrium again after this change. It has been observed that there is a change in a solvent structure which occurs quickly than the chemical reaction which is under consideration. By this method, reactions having half- life ranging from few seconds to 5×10^{-10} second are measured. Let us now derive the rate constant expression by considering a reversible first-order reaction:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$
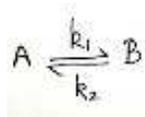
Suppose at any instant, the total concentration of the reaction that consist of A and B is represented by a while x be the concentration of B. As rate of reaction is defined as the change in the concentration of reactant or product per unit time, therefore rate of formation of product (r) is given by:

$r = dx/ dt = k_1 (a - x) - k_2 x$ ………. (1)

where $(a - x)$ is the concentration of A at any instant. If x_e represents the equilibrium concentration, the change in concentration (Δx) is given by: $\Delta x = x - x_e$ or $x = \Delta x + x_e$

Now on putting the value of x in equation 1:

$r = dx/ dt = d(\Delta x) /dt = k_1 (a - \Delta x - x_e) - k_2 (\Delta x + x_e)$

$d(\Delta x) /dt = k_1 a - k_1 \Delta x - k_1 x_e - k_2 \Delta x + k_2 x_e$ ………. (2)

We know that at equilibrium: $r = dx/ dt = 0$ and $x = x_e$

Hence equation (1) at equilibrium becomes: $k_1 (a - x_e) - k_2 x_e = 0$

$k_1 (a - x_e) = k_2 x_e$

On putting the value of $k_2 x_e$ in equation 2: $d(\Delta x)/dt = k_1 a - k_1 \Delta x - k_1 x_e - k_2 \Delta x + k_1 (a - x_e)$

$d(\Delta x)/dt = k_1 a - k_1 \Delta x - k_1 x_e - k_2 \Delta x + k_1 a - k_1 x_e$

$d(\Delta x)/dt = - k_1 \Delta x - k_2 \Delta x$

$d(\Delta x)/dt = - (k_1 + k_2) \Delta x$

$d(\Delta x)/dt = - k_r \Delta x$; where $(k_r = k_1 + k_2)$

Where k_r is the relaxation rate constant which is equal to $k_1 + k_2$. Relaxation time (t) is a reciprocal of relaxation rate constant, hence:

$t = 1/k_r = 1/k_1 + k_2$

Relaxation time is obtained by different methods that includes pressure - jump method and temperature- jump method which measures relaxation time of more than 10^{-5} second whereas for measuring relaxation time less than 10^{-5} second, high electric field methods are there.

7.3.2 Flow method

This method is one of the commonly used method for determining the rate of fast reactions and was the first method to be employed for studying the kinetics of fast reactions having half-life in the range 10 to 10^{-3} seconds. This technique was proposed by Roughton and Hastridge in 1923. There are various flow methods that include stopped-flow method, continuous –flow method and quenched flow method. Out of these three methods, stopped-flow method is commonly used method in comparison to continuous –flow method and quenched flow method. Let us discuss these methods:

- Stopped- flow method: As discussed above, this is commonly used flow method. The apparatus for this method is shown in Figure 1.
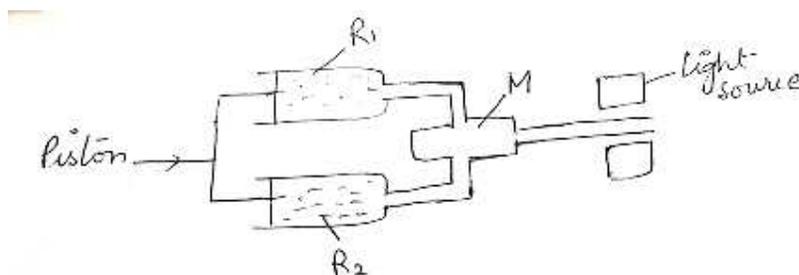
Figure 1. Apparatus for flow method

It is clear from Figure 1 that apparatus consist of two reservoir having reactants (reagents) R_1 and R_2. These two reservoirs is attached to a piston. By using piston, two reactants are allowed to mix in a chamber known as mixing chamber indicated by M in Figure 1. From M, the solution of two reagents then move through observation tube having light source in the ultraviolet and visible region. After mixing the reagents, observations are made within a few milliseconds. In this method, with different flow from the value of absorption, rate versus time graph is plotted. In this method as the name indicates, the flow is stopped suddenly at a particular point and the equilibrium rate is measured as a function of time by using absorption data. One point to be noted is that in this method, measurements are done at a particular point. For example, aqueous solution of Fe^{3+} and CNS^- is studied by using this method.

- Continuous –flow method: In this method, absorption is recorded at different distance from the mixing chamber. This method is more superior than stopped- flow method in terms of time resolution but this method consume large amount of reagents (reactants).
- Quenched flow method: In this method, the solution produced after mixing of reagents passes into quenching solution where reaction stops. This method best suits to those reactions which occur very fast like exchange reactions. Measurements are made at various distance or at a different rate of flow of solution.

7.3.3 Flash photolysis

In this method, as the name indicates a strong flash of high intensity or energy of the order 10^5 J is allowed to fall on a sample for microseconds or 10^{-6} second. On the interaction of high energy flash with the sample, almost all the molecules of the sample get excited that results in the formation of free radicals (reaction intermediates). The concept of flash photolysis was given by R. G. W. Norrish and G. Porter (1950). For this great achievement, they were awarded by Nobel Prize. As free radicals are produced on the exposure of flash on the sample therefore this photolysis is used from determining absorption spectra of free radicals like $^•CH3$, $^•Cl$ and $^•NH_2$ for studying reactions occurring in solution as well as in gas phase. The apparatus for flash photolysis is shown in Figure 2.
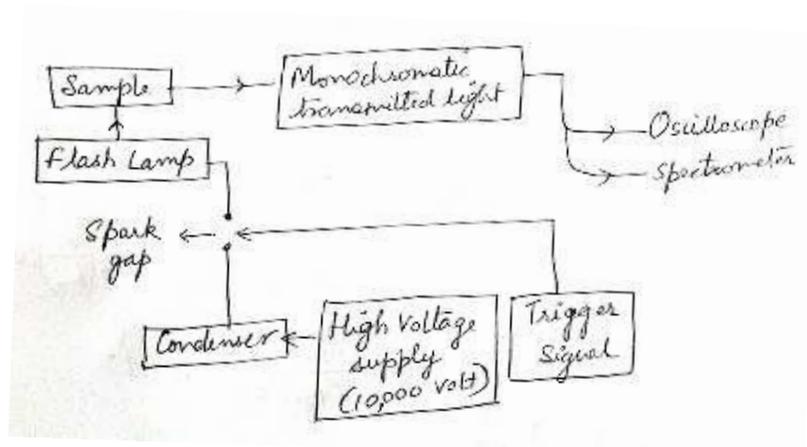
Figure 2. Flash-photolysis apparatus

It is clear from Figure 2 that there is a high voltage supply that provide 10,000 volt to a condenser. In the spark gap, a spark is generated by a trigger signal which is responsible for passing current through the flash lamp above which sample is placed. Within few microseconds, the condenser gets discharge resulting in the automatic stop of flash lamp. Hence on exposure to flash, reactant or sample get excited and form free radicals. More is the disappearance of excited molecules, more is the increase in transmitted light (monochromatic). Figure 2 shows that transmitted light passes the oscilloscope which shows the variation of the instantaneous signal voltage with time by means of graph. The spectrometer is placed in such a way that the wavelength absorbed by the excited reactant molecule or excited sample is same as the light the light passing through the condenser. In this way absorption spectra is taken by using spectrometer. The rate of very fast reactions like recombination of iodine atom, formation of chlorine atom in chlorine- oxygen reaction are determined by flash photolysis.

7.4 MOLECULAR REACTION DYNAMICS

Molecular reaction dynamics is also known by name microscopic kinetics. D. R. Herschbach, Y.T. Lee and J. C. Polanyi gave the concept of molecular reaction dynamics and won Nobel Prize for this great work. Molecular reaction dynamics deals with the quantum state of reactants and products along with intramolecular (within the molecule) and intermolecular (in between the molecules) motions that take place during a simple chemical reaction (elementary reaction). With quantum state we mean state of a quantized system having a particular set of quantum number. By this dynamics, we can simply have a detailed

knowledge of basic chemical change. For studying molecular reaction dynamics, there is an experimental method known as molecular beam method. In this method, a mono-energetic beam of atoms or molecules is used. Molecular beam apparatus used in molecular beam method is given in Figure 3.
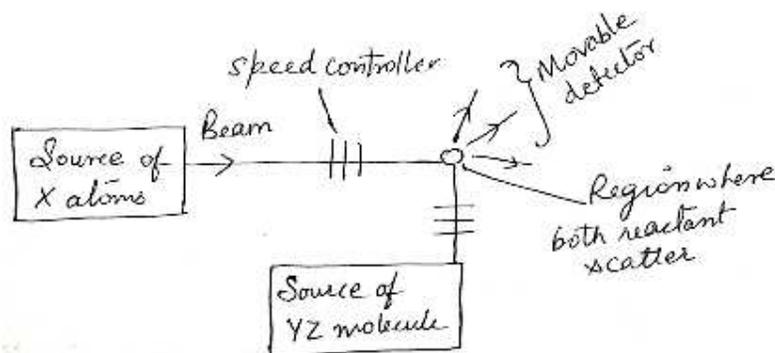

Figure 3. Molecular beam apparatus

This apparatus is designed in such a way that narrow beam of reactants are produced in which speeds of the molecules or atoms are controlled along with rotational, vibrational and electronic states. In addition to this, apparatus also consist of a movable detector for detecting the direction along with the speed of reactants and products. By this method, we can obtain detailed information regarding the reaction product that deals with energy distribution, distribution of angular momentum and quantum states of products and reactants. In old molecular beam method, reactants are taken in a small container having opening (very small) and beams are produced which are of very low intensity. In this method, there are differential surface ionization detectors. It has been found that old molecular beam method is only for alkali metals (first group elements). But in modern beam method, there is a use of supersonic nozzle source that produces beams having more intensities (about third order of magnitude than old beam method). For analyzing the scattered beam in modern beam method, mass spectrometers are used in place of movable detector and all types of reactions are studied by this modern beam method. It has been observed that on collision of reactant molecules, there case of scattering arises. In first case, there is no transfer of energy among different degree of freedom that refers to elastic scattering. In second case, there is no chemical reaction but transfer of energy among different degree of freedom takes place. In third case, there is transfer of energy along the chemical reaction.

7.5 CHAIN REACTION

As we know that reactions are classified into elementary and complex reaction. Elementary reactions are those reactions that take place in a single step while complex reaction takes place in two or more steps. These complex reactions are further classified into three types: reversible reaction, consecutive reaction and chain reaction. Reversible reactions as the name indicates, the rate of forward and backward reaction is same. In case of consecutive reactions, steps take place one after another. Now coming to chain reaction, which is a type of complex reaction in which highly reactive intermediates are formed which carry out a fast reaction for a long time. Intermediates are short-lived chemical species formed during the conversion of reactants into products. In place of short lived species we can also use a term transient existence. In 1943, Frank O. Rice and Karl F. Herzfeld first studied the chain reaction. In the mechanism of chain reaction, there are three steps: first is chain initiation, next is chain propagation and last is chain termination. For studying the kinetics of chain reaction, we must have knowledge of steady state approximation. According to steady state approximation, the rate of formation of an intermediate is equal to the rate of its decomposition. Thus: $d[R]/dt = 0$

where $[R]$ is the concentration of intermediate. Several chain reactions that includes reaction of hydrogen with halogens (chlorine and bromine), polymerization reaction, pyrolysis of hydrocarbon, aldehydes. Let us now discuss the kinetics of reaction between hydrogen and bromine.

7.5.1 Kinetics of hydrogen –bromine chain reaction

The reaction between hydrogen and bromine is given below along with its mechanism:

H_2 (g) + Br_2 (g) $\longrightarrow$ 2HBr (g)
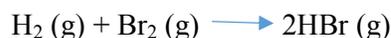
Mechanism:

1. Chain initiation: (i) Br_2 $\longrightarrow$ 2 Br; rate constant: k_1

2. Chain propagation: (ii) H_2 + Br $\longrightarrow$ HBr + H; rate constant: k_2

                  (iii) H + Br_2 $\longrightarrow$ HBr + Br; rate constant: k_3

3. Chain inhibition: (iv) H + HBr $\longrightarrow$ H_2 + Br; rate constant: k_4

4. Chain termination: (v) Br + Br $\longrightarrow$ Br_2; rate constant: k_5

In chain initiation step, bromine molecule acquire energy due to collision and form two bromine atoms. Here H and Br are the intermediates.

Rate of formation of HBr is the rate of reaction which is given by:

$r = d[HBr]/dt = k_2 [H_2] [Br] + k_3 [H] [Br_2] - k_4 [H] [HBr]$ .... (1)

There are two intermediates, H and Br having rate of formation:

$d[H]/dt = k_2 [H_2] [Br] - k_3 [H] [Br_2] - k_4 [H] [HBr]$

$d[Br]/dt = 2 k_1 [Br_2] - k_2 [H_2] [Br] + k_3 [H] [Br_2] + k_4 [H] [HBr] - 2 k_5 [Br]^2$

On applying steady state, $d[H]/dt = 0$; $d[Br]/dt = 0$

$k_2 [H_2] [Br] - k_3 [H] [Br_2] - k_4 [H] [HBr] = 0$ .... (2)

$2 k_1 [Br_2] - k_2 [H_2] [Br] + k_3 [H] [Br_2] + k_4 [H] [HBr] - 2 k_5 [Br]^2 = 0$ .... (3)

From equation 2, $k_2 [H_2] [Br] = k_3 [H] [Br_2] + k_4 [H] [HBr]$

$k_2 [H_2] [Br] = [H] (k_3 [Br_2] + k_4 [HBr])$

$[H] = k_2 [H_2] [Br] / (k_3 [Br_2] + k_4 [HBr])$

From equation 3,

$k_2 [H_2] [Br] = 2 k_1 [Br_2] + k_3 [H] [Br_2] + k_4 [H] [HBr] - 2 k_5 [Br]^2 = 0$ ....(4)

Now equation 2 can be written as:

$k_2 [H_2] [Br] = k_3 [H] [Br_2] + k_4 [H] [HBr]$ .... (5)

On subtracting equation 5 from equation 4,

$k_2 [H_2] [Br] - k_2 [H_2] [Br] = 2 k_1 [Br_2] + k_3 [H] [Br_2] + k_4 [H] [HBr] - 2 k_5 [Br]^2 - k_3 [H] [Br_2] - k_4 [H] [HBr]$

$2 k_1 [Br_2] - 2 k_5 [Br]^2 = 0$

$k_1 [Br_2] = k_5 [Br]^2$

$[Br]^2 = k_1 [Br_2] / k_5$

$[Br] = (k_1 [Br_2] / k_5)^{1/2}$

The expression for [H] contains [Br], hence on putting the value of [Br] in [H], we obtain:

$[H] = k_2 [H_2] (k_1 [Br_2]/ k_5)^{1/2} / (k_3 [Br_2] + k_4 [HBr])$

Now the value of [H] and [Br] in placed in equation 1,

$r = d[HBr]/ dt = (k_1^{1/2} k_2 [H_2] [Br_2]^{1/2}) / k_5^{1/2} + (k_1^{1/2} k_2 k_3 [Br_2] [H_2] [Br_2]^{1/2}) / k_5^{1/2} (k_3 [Br_2] + k_4 [HBr]) - k_1^{1/2} k_2 k_4 [H_2] [Br_2]^{1/2} [HBr] / k_5^{1/2} (k_3 [Br_2] + k_4 [HBr])$

$r = d[HBr]/ dt = k_1^{1/2} k_2 [H_2] [Br_2]^{1/2} / k_5^{1/2} [1 + \{k_3 [Br_2] / (k_3 [Br_2] + k_4 [HBr])\} - \{k_4 [HBr] / (k_3 [Br_2] + k_4 [HBr])\}]$

$r = d[HBr]/ dt = k_1^{1/2} k_2 [H_2] [Br_2]^{1/2} / k_5^{1/2} (k_3 [Br_2] + k_4 [HBr] + k_3 [Br_2] - k_4 [HBr])/ (k_3 [Br_2] + k_4 [HBr])$

$r = d[HBr]/ dt = k_1^{1/2} k_2 [H_2] [Br_2]^{1/2} / k_5^{1/2} [2 k_3 [Br_2] / (k_3 [Br_2] + k_4 [HBr])]$ ………. (6)

Equation 6 shows the rate of formation of HBr or rate of reaction for hydrogen- bromine chain reaction. It is clear from the above expression that with increase in time, the rate of formation of HBr decreases.

7.5.2 Kinetics of hydrogen –chorine chain reaction

The reaction between hydrogen and chlorine is given as: H_2 (g) + Cl_2 (g) $\longrightarrow$ 2HCl (g)

Bodenstein and Nernst proposed the mechanism of reaction that occurs between hydrogen and chlorine:

Mechanism:

1. Chain initiation: (i) $Cl_2 \longrightarrow$ 2 Cl; rate constant: k_1

2. Chain propagation: (ii) Cl + $H_2 \longrightarrow$ HCl + H; rate constant: k_2

(iii) H + $Cl_2 \longrightarrow$ HCl + Cl; rate constant: k_3

4. Chain termination: (iv) Cl + wall $\longrightarrow$ ½ Cl_2; rate constant: k_4

Rate of formation of HCl is the rate of reaction which is given by:

$r = d[HCl]/ dt = k_2 [Cl] [H_2] + k_3 [H] [Cl_2]$ ………. (1)

There are two intermediates H and Cl. The rate of formation of H is given by:

$d[H]/ dt = k_2 [Cl] [H_2] - k_3 [H] [Cl_2]$

Similarly rate of formation of Cl is given by:

$d[Cl]/dt = k_1 I_{abs} - k_2 [Cl][H_2] + k_3 [H][Cl_2] - k_4 [Cl]$

where I_{abs} is the intensity of radiation absorbed. Applying steady –state approximation to intermediates:

$d[H]/dt = 0; d[Cl]/dt = 0$

$k_2 [Cl][H_2] - k_3 [H][Cl_2] = 0$ ……… (2)

$k_1 I_{abs} - k_2 [Cl][H_2] + k_3 [H][Cl_2] - k_4 [Cl] = 0$ ………… (3)

On adding equation 2 and 3;

$k_2 [Cl][H_2] - k_3 [H][Cl_2] + k_1 I_{abs} - k_2 [Cl][H_2] + k_3 [H][Cl_2] - k_4 [Cl] = 0$

$k_1 I_{abs} - k_4 [Cl] = 0$

$k_1 I_{abs} = k_4 [Cl]$

$[Cl] = k_1 I_{abs} / k_4$

From equation 2, $k_2 [Cl][H_2] = k_3 [H][Cl_2]$

Now from equation 1, $r = d[HCl]/dt = k_2 [Cl][H_2] + k_2 [Cl][H_2]$

$r = d[HCl]/dt = 2 k_2 [Cl][H_2]$

Now the value of [Cl] is placed in above expression of rate of reaction, we obtain:

$r = d[HCl]/dt = 2 k_1 k_2 [H_2] I_{abs} / k_4$

The above expression shows that rate of formation of HCl for hydrogen- chlorine reaction is directly proportional to the concentration of hydrogen gas taken as a reactant.

7.5.3 Pyrolysis of acetaldehyde

Pyrolysis means decomposition of a substance at high temperature. Here in this section, we will study the pyrolysis of acetaldehyde or decomposition of acetaldehyde at very high temperature at wavelength ranging from 2500 to 3100 ^{o}A. The reaction is given below:

$CH_3CHO \longrightarrow CH_4 + CH_3CH_3 + CO$ + other products
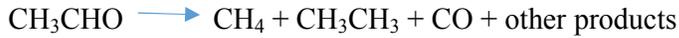
Mechanism:

(i) Chain initiation: $CH_3CHO \longrightarrow CH_3 + CHO$; rate constant: k_1

(ii) Chain propagation: $CH_3CHO + CH_3 \longrightarrow CH_4 + CH_3CO$; rate constant: k_2

$$CH_3CO \longrightarrow CO + CH_3; \text{ rate constant: } k_3$$

(iii) Chain termination: $CH_3 + CH_3 \longrightarrow CH_3CH_3$; rate constant: k_4

Rate of formation of intermediate, CH_3CO and CH_3 is given by:

$d\,[CH_3]/\,dt = k_1\,I_{abs} - k_2\,[CH_3CHO]\,[CH_3] + k_3\,[CH_3CO] - k_4\,[CH_3]^2$

$d\,[CH_3CO]/\,dt = k_2\,[CH_3CHO]\,[CH_3] - k_3\,[CH_3CO]$

On applying steady-state approximation to the intermediates, we have:

$d\,[CH_3]/\,dt = 0$; $d\,[CH_3CO]/\,dt = 0$

Hence: $k_1\,I_{abs} - k_2\,[CH_3CHO]\,[CH_3] + k_3\,[CH_3CO] - k_4\,[CH_3]^2 = 0$ ………. (1)

$k_2\,[CH_3CHO]\,[CH_3] - k_3\,[CH_3CO] = 0$ ………. (2)

On adding equation 1 and 2:

$k_1\,I_{abs} - k_2\,[CH_3CHO]\,[CH_3] + k_3\,[CH_3CO] - k_4\,[CH_3]^2 + k_2\,[CH_3CHO]\,[CH_3] - k_3\,[CH_3CO]$
$= 0$

$k_1\,I_{abs} - k_4\,[CH_3]^2 = 0$

$k_1\,I_{abs} = k_4\,[CH_3]^2$

$[CH_3]^2 = k_1\,I_{abs}/\,k_4$

$[CH_3] = (k_1\,I_{abs}/\,k_4)^{1/2}$

Now in order to find the concentration of CH_3CO, we put the value of $[CH_3]$ in equation 2.

$k_2\,[CH_3CHO]\,(k_1\,I_{abs}/\,k_4)^{1/2} - k_3\,[CH_3CO] = 0$

$k_2\,[CH_3CHO]\,(k_1\,I_{abs}/\,k_4)^{1/2} = k_3\,[CH_3CO]$

$[CH_3CO] = k_2\,[CH_3CHO]\,k_1^{1/2}\,I_{abs}^{1/2}\,/\,k_3\,k_4^{1/2}$

Now we know that the rate of reaction is the rate of formation of CO, therefore:

$r = d\,[CO]/\,dt = k_3\,[CH_3CO]$

On putting the value of [CH$_3$CO] in above expression, we obtain:

$r = d [CO]/ dt = k_3 k_2 [CH_3CHO] k_1^{1/2} I_{abs}^{1/2} / k_3 k_4^{1/2}$

$r = d [CO]/ dt = k_2 [CH_3CHO] k_1^{1/2} I_{abs}^{1/2} / k_4^{1/2}$

$r = d [CO]/ dt = k [CH_3CHO] I_{abs}^{1/2}$ ……….. (3)

Where $k = k_2 k_1^{1/2}/ k_4^{1/2}$, another constant. Equation 3 represents the rate expression for pyrolysis of acetaldehyde. It is clear from above expression that rate of reaction is directly proportional to the concentration of acetaldehyde.

7.6 ENZYME REACTIONS

Enzymes as we know are biological catalyst that catalyzes the reactions taking place in a biological system. The catalysis by enzymes is known as micro- heterogeneous catalysis. These are complex organic compounds (proteins) formed by living plants and animals. Enzymes when dissolved in water forms colloidal solution. A particular reaction is catalyzed by a specific enzyme like hydrolysis of maltose into two glucose is catalyzed by enzyme maltase, similarly the enzyme zymase catalyze the conversion of glucose into ethyl alcohol and carbon dioxide. Enzymes are used in small amount and increase the rate of reaction by lowering the activation energy. Let us consider the kinetics of enzyme- catalyzed reaction.

7.6.1 Kinetics of enzyme reactions

There are three equations of enzyme- catalyzed reactions which are Michaelis- Menten equation, Lineweaver – Burk equation and Eadie- Hofstee equation. Let us discuss these equations one by one:

7.6.1.1 Michaelis- Menten equation

L. Michaelis and M. Menten in 1913 proposed the mechanism of enzyme- catalyzed reactions. According to them, enzyme (E) combines with substrate (S) and form enzyme- substrate complex (ES). This enzyme-substrate complex (ES) may form enzyme and substrate or may form products (P). Here ES is an intermediate. The mechanismis as follows:

(i) E + S $\longrightarrow$ ES; rate constant = k_1

(ii) ES $\longrightarrow$ E + S; rate constant = k_2

(iii) ES $\longrightarrow$ Products + E; rate constant = k_3

Rate of reaction is equal to rate of formation of products (P), therefore:

$r = d[P]/dt = k_3 [ES]$ ………. (1)

Rate of formation of enzyme- substrate complex (ES) is given by:

$d[ES]/dt = k_1 [E] [S] - k_2 [ES] - k_3 [ES]$

Applying steady –state approximation: $d[ES]/dt = 0$, Therefore:

$k_1 [E] [S] - k_2 [ES] - k_3 [ES] = 0$ ………. (2)

If $[E_o]$ represents the total enzyme concentration, then: $[E_o] = [E] + [ES]$

Where [E] is the concentration of free enzyme (enzyme without substrate) while [ES] represents the concentration of enzyme- substrate complex.

$[E] = [E_o] - [ES]$

Now on putting the value of [E] in equation 2, we obtain:

$k_1 ([E_o] - [ES]) [S] - k_2 [ES] - k_3 [ES] = 0$

$k_1 [E_o] [S] - k_1 [ES] [S] - k_2 [ES] - k_3 [ES] = 0$

$k_1 [E_o] [S] = k_1 [ES] [S] + k_2 [ES] + k_3 [ES]$

$k_1 [E_o] [S] = [ES] (k_1 [S] + k_2 + k_3)$

$[ES] = k_1 [E_o] [S] / k_1 [S] + k_2 + k_3$

Now the value of [ES] is placed in equation 1, therefore:

$r = d[P]/dt = k_3 k_1 [E_o] [S] / k_1 [S] + k_2 + k_3$

On dividing the numerator and denominator by k_1, we obtain:

$r = d[P]/dt = k_3 [E_o] [S] / [S] + (k_2 + k_3) / k_1$

$r = d[P]/dt = k_3 [E_o] [S] / [S] + K_M$ ………. (3)

Equation 3 is Michaelis- Menten equation where K_M is Michaelis constant which is equal to $(k_2 + k_3) / k_1$. When all enzyme reacts with substrate then there will be no free enzyme or we can say $[E_o] = [ES]$. In this case, rate of reaction is maximum and is represented by V_{max}.

$V_{max} = k_3 [E_o]$

$r = V_{max} [S]/ [S] + K_M$

Three case arises:

- Case 1: When $[S] >>> K_M$

$r = V_{max}$ (This shows that rate does not depend on the concentration of the substrate or we can say that reaction obey zero- order kinetics).

- Case 2: When $[S] <<< K_M$

$r = V_{max} [S]/ K_M$ (This shows that with increase in concentration of substrate, rate of reaction increases or we can say that reaction obey first order kinetics)

- Case 3: When $[S] = K_M$

$r = V_{max} /2$ (This shows that when rate of reaction is half the maximum rate, concentration of the substrate is equal to Michaelis constant). All these three cases are given in Figure 4.
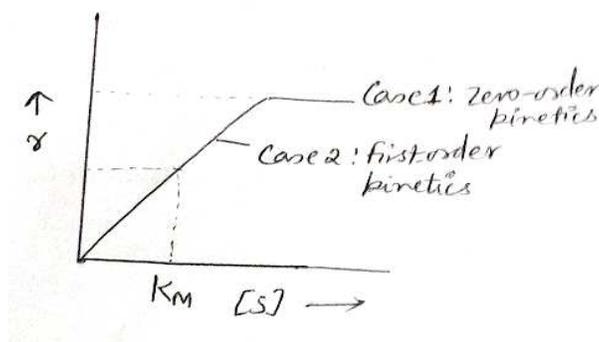

Figure 4. Michaelis- Menten plot

There is a term known as turnover number of an enzyme which is defined as the number of molecules of reactants which forms the product in unit time by one molecule of an enzyme. This number is represented by k_3.

7.6.1.2 Lineweaver- Burk equation

This equation is reverse of Michaelis- Menten equation. This equation was proposed by Lineweaver and Burk and is given by:

$1/ r = (K_M/ V_{max} [S]) + (1/ V_{max})$

This equation is Lineweaver- Burk equation, where K_M is Michaelis constant, V_{max} is maximum rate, r is rate of reaction while $[S]$ is concentration of the substrate. The plot is given in Figure 5 which is known as Lineweaver- Burk plot.
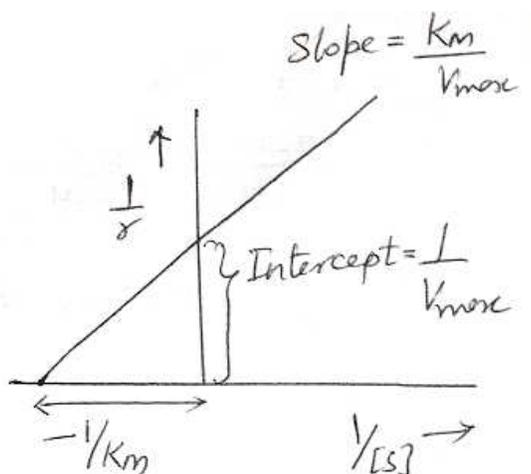
Figure 5. Lineweaver- Burk plot

7.6.1.3 Eadie- Hofstee equation

This equation of enzyme- catalyzed reaction is given by Eadie and Hofstee which is given as:

$r/[S] = V_{max}/K_M - r/K_M$

This equation is Eadie- Hofstee equation, where K_M is Michaelis constant, V_{max} is maximum rate, r is the rate of reaction while [S] is concentration of the substrate. The plot is given in Figure 6 which is known as Eadie- Hofstee plot.
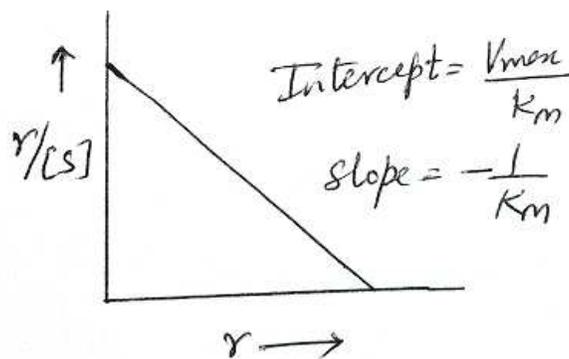

Figure 6. Eadie- Hofstee plot

7.7 SUMMARY

We have discussed about the kinetics of fast reactions in which we have studied various methods like relaxation method, flow method and flash photolysis in order to find the rate of fast reactions. Along with this, we have also discussed an elementary idea of microscopic kinetics which is also known by name molecular reaction dynamics. Then we talked about

chain reactions that include mechanism and kinetics of several chain reactions like hydrogen-chlorine, hydrogen- bromine and pyrolysis of acetaldehyde. After discussing the chain reaction, we studied about biological catalyst i.e. enzymes in which its mechanism and kinetics are studied by considering three equations: Michaelis- Menten equation, Lineweaver – Burk equation and Eadie- Hofstee equation.

7.8 SELF- ASSESSMENT QUESTIONS (SAQ)

- Fill in the blanks:

1. In old molecular beam method, beam produced possess ………. intensities.

2. In modern molecular beam method, beam produced are of ………. intensities.

3. Molecular reaction dynamics is also known by name ………. kinetics.

4. In molecular reaction dynamics, ………… states of reactants and products are considered.

5. ………. method is commonly used method for determining the rate of fast reactions.

6. In relaxation method, there is change in ………., ………. and ……….

7. For measuring relaxation time, the methods employed are ………. and ……….

8. Molecular reaction dynamics deals with ………. systems.

9. Chain reaction is a type of ………. reaction.

10. According to steady– state approximation, rate of disappearance of an intermediate is ………. to rate of appearance of an intermediate.

11. In hydrogen- bromine reaction, there are to intermediates, ………. and ……….

12. Br_2 form two bromine atom by acquiring an energy which is due to ……….

13. In hydrogen- chlorine reaction, there are to intermediates, ………. and ……….

14. ………. is defined as the decomposition of a substance at high temperature.

15. Enzymes are ………. catalysts.

16. Enzymes catalysis is known as ………. catalysis.

17. The complex formed by enzyme with substrate is known as ………. complex.

18. Michaelis constant (K_m) is equal to the concentration of the substrate when rate of reaction is ………. the maximum rate.

19. When concentration of a substrate is greater than Michaelis constant, then reaction obeys ………. order kinetics.

20. When Michaelis constant is more than the concentration of a substrate, then reaction obeys ………. order kinetics.

7.9 GLOSSARY

- **Relaxation**: Time required attaining the equilibrium after changing temperature, pressure and electric field of a system.
- **Catalysis**: Process by which rate of reaction is changed.
- **Enzymes**: Biological catalysts that catalyze the reaction occurring in living plants and animals.
- **Pyrolysis**: Decomposition of a substance at high temperature.
- **Chain reaction**: Highly reactive intermediates are formed which carry out a fast reaction for a long time.

7.10 ANSWERS TO SAQ's

- Fill in the blanks:

1. Low; 2. High; 3. Microscopic; 4. Quantum; 5. Flow; 6. Temperature, Pressure and Electric field; 7. Temperature- jump method and pressure-jump method; 8. Quantized; 9. Complex; 10. Equal; 11. H and Br; 12. Collision; 13. H and Cl; 14. Pyrolysis; 15. Biological; 16. Heterogeneous; 17. Enzyme- substrate; 18. Half; 19. Zero; 20. First.

7.11 REFERENCES

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7.12 TERMINAL QUESTIONS

- Describe various methods which are used for the determination of kinetics of fast reactions.

- Explain kinetics of enzyme-catalyzed reaction by giving all the three equations: Michaelis- Menten equation, Lineweaver- Burk equation and Eadie- hofstee equation.

- Discuss the kinetics of reaction between hydrogen-bromine and hydrogen–chlorine reaction.

UNIT 8: CATALYSIS

8.9 Summary

8.10 Self-Assessment Questions (SAQ)

8.11 Glossary

8.12 Answers to SAQ's

8.13 References

8.14 Terminal Questions

8.1 INTRODUCTION

As we know that there are some substances that change the rate of reaction either by increasing the rate of reaction or by decreasing the rate of reaction without being used up. These substances are refers to as catalyst and the process by which they change the rate of reaction is called catalysis. Catalysis is further classified into various types like positive catalysis, negative catalysis, auto- catalysis, homogeneous catalysis, heterogeneous catalysis. All these types of catalysis are discussed in detail in upcoming sections.

The present unit deals with the concept of catalysis which is quite interesting. Unit also contains several headings like types of catalysis, adsorption, types of adsorption, factors affecting adsorption, adsorption isotherm that includes Freundlich adsorption isotherm, Langmuir's adsorption isotherm, Gibbs adsorption isotherm and B.E.T. equation. After going through the unit it will be clear that how the process of catalysis works at the surface.

There is a catalytic converter in automobiles that contain platinum as catalyst. The platinum that acts as catalyst convert toxic carbon monoxide into carbon dioxide thereby decreasing the air pollution. There are several examples of catalysis that are eco- friendly (environment loving) thereby making the chapter more and more interesting to the reader. Let us now discuss the complete unit in detail.

8.2 OBJECTIVES

After reading this unit you will be able to:

- Define catalysis.

- Classify catalysis

- List the characteristics of catalyst.

- Explain the process of adsorption including its types.

- Write the factors that affect the phenomenon of adsorption.

- Describe adsorption isotherm, adsorption isobar, adsorption isostere.

- To determine the surface area by using the process of adsorption.

- Explain adsorption isotherm given by Gibbs known as Gibbs adsorption isotherm.

- Describe catalytic activity at a surface.

- List all considerations made by B.E.T.

8.3 CATALYSIS

As discussed above that there are certain substances that change the rate of reaction without being consumed in the reaction. These substances are known as catalysts and the process or phenomenon is known as catalysis. The term catalysis was coined by Berzelius. These substances either increase the rate of reaction or decrease the rate of reaction. There are several characteristics of catalyst which are discussed below:

- As said above that catalyst remains unchanged in the reaction. Catalyst remains unchanged in terms of mass and chemical composition but it has been observed that catalyst undergoes a physical change in which there is change in physical appearance like if the catalyst is taken in a form of small pellets then at the end of the reaction, it appears in a form of powder.

- Generally a small amount of a catalyst is needed to change the reaction rate. Like finely divided (pore size is very small) platinum acts as a catalyst in the decomposition of hydrogen peroxide. In certain like Friedel Craft's reactions where anhydrous $AlCl_3$ is taken as a catalyst, the amount of catalyst is in large amount.

- Specific catalyst can catalyze a particular reaction. This shows that catalyst is specific in its action. For example, when ethyl alcohol is passed over hot aluminum oxide (Al_2O_3), dehydration occurs. Dehydration as the name indicates is the loss of water thus ethyl alcohol loss water and form ethylene ($CH_2=CH_2$). On the other hand, when ethyl alcohol is passed over hot copper, there is dehydrogenation (loss of hydrogen molecule) which leads to the formation of acetaldehyde. (CH_3CHO). This shows that Al_2O_3 is the catalyst that causes dehydration and copper is the catalyst that

causes dehydrogenation of ethyl alcohol which confirm that a particular catalyst catalyze a particular reaction.

- Finely divided catalyst is more specific in its action in comparison to those that are not finely divided. It has been observed that solid nickel in the form of lumps possesses less catalytic activity than when it is taken in the form of powder.

- In case of reactions that exist in equilibrium or the reaction is reversible then catalyst reduces the time needed to establish equilibrium but do not affect the final position of the equilibrium. It means that the equilibrium can attained earlier by adding the catalyst. For example, in Haber's process of synthesis of ammonia, finely divided iron is used as a catalyst by which equilibrium is attained earlier. The effect of catalyst on equilibrium is shown in Figure 1.
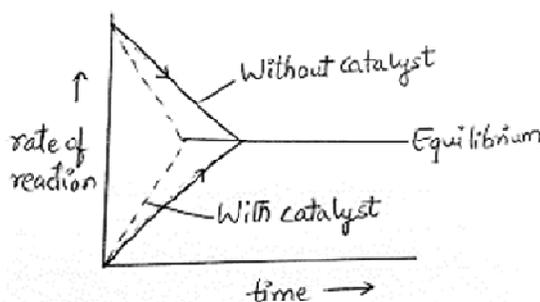

Figure 1. Effect of catalyst on equilibrium

It is clear from the Figure 1 that with time, rate of forward reaction decreases while that of reverse reaction increases. When the rate of both the reaction becomes equal, then there is a state of equilibrium.

- Catalyst generally alters or changes the rate of reaction but do not start the reaction. But there are certain reactions in which catalyst acts as initiator. There is no reaction between hydrogen and oxygen at room temperature but in presence of catalyst (platinum), they react.

- The catalytic activity of a catalyst can be increased by adding certain substance known as promotors. As discussed above, in Haber's process of ammonia synthesis, finely divided iron is used as catalyst. Its activity is increased by adding molybdenum which acts as promotor.

- There are certain substances that destroy the catalytic activity. These substances are known as catalytic poisons. Catalytic poisons are also known as anti-catalysts. In

case of Haber's process of ammonia synthesis, finely divided iron is used as catalyst while hydrogen sulphide (H_2S) destroy the activity of iron catalyst.

- Catalytic activity attains a maximum height or maximum rate at a particular temperature. This temperature when catalytic activity is maximum is called optimum temperature. For example, in case of an enzyme which acts as a biological catalyst, the optimum temperature is 35^oC to 37^oC.

8.3.1 Types of catalysis

Now coming to the classification of catalysis, we have discussed earlier that catalyst increases or decreases the rate of reaction. On this basis, catalyst is classified into two types:

- Positive catalysis: A catalysis in which there is increase in the rate of reaction is known as positive catalysis and catalyst are known as positive catalysts. For example, finely divided iron as catalyst in Haber's process act as positive catalyst and the process is called positive catalysis. Similarly in contact process of sulphuric acid synthesis, finely divided platinum is used as a positive catalyst. Positive catalyst lowers the activation energy thereby increasing the rate of reaction as given in Figure 2.
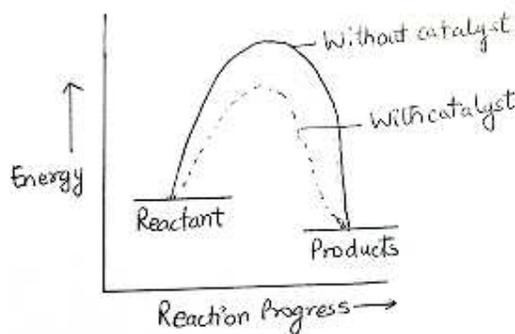

Figure 2. Effect of catalyst on activation energy

- Negative catalysis: A catalysis in which there is a decrease in rate of reaction is known as negative catalysis and catalysts are known as negative catalyst. In some cases, negative catalyst even stops the reaction. Negative catalysts are also known as inhibitors. For example, in the decomposition of hydrogen peroxide (H_2O_2), dilute solution of acid (H^+) lowers the reaction rate. A very common example of negative catalyst is of TEL. TEL refers to tetraethyl lead. This catalyst added to petrol which thereby decreases the rate of

combustion of petrol. In absence of catalyst, combustion takes place very rapidly. These catalyst increases the activation energy thereby decreasing the reaction rate.

Another classification of catalyst depends on the phase of catalyst and reactant. A phase is defined as a homogeneous part of a system that possesses same chemical and physical properties. For example, mixtures of gases consist of one phase. It means that when gases are mixed, we cannot differentiate individual gases which thereby form a homogeneous system consisting of one phase. Practically, we all know that atmosphere contains several gases that form one phase. Similarly when sugar is dissolved in water then a clear solution is formed which is homogeneous and this solution consist of one phase. We say that water exist in three phase solid, liquid and gas. On the basis of phase, catalysis is classified into two types:

- Homogeneous catalysis: As we know that a system that contains only one phase is called homogeneous system. Here we are talking about catalysis, then homogeneous catalysis is defined as a catalyst in which the reactant and catalyst are in same phase. For example, when reactants and catalyst are in gaseous phase then catalysis is homogeneous catalysis. When carbon monoxide gas (CO) combines with oxygen gas (O_2) in presence of nitric oxide (NO) as catalyst, there is a formation of carbon dioxide (CO_2). Here reactant CO, O_2 and catalyst NO are in gaseous phase. Similarly sulphur dioxide combines with oxygen in presence of nitric oxide as catalyst to form sulphur trioxide (gas).

$$2CO + O_2 + NO \longrightarrow 2CO_2 + NO$$

$$2SO_2 + O_2 + NO \longrightarrow 2SO_3 + NO$$

As also discussed earlier that when sugar is added to water, it forms homogeneous system having one phase. Therefore another example of homogeneous catalysis is reaction of cane – sugar with water (hydrolysis of cane-sugar). In the hydrolysis of cane sugar, the catalyst used is acid which may be sulphuric acid, hydrochloric acid, nitric acid etc. For this, cane-sugar is dissolved in water making a clear solution, then acid is added which acts as catalyst. Acid added is also in liquid phase. Thus we can say that the reactants and catalyst possess only one phase. It has been found that rate of homogeneous catalysis is more than that of heterogeneous catalysis.

- Heterogeneous catalysis: A system that consist of more than one phase constitute a heterogeneous system. When reactants and catalyst possess different phase then the catalysis is known as heterogeneous catalysis. The rate of this catalysis is less than

that of homogeneous catalysis. For example, when above reaction of sulphur dioxide and oxygen (both in gaseous phase) reacts in presence of finely divided platinum as catalyst (solid), then the phase of reactants and catalyst is different. Thus it constitute heterogeneous catalysis. The chemical reaction is given below:

$$2SO_2 + O_2 + Pt \longrightarrow 2SO_3 + Pt$$

Another example of heterogeneous catalyst is

$$N_2 + 3H_2 + Fe \longrightarrow 2NH_3 + Fe$$

$$2 H_2O_2 + Pt \longrightarrow 2 H_2O + O_2 + Pt$$

Here H_2O_2 is present in liquid phase while catalyst, platinum is present is present in solid phase. When the reactant is in solid phase and catalyst also in solid phase, then the catalysis is heterogeneous catalysis as two solid constitute two different phase.

In addition to these types of catalysis, there is another type of catalysis known as enzyme catalysis. Enzymes are large organic molecules produced by living plants and animals. These are proteins having amino acid as a repeating unit. The catalysis carried by enzyme is called enzyme catalysis. This catalysis is heterogeneous catalysis. For example, an enzyme diastase catalyzes the hydrolysis of starch, similarly enzyme zymase convert glucose to ethyl alcohol and carbon dioxide. Enzymes are considered as biological catalyst each having specific function. Another type of catalysis is auto-catalysis. In this catalysis, one of the product formed in the reaction itself acts as a catalyst. For example, when ethyl acetate ($CH_3COOC_2H_5$) reacts with water, there is formation of acetic acid (CH_3COOH) and ethyl alcohol (C_2H_5OH). Acetic acid thus formed acts as a catalyst.

8.4 ADSORPTION

Now the question arises that why solid acts as adsorbent. The reason is that in solid the molecules are very close to each other or has compact arrangement of molecules having strong intermolecular force of attraction. The molecules that are present towards the inner side are attracted equally by other molecules surrounding it from all direction but the molecules at the surface are attracted by other molecules that are present towards the inner side. Therefore on the surface unbalanced residual forces are present. In order to balance these residual forces, the solid surface attracts the molecular species (gas/ vapour / liquid) towards itself that result in the process of adsorption. Solids with large surface area show more adsorption. It means that powder of chalk is a better adsorbent than a piece of chalk.

The reverse of adsorption is known as desorption which is defined as a removal of adsorbate from the surface of adsorbent. Adsorption is an important phenomenon having several applications like we can remove color of cane-sugar by using animal charcoal (adsorbent), play an important role in heterogeneous catalysis where reactant and catalyst are in different phase, softening of hard water, chromatographic analysis. Plants receive nutrients from soil which is due to adsorption. Certain adsorbent like activated charcoal is used in gas masks which adsorb harmful gases and provide pure air to breath. Let us now discuss the thermodynamics of adsorption.

8.4.1 Thermodynamics of adsorption

It is clearly explained above that when adsorption takes place, there is decrease in residual force that results in the decrease in energy. This shows that during adsorption some energy is released which is in the form of heat, hence adsorption is an exothermic process. In exothermic process, energy in a form of heat is evolved hence ΔH is negative. ΔH represents change in enthalpy which is a measure of heat content of a system. When one mole of adsorbate (gas or vapour) is adsorbed on a surface of adsorbent, then the amount of heat evolved or released is called molar enthalpy of adsorption. Now coming to another thermodynamic function, entropy. Entropy as we know is a measure of randomness or disorderness of the molecules present in the system. Suppose we have four numbers: 1,2,3,4. If these are arranged like 1,2,3,4 in a proper order, we say that randomness or disorderness is zero therefore entropy is zero. If these numbers are arranged like 1,3,2,4 then disorderness occurs that results in increase of entropy. In adsorption, adsorbate (generally gas) adsorbed on slid surface. So in adsorption there is decrease in entropy when gas (adsorbate) accumulates on the surface of solid (adsorbent) as its randomness decreases. Before adsorption the gas molecules are free to move (more entropy) but after adsorption the molecules get attached on the surface thereby decreasing its disorderness or randomness. Here ΔS is negative where S represent entropy and negative sign represents decrease in entropy. Now coming to another thermodynamic function free energy (G). The relation between ΔG (change in free energy), ΔH (change in enthalpy) and ΔS (change in entropy) is given by: $\Delta G = \Delta H - T\Delta S$. As adsorption is a spontaneous process (process that takes place naturally without any external help) so ΔG is negative. For this ΔH should be more negative than ΔS.

8.4.2 Types of adsorption

On the basis of nature of interaction between adsorbate and adsorbent, adsorption is classified into two types: physical adsorption and chemical adsorption.

7.4.2.1 Physical adsorption

Physical adsorption is known as physisorption or van der Waals adsorption. In this type of adsorption, there is physical force of attraction between adsorbate and adsorbent which may be due to polarization, dipole moment. The force that exists is weak van der Waals forces. In this adsorption, more than one layer (multilayer) of adsorbate can form on the surface of the adsorbent as the force is physical in nature. Therefore it can attract adsorbate molecules that come under the influence of force. As the force between adsorbate and adsorbent is weak, therefore heat evolved is low about 4 to 40 kJ mol^{-1}. Physical adsorption is reversible in nature it means that adsorbed gas or adsorbate can be easily recovered from the surface of the adsorbent simply by lowering the pressure of a system at the same temperature at which the adsorption occurs. As we know that desorption is reverse of adsorption, therefore small amount of energy is required to remove the adsorbate from the surface of the adsorbent. Hence we say that activation energy of desorption is very low. It has been observed that with rise in temperature, physisorption decreases. For example, adsorption of gas (hydrogen) on charcoal.

8.4.2.2 Chemical adsorption

Chemical adsorption is also known as chemisorption. In this type of adsorption, there is chemical force of attraction between adsorbate and adsorbent that involve electrons. The force that exist is a strong valence force. In this adsorption only one layer of adsorbate is formed on the surface of the adsorbent as the force are chemical (ionic bond or chemical bond) in nature. No multilayer is formed in chemisorption. As the force between adsorbate and adsorbent is strong, heat evolved during adsorption is high about 40 to 400 kJmol^{-1}. Chemical adsorption is irreversible in nature it means that gas (adsorbate) once accumulate at the surface cannot be removed by lowering the pressure of the gas at the same temperature at which adsorption occurs. As the force is strong, hence activation energy of desorption is very high. It has been observed that with increase of temperature, chemical adsorption increases. For example, adsorption of hydrogen gas on the surface of nickel.

Another classification of adsorption is based on the amount of adsorbate on the surface of the adsorbent. On this basis, adsorption is classified into positive adsorption and negative adsorption. In positive adsorption as the name indicates, the amount of adsorbate on the surface of adsorbent is more while in negative adsorption, the amount of adsorbate on the surface of adsorbent is less. This is all about the classification of the adsorption.

8.4.3 Factors affecting adsorption

We know that as in adsorption, there is an adsorbate and adsorbent. Therefore adsorption depends on the nature of adsorbate (gas generally) and nature of adsorbent (solid). In addition to these two factors, adsorption also depends upon temperature and pressure. Let us discuss these factors one by one:

8.4.3.1 Nature of gas (adsorbate)

It has been observed that gases which are easily liquefiable and readily soluble like NH_3, SO_2 are adsorbed more readily in comparison to permanent gases O_2, N_2 because easily liquefiable gases possess more force of attraction than those gases that are not easily liquefiable. Critical temperature of a substance is defined as a temperature at which vapour of a substance cannot be liquefied (change to liquid) no matter how much pressure is applied. It has been noticed that higher the critical temperature of a gas (adsorbate) more is adsorption.

8.4.3.2 Nature of adsorbent

Adsorption depends on the surface area of adsorbent. More is the surface exposed for adsorption; more will be the process of adsorption. Hence adsorbent in powder form possess more surface area resulting in more adsorption. Charcoal, silica gel in powder (porous) form, finely divided nickel or platinum metal show more adsorption.

8.4.3.3 Temperature

The process of adsorption depends upon the temperature at which it takes place. As we know that adsorption is an exothermic process, it means that in adsorption heat is evolved. We also know that heat is related to temperature so with adsorption, temperature decreases. In short adsorption is inversely proportional to temperature i.e. with increase of temperature, adsorption decreases and vice-versa. It has been observed that when temperature dropped from -29^oC to -78^oC, adsorption of nitrogen gas increases in case of coconut charcoal as an adsorbent.

8.4.3.4 Pressure

The phenomenon of adsorption depends upon the pressure of gas (adsorbate). With adsorption, pressures of gas decreases as gas molecules are notfree to move after adsorption. Therefore more decrease in pressure leads to more adsorption while less decrease in pressure leads to less adsorption.

8.5 ADSORPTION CURVES

We have discussed earlier that adsorption depends upon temperature and pressure. Therefore adsorption is a function of temperature (T) and pressure (P).

$$a= f (P, T)$$

The commonly studied adsorption is adsorption of gas on solid. Here a represents adsorption or amount of gas adsorbed. In the above expression, there are three terms P, T and a. By keeping one term constant, a graph is plotted between other two terms. In this way we obtain three adsorption curves which are discussed one by one below:

- Adsorption isotherm: In this curve, temperature remains constant therefore a graph is plotted between pressure of a gas (P) and amount of gas adsorbed (a). The graph thus obtained is called adsorption isotherm which is given in Figure 3.
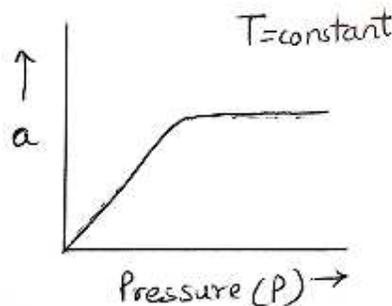

Figure 3. Adsorption isotherm

- Adsorption isobar: In this curve, pressure remains constant therefore a graph is plotted between amount of gas adsorbed (a) and temperature (T). The graph thus obtained is called adsorption isobar which is given in Figure 4.
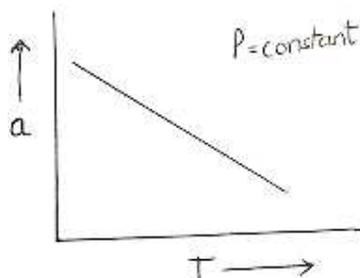
Figure 4. Adsorption isobar

- Adsorption isostere: In this curve, amount of gas adsorbed (a) remains constant therefore a graph is plotted between temperature (T) and pressure of a gas (P). The graph thus obtained is called adsorption isostere which is given in Figure 5.
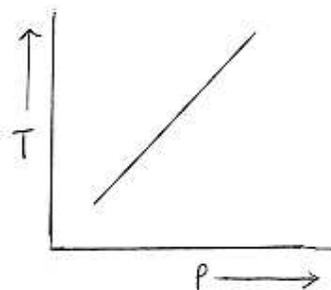

Figure 5. Adsorption isostere

8.6 ADSORPTION ISOTHERM

Adsorption isotherm as discussed above is obtained by plotting a graph between amount of gas adsorbed (a) and pressure of a gas (P) at constant temperature. Let us discuss the types of adsorption isotherm.

8.6.1 Freundlich's adsorption isotherm

Freundlich proposed an adsorption isotherm known as Freundlich's adsorption isotherm. He proposed an empirical equation that relates adsorption (a) with pressure of a gas (P) by a relation:

$$a = k\, P^{\,n}$$

where k and n are constant that depends on the nature of adsorbate (gas) and adsorbent. According to Freundlich, the value of n lies in between zero and one. It means that with

increase of pressure of a gas, the amount of gas adsorbed do not increase to the same extent as n is less than one. The plot of Freundlich's adsorption isotherm is same as Figure 3. It is clear initially with increase of pressure, adsorption increases but after a certain value of pressure (high pressure), there is no adsorption. Here Freundlich fails as according to him with increase of pressure of a gas, adsorption increases but the curve shows that at high pressure, their dependency vanishes. Thus we say that Freundlich's adsorption isotherm is valid over a certain range of pressure only.

8.6.2 Langmuir's adsorption isotherm

Langmuir proposed an adsorption isotherm known as Langmuir's adsorption isotherm in which gas is adsorbed in solid. Langmiur made the following assumptions:

- The adsorption is chemical in nature or chemisorption takes place which shows that only one layer of adsorbate is formed on the surface of adsorbent (solid).
- The surface of adsorbent (solid) possesses equivalent sites that adsorb gas molecules (one site adsorbs one gas molecule). Thus the surface of solid is homogeneous.
- Adsorbed gas molecules do not interact with each other.
- As the adsorption is chemical in nature, the adsorbed gas molecules do not move over the surface of the adsorbent i.e. gas molecules are localized.
- There exist a dynamic equilibrium between the adsorbed gas molecules and free gas molecules.

Langmuir's adsorption isotherm is given in terms of θ which is thefraction of surfacewhere adsorption takes place.

$$\theta = KP/1 + KP$$

where K is constant which is the ratio of rate constant of adsorption process to the rate constant of desorption process, P represents pressure of gas (G). Two conditions are applied to the above expression:

- Case 1: When pressure is low: $KP \ll 1$, hence KP can be neglected: $\theta = KP$

This shows that fraction of surface covered (θ) is directly proportional to pressure of the gas raised to power one. Hence it obeys first order kinetics i.e. with increase of pressure θ increases.

- Case 2: When pressure is high: $KP \gg 1$, hence KP cannot be neglected : $\theta = 1$

This shows that fraction of surface covered or adsorption does not depend on pressure of the gas and the surface pf solid (adsorbent) is covered completely by monolayer. Both these cases are represented in Figure 6.
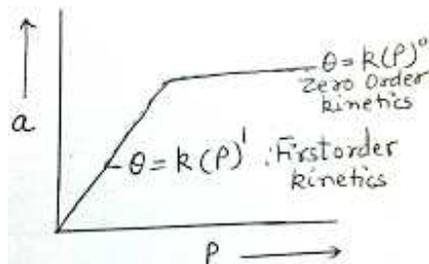

Figure 6. Langmuir's adsorption isotherm plot

At an intermediate pressure $\theta = K \, (P)^n$; where value of n is between zero and one. This expression is same as Freundlich's adsorption isotherm, thus we say that at an intermediate pressure, Langmuir's adsorption isotherm obeys Freundlich's adsorption isotherm.

8.6.3 Gibbs adsorption isotherm

We have discussed earlier that a commonly studied adsorption is gas on solid. Now coming to adsorption of a solute from a solution (liquid on solid). American physicist, J. W. Gibbs in 1878 proposed an adsorption isotherm called Gibbs adsorption isotherm where solute is adsorbed from the solution. He relates adsorption with surface tension of a solvent which changes on adding a solute. Let us consider a solution having two components (solute and solvent), free energy (G) is given by:

$$G = n_1\mu_1 + n_2 \mu_2$$

Where n_1 is the number of moles of a solvent at the surface; n_2 is the number of moles of a solute at the surface, μ_1 and μ_2 are chemical potential of solvent and solute respectively. Gibbs considers the adsorption of solute from the solution due to which there is change in free energy. Thus:

$$G = n_1\mu_1 + n_2 \mu_2 + \gamma A \; .... (1)$$

Where γ is surface tension and a represent surface area. On complete differentiation of equation 1, we obtain:

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 \, d\mu_2 + \mu_2 \, dn_2 + \gamma \, dA + A \, d\gamma \; .... (2)$$

It is clear from equation 2 that free energy (G) depends on n_1, n_2, A, T, P. Hence we can write:

$$G = f(T, P, n_1, n_2, A)$$

$$dG = (\partial G/\partial T)_{P, n1, n2, A}\, dT + (\partial G/\partial P)_{T, n1, n2, A}\, dP + (\partial G/\partial n1)_{T, P, n2, A}dn_1 + (\partial G/\partial n2)_{T, P, n1, A}dn_2$$
$$+ (\partial G/\partial A)_{T, P, n1, n2}dA$$

From thermodynamic relations:

$$1.\ (\partial G/\partial T)_{P, n1, n2, A} = -S$$

$$2.\ (\partial G/\partial P)_{T, n1, n2, A} = V$$

$$3.\ (\partial G/\partial n1)_{T, P, n2, A} = \mu_1$$

$$4.\ (\partial G/\partial n1)_{T, P, n2, A} = \mu_2$$

$$5.\ (\partial G/\partial A)_{T, P, n1, n2} = \gamma$$

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \gamma dA$$

At a particular temperature and pressure; dP = 0; dT = 0

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma dA \dots\dots (3)$$

On comparing equation (2) and equation (3);

$$\mu_1 dn_1 + \mu_2 dn_2 + \gamma dA = n_1 d\mu_1 + \mu_1 dn_1 + n_2\, d\mu_2 + \mu_2\, dn_2 + \gamma\, dA + A\, d\gamma$$

$$n_1 d\mu_1 + n_2\, d\mu_2 + A\, d\gamma = 0 \dots\dots (4)$$

According to Gibb's Duhem equation: $n_1 d\mu_1 + n_2\, d\mu_2 = 0$

The above equation is for surface of solution which undergoes modifications during adsorption. There is no change in the bulk phase of a solution as adsorption is a surface phenomenon. Therefore in bulk phase n_1^o represents number of moles of solvent and n_2^o represents number of moles of solute. According to Gibb's Duhem equation: $n_1^o\, d\mu_1 + n_2^o\, d\mu_2 = 0 \dots\dots (5)$

On multiplying equation (5) by n_1/n_1^o, we obtain:

$$n_1 d\mu_1 + n_1 n_2^o d\mu_2 / n_1^o = 0$$

Now on subtracting from equation (4), we obtain:

$$n_2\, d\mu_2 - n_1 n_2^o d\mu_2 /\ n_1^o + A\, d\gamma = 0$$

$$d\mu_2\, (n_2 - n_1 n_2^o/\ n_1^o) + A\, d\gamma = 0$$

$$d\mu_2\, (n_2 - n_1 n_2^o/\ n_1^o) = -\,A\, d\gamma$$

$$-\ d\gamma/\, d\mu_2 = (n_2 - n_1\, n_2^o/\ n_1^o)/\ A$$

The quantity on right side represents excess concentration of solute per unit area (A) of the surface. This excess concentration is represented by Γ. As Γ is for soluteso we write Γ_2 in place of Γ.Thus

$$\Gamma_2 = -\, d\gamma/\, d\mu_2 \ldots\ldots (6)$$

The chemical potential of solute is given by: $\mu_2 = \mu_2^o + RT\ \ln a_2$; where $\mu_2^o$is the chemical potential of the pure solute when it is in liquid state which is constant and $a_2$is the activity of the solute.

On differentiation: $d\mu_2 = RT\, d\ln a_2$ ($d\mu_2^o = 0$), On putting the value of $d\mu_2$in equation (6), we obtain:

$$\Gamma_2 = -\, d\gamma/\, RT\, d\ln a_2$$

$$\Gamma_2 = -\, 1/RT(\, d\gamma/\, d\ln a_2)$$

$$\Gamma_2 = -\, a_2\, /RT(d\gamma/\, da_2) \ldots\ldots (7)$$

Equation 7 represents Gibb's adsorption isotherm or equation. When graph is plotted between γ and a_2 (Figure 7), two case arises:

- Case 1: If $d\gamma/\, da_2 =$ negative; $\Gamma_2 =$ positive

  This shows that excess concentration of solute on the surface increases or adsorption increases which results in the decrease of surface tension. Here the solute is generally organic compounds that are not ionized.

- Case 2: If $d\gamma/\, da_2 =$ positive; $\Gamma_2 =$ negative

This shows that excess concentration of solute on the surface decreases or adsorption decreases which results in the increase of surface tension. Here the solute is generally highly hydrated organic compounds or inorganic electrolytes.
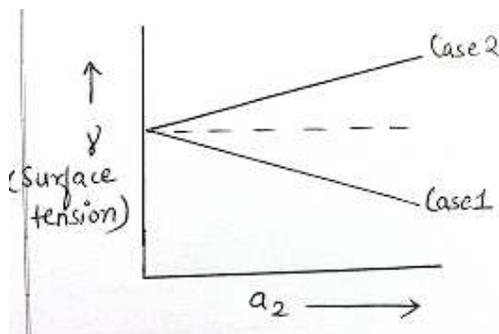
Figure 7. Gibbs adsorption isotherm plot

In this way, Gibb's relates adsorption with surface tension of a solvent that changes on adding a solute. In case of dilute solution, activity is replaced by concentration. Therefore equation 7 can be written as: $\Gamma_2 = - c_2 / RT(d\gamma/ dc_2)$

8.7 B.E.T. EQUATION

B.E.T. equation refers to Brunauer, Emmett and Teller. These are three scientists who proposed an equation called B.E.T. equation. They consider physical adsorption that a result in the formation of multilayer means that in addition to monolayer of adsorbate molecules, bimolecular layer or trimolecular layer also form.B.E.T. consider Langmuir's adsorptionbut Langmuir considered chemical adsorption that results in the formation of monolayer of adsorbate molecules while B.E.T. consider multi-molecular layer formation of adsorbate in case of physical adsorption. They proposed different postulates:

- The surface of adsorbent is homogeneous (uniform) that contains sites over which adsorbate molecules attached.
- There is no interaction among the adsorbed molecules.
- Adsorbate molecules form multi-layer on the surface of adsorbent.
- Between successive layers, there is a dynamic equilibrium.

On considering these postulates, B.E.T. derived an equation called B.E.T. equation which is given below:

$$\frac{P}{V_{total}(P^o-P)} = \frac{1}{V_{mono}C} + \frac{C-1}{V_{mono}C}\left(\frac{P}{P^o}\right)$$

Where P is the pressure of gas, $P^o$is saturated pressure of the gas;V_{mono} represents the volume of gas adsorbed over the solid adsorbent when it is covered by monolayer of the gas

(adsorbate); V_{total} is the total volume of gas adsorbed when it forms unimolecular layer, bimolecular layer, trimolecular layer and so on while C is a constant that depends on the nature of gas. When P/V_{total} $(P^o - P)$ is plotted against P/P^o, we obtain a straight line having intercept $1/V_{mono}$ C and slope $(C-1)/C$ V_{mono}. The graph thus obtained is called B.E.T. graph or B.E.T. plot which is given below in Figure 8.
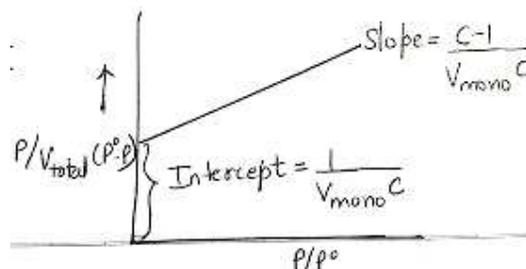

Figure 8.B.E.T. plot

Adsorption of nitrogen gas on silica gel (porous form) at -183^oC obeys B.E.T. equation. It has been observed that when P/P^o is less than 0.05 or more than 0.35, B.E.T. equation fails. By using B.E.T. equation we can determine the surface area of the adsorbent.

8.7.1 Determination of surface area

B.E.T. method of determining a surface area is easy. We know that B.E.T. equation is as follows:

$$\frac{P}{V_{total}\,(P^o - P)} = \frac{1}{V_{mono}\,C} + \frac{C-1}{V_{mono}\,C}\left(\frac{P}{P^o}\right)$$

It obeys straight line having intercept $1/V_{mono}$ C and slope $(C-1)/C$ V_{mono}

Intercept + slope = $1/V_{mono}$ C + $(C-1)/C$ V_{mono}

Intercept + slope = $1/V_{mono}$ [1/ C + $(C-1)/C$]

Intercept + slope = $1/V_{mono}$ [1+ C $-$ 1/ C]

Intercept + slope = $1/V_{mono}$

V_{mono}= 1/ Intercept + slope

From this expression, V_{mono} is calculated by knowing the value of intercept and slope.

At NTP, 22400 ml of gas contains N molecules. Therefore, 1 ml of gas contains N/ 22400 molecules. V_{mono}ml of gas contains $V_{mono} \times$ N/ 22400 molecules.

$$\text{Surface area of solid adsorbent} = A \times V_{mono} \times N/ 22400$$

Where A is the area of each adsorbed gas molecule. From this expression, we can calculate or determine surface area of solid adsorbent in which $V_{mono}$is calculated by using B.E.T. equation. By knowing the surface area, we can also determine specific surface area which is given by the relation: Specific surface area = surface area/ mass of adsorbent

8.8 CATALYTIC ACTIVITY AT SURFACE

Catalytic activity at surface refers to the activity of catalyst that occurs at the surface or that involves process of adsorption that shows catalysts works at the surface. Catalytic activity at surface refers to heterogeneous catalysis in which catalyst and reactant are in different phase. There are free valencies on the surface of catalyst by which it allow the reactants to react chemically on its surface. Catalyst activity at surface involves the following steps: suppose we have two gaseous reactant X and Y. Now when these reactants come in contact with a catalyst, they spread over the surface of the catalyst. This process is called diffusion (a). On the surface of catalyst as we know free valencies are present due to these free valencies, reactant molecules get adsorbed on the surface of the catalyst by forming a chemical bond (b). Hence the adsorption is chemical adsorption. Now after adsorption, reactant molecules (X and Y) interact with each other and form an activated complex (c). In activated complex as we know that no bond is rigid and it is a state of high energy. Activated complex thus formed decompose to give products which then diffuse from the catalyst surface by desorption thereby regenerating the free valencies on the surface of the catalyst (d). All these steps are consecutive i.e. takes place one after the other. The slowest step or rate determining step in heterogeneous catalyst is the step in which products formation takes place. The complete process is described below in Figure 9 by considering the reactant (X and Y) while catalyst is finely divided metal.
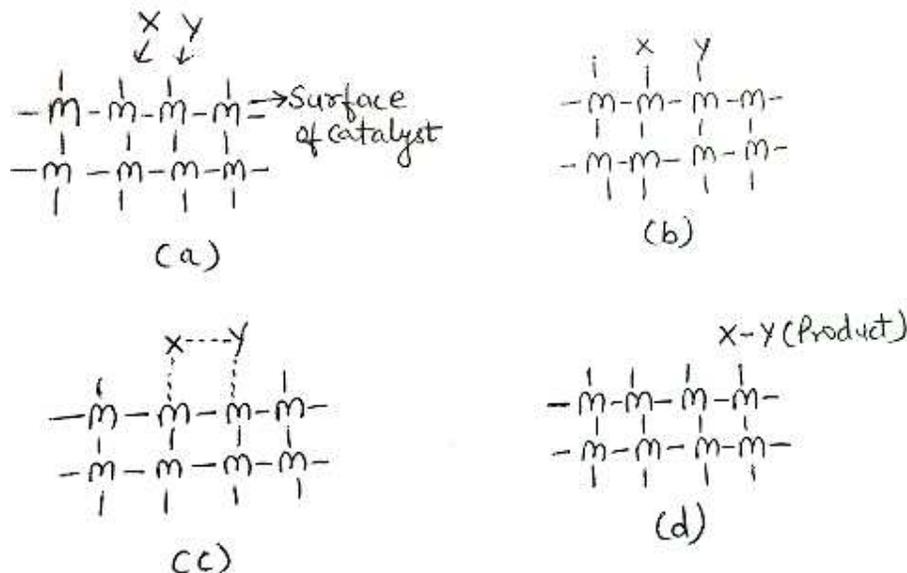
Figure 9. Catalytic activity at surface

8.9 SUMMARY

In this unit, we have discussed about the concept of catalysis in detail that includes definition, types of catalysis. Then we move to adsorption, factors affecting the adsorption, types of adsorption and various adsorption isotherms that include Freundlich's adsorption isotherm, Langmuir's adsorption isotherm, Gibb's adsorption isotherm and B.E.T. equation.

8.10 SELF ASSESSMENT QUESTIONS (SAQ)

- Fill in the blanks:

1. Positive catalyst ………. the rate of reaction.

2. Negative catalyst……… the rate of reaction.

3. The term catalysis was coined by ……….

4. Positive catalyst increases the rate of reaction by ………. the activation energy.

5. Negative catalyst decreases the rate of reaction by ………. the activation energy.

6. In Haber's process of ammonia synthesis, finely divided ………. is used as a catalyst.

7. Catalytic activity increases by adding certain substances known as ……….

8. In homogeneous catalysis, both reactant and catalyst possess ………. phase.

9. In heterogeneous catalysis, both reactant and catalyst possess ………. phase.

10. Enzymes acts as ………. catalysts.

11. Adsorption is a ………. phenomenon while absorption is a ………. phenomenon.

12. Reverse of adsorption is ……….

13. Catalyst possess ………. on their surface in order to show the phenomenon of catalysis.

14. ………. adsorption isotherm relates adsorption with surface tension of a solvent.

15. B.E.T. equation was proposed by ………., ………. and ……….

8.11 GLOSSARY

- **Catalysis**: Phenomenon by which there is a change in the rate of reaction.
- **Promotors**: Substances that increases the catalytic activity.
- **Inhibitors**: Substances that decreases the catalytic activity.
- **Positive catalyst:** Catalyst that increases the rate of reaction.
- **Adsorption:** Phenomenon of accumulation of a substance on the surface of a solid.

8.12 ANSWERS TO SAQ's

- Fill in the blanks:

1. Increases; 2. Decreases; 3. Berzelius; 4. Lowering; 5. Increasing; 6.Iron; 7. Promotors; 8. Same; 9. Different; 10. Biological; 11. Surface, bulk; 12. Desorption; 13. Free valencies; 14. Gibb's; 15. Brunauer, Emmett and Teller

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8.14 TERMINAL QUESTIONS

- Explain the phenomenon of catalysis in detail along with its classification.

- Define adsorption and discuss the various factors that affects the process of adsorption along with its classification.

- Explain B.E.T. equation along with its application in determining the surface area of the adsorbent.

UNIT 9- ELECTROCHEMISTRY-I

CONTENTS

9.8   Terminal questions

9.9   References

9.1   OBJECTIVES

After you have studied this chapter, you should be able to:

1. Describe the drawbacks of Arrhenius theory of weak electrolytes and need of a theory to explain the behavior of strong electrolytes.

2. Define activity, activity coefficients of solutions and mean ionic activity, mean activity coefficient of electrolytes.

3. Elucidate the need of mean ionic activity and mean activity coefficient for electrolytic solutions.

4. Explain the concept of ionic strength and calculate the ionic strength of electrolytic solutions.

5. List different methods to determine mean activity coefficient of electrolytes.

6. Describe different methods to determine mean activity coefficient of electrolytes

7. Describe the salient features of Debye-Huckel theory for electrolytic solution.

8. Explain ionic atmosphere of a given ion in electrolytic solution and its effect on conductivity of electrolytic solutions.

9. Apply Debye-Huckel treatment to explain electrochemistry of dilute solutions. .

9.2   INTRODUCTION

Electrochemistry is the branch of chemistry which deals with the relationship between electrical and chemical energy and their interconversion. Electrochemistry generally deals with the electrical properties of electrolytes in their aqueous solutions. There are two types of electrolytes, namely, weak and strong electrolytes. The weak electrolytes have low degree of dissociation and furnish very few ions in their solutions. Strong electrolytes have high degree of dissociation and give large number of ions in their aqueous solutions.

Arrhenius theory of electrolytes states that there is partial dissociation of electrolytes into ions in their aqueous solution. There exists a dynamic equilibrium between the ions and undissociated electrolyte. This theory is readily applicable to weak electrolytes but fails to explain the behavior of strong electrolytes. There are several limitations of Arrhenius theory out of which one is the Ostwald dilution law. This law is based on Arrhenius theory of dissociation that holds good for weak electrolytes but fails to explain the dissociation of

strong electrolytes. The limitations of Arrhenius theory have originated the need of more acceptable theory for strong electrolytes. Debye Huckel theory which assumes complete dissociation of electrolytes in aqueous solution holds interionic interactions responsible for the deviation of strong electrolytic solutions from ideal behavior. Before describing the salient features and application of this theory, we shall discuss some of the basic thermodynamic properties of the ionic solutions viz. ionic strength , activity, mean activity etc. which will help us to understand the Debye Huckel treatment of the electrolytic solutions.

9.3 ACTIVITY, ACTIVITY COEFFICIENT, MEAN IONIC ACTIVITY AND MEAN ACTIVITY COEFFICIENT OF ELECTROLYTES, IONIC STRENGTH OF ELECTROLYTIC SOLUTION

9.3.1 Activity and Activity Coefficient of Electrolytes

9.3.1.1 Activity

Thermodynamic properties of ideal solutions can be explained in terms of chemical potentials and activities. Electrolytic solutions on the other hand differ from non electrolytic solutions since electrolytes dissociate into ions in their solutions and there are strong interactions among these ions. It results into deviation from the ideal behavior.

For ideal solutions, molal concentrations can be used to describe the activity of the solution but for ionic solutions this approximation is correct only for very dilute solutions where ionic interaction in the solution can be neglected. The term activity and activity coefficients become significant in such cases.

Activity of a component of solution can be defined as its effective concentration. For an ideal solution activity of a component is equal to its concentration whereas in case of non-ideal solutions, activity (a) of a component is directly proportional to the concentration of the component.

a= γ C   where γ is called as activity coefficient of the component.

So, Activity of a component can be expressed in terms of molarity (*M*), molality (*m*) or mole fraction (χ) of the component as

$$a=\gamma.M$$

$$a=\gamma.m$$

$$a=\gamma.x$$

For ideal solutions, $\gamma=1$, so $a=C$

9.3.1.2 Activity Coefficient of a Solution:

Activity coefficient is a factor used in thermodynamics to express the properties of non-ideal solutions such as solutions of electrolytes. It can be defined as the ratio of activity of a component and concentration of the non-ideal solution: $\gamma = a/C$, where C may be in terms of molality, molarity or mole fraction . The value of γ is unity for ideal solutions so its values other than 1 indicate the extent of deviation from the ideal behavior. Since activity coefficient is a ratio it is a dimensionless quantity with no unit.

89.3.2 Mean Ionic Activity and Mean Activity Coefficient of Electrolytes

9.3.2.1 Mean Ionic Activity of Electrolytes

In case of nonelectrolytic solutions viz. solution of sugar in water, activity of solution refers to the activity of its component i.e. sugar in the solution. In similar manner, activity of salt present in solution refers to the activity of salt dissolved in the solution. Since dissolved salt dissociates into ions, activity of solution should refer to activity of cations and anions. In other words, activity of electrolytic solutions depends on activities of its ions but it is not possible to measure the activities of individual ions due to following reason. Solutions of electrolytes are electrically neutral. Any additions of cation or anions alone, if at all possible, make the solutions electrically charged. The properties of ions in such a charged solution will be different from that of electrically neutral situation. Since there is no way to measure individual effect of cations and anions so it is not possible to measure the individual ionic activity. So, activity of an electrolytic solution is defined in such a way that it includes the equal contribution from cations and anions. This definition includes a term; Mean activity of electrolytes ($\gamma_{\pm}$).

Mean activity of electrolytic solution is defined as the geometric mean of the ionic activities.

Mathematically, for an electrolyte A_xB_y which dissociates as

$$A_xB_y \longrightarrow xA^+ + yB^-$$

Where, total number of ions present in solution $=x+y$

Mean activity coefficient of electrolyte is expressed as:

$$\gamma_{\pm}=[(a_+)^x.(a_-)^y]^{\ 1/x+y}=(a_\pm)^{x+y}$$
(8.01)

Let us understand it in terms of chemical potential of a solute in a solution.

Chemical potential (μ) of a solute in an ideal solution is mathematically defined as,

$$\mu_{real}= \mu^0+RT\ \text{In}\ m \qquad\qquad (8.02)$$

Where, μ^0 is standard chemical potential of solute and m is the molality of solution.

For non-ideal (real) solutions the chemical potential of a solute is expressed in terms of its activity in the solution.

$$\mu_{real}= \mu^0+RT\ \text{In}\ a$$

$$\mu_{real}= \mu^0+RT\ \text{In}\ m.\ \gamma \qquad\qquad (\text{Since } a= m.\ \gamma\ )$$

Or, $\qquad\qquad\qquad\qquad \mu_{real}= \mu^0+RT\ \text{In}\ m+RT\ \text{In}\ \gamma \qquad\qquad (8.03)$

Substituting value from Equation No. 8.02 in Equation No.8.03,

$$\mu_{real}= \mu_{ideal}+RT\ \text{In}\ \gamma \qquad\qquad (8.04)$$

In the Equation No. 8.04,

$\mu_{real}= \mu_{ideal}$ as $RT\ ln\ \gamma \rightarrow 0$

So, the deviation from ideality lies in the activity coefficient of solute.

For an electrolytic solution, components of solution include cations and anions. The total molar Gibbs energy of an ideal solution of an electrolyte AX where A^+ is univalent cation and X^- is univalent anion, is given by the expression

$$G_{ideal}=\mu^+_{ideal}+ \mu^-_{ideal}$$

Where μ^+_{ideal} and μ^-_{ideal} are the chemical potentials of cation and anion respectively.

Similarly, total molar Gibbs energy of a non-ideal (real) solution is given by the expression

$G_{real}=\mu^+_{real}+ \mu^-_{real} \qquad\qquad (8.05)$

From Equation No. 8.04,

$$\mu^+_{real}= \mu^+_{ideal}+RT\ \text{In}\ \gamma_+ \qquad\qquad (8.06)$$

And

$$\mu^-_{real}= \mu^-_{ideal}+RT\ \text{In}\ \gamma_- \qquad\qquad (8.07)$$

Where, γ_+ and γ_- are activity coefficients of cation and anion respectively.

Substituting these values from Equation No.8.06 and 8.07 in Equation No.8.05

$$G_{real}=\mu^+_{real+}RTln\gamma_+ + \mu^-_{ideal} +RT \ln \gamma_-$$

Or $\quad G_{real}=\mu^+_{ideal+} + \mu^-_{ideal} +RT \ln \gamma_+\gamma_-$

Or $\quad G_{real}=\mu^+_{ideal+} + \mu^-_{ideal} +RT \ln \gamma_+\gamma_-$ (8.08)

So, the total molar Gibbs energy of a solution of electrolyte depends on the activity coefficients of cation and anion.

9.3.2.2 Mean Activity Coefficient of Electrolytes

An electrolyte undergoes dissociation in its aqueous solution. So the components of electrolytic solutions include cations and anions. Theoretically, like a nonelectrolytic solution, activity of an electrolytic solution should be the total contribution of activities of cations and anions. But in an electrolytic solution, since cations and anions are inseparable, it is not possible to measure their activity and activity coefficients separately.

So, for a real solution of electrolytes, a new term mean activity coefficient is introduced to assign the nonideality of solution to the constituent ions. Mean activity coefficient is defined as the geometric mean of the activity coefficients of cation and anion.

Mathematically, for a 1:1-electrolyte i.e. electrolyte having univalent cation and univalent anion, the mean activity coefficient is defined as $(\gamma_+ \gamma_-)^{1/2}$.In general, for an electrolyte A_xB_y that dissociates in the aqueous solution as follows,

$$A_xB_y \longrightarrow xA^+ +yB^-$$

The mean activity coefficient $= [(\gamma_+)^x (\gamma_-)]^{1/(x+y)}$ (8.09)

9.3.2.3 Relation between Mean Activity And Mean Activity Coefficient Of Electrolyte

For an electrolyte A_xB_y this dissociates in the aqueous solution as follows,

$$A_xB_y \rightarrow xA^+ + yB^-$$
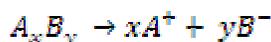
Total number of ions=x+y

$$a_{\pm} = \left((a_+)^x \cdot (a_-)^y\right)^{1/x+y}$$ (8.10)

By definition of activity coefficient, $a_+ = \gamma_+ \, m_+$ and $a_- = \gamma_- \, m_-$

Substituting it in Equation No 8.10,

$$a_{\pm} = ((\gamma_+ m_+)^x \cdot (\gamma_- m_-)^y)^{1/x+y}$$

Or, $$\qquad\qquad a_{\pm} = ((\gamma_+)^x \cdot (\gamma_-)^y)^{1/x+y}((m_+)^x \cdot (m_-)^y)^{1/x+y}$$

Or, $$\qquad\qquad a_{\pm} = \gamma_{\pm}[(m_1)^x \cdot (m_-)^y]^{1/x+y} \qquad\qquad (8.11)$$

As, the term in square bracket in Equation No. 8.11 is the geometrical mean of molality of cations and anions, it can be written as mean molality of the solution

So the Equation No. 8.11 can be rewritten as,

$$a_{\pm} = \gamma_{\pm} m_{\pm} \qquad\qquad (8.12)$$

9.4 METHODS OF DETERMINATION OF MEAN ACTIVITY COEFFICIENT OF ELECTROLYTES

In order to ascertain whether a strong electrolyte in its solution behaves as an ideal or showing deviation from ideality, it is important to know its activity. If its activity is equal to its concentration it behavior is ideal. In case, if it deviates from this behavior it has activity lower than its solution. It is easy to Calculate its activity if its   activity is known to us. There are several methods of determination of activity coefficients. Important among them are:

1. EMF measurement method
2. Measurement of Solubility of sparingly soluble salts
3. Freezing point depression measurement method
4. Debye- Huckel method

9.4.1 EMF Measurement Method

This method is explained taking the example of determination of activity coefficient of HCl.

A cell is setup by coupling Hydrogen electrode with Ag-AgCl electrode.
The hydrogen electrode contains the HCl solution for which activity coefficient is to be determined. Both the electrodes are immersed in the same solution i.e. a cell without transference is setup.

Representation of cell: Pt, H_2 (g) (P= 1atm) // HCl (m_1) AgCl(s) / Ag(s)

As the representation shows, hydrogen electrode acts as anode and Ag-AgCl electrode as cathode.

Following half cell reactions take place in the cell:

At Anode: $1/2H_2(g)=H^+(aq)+e^-$

At Cathode: $AgCl(s)+e^-=Ag(s)+Cl^-$ (*aq*)

Cell Reaction: $1/2H_2(g)+AgCl(s)=Ag(s)+H^+(aq)$ $Cl^-(aq)$
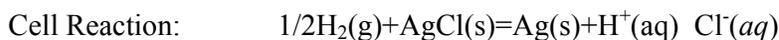
The emf of this cell can be given by Nernst equation as:

$$E = E^0 - \frac{2.303RT}{nF}\log\frac{a_{H^+} \cdot a_{Cl^-}}{\left(P_{H_2}\right)^2}$$ (8.13)

If p_{H2} $P_{H_2} = 1\,atm$ then Equation (17) becomes,

$$E = E^0 - \frac{2.303RT}{1 \times F}\log a_{H^+} \cdot a_{Cl^-}$$

Since, $a_{\pm} = (a_+ \cdot a_-)^{\frac{z}{x+y}}$

For HCl, $HCHCl \rightarrow H^+ + Cl^-$ So, $x = 1$ and $y = 1$
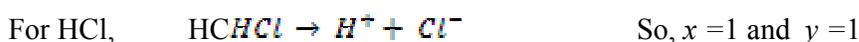
So, $a_{\pm} = (a_+ \cdot a_-)^{\frac{z}{2}}$ Or, $a_+ \cdot a_- = (a_{\pm})^2$

So,

$$E = E^0 - \frac{2.303RT}{1 \times F}\log(a_{\pm})^2$$

Or,

$$E = E^0 - 2 \times \frac{2.303RT}{1 \times F}\log(a_{\pm})$$

Since, $a = \gamma m$ And $a_{\pm} = \gamma_{\pm} m_{\pm}$

Again for HCl, $HCHCl \rightarrow H^+ + Cl^-$

                         m   *m*   *m*

So $m_{\pm} = (m_+^x \cdot m_-^y)^{\frac{z}{x+y}}$

Or, $m_{\pm} = (m_+^1 \cdot m_-^1)^{\frac{z}{2}}$

Or, $m_{\pm} = m^1 m^1$

Or, $m_{\pm} = m^{2 \times 1/2} = m$

So, $a_{\pm} = \gamma_{\pm} m$

So,

$$E = E^0 - 2 \times \frac{2.303RT}{1 \times F} \log(\gamma_\pm \, m)$$

$$E = E^0 - \frac{4.606RT}{F} \log m - \frac{4.606 \, RT}{F} \log \gamma_\pm$$

Or,

$$E + \frac{4.606RT}{F} \log m = E^0 - \frac{4.606 \, RT}{F} \log \gamma_\pm \qquad (8.14)$$

The above equation is used to determine the mean activity coefficient of the electrolyte

Procedure:

A number of electrodes having different known concentration of HCl are setup and EMF of each such setup is measured. A graph is plotted between $E + \frac{4.606RT}{F} \log m$ and $\sqrt{m}$.

So,

$$E + \frac{4.606RT}{F} \log m = E^0 - \frac{4.606 \, RT}{F} \log 1$$

Or,

$$E + \frac{4.606RT}{F} \log m = E^0$$
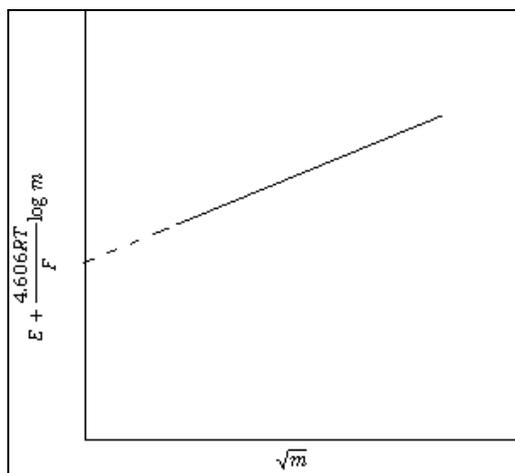
Fig.8.01: Determination of mean activity coefficient by EMF method

9.4.2 Solubility Method:

Solubility of sparingly soluble salts depends on charge and concentration of ions in solution. The mean activity coefficients of the sparingly soluble electrolytes can be determined by solubility method.This method of determination of mean activity coefficient involves the following principle.

When a sparingly soluble electrolyte A_xB_y is dissolved in water, it undergoes ionization. There exists a dynamic equilibrium between undissolved salt and its ions in a saturated solution. According to law of mass action,

$$k = \frac{(a_{A^+})^x (a_{B^-})^y}{a_{A_xB_y}} \qquad (8.15)$$

Since activity of A_xB_y is assigned as unit, equation No. 8.15 becomes

$$K=(a_{A+})^x(a_{B-})^y$$

The constant K is known as activity product of electrolyte. Since $a=\gamma c$

So, $\qquad\qquad a_+=\gamma_+C_+$

And $\qquad a_-= \gamma_-C_-$

So, $\qquad\qquad K k_\alpha = (c_+)^x (c_-)^y (\gamma_+)^x (\gamma_-)^y$

Let S is the solubility of electrolyte

Or, $\qquad\qquad K\ k_\alpha = (x)^x (y)^y (\gamma_\pm)^{x+y} S^{x+y}$

Procedure:

For the experimental determination of mean activity coefficient by solubility method, solubility of a given salt at various ionic strengths is experimentally measured. It is important to know that solubility of sparingly soluble salts is the function of ionic strength.

Solubility values are plotted against square root of ionic strength .Plot results into a straight line with positive slope (Fig. 8.02).

As, $c \to 0 \qquad \gamma_\pm \to 1\ and\ \sqrt{I} \to 0$

So, at $\sqrt{I} = 0 \qquad S_0 = k$

Once the value of k is known, it is possible to calculate the value of $\gamma_\pm$ by inserting the value of k in the equation $\quad \gamma_\pm = \frac{k}{S}$.
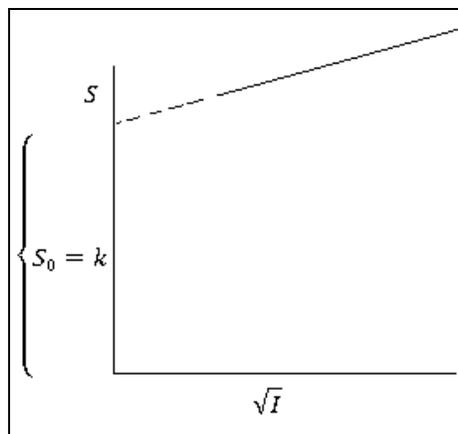
Fig. 8.02: Determination of mean activity coefficient by solubility product method

9.4.3. Freezing Point Depression Measurement Method

Activity coefficient of electrolytes can be calculated by measuring the depression in freezing points of solutions of different strength. A detailed theory of the method is given below:

If in a binary solution,1 stand for solute and 0 for solvent, then its chemical potential given by Gibbs-Duhem equation is,

$$n_o d\mu_o + n_1 d\mu_1 = 0 \tag{8.18}$$

Where,

n_o = number of moles of solvent

n_1 = number of moles of solute

$n_0 \, n_1$ μ_o = chemical potential of solvent

μ_0 μ_1 = chemical potential of solute

In general, chemical potential of a component A in a nonideal solution is given by the expression,

$$\mu\mu_A = \mu_A^0 + RT \, ln a_A \tag{8.19}$$

Where, $\mu^o{}_A$ is the Chemical potential of A in its standard state and a_A is Activity of A

Equation No. 8.18 can be expanded by using Equation No 8.19,

$$n_1 d(\mu_1^2 + RT \, ln a_1) + n_0 d(\mu_0^0 + RT \, ln a_0) = 0 \tag{8.20}$$

According to Gibbs- Duhem equation, $n_o d\mu_o + n_1 d\mu_1 = 0$, The Equation No.8.18 can be rearranged as,

$$n_1 RT d\ln a_1 + n_o RT d\ln a_o = 0$$

Dividing this equation by RT, we get,

$$n_1 d\ln a_1 + n_o d\ln a_o = 0$$

$$d\ln a_1 = -\left(\frac{n_0}{n_1}\right) d\ln a_0 \qquad (8.21)$$

The following expression correlates activity of solvent with temperature variation

$$\frac{d\ln a_0}{dT} = \frac{\Delta H_f}{RT^2} \qquad (8.22)$$

Where ΔH_f, is the Latent heat of fusion.

Depression in Freezing point is given by $\Delta T = (T_o - T)$

Where, T_o is the freezing point of pure solvent and T is freezing point of the solution.

On differentiation, $d(\Delta T) = d(T_o - T) = -d(T)$, therefore equation (8.22) can be written as

$$\frac{-d\ln a_0}{d(\Delta T)} = \frac{\Delta H_f}{RT^2}$$

$$-d\ln a_0 = \frac{\Delta H_f}{RT^2} d(\Delta T) \qquad (8.23)$$

Substituting value from Equation No. 8.23 into Equation No. 8.21 we get,

$$d\ln a_1 = \left(\frac{n_0}{n_1}\right)\left(\frac{\Delta H_f}{RT^2}\right) d(\Delta T)$$

Since $K_f = \frac{RT_0^2 M_A}{\Delta H_f \times 1000}$ where M_A is the molar mass of A

So,

$$d\ln a_1 = \frac{1}{mK_f} \times d(\Delta T) \qquad (8.24)$$

By definition, activity $a = a_\pm^v = \gamma_\pm^v m^v (x^x y^y)$ where, $v = x + y$

So, $d\ln a = v d\ln a_\pm = v d\ln\gamma_\pm + v d\ln m$

$$\frac{d\ln a}{v} = d\ln a_1 = d\ln\gamma_1 + d\ln m \qquad (8.25)$$

Or,

Substituting value from Equation No.8.25 into equation No. 8.24

$$d \ln a_{\pm} = d \ln \gamma_{\pm} + d \ln m = \frac{1}{v \, m \, K_f} \times d \, (\Delta T) \tag{8.26}$$

Let,

$$1 - \frac{1}{v \, m \, K_f} \times \Delta T = x$$

Then, on differentiation,

$$dx = -\frac{d \, (\Delta T)}{v \, m \, K_f} + \frac{\Delta T}{v \, m^2 \, K_f} \times dm$$

On rearranging the above equation,

$$\frac{d \, (\Delta T)}{v \, m \, K_f} = -dx + \frac{\Delta T}{v \, m \, K_f} \times \frac{dm}{m}$$

On substituting value of x back,

$$\frac{d \, (\Delta T)}{v \, m \, K_f} = -dx + (1 - x) \times \frac{dm}{m} \tag{8.27}$$

Equating Equation No. 8.26 and 8.27,

$$d \ln \gamma_{\pm} + d \ln m = -dx + (1 - x) \times \frac{d \, m}{m}$$

On integrating the Equation

$$\int_{1}^{\gamma_{\pm}} d \ln \gamma_{\pm} = -\int_{0}^{x} dx - x \int_{0}^{m} d \ln m$$

$$\gamma \ln \gamma_{\pm} = x \quad \int_{0}^{m} \frac{x}{m} \, dm) \tag{8.29}$$

In the actual experiments, a number of solutions of electrolyte of known concentrations are prepared and the depression in freezing point is determined for each of them. A graph is plotted between x and molality. Area under this graph gives the value of $\int_{0}^{m} \frac{x}{m} dm$ (Fig. 8.03).

This value is substituted in the Equation No 8.29 to get the value of $\gamma_{\pm}$.
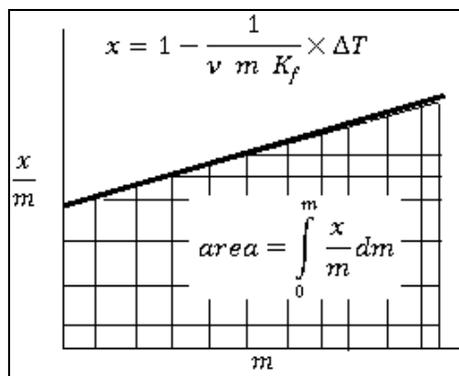
Fig. 8.03: Determination of mean activity coefficient by Freezing Point method

9.4.4 By Debye- Huckel Limiting law

In 1923, Dutch chemist Peter Debye and German physicist Erich Huckel put forward a new theory of strong electrolytes was which holds interionic forces responsible for deviation of electrolytic solutions from ideality. A detail discussion of this theory will be given in Chapter No.9.

Based on assumptions of complete dissociation of strong electrolytes at any concentration and presence of extra free energy in solution due to interionic interaction, Debye and Huckel arrived at an expression for mean activity coefficient of electrolytic solution with ionic strength of solution as below:

$$\gamma_\pm = -A\left|z_+z_-\right|\sqrt{I} \qquad\qquad (8.30)$$

Where, *A* is a constant. For water A = 0.509 at 298 K, $\gamma_\pm$ is the mean activity coefficient of electrolyte. z_+ and z_- are magnitude of valence of cations and anions respectively and I is the ionic strength of electrolytic solution.

This equation shows the value of mean activity coefficient of an electrolyte decreases with increase in the ionic strength. The decrease is higher with increase in valence and decrease in the dielectric constant of the solvent. This equation is called as a limiting law because while deriving the equation it has been consistently assumed that these approximations are applicable only when dilution approaches to infinity. So this equation is not expected to hold good for concentrated solutions. Practically, this equation has been substantiated by the data obtained for electrolytic solutions having concentration less than 1mmolkg-[1] or with ionic strength less than 0.001.

This equation can be used to determine mean activity coefficient of an electrolyte experimentally in dilute solutions.

9.4.5 Ionic Strength of Electrolytic Solutions

Many of the properties of electrolytic solution depend upon the combined effect of electrostatic field of various ions present in solution. Solubility of sparingly soluble salts, activity coefficient of electrolytes, rate of ionic reactions are some of the properties which depend on the total strength of ionic interaction in solution. For example $CaSO_4$ is a sparingly soluble salt but its solubility in sea water is much higher than that in fresh water. The reason behind this fact is the ionic interaction in sea water is higher due to high concentration of ions.

Lewis and Randall introduced a new function for electrolytic solutions in order to show the dependency of properties of electrolytic solutions on the electrostatic interactions between ions. This function of ionic concentration is known as Ionic Strength (I).

Ionic strength of a solution is defined by

$$I = I = \frac{1}{2} \sum m_i z_i^2 \qquad\qquad (8.31)$$

Where, m_i is molality of ith ion and z_i is charge on i^{th} ion.

Concept of ionic strength takes in consideration both the factors, concentration of charge and magnitude (valence) of ion. In the above example, ionic strength of sea water is around $7.2 \times 10^{-1} mol\, kg^{-1}$ against $1.5 \times 10^{-3} mol\, kg^{-1}$ that of lake water. High ionic strength of sea water can be attributed to high concentration of ions viz. concentration of Na^+ is $0.49\, mol\, kg^{-}$ whereas it's just $0.2 \times 10^{-3} mol\, kg^{-1}$ in lake water. Other ions viz. Mg^{2+}, Ca^{2+}, K^+, Cl^- etc. also add to ionic strength of sea water.

9.5 DRAWBACKS OF ARRHENIUS THEORY AND ADVENT OF DEBYE HUCKEL THEORY

9.5.1 Drawbacks of Arrhenius Theory

Swedish chemist Svante August Arrhenius (1859-1927) proposed theory of electrolytic solution in 1887. It was based on the findings of Kohlrausch Law and enthalpy of neutralization data. As stated earlier in this chapter, Arrhenius theory of electrolytes states that there is partial dissociation of electrolytes into ions in their aqueous solution and also, there exists a dynamic equilibrium between the ions and undissociated electrolyte. The dissociation increase with dilution accordingly equivalent and molar conductivity of solution

also increases with dilution. The reverse is also true which states, concentrated solutions of electrolytes have lower degree of dissociation and thus lower molar and equivalent conductivity. This theory is readily applicable to weak electrolytes but fails to explain the behavior of strong electrolytes.

Main limitations of Arrhenius theory are:

(i). Ostwald Dilution Law which is an important outcome of Arrhenius theory, holds good for weak electrolytes but fails miserably for strong electrolytes.

(ii). Degree of dissociation of strong electrolytes could be calculated from Kohlrausch Law

(i.e. $\alpha = \alpha = \lambda/\lambda_0$) and also from van't Hoff factor. In actual, when calculated from these two methods, values of degree of dissociation were far from concordant and varied to great extent which raised doubts about following of Arrhenius theory by strong electrolytes.

(iii). Enthalpy of neutralization for the reaction between a strong acid and a strong base is always constant(i.e.57.3 KJmol^{-1}). It does not change with dilution. According to Arrhenius theory, strong electrolytes (and therefore, strong acids and strong bases) have high degree of dissociation (not completely dissociated!!!) so there should be some change, howsoever small, in their degree of dissociation with dilution which should be reflected by change in enthalpy of neutralization. But there is no such observation for neutralization reaction between strong acid and strong base.

(iv). Danish physical chemist N J Bjerrum examined absorption spectra of solutions of many strong electrolytes between 1909 to 1916 and he observed no evidence for the existence of undissociated molecules of electrolytes in solution.

(v). Arrhenius theory gives no emphasis on the role of solvent in the behavior of strong electrolytes in solution. In this theory solvent remains passive and merely plays as a medium of ionic behavior.

These drawbacks rejected Arrhenius theory of strong electrolytes and posed a challenge before the scientific community to devise a new theory that could explain the behavior of strong electrolytes in solution, deviation of such solutions from ideality in more satisfactory manner.

9.5.2 Debye Huckel Theory of Strong Electrolytes

Theory of strong electrolytes was put forward by Dutch chemist Peter Debye and German physicist Erich Huckel In 1923, which addresses anomalies of Arrhenius theory. It's a mathematical treatment for the behavior of strong electrolytes in solution that holds interionic forces responsible for deviation of electrolytic solutions from ideality.

Main postulates of Debye- Huckel theory are:

(i). Complete dissociation of strong electrolytes: Strong electrolytes are completely dissociated into ions in their aqueous solutions. This is in contrast to the postulate of Arrhenius theory which states about high degree of dissociation of strong electrolytes (but not complete dissociation!!!).The 100% dissociation of strong electrolytes in aqueous solution is in agreement with Bjerrum's observation of spectroscopic studies of aqueous solution of electrolytes.

(ii).Electrostatic interactions between ions in aqueous solution and ionic atmosphere: Ions present in the solution exhibit electrostatic interaction. As a result, distribution of ions in aqueous solution is not completely at random. In the immediate vicinity of a given central ion, chances of finding a counter ion are more due to electrostatic attraction i.e. more anions tend to be present around a cation and vice versa. Thus, on an average, a given central ion is surrounded by ions of opposite charge. This results into formation of a screening layer of oppositely charged ions around a central ion. This hallow of counter ions surrounding a given central ion is termed as its ionic atmosphere. A pictorial representation of ionic atmosphere is given in Fig. 8.01.
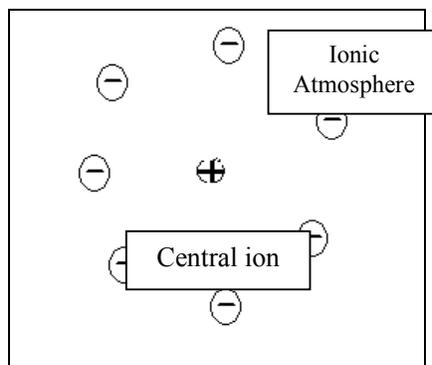

Fig. 8.01: Symmetrical ionic atmosphere around a central ion

(iii). Reason for deviation from ideality: Though the strong electrolytes are completely ionized in their aqueous solutions, they show nonideality in their behavior viz. fall in molar

conductivity. These deviations from ideality become more pronounced with increase in concentration. There are two reasons behind this deviation:

  (i) Asymmetry Effect   (ii) Electrophoretic Effect

Let us understand these two terms one by one:

  (i) Asymmetry Effect: For a stationary given central ion, its ionic atmosphere tends to be spherically symmetrical around it. When the central ion moves towards its electrode under the influence of applied electrical field, the ionic atmosphere still relaxes around it so the symmetry of ionic atmosphere gets distorted. Though this decay in ionic atmosphere is overcome by formation of new ionic atmosphere but there is a time lag between development of asymmetry and regaining of symmetry in ionic atmosphere. As a result, ionic charge density in the ionic atmosphere is more behind the moving ion than in front of it (Fig. 8.02). This distortion of symmetry of charge density and accumulation of oppositely charged ions more on back side of the ions exert a net backward electrostatic pull on the moving ion which retards it. This retardation effect of distorted ionic atmosphere on the ionic velocity is known as Asymmetry or relaxation effect. This effect is greater at higher concentration; thereby retardation of ionic mobility is higher at higher concentration.

Debye-Huckel derived expression for force due to relaxation effect on the basis of theoretical consideration of this effect.

According to them,

$$relaxation\ force = \frac{e^3 z_i K}{24 \varepsilon \varepsilon_0 k_B T} wV \tag{8.32}$$
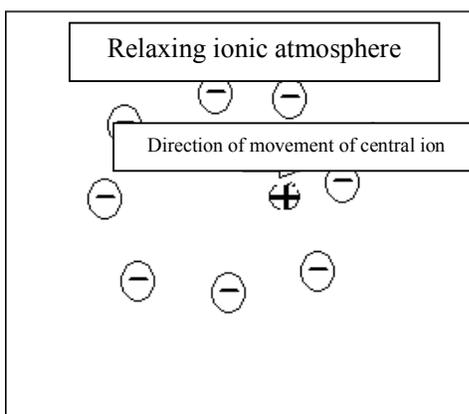

Fig.8.02: Ionic atmosphere showing asymmetry effect

  (ii) Electrophoretic effect: There is one more way by which the ionic atmosphere of a given central ion hampers its motion and retards ionic mobility. The counter ions of ionic

atmosphere are solvated i.e. the ions are attracted to solvent molecules around them by ion-dipole interactions. The ions of ionic atmosphere also move towards respective electrode under the influence of applied electrical field (and of course it's the direction opposite to the direction of movement of central ion). These moving ions tend to drag the associated solvent molecules with them. As a result, a moving central ion has to move against the stream of these counter ions and solvent molecules which move along the counter ions present in ionic atmosphere. This upstream movement further reduces the mobility of central ion. This impediment of ionic mobility of central ion due to movement of solvent molecules bound with counter ions of ionic atmosphere is termed as Electrophoretic effect.

Debye and Huckel derived expression for electrophoretic force acting on i^{th} ion applying Stokes law to the electrolytic solution. It comes out to be,

$$electrophoretic\ force = \frac{ez_i\kappa}{6\pi\eta}K_iV \qquad (8.33)$$

Various symbols used in the above Equation No.8.32 and 8.33 stands for,

k_i=Frictional coefficient on i^{th} ion due to solvent

e=Electronic charge

k=Reciprocal of thickness of ionic atmosphere

V=Potential gradient under which i^{th} ion is moving

η=Coefficient of viscosity

a number defined by, $w = z_+z_-\frac{2q}{1+\sqrt{q}}$

Where $q = z_+ . z_- \frac{\lambda_+ + \lambda_-}{z_+\lambda_- + z_-\lambda_+}$

As these two effects namely; asymmetry and Electrophoretic effect are more pronounced at higher concentration, ionic mobility is adversely affected more at higher concentration. As a result, even after complete ionization, strong electrolytic solutions show deviation from ideal behavior viz. lower molar conductivity.

Theoretical treatment of ionic movement, led Debye and Huckel to calculate the retarding forces acting on the central ion due to asymmetry and electrophoretic effect. This helped to refine the concept of conductivity of strong electrolytes and led to another important relationship in electrochemistry known as Debye-Huckel-Onsager equation. It has been treated in detail in the next chapter.
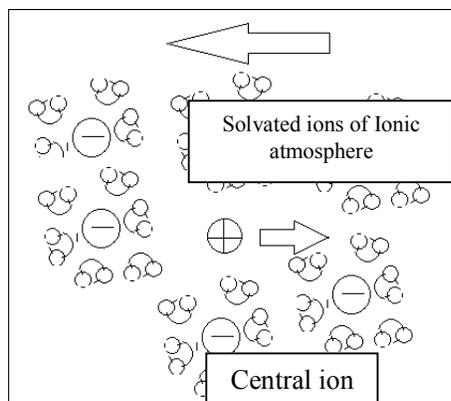
Fig.8.03: Electrophoretic effect

9.6 ELECTROCHEMISTRY OF SOLUTIONS AND DEBYE-HUCKEL TREATMENTOF DILUTE SOLUTIONS

Debye-Huckel theory is quite successful in explaining electrochemistry of dilute solutions of strong electrolytes. Debye-Huckel treatment considers complete ionization of strong electrolytes in their aqueous solution at any concentration. Unlike Arrhenius theory, the strong electrolytes are although completely ionized but not dissociated.The ions interact with each other in the solution. This interionic interaction results into extra free energy in solution. This is responsible in deviation of strong electrolytes solution from ideal behavior and decreased observed molar conductivity.

According to it, under the influence of external electrical field when a given ion moves through the solution towards its respective electrode its mobility is impeded by presence of ionic atmosphere as well as solvation of ions of ionic atmosphere. As the ion moves to new position, it tends to drag its ionic atmosphere. However, the ionic atmosphere still relaxes so the symmetry of ionic atmosphere gets distorted. There is a time lag between development of asymmetry and regaining of symmetry in ionic atmosphere. As a result, there is net increase of ionic charge density behind the moving ion than in front of it. This accumulation of oppositely charged ions exerts a net backward electrostatic pull on the moving ion which retards it. This retardation effect on the ionic velocity is known as *asymmetry* or *relaxation effect*. Apart from this, there is one more way by which the ionic atmosphere retards ionic mobility. The counter ions of ionic atmosphere are solvated. The ions of ionic atmosphere also move towards respective electrode under the influence of applied electrical field in a direction opposite to that of central ion. These moving ions tend to drag the associated solvent molecules with them. As a result, a moving central ion has to move against the stream

of these counter ions and solvent molecules which move along the counter ions present in ionic atmosphere. This upstream movement further reduces the mobility of central ion. This impediment of ionic mobility of central ion due to movement of solvent molecules bound with counter ions of ionic atmosphere is termed as *electrophoretic effect*. Magnitude of relaxation and electrophoretic effect increases with the concentration of the electrolytic solution as well as with the charge of ions present in solution.

It is worth mentioning here, Norwegian-born American physical chemist Lars Onsager modified this concept of conductivity of strong electrolytes later on. He proposed that moving ions collide with the solvent molecules of which are almost of similar dimension to that of ions. These collisions reduce the ionic mobility as this result into zigzag Brownian movement of the ions. It can be considered as frictional resistance of solvent to the ionic mobility.

A moving ion, sooner or later, gains a steady state motion at which propelling electrical force of forward motion is balanced by sum of opposing forces i.e. asymmetry force, electrophoretic force and frictional force of solvent.

In case of weak electrolytes viz. ammonium hydroxide or acetic acid, only partial hydrolysis takes place in their aqueous solution giving very few ions. These ions at normal concentration are far from each other. The large distance between these ions rules out ionic interactions and any effect such as electrophoretic or asymmetry effect arising thereby. There behavior in aqueous solution can be explained by Arrhenius theory.

9.7 SUMMARY

Electrolytes are the substances which undergo ionization in their aqueous solution. As a result electrolytic solutions are good conductor of electricity. Weak electrolytes undergo partial dissociation in water and there exists a dynamic equilibrium between ions and undissociated molecules. Conductivity and behavior of weak electrolytes can be explained on the basis of Arrhenius- Ostwald theory. Strong electrolytes on the other hand ionize but not completely dissociated at any concentration in their aqueous solution. This deviation from ideality is measured in terms of their mean activity. Depressions in freezing point, EMF method, solubility method, Debye-Huckel limiting law method are some of the methods to determine the mean activity coefficient of electrolyte. Behavior of strong electrolyte and their deviation from ideality can be explained by Debye-Huckel theory. This theory claims that ions are not free even in solution and there exists interionic interactions in electrolytic solution. These interactions lead to extra free energy in solution which can be held responsible for deviation

from ideality. Interionic interaction leads to formation ionic atmosphere around a given ion. This ionic atmosphere impedes the ionic mobility of central ion by relaxation effect an electrophoretic effect. This is why, strong electrolytes show lower molar conductivity than expected even though they are completely ionized in their aqueous solution.

9.8 TERMINAL QUESTIONS

1. List four drawbacks of Arrhenius theory that forced scientist to develop new theory of strong electrolytes.

2. What is meant by activity of a solution? Why is it necessary to use the term mean activity instead of activity for electrolytic solutions?

3. What is meant by ionic strength of a solution? Calculate ionic strength of a solution which is prepared by mixing 50ml of 0.1M NaCl and 50ml of 0.2M $CaCl_2$?

4. List four methods to determine mean activity coefficient of electrolytes? Explain principle of solubility method for determination of mean activity coefficient.

5. Explain principle and method of determination of mean activity coefficient of strong electrolytes by EMF method.

6. Write short notes on the following:

(i) Ionic atmosphere   (ii) Electrophoretic effect   (iii) Relaxation effect

7. Account for the following:

(i) Strong electrolytes, though completely ionized show lower molar conductivity than expected from their concentration.

(ii) It is better to use term 'mean activity' for electrolytic solution rather than 'activity'.

8. Explain mechanism of conductivity of strong electrolytic solution in the light of Debye-Huckel theory.

9.9 REFERENCES

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UNIT 10 ELECTROCHEMISTRY-II

CONTENTS

10.1 OBJECTIVES

After you have studied this chapter, you should be able to:

1.   Define activity, activity coefficient of components of solution.

2.   Explain need for the new term mean activity and mean activity coefficient for electrolytic solutions.

3.   Define mean activity and mean activity coefficient of electrolytes.

4.   Explain various methods of determination of mean activity coefficient of electrolytes.

5.   Explain salient features of Debye –Huckel theory of strong electrolytes including ionic atmosphere.

6.   Derive Debye- Huckel limiting law.

7.   Derive the expression for thickness of ionic atmosphere.

8.   Explain modification of Debye- Huckel theory by Onsager.

9.   Derive Debye-Huckel-Onsager equation.

10.   Explain theory of conduction of strong electrolytes.

11.   Define overvoltage and its possible causes.

12.   Define decomposition potential and its importance.’

10.2 INTRODUCTION

As we have studied in the previous chapter, weak and strong electrolytes behave differently in their aqueous solutions. Weak electrolytes undergo partial dissociation and show low molar conductivity at normal concentration. Their molar conductivity increases with dilution due to increase in degree of dissociation. This fact can be explained by Arrhenius theory of weak electrolytes. Strong electrolytes, on the other hand, undergo complete dissociation at any concentration. Still their molar conductivities are also less than that of expected value. This is expressed as their deviation from ideality. Debye-Huckel theory of strong electrolytes holds interionic interactions in solution responsible for this deviation. This behavior of strong electrolytes has been dealt in detail in the previous chapter in the light of Debye-Huckel theory. This chapter will explore the mathematical aspects of Debye-Huckel theory, Debye-Huckel limiting Law, its modification by Onsager and an important relationship between molar

conductivity and concentration of electrolytic solution i.e. Debye-Huckel-Onsager equation. At the end we shall discuss two important concepts of electrode kinetics namely decomposition potential and overvoltage. These two experimental observations help us to understand reversible nature of standard EMF and deviation from it as some of the electrode processes take place irreversibly. These two concepts will help us to explain formation of unexpected products during electrolysis and role of electrode in deciding the product of electrolysis.

10.3 ACTIVITY, ACTIVITY COEFFICIENT, MEAN IONIC ACTIVITY AND MEAN ACTIVITY COEFFICIENT OF ELECTROLYTES, IONIC STRENGTH OF ELECTROLYTIC SOLUTION

10.3.1 Activity and activity coefficient of electrolytes

10.3.1.1 Activity

Thermodynamic properties of ideal solutions can be explained in terms of chemical potentials and activities. Electrolytic solutions on the other hand differ from non electrolytic solutions since electrolytes dissociate into ions in their solutions and there are strong interactions among these ions. It results into deviation from the ideal behavior.

For ideal solutions, molal concentrations can be used to describe the activity of the solution but for ionic solutions this approximation is correct only for very dilute solutions where ionic interaction in the solution can be neglected. The term activity and activity coefficients become significant in such cases.

Activity of a component of solution can be defined as its effective concentration. For an ideal solution activity of a component is equal to its concentration whereas in case of non-ideal solutions, activity of a component is directly proportional to the concentration of the component.

Or, for a non-ideal solution, $a = \gamma C$

For ideal solutions, γ $\gamma = 1$ so, $a = C$.

Where a is the activity of a component of solution, C is its concentration and γ is called as activity coefficient of the component.

So, Activity of a component can be expressed in terms of molarity (M), molality (m) or mole fraction (χ) of the component as $a=\gamma m$, $a=\gamma M$ or $a=\gamma\chi$

10.3.1.2 Activity coefficient of a solution:

Activity coefficient is a factor used in thermodynamics to express the properties of non-ideal solutions such as solutions of electrolytes. It can be defined as the ratio of activity of a component and concentration of the non-ideal solution.

Since $a=\gamma C$ where $\gamma =a/C$ is called as activity coefficient of the component.

So, Activity of a component can be expressed in terms of molarity (M), molality (m) or mole fraction (χ) of the component as $\gamma =a/M$, $\gamma =a/m$ or $\gamma =a/x$

The symbol γ in the above expressions is known as activity coefficient.

The value of $\gamma = 1$ for ideal solutions so its values other than 1 indicate the extent of deviation from the ideal behavior. Since activity coefficient is a ratio it is a dimensionless quantity.

10.3.2 Mean ionic activity and mean activity coefficient of electrolytes

10.3.2.1 Mean ionic activity

The **activity** of nonelectrolytic solutions, such as solution of sugar in water, refers to activity of its solute component. Similarly, activity of a salt present in solution refers to the activity of cations and anions present in solution. Since there is no way to measure individual effect of cations and anions so it is not possible to measure the individual ionic activity. So, activity of an electrolytic solution is defined in such a way that it includes the equal contribution from cations and anions. This definition includes a term; Mean activity of electrolytes ($\gamma_{\pm}$).

Mean activity of electrolytic solution is defined as the geometric mean of the ionic activities.

Mathematically, for an electrolyte A_xB_y which dissociates as

$$A_xB_y \longrightarrow xA^+ +yB^-$$

Where, total number of ions present in solution $=x+y$

Mean activity coefficient of electrolyte is expressed as:

$$\gamma_{\pm}=[(a_+)^x.(a_-)^y]^{1/x+y}=(a_{\pm})^{1/x+y} \tag{9.01}$$

Let us understand it in terms of chemical potential of a solute in a solution.

Chemical potential (μ) of a solute in an ideal solution is mathematically defined as,

$$\mu_{real}=\mu^0+RT\ In\ m \tag{9.02}$$

Where, μ^0 is standard chemical potential of solute and m is the molality of solution.

For non-ideal (real) solutions the chemical potential of a solute is expressed in terms of its activity in the solution.

$$\mu_{real}=\mu^0+RT\ In\ a$$

$$\mu_{real}=\mu^0+RT\ In\ m.\ \gamma \qquad\text{(Since a= m. }\gamma\text{)}$$

Or, $$\mu_{real}=\mu^0+RT\ In\ m+\ RT\ In\ \gamma \tag{9.03}$$

Substituting value from Equation No 9.02 in Equation No.9.03,

$$\mu_{real}=\mu_{ideal}+RT\ In\ \gamma \tag{9.04}$$

In the Equation No. 9.04,

As $In\gamma$ tends to zero, $\mu_{real}=\mu_{ideal}$

For an electrolytic solution, components of solution include cations and anions. The total molar Gibbs energy of an ideal solution of an electrolyte AX where A^+ is univalent cation and X^- is univalent anion, is given by the expression

$$G_{ideal}=\mu^+_{ideal}+\mu^-_{ideal}$$

Where μ^+_{ideal} and μ^-_{ideal} are the chemical potentials of cation and anion respectively.

Similarly, total molar Gibbs energy of a non-ideal (real) solution is given by the expression

$$G_{real}=\mu^+_{real}+\mu^-_{real} \tag{9.05}$$

From equation (9.04),

$$\mu^+_{real}=\mu^+_{ideal}+RT\ In\ \gamma_+ \tag{9.06}$$

And

$$\mu^-_{real}= \mu^-_{ideal}+RT \ln \gamma_- \qquad (9.07)$$

Where, γ_+ and γ_- are activity coefficients of cation and anion respectively.

Substituting these values from Equation No.9.06 and 9.07 in Equation No.9.05

$$G_{real}=\mu^+_{real}+RT\ln\gamma_++\mu^-_{ideal}+RT \ln \gamma_-$$

$$\text{Or} \quad G_{real}=\mu^+_{ideal+}+\mu^-_{ideal}+RT \ln \gamma_+\gamma_-$$

$$\text{Or} \quad G_{real}=\mu^+_{ideal+}+\mu^-_{ideal}+RT \ln \gamma_+\gamma_- \qquad (9.08)$$

So, the total molar Gibbs energy of a solution of electrolyte depends on the activity coefficients of cation and anion both.

10.3.2.2 Mean activity coefficient of electrolytes

Theoretically, activity of an electrolytic solution should be the total contribution of activities of cations and anions. Since cations and anions of electrolytes in solution are inseparable, it is not possible to measure their activity and activity coefficients separately.

For such reasons, a new term mean activity coefficient is introduced to assign the nonideality of solution to the constituent ions. Mean activity coefficient is defined as the geometric mean of the activity coefficients of cations and anion.

Mathematically, for a uni-uni valent (1:1)-electrolyte i.e. electrolyte having univalent cation and univalent anion, the mean activity coefficient is defined as $(\gamma_+ \gamma_-)^{1/2}$. In general, for an electrolyte A_xB_y that dissociates in the aqueous solution as follows,

$$A_xB_y \longrightarrow xA^+ +yB^-$$

$$(\gamma_+ \gamma_-)^{1/2}= [(\gamma_+)^x (\gamma_-)^y]^{1/(x+y)} \qquad (9.09)$$
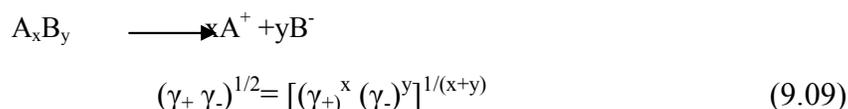
10.3.2.3 Relation between Mean activity and mean activity coefficient of electrolyte

For an electrolyte A_xB_y mean ionic activity coefficient is expressed according to (8.01).Substituting the values of activity coefficients of cations (γ_+m_+) and anions (γ_-m_-) in (8.01), the mean activity of electrolyte is expressed as:

$$a_\pm=[(\gamma_+m_+)^x(\gamma_-m_-)^y]^{1/x+y} \qquad (9.10)$$

$$= \gamma_\pm [(m_+)^x(m_-)^y]^{1/x+y} \qquad (9.11)$$

As, the term in square bracket in Equation No. 9.11 is the geometrical mean of molality of cations and anions, it can be written as mean molality of the solution.

So the Equation No. 9.11 can be rewritten as,

$$a_\pm = \gamma_\pm m_\pm \tag{9.12}$$

10.4 METHODS OF DETERMINATION OF MEAN ACTIVITY COEFFICIENT OF ELECTEROLYTES

In order to ascertain whether a strong electrolyte in its solution behaves as an ideal or showing deviation from ideality, it is important to know its activity. If its activity is equal to its concentration it behavior is ideal. In case, if it deviates from this behavior it has activity lower than its solution. It is easy to Calculate its activity if its activity is known to us. There are several methods of determination of activity coefficients. Important among them are:

5. Freezing point depression measurement method
6. EMF measurement method
7. Measurement of Solubility of sparingly soluble salts

10.4.1 Freezing point depression measurement method

Activity coefficient of electrolytes can be calculated by measuring the depression in freezing points of solutions of different strength. A detailed theory of the method is given below:

If in a binary solution,1 stand for solute and 0 for solvent, then its chemical potential given by Gibbs-Duhem equation is,

$$n_o d\mu_o + n_1 d\mu_1 = 0 \tag{9.13}$$

Where, n_o is number of moles of solvent

n_1 is number of moles of solute

n_0 n_1 μ_o is chemical potential of solvent

μ_0 μ_1 is chemical potential of solute

In general, chemical potential of a component A in a nonideal solution is given by the expression,

$$\mu = \mu_A{}^0 + RT \text{ In } a_A \tag{9.14}$$

Where, $\mu^o{}_A$ is the Chemical potential of A in its standard state and a_A is Activity of A

Equation No. 9.13 can be expanded by using Equation No 9.14,

Terms μ_1 and μ_0 of Equation No. 9.13 can be expanded by using Equation No. 9.14,

$$(\mu_1{}^o + RT \text{ in} a_1) + n_o d \, (\mu_o{}^o + RT \text{ in} a_o) = 0 \tag{9.15}$$

According to Gibbs- Duhem equation, $n_o d\mu_o + n_1 d\mu_1 = 0$, The Equation No.8.18 can be rearranged as,

$$n_1 RT d\ln a_1 + n_o RT d\ln a_o = 0$$

Dividing this equation by *RT*, we get,

$$n_1 d\ln a_1 + n_o d\ln a_o = 0 \tag{9.16}$$

The following expression correlates activity of solvent with temperature variation

$$\frac{d \ln a_0}{dT} = \frac{\Delta H_f}{RT^2} \tag{9.17}$$

Where, ΔH_f, is Latent heat of fusion.

Depression in Freezing point is given by $\Delta T = T_0 - T$

Where, T_o is the freezing point of pure solvent and T is freezing point of the solution.

On differentiation, d $(\Delta T) = d(T_o - T) = -d(T)$, therefore equation (8.22) can be written as

$$\frac{-d \ln a_0}{d(\Delta T)} = \frac{\Delta H_f}{RT^2}$$

Or,

$$-d \ln a_0 = \frac{\Delta H_f}{RT^2} d(\Delta T) \tag{9.18}$$

Substituting value from Equation No 9.18 into Equation 9.16   we get,

$$dln\ a_1 = \left(\frac{n_0}{n_1}\right)\left(\frac{\Delta H_f}{RT^2}\right)d(\Delta T)$$

Since $K_f = \frac{RT_c^2 M_A}{\Delta H_f \times 1000}$ where M_A is molar mass of A

So,

$$dln\ a_1 = \frac{1}{mK_f} \times d\ (\Delta T) \tag{9.19}$$

By definition, activity $a = a_{\pm}^v = \gamma_{\pm}^v m^v (x^x y^y)$ where, $v = x + y$

So, $d\ln a = vd\ln a_{\pm} = v\ d\ln\gamma_{\pm} + v\ d\ln m$

Or,

$$\frac{d\ln a}{v} = d\ln a_{\pm} = d\ln\gamma_{\pm} + d\ln m \tag{9.20}$$

Substituting value from Equation No 9.20 into Equation No. 9.19

$$d\ln a_{\pm} = d\ln\gamma_{\pm} + d\ln m = \frac{1}{v\ m\ K_f} \times d\ (\Delta T) \tag{9.21}$$

Let us suppose that

$$x = 1 - \frac{\Delta T}{v\ m\ K_f}$$

Then, on differentiation,

$$dx = -\frac{d\ (\Delta T)}{v\ m\ K_f} + \frac{\Delta T}{v\ m^2\ K_f} \times dm$$

On rearranging the above equation,

$$\frac{d\ (\Delta T)}{v\ m\ K_f} = -dx + \frac{\Delta T}{v\ m^2\ K_f} \times dm$$

$$\frac{d\,(\Delta T)}{v\;m\;K_f} = -dx + \frac{\Delta T}{v\;m\;K_f} \times \frac{dm}{m}$$

On substituting value of x back,

$$\frac{d\,(\Delta T)}{v\;m\;K_f} = -dx + (1-x) \times \frac{dm}{m} \tag{9.22}$$

Equating Equation No. 9.21 and 9.22,

$$d\,\ln\gamma_{\pm} + d\ln m = -dx + (1-x) \times \frac{d\,m}{m}$$

Or, $$d\,\ln\gamma_{\pm} = -dx - x\,d\ln m \tag{9.23}$$

In the above equation, $\ln\gamma_{\pm} \to 0$ as molality approaches zero and also x approaches zero.

So on integrating Equation No. 9.23

$$\int_{1}^{\gamma_{\pm}} d\,\ln\gamma_{\pm} = -\int_{0}^{x} dx - x\int_{0}^{m} d\ln m$$

$$\ln\gamma_{\pm} = -x - \int_{0}^{m}\frac{x}{m}\,dm\,) \tag{9.24}$$

In the actual experiments, a number of solutions of electrolyte of known concentrations are prepared and the depression in freezing point is determined for each of them. A graph is plotted between x and molality. Area under this graph gives the value of $\int_{0}^{m}\frac{x}{m}\,dm$.

10.4.2 EMF measurement method

A suitable cell is setup which includes the electrolyte for which activity coefficient is to be measured.

This method is explained taking the example of determination of activity coefficient of HCl.

A cell is setup by coupling Hydrogen electrode with Ag-AgCl electrode.

The hydrogen electrode contains the HCl solution for which activity coefficient is to be determined. Both the electrodes are immersed in the same solution i.e. a cell without transference is setup.

Representation of cell: Pt, H_2 (g) (P= 1atm) // HCl (m_1) AgCl(s) / Ag(s)

As per representation, hydrogen electrode acts as anode and Ag-AgCl electrode as cathode.

Following half cell reactions take place in the cell:

At Anode: ½ H_2(g) =H^+ (aq)+e^-

At Cathode: AgCl(s)+ e^- =Ag(s)+Cl^-(aq)

Cell Reaction: ½H_2(g)+AgCl(s)=H^+(aq)+Ag(s)+Cl^-(aq)

The EMF of this cell can be given by Nernst equation as:

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{a_{H^+} \cdot a_{Cl^-}}{\left(P_{H_2}\right)^2}$$ (9.25)

If P_{H2} =1 atm, Equation No. 9.25 becomes,

$$E = E^0 - \frac{2.303RT}{1 \times F} \log a_{H^+} \cdot a_{Cl^-}$$

Since, $a_{\pm} = (a_+ \cdot a_-)^{\frac{1}{x+y}}$

And for HCl, x =1 and y =1

So,

$$E = E^0 - \frac{2.303RT}{1 \times F} \log(a_{\pm})^2$$

Or,

$$E = E^0 - 2 \times \frac{2.303RT}{1 \times F} \log(a_{\pm})$$

Since a=γm, then for HCl, the above equation may be simplified as

$$E = E^0 - 2 \times \frac{2.303RT}{1 \times F} \log(\gamma_{\pm} m)$$

$$E = E^0 - \frac{4.606RT}{F}\log m - \frac{4.606\ RT}{F}\log \gamma_{\pm}$$

Or,

$$E + \frac{4.606RT}{F}\log m = E^0 - \frac{4.606\ RT}{F}\log \gamma_{\pm} \tag{9.26}$$

The above equation is used to determine $\gamma_{\pm}$ of 1:1 electrolytes

10.4.3 Solubility Method:

The mean activity coefficients of the electrolytes, particularly sparingly soluble electrolytes can be determined by solubility method as follows;

In a saturated solution of sparingly soluble electrolyte A_xB_y following equilibrium exists,

$$A_xB_y \rightleftharpoons xA^+ + yB^-$$
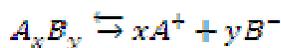
According to law of mass action,

$$k = \frac{(a_{A^+})^x (a_{B^-})^y}{a_{A_xB_y}} \tag{9.27}$$

Or,   k a_{AxBy} =(a_{A+})x$(a_{B-})^y$=K   , where a_{AxBy}=1

So Equation No. 9.27 becomes, K $k_a = (a_{A^+})^x (a_{B^-})^y$

The constant K is known as activity product of electrolyte.

Since activity a=γC

So, $a_+ a_+ = \gamma_+ c_+$

And $a_- a_- = \gamma_- c_-$

So $K k_a = (\gamma_+ c_+)^x (\gamma_- c_-)^y$

Or, $k_a = (c_+)^x (c_-)^y (\gamma_+)^x (\gamma_-)^y$

By definition, $\gamma_{\pm} = (\gamma_+^x\ \gamma_-^y)^{\frac{1}{x+y}}$

So, $(\gamma_+^x \gamma_-^y)= (\gamma_\pm)^{x+y}$

So, $K=(C_+)^x(C_-)^y (\gamma_\pm)^{x+y}$ (9.28)

Let S is the solubility of A_xB_y in water, then

Concentration of cation $C_+=xS$

And   Concentration of anion $C_-=yS$

Or, $K \ k_\alpha = (x)^x (y)^y(\gamma_\pm)^{x+y}S^{x+y}$ (9.29)

Procedure:

For the experimental determination of mean activity coefficient by solubility method, solubility of a given salt at various ionic strengths is experimentally measured. It is important to know that solubility of sparingly soluble salts is the function of ionic strength.

These solubilities are plotted against square root of ionic strength $(\sqrt{I})$.Plot results into a straight line with positive slope.

As, $c \rightarrow 0 \qquad \gamma_\pm \rightarrow 1 \ and \ \sqrt{I} \rightarrow 0$

So, at $\sqrt{I} = 0 \qquad S_0 = k$

Once the value of k is known, it is possible to calculate the value of $\gamma_\pm$ by inserting the value of k in the equation $\gamma_\pm = \dfrac{k}{S}$.

10.5 DEBYE - HUCKEL THEORY

In 1923, a new theory of strong electrolytes was put forward by Dutch chemist Peter Debye and German physicist Erich Huckel which addresses anomalies of Arrhenius theory. It's a mathematical treatment for the behavior of strong electrolytes in solution which holds interionic forces responsible for deviation of electrolytic solutions from ideality.

10.5.1 Main Postulates of Debye-Huckel theory

Main postulates of Debye- Huckel theory are:

(i). Complete dissociation of strong electrolytes: Strong electrolytes are completely dissociated into ions in their aqueous solutions. This is in contrast to the postulate of Arrhenius theory which states about high degree of ionization of strong electrolytes.The 100% dissociation of strong electrolytes in aqueous solution is in agreement with Bjerrum's observation of spectroscopic studies of aqueous solution of electrolytes.

(ii).Electrostatic interactions between ions in aqueous solution and ionic atmosphere: Ions present in the solution exhibit electrostatic interaction. As a result, distribution of ions in aqueous solution is not completely at random. In the immediate vicinity of a given central ion chances of finding a counter ion are more due to electrostatic attraction i.e. more anions tend to be present around a cation and vice versa. Thus, on an average, a given central ion is surrounded by ions of opposite charge. This results into formation of a screening layer of oppositely charged ions around a central ion. This hallow of counter ions surrounding a given central ion is termed as its ionic atmosphere.

(iii). Reason for deviation from ideality: Though the strong electrolytes are completely ionized in their aqueous solutions, they show nonideality in their behavior viz. fall in molar conductivity. These deviations from ideality become more pronounced with increase in concentration. There are two reasons behind this deviation:

    (ii) Asymmetry Effect   (ii) Electrophoretic Effect

Let us understand these two terms one by one:

    (iii) **Asymmetry Effect:** For a stationary given central ion, its ionic atmosphere tends to be spherically symmetrical around it. When the central ion moves towards its electrode under the influence of applied electrical field, the ionic atmosphere still relaxes so the symmetry of ionic atmosphere gets distorted. Though this decay in ionic atmosphere is overcome by formation of new ionic atmosphere but there is a time lag between development of asymmetry and regaining of symmetry in ionic atmosphere. As a result, ionic charge density in the ionic atmosphere is more behind the moving ion than in front of it. This distortion of symmetry of charge density and accumulation of oppositely charged ions more on back side of the ions exert a net backward electrostatic pull on the moving ion which retards it. This retardation effect of distorted ionic atmosphere on the ionic velocity is known as Asymmetry or relaxation effect. This effect is

greater at higher concentration; thereby retardation of ionic mobility is higher at higher concentration.

(iv)**Electrophoretic effect:** There is one more way by which the ionic atmosphere of a given central ion hampers its motion and retards ionic mobility. The counter ions of ionic atmosphere are solvated i.e. the ions are attracted to solvent molecules around them by ion- dipole interactions. The ions of ionic atmosphere also move towards respective electrode under the influence of applied electrical field (and of course it's the direction opposite to the direction of movement of central ion). These moving ions tend to drag the associated solvent molecules with them. As a result, a moving central ion has to move against the stream of these counter ions and solvent molecules which move along the counter ions present in ionic atmosphere. This upstream movement further reduces the mobility of central ion. This impediment of ionic mobility of central ion due to movement of solvent molecules bound with counter ions of ionic atmosphere is termed as Electrophoretic effect.

As these two effects namely; asymmetry and Electrophoretic effect are more pronounced at higher concentration, ionic mobility is adversely affected more at higher concentration. As a result, even after complete ionization, strong electrolytic solutions show deviation from ideal behavior viz. lower molar conductivity.

Theoretical treatment of ionic movement, led Debye and Huckel to calculate the retarding forces acting on the central ion due to asymmetry and electrophoretic effect. This helped to refine the concept of conductivity of strong electrolytes and led to another important relationship in electrochemistry known as Debye-Huckel-Onsager equation.

10.5.2 Thickness of Ionic atmosphere:

As postulated in Debye-Huckel theory, strong electrolytes, though completely ionized in aqueous solution, yet their ions are not entirely free. Interionic and ion-solvent interaction result in impediment of ionic mobility which is observed as decrease in molar conductivity and deviation from ideal behavior. A given central ion in strong electrolytic solution is surrounded by spherical haze of counter ions which is known as its ionic atmosphere.

Let us take a small part of this system in which a given central ion with certain positive charge, is present at point A and it is surrounded by ionic atmosphere in solution (Fig.9.01).

Let dv the small part of the volume of ionic atmosphere in the vicinity of central ion at distance r from it and ψ is the average electrical potential at this volume element. By definition, electrical potential is the work done in bringing a unit positive charge from infinity to that point.
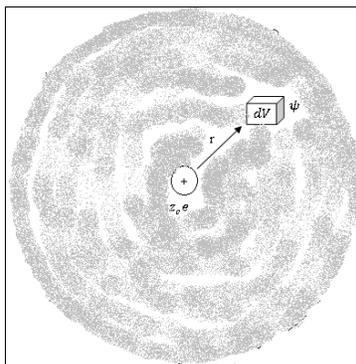
Fig. 9.01: Thickness of ionic atmosphere

So work done to bring unit positive charge from infinity to volume element=e^+ ψ

Work done to bring unit negative charge from infinity to volume element= $e^-\psi$

Where, e^+ and e^- are number of charges carried by cations and anions respectively

If N_+ and N^- are the number of cations and anions present in unit volume of electrolytic solution then according to Boltzmann distribution law.

So,

$$dN_+ = N_+ \, e-^{z_+e\,\psi/k_BT} \, dV$$

And

$$dN_- = N_- \, e-^{(-z_-e\,\psi/k_BT)} \, dV$$

Or

$$dN_- = N_- \, e^{+z_-e\,\psi/k_BT} \, dV$$

Electrical charge density (ρ) in this volume element can be defined as excess of positive charge (or negative charge) present per unit volume.

Or,

Electrical charge density in dV

$$= \frac{total\ positive\ charge\ in\ dV - total\ negative\ charge\ in\ dV}{dV}$$

$$\rho = \frac{(dN_+ \times z_+ \times e) - (dN_- \times z_- \times e)}{dV}$$

$$= \frac{(N_+ e^{-z_+ e\psi/k_B T} dV \times z_+ \times e) - (N_- e^{+z_- e\psi/k_B T} dV \times z_- \times e)}{dV}$$

$$\rho = e\left((N_+ e^{-z_+ e\psi/k_B T} \times z_+) - (N_- e^{+z_- e\psi/k_B T} \times z_-)\right) \tag{9.30}$$

For a 1:1 electrolyte, $z_+ = z_- = 1$ and $N_+ = N_- = N_i$

So, the Equation No. 9.30 becomes, $\hspace{5cm}$ (9.31)

$$\rho = e N_i \left(e^{-e\psi/k_B T} - e^{e\psi/k_B T}\right)$$

Expanding the exponential terms by formulae,

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots, -\infty < x < \infty$$

And $\hspace{1cm} e^{-x} = 1 - \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots, \ -\infty < x < \infty$

As $\frac{e\psi}{kT} \ll 1$ so higher term in the expansion can be neglected so Equation No. 9.31

becomes,

$$\rho = -\frac{2N_i e^2 \psi}{k_B T} \tag{9.32}$$

There is a well established relationship in electrostatics, between electrostatic potential ψ and

charge density ρ at a point. It is given as Poisson equation, which can be expressed as,

$$\nabla^2 \psi = -\frac{\rho}{\varepsilon_0}$$

Where, ε_o is the permittivity of vacuum (= 8.854 x 10^{-12} $C^2 N^{-1} m^{-2}$) and ∇ is Laplacian operator. If ε is the dielectric constant or relative permittivity of the medium then absolute permittivity is given as $\varepsilon_0 \varepsilon$. Poisson equation, then becomes as,

$$\nabla^2 \psi = -\frac{\rho}{\varepsilon_0 \varepsilon}$$

For rectangular coordinates

$$\nabla^2 \psi = \frac{d^2 \psi}{dx^2} + \frac{d^2 \psi}{dy^2} + \frac{d^2 \psi}{dz^2}$$

As the electrostatic potential around central ion is spherically symmetrical, the above equation can be expressed in terms of polar coordinates. Poisson equation, thus becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = -\frac{\rho}{\varepsilon_0 \varepsilon}$$

Using equation No 9.32, this equation becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = -\frac{\left(-\left(\frac{e^2\psi}{k_B T}\right)\Sigma N i z_i^2\right)}{\varepsilon_0 \varepsilon}$$

Or,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = \frac{\left(\frac{e^2\psi}{k_B T}\right)\Sigma N i z_i^2}{\varepsilon_0 \varepsilon}$$

Or,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = \frac{e^2\psi}{k_B T \, \varepsilon_0 \varepsilon}\sum N i z_i^2$$

Let

$$\frac{e^2}{k_B T \, \varepsilon_0 \varepsilon}\sum N i z_i^2 = \kappa^2$$

then the above equation becomes,

$$\kappa^2 = \frac{2e^2 N_A I}{k_B T \, \varepsilon_0 \, \varepsilon}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = \kappa^2 \, \psi \tag{9.33}$$

Since

$$\kappa^2 = \frac{e^2 \sum N_i z_i^2}{k_B T \, \varepsilon_0 \, \varepsilon}$$

And $N_i = C_i N_A$, where C_i is concentration of ith ion and N_A is Avogadro's number.

So the above equation can be rewritten as

$$\kappa^2 = \frac{e^2 \sum C_i z_i^2 N_A}{k_B T \, \varepsilon_0 \, \varepsilon} \tag{9.34}$$

Or,

$$\kappa = \left(\frac{e^2 \sum C_i z_i^2 N_A}{k_B T \, \varepsilon_0 \, \varepsilon}\right)^{\frac{1}{2}}$$

Or,

$$\kappa^2 = \frac{2e^2 \frac{1}{2}\sum C_i z_i^2 N_A}{k_B T \, \varepsilon_0 \, \varepsilon}$$

Since $\frac{1}{2}\sum C_i z_i^2 = I$, the ionic strength of solution,

So $\tag{9.35}$

$$k = \left(\frac{2e^2 N_A I}{k_B T \, \varepsilon_0 \, \varepsilon}\right)^{\frac{1}{2}}$$

Equation No. 9.33 is a differential equation. Its solution is given as:

$$\psi = \frac{A e^{-\kappa r}}{r} + \frac{A' e^{\kappa r}}{r}$$

Where A and A' are the integration constants. In order to get the values of these constants, let us consider a situation. For larger values of r, the above equation becomes,

$$\psi = \frac{Ae^{-\kappa r}}{r} \tag{9.36}$$

For dilute solutions,

$$\psi = \frac{A}{r} \tag{9.37}$$

But at the same time, at infinite dilution, potential at a point at distance *r* from the central ion will solely be the potential of central ion. It is given by,

$$\psi = \frac{z_c e}{4\pi \varepsilon \varepsilon_0 r} \tag{9.38}$$

Equating Equation No. 9.37.and 9.38 we get,

$$A = \frac{z_c e}{4\pi \varepsilon \varepsilon_0}$$

On substituting this value of A in Equation No. 9.36

$$\psi = \frac{z_c e}{4\pi \varepsilon \varepsilon_0} \frac{e^{-\kappa r}}{r} \tag{9.39}$$

In a very dilute solution, $e^{-\kappa r} = 1 - kr$ so Equation No. 9.39 becomes,

$$\psi = \frac{z_c e}{4\pi \varepsilon \varepsilon_0 r} - \frac{z_c ek}{4\pi \varepsilon \varepsilon_0} \tag{9.40}$$

Above discussion brings forth the value of the electrical potential on central ion due to its ionic atmosphere is,

$$\psi_i = -\frac{z_c ek}{4\pi \varepsilon \varepsilon_0} \tag{9.41}$$

10.5.3 Derivation of Debye-Huckel Limiting Law:

According to Debye-Huckel theory, there exists an interionic interaction in electrolytic solutions. These interactions result into extra free energy of the solution which in turn leads to deviation from ideal behaviour. This extra free energy is equal to reversible work done to give an ion (central ion) of potential ψ_i (this is the potential at central ion due to its ionic atmosphere). The extra free energy is measure of deviation from ideality and may be correlated with the ionic activity.

The chemical potential of an ith ion (μ_i) in a solution is related to concentration m_i as below:

μ_i (ideal) $= \mu_i^o$ (ideal) $+RT$ in m_i

In an electrolytic solution which is a non-ideal solution, chemical potential of ith ion (μ_i)

depends on its activity (a_i) and can be given by

μ_i (electrolyte solution) $= \mu_i^o$ $+RT$ in a_i

Substituting $a_i = m_i\gamma_i$ may result

μ_i (electrolyte solution) $= \mu_i^o$ $+RT$ in $m_i\gamma_i$

Since μ_i (ideal)$= \mu_i^o$ $+RT$ in m_i

Therefore μ_i (electrolyte solution) $-\mu_i$ (ideal) $=RT$inγ_i

The above difference in chemical potential is the extra free energy per mole. In other words, it is the energy wise contribution of the ionic atmosphere to the total energy of the one mole of central ion.

So, the extra free energy per ion $\Delta G = k_B T \, ln\gamma_i$ (9.42)

Where k_B is Boltzmann constant

The workdone (dw) to increase the charge of central ion by de at potential, ψ_i can be given by

w $dw = \psi_i de$ (9.43)

So, the reversible workdone w, to charge the ion from zero to z_c^θ is given by

w $w = \int_0^{z_c^\theta} \psi_i de$ (9.44)

According to equation 9.41, the value of the electrical potential on central ion due to its ionic atmosphere is expressed as:

$$\psi_i = -\frac{z_c e k}{4\pi \varepsilon \varepsilon_0}$$

On substituting the value of ψ_i from Equation No.9.41 into Equation No. 9.44 results

$$w = -\frac{z_c^2 e^2 k}{8\pi \varepsilon \varepsilon_0} \tag{9.45}$$

As this work done is equal to the extra free energy per ion present in the solution, Equation No. 9.42 and 9.45 can be equated and thus, we get

$$k_B T \ln \gamma_i = -\frac{z_c^2 e^2 k}{8\pi \varepsilon \varepsilon_0} \tag{9.46}$$

On substituting the value of κ from Equation No. 9.35 to 9.46, and rearranging we get,

$$\ln \gamma_i = -\frac{z_c^2 e^2 \left(\dfrac{2e^2 N_A}{k_B T \; \varepsilon_0 \; \varepsilon}\right)^{\frac{1}{2}}}{8\pi \varepsilon \varepsilon_0 \; k_B T} \sqrt{I}$$

On substituting k_B $k_B = R/N$ and further rearranging the above equation,

$$\log \gamma_i = -\frac{e^2 N_A}{2.303 \times 8\pi \varepsilon \varepsilon_0 RT} \left(\frac{2e^2 N_A^2}{RT \; \varepsilon_0 \; \varepsilon}\right)^{\frac{1}{2}} z_c^2 \sqrt{I}$$

$$\log \gamma_i = -A \, Z_c^2 \; z_c^2 \sqrt{I} \tag{9.47}$$

Where,

$$A = -\frac{e^2 N_A}{2.303 \times 8\pi \varepsilon \varepsilon_0 RT} \left(\frac{2e^2 N_A^2}{RT \; \varepsilon_0 \; \varepsilon}\right)^{\frac{1}{2}} \tag{9.48}$$

The Equation No. 9.47 is one form of Debye-Huckel Limiting Law that correlates mean activity coefficient of ith ion with its charge and ionic strength of the solution. In this equation A is a constant for a given solvent at a given temperature.

Using equation 9.48, at 298K the value of A for water is 0.507 $\mathrm{mol}^{-1/2} \mathrm{kg}^{1/2}$

If one mole of electrolyte gives x cations and y anions then by definition of mean activity coefficient,

$$\gamma_{\pm} = ((\gamma_+)^x (\gamma_-)^y)^{\frac{1}{x+y}}$$

On taking log of the above equation,

$$\log \gamma_{\pm} = \frac{x \log \gamma_+ + y \log \gamma_-}{x + y} \tag{9.49}$$

$$x \times z_+ = y \times z_- \tag{9.50}$$

Dividing RHS of Equation No. 9.49 by y we get,

$$\log \gamma_{\pm} = \frac{\frac{x}{y} \log \gamma_+ + \frac{y}{y} \log \gamma_-}{\frac{x}{y} + \frac{y}{y}} \tag{9.51}$$

On substituting values in Equation No. 9.51 from Equation No. 9.50,

$$\log \gamma_{\pm} = \frac{\frac{z_-}{z_+} \log \gamma_+ + \frac{y}{y} \log \gamma_-}{\frac{z_-}{z_+} + \frac{y}{y}}$$

Or,

$$\log \gamma_{\pm} = \frac{z_- \log \gamma_+ + z_+ \log \gamma_-}{z_- + z_+} \tag{9.52}$$

Substituting $\log \gamma_i = -A\, Z_c^2\, z_c^2 \sqrt{I}$ from Equation No. 9.47 into Equation No. 9.52,

$$\log \gamma_{\pm} = \frac{z_- \left(- A z_+^2 \sqrt{I}\right) + z_+ \left(- A z_-^2 \sqrt{I}\right)}{z_- + z_+}$$

or $\log \gamma_i = -A\, Z_+ Z_-\, z_c^2 \sqrt{I}$

As, only the magnitude of the valence is considered for calculation, this equation can be written as,

$$\log \gamma_i = -A\, |Z_+ Z_-|\, z_c^2 \sqrt{I} \tag{9.53}$$

This Equation No. 9.53 is known as Debye Huckel Limiting Law.

Practically, above equation has been substantiated by the data obtained for electrolytic solutions having concentration less than 1mmolkg^{-1} or with ionic strength less than 0.001.In this equation, *A* is a constant. For water at 298 K, A = 0.509. Other symbols have their usual significance

$\gamma_{\pm}$ The general inference that can be drawn from this equation is that the value of mean activity coefficient of an electrolyte decreases with increase in the ionic strength. The decrease is higher with increase in valence and decrease in the dielectric constant of the solvent. This equation is called as a limiting law because while deriving the equation it has been consistently assumed that these approximations are applicable only when dilution approaches to infinity. So this equation is not expected to hold good for concentrated solutions.

10.6 DEBYE-HUCKEL-ONSAGER THEORIES AND ONSAGER EQUATION

Norwegian-born American physical chemist and theoretical physicist Lars Onsager (1903-1976) improved Debye-Huckel theory in 1926. Debye and Huckel assumed the ionic movement in solution in straight line. They neglected the fact that moving ions collide with the solvent molecules and these collisions also affect their mobility along with electrophoretic and relaxation effect. Onsager considered the effect of this collision and not only modified the Debye-Huckel theory but also improved the expression derived by the former for relaxation effect.

10.6.1 Main Postulates of Debye – Huckel- Onsager Theory:

Lars Onsager modified the already proposed Debye-Huckel theory of strong electrolytes by including the effect of ionic collisions with the solvent molecules. This version of Debye-Huckel theory gets improved on adding Onsager's modification and it can be called as Debye-Huckel-Onsager theory of strong electrolytes. The main postulates of this theory are:

1. In electrolytic solution of strong electrolyte, ions moving towards respective electrode under the influence of external electrical field collide with the solvent molecules. As a result of these collisions, ions move not in straight line but in a zigzag Brownian movement. This also reduces ionic mobility.
2. This effect of Brownian movement of ions should be taken into consideration while deriving an expression for relaxation force acting on ion.

3. Three forces act upon moving ion opposite to direction of motion. These are;

(i)Relaxation force   (ii) Electrophoretic force   (iii) Frictional force of solvent

4. An ion moving with a steady velocity, experience zero resultant force as the force due the external electrical force is exactly balanced by sum of these three forces acting on opposite direction.

10.6.2 Derivation of Onsager Equation:

Onsager equation is an expression relating molar conductivity of strong electrolyte with concentration. This can be derived by considering the three forces acting on an ion moving with steady velocity in the direction opposite to external electrical field and equating sum of these forces with force due to external electrical field.

Onsager derived the expression for Relaxation force acting on the ith ion making allowance for Brownian movement.

According to it,

$$relaxation\ force = \frac{e^3 z_i \kappa}{24 \varepsilon \varepsilon_0 k_B T} wV \tag{9.54}$$

Debye and Huckel derived expression for electrophoretic force acting on i^{th} ion applying stokes law to the electrolytic solution. It comes out to be,

$$electrophoretic\ force = \frac{e z_i \kappa}{6 \pi \eta} K_i V \tag{9.55}$$

Frictional force of solvent is related to the ionic mobility as per the following relationship,

$$Frictional\ force = K_i u_i \tag{9.56}$$

Various symbols used in the above Equations from 9.54 to 9.56 stands for,

K_i=Frictional coefficient on i^{th} ion due to solvent

k= ionic mobility (i.e. the steady velocity of the ith ion)

e= electronic charge

z_i=valence of ith ion

V=potential gradient under which i^{th} ion is moving

η=coefficient of viscosity

a number defined by, $w = z_+ z_- \dfrac{2q}{1+\sqrt{q}}$

Where $q = z_+ \cdot z_- \dfrac{\lambda_+ + \lambda_-}{z_+ \lambda_- + z_- \lambda_+}$

Let us understand value of w and q for NaCl.

For NaCl, valence of cation, $z_+ = 1$ and valence of anion, $z_- = 1$.

So $q = 1 \times 1 \dfrac{\lambda_+ + \lambda_-}{\lambda_- + \lambda_+} = \dfrac{1}{2}$

So, $w = 1 \times 1 \dfrac{2 \times 1}{1 + \sqrt{\frac{1}{2}}} = 2 - \sqrt{2}$

At steady velocity of moving ion, sum of three opposing forces is equal to electrical force on it.

So, from Equation No. 9.54, 9.55, 9.56 and 9.57,

$$ez_i V = K_i u_i + \frac{ez_i \kappa}{6\pi\eta} K_i V + \frac{e^3 z_i \kappa}{24\varepsilon\varepsilon_0 k_B T} wV \tag{9.57}$$

$$\frac{ez_i V}{K_i V} = \frac{K_i u_i}{K_i V} + \frac{ez_i \kappa}{6\pi\eta} \frac{K_i V}{K_i V} + \frac{e^3 z_i \kappa}{24\varepsilon\varepsilon_0 k_B T} \frac{wV}{K_i V} \tag{9.58}$$

On rearranging the above equation,

$$\frac{u_i}{V} = \frac{ez_i}{K_i} - e\kappa \left(\frac{z_i}{6\pi\eta} + \frac{e^2 z_i}{24\varepsilon\varepsilon_0 k_B T} \frac{w}{K_i} \right)$$

Let the ith ion is moving under the influence of unit potential gradient, i.e. $V = {}^1/_{300}$ then, Equation No.9.58 becomes as,

$$u_i = \frac{ez_i}{300\, K_i} - \frac{e\kappa}{300} \left(\frac{z_i}{6\pi\eta} + \frac{e^2 z_i}{24\varepsilon\varepsilon_0 k_B T} \frac{w}{K_i} \right) \tag{9.59}$$

Equivalent conductance of ith ion (λ_i) is related to its ionic mobility (u_i) by the following expression

$$\lambda_i = u_i\, F \tag{9.60}$$

At infinite dilution, k=0, so the Equation No 9.59 may reduced to

$$u_i^0 = \frac{ez_i}{300\, K_i} \tag{9.61}$$

Also at infinite dilution, limiting equivalent conductance of ith ion $(\lambda_i{}^o)$ and its ionic mobility $(u_i{}^o)$ are related as,

$$\lambda_i{}^o = u_i{}^o \, F \tag{9.62}$$

Equating Equations No 9.61 and 9.62,

$$\frac{\lambda_i^0}{F} = \frac{ez_i}{300 \, K_i} \tag{9.63}$$

On rearrangement, 9.63 is reduced to $\qquad\qquad\qquad\qquad\qquad$ (9.64)

$$\frac{ez_i}{K_i} = \frac{300 \, \lambda_i^0}{F}$$

On substituting values from equation No (9.60) and (9.63) into (9.59) results

$$\frac{\lambda_i}{F} = \frac{\lambda_i^0}{F} - \frac{e\kappa}{300}\left(\frac{z_i}{6\pi\eta} + \frac{ew}{24\varepsilon\varepsilon_0 k_B T}\frac{ez_i}{K_i}\right) \tag{9.65}$$

Substituting the value from Equation No. 9.64 into 9.65,

$$\frac{\lambda_i}{F} = \frac{\lambda_i^0}{F} - \frac{e\kappa}{300}\left(\frac{z_i}{6\pi\eta} + \frac{ew}{24\varepsilon\varepsilon_0 k_B T} \times \frac{300 \, \lambda_i^0}{F}\right)$$

On dividing this equation by F we get,

$$\lambda_i = \lambda_i^0 - \frac{e\kappa}{300}\left(\frac{z_i F}{6\pi\eta} + \frac{ew}{24\varepsilon\varepsilon_0 k_B T} \times 300 \, \lambda_i^0\right) \tag{9.66}$$

Substituting the value of κ $\kappa = \left(\frac{e^2 \sum C_i z_i^2 N_A}{k_B T \, \varepsilon_0 \varepsilon}\right)^{\frac{1}{2}}$ from Equation No. 9.35 in Equation No. 9.66 ,

$$\lambda_i = \lambda_i^0 - \frac{e}{300}\left(\frac{e^2 \sum C_i z_i^2 N_A}{k_B T \, \varepsilon_0 \varepsilon}\right)^{\frac{1}{2}}\left(\frac{z_i F}{6\pi\eta} + \frac{ew}{24\varepsilon\varepsilon_0 k_B T} \times 300 \, \lambda_i^0\right)$$

On substituting the values of the constants and calculating, we get

$$\lambda_i = \lambda_i^0 - \left[\frac{29.15 z_i}{(\varepsilon_0 \varepsilon T)^{\frac{1}{2}}\eta} + \frac{9.9 \times 10^5}{(\varepsilon_0 \varepsilon T)^{\frac{3}{2}}} w\lambda_i^0\right]\left(\sum C_i z_i^2\right)^{\frac{1}{2}} \tag{9.67}$$

Where C_i is the concentration of ith ion and z_i is its valence. If C_i is replaced with C the equivalent per litre , thenequivalent conductance of ith ion in electrolytic solution becomes

$$\lambda_i = \lambda_i^0 - \left[\frac{29.15z_i}{(\varepsilon_0 \varepsilon T)^{\frac{1}{2}}\eta} + \frac{9.9 \times 10^5}{(\varepsilon_0 \varepsilon T)^{\frac{3}{2}}} w\lambda_i^0\right]\left(\sum C z_i\right)^{\frac{1}{2}} \tag{9.68}$$

Since equivalent conductance of an electrolyte is the sum of equivalent conductance of its constituent ions, it can be given from the above equation as,

$$\Lambda = \Lambda^0 - \left[\frac{29.15(z_+ + z_-)}{(\varepsilon_0 \varepsilon T)^{\frac{1}{2}}\eta} + \frac{9.9 \times 10^5}{(\varepsilon_0 \varepsilon T)^{\frac{3}{2}}}w\Lambda^0\right](C(z_+ + z_-))^{\frac{1}{2}} \tag{9.69}$$

Equation 9.69 is the general form of Debye-Huckel-Onsager equation for equivalent conductivity of strong electrolyte.

For a 1:1 electrolyte $w = 2 - \sqrt{2}z_+$, $z_+ = z_- = 1$ and C, the equivalent conductivity can be replaced by c, the molar conductivity as both are same for 1:1 electrolyte. Thus, the equation can be simplified as,

$$\Lambda = \Lambda^0 - \left[\frac{82.4}{(\varepsilon_0 \varepsilon T)^{\frac{1}{2}}\eta} + \frac{8.2 \times 10^5}{(\varepsilon_0 \varepsilon T)^{\frac{3}{2}}}\Lambda^0\right](c)^{\frac{1}{2}} \tag{9.70}$$

Equations 9.68 to 9.70 are the various forms of Debye-Huckel-Onsager equation. It accounts for the decrease in equivalent conductivity of strong electrolyte. First term in the square bracket implies to electrophoretic force and the second term stands for relaxation force.

The above equation for 1:1 electrolyte can be represented in a simplified Debye-Huckel-Onsager equation as,

$$\Lambda= \Lambda = \Lambda^0 - [A + B\Lambda^0]\sqrt{c} \tag{9.71}$$

Where, A and B are the constants which depend on nature of solvent and the temperature.

$$A = \frac{82.4}{(\varepsilon_0 \varepsilon T)^{\frac{1}{2}}\eta} \quad \text{and} \quad B = \frac{8.2 \times 10^5}{(\varepsilon_0 \varepsilon T)^{\frac{3}{2}}}$$

10.7 THEORY OF CONDUCTIVITY OF STRONG ELECTROLYTES

Conductivity of strong electrolytes in a solution is explained on the basis of Debye-Huckel theory in the light of Onsager's modification. According to it, strong electrolytes are completely ionized in aqueous solution at all concentrations. Oppositely charged ions thus formed, interact in solution that leads to formation of spherically symmetrical ionic atmosphere of oppositely charged ions around a given ion. So it can be said that ions are completely not free even in solution. Under the influence of external electrical field, a given ion moves through the solution towards its respective electrode. Ionic mobility is impeded by presence of ionic atmosphere as well as solvent molecules around the given ion. As the ion moves to new position, it tends to drag with it, its ionic atmosphere. However, the ionic atmosphere still relaxes so the symmetry of ionic atmosphere gets distorted. There is a time lag between development of asymmetry and regaining of symmetry in ionic atmosphere. As a result, there is net increase of ionic charge density behind the moving ion than in front of it. This accumulation of oppositely charged ions exerts a net backward electrostatic pull on the moving ion which retards it. This retardation effect on the ionic velocity is known as *asymmetry* or *relaxation effect*.

Apart from this, there is one more way by which the ionic atmosphere retards ionic mobility. The counter ions of ionic atmosphere are solvated. The ions of ionic atmosphere also move towards respective electrode under the influence of applied electrical field in a direction opposite to that of central ion. These moving ions tend to drag the associated solvent molecules with them. As a result, a moving central ion has to move against the stream of these counter ions and solvent molecules which move along the counter ions present in ionic atmosphere. This upstream movement further reduces the mobility of central ion. This impediment of ionic mobility of central ion due to movement of solvent molecules bound with counter ions of ionic atmosphere is termed as *electrophoretic effect*.

Fig.9.02: Relaxation Effect

The moving ion gets drifted towards the respective electrode under the continuous influence of the external electrical field. But this movement is not in straight line as the moving ion gets constantly collided with the solvent molecules which are almost of similar size. This results into a zigzag Brownian movement of ion towards its electrode. This retarding effect on its motion is termed as *frictional force of solvent.* A moving ion, sooner or later, gains a steady state motion at which propelling electrical force of forward motion is balanced by sum of opposing forces i.e. asymmetry force, electrophoretic force and frictional force of solvent.

10.8 DECOMPOSITION POTENTIAL AND OVERVOLTAGE

A lot of reactions take place at electrode surface. Rate of these reactions and are studied under the branch *electrochemical kinetics*. Decomposition potential and overvoltage or overpotential are the phenomena that deals with electrochemical kinetics.

10.8.1. Decomposition Potential

Le Blanc in 1893 set up an experiment in which he took an electrolytic cell and increased the external EMF gradually and measured the current flowing through the cell and also the potential across it simultaneously. Proceeding, in this manner, he plotted current density against potential (cell voltage). Current density is defined as, magnitude of current per unit area of the electrode. The graph thus obtained has been shown in Fig. 9.03.
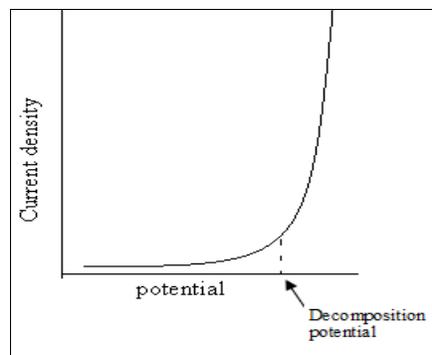
Fig. 9.03: Decomposition potential

Such a graph of current density versus potential shows, potential keeps on increasing regularly and rapidly but there is no appreciable increase in the current density. But there is a potential at which there is sudden rise in the current density and beyond which the potential subsequently changes by only a small degree. This potential is known as decomposition potential of the solution. This potential can be obtained by extrapolation of the steeping part of the curve to the potential axis. Theoretically, decomposition potential of a solution can be defined as the minimum potential that must be applied between a pair of electrodes to pass the current of appreciable strength.

When such experiments were performed with aqueous solutions of a number of acids and bases taking smooth platinum as anode and cathode, following facts were evident:

1. Decomposition potential was almost constant irrespective of nature of electrolyte. It was in the vicinity of 1.70 V.
2. Evolution of hydrogen and oxygen gases was observed with the passage of current in each case.

These observations led le Blanc conclude that the same process takes place during the experiment in all electrolytic solution under study. The only common process to these electrolytic solutions could be the decomposition of water leading to formation of hydrogen and hydroxyl ions. Their discharge at cathode and anode respectively form hydrogen and oxygen gases. However, decomposition potential of solutions has no theoretical significance as it depends on two individual electrodes, resistance of solution and concentration of solution.

10.8.2. Overvoltage or Over Potential

10.8.2.1 Overvoltage: definition and explanation

Le Blanc's reveals decomposition potential for a number of aqueous solutions of acids and bases remain around 1.70 V over platinum electrodes. The constant value of decomposition potential attributes to the similar reaction i.e. decomposition of water and discharge of hydrogen and hydroxyl ions in all the solutions.

The reaction that occurs during this electrolysis is,

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g) \qquad \Delta G^0 = 23.81 \, KJ \, mol^{-1}$$

Theoretical decomposition potential for this reaction can be calculated as follows:

Since, $\Delta G = -nFE^o$

Or,

$$E^0 = \frac{-\Delta G^0}{nF}$$

On substituting the values, $E^o \quad E^0 = \frac{-23.81 \times 10^3}{2 \times 96500} = 1.23$ V

This theoretical value of decomposition is quite different in fact quite lower than the observed value that is 1.70 V.

German scientist Caspari in 1899 studied the dependence of decomposition potential on the nature of the electrodes. Caspari performed the experiments similar to those of Le Blanc using different metals as electrode and concentrated on the relation of potential at which evolution of oxygen and hydrogen was actually observed with the nature of electrode.

The difference between the potential of the electrode when the gas evolution is actually observed i.e. the observed decomposition potential and its theoretical reversible value is known as over voltage or over potential. It is generally represented by η. Original word used by Caspari for this difference in potential was 'Uberspannung' in German which was translated as "Overvoltage".

In this case, for smooth platinum electrodes, Over voltage, η =1.70 V – 1.23 V = 0.47 V.

Caspari's studies revealed that overpotential (overvoltage) value for the same reaction changes with the change in nature of electrode. e.g. hydrogen overpotential at smooth platinum is 0.09 V whereas at platinised platinum it is 0.00 V. It is as high as 0.78 V at mercury electrode.

10.8.2.2 Types of Overvoltage

Different types of overvoltage come across in the course of electrochemical reaction. These can be classified as:

(i) Activation overvoltage (ii) Resistance overvoltage (iii) Concentration over voltage
Let us discuss them one by one.

10.8.2.2.1 Activation overvoltage

If a reaction at electrode is has high activation energy, it proceeds with slow transfer of electrode. As a consequence, in order to get the product at electrode at an appreciable rate, extra potential over the equilibrium potential is must be applied. This extra potential gives the activation over voltage.

10.8.2.2.2 Resistance overvoltage

Electrolytic solution around an electrode is of limited conductivity and it resists the flow of current. Therefore, there is drop of potential between two electrodes. It is known as resistance or ohmic over voltage. It can also be caused by formation and deposition of a resistive film of product on electrode.

10.8.2.2.3 Concentration overvoltage

It is caused by change in concentration around an electrode during an electrochemical reaction. The imbalance in number of ions discharged and produced at an electrode cause decrease in concentration in the vicinity of cathode or increase in concentration around anode. As a result electrodes are said to be polarized and need extra potential to eliminate this polarization and maintain current flow. This extra potential is known as concentration over voltage. Stirring the solution around an electrode reduces the extent of concentration over- voltage.

10.9 SUMMARY

Arrhenius theory was unable to explain the behavior of strong electrolytes. This is because, strong electrolytes, though completely ionized but remain in undissociated state at all concentrations. Molar conductivity of the solution of strong electrolyte is lower than that is expected. For such reasons, the concentration of strong electrolytes in solution is expressed in terms of activity which is the effective concentration of a solution. The ratio of activity and concentration of a component of solution is known as its activity coefficient. Since, failure of Arrhenius theory, a new theory was put forward by Debye and Huckel and later on modified by Onsager to explain the behavior of strong electrolytes through introducing the concept of interionic attractions. The ionic interaction result into formation ionic atmosphere around a given ion in solution. This ionic atmosphere predominantly consists of oppositely charged ions. It impedes the mobility of central ion by relaxation effect and electrophoretic effect. The interionic interactions are responsible for decrease in molar conductivity and deviations of solutions of strong electrolytes from ideal behavior. Onsager further added to Debye-Huckel theory, the role of ionic collisions with solvent molecules which result into Brownian movement of the ions and further decelerate a moving ion. Relation between mean activity coefficient of solution with the ionic strength and valence of the ions is expressed through -Huckel limiting law. At the last part of the chapter, two basic experimental observations of electrolysis, namely decomposition potential and overvoltage have been discussed. Over voltage of an individual electrode can be the collective contribution from three overvoltage namely; activation, resistance and concentration over voltage.

10.10 TERMINAL QUESTIONS

1. List four methods to determine mean activity coefficient of electrolytes? Explain principle of determination of mean activity coefficient by depression in freezing point.

2. Explain salient features of Debye-Huckel theory. How is it different from Arrhenius theory?

3. Explain Onsager's modification of Debye-Huckel theory of strong electrolytes.

4. Account for the following:

(i) Weak electrolytic solutions do not face electrophoretic and relaxation effect.

(ii) $CaSO_4$ is a sparingly soluble salt but its solubility in sea water is several times higher than that of in lake water.

(iii) During electrolysis of aqueous NaCl, Cl_2 is liberated at anode instead of O_2 though its E^0 value is more positive than the later.

5. Derive expression for thickness of ionic atmosphere.

6. Derive Debye- Huckel Limiting law. Why is it called as limiting law?

7. Derive Onsager equation of molar conductivity of strong electrolyte.

8. What is meant by decomposition potential? What was Le Blanc's explanation for its constant value?

9. Define overvoltage. What are the reasons for overvoltage?

10. Explain mechanism of conductivity of strong electrolyte.

10.11 REFERENCES

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