# MARUDHAR KESARI JAIN COLLEGE FOR WOMEN (AUTONOMOUS) VANIYAMBADI PG Department of Chemistry

III B.Sc. Chemistry- semester- V

**E-Notes** 

### COURSENAME: PHYSICAL CHEMISTRY-I CODE: FCH53

### UNIT-II COLLIGATIVE PROPERTIES AND CHEMICAL EQUILIBRIUM

Colligative properties - Lowering of vapour pressure - Osmosis and osmotic pressure -Thermodynamic Derivation of Elevation of boiling point and Depression of freezing point -Determination of molar mass - Van't Hoff factor - Chemical Equilibrium - Law of Chemical Equilibrium - Thermodynamic derivation of Law of Chemical Equilibrium. Relationship between Kp,Kc and Kx for reactions involving Ideal Gases - Van't Hoff Reaction Isotherm - Temperature Dependence of Equilibrium Constant - Van't Hoff Isochore - Le Chatelier's Principle and Its Applications.

**Learning Objective:**To impart knowledge about the Colligative properties and Van't Hoff Reaction Isotherm

**Learning Outcome:** To understand thelaw of Chemical equilibrium and Van't Hoff isotherm and  $\Box$  Determine molar mass from the colligative properties.

### **COLLIGATIVE PROPERTIES AND CHEMICAL EQUILIBRIUM:**

Colligative properties are solution properties that depend on the concentration of solute particles, but not on the type of particles. Chemical equilibrium is the state in which the concentrations of reactants and products in a chemical reaction do not change over time.

### Colligative properties and vapor pressure

In a closed container, a liquid will evaporate until the pressure of the vapor phase above the liquid is equal to the pressure of the molecules returning to the liquid state. This pressure is called the equilibrium vapor pressure.



#### **UNIT-III**

### **Colligative properties and Chemical Equilibrium**

### **Colligative properties**

- 1) When certain amount of non-volatile solute added to volatile solvent; the **vapour pressure** of the solution is decreased as well as **chemical potential** ( $\mu$ )
- These vapour pressure depends upon only solvent not for solute nature such a solution is called ideal solution that obey Raoult's law.
- 3) The vapour pressure relates the following properties of solution, they are
  - I. Lowing of vapour pressure  $(\Delta p)$
  - II. Osmosis and Osmotic pressure  $(\pi)$
  - III. Elevation of boiling point  $(\Delta T_b)$
  - IV. Depression of freezing point  $(\Delta T_f)$
- 4) All this properties depends on the number of solute particles related to the total number of particles present in the solution, is called Colligative properties.

### I. Lowering of vapour pressure( $\Delta p$ )

The vapour pressure of the solvent in solution is less than that of pure solvent. Consider x<sub>1</sub> be solvent and x<sub>2</sub> is solute in solvent

#### According to Raoult's law

Where p is vapour pressure of solvent

x is mole fraction of solution (or concentration)

k is proportionality constant

2) For pure solvent  $x_1 = 1.0$  and p become  $p^0$ , substitute these value in Eq: (1)

$$p^0 = k \ (1.0)_1$$

$$k = p^0 x_1$$

Substitute k values in Eq: (1)

Where  $p^0$  is vapour pressure of pure solvent

3) When solute added to solvent, it reduced the vapour pressure of solvent ( $\Delta p$ ) is given as

$$\Delta p = p^0 - p$$
  
=  $p^0 - p^0 x_1$   $\therefore p = p^0 x_1$ 

$$\Delta p = p^{0}(1 - x_{1}) \dots (3)$$
Knowing that  $x_{2} = (1 - x_{1})$ 

$$\Delta p = p^{0}x_{2} \dots (4)$$

$$x_{1} - x_{2} = 1$$

$$x_{2} = (1 - x_{1})$$

4) In a solution contain several non-volatile solute, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes.

Eq: (4) can be written as

 $\Delta p$ 

 $\frac{1}{n^0}$  is called **relative lowering of vapour pressure** and is equal to the mole fraction (x) of the solute.

Eq: (5) become

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Where  $n_1$  and  $n_2$  are the number of moles of solvent and solute respectively, for dilute solution,  $n_2 < n_1$ , hence  $n_2$  is negligible

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 $n_{2}$ 

$$\frac{p^{0}-p}{p^{0}} = \frac{n_{2}}{n_{1}} \dots (7)$$

$$\boxed{\frac{p^{0}-p}{p^{0}} = \frac{w_{2} \times M_{1}}{M_{2} \times w_{1}}}_{Where , w \text{ are mass and } M, M_{1 - 2}} \text{ are molar}$$

$$= \frac{w_{2} \times M_{1}}{M_{2} \times w_{1}}$$

$$= \frac{w_{2} \times M_{1}}{M_{2} \times w_{1}}$$

$$= \frac{w_{2} \times M_{1}}{M_{2} \times w_{1}}$$

mass of solvent and solute respectively.

Eq: (8) is known as lowering of vapour pressure is colligative properties

#### **Osmosis and Osmotic pressure** II.

#### **Osmosis:**

1) When two different concentrated solution are separated by membrane, spontaneous movement of solvent particles from dilute solution (pure solvent) to concentrated solution across the membrane is known as Osmosis. (in Greek 'Osmos' = to push).

 The membrane has sub microscopic holes or pores that allows only the smaller particles not bigger molecules such a property of membrane is called semipermeable membrane (SPM).

Ex: Cellophane and cellulose acetate

3) Osmosis is prime importance in living organisms.

### Osmotic pressure $(\pi)$



- The osmosis process is just stop by applying external force or pressure at high concentrated solution side that external pressure is called Osmotic pressure.
- Since Osmotic pressure depends on the number of solute molecules, it is colligative property.
- At constant temperature (T), Osmotic pressure (π) directly proportional to the concentration (C) of the solution is given by Boyle's –Vant Hoff law,

 $\therefore \pi \ a \ C$  (*C* is molar concentration)

4) At constant concentration, the Osmotic pressure  $(\pi)$  directly proportional to the temperature (T), is given by Charle's Vant Hoff law.

#### $\therefore \pi \ \mathrm{a} \ T$

Combining these two law,

 $\pi$  a *CRT* (*or*)  $\pi$  = *CRT* .....(1)

Where  $\pi$  is Osmotic pressure

*C* is molar concentration

R is gas constant

T is temperature

The above Eq: (1) is known as **Vant Hoff factor** 

Molar concentration (C) can be taken as  $\binom{n_2}{V}$ 

$$\pi = \binom{n_2}{V}RT$$

Where  $n_2$  is mole of the solute  $[n_2 = \frac{w_2}{M_2}]$ 

5) Eq: (2) is the Osmotic pressure of the solution using this equation; molar mass of the solute can be determined.

$$M_2 = \left(\frac{\underline{w_2} \, \underline{RT}}{\pi \times V}\right)$$

#### **Characteristic of Osmotic pressure:**

- The minimum external pressure is applied at high concentrated solution side to just stop the osmosis process, if two different concentrated solution separated by semipermeable membrane.
- If two solution having same osmotic pressure at a given temperature, are called isotonic solution (solution having same concentration)
- The solution having lower or higher Osmotic pressure compare to other solution, is said to be hypotonic or hypertonic solution respectively.
- 4) Osmotic pressure is prime important in living organism

Ex:

- In our blood plasma, osmotic pressure is balanced by  $Na^+$  and  $K^+$  ion (equivalent to 0.9% M/V is normal saline solution),
- if we place the blood cell in more than 0.9% *M/V NaCl* solution (hypertonic) water will flow out from the cells to shrink.
- If the salt concentration is less than 0.9%, (**Hypotonic solution**), water will flow into the blood cells to swell.

#### Thermodynamic derivation of Elevation of Boiling point

1) When a non-volatile solute is added to a pure solvent, the **vapour pressure** of the solvent is **decreased and its boiling point**  $(T_b)$  is raised (elevates).

2) At a given temperature (*T*) and pressure (*P*), chemical potential ( $\mu$ ) is same in both liquid and vapour phase of solvent when exhibit in equilibrium.

$$\mu_1^l = \mu_1^v$$

 At any temperature, boiling point of solvent, solution and it chemical potential(µ) at higher temperature would be different and equal at equilibrium.

$$d\mu_1^l = d\mu_1^v$$

The chemical potential of the solvent in solution depends upon T, P, and concentration (mole fraction)

$$\mu_1^l = f(T, P, x_1)$$
 .....(1)

Chemical potential in the vapour phase would depend only on T and P

$$\mu_1^v = (T, P)$$
 .....(2)

Differentiate Equ: (1) w.r.t T, P and concentration (x)

Also differentiate Equ: 2 w.r.t T, P only

At constant pressure, dP = 0, so that the Equ: (5) become

Where  $\Delta \overline{S}_{v}$  is the partial molar entropy of solvent vapour.

For ideal solution chemical potential  $\mu$  is

$$\mu_1 = \mu^0 + RT \ln x_1$$

Differentiate w.r.t  $x_1$  at constant T and P

$$\left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,P} = \frac{RT}{x_1}.$$

From Equ: (6) & (7)

But 
$$\Delta \overline{S}_v = \frac{\Delta \overline{H}_v}{T}$$
 substitute in Equ:(8)

$$\frac{\Delta H_{\nu}}{T} dT = -RT d \ln x_1$$

$$-\left(\frac{\Delta H_{\nu}}{RT^2}\right) dT = d \ln x_1.....9$$

Where  $\Delta \overline{H}_{\nu}$  is the partial molar enthalpy of solvent vapour.

We assumed that  $\Delta \overline{H}_{\nu}$  is independent at give temperature, so

Equ: (9) is integrated from  $x_1 = 1$ ,  $T = T_b$  (for pure solvent Boiling point)

 $x_1 = x_1, T = T$  (for solution Boiling point)

$$\int_{1}^{x_{1}} d\ln x_{1} = -\frac{\Delta \overline{H}_{v}}{R} \int_{T_{b}}^{T} \frac{dT}{T^{2}}$$

$$\ln x_{1} = -\frac{\Delta \overline{H}_{v}}{R} \left[\frac{1}{T} - \frac{1}{T_{b}}\right]$$

$$\ln x_{1} = -\frac{\Delta \overline{H}_{v}}{R} \times \frac{\Delta T_{b}}{T T_{b}}$$
(10)

Where  $\Delta T_b = T - T_b$  is elevation of boiling point.

For dilute solution  $T \approx T_b$  and  $\ln x_1 = \ln(1 - x_2) \approx -x_2$  where  $x_2$  is small, so that Equ: (10) become

For infinitely dilute binary solution  $\Delta \overline{H}_v = \Delta H$ 

$$\Delta T_b = \left(\frac{R T_b^2}{\Delta H_v}\right) \chi_2....(12)$$

Where  $\Delta H_v$  is the molar heat of solvent vapour.

#### $x_2$ is mole fraction

$$x_{2} = \frac{n_{2}}{(n_{1}+n_{2})} \qquad n_{2} < n_{1} \text{ so it is negligible}$$

$$x_{2} = \frac{n_{2}}{n_{1}} \qquad \boxed{\frac{n_{2}}{n_{1}} = \frac{w_{2}}{M_{2}} \times \frac{M_{1}}{w_{1}}}$$

$$x_{2} = \frac{w_{2}}{M_{2}} \times \frac{M_{1}}{w_{1}}$$

If *m* mole of the solute dissolved in 1kg of the solvent. *i.e.*,  $m = \frac{w_2}{M_2}$  and  $w_1 = 1kg$ , then

$$x_2 = \frac{m \times M_1}{1kg}$$

Where m is molality of the solution.

From above expression, Equ: (12) may be written as

$$\Delta T_b = \frac{R T_b^2 M_m}{\Delta H_v}$$

 $k_b = \frac{R T_b^2 M_1}{\Delta H_v}$  is constant for a given solvent called as **molal boiling point elevation constant** 

 $\Delta T_b = k_b m \quad (13)$ 

According to Equ: (13), the elevation of boiling point depends only on the molality of the solute and is independent of the nature of the solute. So it is a colligative property.

### Thermodynamic derivation of Depression of Freezing point

- 1) There is an equilibrium between solid and liquid at freezing point of pure liquid.
- 2) So that vapour pressure of solid and vapour phase are equal and also its chemical potential, escaping tendencies.
- 3) When a non-volatile solute added to the liquid, the escaping tendency of solvent molecules from liquid to solid phase decrease whereas the reverse escaping tendency from solid to liquid remains unaffected. So that liquid equilibrium is losses.
- 4) In order to restore the equilibrium, at certain lower temperature, the two escaping tendencies become equal and equilibrium is formed.

The chemical potential

$$\mu = \mu_0 + RT \ln x$$

At equilibrium,  $\mu_1^s = \mu_1^l$ 

Where  $\mu_1^{s}$  is chemical potential of solid phase

 $\mu_1^l$  is chemical potential of liquid phase

$$\mu_1 = f(T, P, x_1)$$
 .....(2)

A small changes in  $T, P, x_1$  at equilibrium is

Differentiate Equ: 1) w.r.t T, P only

$$d\mu_1^s = \left(\frac{\partial \mu_1^s}{\partial T}\right)_P dT + \left(\frac{\partial \mu_1^s}{\partial P}\right)_T dP \dots 3$$

Similarly differentiate Equ: (2) w.r.t T, P and concentration  $x_1$ 

$$\stackrel{l}{=} \begin{pmatrix} \partial \mu^l \\ 1 \end{pmatrix}_{P,1} dT + \begin{pmatrix} \partial \mu^l \\ 1 \end{pmatrix}_{T,1} dP + \begin{pmatrix} \partial \mu^l \\ 1 \end{pmatrix}_{T,P} dx_1 \dots (4)$$

At constant P, dP = 0 so that Equ: (3) & (4) become

$$d\mu_1^s = \left(\frac{\partial \mu^s}{\partial T}\right)_p dT$$
$$d\mu_1^s = -\overline{S}_1^s dT$$

For infinite dilution binary solution,  $\overline{S}_1 = S$  so that above Equ. become  $d\mu^s = -S^l dT$ .....

Similarly

$$d\mu_{1}^{s} = -S^{l} dT.....(5)$$

$$d\mu_{1}^{l} = \left(\frac{\partial l}{\partial T}\right)_{P,1} dT + \left(\frac{\partial \mu^{l}}{\partial x_{1}}\right)_{T,P} dx_{1}$$

$$= \frac{l}{1} - S \ \overline{d}_{1}^{l} + \left(\frac{\partial \mu^{l}}{\partial x_{1}}\right)_{T,P} dx_{1}$$

$$\therefore \overline{S}_{1} = S \text{ so that above Equ. become}$$

For ideal solution chemical potential  $\mu$  is

$$\mu_1 = \mu^0 + RT \ln x_1$$

Differentiate w.r.t  $x_1$  at constant *T* and *P* 

$$\left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,P} = \frac{RT}{x_1}$$
.....(7)

From Equ: 6 & 7

 $\Delta H_{fus}$  is the molar enthalpy of fusion.

Assuming  $\Delta H_{fus}$  is constant at given temperature, so Equ: (10) is integrated from

 $\Delta T_{fus} = (T_0 - T_{fus})$  is the depression of freezing point of the solution.

For dilute solution  $T_0 = T_{fus}$  and  $\ln x_1 = \ln(1 - x_2) \approx -x_2$  where  $x_2$  is small, so that Equ: (1) become

Where  $\Delta H_{fus}$  is the molar heat of solvent vapour.

 $x_2$  is mole fraction

$$x_{2} = \frac{n_{2}}{(n_{1}+n_{2})} \qquad n_{2} < n_{1} \text{ so it is negligible}$$

$$x_{2} = \frac{n_{2}}{n_{1}} \qquad \boxed{\frac{n_{2}}{n_{1}} = \frac{w_{2}}{M_{2}} \times \frac{M_{1}}{w_{1}}}$$

$$x_{2} = \frac{w_{2}}{M_{2}} \times \frac{M_{1}}{w_{1}}$$

If *m* mole of the solute dissolved in 1kg of the solvent. *i.e.*,  $m = \frac{w_2}{M_2}$  and  $w_1 = 1kg$ , then

$$x_2 = \frac{m \times M_1}{1kg}$$

Where m is molality of the solution.

From above expression, Equ: (12) may be written as

$$\Delta T_{fus} = \frac{R T_0^2 M_1 m}{\Delta H_{fus}}$$

 $k_f = \frac{R T_0^2 M_1}{\Delta H_{fus}}$  is constant for a given solvent called as **molal boiling point freezing constant** 

$$\Delta T_{fus} = k_f m \tag{13}$$

According to Equ: <sup>(13)</sup> the elevation of freezing point depends only on the molality of the solution and is independent of the nature of the solute. So it is a colligative property.

### **Determination of molar mass**

### a) By determination of elevation of boiling point $(\Delta T_b)$ [Cottrell's method]



- 1) A known *wt* of the solvent  $(w_1)$  is taken in the boiling tube and heated with piece of porcelain bits.
- 2) The boiling point of pure solvent  $(T_0)$  is determined by **Beckmann thermometer**
- 3) The contents are cooled, then a known wt of solute ( $w_2$ ) whose molecular wt M<sub>2</sub> is added.
- 4) The boiling point of the solution  $(T_1)$  is noted, then the elevation of boiling point  $(\Delta T_b)$  is given by

$$\Delta T_b = (T_1 - T_0)$$

 $\Delta T_b$  a m (or)  $\Delta T_b = k_b m$ 

Here *m* is molality of solution  $[m = \frac{w^2 \times 1000g}{M_2 \times w_1}]$ 

*k<sub>b</sub>* is boiling point (or) Molal elevation constant (or) (Ebullioscopic constant)

$$\Delta T_b = \frac{k_b \times w_2 \times 100g}{M_2 \times w_1}$$

Knowing  $w_1$ ,  $w_2$ ,  $\Delta T_b$  then  $k_b$  and  $M_2$  values are determined using above formula.

5) To determinate  $(k_b)$  value

$$k_b = \frac{M_2 \times W_1 \times \Delta T_b}{W_2 \times 1000g}$$

6) To determine molar mass of solute  $(M_2)$ 

$$M_2 = \frac{k_b \times w_2 \times 100g}{\Delta T_b \times w_1}$$

#### Limitation:

Elevation of boiling point is a colligative property which depends on the number of solute particles. So this method cannot be used to determine the molecular wt.of electrolytes. They dissociate into ions when dissolved in water.

### b) By determination of Freezing point $(\Delta T_f)$ [Beckmann Method]

The Beckmann's apparatus is shown in fig.



1) A known *wt* of the pure solvent  $(w_1)$  is taken in the freezing tube A. heated and cooled gently to note the freezing point  $(T_0)$ 

- 2) The tube A is taken out and then a known wt of solute ( $w_2$ ) whose molecular wt M<sub>2</sub> is added through the side tube.
- 3) The tube A is put back in its original position and the freezing point of the solution  $(T_1)$  is noted.
- 4) Then the depression of freezing point  $(\Delta T_f)$  is given by

$$\Delta T_f = (T_1 - T_0)$$

$$\Delta T_f$$
 a  $m$  (or)  $\Delta T_f = k_f m$ 

Here *m* is molality of solution  $[m = \frac{w^2 \times 1000g}{M_2 \times w_1}]$ 

 $k_f$  is freezing point (or) Molal depression (or) **Cryoscopic** constant.

$$\Delta T_f = \frac{k_f \times w_2 \times 100g}{M_2 \times w_1}$$

Knowing  $w_1$ ,  $w_2$ ,  $\Delta T_f$  then  $k_f$  and  $M_2$  values are determined using above formula.

1) To determinate  $(k_b)$  value

$$k_f = \frac{M_2 \times W_1 \times \Delta T_f}{W_2 \times 1000g}$$

2) To determine molar mass of solute  $(M_2)$ 

$$M_2 = \frac{k_f \times w_2 \times 100g}{\Delta T_f \times w_1}$$

#### Limitation:

Depression of freezing point is a colligative property which depends on the number of solute particles. So this method cannot be used to determine the molecular wt.of electrolytes. They dissociate into ions when dissolved in water.

### Van't Hoff factor

- 1) Since colligative properties depends upon the number of particles of solute. In some cases solution may **associates or dissociates** to give abnormal results.
- This abnormal results accounted by Van't Hoff, he introduced a factor "i" known as Van't Hoff defined as

$$i = \frac{observed \ Osmotic \ effect}{Normal \ Osmotic \ effect}$$

 Osmotic effect indicates colligative property, its property inversely vary with molar mass of solute.

$$i = \frac{Normal\ molar\ mass}{Observed\ molar\ mass}$$

#### **Degree of Association:**

- 1) It means the fraction of total number of molecules combined to form bigger molecules.
- Consider 1 mole of a solute dissolved in a given volume of a solvent. Let n be the simple molecule combine to form an associated molecule.

$$nA \implies (A)_n$$

Let  $\alpha$  be the degree of Association, then

The number of unassociated moles =  $1 - \alpha$ 

- The number of associated moles  $= (\frac{\alpha}{n})$  $\therefore$  The total number of effective moles  $= 1 - \alpha + (\frac{\alpha}{n})$
- Since Osmotic effect (colligative property) is proportional to the number of moles of solute, the Van't Hoff factor "i" is given by

$$i = \frac{\substack{observed \ Osmotic}}{\substack{effect\\ Normal \ Osmotic \ effect}} = \frac{1 - \alpha + \binom{\alpha}{n}}{1}$$

Alternative with respect to molar mass of solute

$$i = \frac{normal\ molar\ mass}{\frac{observed\ molar\ mass}{mass}} = \frac{1 - \alpha + \frac{\alpha}{\binom{n}{2}}}{1}$$

4) If we know *n* value is simple molecule combine to form an associated molecules whose molar mass  $(\frac{\alpha}{n})$ , the degree of association and Van't Hoff factor can be calculated.

#### **Degree of dissociation of solute**

 It meant the ration between the number of molecules dissociated and total number of molecules taken.

$$\alpha = \frac{number \ of \ molecules \ (or) \ moles \ dissociated}{number \ of \ molecules \ (or) \ moles \ dissolved}$$

2) Consider 1 *mole* of an electrolyte dissolved in a given volume of solvent. Let  $\alpha$  be the degree of dissociation and *n* molecules gives  $n\alpha$  moles of ions.

Ex:

The number of undissociated ions =  $(1 - \alpha)$ 

The number of dissociated ions  $= n \alpha$ 

- $\therefore$  The total number of effective dissociated ions =  $1 \alpha + n \alpha$
- Since Osmotic effect (colligative property) is proportional to the number of moles of solute, the Van't Hoff factor "*i*" is given by

$$i = \frac{observed \ Osmotic \ effect}{Normal \ Osmotic \ effect} = \frac{1 - \alpha + \ n \ \alpha}{1}$$

Alternative with respect to molar mass of solute

$$i = \frac{normal \text{ moles of ions}}{observed \text{ moles of ions}} = \frac{1 - \alpha + n \alpha}{1}$$
$$i = \frac{1 - \alpha + n \alpha}{1}$$
$$i = \frac{1 + (n - 1)\alpha}{1}$$

4) From above equation Van't Hoff factor and dissociation ( $\alpha$ ) can be calculated.

$$i = 1 + (n - 1)$$
$$\alpha = \frac{i - 1}{n - 1}$$

### **Chemical Equilibrium**

- A chemical reaction is said to be an equilibrium state when the rates of forward reaction and back ward reaction become equal.
- At equilibrium state, the system appears stationary at a given temperature and pressure.

### Law of active mass

The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is directly proportional to the product of the active masses of the reacting substances.

Chemical equilibrium

Let general equilibrium reaction.

a A + b B < m M + n N

According to the law of mass action,

Assuming that active masses are equivalent to molar concentration.

The rate of the forward reaction,

$$r_f a [A]^a + [B]^b$$
  
 $r_f = k_f [A]^a + [B]^b$ 

The rate of the backward reaction,

 $r_b$  a  $[M]^m + [N]^n$  $r_b = k_b [M]^m + [N]^n$ 

At equilibrium, the rate of forward and backward reaction are equal,

$$r_{f} = r_{b}$$

$$k_{f} [A]^{a} + [B]^{b} = k_{b} [M]^{m} + [N]^{n}$$

$$\frac{k_{f}}{k_{b}} = \frac{[M]^{m} + [N]^{n}}{[A]^{a} + [B]^{b}}$$

$$\therefore k_{c} = \frac{k_{f}}{k_{b}}$$

$$k_{c} = \frac{[M]^{m} + [N]^{n}}{[A]^{a} + [B]^{b}}$$

This equation is called low of chemical equilibrium. Where  $k_c$  is equilibrium constant.

### Thermodynamic derivation of low of chemical equilibrium

The general reversible reaction

a A + b B 🗲 m M + n N

Where reactants and the products are assumed to be an ideal gases.

The **chemical potential** of reactants of a moles of A and b moles of B is given by the expression.

Where  $\mu_A$  and  $\mu_B$  are chemical potentials

III<sup>ly</sup> for the products,

$$G_{products} = m\mu_M + n\mu_N \dots (2)$$

The difference between the free energy of the products and reactant

$$\Delta G_{reaction} = G_{product} - G_{reactants}$$
$$= m\mu_M + n\mu_N - a\mu_A + b\mu_B \dots (3)$$

At equilibrium, the free energy change  $\Delta G = 0$ ,

$$0 = m\mu_M + n\mu_N - a\mu_A + b\mu_B \dots (4)$$

The **chemical potential** of the  $i^{th}$  species in the gaseous state is given by,

$$\mu_i = \mu_i^0 + RT \ln p_i \tag{5}$$

Where  $p_i$  is partial pressure of the  $i^{th}$  component,

### $\mu_i^0$ is standard chemical potential

Substitute Equ: (4) in (3)

$$(\mu^{0} + RT \ln p_{M}) + (\mu^{0} + RT \ln p_{N}) - a(\mu^{0} + RT \ln p_{A}) + b(\mu^{0} + RT \ln p_{B}) = 0 \dots (6)$$

$$RT \ln \frac{(p_{M}^{m})_{N}}{(p_{A}^{a} p_{B}^{b})} = -[(m\mu_{M}^{0} + n\mu_{N}^{0}) - (a\mu_{A}^{0} + b\mu_{B}^{0})]$$

$$= -[G_{products}^{0} - G_{reactants}^{0}]$$

$$RT \ln \frac{(m_{M}^{m} p_{N}^{n})}{(p_{A}^{a} p_{B}^{b})} = -(\Delta G^{0})_{reaction} \text{ (or)}$$

$$\frac{(p_{M}^{m} p_{R}^{n})}{(p_{A}^{m} p_{B}^{b})} = e^{-\Delta G^{0}}/RT \dots (7)$$

Since,

 $\Delta G^0$  depends only on temperature

R is the gas constant

$$\frac{(p_{M} p_{R})}{(p_{A}^{a} p_{B}^{b})} = constant = k_{p}$$

This equation is called thermodynamic derivation of law of chemical equilibrium.

### Van't Hoff reaction isotherm

Consider a mixture of four ideal gases A, B, C and D, the following reaction takes place.

$$a A + b B \iff c C + d D$$
 .....(1)

The chemical potential of various gases are,

$$\mu_A = \mu_A^0 + RT \ln p_A$$
$$\mu_B = \mu_B^0 + RT \ln p_B$$

$$\mu_{C} = \mu_{C}^{0} + RT \ln p_{C}$$
$$\mu_{D} = \mu_{D}^{0} + RT \ln p_{D}$$

The free energy change of the reaction

$$\Delta G_{reaction} = G_{product} - G_{reactants}$$

$$\Delta G = (c\mu_{c} + d\mu_{D}) - (a\mu_{A} + b\mu_{B}) \dots (2)$$

$$\Delta G = (c\mu_{c}^{0} + cRT \ln p_{c} + d\mu_{D}^{0} + dRT \ln p_{D})$$

$$-(a\mu_{A}^{0} + aRT \ln p_{A} + b\mu_{B}^{0} + bRT \ln p_{B}) \dots (3)$$

$$\Delta G = (c \stackrel{0}{+} d\mu_{D}) \stackrel{0}{-} (a\mu_{A} \stackrel{0}{+} b\mu_{B}) \stackrel{0}{+} RT \ln \frac{c}{p_{A}^{c} + p_{B}^{d}}$$

$$\Delta G = \Delta G^{0} + RT \ln \frac{p_{A}^{c} + p_{B}^{d}}{p_{A}^{a} + p_{B}^{b}} \dots (4)$$

If the reaction is at equilibrium  $\Delta G = 0$ ,

$$0 = \Delta G^{0} + RT \ln \frac{p_{C}^{c} + p_{D}^{a}}{p_{A}^{a} + p_{B}^{b}}$$

$$\Delta G^{0} = -RT \ln \frac{p_{C}^{c} + p_{D}^{d}}{p_{A}^{a} + p_{B}^{b}}$$

$$\frac{p_{C}^{c} + p_{D}^{d}}{p_{A}^{a} + p_{B}^{b}}$$
is known as equilibrium constant, it is denoted as  $k_{p}$ 

$$\Delta G^{0} = -RT \ln k_{p}$$
(5)

Since,

 $\Delta G^0$  is standard free energy change  $k_p$  is depends on temperature only,

Substitute Equ: (5) in (4)

$$\Delta G = -RT \ln k_p + RT \ln \frac{p_C^c + p_D^d}{p_a + p_b}$$

$$\Delta G = -RT \ln k_p + RT \ln Q_p$$

$$\Delta G = -RT \ln k_p + RT \ln J_a$$
(8)

Equations (6), (7) and (8) are different forms of Van't Hoff reaction isotherm.

### Temperature dependence of equilibrium constant.

### [Van't Hoff equation (or) Van't Hoff isochore]

The temperature of a chemical equilibrium is altered, there is a change in the value of equilibrium constant.

Consider Van't Hoff isotherm for a chemical equilibrium,

 $\Delta G^0 = -RT \ln k_p \tag{1}$ 

Rearranging the above equation

$$\ln k_p = -\frac{1}{R} \frac{\Delta G^0}{T} \dots (2)$$

Differentiating Equ: (2) w.r.t 'T'

$$\frac{d\ln k_p}{dT} = -\frac{1}{R} \frac{\Delta G^0}{dT} \dots (3)$$

According to Gibb's – Helmholtz equation

$$\frac{d \Delta G^0/T}{dT} = -\frac{\Delta H^0}{T^2}$$

Δ

Substituting the above equation in Equ: ③

$$\frac{d\ln k_p}{dT} = -\frac{\Delta H^0}{RT^2}.....(4)$$

#### This equation is known as Van't Hoff isochore (or) Van't Hoff equation.

 $\Delta H^0$  is standard enthalpy change for the chemical reaction, if  $\Delta H^0$  is constant, Van't Hoff isochore can be integrated.

$$d\ln k_p = \frac{\Delta H^0}{R} \frac{dT}{T^2} \dots (5)$$

Integrating between limits,

This equation is called integrated Van't Hoff equation (or) Van't Hoff isochore.

### Le Chatelier principle and its applications

- There are three main factors which alter the state of equilibrium there are,
  - 1. Concentration
  - 2. Temperature
  - 3. Pressure
- The addition of catalyst has no effect. The **function of a catalyst**, **is hastened the equilibrium** (speed up the forward as well as the backward reaction.)
- Henri Louis Le Chatelier (1850 1936), the French chemist, studied the effect of concentration, temperature and pressure on a large number of chemical equilibria. He summed up his conclusion the form of an equilibrium known as Le Chatelier's principle.
- If an equilibrium is subjected to a stress, the equilibrium shifts in such a way as to reduce the stress.
- A system at equilibrium is subjected to a change of concentration, pressure and temperature the equilibrium shits in the direction that tends to undo the effect of the change.

### **Application:**

a) Effect of change of concentration

${\rm F}{\rm e}^{3+}$ +	SCN-	$[Fe (SCN)]^{2+}$
(aq)	(aq)	(aq)
(Pale yellow)	(colourless)	(Dark brown)

- 1) Some ferric ( $Fe^{3+}$ ) salts is added to this equilibrium. The colour of the solution will be darken immediately showing that there is increase in the concentration of the coloured complex ion [Fe(SCN)]<sup>2+</sup>
- 2) Addition of more ( $Fe^{3+}$ ) and sulphocyanide salt resulted in increasing the concentration of the complex.
- 3) In a chemical equilibrium, increasing the concentration of the reactants results in shifting the equilibrium in favour of the products while increasing the concentrations of the products results in shifting the equilibrium in favour of the reactants.

#### b) Effect of change of Temperature

 A chemical equilibrium actually involves two opposing reactions. One favouring the products and the other favouring the reactants. If one of these is exothermic (i.e., accompanied by evolution of heat), the other must be endothermic (i.e., accompanied by absorption of heat).

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

2) The reaction favouring the product  $(NO_2)$  is seen to be **endothermic**. Therefore, the opposing reaction favouring the reactant  $(N_2O_4)$  must be **exothermic**. Then temperature is allowed to rise the equilibrium will shift in the direction which tends to undo the effect of heat. i.e., which tends to produce cooling.

$$\begin{array}{ccc} N_2 &+ & 3 H_2 \\ (g) & (g) \\ \end{array} \begin{array}{c} 2 & NH_3 \\ (g) \\ \end{array}$$

 The forward reaction is exothermic. The back reaction must be endothermic. The increase of temperature will favour the back reaction. i.e., the dissociation of ammonia.

#### c) Effect of change of pressure

1) If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure.

$$N_2O_4_{(g)} \iff 2 NO_2_{(g)}$$
  
1 mole 2 moles

2) The pressure on the system is increased. The volume of the system will be decrease proportionately. The total number of moles per unit volume will be more than before. The change can be counteracted if equilibrium shifts in that direction in which the total number of moles is decreased.

$$N_2 + 3 H_2 \rightleftharpoons 2 NH_3$$
(g) (g) (g)
$$1 \text{ mole } 3 \text{ mole} 2 \text{ moles}$$

$$4 \text{ moles}$$

3) The forward reaction is accompanied by a decrease in the number of moles. If the pressure is increased. The volume will decrease and, therefore, the number of moles per unit volume will increased.

CO +	H₂O <b>⇐</b>	$CO_2$ +	Н2
(g)	-	(g)	(g)
1 mole	1 mole	1 mole	1 molę
$\smile$			
2 moles		2 moles	

 The above reaction proceeds in either direction without any change in the number of moles. Therefore, the pressure will have no effect on this equilibrium.

## **PRACTICE QUESTIONS:**

- 1. Define Van't Hoff factor
- 2. Explain the types of Colligative properties
- 3. Discuss about Determination of molar mass
- 4. Evaluate the application of Le Chatelier's Principle
- 5. Derive Thermodynamic derivation of Law of Chemical Equilibrium

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