

## Department of Chemistry

**Attention: All the students of Semester IV having Chemistry as General Paper ( GE 4 and C 4)**

The concerned students are hereby informed that the following items from their respective syllabi has to be taken care of for their Semester IV Examination, 2020. The students should consult **any text book** they possess, even books from their Higher Secondary classes may be helpful.

Paper GE4T and COR4T in Chemistry contains two sections.

Section A: **Physical Chemistry-III** which includes four different topics- solution, phase equilibria, conductance and electromotive force

### **Solution**

1. Ideal solution
2. Raoult's law
3. Non ideal solution
4. Azeotrope
5. Critical solution temperature
6. Nernst Distribution Law

### **Phase Equilibria**

1. Definition of phase, component, degrees of freedom
2. Gibb's Phase Rule
3. Phase diagram of water
4. Eutectic mixture
5. Clausius Clapeyron equation
- 6.

### **Conductance**

1. Definition of conductance, specific conductance, equivalent conductance, molar conductance. Its units and factors on which they depend
2. Variation of specific and equivalent conductance with dilution for strong and weak electrolyte
3. Kohlrausch's law
4. Ostwald dilution law
5. Conductometric titration

### **Electromotive force**

1. Galvanic cell
2. Reversible and irreversible cell
3. Types of electrodes and cell representation
4. EMF, standard electrode potential, Nernst equation
5. Electrochemical series
6. Liquid junction potential

## SOLUTIONS

### Ideal Solution:

- The components of an ideal solution obey Raoult's law for all concentrations.
- The molecules of both solute and solvent are roughly the same size and shape, and the intermolecular forces in the pure liquids and in their mixture are all similar.
- Also note that  $\Delta H$  and  $\Delta V$  due to mixing are zero.

### Raoult's law:

If an involatile substance (solute) is dissolved in a volatile liquid (solvent), then the equilibrium vapour pressure over the solution is observed to be less than over the pure liquid. The temperature of the system is kept constant.

If  $p^0$  be the vapour pressure of the pure liquid and  $p$  be the vapour pressure over the solution at the temperature T, then  $p = x_1 p^0$  where  $x_1$  is the mole fraction of the solvent in the solution. This is Raoult's law.

In the binary solution, the mole fraction of the solute in the solution  $x_2$  is given by  $x_2 = 1 - x_1$ . Therefore,  $p = (1 - x_2)p^0 \therefore p = p^0 - x_2 p^0$

The vapour pressure lowering  $\Delta p = p^0 - p = x_2 p^0$

### Two volatile liquids forming an ideal solution:

Consider at a certain temperature two volatile liquids A and B, miscible with each other in all proportions, are forming an ideal solution. Since the solution is an ideal one, both the constituents of the binary mixture will obey Raoult's law. The partial pressures exerted by vapours of these constituents over the solution will be given by

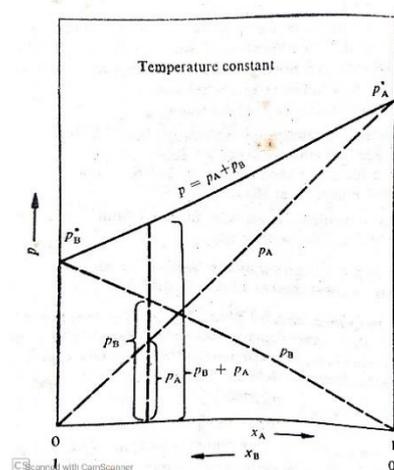
$p_A = x_A p_A^0$  and  $p_B = x_B p_B^0$ ; where  $x_A$  and  $x_B$  are the mole fractions of A and B in the liquid phase and  $p_A^0$  and  $p_B^0$  are the vapour pressures of the pure liquids respectively.

The total vapour over the solution  $p = p_A + p_B = x_A p_A^0 + x_B p_B^0$ .

Since  $x_A + x_B = 1$  (binary solution), therefore,  $p = x_A p_A^0 + (1 - x_B) p_B^0 = p_B^0 + (p_A^0 - p_B^0) x_A$ .

or it can be written as  $p = (1 - x_B) p_A^0 + x_B p_B^0 = p_A^0 + (p_B^0 - p_A^0) x_B$ .

So, at a certain temperature the total vapour pressure over the solution will vary linearly with the mole fraction of either component. (Both  $p_A^0$  and  $p_B^0$  are constants at any certain temperature.)



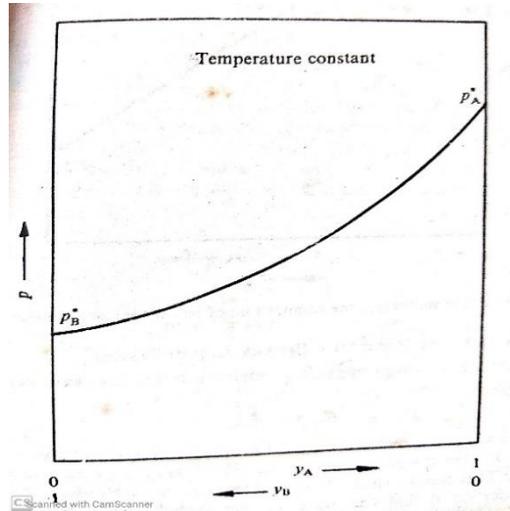
Slope of the line of  $p$  versus  $x_A$  or  $x_B$  will depend upon the values of  $p_A^0$  and  $p_B^0$ . Here in the adjoining diagram of  $p$  versus  $x_A$  the slope is shown positive, because  $p = p_B^0 + (p_A^0 - p_B^0) x_A$  and  $p_A^0 > p_B^0$ .

So far we have seen the variation of total vapour pressure with the mole fraction of the either constituent in the liquid. Now, in order to find the variation of total vapour pressure with the mole fraction of either A or B in the vapour we have to use Dalton's law of partial vapour pressure. If  $y_A$  and  $y_B$  are the mole fraction of A and B in the vapour then

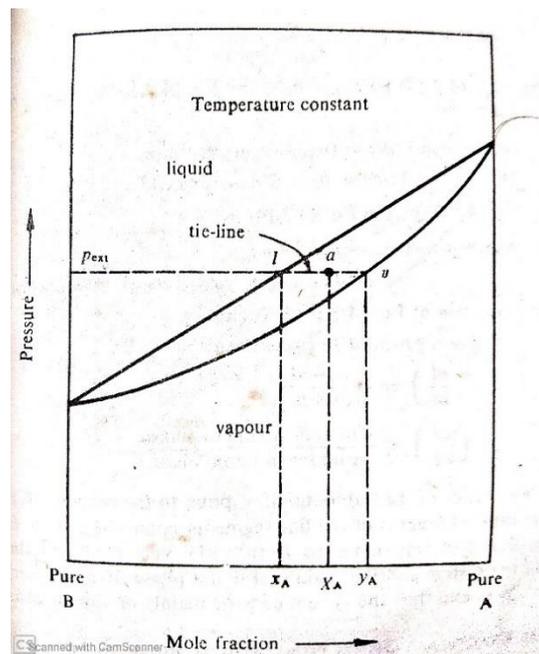
$$y_A = \frac{p_A}{p} = \frac{x_A p_A^0}{p_B^0 + (p_A^0 - p_B^0) x_A} \quad \therefore x_A = \frac{y_A p_B^0}{p_A^0 + (p_B^0 - p_A^0) y_A}$$

Therefore, the total vapour pressure  $p = p_B^0 + (p_A^0 - p_B^0) x_A = p_B^0 + (p_A^0 - p_B^0) \frac{y_A p_B^0}{p_A^0 + (p_B^0 - p_A^0) y_A}$

$p = \frac{p_A^0 p_B^0}{p_A^0 + (p_B^0 - p_A^0) y_A}$  This clearly shows that  $p$  will not vary linearly with  $y_A$  i.e. the vapour composition. The plot of  $p$  versus  $y_A$  is shown in the following figure.



When the two plots drawn earlier, are plotted together in one graph, then we have



Above the straight line (liquid composition line), i.e. at high pressure region we have only liquid (mixture of A and B) and below the curved line (vapour composition line) i.e. at low pressure region we have only vapour. In between these two lines we have liquid in equilibrium with the vapour. The amount of two phases in equilibrium can be obtained using Lever Rule.

The distance  $al$  (in the last fig)  $\propto$  amount of the vapour formed  
 $av$  (in the last fig)  $\propto$  amount of the liquid formed. Taking the ratio we have

and the distance

$$\frac{al}{av} = \frac{\text{Amount of vapour}}{\text{Amount of liquid}}, \text{ this equation is known as the lever rule.}$$

Distillation of solutions:

In order to understand the phenomenon of fractional distillation of a solution we have to draw the *temperature – composition* diagram at a constant pressure. For an ideal solution the *temperature – composition* diagram is shown below.

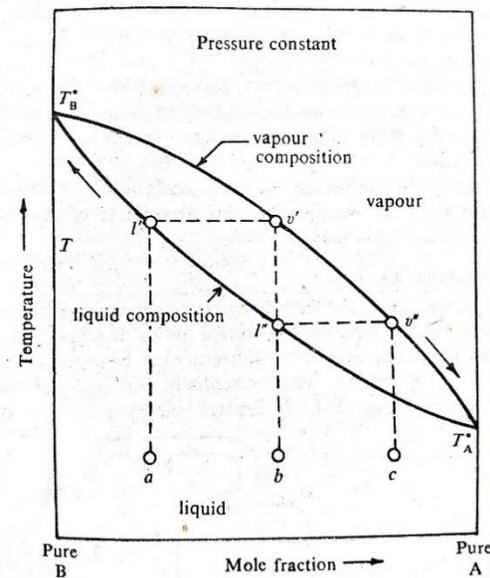


Fig. 4.7.8 Principle of isobaric distillation

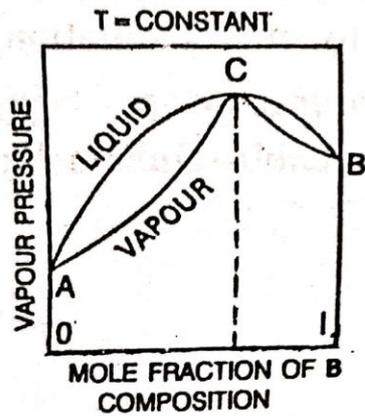
Note that (i) neither the liquid nor the vapour curve is a straight line, and (ii) the lower region in the figure represents the liquid phase (low temperature) whereas the upper region represents the vapour phase (high temperature).

By fractional distillation it is possible to separate both the liquids A and B completely. The more volatile component will be distilled out completely leaving the less volatile component as the residue.

#### Non-ideal solutions:

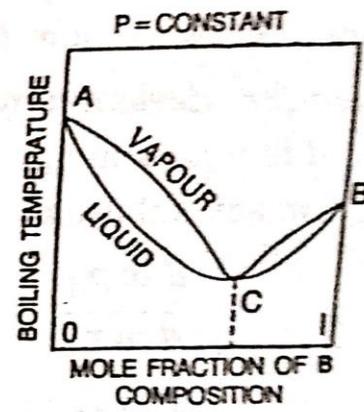
For non-ideal solutions (constituents do not obey Raoult's law) both the *pressure – composition* and the *temperature – composition* curves are entirely different. The following points are to be noted.

1. Total vapour pressure either passes through a maximum or a minimum in the *vapour pressures – composition* diagram.
2. Since boiling point is inversely related to vapour pressure, it is expected that the solution will exhibit either a minimum or a maximum in the *temperature – composition* curve where maximum or minimum in the total vapour pressure is observed.
3. In both the *pressure – composition* and the *temperature – composition* curves, the liquid line and the vapour line intersect with each other.

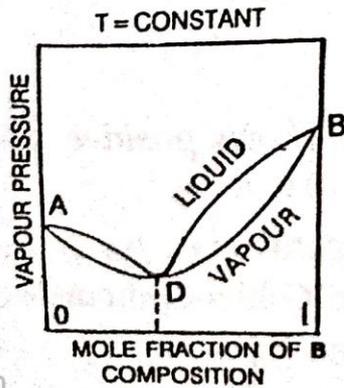


(ii)

TYPE II

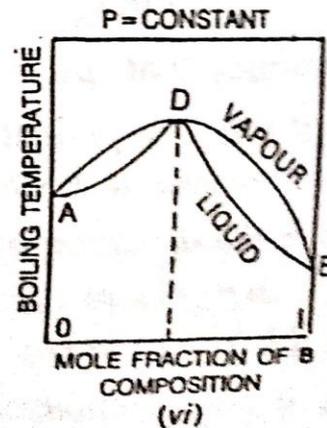


(v)



(iii)

TYPE III



(vi)

Type II. Here vapour pressure shows a maximum in its *vapour pressures - composition* curve and corresponding minimum in the *temperature - composition* curve.

Type III. Here vapour pressure shows a minimum in its *vapour pressures - composition* curve and corresponding maximum in the *temperature - composition* curve.

For fractional distillation (at constant pressure) we will consider only the *temperature - composition* curves in both Type II and Type III cases.

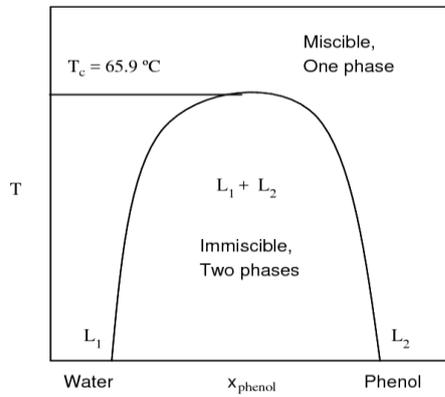
In Type II, the liquid composition and the vapour composition curves intersect at point C. The solution of that composition will boil at the lowest temperature. The liquid and the vapour phases at this point have the same composition. Therefore, the liquid mixture represented by the point C will boil at a constant temperature and will distil over completely without change of composition. ***Such a mixture which boils at a constant temperature and distils over completely at the same temperature without change in composition is called an azeotropic mixture.***

In Type III, the liquid composition and the vapour composition curves intersect at point D. The solution of that composition will boil at the highest temperature. The liquid and the vapour phases at this point have the same composition. Therefore, the liquid mixture represented by the point D will boil at a constant temperature and will distil over completely without change of composition, ***an azeotropic mixture.***

#### Partially miscible liquids, critical solution temperature (CST):

*The temperature above (or below) which a pair of partially miscible liquids becomes miscible in all proportions, is called critical solution temperature (CST) or consolute temperature for the pair.*

Phenol and water are only partially miscible at ordinary temperature. On shaking these two liquids with each other, two saturated solutions of different compositions, one of phenol in water and the other of water in phenol, are obtained. Such solutions of different compositions co-existing with one another are termed conjugate solutions. The mutual solubility of phenol and water increases with rise in temperature and ultimately at a certain temperature (CST) the two conjugate solutions change into one homogeneous solution. The CST for phenol-water system is around 66°C and the composition of the solution then is around 34 mass per cent of phenol.



Outside the curve we have a homogeneous solution of phenol and water and inside the curve we have two conjugate solutions  $L_1$  (phenol in water) and  $L_2$  (water in phenol) in equilibrium with each other.

Nernst distribution law:

If a solute is added in a system containing two immiscible liquids  $\alpha$  and  $\beta$  and if the solute is soluble in both the liquids, then it distributes itself between the two liquids in a definite manner, such that

$\frac{c^\alpha}{c^\beta} = K_D$  where  $c^\alpha$  and  $c^\beta$  are the molar equilibrium molar concentrations of the solute in the two liquids and  $K_D$  is a constant known as the distribution coefficient or the partition coefficient. The value of the constant  $K_D$  depends only on the temperature of the system and is independent of the relative amounts of the two layers and also that of the solute provided the solute has the same molar mass in both the layers.

## CONDUCTANCE

### Conductance

**Definition:** Current carrying capacity of an electrolyte. It is the reciprocal of resistance

**Symbol:** L

**Formula :**  $L = 1/R$ , where R is resistance in ohms

**Unit:** ohm<sup>-1</sup>(Ω<sup>-1</sup>) or Seimens(S) or mho

**Properties:**

1. It is additive
2. It depends on (a) total number of ions in the solution ie on volume and concentration of solution. (b) charge of ions (c) velocity of ions i.e. on size of ions and potential difference across electrodes.
3. It is experimentally measurable by Wheatstone Bridge principle

### Specific conductance/Conductivity

**Definition:** It is the conductance of an electrolyte placed between two parallel electrodes 1cm apart and effective common area of 1sq.cm.

**Symbol:**  $L_s$  or  $\kappa$  (kappa)

**Formula:**  $L_s = L \times (l/A)$ , where l = distance between electrodes in cm, A = common area of electrodes in cm<sup>2</sup>, (l/A) = cell constant in cm<sup>-1</sup>.

**Unit:** ohm<sup>-1</sup>cm<sup>-1</sup> (CGS system) S<sup>-1</sup>m<sup>-1</sup>(SI system)

**Properties:**

1. It depends on (a) concentration of electrolyte (b) nature of electrolyte (strong/weak)
2. It is independent of volume of electrolyte taken i.e. the type of conductivity cell used
3.  $L_s$  of weak electrolytes less than that of strong electrolytes at same concentration.
4. As dilution increases( concentration decreases)  $L_s$  of both strong and weak electrolytes decrease.
5.  $L_s$  decreases more for strong as compared to weak electrolytes with dilution.
6. It is directly measurable experimentally by using cell of cell constant unity.

### Equivalent conductance

**Definition:** It is the conducting power of 1gm equivalent of electrolyte placed between two parallel electrodes 1cm apart.

**Symbol:**  $\lambda$  (lamda)

**Formula:**  $\lambda = L_s \times (1000/C)$ , where C = concentration of electrolyte in normality (gm equivalents per litre)

**Unit:** ohm<sup>-1</sup>cm<sup>2</sup>gm.eqv<sup>-1</sup> (CGS system) Sm<sup>2</sup> gm.eqv<sup>-1</sup> (SI system)

**Properties:**

1. Equivalent conductance of both strong and weak electrolytes increase with dilution
2. Equivalent conductance of weak electrolytes increase more with dilution than strong electrolytes
3. It cannot be measured by direct experiment.

### Molar conductance

**Definition:** It is the conducting power of 1gm mole of electrolyte placed between two parallel electrodes 1cm apart.

**Symbol:**  $\lambda_M$  (lamda)

**Formula:**  $\lambda_M = L_s \times (1000/C_M)$ , where  $C_M$  = concentration of electrolyte in molarity (gm moles per litre)

**Unit:** ohm<sup>-1</sup>cm<sup>2</sup>gm.mole<sup>-1</sup> (CGS system) Sm<sup>2</sup> gm.mole<sup>-1</sup> (SI system)

**Relation with  $\lambda$ :**  $\lambda_M = \lambda \times \text{charge}$

Example: Find  $\lambda_M$  of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> if  $\lambda$  is 150 Sm<sup>2</sup> gm.eqv<sup>-1</sup>.  $\lambda_M = \lambda \times \text{charge} = 150 \times (2 \times 3) = 900 \text{ Sm}^2 \text{ gm.mole}^{-1}$

### Variation of specific conductance ( $L_s$ ) with dilution:

1.  $L_s$  of weak electrolytes (eg. Acetic acid,  $\text{NH}_4\text{OH}$ ) less than that of strong electrolytes ( eg.  $\text{HCl}$ ,  $\text{NaOH}$ ,  $\text{NaCl}$ ) at same concentration.

Strong electrolytes dissociate completely, producing more number of ions hence their specific conductance is higher than incompletely dissociated weak electrolytes.

2. As dilution increases( concentration decreases)  $L_s$  of both strong and weak electrolytes decrease.

With decrease of concentration number of ions per unit volume decreases. Specific conductance depends on number of ions, hence it decreases.

3.  $L_s$  decreases more for strong as compared to weak electrolytes with dilution.

Strong electrolytes dissociate completely. On decrease of concentration the number of ions per unit volume decrease, hence specific conductance decreases.

Weak electrolytes on the other hand are incompletely dissociated. On dilution the number of undissociated molecules per unit volume of weak electrolytes decrease, but the degree of dissociation increases, i.e. the electrolyte molecules now produce more number of ions. Hence although there is a net decrease in number of ions, the decrease is less pronounced than that of strong electrolytes.

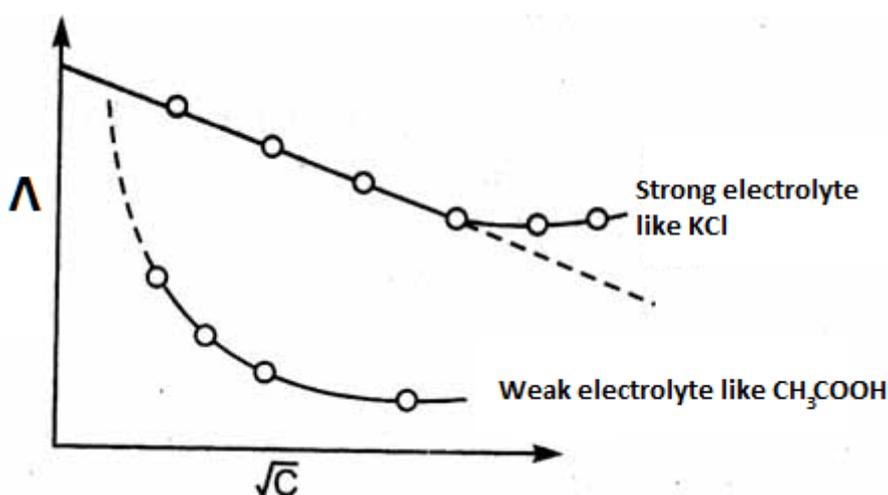
### Variation of equivalent conductance ( $\lambda$ ) with dilution:

1. Equivalent conductance of strong electrolytes increase with dilution.

On dilution, the ions move further apart. This decreases the interionic interaction between ions and results in increase of their velocities. Hence equivalent conductance increases.

2. Equivalent conductance of weak electrolytes increase with dilution.

On dilution degree of dissociation of weak electrolytes increase. Hence 1 gm equivalent of electrolyte produce more number of ions. Therefore equivalent conductance increases rapidly.



### Kohlrausch's law of independent migration of ions

At infinite dilution (where no interionic interaction exists) each ion migrates independently of its counter ion i.e. they have equivalent conductance values independent of its counter ion.

At infinite dilution ( $C \rightarrow 0$ ) equivalent conductance of an electrolyte is the sum of individual ion conductances.

$$\lambda^\circ (\text{AB}) = \lambda^\circ (\text{A}^+) + \lambda^\circ (\text{B}^-)$$

### Determination of equivalent conductance at infinite dilution

For **strong electrolytes** by the extrapolation of the linear  $\lambda$  vs  $\sqrt{C}$  plot to  $\sqrt{C} = 0$ , i.e. from the Y axis intercept of the plot.

For **weak electrolytes** the  $\lambda$  vs  $\sqrt{C}$  plot is asymptotic, hence extrapolation method cannot be used. Kohlrausch's law is used for the determination.

Example : (1) To determine  $\lambda^\circ$  of acetic acid ( $\text{CH}_3\text{COOH}$ ) a weak electrolyte, the  $\lambda^\circ$ 's of strong electrolytes  $\text{NaCl}$ ,  $\text{CH}_3\text{COONa}$  (sodium acetate) and  $\text{HCl}$  are determined from the  $\lambda$  vs  $\sqrt{C}$  plot.

According to Kohlrausch's law-

$$\begin{aligned}\lambda^\circ(\text{HCl}) + \lambda^\circ(\text{CH}_3\text{COONa}) - \lambda^\circ(\text{NaCl}) &= \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{Cl}^-) + \lambda^\circ(\text{CH}_3\text{COO}^-) + \lambda^\circ(\text{Na}^+) - [\lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-)] \\ &= \lambda^\circ(\text{CH}_3\text{COO}^-) + \lambda^\circ(\text{H}^+) \\ &= \lambda^\circ(\text{CH}_3\text{COOH})\end{aligned}$$

(2) To determine  $\lambda^\circ$  of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) a weak electrolyte, the  $\lambda^\circ$ 's of strong electrolytes  $\text{NH}_4\text{Cl}$ ,  $\text{NaOH}$  and  $\text{NaCl}$  are determined from the  $\lambda$  vs  $\sqrt{C}$  plot.

According to Kohlrausch's law-

$$\begin{aligned}\lambda^\circ(\text{NH}_4\text{Cl}) + \lambda^\circ(\text{NaOH}) - \lambda^\circ(\text{NaCl}) &= \lambda^\circ(\text{NH}_4^+) + \lambda^\circ(\text{Cl}^-) + \lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{OH}^-) - [\lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-)] \\ &= \lambda^\circ(\text{NH}_4^+) + \lambda^\circ(\text{OH}^-) \\ &= \lambda^\circ(\text{NH}_4\text{OH})\end{aligned}$$

(3) At  $25^\circ\text{C}$  and in infinite dilution the value of equivalent conductance of  $\text{CH}_3\text{COONa}$ ,  $\text{HCl}$  and  $\text{NaCl}$  are 78.0, 384.0 and 109.0  $\text{mho cm}^2 \text{equiv}^{-1}$  respectively. Calculate equivalent conductance of  $\text{CH}_3\text{COOH}$  at infinite dilution in that temperature.

Ans:  $\lambda^\circ(\text{CH}_3\text{COOH}) = \lambda^\circ(\text{HCl}) + \lambda^\circ(\text{CH}_3\text{COONa}) - \lambda^\circ(\text{NaCl}) = 384 + 78 - 109 = 353 \text{ mho cm}^2 \text{equiv}^{-1}$

### Ostwald's Dilution Law

The degree of dissociation of a weak electrolyte is inversely proportional to the square root of concentration.

$$\alpha = \sqrt{\frac{K}{C}}$$

**Derivation:** A weak electrolyte  $\text{AB}$  incompletely dissociates into its corresponding ions  $\text{A}^+$  and  $\text{B}^-$ . There exists an equilibrium between the undissociated molecule ( $\text{AB}$ ) and the dissociated ions  $\text{A}^+$  and  $\text{B}^-$ .

i.e.	$\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$
Concentration before dissociation	C      0      0
Concentration after dissociation	$C(1-\alpha)$ $C\alpha$ $C\alpha$

Hence Equilibrium constant ( $K$ ) =  $\frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} = \frac{[C\alpha][C\alpha]}{C[1-\alpha]} = \frac{C\alpha^2}{1-\alpha}$ .

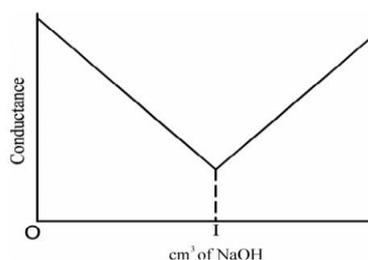
When  $\alpha \ll 1$ ,  $K = \alpha^2 C$  and  $\alpha = \sqrt{\frac{K}{C}}$

### Conductometric titrations

**Principle:** During titration ions replace one another, which differ in mobility, resulting in difference in conductance. The mobility of  $\text{H}^+ \gg \gg$  mobility of  $\text{OH}^- \gg \gg$  mobility of all other ions. Hence conductance also follows the same sequence.

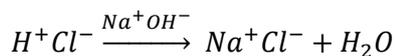
### Conductometric titration of strong acid (HCl) by strong base (NaOH)

Plot:



Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

**Explanation:**

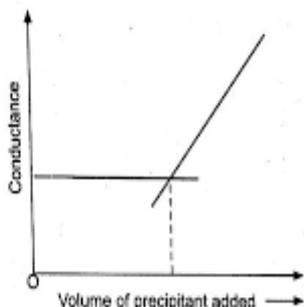


Before equivalence point: H<sup>+</sup> of higher mobility replaced by Na<sup>+</sup> of lower mobility during titration Hence conductance decreases.

After equivalence point: System contains excess OH<sup>-</sup> ions of high mobility. Therefore conductance increases.

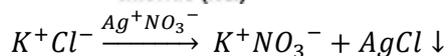
**Conductometric titration of a precipitation reaction of KCl by AgNO<sub>3</sub>**

**Plot:**



**Conductometric titration of silver nitrate (AgNO<sub>3</sub>) and potassium chloride (KCl)**

**Explanation:**



Before equivalence point: Cl<sup>-</sup> replaced by NO<sub>3</sub><sup>-</sup> of similar mobility during titration Hence conductance remains constant.

After equivalence point: System contains excess Ag<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions. Therefore conductance increases.

**Notes on other topics will be uploaded in future**