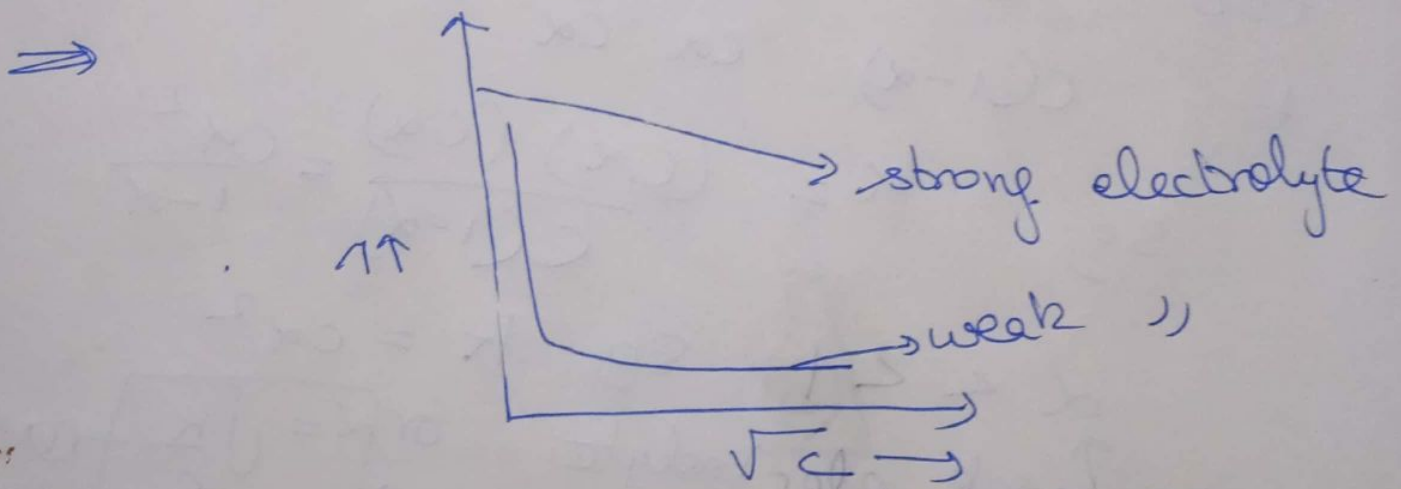


Lecture 3

⇒ Variation of molar conductivity with \sqrt{c} shows different behaviour for strong and weak electrolytes.

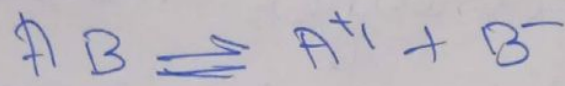
⇒ Strong electrolytes molar conductivity decreases sharply with increase in concentration while ~~increases~~. For weak electrolyte molar conductivity increases slowly and then sharply with dilution.



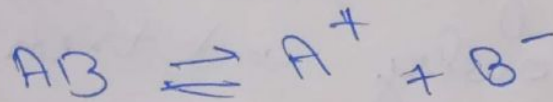
⇒ Behaviour of weak electrolyte can be explained on the basis of Arrhenius theory of Electrolytic dissociation while strong electrolyte on the basis of Debye-Huckel-Onsager theory.

Arrhenius theory of electrolyte dissociation

Weak electrolyte undissociated molecule $AB \rightleftharpoons A^+ + B^-$ ions are in equilibrium with each other.



$$K = \frac{[A^+][B^-]}{[AB]}$$



$t=0$

C

0

0

t

$C(1-\alpha)$

$C\alpha$

$C\alpha$

so,

$$K = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$\alpha \ll 1$ so $K = C\alpha^2$

weak electrolyte or $\alpha = \sqrt{\frac{K}{C}}$ (1)
Oswald's dilution law

From this eq (1) we can see for weak electrolyte when conc decreases (dilution) degree of dissociation ~~is~~ increases so, no of ions per unit volume increases hence on dilution molar conductivity increases.

Ostwald dilution law \rightarrow When α conc. increases, degree of dissociation decreases

Relation between α & Λ

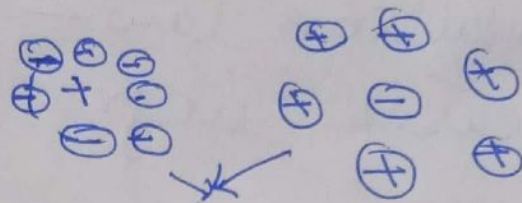
$$\alpha = \frac{\Lambda_c}{\Lambda^\infty} = \frac{\text{molar conductivity at conc. } c}{\text{molar conductivity at infinite dilution}}$$

$$k = \frac{c\alpha^2}{1-\alpha} = \frac{c \left(\frac{\Lambda_c}{\Lambda^\infty} \right)^2}{\left(1 - \frac{\Lambda_c}{\Lambda^\infty} \right)}$$

$$k = \frac{c \Lambda_c^2}{\Lambda^\infty (\Lambda^\infty - \Lambda_c)}$$

Debye Huckel Onsager theory of ionic atmosphere for strong electrolyte

\Rightarrow Acc. to this theory, each ion in solution is surrounded by an ionic atmosphere consisting of other ions whose net average charge is opposite to that of central ion.

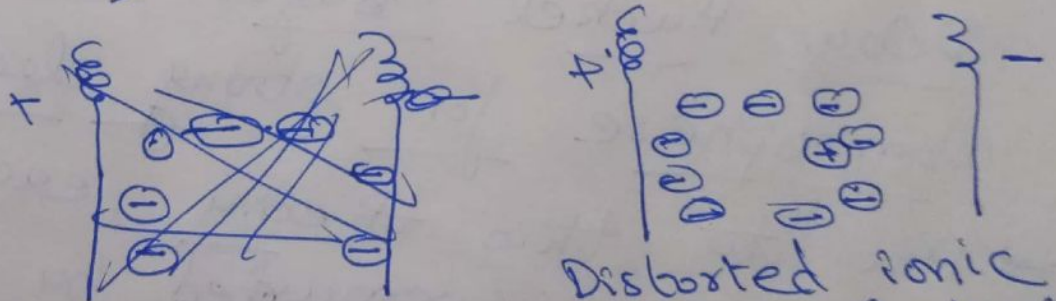


Ionic atmosphere

→ spherical & symmetrical (in the absence of any disturbing factors like potential etc.)

⇒ When the potential is applied the ions start moving towards respective electrodes as a result ionic atmosphere distorted which result in decrease in speeds on ions. This is due to 2 effects or factors:-

a Relaxation of an ionic atmosphere due to an applied potential or asymmetry effect →



atmosphere due to applied field

⇒ Due to applied field distortion of ionic atmosphere as cations move towards cathode & anions ~~move~~ towards

anode. Thus force ~~este~~ exerted by the atmosphere on the central ion is no longer uniform in all directions, it is greater behind the ion than in front of it so, central ions experience retarding force opposite to direction of its motion so, speed is lowered down and hence conductivity

b Electrophoretic effect

- ⇒ Ions in solutions are solvated
- ⇒ Cations and anions move in the opposite directions
- ⇒ Let central ion move through a medium in which solvent molecules carried by the ions of the atmosphere move in the opposite direction.
- ⇒ Similarly the ions involved in ionic atmosphere move in a medium of opposite moving solvent molecules carried by the central ion.
- ⇒ Thus both types of ions moving in solution do not travel through a stationary medium but through a

medium which moves in the opposite direction.

→ These counter currents make it more difficult for the ions to move through the solution & slow down its motion. This is known as electrophoretic effect.

→ Because of these 2 effects speed of ions lowers down hence conductivity decreases and as the conc. of strong electrolyte decreases, these 2 effects decrease ~~causes more which~~ hence more conductivity of strong electrolyte on dilution.

Wien effect → At very high electric field i.e. $E > 10^5 V$ an increase in conductivity. This is because finite time (relaxation time) required to make ionic atmosphere. At very high electric field ions are moving very fast so no ionic atmosphere forms hence ions freely move. Thus conductance ↑.

Debye Falkenhagen effect

At high frequency ($> 3 \times 10^6$ Hz) conductivity increases. "Due to high frequency, ionic atmosphere doesn't form, ions freely move so conductivity increases."

Kohlrausch's law of independent migration of ions

Acc. to this law at infinite dilution dissociation of all electrolyte is complete. [weak electrolyte], all interionic effect disappears, each ion migrates independently of its companion and contributes to the total molar

conductivity of an electrolyte

$$\text{Eg } \lambda_m^\infty(AB) = \lambda_m^\infty(A^+) + \lambda_m^\infty(B^-)$$

This law helps to find conductance of these solution whose "

determination is difficult practically.

$$\text{Eg } \lambda^\infty(\text{HAc}) = \lambda^\infty(\text{NaAc}) + \lambda^\infty(\text{HCl}) - \lambda^\infty(\text{NaCl})$$

Conductance Comparison of alkali metal ions
Molar conductivities
Exp λ_{+}^{∞} S cm² mol⁻¹

Li ⁺	38.66
Na ⁺	50.11
K ⁺	73.52
Rb ⁺	77.8
Cs ⁺	77.3

Acc. to Stokes' law $\lambda_{+}^{\infty} = \frac{F e z_{+}}{6 \pi \eta r_{+}}$

$$\lambda_{+}^{\infty} \propto \frac{1}{r_{+}} \text{ (radius of cation)}$$

Li⁺ has smallest radii so, λ_{+}^{∞} must be maximum in Ist group but experimental data is reversed.

⇒ This can be explained as conductivity is measured in solution so, ions are solvated. Since Li⁺ has smallest size so maximum charge density hence maximum solvated and maximum or largest radii among Ist group element. As we go down less charge density, less solvation so size decreases and conductance increases in solution.