

Chapter 4

ELECTROCHEMISTRY

Lecture/Lession Plan -1

ELECTROCHEMISTRY

4.1 Concept of electrochemistry

Electrochemistry is a branch of chemistry where we will study how chemical energy can be transformed into electrical energy and vice versa. Substances which conduct electricity or current are termed as conductors. Metals and electrolytes are good conductor of electricity; metal carries current by flow of electron where no matter is being transported during current flow whereas in case of electrolytes, movement of ions (matter) is responsible for electricity flow. During current flow an internal force of the conductor resist the flow of current through it which is known as resistance of the conductor.

4.2 Conductance

According to Ohm's law, resistance (R) of any conductor is directly proportional to its length (l) and inversely proportional to its area of cross section (a). Ohm's law can be expressed as:

$$R = \rho \frac{l}{a}$$

; where ρ is specific resistance or resistivity. When $l=1$ cm and $a=1$ cm² then ρ will be equal to R. Hence specific resistance or resistivity of a conductor can be defined as the resistance of the conductor having 1 cm length and 1 cm² area of cross section.

Unit of resistance is "ohm" and unit of specific resistance can be determined as:

$$R = \rho \frac{l}{a}$$
$$\text{or, } \rho = R \frac{a}{l}$$

Unit of specific resistance

$$\begin{aligned} &= \frac{\text{ohm.cm.cm}}{\text{cm}} \\ &= \text{ohm.cm} \end{aligned}$$

Conductance (Λ) can be defined as reciprocal of resistance.

4.2.1 Specific conductance

specific conductance (κ) can be defined as reciprocal of specific resistance. Conductance is basically the ease of current flow through a liquid conductor. specific conductance is defined by the conductance of a solution of the dissolved electrolyte and the whole solution is being placed between two electrode of 1 sq. cm area and 1 cm. Unit of conductance will simply be reciprocal of unit of resistance i.e.,

$$\frac{1}{\text{ohm}} = \text{ohm}^{-1} = \text{mho.}$$

Unit of specific conductance =

$$\frac{1}{\text{ohm.cm}} = \text{mho.cm}^{-1}$$

4.2.2 Equivalent conductance

Form the expression of conductance, we know that

$$\begin{aligned} \Lambda &= \frac{1}{R} \\ &= \frac{1}{\rho \frac{a}{l}} \\ &= \frac{1}{\rho} \frac{l}{a} \\ &= \kappa \frac{V}{1^2}; \end{aligned}$$

where $V = \text{volume of the solution} = \text{area} \times \text{length} = a \times l$

Equivalent conductance is defined by the conductance of a solution containing 1 gm-equivalent of the dissolved electrolyte and the whole solution is being placed between two electrode of 1 sq. cm area and 1 cm apart.

Thus equivalent conductance

$$(\Lambda) = \kappa V$$

(as $l = 1 \text{ cm}^2$)

Now, say c gm-equivalent dissolved in 1000 cc of solution

So, 1 gm-equivalent will be present in

$$\frac{1000}{c} \text{cc solution.}$$

So, equivalent conductance

$$(\Lambda) = \frac{1000\kappa}{c}$$

Unit of equivalent conductance =

$$\frac{\text{mho.cm}^{-1}}{\text{gm-equivalent.cc}} = \frac{\text{mho.cm}^{-1}}{\text{gm-equivalent.cm}^3} = \text{mho.cm}^2.\text{gm-equivalent}^{-1}$$

4.2.3 Molar conductance

Molar conductance is defined by the conductance of a solution containing 1 gm-mole of the dissolved electrolyte and the whole solution is being placed between two electrode 1 cm apart.

Molar conductance

$$(\Lambda_m) = \kappa V$$

(V = volume of a solution containing 1 gm-mole dissolved electrolyte)

Now, say c gm-mole dissolved in 1000 cc of solution

So, 1 gm-mole will be present in

$$\frac{1000}{c} \text{cc solution.}$$

So, equivalent conductance

$$(\Lambda) = \frac{1000\kappa}{c}$$

Unit of equivalent conductance =

$$\begin{aligned} \frac{\text{mho.cm}^{-1}}{\text{gm-mole.cc}} &= \frac{\text{mho.cm}^{-1}}{\text{gm-mole.cm}^3} \\ &= \text{mho.cm}^2.\text{gm-mole}^{-1}. \end{aligned}$$

Relation between equivalent conductance and molar conductance Let us consider an electrolyte (molecular weight M) having weight W gm taken in between two electrode (in the cubic core); p and q are the valency and number of cations are respectively.

$$\text{Now, equivalent weight of the electrolyte is; } E = \frac{M}{pq}$$

$$\begin{aligned} \text{C gm equivalent equivalent} &= \frac{W}{E} \\ &= \frac{W}{\frac{M}{pq}} \\ &= \frac{W \times pq}{M} \end{aligned}$$

$$\begin{aligned}
 \text{Now, equivalent conductance} &= \Lambda = \frac{1000\kappa}{c} \\
 &= \frac{1000\kappa}{\frac{W \times pq}{M}} \\
 &= \frac{1000\kappa}{M \text{ gram mole} \times pq} \\
 &= \frac{\Lambda_m}{pq}
 \end{aligned}$$

So,

$$\Lambda_m = \Lambda \times pq$$

4.3 Effect of temperature on equivalent conductance

In general equivalent conductance should increase with temperature as with increased temperature, the dissociation of electrolyte and ionic mobility of ions increases. Conductance and temperature are correlated by this equation:

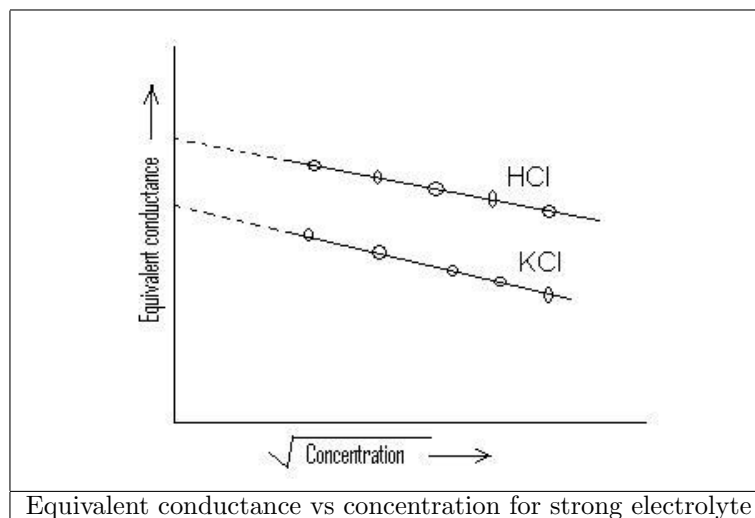
$$\Lambda_T^0 = \Lambda_{25^\circ\text{C}}^0 [1 + \alpha(T - 25^\circ\text{C})]$$

; where Λ_T^0 and $\Lambda_{25^\circ\text{C}}^0$ are the equivalent conductance at $T^\circ\text{C}$ and 25°C respectively; α is the temperature coefficient.

4.4 Effect of concentration on equivalent conductance

Conductance of an electrolyte depends on the number of ions present in the solution and the speed of the ions which is known as ionic mobility. As strong electrolyte already completely dissociated in solution hence number of ions do not changes with dilution. Therefore, the conductance of a strong electrolyte depends upon only the ionic mobility of the ions present in solution. In a concentrated solution, the density of ions are high as the the attraction between ions are high. According to Debye and Huckel, at high concentration a particular type of ion is surrounded by the opposite charged ions and thus a ionic cloud is being created. A cationic cloud formed on an anion and vice versa. These ionic clouds are generally spherical when no electric fields is present. But in presence of an external electrical field these ionic spheres get distorted. As the extend of ionic cloud distortion increases the the ionic mobility decreases. This is commonly known as relaxation effect. As dilution increases, the extend of this distortion decreases or the attraction between ions decreases; as a result the ionic mobility or the conductance of the solution increases. With increase in concentration, the equivalent conductance of any electrolyte decreases but the pattern of the graph is different for strong and weak electrolyte. Conductance generally depends upon the number of ions and speed of ions (ionic mobility).

Strong electrolytes are completely dissociated in solution and hence decrease in concentration or increase in dilution will increase the ionic mobility only. Hence the with dilution equivalent conductance will increase slightly in a regular straight line. At infinite dilution this value will reach at its maximum which is termed as limiting equivalent conductance (Λ^0). Example of strong electrolytes are NaCl, KCl, K_2SO_4 , HCl, H_2SO_4 , HNO_3 , NaOH, KOH etc.



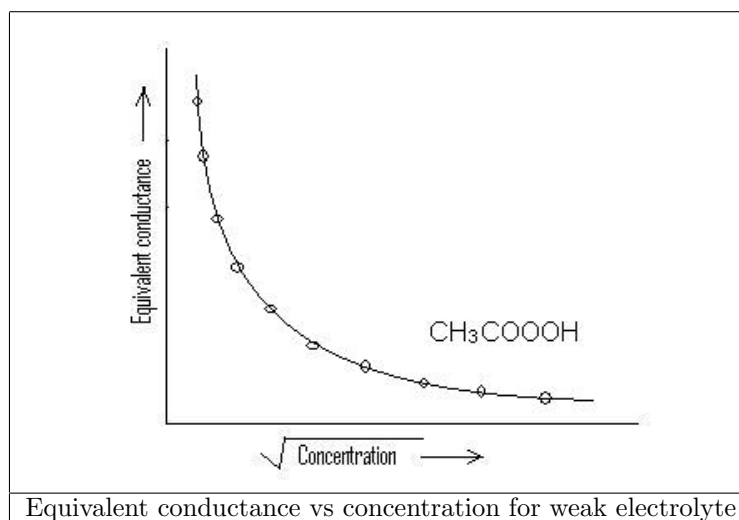
Equivalent conductance vs concentration for strong electrolyte

The relationship between concentration of any electrolyte and its equivalent conductance is given by Debye-Huckel-Onsager equation:

$$\Lambda_{\text{eqv.}} = \Lambda_0 - b\sqrt{c};$$

where b is a constant and its value depends upon stoichiometry of the electrolyte of interest, c is the concentration of the electrolyte in gm-eqv./L.

Weak electrolytes are partially dissociated in solution and hence with increase in dilution or decrease in concentration both the dissociation of electrolytes and the number of ions increases. These two combine effect increases equivalent conductance exponentially and becomes almost equal parallel to y-axis.



Equivalent conductance vs concentration for weak electrolyte

Thus at infinite dilution, the equivalent conductance of a weak electrolyte can not be determined. But from Kohlrausch's law, indirectly we can calculate that. So for weak electrolyte when equivalent conductance reaches maximum at almost complete dissociation, i.e.; dissociation constant (α) is close to unity. α can be expressed as a ratio of equivalent conductance at a certain concentration of a electrolyte(Λ) with equivalent conductance at infinite dilution Λ_0 of same electrolyte.

4.5 Transport number and Ionic conductance

Transport number can be defined as fraction of current transported by a particular type of ion in a solution of electrolyte.

So, transport number for cation

$$t_+ = \frac{I_+}{I}$$

and transport number for anion

$$t_- = \frac{I_-}{I};$$

where I_+ is the amount of current carried by cation and I_- is the amount of current carried by anion. Current carried by any type of ion depends upon speed of ions (u), charge of the ions (c) and valency of ion (z). Thus

$$I_+ \propto u_+ c_+ z_+$$

and

$$I_- \propto u_- c_- z_-$$

Hence,

$$t_+ = \frac{u_+ c_+ z_+}{(u_+ c_+ z_+) + (u_- c_- z_-)}$$

and

$$t_- = \frac{u_- c_- z_-}{(u_+ c_+ z_+) + (u_- c_- z_-)}$$

Thus,

$$t_+ = \frac{u_+}{(u_+) + (u_-)}$$

and

$$t_- = \frac{u_-}{(u_+) + (u_-)}$$

Let us consider at infinite dilution the ionic conductance of cation is λ_c and ionic conductance of anion is λ_a . Now as ionic conductance varies directly proportional to speed of that particular type of ion-

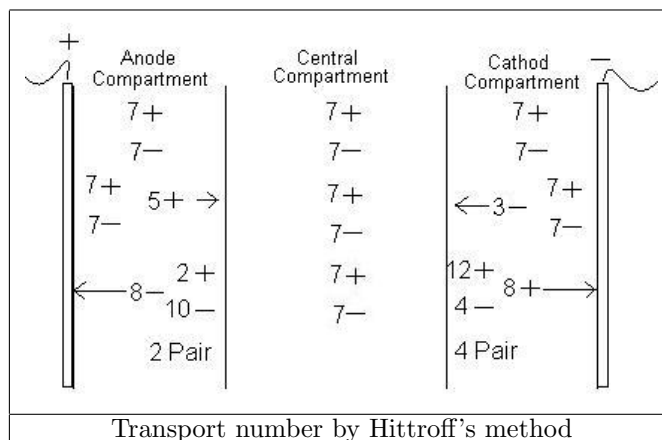
$$u_+ \propto \lambda_c \text{ and } u_- \propto \lambda_a$$

Thus,

$$t_+ = \frac{\lambda_c}{(\lambda_c + \lambda_a)} \text{ and } t_- = \frac{\lambda_a}{(\lambda_c + \lambda_a)}$$

$$\text{or, } t_+ = \frac{\lambda_c}{\Lambda_0} \text{ and } t_- = \frac{\lambda_a}{\Lambda_0}$$

So, transport number of a particular type of ion can be expressed as fraction of conductance at infinite dilution offered by that particular type of ion.



4.6 Mobility of H^+ and OH^- ions in aqueous solution

The ionic mobility and hence the conductance value of both H^+ and OH^- ion is very high. The conductance value of H^+ and OH^- ions are $350 \text{ mho.cm}^2.\text{mole}^{-1}$ and $200 \text{ mho.cm}^2.\text{mole}^{-1}$ respectively.

Earlier it was considered that high charge density of both the ion is responsible for this abnormal high conductance. But in aqueous solution the H^+ ion basically exists as a hydroxonium ion H_3O^+ . The high mobility can be explained by the fact that from hydroxonium ion the H^+ ion migrates to neighboring water molecule and thus the proton molecule is transported from one molecule to other molecule of water. Thus in presence of an external field water molecule migrates from one molecule to another molecule. A proton does not travel an entire distance up to the electrode rather it only travels the distance between two water molecule. This mechanism is known as Grotthus-type mechanism.

Hydroxyl ion are getting transported in similar manner. The major difference is that in proton transfer proton transported from hydroxonium ion to water molecule but in case for hydroxide ion transport proton transported from water to adjacent hydroxide ion.