Electrolytic Conductance

Conductance that results from the presence in the electrolytes of positive and negative ions (cations and anions) Electrolyte solutions obey Ohm's law just as metallic conductors do. Thus the current, I, passing through a given body of solution is proportional to the applied potential difference, V. The resistance, R, of the solution in ohms (Ω) is given by R = V/I, where the potential difference is expressed in volts and the current in amperes. The reciprocal of the resistance is called conductance. It is denoted by C with units in in ohm⁻¹ or mho or Siemen(S). It is direct proportional to the cross-sectional area A, in cm² and inversely proportional to the length ℓ, in cm:

\[
\frac{1}{R} = \kappa A / ℓ
\]

\[
ℓ / A = K
\]

Where K is the cell constant with units of cm⁻¹

Where κ (Kappa) is the specific conductance with units cm⁻¹

\[
\frac{1}{R} = \bar{C}
\]

\[
R = ℓ / κ A
\]

\[
R = ℓ \rho / A
\]

Where ρ (rho) is the specific resistance (resistivity) with units cm

(By international agreement, the reciprocal ohm Ω⁻¹ is now called a Siemens, S=1 Ω⁻¹). One can think of the specific conductance as the conductance of a cube of material, 1 m on each edge. Since it is difficult to build a cell with well defined geometrical parameters A and ℓ, any cell should be calibrated with a solution of exactly known specific conductance. From equation cell constant K can be determine:

\[
κ R = ℓ / A
\]

\[
K \equiv ℓ = κ \cdot R
\]
The cell constant, $K$, with units cm$^{-1}$, is determined by measuring the resistance of a cell filled with a solution of known specific conductance, which is here KCl. Once the cell constant $K$ has been determined, specific conductance of any solution can be calculated from experimental resistances by using equation. The specific conductance $\kappa$ increases as the concentration increases.

Equivalent conductance is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution. It is expressed as $\Lambda$ and is related to specific conductance as

$$\Lambda = k \times 1000/c$$

And

$$\Lambda_m = k \times 1000/M$$

($M$ is Molarity of the solution)

The units of concentration, $c$, are equiv/L and the units of $\Lambda$ are cm$^2$ equiv$^{-1}$ ohm$^{-1}$. This is a CGS unit and is the unit of equivalent conductance most frequently tabulated in the literature. The SI unit is obtained by multiplying the CGS unit by $10^{-4}$. Note, that in the case of simple one-one electrolytes $A^+B^-$, there is no distinction between equivalents and moles and the equivalent conductance is the same as the molar conductance.

**Example**

The resistance of cell contains 0.1 equiv/L of KCl is measured which was 3468.9 ohm at 25°C. Then, the same cell was used to measure of resistance of 0.1 N for an electrolyte at same temperature which was 4573.4 ohm. Calculate the equivalent conductance for later solution given that the specific conductance of KCl solution at 25°C is 0.012856 ohm$^{-1}$ cm$^{-1}$.

**Solution**

$$1/R = k \Lambda / \ell$$

$$K = \ell / A$$

$$1/R = k/K$$

$$K = kR$$
K=(0.012856 ohm\(^{-1}\)cm\(^{-1}\))( 3468.9 ohm)
=44.597 cm\(^{-1}\)

For 2\(^{\text{nd}}\) esolution

K=K/R
=44.597 cm\(^{-1}\)/4573.4 ohm
=0.009751 ohm\(^{-1}\)cm\(^{-1}\)

c=0.1 equi/1000 cm\(^3\)

\[ \Lambda = \frac{k}{c} \]
=0.009751 ohm\(^{-1}\)cm\(^{-1}\)/0.0001 equi cm\(^{-3}\)
=97.51 equi\(^{-1}\)ohm\(^{-1}\)cm\(^2\)

**Factors Affecting the Electrolytic Conductance**

The conductance of an electrolyte depends upon the following factors:

(I) **Nature of electrolyte**: Electrolytic conduction is greatly affected by the nature of electrolytes. The degree of dissociation of electrolytes determines the concentration of ions in the solution and hence the conductivity of electrolytes. Substances such as CH\(_3\)COOH, with low degree of dissociation will have less number of ions in the solution and hence their conductivity will also be low and these are called weak electrolytes. Strong electrolytes such as KNO\(_3\) have high degree of dissociation and hence their solutions have high concentration of ions and so they are good electrolytic conductance.

(II) **Concentration of the solution**: The molar conductance of electrolytic solution varies with the concentration of the electrolyte. In general, the molar conductance of an electrolyte increases with decrease in concentration or increase in dilution.

For weak electrolytes the variation of \(\Lambda\) with dilution can be explained on the bases of number of ions in solution. The number of ions furnished by an electrolyte in solution depends upon the degree of dissociation with dilution. With the increase in dilution, the degree of dissociation increases and as a result molar conductance increases. The limiting value of molar conductance \((\Lambda_\infty)\) corresponds to degree of dissociation equal to 1 i.e., the whole of the electrolyte dissociates.

Thus, the degree of dissociation can be calculated at any concentration as,

\[ \alpha = \frac{\Lambda}{\Lambda_\infty} \]
where \( \alpha \) is the degree of dissociation,

\[ \Lambda^* \] is the molar conductance at concentration \( C \) and

\[ \Lambda^I \] is the molar conductance at infinite dilution.

**Strong Electrolytes.** A strong electrolyte is a solute that completely, or almost completely, ionizes or dissociates in a solution. While the specific conductance of a solution increases with concentration, the equivalent conductance decreases as the concentration increases. **Onsager** showed theoretically for strong electrolytes in dilute solution that the effect of ionic attraction reduces the equivalent conductance.

\[
\Lambda = \Lambda_0 - k \cdot c^{1/2}
\]

there is no increase in the number of ions with dilution because strong electrolytes are completely ionised in solution at all concentrations (By definition). However, in concentrated solutions of strong electrolytes there are strong forces of attraction between the ions of opposite charges called inter-ionic forces. Due to these inter-ionic forces the conducting ability of the ions is less in concentrated solutions. With dilution, the ions become far apart from one another and inter-ionic forces decrease. As a result, molar conductivity increases with dilution. When the concentration of the solution becomes very-very low, the inter-ionic attractions become negligible and the molar conductance approaches the limiting value called molar conductance at infinite dilution. This value is characteristic of each electrolyte.

(III) **Temperature:** The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increases.

### 2. Strong Electrolytes

Kohlrausch law states that, “At time infinite dilution, the molar conductivity of an electrolyte can be expressed as the sum of the contributions from its individual ions i.e at infinite dilution the ions act completely independently, and it is then possible to express \( \Lambda_0 \) as the sum of the limiting conductances of the separate ions. For a one-one electrolyte”

\[ \Lambda_0 = \lambda_0^+ + \lambda_0^- \]
Where $\lambda_0^+ = F \cdot U_0^+$ and $\lambda_0^- = F \cdot U_0^-$, $F$ is a Faraday number, and $\lambda_0^+$ and $\lambda_0^-$ are the ionic equivalent conductance of positive and negative ions, respectively. Note that $U$ is the mobility of the ion, defined as the speed of the ion under the influence of an electric field:

$$U_0^\pm = z^\pm \cdot \frac{v}{E}$$

Where $z^+$ and $z^-$ are valences of positive and negative ions, respectively, and therefore the mobility has units of $\text{m}^2\text{s}^{-1}\text{V}^{-1}$. A table of equivalent conductance at infinite dilution of some strong electrolytes is presented below:

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$\Lambda_0$</th>
<th>Electrolyte</th>
<th>$\Lambda_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>426.16</td>
<td>CaCl$_2$</td>
<td>135.84</td>
</tr>
<tr>
<td>LiCl</td>
<td>115.03</td>
<td>Ca(NO$_3$)$_2$</td>
<td>130.94</td>
</tr>
<tr>
<td>NaCl</td>
<td>126.45</td>
<td>BaCl$_2$</td>
<td>139.98</td>
</tr>
<tr>
<td>KCl</td>
<td>149.86</td>
<td>NaNO$_3$</td>
<td>121.55</td>
</tr>
<tr>
<td>KBr</td>
<td>151.90</td>
<td>KNO$_3$</td>
<td>144.96</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>149.70</td>
<td>NaO$_2$CCH$_3$</td>
<td>91.00</td>
</tr>
</tbody>
</table>

The following table shows Limiting ion conductivity in water at 298 K.

<table>
<thead>
<tr>
<th>Cations</th>
<th>$\lambda_+^0$ / mS m$^2$ mol$^{-1}$</th>
<th>anions</th>
<th>$\lambda_-^0$ / mS m$^2$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>34.96</td>
<td>OH$^-$</td>
<td>19.91</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>3.869</td>
<td>Cl$^-$</td>
<td>7.634</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>5.011</td>
<td>Br$^-$</td>
<td>7.84</td>
</tr>
</tbody>
</table>
4. Equilibrium Constant for Weak Electrolyte

Knowing the concentration $c$ of the weak electrolyte, say HAc, and its degree of ionization $\alpha$ at that concentration, the concentrations of $H^+$ and Ac$^-$ ions and of un-ionized HAc can be calculated. Then the equilibrium constant in terms of concentrations $K_c$ can be calculated from

$$K_c = \frac{[H^+][Ac^-]}{[HAc]} = c \frac{\alpha^2}{1-\alpha}$$

Once we know $K_c$, we can predict the concentration dependence of the equivalent conductance. More usefully, we can use the concentration dependence of $\Lambda$ in measurements of the limiting conductance. Using Equations and we obtain Ostwald’s law:

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{\Lambda \cdot c}{K_c \cdot (\Lambda_0)^2}$$

This equation implies that, if $1/\Lambda$ is plotted against $\Lambda \cdot c$, then the intercept at $c=0$ will be $1/\Lambda_0$.

**Difference between Electrochemical Cell and Electrolytic Cells.**

<table>
<thead>
<tr>
<th>Electrochemical Cell</th>
<th>Electrolytic Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>It converts chemical energy into electrical energy.</td>
<td>It converts electrical energy into chemical energy.</td>
</tr>
<tr>
<td>It is based upon the redox reactions which are spontaneous.</td>
<td>The redox reactions are non-spontaneous and take place only when energy is supplied.</td>
</tr>
<tr>
<td>The chemical changes occurring in the reaction occur.</td>
<td>Only one chemical compound</td>
</tr>
<tr>
<td>Electrochemical Cell</td>
<td>Electrolytic Cell</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>--------------------------------------------------------</td>
</tr>
<tr>
<td>two beakers are different.</td>
<td>undergoes decomposition.</td>
</tr>
<tr>
<td>Anode (-ve) - Oxidation takes place.</td>
<td>Anode (+ve) - Oxidation takes place.</td>
</tr>
<tr>
<td>Cathode (+ve) - Reduction takes place.</td>
<td>Cathode (-ve) - Reduction takes place</td>
</tr>
</tbody>
</table>