Conductance of solutions
Theoretical background

1. Introduction
In this experiment we shall be concerned with electrical conduction through aqueous solutions. Although water is itself a very poor conductor of electricity, the presence of ionic species in solution increases the conductance considerably. The conductance of such electrolytic solutions depends on the concentration of the ions and also on the nature of the ions present (through their charges and mobilities). Conductance behavior as a function of concentration is different for strong and weak electrolytes. In this experiment we will study both strong and weak electrolytes, at a number of dilute concentrations. The acid dissociation constant (also called acidity constant or acid-ionization constant) for a weak electrolyte will be calculated from the data obtained.

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 body of solution in ohms (Ω) is given by R = V/I. where the potential difference is expressed in volts and the current in amperes. The conductance, defined as the reciprocal of the resistance, of a homogeneous body of uniform cross section is proportional to the cross-sectional area A and inversely proportional to the length ℓ:

\[
\frac{1}{R} = \frac{κ \cdot A}{ℓ}
\]

where κ is the specific conductance with units Ω⁻¹ m⁻¹ (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 (1) we can determine the cell constant K:
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 conductances of any solution can be calculated from experimental resistances by using equation (2). The specific conductance $\kappa$ increases as the concentration increases. A more fundamental unit of electrolytic conductance is the **equivalent conductance** $\Lambda$, which can be thought as the value of $\kappa$ contributed by one equivalent of ions contained in 1000 cm$^3$ (1 Liter) of solvent. It is defined as:

$$\Lambda = \frac{1000 \cdot \kappa}{c}$$

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**.

### 2. 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.

$$\Lambda = \Lambda_0 - A \cdot c^{1/2}$$

Below concentrations of about 0.1 M, a plot of $\Lambda$ against $c^{1/2}$ gives a straight line, the intercept of which equals $\Lambda_0$, the equivalent conductance at infinite dilution. 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 $A^+B^-$
\( \Lambda_0 = \lambda_0^+ + \lambda_0^- \)

where \( \lambda_0^+ = \mathcal{F} \cdot U_0^+ \) and \( \lambda_0^- = \mathcal{F} \cdot U_0^- \), \( \mathcal{F} \) is a Faraday number, and \( \lambda_0^+ \) and \( \lambda_0^- \) are the ionic mobilities of positive and negative ions, respectively. Note that the mobility is defined as the speed of an ion, \( U \), under the influence of unit electric field:

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

where \( z^+ \) and \( z^- \) are a valences of positive and negative ions, respectively. Hence the mobility has the units \( \text{m}^2\text{s}^{-1}\text{V}^{-1} \). The Table of equivalent conductances 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>

### 3. Weak Electrolytes

For a weakly ionized substance, \( \Lambda \) varies much more markedly with concentration because the degree of ionization, \( \alpha \), varies strongly with concentration. The equivalent conductance, however, must approach a constant finite value at infinite dilution, \( \Lambda_0 \), which again corresponds to the sum of the limiting ionic conductances. It is usually impractical to determine this limiting value from extrapolation of \( \Lambda \) values obtained with the weak electrolyte itself, since to obtain an approach to complete ionization the concentration must be made too small for effective measurement of conductance. However, \( \Lambda_0 \) for a weak electrolyte can be
deduced from \( \Lambda_0 \) values obtained for strong electrolytes by the use of equation (5). As an example, let us consider acetic acid (CH3COOH, denoted as HAc) as a typical weak electrolyte. It follows from equation (5) that

\[
\Lambda_0(\text{HAc}) = \Lambda_0(\text{HX}) + \Lambda_0(\text{MAc}) - \Lambda_0(\text{MX})
\]

where \( M^+ \) is any convenient univalent positive ion such as K\(^+\) or Na\(^+\) and \( X^- \) is a univalent negative ion such as Cl\(^-\) or Br\(^-\). The only restriction on \( M \) and \( X \) is the requirement that \( \text{HX}, \text{MAc}, \) and \( \text{MX} \) must all be strong electrolytes so that their \( \Lambda_0 \) values can be obtained by extrapolation using equation (4). For sufficiently weak electrolytes, the ionic concentration is small and the effect of ion attraction on the mobilities is slight; thus we may assume the mobilities to be independent of concentration and obtain the approximate expression:

\[
\alpha = \frac{\Lambda}{\Lambda_0}
\]

If one measures for a weak electrolyte at a concentration \( c \) and calculates \( \Lambda_0 \) from the conductivity data for strong electrolytes as described above, it is possible to obtain the degree of ionization of the weak electrolyte at concentration \( c \).

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 \( \text{H}^+ \) and \( \text{Ac}^- \) ions and of un-ionized HAc can be calculated. Then the equilibrium constant in terms of concentrations \( K_c \) can be calculated from

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

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 (8) and (9) we obtain Ostwald’s law:

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

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