Related concepts
Kohlrausch’s law, equivalent conductivity, temperature-dependence of conductivity, Ostwald’s dilution law.

Principle
It is possible to differentiate between strong and weak electrolytes by measuring their electrical conductance. Strong electrolytes follow Kohlrausch’s law, whereas weak electrolytes are described by Ostwald’s dilution law. The examination of the concentration dependence of the conductivity allows the molar conductivities of infinitely diluted electrolytes to be determined, and facilitates the calculation of the degree of dissociation and the dissociation constants of weak electrolytes.

Tasks
1. Determine the concentration dependence of the electrical conductivity of potassium chloride and acetic acid solutions.
2. Calculate the molar conductivity using data from the measurements taken and determine the molar conductivity at infinite dilution by extrapolation.
3. Determine the dissociation constant of acetic acid.

Equipment

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<th>Item</th>
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<tr>
<td>Cobra3 Chem-Unit</td>
<td>12153.00*</td>
<td>1</td>
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<td>Power supply 12 V/2 A</td>
<td>12151.99</td>
<td>1</td>
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<td>Data cable, RS232</td>
<td>14602.00</td>
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<td>Software Cobra3 Chem-Unit</td>
<td>14520.61*</td>
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<td>Conductivity / temperature electrode</td>
<td>13701.01*</td>
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<tr>
<td>Magnetic stirrer, mini</td>
<td>47334.93</td>
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<tr>
<td>Magnetic stirrer bar, ( l = 15 \text{ mm} )</td>
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<tr>
<td>Retort stand, ( h = 750 \text{ mm} )</td>
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<td>Right angle clamp</td>
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<td>Spring balance holder</td>
<td>03065.20</td>
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<tr>
<td>Support rod with hole, ( l = 100 \text{ mm} )</td>
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Changes in the equipment required for use of the Basic-Unit:

<table>
<thead>
<tr>
<th>Item</th>
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<th>Amount</th>
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<tbody>
<tr>
<td>Cobra3 Basic-Unit</td>
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<tr>
<td>Measuring module Conductivity</td>
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<td>Software Cobra3 Conductivity</td>
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</tr>
<tr>
<td>Conductivity probe</td>
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</tbody>
</table>

Fig. 1. Experimental set-up.
Set-up and procedure
Perform the experimental set-up according to Fig. 1.
Prepare the solutions required for the experiment in the following manner:

- 0.1 molar KCl solution: Weigh 7.4551 g of dried potassium chloride into a 1000 ml volumetric flask, add some distilled water to dissolve it, and then make up to the calibration mark with distilled water.
- 0.05 molar KCl solution: Weigh 3.7275 g of dried potassium chloride into a 1000 ml volumetric flask, add some distilled water to dissolve it, and then make up to the calibration mark with distilled water.
- 0.01 molar KCl solution: Pipette 25 ml of the 0.1 molar KCl solution into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.005 molar KCl solution: Pipette 25 ml of the 0.05 molar KCl solution into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.001 molar KCl solution: Pipette 5 ml of the 0.1 molar KCl solution into a 500 ml volumetric flask and make up to the mark with distilled water.
- 0.0005 molar KCl solution: Pipette 5 ml of the 0.05 molar KCl solution into a 500 ml volumetric flask and make up to the mark with distilled water.
- 0.0001 molar KCl solution: Pipette 1 ml of the 0.1 molar KCl solution into a 1000 ml volumetric flask and make up to the mark with distilled water.

- 0.1 molar CH₃COOH solution: Pipette 100 ml of the 1 molar acetic acid solution into a 1000 ml volumetric flask and make up to the mark with distilled water.
- 0.05 molar CH₃COOH solution: Pipette 50 ml of the 0.1 molar acetic acid solution into a 1000 ml volumetric flask and make up to the mark with distilled water.
- 0.01 molar CH₃COOH solution: Pipette 25 ml of the 0.1 molar acetic acid solution into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.005 molar CH₃COOH solution: Pipette 25 ml of the 0.05 molar acetic acid solution into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.0005 molar CH₃COOH solution: Pipette 5 ml of the 0.05 molar acetic acid solution into a 500 ml volumetric flask and make up to the mark with distilled water.
- 0.0001 molar CH₃COOH solution: Pipette 1 ml of the 0.1 molar acetic acid solution into a 1000 ml volumetric flask and make up to the mark with distilled water.

Connect the conductivity / temperature probe to the appropriate input of the Cobra3 Chem-Unit.
Call up the ‘Measure’ programme in Windows and enter <Chem-Unit> as measuring instrument. Set the measurement parameters as shown in Fig. 2.
In <Preferences>, under <Conductivity>, select <Conductivity> as mode, <auto> as range, <µS> as unit, and in Temperature compensation select < with Pt 1000> and <linear>. Under <Temperature> select <°C> as unit and <Average over 1 value>. Under the menu point <Displays>, set the <Range> for Conductivity to 0 – 12000 µS. Set digital display 1 to <Conductivity>. Under Diagrams select <Line diagram> for Diagram1, <Conductivity> for Diagram 1a, and <from 0 to 10> and <no auto range> for the display range.
Confirm your entries with <OK>. Now calibrate your sensor under the menu point <Calibrate> at <Conductivity>, either by entering the value of the calibration solution and, after immersion of the sensor, pressing <Calibrate>, or by entering the value of the cell constant of your sensor. For <Temperature> you can either enter a temperature value measured with a thermometer, or calibrate against the level of a temperature probe connected to T1, T2 or T3. After having made these settings, press <Continue> to reach the field for the recording of measured values. Arrange the displays as you want them.
When measuring the conductivity, always begin with the solution having the lowest concentration in each series of measurements. Before each new measurement, thoroughly rinse the probe, the glass beaker and the magnetic stirrer bar, first with distilled water and then with the solution to be subsequently measured.
Determine the conductivity of the distilled water that is used for the dilution of the solutions and note the result. This is to enable the conductivity of the water used to be taken into consideration in the evaluation.
Place a glass beaker containing a magnetic stirrer bar on the magnetic stirrer. Pour the first potassium chloride solution to be measured into the glass beaker, and immerse the previously well-rinsed conductivity cell to a depth of approximately 5 cm in the solution. Adjust the magnetic stirrer to a medium stirring speed. Record the first value by pressing <Save value>.

Fig. 2: Measurement parameters

![Measurement parameters table]

Fig. 3: Conductivity of potassium chloride solutions as a function of the concentration

![Conductivity graph]
Subsequently determine the respective conductivities of the other solutions in the same manner, whereby in each case the solution with the next higher concentration is measured. While recording the measuring series, pay strict attention to cleanliness as even the slightest trace of contaminants (e.g. by carrying over some of one solution into another) would result in the registration of erroneous data. Stop the measurement by pressing <Close> and save the data with <File> <Save the measurement as...>. To have the plot of conductivity versus concentration carried out, make the following alterations. Under the menu point <Information> <x-data> enter <Concentration> as Title, <c> as Symbol, <mol/l> as Unit and <4> for Digits beyond point. Under <Data table> change the numbers 1 – 7 into the corresponding concentrations 0.0001 – 0.1 M in the right order. Fig. 3 shows the graph as it is now presented by the programme. Before measuring the conductivities of the acetic acid solutions, change the <Range> for Conductivity under the menu point <Displays> to 0 – 600 µS. Carry out the measurements and the alterations under <Information> and <Data table> using the same procedure as above. In addition, under <Display options> <left y-axis>, you can select the second button for the Interpolation (spline interpolation), so that the programme constructs a curve.

Theory and evaluation

The resistance of a conductor having a uniform cross section is proportional to the length l and inversely proportional to the cross sectional area A of the conductor.

\[ R = \frac{\rho \cdot l}{A} = \frac{l}{\kappa \cdot A} = \frac{l}{L} \]  

(1)

The substance constant \( \rho \) is known as the specific resistance; its reciprocal \( \kappa \) as the specific conductivity, and the reciprocal of the resistance as the conductance \( L \). It is usual to use \( \rho \) for metallic conductors and \( \kappa \) for electrolytes. The conductivity for an electrolytic solution results in the following:

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

(2)

having the dimension \( \Omega^{-1} \cdot \text{cm}^{-1} \).

If the conductivity of a solution is to be measured, then the measurements of the cell (length and area) must be known. Therefore, the cell is usually calibrated with a solution with a known conductivity. The ratio of the measured to the tabulated conductivity of a calibration solution directly provides the ratio of the length to the cross section. This ratio is also known as the cell constant. Usually it can be found in the accompanying test certificate.

As a result of the strong concentration dependency, the conductivity is not appropriate for comparing electrolytes. For these purposes it is better to determine the molar conductivity \( \Lambda \). This is calculated from the specific conductivity \( \kappa \) and the concentration \( c \) (in mol · l\(^{-1}\)) of the substance in the electrolyte solution:

\[ \Lambda = \frac{\kappa}{c} \]  

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When the concentration dependence of the conductivity in electrolytes is examined, one finds that the conductivity basically increases with the concentration because the number of the charge carriers (ions) increases. The plot of molar conductivity versus concentration can be calculated with <Channel modification> under menu prompt <Analysis> by setting the parameters as given in Fig. 5. In this operation you can also subtract the conductivity of the distilled water. With <Assume channel> under <Measurement> the two diagrams for potassium chloride and acetic acid can be shown in one (Fig. 6).

The molar conductivity approaches a limit $\Lambda_{\infty}$ with increasing dilution. This is the conductivity infinite dilution. Kohlrausch found the following conformity to natural law for the concentration dependency of the molar conductivity for strong electrolytes:

$$\Lambda_m = \Lambda_{\infty} - k \sqrt{c}$$

(4)

According to Kohlrausch’s law, plotting the molar conductivity of KCl against the square root of the concentration should result in a straight line. This line’s intersection with the ordinate is the molar conductivity at infinite dilution.

Weak electrolytes do not dissociate completely and have a lower conductivity than strong electrolytes. As the concentration increases, the dissociation equilibrium shifts in the direction of non-dissociated molecules. The degree of dissociation $\alpha$ of weak electrolytes is the quotient of the molar conductivity divided by the molar conductivity at infinite dilution.

$$\alpha = \frac{\Lambda_m}{\Lambda}$$

(5)

Ostwald’s dilution law is valid for weak electrolytes. It enables dissociation constants to be calculated:

$$K = \frac{\alpha^2 \cdot c}{1 - \alpha} = \frac{\Lambda_m^2 \cdot c}{(\Lambda_{\infty} - \Lambda_m) \Lambda_{\infty}}$$

(6)

The limiting value of the molar conductivity of weak electrolytes at infinite dilution is first reached at extremely low concentrations; therefore, exact measurements in this are no longer possible. Consequently $\Lambda_{\infty}$ cannot be obtained by extrapolating $\Lambda_m/\sqrt{c}$-curves for weak electrolytes. Equation (7) is derived by transforming Ostwald’s law of dilution:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_{\infty}} + \frac{\Lambda_m \cdot c}{\kappa \cdot \Lambda_{\infty}^2}$$

(7)

From equation (7) it can be seen that a linear relationship exists between the reciprocal of the conductivity and the product of the molar conductivity and the concentration of weak electrolytes. Furthermore, Ostwald’s law of dilution shows that the molar conductivity at infinite dilution can be obtained from the line’s point of intersection of the line with the ordinate $1/\Lambda_m$ over $c \cdot \Lambda_m$. 