

A22 Electric conductivity of strong and weak electrolytes

Task:

Determine the concentration dependence of the electric conductivity in aqueous solutions of a strong (NaCl) and a weak (acetic acid) electrolyte at 25 °C.

Basics:

In a conductor with length l and area q the electric resistance is given by

$$R = \sigma \frac{l}{q} = \frac{1}{\kappa} \frac{l}{q} \quad (1)$$

σ is the specific resistance, the corresponding inverse κ is the specific conductivity of the conductor. In general, an electrolyte between two electrodes – this arrangement is called a “cell” – has no specific shape (most often, the electric field is inhomogeneous between the margin electrodes) and hence, l/q cannot be easily calculated. Therefore, one introduces the cell constant $C = l/q$ and equation then reads

$$\kappa = \frac{C}{R} \quad (2)$$

C is determined by measuring the resistance of a calibration solution of well-known specific conductivity and determining C using equation (2).

As the electric conductivity of an electrolyte solution depends on the concentration of the electrolyte, one can define the molar conductivity Λ by dividing the specific conductivity by the concentration

$$\Lambda = \frac{\kappa}{c} \quad (3)$$

Hereby, c is the concentration, i.e. the amount of solved substance per liter. Get acquainted with the units of all quantities mentioned above (electric resistance, specific and molar conductivity).

It turns out that Λ itself depend on concentration where two cases can be distinguished:

a) Strong electrolytes

In this case, one can assume complete dissociation, the mobility, however, is limited by interionic interactions (especially at high concentrations). Kohlrausch empirically found a “square-root law”

$$\Lambda = \Lambda_{\infty} - A\sqrt{c}. \quad (4)$$

Λ_{∞} is the limiting molar conductivity at infinite dilution und results by addition of the individual conductivities of the ions.

b) Weak electrolytes

Weak electrolytes are only dissociated to a certain fraction, though a relationship between the dissociation α and the molar conductivity Λ exists that can mostly be expressed with sufficient accuracy by

$$\alpha = \frac{\Lambda}{\Lambda_{\infty}} \quad (5)$$

Applying mass action law for the equilibrium between ions and non-dissociated molecules one obtains "Ostwald's dilution law" (e.g. each molecule dissociates into two ions)

$$K_c = \frac{\alpha^2}{1-\alpha} c = \frac{\left(\frac{\Lambda}{\Lambda_{\infty}}\right)^2}{1-\frac{\Lambda}{\Lambda_{\infty}}} c \quad (6)$$

where K_c is the dissociation constant with respect to the concentration c .

Experimental procedure:

Determine at 25 °C

- the specific conductivity of water
- the specific conductivity of aqueous NaCl solutions with the following normalities (equivalent concentration): 0.05 n, 0.01 n, 0.005 n and 0.001 n,
- the specific conductivity of aqueous solutions of acetic acids with the following normalities: 0.1 n, 0.05 n, 0.01 n.

The cell constant C has already been saved in the apparatus and needn't to be measured separately. From the conductivity apparatus one can directly read off the specific conductivity.

Solutions listed in b) and c) can be prepared by dilution of the stock solution at hand. Using a thermostat the device is to be temperature-controlled as exact as possible. The measurement cell is filled with the solution to be investigated and the electrodes are plunged in. Make sure that the upper edge of the electrode edge is covered with liquids by at least 1 cm. All vessels (measuring vessel, volumetric flasks and pipettes) are to be used cleaned and dried. Equally, the electrodes and the measuring vessel are to be cleaned after each measurement, advantageously flushed by part of the following measuring solution. If there are two vessels available, one vessel will be cleaned, filled with the new solution and temperature-controlled while the measurement continues in the other cell.

Data analysis:

- In order to obtain the specific conductivity κ , one has to subtract κ_{H_2O} from the measured specific conductivity κ . From this one can calculate the molar conductivity Λ in units of $\text{cm}^2/(\Omega \cdot \text{mol})$. Present your results of weak and strong electrolytes according to the following table:

C	κ	$\kappa - \kappa_{H_2O}$	Λ
-----	-----	-----	-----
...

2. Plot Λ versus \sqrt{c} for NaCl. Determine Λ_{∞} by extrapolation and calculate the constant A from equation (4). Give errors for Λ_{∞} and A.
3. Determine the dissociation degree α and the dissociation constant K_c ($\Lambda_{\infty} = 393,4 \text{ cm}^2/(\Omega \cdot \text{mol})$) from the results for acetic acid. How can one obtain Λ_{∞} for weak electrolytes by extrapolation? Which plot is useful?

What one should know:

Concentration dependence of the specific and molar conductivity of weak and strong electrolytes. Dependency of equivalent conductivity with other transport properties such as viscosity and diffusion. Relationship with ion mobility. Transport numbers. Principle of conductometry. Debye-Hückel-Onsager theory.

Mandatory supplementary question:

1. Sketch the dependency of specific and molar conductivity with respect to the concentration of the electrolyte for strong and weak electrolytes.
2. Discuss the Wheatstone bridge and its applicability to conduction measurements.
3. How does Λ depend on temperature?