Exercise 5

DETERMINATION OF THE LIMITING MOLAR CONDUCTIVITY OF A STRONG ELECTROLYTE

Topics: definition of conductivity, specific conductivity, molar conductivity, limiting molar conductivity, and limiting molar ionic conductivity. Kohlrausch's law of independent ion migration. Determination of molar conductivity and limiting molar conductivity of strong and weak electrolytes. Dependence of electrolyte conductivity on concentration - Kohlrausch's law. Molar conductivity in light of the Debye-Hückel-Onsager theory.

The dependence of the molar conductivity Λ_m of a strong electrolyte on the concentration *c* in the range of low concentrations is given by the empirical law of Kohlrausch:

$$\Lambda_m = \Lambda_m^0 - K c^{1/2} \qquad (1)$$

where Λ_m^0 is the limiting molar conductivity, and K is a constant whose value depends on the stoichiometry of the salt. Kohlrausch's law is derived from the Debye-Hückel-Onsager theory.

The limiting molar conductivity of a strong electrolyte can be determined in the following way. Measure the molar conductivity of the electrolyte for several concentrations, and then, according to equation (1), extrapolate the Λ_m vs. $c^{1/2}$ dependence to zero concentration.

The molar conductivity Λ_m is defined by the formula:

$$\Lambda_m = \frac{\kappa}{c} \qquad (2)$$

where κ is the specific conductivity, also known as the electrolytic conductivity, and *c* is the concentration of the electrolyte solution, expressed in moles per cubic meter. Specific conductivity is the reciprocal of the specific resistance of the electrolyte. Therefore, Ohm's second law can be written in the following form:

$$R = \frac{l}{\kappa A} \qquad (3)$$

After its transformation, we obtain:

$$\kappa = \frac{l}{R A} \qquad (4)$$

where R is the electrical resistance exhibited by the electrolyte between the electrodes (platinum plates coated with platinum black) with a surface area A and separated by a distance l. The electrodes are placed in a vessel, into which the electrolyte under examination is poured. This is the so-called conductometric vessel. The conductometric vessel often takes the shape of a probe that is immersed in the solution being studied. The shape, surface area, and mutual distance of the electrodes do not change during the measurement; these are characteristic quantities for a given conductometric system. Therefore, it is practical to introduce the concept of the vessel constant p:

$$p=\frac{l}{A} \quad (5)$$

Equation (4) takes the form:

$$\kappa=\frac{p}{R} \quad (6)$$

and can be transformed into the relation:

$$\kappa=pG \quad (7)$$

where G [S] is the conductivity of the electrolyte solution. The vessel constant p can be most easily determined by measuring the conductivity of an electrolyte with a precisely known value of κ:

$$p=\frac{\kappa}{G} \quad (8)$$

Note that if Λ_m and κ are expressed in SI units, namely [S m^2 mol^{-1}] and [S m^{-1}] respectively, and the concentration is in [mol dm^{-3}] as per laboratory practice, then in equation (2) a conversion factor for dm^3 to m^3 appears:

$$\Lambda_m=\frac{\kappa}{1000c}\,\frac{[Sm^{-1}]}{\left[dm^3m^{-3}\right][mol\,dm^{-3}]} \quad (9)$$

As implied by equations (7) and (9), measuring molar conductivity essentially involves measuring the conductivity of the electrolyte. The instrument used for conductivity measurements is called a conductometer or conductivity meter.

Performing the exercise

We connect the thermostat and the conductivity meter to the power supply. We verify whether the thermostat is set to a temperature of 25°C. We turn on the heating with mixing, open the cold water tap (cooling the thermostat), and establish a slow flow of cold water. The conductivity measurement is carried out at a temperature of 25°C (which should be set on the conductivity meter screen).

In 100 cm^3 volumetric flasks, we prepare solutions of NaCl with the following concentrations: 0.0016, 0.0025, 0.0036, 0.0049, 0.0064, and 0.0081 mol/dm^3. To prepare them, we use the initial NaCl solution with a concentration of 0.01 mol/dm^3 and freshly distilled water. It's important to note that standing water can dissolve CO_2 over time, and its presence can significantly affect measurement results. Additionally, ensure thorough mixing of the prepared solutions.

We pour the prepared NaCl solutions, the initial NaCl solution, and the 0.01 mol/dm^3 KCl solution into beakers. These beakers are set up on a stand and placed in a thermostat. After 10 minutes (temperature stabilization), we perform conductivity measurements on the prepared electrolytes in order of increasing NaCl concentrations. Finally, we conduct the conductivity measurement of the reference electrolyte - the KCl solution (κ = 0.14114 S m^{-1} for 0.01 M KCl, [M = mol dm^{-3}]).

We conduct the conductivity measurements as follows: we rinse the conductometer electrode several times with distilled water and carefully remove any excess water with blotting paper. We then take the electrode out of the electrolyte a few times and immerse it again to rinse any potential remaining distilled water from the electrode area. Next, we place the electrode into the beaker with the electrolyte and take a conductivity reading from the conductometer. Pay close attention to the precise unit reading on the instrument. We perform the conductivity measurement for each electrolyte three times. From the obtained results, we calculate the arithmetic mean, $\langle G \rangle$.

After completing the measurements, we rinse the electrode and immerse it in distilled water. Then, we turn off the power to the conductivity meter and thermostat, and close the cooling water tap of the device.

Calculations

Based on the measured conductivity values (G_{KCl}) for the reference KCl solution and the calculated arithmetic mean ($\langle G \rangle_{\mathrm{KCl}}$) for them, let's calculate the vessel constant p (equation 8). Knowing p, we can calculate κ (equation 7) and Λ_m (equation 9) for each of the tested solutions. The results should be compiled in a table.

$G_{1\mathrm{KCl}}$ [S] =

$G_{2\mathrm{KCl}}$ [S] =

$G_{3\mathrm{KCl}}$ [S] =

$\langle G \rangle_{\mathrm{KCl}}$ [S] =

Table 1. Results of Conductivity Measurements and Calculations.

c [mol dm^{-3}]	$c^{1/2}$ [mol dm^{-3}]$^{1/2}$	G_{NaCl} [S]			$\langle G \rangle_{\mathrm{NaCl}}$ [S]	κ [S m^{-1}]	Λ_m [S m^2 mol^{-1}]
0.01	0.1						
0.0081	0.09						
0.0064	0.08						
0.0049	0.07						
0.0036	0.06						
0.0025	0.05						
0.0016	0.04						

Based on the experimental data, we create a graph showing the relationship between Λ_m and $c^{1/2}$ (equation 1). We approximate the data points with a straight line of the form y = ax + b using the least squares method. In this case, y corresponds to Λ_m, and x corresponds to $c^{1/2}$. The parameter b represents the sought limiting molar conductivity, Λ_m^0 (equation 1). The literature value of the limiting molar conductivity for NaCl is Λ_m^0 = 0.0126 [S m^2 mol^{-1}].