Determination of the conductivity coefficient with Cobra4 (Item No.: P3060862)

Curricular Relevance

Area of Expertise: Chemistry → **Education Level:** University → **Topic:** Physical Chemistry → **Subtopic:** Electro Chemistry → **Experiment:** Determination of the conductivity coefficient with Cobra4

Difficulty	Preparation Time	Execution Time	Recommended Group Size
Difficult	1 Hour	2 Hours	2 Students

Additional Requirements:

- Compartment drier
- Analytical balance, 120 g / 0.1 mg

Experiment Variations:

Keywords:

Equivalent conductivity, ionic mobility, conductivity, interionic action

Overview

Short description

Principle

The equivalent conductivity of strong electrolytes depends on their concentration. The quotient of the equivalent conductivity at a certain concentration and the equivalent conductivity at infinite dilution is called the conductivity coefficient, which is the result of interionic action.

Fig. 1: Experimental setup.

Safety instructions


Calcium chloride
H319: Causes serious eye irritation
P305+351+338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do – continue rinsing.

Equipment

Position No.	Material	Order No.	Quantity
1	Cobra4 Mobile-Link 2 incl. accessories: battery, USB cable, charger and SD memory card	12620-10	1
2	Cobra4 Sensor-Unit Conductivity+	12632-00	1
3	Conductivity temperature probe Pt1000	13701-01	1
4	Standard solution 1413µS/cm(25°C), 460ml	47070-02	1
5	Protection sleeve for electrode with a diameter of 12 mm	37651-15	1
6	Retort stand, h = 750 mm	37694-00	1
7	Right angle boss-head clamp	37697-00	4
8	Support rod with hole, stainless steel, 10 cm	02036-01	1
9	Spring balance holder	03065-20	1
10	Magnetic stirrer without heating, 3 ltr., 230 V	35761-99	1
11	Magnetic stirring bar 30 mm, cylindrical	46299-02	1
12	Volumetric flask 250 ml, IGJ14/23	36550-00	6
13	Volumetric flask 500 ml, IGJ19/26	36551-00	2
14	Funnel, glass, top dia. 80 mm	34459-00	2
15	Volumetric pipette, 5 ml	36577-00	2
16	Volumetric pipette, 25 ml	36580-00	2
17	Volumetric pipette, 50 ml	36581-00	2
18	Pipettor	36592-00	1
19	Pipette dish	36589-00	1
20	Beaker, high, BORO 3.3, 50 ml	46025-00	2
21	Beaker, high, BORO 3.3, 150 ml	46032-00	8
22	Weighing dishes, square shape, 84 x 84 x 24 mm, 25 pcs.	45019-25	1
23	Spoon, special steel	33398-00	1
24	Pasteur pipettes, 250 pcs	36590-00	1
25	Rubber caps, 10 pcs	39275-03	1
26	Desiccator, vacuum, diam. 150 mm	34126-00	1
27	Porcelain plate f.desiccator150mm	32474-00	1
28	Cristallizing dish,boro3.3, 300ml	46243-00	1
29	Wash bottle, plastic, 500 ml	33931-00	1
30	Silicon grease Molykote, 50 g	31863-05	1
31	Silica gel, orange, granular, 500 g	30224-50	1
32	Potassium chloride 250 g	30098-25	1
33	Calcium chloride, granul. 250 g	48021-25	1
34	Water, distilled 5 l	31246-81	1

Robert-Bosch-Breite 10
D - 37079 Göttingen
Tel: +49 551 604 - 0
Fax: +49 551 604 - 107
info@phywe.de
www.phywe.com

Task

Measure the specific conductivities of various potassium chloride and calcium chloride solutions and calculate the equivalent conductivities. Determine the equivalent conductivities at infinite dilution using the Kohlrausch equation and calculate the conductivity coefficients.

Set-up and procedure

Set up the experiment as shown in Fig. 1. Prepare the solutions required for the experiment as follows:

- 0.05 molar KCl solution: Weigh 1.8638 g of meticulously dried potassium chloride into a 500 ml volumetric flask, add some distilled water to dissolve it, then make up to the mark with distilled water.
- 0.01 molar KCl solution: Pipette 50 ml of 0.05 molar potassium chloride 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 0.05 molar potassium chloride 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 0.05 molar potassium chloride solution into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.05 molar $CaCl_2$ solution: Weigh 2.7746 g of meticulously dried calcium chloride into a 500 ml volumetric flask, add some distilled water to dissolve it, then make up to the mark with distilled water.
- 0.01 molar $CaCl_2$ solution: Pipette 50 ml of 0.05 molar calcium chloride solution into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.005 molar $CaCl_2$ solution: Pipette 25 ml of 0.05 molar calcium chloride solution into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.001 molar $CaCl_2$ solution: Pipette 5 ml of 0.05 molar calcium chloride solution into a 250 ml volumetric flask and make up to the mark with distilled water.

Use the standard solution to calibrate the conductivity / temperature electrode according to the Operation Instructions manual supplied with the conductivity meter. Begin the measurements in each series with the solution of lowest concentration. Rinse the measuring electrode, the beaker and the magnetic stirrer bar in distilled water and then in the solution to be measured. Fill the respective solution into the beaker, immerse the conductivity cell to a depth of approx. 5 cm and read the conductivity. Subsequently continue the measurement series, using the solution of next higher concentration for each successive measurement. Finally determine the conductivity of the distilled water used.

Theory and evaluation

The amperage I is a measure for the sum of the elementary charges passing the cross-section of a conductor in a time unit. A number N_+ of cations per cm^3 having a charge of $z_+ \cdot e_0$ cause an amperage I_+ at a velocity of v_+:

$$I_+ = z_+ \cdot e_0 \cdot N_+ \cdot q \cdot v_+ \quad (1)$$

Similiarly, the portion of the anions is:

$$I_- = z_- \cdot e_0 \cdot N_- \cdot q \cdot v_- \quad (2)$$

where

z Charge number

e_0 Elementary charge

N Number of ions per cm³

q Cross-section of the conductor

v Velocity

If we define the migration velocity u of an ion

$u = \frac{v}{\vec{E}}$ (3)

where

E Field strength

we obtain for the total amperage

$I = e_0 \cdot q \cdot \vec{E}(N_+ \cdot z_+ \cdot u_+ + N_- \cdot z_- \cdot u_-)$ (4)

Considering the field strength, we obtain for Ohm’s law:

$I = \frac{U}{R} = \frac{\vec{E} \cdot L}{R}$ (5)

U Voltage

R Resistance

L Length of the conductor

Equating (4) and (5) results in:

$R = \frac{L}{e_0 \cdot q \cdot (N_+ \cdot z_+ \cdot u_+ + N_- \cdot z_- \cdot u_-)}$ (6)

The specific resistance ρ of a conductor is defined as follows:

$\rho = R \cdot \frac{q}{L}$ (7)

Replacing R by the term in equation (6), we obtain:

$$\rho = \frac{1}{e_0 \cdot (N_+ \cdot z_+ \cdot u_+ + N - - \cdot z_- \cdot u_-)} \quad (8)$$

For the specific conductivity κ as reciprocal value of the specific resistance, we thus obtain:

$$\kappa = e_0 \cdot (N - + \cdot z_+ \cdot u_+ + N_- \cdot z_- \cdot u_-) \quad (9)$$

Conversion of the particle number N per cm [3] into the molar concentration c yields:

$$N_+ = c \cdot (\frac{v_+ \cdot N_\mathrm{L}}{1000}) \quad (10a)$$

$$N_- = c \cdot (\frac{v_- \cdot N_\mathrm{L}}{1000}) \quad (10b)$$

v Ion number per molecule
N_L Avogadro number
c Molar concentration

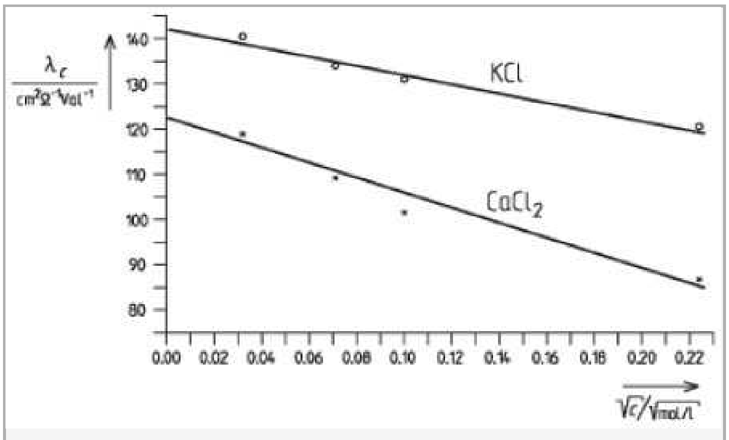

Fig. 2: $\lambda_C - \sqrt{c}$ -curves for potassium chloride and calcium chloride

The electrochemical valence n_e of an electrolyte is

$$n_\mathrm{e} = v_+ \cdot z_+ = v_- \cdot z_- \quad (11)$$

By inserting (10) and (11) into equation (9), we obtain:

$\kappa = \frac{n_e \cdot c \cdot e_0 \cdot N_L}{1000} \cdot (u_+ + u_-)$ (12)

The Faraday constant is defined as the product of e_0 and N_L. After introducing the ionic equivalent conductivies λ_+ and λ_- (acc. to Kohlrausch)

$\lambda_+ = u_+ \cdot F$ (13a)

$\lambda_- = u_- \cdot F$ (13b)

we obtain the fundamental equation for the specific conductivity

$\kappa = n_e \cdot (\frac{c}{1000}) \cdot (\lambda_+ + \lambda_-)$ (14)

The sum of the ion mobilities is called the equivalent conductivity

$\lambda = \lambda_+ + \lambda_-$ (15)

According to equation (14) the conductivity increases linearly with the molar concentration. However, because of interionic action in the case of strong electrolytes, the specific conductivity decreases with increasing concentration. This is the result of the decrease in the equivalent conductivity caused by electrostatic forces, which only cease to exist at infinite dilution. The value λ_∞ is assigned to this condition. The quotient of the equivalent conductivities at a given concentration and at infinite dilution is called the conductivity coefficient:

$f_\lambda = \frac{\lambda_C}{\lambda_\infty}$ (16)

The equivalent conductivity at a given concentration can be calculated from the measured specific conductivity values by means of equation (17):

$\lambda_C = \frac{\kappa \cdot 1000}{n_e \cdot c}$ (17)

For strong electrolytes, the Kohlrausch equation applies :

$\lambda_C = \lambda_\infty - A \cdot \sqrt{c}$ (18)

A Constant

By plotting λ_C versus $\sqrt{C}$ we obtain straight lines which are extrapolated up to $\sqrt{C} = 0$. The point of intersection with the ordinate gives the value for the equivalent conductivity at infinite dilution. The conductivity coefficient can now be calculated for the concentrations used in the measurements.

Data and results

See Tables 1 and 2.

Table 1: Results - KCl

$\frac{c}{\mathrm{mol \cdot l^{-1}}}$	$\frac{\sqrt{c}}{\sqrt{\mathrm{mol \cdot l^{-1}}}}$	$\frac{\kappa}{\mu\mathrm{S \cdot cm^{-1}}}$	$\frac{\lambda_c}{\mathrm{cm^2 \cdot \Omega^{-1} \cdot Val^{-1}}}$	f_c	Lit.-values for f_λ
0.001	0.032	140.5	140.5	0.989	0.979
0.005	0.071	670	134.0	0.943	0.938
0.01	0.1	1310	131.0	0.922	0.919
0.05	0.224	6030	120.6	0.849	0.838

$\lambda_\infty = 142\ \mathrm{cm^2 \cdot \Omega \cdot Val^{-1}}$ (Measuring temperature: 21.5 °C)

Table 2: Results - $CaCl_2$

$\frac{c}{\mathrm{mol \cdot l^{-1}}}$	$\frac{\sqrt{c}}{\sqrt{\mathrm{mol \cdot l^{-1}}}}$	$\frac{\kappa}{\mu\mathrm{S \cdot cm^{-1}}}$	$\frac{\lambda_c}{\mathrm{cm^2 \cdot \Omega^{-1} \cdot Val^{-1}}}$	f_c	Lit.-values for f_λ
0.001	0.032	237.7	118.9	0.981	0.984
0.005	0.071	1092	109.2	0.901	0.937
0.01	0.1	2030	101.5	0.838	0.908
0.05	0.224	8670	86.7	0.715	0.820

$\lambda_\infty = 121\ \mathrm{cm^2 \cdot \Omega \cdot Val^{-1}}$