CONDUCTIVITY OF ELECTROLYTES

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Task 31

CONDUCTIVITY OF ELECTROLYTES

I. Aim of the task

The aim of the task is:

- examination of the dependence of electrolytic and molar electrolytic conductivity on the concentration for strong and weak electrolytes.
- determination of the limit value of molar conductivity of the tested strong and weak electrolytes.
- determination of the degree of dissociation reaction equilibrium constant of weak acids by the conductivity measurements.

II. Introduction

1. Electrolytic conductivity of electrolytes and its dependence on the concentration.
2. The methods of the determination of the electrolytic conductivity of electrolytes.
3. Molar electrolytic conductivity and its dependence on the concentration, limiting molar conductivity, the Kohlrausch's law of the independent movement of ions, determination of the limit value for the molar conductivity of the tested strong and weak electrolytes.
4. Application of the conductivity measurements of electrolyte solutions for the determination of physicochemical parameters.

References:

1. R. Chang, *Physical chemistry for the chemical and biological sciences,* University Science Books, Sausalito, 2000, Chapter 5.
2. G.M. Barrow, *Physical Chemistry,* McGraw-Hill Book, New York, 1966, Chapter 21.
3. I.M.G. Barthel, H. Krienke, W. Kuntz, *Physical Chemistry of electrolyte Solutions,* Springer, New York, Chapter 3.

III. Theory

The flow of the electrical current in a material environment takes place because of the transport of the electric charge whose carriers can be electrons or ions. Depending on the current conduction mechanism, the electrical current conductors are divided into: **electronic** conductors or metallic (metals, semiconductors, superconductors) and **ionic** or **electrolytic**. Typical ionic conductors are solutions of salts, acids and bases, salts - molten or in the solid state.

Pure water does not conduct electricity, but any ionic species would contribute to conductivity of electricity. An ionically conducting solution is called electrolyte solution and the compound which produces the ions while dissolved, is called electrolyte. **A strong electrolyte is a compound that will completely dissociate into ions in water**. Correspondingly, **a weak electrolyte dissolves only partially**. The conductivity of an electrolyte solution depends on its concentration (the ionic species) and changes differently for strong and weak electrolytes. In the case of electrolytic conductors, the flow of electric current is connected with the ions movement. This causes both some chemical changes and those in the concentration of conducting electrolyte. Electrolytes are usually much worse conductors of electricity than metals. Their conductivity is less than 100 [S/m], whereas the metallic conductors show conductivity of the order of 10^6 - 10^8 [S/m]. With the increasing temperature the electric resistivity of electrolytes generally decreases.

The size of the conductivity of the electrolyte solutions depends on their concentration, temperature, chemical nature of the solute (the ability to dissociate into ions), and the type of solvent (the ability to form solvates with the formed ions and the dielectric permittivity). The flow of current through an electrolyte solution (electrolytic conductor) is accompanied by chemical changes occurring at the contacting surfaces of the two types of conductors (and secretion of ions discharge at the electrodes, the electrode reactions or secondary solvent), and changes of the concentration of the electrolyte in the vicinity of electrodes. Chemical processes running in the analyzed systems depend on the chemical properties of the metal electrodes, components of the solution and the potential difference between the electrodes.

Let us consider the electrolyte solution placed in a tube with a length l and cross-sectional area S, connected on the ends with the two electrodes and to which the voltage U is applied. The ions in solution will move in the generated electric field (the field intensity E is equal to U/l) with the uniform motion after finding a balance between:

- **the interaction force of the electric field (F_e)** with the charge of ion ($q = z \cdot e$):

$$F_e = z \cdot e \cdot E \tag{1}$$

where: z - the valence of ion, e - the elementary electric charge of ion,

- **friction force of the center (F_s),** facing the opposite (Stokes law):

$$F_S = 6\pi \cdot \eta \cdot r \cdot v \tag{2}$$

where: η - the viscosity of the solvent, r - the radius of the ion treated as a sphere, v - the ion movement speed.
In an equilibrium state $F_e = F_s$, thus:

$$v = \frac{z \cdot e \cdot E}{6\pi \cdot \eta \cdot r} = u \cdot E \tag{3}$$

As it results from Eq. (3) the ion movement speed v is proportional to the strength of the applied electric field. The proportionality factor u [$m^2/(Vs)$], called **ion mobility** depends on the type of ion and the solvent. The mobility of the ion can be defined as the speed of its movement [m/s] in an electric field of 1 [V/m] strength.

As the temperature increases, the ion mobility increases as a result of the reduction of the solvent viscosity. The intensity of the current flowing through the solution as a result of the migration of the electrolyte ions of charge dQ per unit time dt is:

$$I = \frac{dQ}{dt} \tag{4}$$

Through a unit volume Sdx of the vessel, having the cross-section area S, in the time dt there will flow ions whose total charge carried out charge is equal to:

$$dQ = z \cdot e \cdot n \cdot Sdx = z \cdot e \cdot n \cdot vdt = z \cdot e \cdot c \cdot \alpha \cdot N_a \cdot S \cdot vdt \tag{5}$$

where: $n = c \cdot \alpha \cdot N_a$, n - the number of ions per unit volume of the solution, c - the molar concentration, N_a - the Avogadro number, α - the degree of dissociation, $dx = vdt$.

Hence, the amount of current flowing through the vessel of these dimensions is equal to:

$$I = N_a \cdot e \cdot \alpha \cdot c \cdot z \cdot u \cdot \frac{S}{l} \cdot U = F \cdot c \cdot \alpha \cdot z \cdot u \cdot \frac{S}{l} \cdot U = \kappa \cdot \frac{S}{l} \cdot U = \kappa \cdot S \cdot E \tag{6}$$

where: F - the Faraday constant, κ - the electrical conductivity.

The intensity of the current flowing in the electrolyte solution is proportional to concentration, charge as well as ion mobility and depends on the dimensions of the vessel (its length and cross section area).

Electrical conductivity of the electrolyte solution $\kappa = F \cdot c \cdot \alpha \cdot z \cdot u$ is a measure of the ability of the ions to conduct electricity. It depends on both the concentration of ions and the speed of their movement in the electric field. It is defined as the reciprocal of the resistivity of the electrolyte sample of the cross-section S and length l using the relationship:

$$\kappa = \frac{l}{R \cdot S} \tag{7}$$

The SI unit of conductivity is Siemens per meter [S/m], where $S = \Omega^{-1}$.

Taking into account the presence in the electrolyte solution of both positive and negative ions we can expand the definition of the conductivity:

$$\kappa = F\cdot(c_+\cdot z_+\cdot u_+ + c_-\cdot|z_-|\cdot u_-) = F\cdot c\cdot(\alpha_+\cdot z_+\cdot u_+ + \alpha_-\cdot|z_-|\cdot u_-) \tag{8}$$

From the condition of electroneutrality it results that:

$$\alpha_+\cdot z_+ = \alpha_-\cdot|z_-|$$

$$\kappa = F\cdot c\cdot\alpha_+\cdot z_+(u_+ + u_-) = F\cdot c\cdot\alpha_-\cdot|z_-|\cdot(u_+ + u_-) \tag{9}$$

where: c_+ and c_- is the cation and anion concentration, $c_+ = \alpha_+\cdot c$, $c_- = \alpha_-\cdot c$.

Note: in the case of negative ions do not reflect their characters.

Determination of the electrolyte conductivity is reduced to the measurement of the resistivity of the sample using the calibrated cells. For a given cell the ratio *l*/*S* has a constant value and is called the **cell constant** or **resistance capacity**. It can be determined by measuring the resistance of the reference cell filled with the electrolyte whose conductivity was determined by the direct measurements.

In the case of electrolytes there can not be used the constant current since this will change the composition of the electrolyte and the electrode surface (the polarization of the electrodes). When using the flow current the apparent resistance in the circuit should be eliminated.

The curves of the dependence between the conductivity of electrolyte and its concentration have a characteristic waveform (Fig.1). In the low concentration range an increase of the conductivity with the increasing concentration is observed, which is associated with an increase in the number of ions per a unit volume of the solution. At higher concentrations the interactions between ions increase, thus reducing their mobility and in the case of a weak electrolyte its degree of dissociation also decreases. It causes that the conductivity does not increase, or even it can decrease.

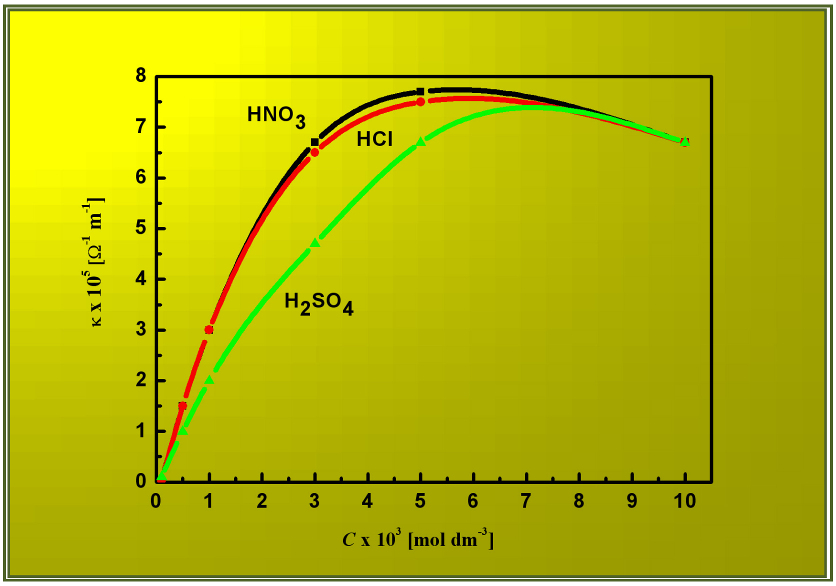

Fig. 1. Dependence of the specific conductivity of HCl, HNO_3 and H_2SO_4 electrolytes on their concentration.

Aside from the specific conductivity, also the **molar conductivity** is used for analysis of properties of the electrolytic conductors:

$$\Lambda = \frac{\kappa}{c} \tag{10}$$

which is defined as the conductivity of an electrolyte placed between two electrodes separated by 1 m (cm) from each other with the cross sectional area S containing 1 mol of the electrolyte. The SI unit of the molar conductivity is the [Sm^2/mol]. Thus, the molar conductivity characterizes the ability of 1 mol of electrolyte to conduct electrical current. The molar conductivity is proportional to the degree of dissociation and a sum of the ions mobility:

$$\Lambda_m = F \cdot \alpha_- \cdot |z_-|(u_+ + u_-) = F \cdot \alpha_+ \cdot z_+(u_+ + u_-) \tag{11}$$

$$\Lambda_m = \alpha_- \cdot |z_-| \cdot \lambda_- = \alpha_+ \cdot z_+ \cdot \lambda_+ \tag{12}$$

where: $\lambda_+ = F \cdot u_+$ and $\lambda_- = F \cdot u_-$ are the molar conductivity of the cation and the anion respectively.

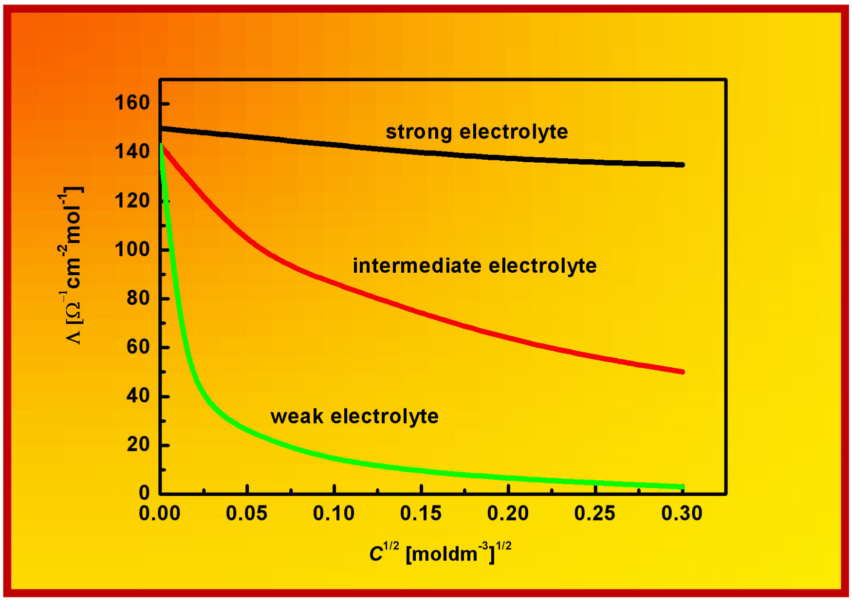

Fig. 2. Dependence of the molar conductivity of strong, intermediate and weak electrolytes on their concentration.

These parameters depend on the concentration of the solution (Fig. 2) and to some extent on the nature of another ion (Table 1). The values of molar conductivity of ions are generally similar, indicating the similarity of their mobility, regardless of their structure and valences. The exceptions are **H^+ and OH^- ions which exhibit much higher conductivity**. This is due to different mechanism of their movement in the solution. The curves of the relation between molar conductivity and concentration show different run for strong and weak electrolytes. At the low concentrations of electrolytes, for both groups of electrolytes, a monotonic decrease in the molar conductivity with concentration is observed, but it is much faster for weak electrolytes. For these electrolytes the conductivity value drops to a low value already in moderately concentrated solutions. It can be explained by decrease of the dissociation degree with the increasing concentration of the electrolyte. The impact of increase in the concentration of strong electrolyte solutions on the decrease in its conductivity is much weaker. At high concentrations of this type of electrolytes, the conductivity level is still high because of the fact that strong electrolytes in solution are almost completely dissociated. The molar conductivity at infinitely large dilution is called the **limiting molar conductivity** Λ_m°. Limiting molar conductivity of the electrolyte is the sum of the contributions from individual ions:

$$\Lambda_m^\circ = \lim_{c \to 0} \Lambda_m(c) \tag{13}$$

$$\Lambda_m^\circ = \nu_+ \cdot \lambda_+^\circ + \nu_- \cdot \lambda_-^\circ \tag{13a}$$

where ν_+ and ν_- are the number of cations or anions formed by the dissociation of one molecule.

This relationship shows that the limit of molar conductivity of a given electrolyte can be calculated by summing up the limit ionic contributions. This is called the **independent movement of Kohlraush's ions law**. Limiting molar conductivity is constant at a constant temperature and characterizes a given ion dissolved in a solvent. The molar conductivity of strong electrolytes depends linearly on the square root of their concentration (Fig. 3). This relationship is known as the **Kohlraush's law** and can be expressed by the equation:

$$\Lambda_m = \Lambda_m^\circ - a\sqrt{c} \tag{14}$$

where a – the empirical constant.

The linear Kohlraush's dependence allows determination of the limiting molar conductivity for strong electrolytes by the extrapolation method. In the case of the weak electrolytes the relationship $\Lambda_m = f(\sqrt{c})$ is not linear (Fig. 3), thus the value of their limiting molar conductivity can be then calculated from the Kohlraush's law of the independent movement of ions.

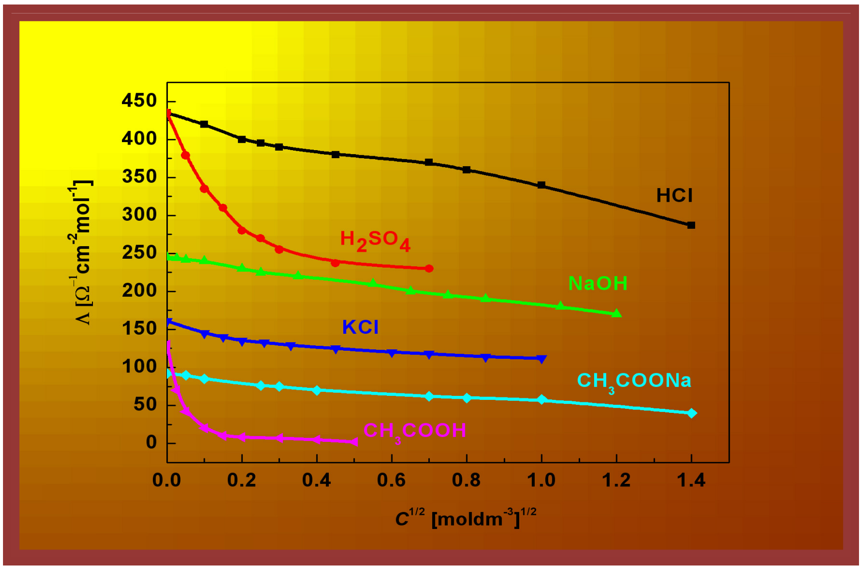

Fig. 3. Dependence of the molar conductivity of weak and strong electrolytes on the square root of their concentration.

Table 1. Electrolyte classification of some common substances

Strong Electrolytes	*Weak Electrolytes*	*Nonelectrolytes*
HCl, HBr, HI $HClO_4$ HNO_3 H_2SO_4 KBr NaCl NaOH, KOH Other soluble ionic compounds	CH_3COOH HF	H_2O CH_3OH (methyl alcohol) C_2H_5OH (ethyl alcohol) $C_{12}H_{22}O_{11}$ (sucrose) Most compounds of carbon (organic compounds)

For the solvents other than water (e.g., organic) curves of the dependences between the conductivity and the concentration have a different course than for aqueous solutions. Measurements of the conductivity of electrolyte solutions are used for different physicochemical and analytical purposes.

III.1. Determination of the degree and equilibrium constant of the dissociation process

According to Arrhenius the degree of dissociation of the electrolyte according to the law of mass action, decreases with the increasing concentration of the solution. He assumed, that the dependence between the conductivity and the concentration of an electrolyte solution depends only on the change of the degree of dissociation. He proposed a method for the degree of dissociation determination based on the following relationship between the molar conductivity in the solution at a given concentration (Λ_m) and in its infinitely dilute solution (Λ°_m), and the degree of dissociation α :

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} \tag{15}$$

This relationship is based on the assumption that the ion mobility is independent of the concentration. Using the mass action law to the dissociation of the weak acid $HA \leftrightarrow H^+ + A^-$ Ostwald defined the equilibrium constant, which can be written as follows:

$$K = \frac{\alpha^2 \cdot c}{1-\alpha} \tag{16}$$

According to the Arrhenius assumption we get the **Ostwald's dilution law** in the following form:

$$K = \frac{\Lambda_m^2 \cdot c}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)} \tag{17}$$

Equation (16) is often also known as the Ostwald's dilution law. The dependence (17) is the simplest experimental method for the determination of equilibrium constants of the dissociation process. It allows to check validity of the assumptions of classical theory of the electrolytic dissociation. According to this theory, the expression (17) should be independent of the concentration. The Ostwald's dilution law is based on the assumption that the ion mobility is independent of the concentration and the assumption about the rightness in the description of ionic equilibria by the mass action law.

III. 2. Determination of the solubility product

The solubility law says that the product of the ions concentrations in the saturated solution of sparingly soluble salt is constant at a given temperature. For monovalent salts dissociating completely, we can write:

$$[M^+][X^-] = L_{MX} = const \cong c_r^2 \tag{18}$$

where c_r - the concentration of the saturated solution.

The concentration of the saturated solution can be determined from the conductivity measurements. The conductivity of a saturated solution of a sparingly soluble salt, due to the low concentration can be expressed by the following relation:

$$\kappa = c_r \cdot (\lambda_+^\circ + \lambda_-^\circ) \tag{19}$$

Thus:

$$L = \left(\frac{\kappa}{\lambda_+^\circ + \lambda_-^\circ}\right)^2 \tag{20}$$

The conductivity value in equations (19) and (20) is the value of saturated salt solution in water (κ_{MX}) reduced by the value of the conductivity of water used to dissolve the salt (κ_{H_2O}).

$$\kappa = \kappa_{MX} - \kappa_{H_2O} \tag{21}$$

This method can be used to determine solubility product for not too much sparingly soluble salts because with small values of the difference ($\kappa_{MX} - \kappa_{H_2O}$) the solubility is charged with too large error.

III.3. Determination of the ionic products of water

Ionic product of water can be determined also by measuring its conductivity:

$$K_w = a_{H_3O^+} \cdot a_{OH^-} = c_{H_3O^+} \cdot c_{OH^-} \cdot \gamma^2 \cong c_{H_3O^+}{}^2 \cong \left(\frac{\kappa_{H_2O}}{\lambda_{H_3O^+}^\circ + \lambda_{OH^-}^\circ}\right)^2 \tag{22}$$

where $a_{H_3O^+}$ and a_{OH^-} - the activity of hydronium and hydroxyl ions, respectively.

For measurement of the ionic product of water, we should use ultrapure water, because the presence of other ions significantly changes its conductivity value.

III. 4. Titration conductivity

Conductometric titration is an analytical method based on examination of the changes in conductivity of the electrolyte during the addition of a titrant. The changes result from those in different mobility.

IV. Experimental

A. Devices and materials

1. **Devices:**
   - RC generator,
   - Wheatstone bridge,
   - zero indicator,
   - vessel with electrodes to measure conductivity.
2. **Equipment:**

– - Volumetric flasks	50 cm^3	8 pcs
– - Graduate pipettes	25 cm^3	2 pcs
– - Precision pipettes	5 cm^3	2 pcs
– - Beaker	400 cm^3	1 pcs
– - Wash bottle		2 pcs

3. **Reagents:**

   Aqueous solutions: 0.02 M KCl, 0.1 M CH_3COONa, 0.1 M NaCl, 0.1 M HCl and 0.1 M CH_3COOH.

B. Program

1. Determination of the resistance cell constant:

   a) Assembly of the measurement system.

   Assembly of the measurement system according to the scheme shown in Figure 4. On the generator set a frequency range by pressing the button corresponding to 100 Hz. Throughout the measurement the frequency should be maintained (read on the display) at 10 Hz.

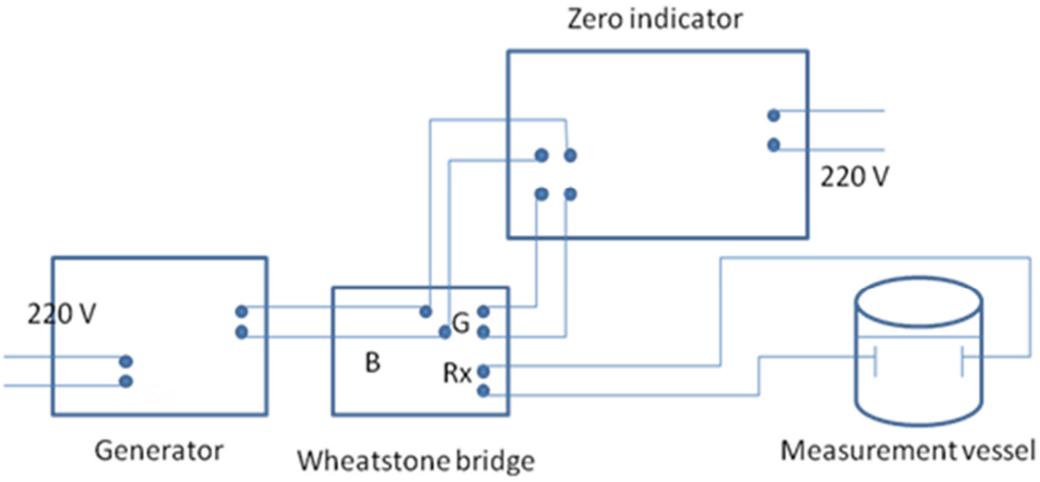

Fig. 4. The conductivity measurement system.

b) Measure the resistance of the electrolyte.
Using the [x] and [:] switches select the appropriate relative resistance of the bridge so as to obtain a clear pointer deflection rate of zero. Then, turning knobs of the bridge bring a hint pointer of the zero indicator to zero. The measured resistance value is calculated by summing up the values read out at five comparison decades and multiplying the resulting value by the integrated relative resistance value [x] and dividing by the second relative resistance value [:].

2. Measurement of conductivity of selected electrolytes

   a) Prepare by diluting the solutions of HCl, NaCl, and CH_3COONa of the following concentrations: 0.01 M; 0.03 M; 0.05 M; 0.07 M; 0.1 M.
   For CH_3COOH prepare the solutions of the concentrations: 0.0025 M; 0.005 M; 0.01 M; 0.05 M; 0.1 M.
   b) Measure the resistance of the prepared electrolytes.

3. Elaboration of the results.

   The measurement results should be presented in Table 2.

Table 2. Measurement of the conductivity; *t* [°C] = ...

Electrolyte	***c* [mol/dm^3]**	**R [Ω]**

C. Methods

1. Determination of the cell resistance constant.

Cell constant, equal to the product of the distance between the electrodes and their surfaces characterizes the dimensions of the electrolyte solution column located between the two electrodes. It is determined from the equation:

$$k = \kappa \cdot R \tag{23}$$

by measuring the resistance R of the electrolyte located in the measurement vessel. Electrical conductivity of the standard electrolyte *k* has been determined through direct measurements. Calculate the resistance cell constant from Eq. (1) using the measured values of the resistance of 0.01 M and 0.02 M KCl and the appropriate values of the electrolytic conductivity of the given electrolyte placed in Table 3.

Table 3. Electrolytic conductivity of the appropriate KCl solutions.

Temp. *t* [°C]	**0.01 M KCl [S/m]**	**0.02 M KCl [S/m]**
15	0.1147	0.2213
16	0.1173	0.2268
17	0.1199	0.2324
18	0.1223	0.2400
19	0.1251	0.2434
20	0.1278	0.2504
21	0.1305	0.2545
22	0.1332	0.2600
23	0.1359	0.2655
24	0.1386	0.2711
25	0.1413	0.2766

2. Examination of the dependence between the electrolyte conductivity and its concentration

a) Calculation of the conductivity of the electrolyte solutions.
Calculate the electrolytic conductivity κ from the relationship:

$$\kappa = \frac{k}{R} \tag{24}$$

using the determined values of the cell resistant constant and the measured values of the resistance R. Plot the dependence $k = \mathrm{f}(c)$ (c - the electrolyte concentration).

b) Calculation of the molar conductivity of the studied electrolytes.

Calculate the molar conductivity Λ_m from equation (10) keeping in mind the appropriate adjustment of the units. Draw the plot of $\Lambda_m = \mathrm{f}(c)$.

c) Determination of the limiting molar conductivity Λ_m° of the studied electrolytes. The molar conductivity values for all tested electrolytes: HCl, NaCl, CH_3COONa and CH_3COOH should be given in one figure $\Lambda_m = \mathrm{f}(\sqrt{c})$.

In the case of the strong electrolytes: NaCl and HCl and CH_3COONa this relationship is linear, and can be expressed by the Kohlrausch's equation (14). Using the least squares method (see Appendix) determine the value of the constant a and limiting molar conductivity Λ_m°.

The obtained results of calculations should be presented in a table according to the specified model. Based on the determined values of parameters of Eq. (14), present linear dependences on the diagram.
In the case of CH_3COOH, which is a weak electrolyte, Λ_m° value can not be determined by extrapolation to $c = 0$. It can be calculated from the Kohlrausch's law of in-

dependent movement of ions using the determined values of Λ°_m for the corresponding strong electrolytes. For CH_3COOH Λ°_m can be calculated based on the values of Λ°_m for CH_3COONa, NaCl and HCl solutions:

$$\Lambda^\circ_{m(CH_3COOH)} = \Lambda^\circ_{m(CH_3COONa)} + \Lambda^\circ_{m(HCl)} - \Lambda^\circ_{m(NaCl)} \tag{25}$$

Calculate the value of Λ°_m for CH_3COOH from Eq. (25).

d) Presentation of the obtained results.

The calculation results should be presented in Table 4.

Table 4. Conductivity of electrolytes; *t* [°C] ……, *k* [m $^{-1}$] = ...

Electrolyte	***c* [mol/dm^3]**	**$\sqrt{c}$**	**R [Ω]**	**κ[S/m]**	**Λ_m [Sm^2/mol]**
$\Lambda^\circ_{m(CH_3COONa)} =$	$\Lambda^\circ_{m(NaCl)} =$		$\Lambda^\circ_{m(HCl)} =$	$\Lambda^\circ_{m(CH_3COOH)} =$	

3. Determination of the equilibrium dissociation constant of CH_3COOH

a) Calculate the degree of dissociation of CH_3COOH, α, from Eq. (15).
b) Calculate the equilibrium dissociation constant, *K*, from the Ostwald law Eq. (16).
c) The obtained results of calculations should be presented in Table 5.

Table 5. Determination of the degree and the equilibrium dissociation constant of CH_3COOH; t [^{o}C] ...; k [m $^{-1}$] = ...; Λ°_{m} [Sm^2/mol] = ...

c [mol/dm^3]	R [Ω]	κ [S/m]	Λ_m [Sm^2/mol]	α	K

$K_{śr}$ = ……….

D. Conclusions

- analyze the dependences between the conductivity, molar conductivity and the concentration of the electrolyte for the weak and strong electrolytes.
- compare the obtained values of the limiting molar conductivity and the equilibrium constant of the CH_3COOH dissociation process with the tabular ones.