First name .... Date ....

Last name .... Degree program name ....

Exercise 240

Determination of specific conductivity of electrolytes

I. Determination of conductivity cell constant

Resistance R_D, [Ω]											
I [mA]											

Resistance of the solution	Temperature of the solution [°C]			Conductivity cell constant
R_1 [Ω]	t_p	t_k	t_1	C [m^{-1}]

II. Determination of specific conductivity of electrolyte

Resistance R_D, [Ω]											
I [mA]											

Resistance of the solution	Temperature of the solution [°C]			Specific conductivity [S/m]	
R_2 [Ω]	t_p	t_k	t_2	at temp. t_2	at 18°C
				σ_2	σ_{02}

Exercise 240. Determination of specific conductivity of electrolytes

Introduction

Electrolyte is defined as a solution that contains ions in addition to neutral molecules. The ions' source are molecules of acids, bases and salts that *dissociate* in a solvent with high dielectric constant (eg, water). If we create an electric field between electrodes immersed in an electrolyte, an electric current will flow through the electrolyte. The carriers of this current are both *cations* (positive ions) and *anions* (negative ions). The intensity of this current, I, is directly proportional to the electric field strength, E, and the cross-sectional area, S, of the current carriers' flux,

$$I = \sigma \cdot E \cdot S . \tag{1}$$

The proportionality factor σ is called the *specific conductivity* of the electrolyte. The dimension of σ is siemens per meter, [S/m]; 1 $S \cdot m^{-1}$ = 1 $\Omega^{-1} \cdot m^{-1}$ (siemens is the inverse of Ohm). Specific conductivity is the inverse of specific resistance ρ,

$$\rho = 1/\sigma .$$

Due to the simultaneous transfer of mass and charge, the conductivity of electrolytes is much lower than the electron conductivity in metals. The specific conductivity depends on the type of solute, its concentration, temperature and the type of solvent. The dependence of σ on temperature is linear:

$$\sigma = \sigma_0 + \gamma (t - 18) ; \tag{2}$$

σ and σ_0 denote the specific conductivity of the electrolyte at temperature t and $t_0 = 18°\mathrm{C}$, respectively,

γ - the temperature coefficient of specific conductivity (it expresses the increase in BB corresponding to a unit change of temperature).

The strength of the electric field, E, between the electrodes can be expressed as the ratio of the voltage on the electrodes, U, to their mutual distance l:

$$E = U/l .$$

We put this relationship into equation (1):

$$I = \frac{\sigma S U}{l} , \tag{3}$$

and considering that $I = U/R$, where R is the electrical resistance of the conductor, we get:

$$R = \frac{1}{\sigma} \cdot \frac{l}{S} . \tag{4}$$

The l/S ratio for a given set of electrode in an electrolytic vessel is constant and is called the *conductivity cell constant C*:

$$C = \frac{l}{S} \tag{5}$$

The measure of C is the reciprocal meter, [m^{-1}]. Applying (5) to (4), we get

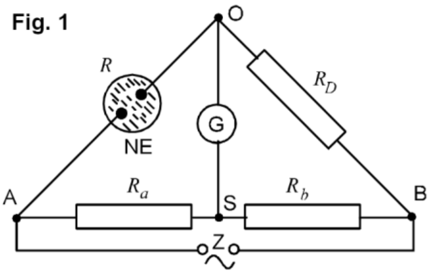
$$\sigma = \frac{C}{R} . \tag{6}$$

By measuring the resistance R of the electrolyte in a vessel of known conductivity cell constant C, we can use formula (6) to determine the specific conductivity. To calculate the conductivity cell constant, we use an electrolyte of known specific conductivity.

Measurement of electrolyte resistance.

We can determine the electrolyte resistance *R* using a Wheatstone bridge. The Wheatstone bridge circuit is made up of 4 resistors connected according to the diagram shown in Fig. 1. The electrolyte is located in the NE vessel. Resistances R_a and R_b are known, whereas R_D is adjustable (decade resistor) and is used to balance the bridge.

Fig. 1



Measurement of resistance *R* requires the selection of such a resistance R_D, so that the current flowing through the galvanometer G has a minimum value. Then the potentials at points O and S are approximately equal and the bridge is in balance.

The Kirchhoff's laws imply the equality of potentials $V_0 = V_S$ at points O and S if:

$$R/R_D = R_a/R_b \,. \tag{7}$$

Resistances R_a and R_b shall be chosen so that $R_a = R_b$. Then, equation (7) implies $R = R_D$, which means that under balanced bridge conditions the resistance *R* of the electrolyte is equal to the resistance of the decade resistor.

Determining the resistance R_1 of the electrolyte with known specific conductivity σ_1 at temperature t_1 allows to calculate the conductivity cell constant *C* from equation (6),

$$C = \sigma_1 \cdot R_1 \,. \tag{8}$$

Aray data of the specific conductivity of an electrolyte are usually given for a defined temperature, such as 18°C – we will denote it as σ_{01}. If we use equation (2), then we obtain *C* from relation:

$$C = R_1\left[\sigma_{01} + \gamma_1 (t_1 - 18)\right], \tag{9}$$

where γ_1 is the temperature coefficient for the standard solution.

After determining *C*, we pour an identical amount of solution of unknown specific conductivity σ_2 into the same vessel and measure its resistance, R_2 . We will calculate the value of σ_2 from the formula

$$\sigma_2 = \frac{C}{R_2} \,. \tag{10}$$

By measuring R_2 values at several different temperatures, we can also determine the temperature coefficient of the electrolyte's specific conductivity — γ_2 (in this exercise, the value of γ_2 is given and will not be determined). This will allow us to determine the value of the specific conductivity σ_{02} at a room temperature of 18C:

$$\sigma_{02} = \sigma_2 - \gamma_2 (t_2 - 18) \,, \tag{11}$$

where t_2 is the temperature at which σ_2 was measured.

Performance of the task

I. Determining the conductivity cell constant C.

1. Pour the standard electrolyte, 5% NaCl solution, into the electrolytic vessel in such an amount that the electrodes are approximately half immersed in the solution. Connect the circuit according to the diagram in Figure 1. Supply the circuit with an alternating voltage of several volts.
2. Measure the initial temperature of the electrolyte — t_p.
3. Set a value of 10 Ω on the decade resistor and turn the power supply on.
4. Look for such a value of resistance R_D on the decade resistor, at which the current in the SO branch is the smallest. Write the value of this resistance in the table, including the corresponding current value from milliammeter (the minimum value of the current is from a dozen to a few tens of mA).
5. Change the value of the resistance on the decade resistor by 1 Ω, in the range of ± a few Ohms, starting from the resistance at which the current is minimum, and note the corresponding values of the milliammeter.
6. After switching off the power supply, measure the final temperaturę t_k of the electrolyte and calculate the average value $t_1 = (t_p + t_k)/2$.
7. On the basis of the results obtained, make a graph $I = f(R)$ and determine graphically the resistance R_1, at which the bridge is balanced, see Figure 2.
8. Using equation (9), calculate the conductivity cell constant C.

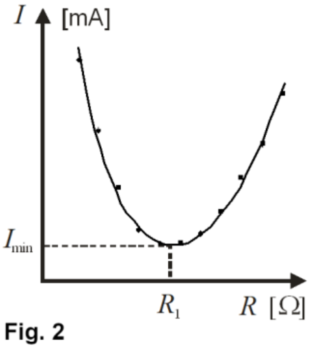


Fig. 2

II. Determination of the specific conductivity of an electrolyte σ_{02}.

1. Determine the resistance R_2 of the investigated electrolyte (eg, an aqueous solution of CuSO4, 15%), following the steps 1÷7 of Part I.
2. Using equations (10) and (11) calculate σ_2 and σ_{02} – specific conductivity of the tested electrolyte at temperaturę t_1 and 18°C, respectively.

Array data

5% NaCl: $\gamma_1 = 0.15\ S/(m \cdot {}^\circ C)$, $\sigma_{01} = 6.7\ S/m$;

15% CuSO4: $\gamma_2 = 0.10\ S/(m \cdot {}^\circ C)$.

Calculation of the uncertainties

We calculate the absolute errors ΔC and $\Delta\sigma_{02}$ using the method of the complete differential, which we apply to equations (9) and (11). For simplicity, we will assume that the array values are not subject to measurement error.

I. $$\Delta C = \frac{C}{R_1}\Delta R_1 + R_1\gamma_1\,\Delta t_1\,;$$

II. $$\Delta\sigma_{02} = \frac{\Delta C}{R_2} + \frac{C}{R_2^2}\Delta R_2 + \gamma_2\Delta t_2\,.$$

For the calculation, we assume: $\Delta R_1 = \Delta R_2 = 0.5\ \Omega,\ \Delta t_1 = \Delta t_2 = 0.5\ ℃$.

After determining ΔC and $\Delta\sigma_{02}$ we also determine the relative percentage errors:

$$B_{p1} = \left(\Delta C/C\right)\cdot 100\%, \qquad B_{p2} = \left(\Delta\sigma_{02}/\sigma_{02}\right)\cdot 100\%\,.$$