Exercise 4

DETERMINATION OF THE ION TRANSPORT NUMBERS FOR K+ AND OH−

Topics: Electrical conductivity of aqueous electrolyte solutions, electrolysis, Faraday's laws of electrolysis, chemical equations for electrode reactions, material balance for the electrolysis process, ion transport numbers, ion mobility.

The flow of current through an electrolyte is based on the migration of ions of both signs in an electric field. The mobility of an ion (*u* [m^2/V×s]) can be characterized as the speed of the ion (*s* [m/s]) moving in an electric field of a given intensity (*E* [V/m]) in the direction of the field forces:

$$u = \frac{s}{E}. \tag{1}$$

The speed at which ions move depends on many factors, primarily the change in electric potential per unit distance between the electrodes (called the potential gradient), but also on ion-ion interactions, ion masses and sizes, their degree of solvation, temperature, and the viscosity of the liquid.

The electric charge *q* [C], transferred by ions of one type in a specific volume of electrolyte, is related to the concentration of these ions (*c* [M]), their elementary charge (z_+e or z_-e, respectively for the charge transferred by cations or anions), and mobility (*u*). Considering the exchange of such an electric charge over time Δ*t* through any cross-section *A*, perpendicular to the direction of current flow, of an electrolyte solution with monovalent cations and anions, in an electric field of intensity E, we get:

$$q_+ = z_+e \cdot c \cdot s\Delta tA \quad \text{oraz} \quad q_- = z_-e \cdot c \cdot s\Delta tA, \tag{2}$$

Substituting *s* from equation (1), the charge transferred by ions takes the form:

$$q_+ = z_+e \cdot u \cdot c \cdot E\Delta\mathrm{t}A \ \text{oraz} \quad q_- = z_-e \cdot u \cdot c \cdot E\Delta tA,$$

The ratio of the electric charge transferred by a particular type of ion to the total charge that flowed through the solution is called the ion's transport number, *t*:

$$t_+ = \frac{|q_+|}{Q} \ \text{oraz} \ t_- = \frac{|q_-|}{Q} \quad , \tag{3}$$

Therefore, the sum of the transport numbers of all ions present in the solution is equal to one:

$$t_+ + t_- = \frac{|q^+| + |q^-|}{Q} = 1 \tag{4}$$

According to Faraday's first law, the total electric charge *Q* transferred over time *t*, conducted with current intensity *I* through the solution, can be divided into two parts: the charge transferred by cations q_+, and the charge transferred by anions q_-,

$$Q = It = \sum |q_+| + |q_-|. \tag{5}$$

Moreover, substituting Faraday's constant into formula (5) defined as the total charge Q for moles of electrons (n) that flowed through the system;

$$F = \frac{Q}{n}, \tag{6}$$

equation 5 and the moles of charges transferred by cations and anions, q_+ and q_-, can be written as:

$$q_+ = z_+ \cdot n_+ \cdot F, q_- = z_- \cdot n_- \cdot F, \tag{7}$$

where n_+ and n_- are the moles of cations (with charge z_+) and anions (with charge z_-), that migrated to the cathode and anode, respectively, while:

$$n = z_+ \cdot n_+ + z_- \cdot n_- \tag{8}$$

is the total number of ion moles that flowed through the system. For the ion transport numbers, we get the following expressions:

$$t_+ = \frac{|z_+|n_+}{n}, t_- = \frac{|z_-|n_-}{n} \tag{9}$$

Usually, ion transport numbers do not show a significant dependence on solution concentration, as long as the electrolyte is fully dissociated. However, sometimes through the formation of complexes a very strong dependence of transport numbers on concentration can be observed. For example, in a concentrated solution of nickel(II) chloride, $NiCl_2$, there is possible to observe formation of $NiCl^+$ complexes which leads to migration of some of the chloride anions (engaged in formation of complex) to the cathode area, resulting in a reduction of the effective transport number of chloride ions. On the other hand, formation of negatively charged complexes may lead to significant drop in the transport number of cation, when such entity migrates towards the anode. Such a phenomenon can be observed, for example, during the electrolysis of a concentrated solution of zinc chloride, $ZnCl_2$.

The aim of the exercise: Gaining both theoretical and practical understanding of the method used to measure ion transport numbers.

Reagents

0.1 M aqueous solution of potassium hydroxide, KOH
0.1 M aqueous solution of sodium sulfate(VI), Na2SO4
0.1 M aqueous solution of hydrochloric acid, HCl

Exercise Execution

The aim of the exercise is the theoretical and practical mastery of the method of measuring transport numbers.

Reagents:

0.1 M aqueous solution of potassium hydroxide, KOH

0.1 M aqueous solution of sodium sulfate(VI), Na_2SO_4

0.1 M aqueous solution of hydrochloric acid, HCl

The total number of moles of charge is determined in a Hoffman coulometer (I), and then the total charge that flowed through the solution during electrolysis can be calculated. The values n^+ and n^- are determined in the Hittorf electrolytic vessel (II) by measuring the electrolyte concentrations near the electrodes after the electrolysis. However there is required to assume that the electrolyte in the individual electrode spaces was not mixing, and that the electrodes were not reacting with the electrolyte or with the products of electrolysis.

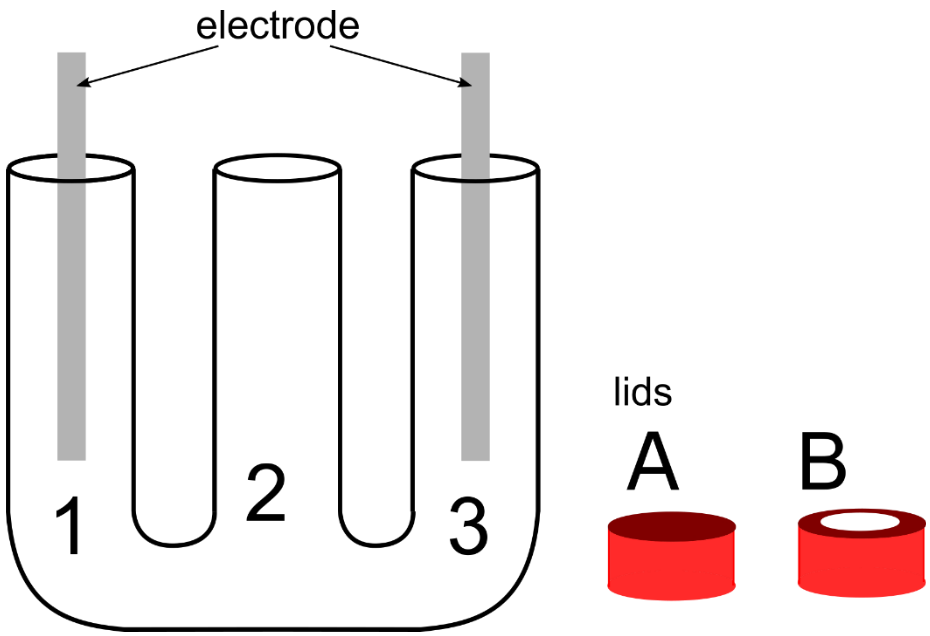
I. Hydrogen-oxygen coulometer, also known as the "Hoffman apparatus" (with a solution of sodium sulfate(VI), Na_2SO_4)

- Before starting the electrolysis experiment, it is necessary to remove the gases contained in the hydrogen-oxygen coulometer. The levels of the solution menisci in both parts of the apparatus should be at the same height - in the upper part in the range of 2 to 6 ml. This exact value should be noted. Instructions for opening and closing the leads will be given by the instructor.

<u>After electrolysis::</u>

- Determine the volume of the produced hydrogen (V_H). The V_H is determined by the difference between the meniscus levels before and after electrolysis.

II. Three-chamber electrolyzer - Hittorf's electrolytic apparatus (filled with KOH solution)



Rys 1. Schematic drawing of the Hittorf vessel

- Before using the Hittorf vessel, it's essential to clean it with distilled water. Subsequently, rinse it with a 0.1 M KOH solution, pouring approximately 5 cm^3 of this solution into each chamber (1), (2), and (3).
- Next, pour 10 cm^3 of the 0.1 M KOH solution into the central part (2), which will undergo electrolysis. Attach the full "A" (white) cap and gently tighten it until slight resistance is felt. Immediately, pour 25 cm^3 of the KOH solution into two graduated cylinders and transfer them sequentially to chambers (1) and (3).
- Unscrew the "A" cap from the central chamber and add 25 $cm^3$of the KOH solution.

Note: The central chamber remains open during electrolysis.

- For chambers (1) and (3), attach the "B" type lid (red) with concentric holes and gently tighten them.
- Mounting the electrodes in the Hittorf electrolyzer should be done under the supervision of the exercise instructor. The current intensity should be 0.04 A – this value will be visible on the digital indicator screen on the left side of the device. Conduct the electrolysis for approximately 60 minutes

<u>After electrolysis</u>:

- Finishing the electrolysis with the assistance of the instructor, remove the electrodes from chamber (1) and chamber (3) of the three-chamber Hittorf electrolyzer and transfer them to a separate empty conical flask.
- Unscrew the "B" (red) lid from chamber (1) and (3) and rinse with water. Close the openings of chambers (2) and (3) with "A" type (white) lid and pour the solution from chamber (1) into a 250 ml beaker. Immediately after this operation, remove the "A" cap from chamber (3) and pour its contents into the next beaker.
- Take two samples (each 5 cm^3) for titration with a 0.1 M HCl solution.

- After titrating the initial solution, use the obtained results to calculate the initial concentration of OH^- (c_0), and after electrolysis in the anode space (c_A) and cathode space (c_K).
- Using dry pipettes, take two samples (each 5 cm^3) from the solutions in the beakers for titration with a 0.1 M HCl solution.
- Titrate the initial solution.
- Pour the contents of the central chamber into beakers. Rinse the vessel several times with water.

Results processing:

- Calculate the initial concentration of OH^- (c_0), and after electrolysis in the anode space (c_A) and cathode space (c_K).
- Measure the room temperature, *T*, and atmospheric pressure p_a.
- Calculate the vapor pressure, p_w, over the Na_2SO_4 in the coulometer. Assuming that p_w (Table 1) changes linearly, apply linear interpolation to calculate the partial pressure of hydrogen:

$$p_H = p_a - p_w \tag{10}$$

Table 1. Vapor pressure p_w over the Na_2SO_4 solution depending on temperature

T [K]	273	283	293	303	313	323
p [Pa]	599.95	1213.23	2293.145	4172.991	7266.07	12159

- sing the Clapeyron equation for ideal gases and the electrode reaction equations in the coulometer, determine the total number of moles of charge, *n*, that flowed through the system:

$$n = \frac{2p_H V_H}{\mathrm{RT}}, \tag{11}$$

where R = 8,314 m^3·Pa/K·mol represents the gas constant.

- From the material balance of the processes, it can be deduced that the increase in the number of moles of OH^- ions in the cathode space is the same as the decrease in the number of moles of OH^- ions in the anode space, and they are equal to the product nt_+

$$(c_K - c_0)V_K = (c_0 - c_A)V_A = nt_+ \tag{12}$$

- The volumes of the electrode spaces, V_K i V_A (converted to m^3), can be eliminated from this equation by introducing the total volume

$$V = V_K - V_A, \tag{13}$$

resulting in:

$$nt_+ = \frac{(c_K - c_0)\,(c_0 - c_A)V}{c_K - c_A} \tag{14}$$

- By combining equations (11) and (14), we obtain the following expression for the cation transport number:

$$t_+ = \frac{(c_K - c_0)\,(c_0 - c_A)}{c_K - c_A} \cdot \frac{\mathrm{RT}}{2p_H V_H} \tag{15}$$

- Knowing the cation transport number, calculate the anion transport number.