PHYSICAL CHEMISTRY LABORATORY II

NUMBER OF THE EXPERIMENT: 3

NAME OF THE EXPERIMENT: Determination of Transference Number by Hittorf's Method

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DATA SHEET

Table 1. Data Sheet

Before Electrolysis	After Electrolysis
V_{KSCN} (initial, for stock AgNO3) = 25,6 mL	t(s)= 4500 seconds
w_i (anode, copper plate) = 1,0658 grams	735 mA
w_i (cathode, copper plate) = 1,1432 grams	w_f (anode, copper plate) = 1,0898 grams
	w_f (cathode, copper plate) = 1,1334 grams
	V_{total} (AgNO3, for anode compartment) = 45 mL
	V_{total} (AgNO3, for middle compartment = 35 mL
	V_{KSCN} (final, for anode compartment) = 25 mL
	V_{KSCN} (final, for middle compartment) = 21,2 mL

CALCULATION

1) Calculate initial number of moles of Ag+ ions (ni) from 25 mL stock solution.

ni = M$_{KSCN}$ x V$_{KSCN}$ = M$_{AgNO3}$ x V$_{AgNO3}$

number of equivalents of SCN- = number of equivalents of Ag+

M$_{KSCN}$ = 0,1 M V$_{KSCN}$ = 25,6 mL   V$_{AgNO3}$ = 25 mL

(0,1M) x (25,6 mL) = M$_{AgNO3}$ x (25 mL)   => M$_{AgNO3}$ = 0,1024 M

$$ni = \left(0,1\frac{mol}{L}\right) \times (25,6\ mL) \times \left(\frac{1L}{1000mL}\right) = 2,56 \times 10^{-3}\ mol$$

2) V_{total} = 45 mL for anode comparment

n = M$_{AgNO3}$ x V$_{AgNO3}$ => n $= \left(0,1024\frac{mol}{L}\right) \times (45\ mL) \times \left(\frac{1L}{1000mL}\right) = 4,608 \times 10^{-3}\ mol$

$4,608 \times 10^{-3}\ mol$ = Ag$^+$ total at Anode at initial

3)   **n$_f$ = M$_{KSCN}$ x V$_{KSCN}$ = M$_{AgNO3}$ x V$_{AgNO3}$** then

n$_f$ = (0,1 M) x (25 mL) = M$_{AgNO3}$ x (25 mL)   => M$_{AgNO3}$ = (0,1M)

n$_f$ $= \left(0,1\frac{mol}{L}\right) \times (25\ mL) \times \left(\frac{1L}{1000mL}\right) = 2,5 \times 10^{-3}\ mol$

4)   **n$_f$ = M$_{KSCN}$ x V$_{KSCN}$ = M$_{AgNO3}$ x V$_{AgNO3}$** V$_T$ = 45 mL for anode part

n$_f$ = $(2,5 \times 10^{-3}$ mol$) \times (\frac{45\ mL}{25\ mL}) =$ $4,5 \times 10^{-3}$ mol

5) n_{Ag^+} at the middle part, $\quad \mathbf{n = M_{KSCN} \times V_{KSCN} = M_{AgNO3} \times V_{AgNO3}}$

$\quad$ V_{AgNO3} = 35 mL , $\mathbf{(0,1M)}$ x (21,2 mL) = M_{AgNO3} x (25 mL) => M_{AgNO3} = 0,0848 M

$$\left(0,0848 \frac{mol}{L}\right) \times (35\ mL) \times \left(\frac{1L}{1000mL}\right) = 2,968 \times 10^{-3}\ mol \text{ equal to moles of } Ag^+ \text{at the}$$

$$\text{middle part}$$

6) q=(I x time) , n_e =q/F $\quad$ F: Faraday constant = 96485,322 C/mol[1]

$\quad$ I= 7,35 mA = 7,35x 10A $\quad\quad$ time = 4500 seconds
$\quad$ Q = (0,735 A) x (4500 s) = 33,075 C

$\quad$ $n_e = \frac{33.075\ C}{\left(96485,322 \frac{C}{mol}\right)}$ = 3,427982 10^{-4} mol ≈ 3.43 x 10^{-4} mol is theoretical value

7) $\mathbf{Q = \dfrac{\Delta w \times 2F}{\dfrac{g\ of\ Cu}{1\ mol\ Cu}}}$ **(experimental) Δw equal to final mass of Cu^{+2} plate – initial mass of Cu^{+2} plate**

$\quad\quad$ From Data sheet, $w_{initial}$ (anode) = 1,0658 g
$\quad\quad\quad\quad\quad\quad\quad\quad$ w_{final} (anode) = 1,0898 g $\quad$ then

$\quad\quad$ Δw = (1,0898 -1,0658 grams) = 0,024 grams

$$Q = \frac{(0.024\ g)\ x\ (2)\ x\ (96485,322\ C)}{63.546\ g/mol} = 71,751858 \approx 71,75 \text{ Coulomb}$$

$\quad\quad$ n_e **(experimental) =** $\frac{Q(experimental)}{F}$ **then,**

$$\frac{71,75\ C}{\left(96485,322 \frac{C}{mol}\right)} = 7.436556\ x\ 10^{-4}\ mol \approx 7,437 \times 10^{-4}\ mol$$

$\quad\quad$ **%Error for n_e =** $\frac{\text{Experimental value} - \text{Theoretical value}}{\text{Theoretical Value}}$ **x 100 then**

$$\frac{(7,43710^{-4}) - (3.43\ x\ 10^{-4})}{(3.43\ x\ 10^{-4})} \text{ x 100 = \% 116,809} \approx \%116,8$$

$\quad$ **8)** $\quad$ **$n_f = n_i - n_{e,theoretical} + n_{mig(theoretical)}$**
$\quad\quad$ n_f = 4,608 x 10^{-3} mol n_i = 2,56 x 10^{-3} mol Theoretical value of n_e = 3.43 x 10^{-4} mol

$$(4,608\ x\ 10^{-3}) = (2,56\ x\ 10^{-3}) - (3,43 x\ 10^{-4}) + n_{mig} \text{ then}$$
$$n_{mig} = 2,391\ x\ 10^{-3}$$

9) $n_f = n_i - n_{e(experimental)} + n_{mig(experimental)}$

$n_f = 4,5 \times 10^{-3}$ mol $n_i = 4,608 \times 10^{-3}$ mol $n_{e(experimental)} = 7.55 \times 10^{-4}$ mol

$(4,5 \times 10^{-3}) = (4,608 \times 10^{-3}) - (7,55 \times 10^{-4}) + n_{mig}$ then

$n_{mig} = 6,47 \times 10^{-4} \, mol$

% Error $= \dfrac{\text{Experimental value} - \text{Theoretical value}}{\text{Theoretical Value}} \times 100$ then

$\dfrac{(6.47 \times 10^{-4}) - (2.391 \times 10^{-3})}{(2.391 \times 10^{-3})} \times 100 = \% \, \text{-72,94}$

10) $t_{+ \, (theoretical)} = \dfrac{n_{mig}(theo)}{n_e(theo)}$ then

$t_{+ \, (theoretical)} = \dfrac{(2.391 \times 10^{-3})}{(3.43 \times 10^{-4})} = 6.971$ **$t_+ + t_- = 1$ then** $t_- = (1 - t_+) = (1 - 6.97) = -5.97$

$t_{+ \, (experimantal)} = \dfrac{n_{mig}(exp)}{n_e(exp)}$

$t_{+ \, (experimental)} = \dfrac{(6.47 \times 10^{-4})}{(7.55 \times 10^{-4})} = 0,857$ **$t_- = 1 - t_+$ then** $t_- = (1 - 0.857) = 0.143$

11) % Error $= \dfrac{\text{Experimental value} - \text{Theoretical value}}{\text{Theoretical Value}} \times 100$ then

Percent error for t_+ $= \dfrac{(0.857 - 6.97)}{(6.97)} x \, 100 = \text{-87.7 \%}$

Percent error for t_- $= \dfrac{(0.143 - (-5.97))}{(-5.97)} x \, 100 = \text{-102.395} \approx \text{-102,4 \%}$

QUESTIONS

1) The Hittorf method is a method used to determine the transfer number. In addition to this method, the transfer number can be resolved with the moving boundary method, and concentration cells.. The color of the solution allows the calculation of the movement speed of the ions, and the number of transfers can be found with this method.[2]

   In the concentration cells method, the occurrence or absence of movement of ions does not affect the determination of the transfer number because the transfer number and activity coefficients are already present in the EMF formula under all conditions. At the same time, in this method, the slope of the ET = f(E) function can be calculated with the transfer number. [2]

2) The reactions on the electrodes affect the mass of the copper plates used in the experiment. $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ reaction occurs in the anode section. As a result of this reaction, the mass of the copper plate has decraesed because this reaction gives electrons and ions to the solution ,and this causes a loss of mass in the plate. The reaction in the cathode chamber is $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$. As a result of this reaction, the mass of the copper plate will increase because copper solids will form on the plate.

3) Mass change is observed in the anode and cathodes used in the Hittorf method, as in the copper plates. The reason for the decrease in mass at the anode can be explained by the reaction $Ag_{(s)} \rightarrow Ag^+_{(aq)} + e^-$. On the cathode, with the reaction of $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$ the formation of silver solids results in an increase in mass in the cathode section.

4) Among the duties of the middle chamber in the experimental system are to ensure the transport of ions passing from the anode to the cathode and maintain the system's neutrality. The passage of ions in liquids is by diffusion logic. In this case, there must be a concentration difference between the ions for the ion transition from the anode to the cathode using the "middle chamber". It does not appear to occur**.**

5) The temperature affects the number of transference. When establishing a relationship between the increase in temperature and the number of transports, if the total number of transports is equal to one, this number decreases as the temperature increases. The effect of electrolyte concentration on the transport number is as follows, as a result of the increase in concentration, the interaction of the ions in the solutions with each other additions because they are in a more congested environment, in this case, the transport number decreases therefore diluted solutions can be used to increase this number. The structure of the ions also affects this number.[3]

6) A coulometer is a device that measures electrical charges and contributes to calculations using electrical charges. It gives its measurements in coulombs.[4]

7) In an ionic medium or matrix, the ability of ions to move with the electric field or the repulsion and pull forces created by the effect of charged particles is called the Electrophoretic effect. The attack of ions with opposite charges with the electric field applied with the electrodes is known as the relaxation effect. The movement of negative NO_3^- ions toward the anode and the positive charged silver ions toward the cathode can be given as an example of the electrophoretic effect. [5]

DISCUSSION

The purpose of this experiment is to find the transference number by using the Hittorf Method. The copper plates used in the experiment were sanded before starting the experiment so that the remaining substances from the previous experiments did not affect the test data. Since the transference numbers were found based on the accumulation of electrons on the copper plates, the weight of the plates was measured before and after the experiment.The sanding process was also performed for the anode and cathodes. The experiment was carried out in an $AgNO_3$ solution. Ag^+ ions moved to the cathode, and NO_3^- ions to the anode. The middle part of the assembly helped this process by creating space in these ion transitions. Electrolysis was carried out in seventy-five minutes. While electrolysis continued, $AgNO_3$ The solution was titrated with KSCN to determine the concentration. After electrolysis, the solutions in the anode and middle parts of the experiment were titrated separately with KSCN. With this process, it was aimed to find the moles of Ag ions in these parts.

As a result of the calculations made for the experiment, error data were obtained. Before talking about the reasons for these errors, the other group's data that did the same experiment as we were used because our experimental data did not come as desired. Inaccurate readings or poor sanding during the weight measurement of the copper plates are also among the causes of error.During the seventy-five-minute waiting period during electrolysis, a situation that was overlooked and affected the current occurred.The ground where the test is made is conductive. The connection points of the conductor cables connected to the anode and cathodes and connected to the device during the test should not come into contact with the ground because this affects the measured current amount.The copper plates are in the coulometer filled with $CuSO_4$ solution, and the copper plates were dipped into this solution with the help of paper clips; if the paper clips contacted the $CuSO_4$ solution and it was not noticed, this is also a cause of the error.

References

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