DETERMINATION OF THE LIQUID JUNCTION POTENTIAL

When two solutions of different concentrations of the same electrolyte are in contact with each other, an additional electrical potential is formed. Its formation is related to the irreversible diffusion of the electrolyte from a solution of higher concentration to that of lower concentration. This potential is called **diffusion potential** or **liquid junction potential** (**LJP**). Its magnitude depends on the relative speed of the ion's movement. LJP cannot be measured directly, The measured electromotive force (EMF) of a cell with transference includes the liquid junction potential. Concentration cells, in which the diffusion potential is created are called **concentration cells with transference**. An example of such a cell presents the scheme:

$$Ag|AgCl|HCl(c_1) \vdots HCl(c_2)|AgCl|Ag \tag{1}$$

The dotted line ⁝ in the scheme (1) means the place where the two solutions are in contact. While the continuous vertical line | represents the liquid-solid or gas-solid contact interface. The diffusion potential at the liquid-liquid interface, E_{dif}, is unmeasurable. One of the attempts at estimation of the diffusion potential is the Henderson equation:

$$E_{dif} = (t_+ - t_-)\frac{RT}{nF} ln\frac{c_2}{c_1} \tag{2}$$

In this equation difference of the transport numbers ($t_+ - t_-$) defines, in addition to the concentration ratio of c_2/c_1, the value of the resulting diffusion potential. If the ions of dissociated electrolytes have the same transport numbers, the diffusion potential can be reduced to zero. On that idea, **the concept of the salt-bridge device** is based.
The essence of this idea is to introduce between two half-cells, the salt-bridge device filled with an electrolyte solution, with ions that have similar transfer numbers. Such properties have electrolytes such as KCl, KNO_3, or NH_4NO_3. What is also important, is the concentration of salt in a salt bridge. It should be higher than the concentration of the electrolyte, too low a concentration does not provide effective elimination of diffusion potential. The salt bridge present in the cell is marked by the double dotted line. For example, the scheme of the cell (1) with salt-bridge will be written as follows:

$$Ag|AgCl|HCl(c_1) \vdots\vdots HCl(c_2)|AgCl|Ag \tag{3}$$

Diffusion potential, E_{dif}, can be measured indirectly by the potentiostatic method. For this purpose, two cells will be investigated: the concentration cell with a salt bridge (3), and without the device (1). If the values of electromotive force (EMF) of cells (1) and (3) are expressed E_1 and E_2 respectively, the value of the diffusion potential between solutions of HCl of different concentrations c_1 and c_2 is given by the equation:

$$E_{dif} = E_1 - E_2 \tag{4}$$

EXERCISE PURPOSE

The aim of the exercise is the determination of the diffusion potential at the interface of different concentrations of HCl solutions.

APPARATUS

- Voltmeter of high internal resistance.
- Salt bridge (glass vessel).
- Stand.
- Electrode Ag|AgCl - 2 pieces (identical).
- Connecting wires.

LAB GLASS

- Beaker 75 ml (narrow) - 2 pieces
- Volumetric flask - 50 ml - 3 pieces
- Pipette - 5 ml
- Wash bottle
- Beaker 150 ml - 2 pieces

CHEMICALS

- Solution of KCl - 3 mol·dm^{-3}.
- Solution of NH_4NO_3 - 3 molndm^{-3}.
- Solution of HCl - 0.1 mol·dm^{-3}.
- Saturated solution of KCl.
- Saturated solution of NH_4NO_3.

EXPERIMENT PROCEDURES

1. Construction of the cell without salt-bridge (1): fill one half-cell with the 0.1 mol·dm^{-3} HCl solution and the second with 0.01 mol·dm^{-3}. Place the half-cells in the stand and dip them in the beaker filled with the same solution as in electrodes 0.01 mol·dm^{-3} or 0.1 mol·dm^{-3}. Measure the EMF value of the cell (1)
2. Construct the cell equipped with salt-bridge (3): the same half-cells should be placed in a beaker filled with appropriate solutions (KCl and then NH_4NO_3) of different concentrations: 0.03 mol·dm^{-3}, 0.3 mol·dm^{-3}, 3 mol·dm^{-3} and saturated respectively. Measure the values of the electromotive force of cell (3)
3. The electromotive force of the cells should be read after a 10 - 20-minute period until the voltmeter is stabilized.

CALCULATIONS

1. Draw the figure presenting the dependence of EMF of the cell (3) on the concentration of salt in the salt bridge. Determine the concentration at which the EMF is not further changed (i.e. the concentration for which Ed reaches a minimum value).

2. Calculate the diffusion potential, which arises at the interface of HCl solutions of different concentrations.

Template of the table and draft of the study

…………………………….. *Faculty* ……………………………….. *Field of study* *Full-time/ part-time studies*	……………………………………………… *Name and surname*	…………………………………... *Date:*
Group no.: ………………… *Team no.:* …………………	……….…………… *Exercise no.:*	………………………………….. *Instructor:*

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Nr grupy: …………………... *Nr zespołu:* …………………..	……….…………… *Nr ćwiczenia:*	………………………………….. *Nazwisko Prowadzącego:*

1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiary:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: