Exercise 25

ELECTROLYTE CONCENTRATION CELL

Key concepts: Electrode compartment, types of electrodes, half-reactions. Galvanic cells, notation for cells, overall cell reactions, cell potential Electrolyte concentration cell with and without transference, chemical cell. Liquid junction potential, salt bridge. Ionic strength.

Galvanic cells are usually divided into chemical and electrolyte concentration cells. In chemical cells, the source of electrical energy is the chemical reaction occurring in the cell when the circuit is closed. In electrolyte concentration cells, the electrical energy is obtained from the process of reaching chemical equilibrium, so the concentrations of both electrolytes are equal. An electrolyte concentration cell consists of two identical electrodes placed in the same two solutions, but with different concentration of ions involved in the electrode reaction. They can be further classified as cells with or without transference, depending on the way of the two electrolyte solutions contact. If there is a direct border of contact between the solutions in a cell, the cell is called a concentration cell with transference. The second type of cell is the so-called concentration cell without transference, in which there is no direct contact between the solutions or it is only through the salt bridge. An example of a concentration cell with transference can be a cell consisting of two silver electrodes, one of which is placed in AgNO₃ solution with a concentration of c_1 and the other in AgNO₃ solution with a concentration of c_2 and connected directly to each other by a membrane. Schematically, such a cell is written as follows:

$Ag(s) \mid AgNO_3(aq, c_1) : AgNO_3(aq, c_2) \mid Ag(s)$

If $c_1 < c_2$, then the electric charge flow through the cell, equal to Faraday constant (*F*=96 485 $\left[\frac{C}{mol}\right]$), will be accompanied by the release of 1 mole of silver ions on the cathode and the transfer into solution of 1 mole of silver ions from the anode. Simultaneously with the electrode reactions in the cell, there is a migration of ions associated with the flow of electric charge. Through the solutions boundary, it flows t_+ moles of silver ions from a solution of concentration c_1 to a solution of concentration c_2 , and t_- moles of nitrate ions in the opposite direction. The total change is the transfer of 1 - $t_+ = t_-$ moles of AgNO₃ electrolyte from a solution of concentration c_2 to a solution of concentration c_1 .

In a cell with two electrolyte solutions of different concentration in contact, there is an additional source of potential difference across the interface of the two electrolytes. This potential is called the liquid junction potential (E_{ij}). The mechanism of the formation of the liquid junction potential can be explained using the example of the cell studied in this exercise: due to the difference in concentration of the electrolyte, diffusion occurs, which is directed from a more concentrated solution to a less concentrated one. If the cations and anions of the electrolyte differ in mobility, then the ions moving at a higher speed overtake the slower ions. However, the two types of ions are not able to diffuse separately, because of the ionic interactions between the ions. Therefore, ions moving faster are inhibited by slower-moving ions, and lower-speed ions are accelerated by faster ions. As a result a layer of the fast-moving ions is formed, which is directly followed by a second layer consisting of slower-moving ions of the opposite sign. A stationary state is reached, characterized by a certain

potential difference between the contacting solutions, called the liquid junction potential. In this state, reached immediately after contact between the solutions, the rate of diffusion of cations and anions toward the dilute solution is equal.

It should be noted that the presence of an additional potential, the liquid junction potential, affects the measured value of the cell potential (E_{cell}). Since this does not correspond to the equilibrium state of the system, the value of E_{cell} containing this potential cannot be used to determine thermodynamic quantities. To obtain the value of E_{cell} without the liquid junction potential, one can either calculate its value theoretically or attempt to remove it experimentally.

Attempts to theoretically estimate the value of the liquid junction potential by Henderson and Planck were based on certain simplified models of the phenomenon. Moreover, this method can be applied only if the difference in the concentrations of the two solutions is small. Therefore, only an approximation of the value of the liquid junction potential is possible. Henderson's equation has a relatively complicated form. However, the general Henderson equation can be applied for some simple models. For example, if the same binary electrolyte with concentrations c_1 and c_2 is present on both sides of a liquid junction, then Henderson's equation takes the form:

$$E_{\rm d} = (t_- - t_+) \frac{RT}{F} \ln \frac{c_2}{c_1}$$

where R – gas constant (R=8.314 $\left[\frac{J}{mol \times K}\right]$), T – temperature [K].

Because of the difficulties with calculating the liquid junction potentials (except in the simplest cases), numerous attempts have been made to develop such a method of measuring E_{cell} that would minimize the influence of this potential. The most common method is to connect the solutions with the salt bridge, which is filled with a concentrated solution of an electrolyte in which ions show similar mobility ($t_{-} = t_{+}\approx 0,5$). Then the notion for the previously discussed concentration cel is written as follows:

$$Ag(s) \mid AgNO_3(aq, c_1) \parallel AgNO_3(aq, c_2) \mid Ag(s)$$

If the electrolyte solutions are separated by a salt bridge (the || sign in the cell notion), the transfer does not occur across the boundary of between the solutions, but is only the result of the electrode process. Therefore, the above cell belongs to the group of concentration cells without transference.

A salt bridge is an inverted U tube containing a concentrated electrolyte solution with equal or very similar mobility of anions and cations (*e.g.,* KNO₃). The salt bridge operation is based on the fact that at the boundary of two solutions with very different concentrations, the liquid junction potential is the result of the diffusion of the more concentrated electrolyte solution only and therefore it is determined by the properties of this solution. If the ions of the electrolyte solution have almost the same mobility, then the liquid junction potential at the boundary between this solution and any dilute solution will not appear. On the other hand, if the salt bridge, containing concentrated solution, joins two diluted solutions, the liquid junctions potential appearing at the boundaries of a salt bridge and the two diluted electrolyte solutions are equal in the value and different in sign. As a consequence, these liquid junction potentials should compensate for each other even if the salt bridge contains an electrolyte with ions having different mobility. In practice, the salt bridge does not eliminate the liquid junction potential of 1 [mV]. However, it is possible to eliminate it and obtain a cell without transference. In such cells, there is no boundary of contact

between the two solutions at which the liquid junction potential could appear, and it can be achieved by connecting two chemical cells in series without liquid connections, differing only in the concentration of the electrolyte.

In the exercise, a neutral electrolyte, which is KNO₃, is added to the studied solution, in order to reduce the liquid junction potential and to obtain a solution of appropriate ionic strength, moreover it allows to neglect changes in the activity coefficients of AgNO₃. The activity of an electrolyte in a solution depends on both its concentration and the concentration of all other ions present in the solution. According to the Lewis-Randall law, the activity coefficients of an electrolyte solution have the same value in different solutions with the same ionic strength.

Experiment method

The aim of the exercise is to measure the potential of the concentration cells without ion transference, which are noted below:

for $c_1(AgNO_3)=0.040$; 0.020; 0.010; 0.005; 0.003; 0.002 M and to compare the obtained values with the theoretical values calculated according to the equation:

$$E_{\text{cell}} = \frac{RT}{F} \ln \frac{c_2}{c_1}$$

The left-hand electrode compartment contains a solution with a variable concentration of $AgNO_3$, to which KNO_3 is added, in order to obtain an ionic strength of 0,15. The addition of a neutral electrolyte such as KNO_3 reduces the liquid junction potential and also allows to neglect the changes in the activity coefficients of $AgNO_3$ (Lewis-Randall law).

Procedure

- (a) prepare in flasks the 0,040, 0,020, 0,010, 0,005, 0,003 and 0,002 M AgNO₃ solutions by diluting the 0,150 M AgNO₃ solution with 0,150 M KNO₃ solution;
- (b) fill the beaker with 1 cm of the prepared $AgNO_3$ solution;
- (c) rinse one of the silver electrode with the distilled water and place it in the beaker containing 0,150 M AgNO₃. This electrode compartment will be the reference one;
- (d) rinse the second electrode with the distilled water and place it in the beaker containing AgNO₃ solution of different concentration;
- (e) connect both of the elctrode compartments with a salt bridge filled with saturated KNO₃ solution;
- (f) using the voltmeter measure the cell potential, *E*_{cell}, three times: first one after 3 minutes, the second after further 3 minutes and the last one after furtjer 2 minutes;
- (g) build the next cel by using the reference electrode compartment and the one containing different solution of AgNO₃ and repeat step (f);
- (h) repeat steps (g) and (f) till potential of all cells are measured

Calculations

- (a) calculate the theoretical E_{cell} value from the following equation: $E_{cell} = \frac{RT}{F} \ln \frac{c_2}{c_*}$;
- (b) calculate the average value of the measured cell potentials, E_{cell} , for each cell, and plot the following dependency: $E_{cell} = a \ln \frac{c_2}{c_c}$;
- (c) determine the *a* coefficient from the linear equation and compare it to the theoretical, calculated value;
- (d) calculate the deviation;
- (e) write down the results in Table 1;
- (f) give possible explanation of the difference between the calculated and measured values.

Tabele 1.

<i>c</i> ₁ (AgNO ₃)	$E_{cell(calc)}$	E _{cell(meas1)}	E _{cell(meas2)}	E _{cell(meas3)}	E _{cell(meas-}	deviation [%]
					average)	$(E_{\text{cell(calc)}} - E_{\text{cell(meas-average}}) \times 100\%$
						E _{cell(calc)}