APPLICATION OF GALVANIC CELLS EMF MEASUREMENT FOR PHYSICAL AND CHEMICAL PROPERTIES

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Task 36

APPLICATION OF GALVANIC CELLS EMF MEASUREMENT FOR PHYSICAL AND CHEMICAL PROPERTIES

I. Aim of the task

The aim of the task is:

- determination of solubility ratio of sparingly soluble salts AgX using EMF measurements of appropriate cells,
- determination of half-cell Ag|Ag^+ standard potential and silver ion activity coefficient using EMF measurements of appropriate cell.

II. Introduction

1. Definitions: galvanic cell, half-cell, cell EMF, half-cell potential, electrolytic cell.
2. Galvanic half-cell types: electrode reactions, cell schemes, the potential expression.
3. Concentration cells: classification, exemplary cells scheme, electrode reaction equations, cell SEM, potential of diffusion, formation mechanism, electrolytic key.
4. Application of EMF measurement for thermodynamic parameters determination: solubility product, standard cell EMF and standard half-cell potential, average electrolyte activity coefficient.

References:

1. P. W. Atkins, *Physical Chemistry*, 4th edition, Oxford University Press 1992, 249-270.
2. D.W. Rogers, *Concise Physical Chemistry*, Wiley 2011, 220-234.
3. H. Kuhn, H-D. Försterling, D.H. Waldeck, *Principles of Physical Chemistry*, 2nd edition, Wiley, 2009.

I. Theory

III. 1. Electromotive force of galvanic cells

The energy effect of chemical reaction can manifest itself as a heat of reaction, mechanical work or electric work. The source generating electricity in a chemical reaction are redox reactions related with the electron transfer from the molecule of one compound to another molecule. This process takes place not through the direct exchange, but through an outside conductor connecting the circuit between the cell electrodes.

An electrochemical cell consists of two electrodes (electricity conductors) dipped in an electrolyte (electrolytic conductor). The electrode dipped in the electrolyte is a **half-cell**. Half-cells can have different or the same electrolyte. In the case of the same electrolyte, the solutions of both half-cells can contact directly with the liquid interface formation or via ion conductive solution **(electrolytic bridge**).

In this case, the electrolytic bridge allows to eliminate (almost completely) the effects associated with the liquid interface (diffusion potential). When the cell electrodes are dipped in two different electrolytes, the electrical contact between them can be obtained for example by using the electrolytic bridge.

An **electrochemical cell** in which a spontaneous chemical reaction proceeds, thereupon the electricity is produced, is called the galvanic cell. If as a result of voltage applied between two electrodes in the electrolytic cell unspontaneous chemical reaction is enforced, then the electrolysis is observed.

During the current flow in the galvanic cell partial oxidation and reduction reactions on the electrodes can be set. Electrons released in the oxidation reaction set on the lower potential electrode:

$$M_{red} \rightarrow M_{utl} + n\bar{e} \tag{1}$$

flow by the external circuit to the higher potential electrode and the reduction reaction proceeds:

$$M_{utl} + n\bar{e} \rightarrow M_{red} \tag{2}$$

where n – the number of electrons taking part in the cell’s reaction.

The substance which takes part in the reduction reaction gets the electrons from the electrode, thus imparts positive charge, corresponding to a higher potential value. On the other electrode, during the oxidation reaction the electrons are evolved causing negative charge appearance (corresponding to lower value of the electrode potential).

Analysing the processes taking place in the galvanic cells two types of cells can be distinguished:

- **chemical cells** - the source of electricity is chemical reaction,
- **concentration cells** - the source of electricity is the electrolyte activity change (the electrolytic concentration cell - in both half - cells the electrolyte concentration is different; the electrode concentration cell - different electrolyte concentrations, e.g.

gaseous electrodes with different gas pressure or amalgam electrodes of different amalgam concentration).

The galvanic cells schemes:

$$\begin{gathered}(-)E_1\left|M^{n_1^+}\right|\left|M^{n_2^+}\right|E_2(+)\\(-)E_1\left|M^{n_1^+}\right|M^{n_2^+}\left|E_2(+)\right.\\(-)E_1\left|M^{n_1^+} \vdots M^{n_2^+}\right|E_2(+)\end{gathered} \tag{3}$$

where: (–) (+) – the negative and positive cell electrode, | - the interface: electrode (*E*) - the electrolyte solution (*M*), ||- the interface at which the diffusion potential was eliminated (electrolytic bridge), ⋮ - the fluid interface (diffusion potential).

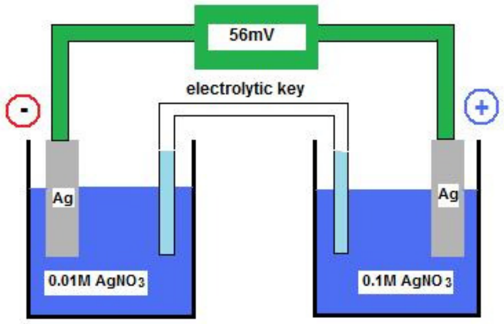


Fig. 1. The example of the concentration cell.

According to the IUPAC recommendation, a scheme of galvanic cells should be written in such a way that the reduction reaction in the scheme always proceeds on the right half-cell.

The reversible cell is the cell in which the reversible processes at the interface are observed.

The electron transfer during the reaction in the cell is the source of the work which depends on the potential difference between cell electrodes. The electric work can be done by the cell in which the total reaction does not achieve equilibrium (this reaction makes electrons flow in the external circuit). If the potential difference between the electrodes of the cell is high, then the electric work which is the result of electrons flow in the cell is high as well. If the potential difference between the electrodes is small then the electric work is small. When the reaction reaches equilibrium in the cell, the potential difference of its half-cell is equal to zero and such a cell cannot do work (e.g. discharged car battery). Maximum work can be obtained only in the reversible cell. To measure thermodynamic parameters using cell work measurements, reversible work must be secured. When the potential difference between the cell electrodes is balanced with opposite external voltage, the spontaneous reaction in the cell is stopped and the system as the whole will be in equilibrium (the reaction in the cell is not at equilibrium, but is measured in the equilibrium state) and then the partial processes proceeding in the cell are reversible. The potential difference between the cell electrodes measured under those conditions is known as **the electromotive force of cell (EMF),** *E* or the cell voltage under powerless conditions. If both half-cells are under standard conditions (activity or fugacity of the redox reaction reagents is equal to unity) then EMF of such a cell is called **the**

standard electromotive force, E^o. The electromotive force (EMF) can be presented using **the Nernst equation:**

$$\mathrm{E} = \mathrm{E_0} - \frac{\mathrm{RT}}{\mathrm{nF}} \ln \mathrm{Q} \tag{4}$$

where: R – the gaseous constant, T- the temperature [K], F – the Faraday constant, Q – the reaction quotient, the quotient of the activity (concentration) of ions involved in the reaction proceeding in the cell.

The electromotive force of the cell can be expressed by two electrodes potential difference:

$$\mathrm{E} = \Pi_\mathrm{R} - \Pi_\mathrm{L} \tag{5}$$

where: Π_R, Π_L- the potentials of right and left half-cells.

A similar dependence can be expressed for the standard electromotive force of cell as the potential difference of two standard half-cells:

$$E^0 = \Pi_R^0 - \Pi_L^0 \tag{6}$$

where: Π^0_R, Π^0_L are the standard potentials of right and left half-cells.

The measurable quantity which characterizes half-cell is its potential. It can be defined as the electromotive force of the examined half-cell and standard hydrogen half-cell.

III. 2. Galvanic half-cell types

There can be distinguished a few different galvanic half-cell types:

III. 2.1. Half-cells reversible to the cation

Half-cells with the active metal electrode

Half-cell of this type is formed by metal dipped in its ions solution MelMe^{n+}. The reaction proceeds:

$$\mathrm{M}^{n+} + n\bar{\mathrm{e}} \rightarrow \mathrm{Me} \tag{7}$$

and its potential can be expressed:

$$\Pi = \Pi^0 - \frac{\mathrm{RT}}{\mathrm{nF}} \ln \frac{\mathrm{a_{Me}}}{\mathrm{a_{Me^{n+}}}} = \Pi^0 + \frac{\mathrm{RT}}{\mathrm{nF}} \ln \mathrm{a_{Me^{n+}}} \tag{8}$$

where: a_{Me}, $a_{Me^{n+}}$- metal and its activity, $a_{Me} = 1$.

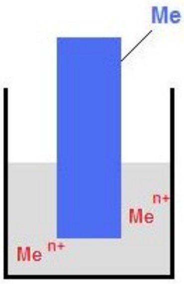


Fig. 2. Scheme of half-cell with active metal electrode.

Gaseous half-cell

Gaseous half-cell consists of metal (very often noble metal) dipped in a solution saturated with appropriate gas containing the potential-creative ions. The example of that type of half-cell is the hydrogen half-cell Me|H_2|H^+, in which there proceeds the reaction:

$$2H^{+} + 2\bar{e} \rightarrow H_{2(g)} \qquad (9)$$

and its potential can be expressed by the equation:

$$\Pi = \frac{RT}{2F}\ln\frac{a_{H_2}}{a_{H^+}^2} = -\frac{RT}{F}\ln\frac{(a_{H_2})^{\frac{1}{2}}}{a_{H^+}} \qquad (10)$$

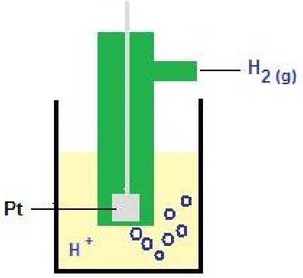


Fig. 3. Scheme of the hydrogen half-cell.

III. 2.2. Half-cells reversible towards the anion

Gaseous half-cells

An example of this type of half-cell is the chlorine Me|Cl_2|Cl^- (platinum electrode rinsed with a chlorine gas stream dipped in a chloride solution), in which the reaction takes place:

$$Cl_2 + 2\bar{e} \rightarrow 2Cl^- \qquad (11)$$

and its potential can be expressed with the equation:

$$\Pi = \Pi^0 - \frac{RT}{2F}\ln\frac{a_{Cl^-}}{a_{Cl_2}^2} = \Pi^0 - \frac{RT}{F}\ln\frac{a_{Cl^-}}{(a_{Cl_2})^{\frac{1}{2}}} \qquad (12)$$

Second type half-cells

The second type half-cell is formed from the metal electrode coated with a tight layer of sparingly soluble metal salt and dipped in a solution containing anions of this salt. The example of such a half-cell is **silver-chloride half-cell** Ag|AgCl|Cl^- in which the following reaction takes place:

$$AgCl + \bar{e} \rightarrow Ag + Cl^- \qquad (13)$$

and its potential can be expressed by the equation:

$$\Pi = \Pi^0 - \frac{RT}{F}\ln\frac{a_{Ag}\cdot a_{Cl^-}}{a_{AgCl}} = \Pi^0 - \frac{RT}{F}\ln a_{Cl^-} \qquad (14)$$

where from the definition the solid activity $a_{Ag} = 1$ and $a_{AgCl} = 1$.

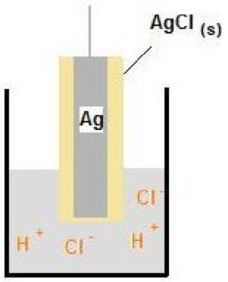


Fig. 4. Scheme of the silver-chloride half-cell.

The other example of the second type half-cell is the very widely applied **calomel half-cell** Hg|Hg_2Cl_2|Cl^- in which the following reaction takes place:

$$Hg_2Cl_2 + 2\bar{e} \rightarrow 2Hg + 2Cl^- \qquad (15)$$

and its potential can be expressed by the equation analogous to (14).

III. 2.3. Redox half-cells

Redox half-cells are constructed of chemically neutral metal dipped in a solution containing the oxidized and reduced forms of an ion $\mathrm{Me}|\mathrm{Me}^{n_1^+}, \mathrm{Me}^{n_2^+}$. The electrochemical oxidation-reduction reaction taking place in that type of half-cell runs with contribution of the electrons provided by the metallic electrode which it does not take direct part in the reaction. The electrode plays here an electric charge conducting role. The potential of such half-cell can be expressed with the equation:

$$\Pi = \Pi^0 - \frac{RT}{nF} \ln \frac{a_{red}}{a_{utl}} \qquad (16)$$

where a_{red} and a_{utl} – the activity of the reduced and oxidized forms, respectively.

An example of such a half-cell is Pt|Fe^{2+},Fe^{3+} half-cell where there proceeds the reaction:

$$Fe^{3+} + \bar{e} \rightarrow Fe^{2+} \qquad (17)$$

and its potential can be expressed by the equation:

$$\Pi = \Pi^0 - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \qquad (18)$$

or quinhydrone half-cell with non-reactive metal dipped in a saturated quinhydrone solution. In an aqueous solution of this compound there is an equimolar amount of quinone (*q*) and hydroquinone (*hq*) molecules. The reaction in the half-cell can be expressed as follows:

$$(q) \quad C_6H_4O_2 + 2H^+ + 2\,\bar{e} \rightarrow C_6H_4(OH)_2 \quad (hq) \qquad (19)$$

and the potential is equal to:

$$\Pi = \Pi^0 + \frac{RT}{F} \ln a_{H^+} + \frac{RT}{2F} \ln \frac{a_q}{a_{hch}} \qquad (20)$$

Another group of cells are **concentration cells**. The source of the electromotive force here is the work of ions transfer from higher concentration (activity) solution to a lower concentration solution. Considering two types of concentration cells, in **the transfer cell** the direct contact between the electrolyte solutions is present. An example there can be a cell constructed from two identical half-cells of different activity electrolyte:

$$(-)\mathrm{E}\left|\mathrm{M}^{n_1^+}(a_1) \,\vdots\, \mathrm{M}^{n_2^+}(a_2)\right|\mathrm{E}(+) \qquad (21)$$

In the case of this cell direct ions migration from higher concentration solution to lower concentration solution is possible for example by porous membrane. Due to the diffusion rate difference of various ions at the two solutions interface, uncompensated charge is accumulated. The ensuing electric field gradient causes rise (for slower moving ion) or lowering (for faster moving ion) of diffusion rate. As a result, a steady state is achieved in the system and all the ions move along with the same speed and the potential difference at the interface does not change. This potential difference is called **the diffusion potential**. The diffusion potential is bigger with bigger difference in the concentration of the two solutions, as well bigger ions mobility difference. The electromotive force of such a cell can be expressed by the equation:

$$\mathrm{EMF} = \mathrm{E} = \mathrm{t} \cdot \frac{\mathrm{RT}}{\mathrm{nF}} \ln \frac{a_2}{a_1} \qquad (22)$$

where t – the number of cation or anion transfer.

In the case of cells without transfer, the solutions of each half-cells are separated from each other (contact is enabled by the electrolytic bridge), which prohibits direct ions migration between half-cells:

$$(-)\ \mathrm{E}|\mathrm{M}^{n+}(a_1)||\mathrm{M}^{n+}(a_2)|\mathrm{E}\ (+) \qquad (23)$$

Because the solutions do not get into contact, the diffusion potential is not formed. The electromotive force of such cell can be expressed with the equation:

$$\mathrm{EMF} = \mathrm{E} = \frac{\mathrm{RT}}{\mathrm{nF}} \ln \frac{a_2}{a_1} \qquad (24)$$

The quotient of transfer of the cell electromotive force (EMF_{transf}) and the electromotive force of the cell without transfer (EMF) with the same ion reversible electrodes is called **the ion transfer number**:

$$\mathrm{t} = \frac{\mathrm{EMF_{transf}}}{\mathrm{EMF}} \qquad (25)$$

Measurement of electromotive force appropriate cells allows determination of various physicochemical properties.

III. 3. Determination of the standard half-cell potential and the standard cell electromotive force

Determination of the standard half-cell potential value is based on accurate EMF measurements of appropriate cell at different electrolyte solution concentrations. Consider a cell with the metallic active electrode Me|Me^{n+} and with the reference half-cell constant potential, e.g. calomel electrode. EMF of that type of cell is equal to the difference of potentials of the two half-cells:

$$\mathrm{E} = \Pi - \Pi_{\mathrm{ref}} = (\Pi^0 - \Pi_{\mathrm{ref}}) + \frac{\mathrm{RT}}{\mathrm{nF}} \ln \mathrm{c} \cdot \mathrm{f} = (\Pi^0 - \Pi_{\mathrm{ref}}) + \frac{\mathrm{RT}}{\mathrm{nF}} \ln \mathrm{c} + \frac{\mathrm{RT}}{\mathrm{nF}} \ln \mathrm{f} \qquad (26)$$

where *c* – the concentration of potential-determining ions, *f* – the coefficient of the potential-determining ions activity.

Expressing the activity coefficient by appropriate function of concentration, depending on the used concentration range:

$$\log \mathrm{f} = -\mathrm{A}\sqrt{\mathrm{c}} \qquad (27)$$

$$\log \mathrm{f} = -\frac{\mathrm{A}\sqrt{\mathrm{c}}}{\mathrm{a}+\mathrm{B}\sqrt{\mathrm{c}}} \qquad (28)$$

$$\log \mathrm{f} = -\mathrm{A}\sqrt{\mathrm{c}} + \mathrm{C} \cdot \mathrm{c} \qquad (29)$$

where *A*, *B*, *C*, *a* – the constants.

Substituting these functions into equation (26) one obtains equation, which allow standard half-cell potential value determination.

In the case of the simplest function (27) application, the following equation is obtained:

$$\mathrm{E} - \frac{\mathrm{RT}}{\mathrm{nF}} \ln \mathrm{c} = \left(\Pi^0 - \Pi_{\mathrm{ref}}\right) - \frac{\mathrm{RT}}{\mathrm{nF}} \cdot 2.303 \cdot \mathrm{A}\sqrt{\mathrm{c}} \qquad (30)$$

then denoting:

$$\mathrm{E} = -\frac{\mathrm{RT}}{\mathrm{nF}} \ln \mathrm{c} = \mathrm{E}' \qquad (31)$$

equation (32) is obtained:

$$\mathrm{E}' = \Pi^0 - \Pi_{\mathrm{ref}} - 2.303 \frac{\mathrm{RT}}{\mathrm{nF}} \cdot \mathrm{A}\sqrt{\mathrm{c}} \qquad (32)$$

Equation (32) is a straight line dependence of E '= f ($\sqrt{c}$):

$$\mathrm{E}' = \mathrm{b} + \mathrm{a}\sqrt{\mathrm{c}_{\mathrm{AgNO_3}}} \qquad (33)$$

from which by the extrapolation to *c* = 0, and taking into account the calomel half-cell potential, standard potential of the examined half-cell can be determined. Similarly, the cell standard electromotive force can be determined using the measurements for the appropriately selected half-cells system.

III. 4. Ion electrolyte activity rate determination

The electromotive force measurement of concentration cell without transfer with known electrolyte concentration allows the electrolyte activity coefficient determination from the equation:

$$\log \mathrm{f} = \frac{\mathrm{F}}{2.303\ \mathrm{RT}} (\mathrm{E} - \mathrm{E}^0) - \log \mathrm{c} \qquad (34)$$

III. 5. Solubility product determination

Knowing the standard potential of an appropriate pair of half-cells of first and second types of the same metal phase (e.g. Ag|Ag$^+$ and Ag|AgCl|Cl$^-$) the solubility product of a salt can be determined:

$$\log \mathrm{I} = \frac{\mathrm{nF}}{2.303\ \mathrm{RT}} \Pi_{\mathrm{II}}^{0} - \Pi_{\mathrm{I}}^{0} \tag{35}$$

The solubility ratio can be determined from measurements of electromotive force of appropriate concentration cells.

II. Experimental

A. Devices and materials

1. **Devices**

- digital voltmeter,
- silver electrodes,
- saturated calomel electrode,
- measurement vessels,
- electrolytic bridge,
- 25 cm^3 flasks,
- 10 cm^3 pipettes,
- 0.5 cm^3 pipettes,
- 100 cm^3 beaker,
- wash bottle.

2. **Materials:**

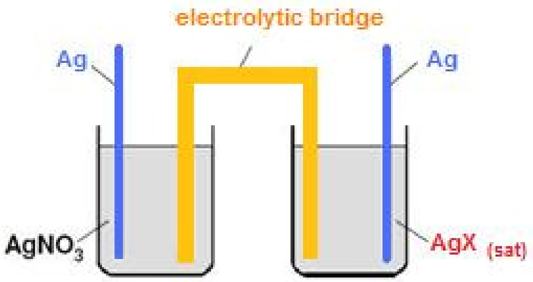
- 0.1 M $AgNO_3$ solution,
- saturated KCl,
- 0.1 M KCl solution,
- 0.1 M KBr solution,
- 0.1 M KI solution,
- 0.1 M KOH solution,
- 0.1 M KSCN solution,
- 0.1 M $K_2Cr_2O_7$ solution.

B. Solubility product determination

1. Cells preparation

Prepare cells according to the scheme (-) Ag|$AgX_{(sat)}$||$AgNO_3$(0.1M)|Ag (+) where X= Cl, Br, I, OH, SCN, Cr_2O_7.

Fill one of the measurement vessels with 9 cm^3 of 0.1M $AgNO_3$. To another vessel put exactly 3 cm^3 of 0.1M $AgNO_3$ and 6 cm^3 of 0.1M KCl (KBr, KI, etc.) and mix carefully. Insert silver electrodes into both measurement vessels and connect them with the electrolytic bridge.



2. *EMF determination*

Connect the electrodes of the cell with the external sockets of digital voltmeter and turn on the electric supply of the meter.

Measure EMF of all cells. After each measurement both electrolytic bridge and electrode should be rinsed with distilled water.

C. Standard potential of half-cell Ag|Ag+ and activity coefficient of silver ions determination

1. *Cells preparation*

Prepare cells according to the scheme $(-)Hg,Hg_2Cl_2|KCl_{(sat)}||AgNO_3(c_x)|Ag(+)$ where c_x = 0.001; 0.002; 0.005; 0.01; 0.05; 0.1M. Dilute 0.1M $AgNO_3$ solution with distilled water in flasks in order to obtain given solutions. Pour 9 cm^3 of $AgNO_3$ solution of appropriate concentration into one of measurement vessels and insert the silver electrode into it. Fill another measurement vessel with saturated KCl solution and put in the calomel electrode. Connect both vessels with the electrolytic bridge.

2. *EMF determination*

Connect the electrodes of cell with the external socket of digital voltmeter and turn on the electricity supply to the meter.

Measure EMF for all cells. After every measurement both the electrolytic bridge and the electrode should be carefully rinsed with distilled water.

D. Results

1. *Solubility ratio determination*

a) Calculation of Ag^+ ions concentration in half cell for each examined electrolyte.

The cell can be examined as the concentration cell:

$$(-)\ Ag\ |\ [Ag^+](c_1)\ ||\ AgNO_3(c_2=0.1M)\ |\ Ag(+)$$

and EMF of that cell is:

$$E = \frac{RT}{nF}\ln\frac{c_2}{c_1} = \frac{RT}{nF}\ln\frac{0.1}{c_1} \tag{36}$$

where: c_1 – the concentration of Ag^+ ions in the left half-cell, c_2 – the concentration of Ag^+ ions in the right half-cell; c_2 is the constant equal to 0.1M ($AgNO_3$ concentration).

Concentration of Ag^+ ions in the left half-cell c_1 can be calculated using equation (36).

b) Solubility product determination.

Solubility product of salts AgX (X= Cl, Br, I, OH, SCN, Cr_2O_7) is expressed:

$$L_{AgX} = [Ag^+]\,[X^-] \tag{37}$$

In the case of $Ag_2Cr_2O_7$:

$$\mathrm{L_{Ag2Cr2O7}} = [\mathrm{Ag^+}][\mathrm{Cr_2O_7^{2-}}] \tag{38}$$

The anion concentration is equal to the concentration of precipitant excess, e.g. for mono-valence anions $[X^-]$:

$$[\mathrm{X^-}] = \frac{(6\cdot 10^{-3}\mathrm{dm^3} - 3\cdot 10^{-3}\mathrm{dm^3})\cdot 0.1\frac{\mathrm{mol}}{\mathrm{dm^3}}}{3\cdot 10^{-3}\mathrm{dm^3} + 6\cdot 10^{-3}\mathrm{dm^3}} = \frac{1}{3}\cdot 10^{-1}\frac{\mathrm{mol}}{\mathrm{dm^3}}$$

c) Results presentation

Results of calculations should be presented in Table 1.

Table 1. Solubility ratio determination.

Cell scheme	**E [V]**	**$c_1 = [Ag^+]$**	**L_{AgX}**	**$L_{from\ the\ table}$**

c_1 = const = 0.1M

2. *Standard potential of half-cell Ag|Ag$^+$ and activity rate of silver ions determination.*

a) Standard potential of half-cell Ag|Ag$^+$ determination

EMF of examined cells can be expressed as the difference between first kind of metal Ag and calomel half-cells:

$$\begin{aligned} \mathrm{EMF} = \mathrm{E} = \Pi_{\mathrm{Ag/Ag^+}} - \Pi_{\mathrm{SCE}} &= \Pi^0_{\mathrm{Ag/Ag^+}} + \frac{\mathrm{RT}}{\mathrm{F}}\ln\left(\mathrm{a_{Ag^+}}\right) - \Pi_{\mathrm{SCE}} = \\ &= \left({\Pi^0}_{\mathrm{Ag/Ag^+}} - \Pi_{\mathrm{SCE}}\right) + \frac{\mathrm{RT}}{\mathrm{F}}\ln\left(\mathrm{c_{Ag}}\cdot \mathrm{f_{Ag}}\right) = \\ &= \left({\Pi^0}_{\mathrm{Ag/Ag^+}} - \Pi_{\mathrm{SCE}}\right) + \frac{\mathrm{RT}}{\mathrm{F}}\ln\left(\mathrm{c_{Ag^+}}\right) + \frac{\mathrm{RT}}{\mathrm{F}}\ln\left(\mathrm{f_{Ag^+}}\right) \end{aligned} \tag{39}$$

where: $\Pi_{Ag/Ag+}$- the potential of Ag|Ag$^+$ half-cell, $\Pi^0_{Ag/Ag+}$- the standard potential of Ag|Ag$^+$ half-cell, Π_{SCE}- the potential of saturated calomel half-cell, a_{Ag+}- the activity of silver ions, c_{Ag+}- the concentration of metal ions, f_{Ag+} - the activity coefficient of metal ions.

The potential of Ag|Ag$^+$ half-cell can be determined by graphical extrapolation using **the limiting Debye-Hückel law** which allows to express the activity coefficient as a function of concentration:

$$-\log \mathrm{f_j} = A|z_+z_-|\sqrt{I} \tag{40}$$

where: I – the ionic strength of the solution,$I = \frac{1}{2}\Sigma c_j z_j^2$, z_+, z_- - the ions valence, A- the constant.

In the case of aqueous electrolyte solutions of type 1:1 (e.g. $AgNO_3$), this dependence is simplified to:

$$\log \mathrm{f_{Ag^+}} = -\mathrm{A}\sqrt{\mathrm{c_{AgNO_3}}} \tag{41}$$

after introducing equation (41) into (39) we obtain:

$$\mathrm{E} - \frac{\mathrm{RT}}{\mathrm{F}}\ln\left(\mathrm{c_{AgNO_3}}\right) = \left(\Pi^0{}_{\mathrm{Ag/Ag^+}} - \Pi_{\mathrm{SCE}}\right) - 2.303\frac{\mathrm{RT}}{\mathrm{F}}\mathrm{A}\sqrt{\mathrm{c_{AgNO_3}}} \tag{42}$$

and denoting

$$\mathrm{E}' = \mathrm{E} - \frac{\mathrm{RT}}{\mathrm{F}}\ln\left(\mathrm{c_{AgNO_3}}\right) \tag{43}$$

we obtain

$$\mathrm{E}' = \left(\Pi^0{}_{\mathrm{Ag/Ag^+}} - \Pi_{\mathrm{SCE}}\right) - 2.303\frac{\mathrm{RT}}{\mathrm{F}}\mathrm{A}\sqrt{\mathrm{c_{AgNO_3}}} \tag{44}$$

Equation (44) is the equation of straight line dependence of $\mathrm{E}' = \mathrm{f}(\sqrt{\mathrm{c_{AgNO_3}}})$:

$$\mathrm{E}' = \mathrm{b} + \mathrm{a}\sqrt{\mathrm{c_{AgNO_3}}} \tag{45}$$

Plotting equation (45) and extrapolating to $c = 0$, one obtains the value of potential difference for the standard silver half-cell and calomel half-cell:

$$\lim_{\sqrt{c}\to 1} E' = \Pi^0{}_{\mathrm{Ag/Ag^+}} - \Pi_{\mathrm{SCE}} \tag{46}$$

Plot the measured experimental results in coordinates of equation (45) $\mathrm{E}' = \mathrm{f}(\sqrt{\mathrm{c_{AgNO_3}}})$ (calculate E' from eq. (43)). The parameters of eq. (46) should be determined using graphical or least squares method (see Appendix). In the case of least squares method, determine the theoretical dependence (46) based on determined values of calculated before parameters. The calculation results should be presented in Table 2.

Knowing that the potential of the saturated calomel half-cell (SCE) against the standard hydrogen half-cell is equal to:

$$\Pi_{\mathrm{SCE}}\,[\mathrm{V}] = 0.2415 - 0.00076(\mathrm{T} - 298) \tag{47}$$

where T- the temperature [K], the standard potential of Ag|Ag$^+$ half-cell can be determined and compared with the theoretical tabular value. The constant A from the limiting Debye-Hückel law should be compared with the theoretical tabular value as well.

b) Determination of activity coefficient of silver ions

Using the measured cell EMF values and the value calculated from equation ($\Pi^0{}_{\mathrm{Ag/Ag+}}$ - Π_{NEK}) calculate the activity coefficients of silver ions in the examined system from the equation:

$$\log f_{Ag^+} = \frac{F}{2.303RT} \cdot [E - (\Pi^0{}_{Ag/Ag^+} - \Pi_{SCE})] - \log c_{AgNO_3} \qquad (48)$$

c) Results presentation

Results of the calculations should be presented in Table 2.

Table 2. Silver ions activity rate determination.

c_{AgNO_3}	E [V]	E’	$\sqrt{c_{AgNO_3}}$	$\log f_{Ag+}$	f_{Ag+}