Exercise 23

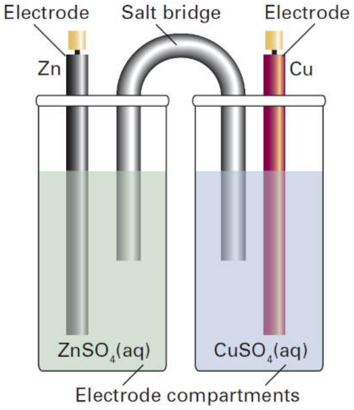
DEPENDENCE OF THE SILVER ELECTRODE POTENTIAL ON THE CONCENTRATION OF Ag^+ IONS IN THE SOLUTION

Key concepts: Electrode compartment, types of electrodes, half-reactions. Galvanic cells, notation for cells, overall cell reaction, cell potential, standard potential, Nernst equation. Reaction quotient. Liquid junction potential. Solution activity, mean activity coefficient, ionic strength, Lewis-Randall rule, Debye–Hückel law.

An electrode compartment consists of two or more phases, including one conducting the electrons (an electrode) and the other being ionic conductor (electrolyte in the solution, a liquid or a solid), between them the electrons or ions are transferred in the electrochemical reaction of oxidation and reduction. Under isothermal-isochoric conditions, in most of the electrode types, the electrochemical equilibrium, determining the potential difference between phases, is quickly established.

The simplest electrode compartments are built of a metal electrode and a metal ion solution (for example: zinc electrode placed in the $ZnSO_4$ solution, $Zn(s)|Zn^{2+}(aq)$). These are the I type. Also gas electrodes compartments are the I type (for example: hydrogen electrode $Pt(s), H_2(g)|H^+(aq)$). The II type are built of metal covered with the insoluble salt of this metal and a solution (for example: $Ag(s)|AgCl(s)|Cl^-(aq)$). The other type is redox one, built of a noble metal in solution, containing particles or ions on different oxidation number (for example: $Pt(s)|Fe^{2+},Fe^{3+}(aq)$). An electrochemical cell consists of two electrodes compartments, which are connected by a salt bridge, membrane or two electrodes sharing the same electrolyte.

In the notation for cell, on the edges the composition of electrodes is given, then the composition and activity, molality or concentration of reactants and the type of solvent; in case of a gaseous reactant also the pressure should be given. On the left there is an electrode with the lower potential (anode), on the right - the one with higher potential (cathode). The phase boundaries are denoted by a vertical bar. A liquid junction potential is denoted by vertical dots. A double vertical line denotes salt/ion bridge. For example:



$$Zn(s)\ |\ ZnSO_4\ (aq, a_1)\ \|\ CuSO_4\ (aq, a_2)\ |\ Cu(s)$$

Both of electrodes can be also placed in the same solution. For example:

$$Pt(s)\ |\ H_2(g)\ |\ HCl(aq, a_1)\ |\ AgCl(s)\ |\ Ag(s)$$

A redox reaction taking place in the electrode compartments can be written as:

$$\mathrm{Ox} + \nu\bar{e} \rightarrow \mathrm{Red}$$

where $\nu\bar{e}$ – number of electrons exchanged in the half-reaction

The reducing agent (reductant) and the oxidizing agent (oxidant) in a half-reaction form a redox couple. During the redox reaction the electrons are removed from one species, transferred and added to other species. The difference between the potential of right-hand and left-hand electrodes is the cell potential.

$$E_{\mathrm{cell}} = E(\mathrm{right}) - E(\mathrm{left}) \qquad (1)$$

In a cell with two different electrolyte solutions 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_{lj}, and has an influence on the measured cell potential value. Its contribution can be reduced by joining the electrolyte compartments through a salt bridge, which contains a concentrated electrolyte solution with equal or very similar mobility of anions and cations (*e.g.,* KNO_3).

The potential difference calculated from the standard potentials of electrodes is called the standard cell potential ($E^{\ominus}_{\mathrm{cell}}$). The standard potential of electrode can be measured by constructing a cell in which it is the right-hand electrode and the left-hand electrode is standard hydrogen electrode (SHE). The value of the SHE potential is assigned to zero at all temperatures. To achieve the standard conditions, the activity of the hydrogen ions must be 1 (that is, pH = 0) and the pressure of the hydrogen gas must be 1 bar.

After connecting the electrodes with an external current conductor, the total chemical reaction of the cell does not reach equilibrium. The course of such a reaction is accompanied by the transfer of electrons in an external electrical circuit and the cell can do electrical work (w_{e}). The maximum work of the cell is obtained in the quasistatic process, in which the current intensity is infinitely small (then there is only a temporary and slight disturbance of the equilibrium of electrode reactions). In this case, the energy released in the total chemical reaction is completely converted into electrical work. This work is expressed by the formula: $w_{\mathrm{e,max}} = \Delta_{\mathrm{r}}G$.

The relation between the reaction Gibbs energy and the cell potential is:

$$\Delta_{\mathrm{r}}G = -\nu F E_{\mathrm{cell}} \qquad (2)$$

where $\nu\bar{e}$ – number of electrons exchanged in the half-reaction, F – Faraday’s constant, equal 96485 $\left[\frac{\mathrm{C}}{\mathrm{mol}}\right]$.

We can relate also the cell potential to the activities of the participants in the overall cell reaction. The dependency of the E_{cell} on the composition of the reaction mixture is called the Nernst equation:

$$E_{\mathrm{cell}} = E^{\ominus}_{\mathrm{cell}} - \frac{RT}{\nu F}\ln Q \qquad (3)$$

where R – gas constant, equal 8.314$\left[\frac{\text{J}}{\text{mol·K}}\right]$, T – temperature [K], Q – the reaction quotient.

The reaction quotient can be defined as Q = $\prod_J a_J^{\nu_J}$, and because reactants have negative stoichiometric numbers, they automatically appear as the denominator when the product is written out explicitly, therefore we can write Q = $\frac{\text{activities of products}}{\text{activities of reactants}}$, with each species raised to the power given by its stoichiometric coefficient. Moreover, for pure solids and liquids, the activity is 1, so such substances make no contribution to Q even though they may appear in the chemical equation For the reaction

Ox + νē → Red, the Q = $\frac{a_{\text{Red}}}{a_{\text{Ox}}}$.

The activity, which is an effective concentration, is dimensionless and can be defined using the molality (b) or molar concentration (c):

$$a = \gamma\frac{b}{b^\ominus} \quad \text{lub} \quad a = \gamma\frac{c}{c^\ominus} \qquad (4)$$

where γ – activity coefficient, in which all the deviation from ideality are captured (dimensionless), b – molality $\left[\frac{\text{mol}}{\text{kg}}\right]$, $b^\ominus$ - standard molality, $b^\ominus$=1$\left[\frac{\text{mol}}{\text{kg}}\right]$, c – molar concentration $\left[\frac{\text{mol}}{\text{dm}^3}\right]$, $c^\ominus$ standard molar concentration, $c^\ominus$=1 $\left[\frac{\text{mol}}{\text{dm}^3}\right]$

For example in the Daniell cell:

$$\text{Zn(s)} \mid \text{ZnSO}_4\,(\text{aq}, a_1) \parallel \text{CuSO}_4\,(\text{aq}, a_2) \mid \text{Cu(s)}$$

the half-reactions are:

$$\text{Cu}^{2+}(\text{aq}) + 2\bar{e} \rightarrow \text{Cu(s)}$$
$$\text{Zn}^{2+}(\text{aq}) + 2\bar{e} \rightarrow \text{Zn(s)}$$

and the overall cell reaction is:

$$\text{Cu}^{2+}(\text{aq}) + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq})$$

and the Nernst equation is:

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{RT}{\nu F}\ln\frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$$

In electrolyte solutions the ion-ion interactions are so strong, that the activity (a) can be replaced by molality (b) only in case of very dilute solutions, because if molality of the substance goes to zero, then the activity coefficient goes to 1 ($\gamma \rightarrow 1$, when $b \rightarrow 0$). In electrolyte solutions there is no experimental way of separating the activity coefficient of anions and cations The best we can do experimentally is to assign responsibility for the nonideality equally to both kinds of ion. Therefore, the mean activity coefficient as the geometric mean of the individual coefficients was introduced. For the M_pX_q compound that dissolves and give a solution of p cations and q anions, we can write:

$$\gamma_\pm = (\gamma_+^p \gamma_-^q)^{1/s}, \text{ where } s = p + q \qquad (5)$$

The long range and strength of the Coulombic interaction between ions means that it is likely to be primarily responsible for the departures from ideality in ionic solutions and to dominate all the other contributions to nonideality. This domination is the basis of the Debye–Hückel theory of ionic solutions, which was devised by Peter Debye and Erich Hückel in 1923. The model leads to the result that at very low concentrations the activity coefficient can be calculated from the Debye–Hückel limiting law:

$$\log\gamma_\pm = -A|z_+z_-|I^{1/2} \qquad (6)$$

where I – ionic strenght of the solution (dimensionless), $I = \frac{1}{2}\sum_i z_i^2(b_i/b^{\ominus})$, A = 0,509 for an aqueous solution at 25°C, z_+ and z_- - the charge number of cation and anion.

When the ionic strength of the solution is too high for the limiting law to be valid, the activity coefficient may be estimated from the extended Debye–Hückel law:

$$\log\gamma_\pm = -\frac{A|z_+z_-|I^{1/2}}{1 + BI^{1/2}} \qquad (7)$$

where B is a dimensionless constant.

According to Lewis-Randall rule the activity coefficient of cations and anions and the average activity coefficient have the same value in different solution and the same ionic strength.

Experiment method

The aim of the exercise is to determine the dependency of silver electrode potential on Ag^+ concentration in the solution with constant ionic strength (I = 0,1) by measuring the potential of the following cell:

$$Ag(s) \mid AgCl(s) \mid KCl\ (aq,\ 1M) \parallel KNO_3\ (aq,\ 0{,}1M - c\ ),\ AgNO_3\ (aq,\ c) \mid Ag(s)$$

and to determine the average activity coefficient of $AgNO_3$ in studied solutions.

Procedure

(a) build the cell according to the above cell notation. The anode is a reference silver chloride electrode with a salt bridge and the cathode is a silver electrode in a solutions with different concertation of $AgNO_3$, but constant ionic strength;
(b) in a volumetric flasks of 50 cm^3, by using the solution (1) c = 0,09 M KNO_3 + 0,01 M $AgNO_3$ and 0,10 M KNO_3, prepare the following solutions of $AgNO_3$ with constant ionic strength I = 0,10:,
(2) $c = 2{,}5{\cdot}10^{-3}$,
(3) $c = 1{,}0{\cdot}10^{-3}$,
(4) $c = 4{\cdot}10^{-4}$,
(5) $c = 1{,}0{\cdot}10^{-5}$ M can be obtained by diluting solution (3);
KNO_3 concentration in each solution is equal (0,1 – c) M;
(c) before starting the measurements both of electrodes should be rinsed several times with distilled water, changing the distilled water about five times in a clean beaker, then dry the electrodes with tissue paper;
(d) the measurements of cell potential (containing the liquid junction potential of E_{lj} = 0,002 [V]) should start from the solution of the lowest concentration of $AgNO_3$;
(e) after placing both electrodes in the solution, leave the electrical circuit opened (no current flows) and wait 10-15 minutes for establishing the equilibrium in the cell; next perform the measurement by closing the electrical circuit for 1 minute; repeat measurement 3 times for each solution;
(f) after finishing the measurements rinse both electrodes with distilled water, leave the silver electrode dry and place the silver chloride electrode in the beaker filled with 0,10 M KNO_3.

Calculations

(a) write the half-reactions and the overall cell reaction;
(b) based on the measured cell potential for different $AgNO_3$ solutions, calculate cell potential E_{cell} without the liquid junction potential E_{lj}= 0,002 [V] from the equation: $E_{cell} = E_{cell\ (measured)} - E_{lj}$;
(c) calculate the potential of silver electrode, using the equation (1), using the potential of silver chloride electrode equal 0,201 [V];
(d) write down all the results in Table 1:

Table 1.

cAgNO$_3$ M	$E_{cell} = E_{cell(measured)} - E_{lj}$ [V]	$E_{Ag^+\|Ag}$ [V]
0.01		
$2{,}5 \cdot 10^{-3}$		
$1{,}0 \cdot 10^{-3}$		
$4 \cdot 10^{-4}$		
$1{,}0 \cdot 10^{-5}$		

(e) the Nernst equation for the studied cell is:

$$E_{Ag|Ag^+} = E^{\ominus}_{Ag|Ag^+} - \frac{RT}{\nu F} \ln \frac{1}{a_{Ag^+}}$$

by replacing the activity of AgNO$_3$ with $\gamma_{\pm} \cdot c$ we obtain:

$$E_{Ag|Ag^+} = E^{\ominus}_{Ag|Ag^+} - \frac{RT}{\nu F} \ln \frac{1}{\gamma_{\pm} \cdot c_{Ag^+}}$$

and after further transformation:

$$E_{Ag|Ag^+} = E^{\ominus}_{Ag|Ag^+} - \frac{RT}{\nu F} \ln \frac{1}{\gamma_{\pm}} - \frac{RT}{\nu F} \ln \frac{1}{c_{Ag^+}}$$

the dependency of silver electrode potential $E_{Ag|Ag^+}$ on $\ln \frac{1}{c_{Ag^+}}$ is linear and can be expressed with linear equation y = ax + b, where

$$y = E_{Ag|Ag^+}$$
$$x = \ln \frac{1}{c_{Ag^+}}$$
$$a = -\frac{RT}{\nu F}$$
$$b = E^{\ominus}_{Ag|Ag^+} - \frac{RT}{\nu F} \ln \frac{1}{\gamma_{\pm}}$$

(f) make plot of this dependency, add the regression line and determine coefficients a i b;

(g) calculate the average activity coefficient $\gamma_{\pm}$ of AgNO$_3$ in studied solutions with constant ionic strength by using the b value determined in point (f), ($E^{\ominus}_{Ag|Ag^+}$ = 0.799 [V]);

(h) which of the prepared cells can do the highest amount of work? Give an explanation.