Exercise 24

GALVANIC CELL THERMODYNAMICS

Key concepts: electrode compartment, types of electrodes, half-reactions. Galvanic cells, notation for cells, overall cell reaction, cell potential, standard potential. The relationship between Gibbs energy, entropy and enthalpy and cell potential. Dependence of the cell potential on temperature. Determination of enthalpy and entropy from the measurement of cell potential at different temperatures.

A galvanic cell is a system of two electrodes placed in the same or different electrolyte solutions, with such a design that when connected by an external source of current, a spontaneous transfer of charge occurs in the circuit. The cell remains in electrochemical equilibrium when no current flows through it. This means that the electrode reactions in both electrode compartments reach equilibrium and in this case the potential difference between the electrodes is equal to the potential of the cell (E_{cell}). In turn, after connecting the electrodes with an external source of current, 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 the external electrical circuit and the cell can perform electrical work (w_e). In parallel with the movement of electrons in the outer circuit, an orderly movement of ions in the electrolyte solution takes place. After opening the outer circuit, the cell gradually returns to equilibrium.

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: $w_{e,\max} = \Delta_r G$.

$$w_{e,\max} = -\nu F E_{\text{cell}} \qquad (1)$$

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

In an elementary, reversible isothermal-isobaric process, the elementary non-expansion work is equal to the change in Gibbs energy, $w_{e,\max} = \Delta_r G$. Thus, if the reactions in the cell proceed in a thermodynamically reversible way, then:

$$\Delta_r G = -\nu F E_{\text{cell}} \qquad (2)$$

This equation expresses a simple relationship between the Gibbs energy of the reaction running in the cell, and its potential. This is one of the most important relations of electrochemical thermodynamics. As a result of differentiation of equation (2) with respect to temperature (under constant pressure), the following are obtained:

$$\left(\frac{\partial \Delta_r G}{\partial T}\right)_p = -\nu F\left(\frac{\partial E_{\text{cell}}}{\partial T}\right)_p \qquad (3)$$

By applying the equivalence of entropy (S) and the partial derivative of Gibbs energy calculated relative to temperature (at $p = const.$):

$$-\Delta_r S = \left(\frac{\partial \Delta_r G}{\partial T}\right)_p \qquad (4)$$

We obtain the equation:

$$\Delta_r S = \nu F\left(\frac{\partial E_{\text{cell}}}{\partial T}\right)_p \qquad (5)$$

It allows to determine the entropy changes of the cell reaction by measuring the change in potential (E_{cell}) together with temperature (T).
From a known relationship:

$$\Delta_r H = \Delta_r G + T\Delta_r S \qquad (6)$$

by $T = const.$ i and after combining equations (2) i (5) we obtain:

$$\Delta_r H = \nu F\left[T\left(\frac{\partial E_{\text{cell}}}{\partial T}\right)_p - E_{\text{cell}}\right] \qquad (7)$$

Therefore the measurement of the cell potential and its dependence on temperature allows to determine the changes in the thermodynamic functions $\Delta_r G$, $\Delta_r S$ oraz $\Delta_r H$ for the reactions occurring in the cell at constant pressure.

Experiment method

The aim of the exercise is to construct a cell and measure its potential (E_{cell}) at different temperature values, and then calculate the change of: Gibbs energy $\Delta_r G$, entropy $\Delta_r S$ and enthalpy $\Delta_r H$ caused by the reaction occurring in the cell. Measurements should be performed at the following temperatures: 20, 25, 30, 35 and 40 °C.

The studied cell consists of a silver chloride electrode (anode) and a redox electrode (cathode). The notation for this cell is:

$$\mathrm{Ag(s)} \mid \mathrm{AgCl(s)} \mid \mathrm{KCl\ (aq)} \parallel \mathrm{Fe(CN)_6^{3-}(aq,\ 0{,}01\ M)},\ \mathrm{Fe(CN)_6^{4-}(aq,\ 0{,}01\ M)} \mid \mathrm{Pt(s)}$$

Procedure

(a) turn on the thermostat and ste the temperature to 20°C;

(b) measure 25 ml of Fe^{3+} and 25 ml of Fe^{2+} solutions, then mix them in a 100 ml beaker and place it in the thermostat so that the part with the solution is immersed in water;

(c) rinse both electrodes with distilled water, dry gently with tissue paper, place the electrodes and the temperature sensor in the studied solution;

(d) the cell potential (E_{cell}) should be measured, when the current flowing through the cell is the smallest, what can be achieved by applying voltmeter with a very high input resistance (about 10^8 – 10^{12} [Ω]), applied in this exercise. Notice that the cell should be connected to the measuring system only for the time of the potential measurement (reading), so the time of current flow through the cell is as short as possible;

(e) turn on a voltmeter with a very high input resistance (in the exercise, the role of such a voltmeter is fulfilled by a pH-meter);

(f) turn on the temperature sensor (see the instructions next to it), wait till the memory and display are tested, then the instrument is set to the temperature measurement mode. According to the attached instructions, select a temperature measurement resolution of 0,1;

(g) thermostate the solution with the electrodes at a given temperature for about 10 minutes, after this time, connect the electrodes to the pH meter and read the E_{cell} value and the temperature measured by the sensor. If the E_{cell} values change, read several of the values and calculate an average of them. After reading the E_{cell} value, disconnect the electrodes from the pH meter (necessarily);

(h) set the thermostat to the next required temperature and repeat the steps described in point (g);

(i) after the measurements are completed, turn off: the temperature meter (see the manual, also disconnect the power supply of the meter from the power source), the pH-meter and the thermostat. Remove the temperature sensor and electrodes from the studied solution and rinse them with distilled water, then place the silver chloride electrode in KNO_3 solution. Remove the beaker with the solution from the thermostat, empty it, wash it and allow it to dry.

Calculations

(a) if the temperature changes are small, the cell potential can be expressed with a good approximation as a linear function of temperature:

$$E_{\text{cell}} = aT + b \qquad (8)$$

where $a = \left(\frac{\partial E_{\text{cell}}}{\partial T}\right)_p$

(b) based of the obtained results, draw a plot of the dependence of the E_{cell} on the temperature and, using the least squares method, determine the coefficients a and b;

(c) calculate $\Delta_r S$ value using equation (5);

(d) for each temperature calculate $\Delta_r G$ (equation (2)) and $\Delta_r H$ (equation (7)) values, as well as E_{cell} values using equation (8);

(e) write down all the results in Table 1;

(f) write down the half-reactions and the overall cell reaction.

Tabela 1. Values of E_{cell} (measured), $\Delta_r G$, $\Delta_r H$ and E_{cell} (calculated) in different temperature values.

T [K]	E_{cell} [V] measured	$\Delta_r G$ $\left[\frac{\text{J}}{\text{mol}}\right]$ calculated	$\Delta_r H$ $\left[\frac{\text{J}}{\text{mol}}\right]$ calculated	E_{cell} [V] calculated