

DETERMINATION OF THE THERMODYNAMIC FUNCTIONS OF CHEMICAL REACTION IN A GALVANIC CELL

INTRODUCTION

Electrochemical cells are devices consisting of two half-cells (electrodes) connected by a conductor enabling the flow of electrons and immersed in the electrolyte, which facilitates migration of charge in the form of ions. When the electrodes have different electrolytes, they are connected by means of a **salt bridge** (ion bridge), which prevents electrolyte mixing and ensures the transfer of charge between these electrolytes.

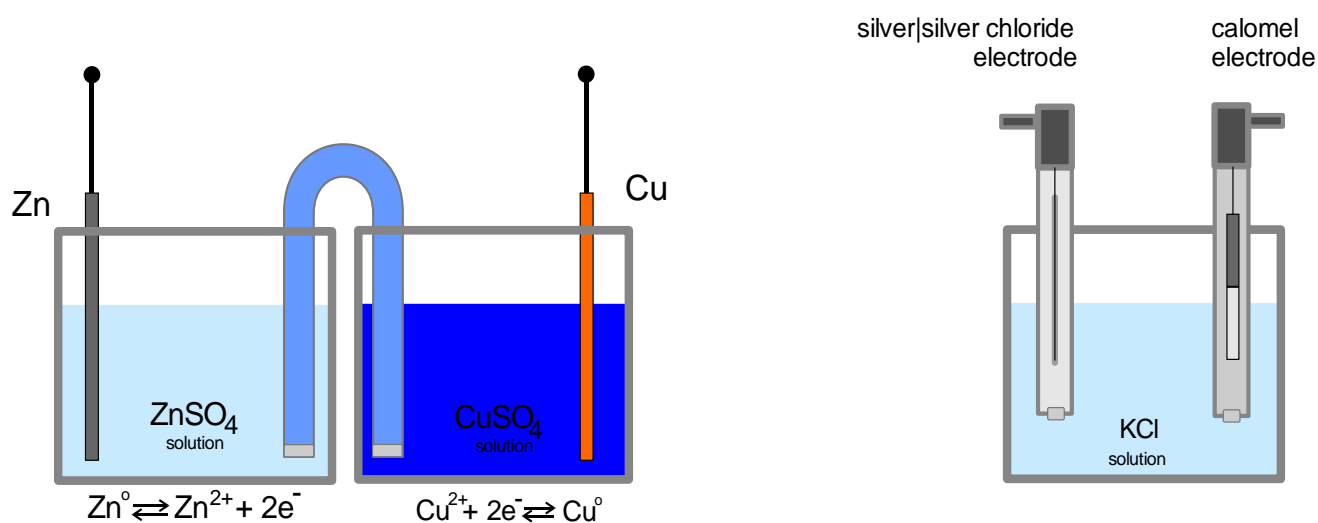


Figure 1. Scheme of a Daniell cell – zinc-copper cell (left) and scheme of the investigated cell (right).

The Standard Electromotive Force of the cell (*EMF*, for the purpose of this exercise marked with the symbol *E*) is the difference of potentials between the electrodes in conditions when the current does not flow through the cell. The resultant reaction in the cell consists of the reactions occurring in the half-cells. According to the IUPAC convention, the cell diagram should be written in such a way that the electrode with the lower potential is placed on the left side of the diagram, and the electrode with the higher potential on the right. The notation (Stockholm convention) of Daniell cell can be written as follows:



After the circuit is short-circuited, an electrochemical reaction will occur whose driving force is the potential difference between the electrodes. On the electrode with a higher potential, a reduction reaction takes place, and on the electrode with a lower potential, the oxidation reaction. The resultant reaction taking place in the cell is represented by the equation:



Each chemical reaction can be described using thermodynamic functions. To describe the thermodynamic work of a galvanic cell, one can use the relationship between the change of the thermodynamic potential ΔG for electrode processes and the electromotive force of cell *E*:

$$\Delta G = -nFE$$
 (3)



The change in the entropy of the process taking place in the cell is related to the temperature dependence of the electromotive force ($\partial E/\partial T$) of the cell as follows:

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right) \quad (4)$$

The dependence of electromotive force E of the cells on temperature in a small temperature range can be described approximately by linear relation:

$$E = a + bT \quad (5)$$

The value of the temperature coefficient b can be expressed by the formula:

$$\left(\frac{\partial E}{\partial T} \right) = b \quad (6)$$

The measurement of electromotive force E and the temperature coefficient $\partial E/\partial T$ allows us to calculate the thermodynamic functions ΔG , ΔS , and ΔH of the reaction occurring in the cell by the equations (3), (4), and (7).

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (7)$$

OBJECTIVE OF THE TASK

The aim of the exercise is to determine thermodynamic functions (ΔG , ΔS , and ΔH), describing the process taking place in a galvanic cell built of two electrodes: silver chloride and calomel.

The silver chloride electrode is made of metallic silver coated with silver chloride and immersed in a solution such as KCl. The equilibrium reaction occurring at the electrode is shown in the equation:



The calomel electrode is made of mercury coated with mercury chloride(I) and immersed in a solution of chloride ions, e.g. KCl, in which the reaction is carried out:



We write the diagram of the tested cell in the following way:



APPARATUS

1. Silver chloride electrode (Hydromet, RL-100)
2. Calomel electrode
3. Thermostatic vessel
4. Digital millivoltmeter V 541
5. Thermostat – IKA HBC-5 BASIC
6. Cables (2 pcs)
7. Digital thermometer (accuracy 0.1 K).



8. 50 cm³ beaker
9. Magnetic stirrer IKA
10. Tweezers.

CHEMICALS

Solution of KCl (3M).

EXPERIMENTAL PROCEDURE

1. Built a cell $(-)\text{Ag}|\text{AgCl}|\text{Cl}^-||\text{Cl}^-|\text{Hg}_2\text{Cl}_2|\text{Hg}(+)$. For this purpose, immerse silver chloride and calomel electrodes in a thermostated vessel filled with solution 3M KCl.
2. Connect the electrodes to the millivoltmeter so that the measured electromotive force has a positive value.
3. Turn on the thermostat (the thermostat's handling will be explained by the instructor), and begin the measurements at 25 °C. Measure electromotive force until 46 °C every 3 °C, and wait for the temperature to stabilize each time (usually 8-10 min.).
4. After the measurements, cool the system to 25 °C.

CALCULATIONS

1. The results of measurements and calculations should be presented in tabular form.
2. Write the equation of the reaction taking place in the cell.
3. On graph paper, draw electromotive force dependence on temperature (in absolute scale).
4. Calculate the slope coefficient of the straight line (temperature coefficient) and the electromotive force at 298K using any application or calculator.
5. Calculate the values ΔG , ΔS , and ΔH .
6. Based on accessible physicochemical data, and thermodynamic tables (specify which sources you used), calculate the thermodynamic functions of the reaction taking place in the cell and compare them with the values calculated on the basis of measurements.



Template of the table and draft of the study

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

<p>..... Wydział</p> <p>..... Kierunek Studia stacjonarne/niestacjonarne</p>	<p>..... Imię i Nazwisko studenta</p>	<p>..... Data wykonywania ćwiczenia:</p>
<p>Nr grupy:</p> <p>Nr zespołu:</p>	<p>..... Nr ćwiczenia:</p>	<p>..... Nazwisko Prowadzącego:</p>

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: