

Determining thermodynamic parameters of a reaction by electrochemical measurements

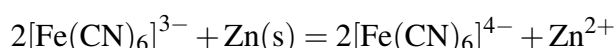
Theoretical background: Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods*, Ch. 2.
(Novák Mihály, Szűcs Árpád, *Elektrokémia*, Ch. 9 (Hungarian)).

Type of practice: Individual.

Purpose of practice: How to determine fundamental thermodynamic values for a redox reaction using potentiometry.

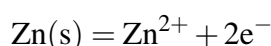
1 Introduction

In the practice you will study the following heterogeneous redox process,

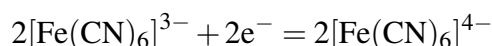


You will determine the Gibbs energy ($\Delta_r G$), the entropy ($\Delta_r S$), the enthalpy ($\Delta_r H$), and the heat of the reaction (q_r) as the function of temperature.

The simplest way to carry out the above reaction is to put a piece of zinc into hexacyanoferrate(III) solution (Fig. 1). Then the oxidation half reaction is



and the reduction half reaction is



The reaction can also be carried out by spatially separating the oxidation and reduction processes in two half-cells of an electrochemical cell (Fig. 2). Then the oxidation half-cell reaction (anodic process) and the reduction half reaction (cathodic process), that is, the overall cell reaction is the same as above, but in this case due to the potential difference in the cell, the system is able to do electrical work, the change in energy can be not only heat but also work. The KCl salt bridge serves two purposes: (1) ensures the electric connection between the two electrolyte solutions without mixing them, and (2) it also prevents the formation of a so-called diffusion potential between the two half-cells due to the different diffusion rates of ions of different mobilities. Within the salt bridge K^+ and Cl^- ions have about the same electric mobility (diffusion coefficient).

Gibbs energy (earlier it was called free enthalpy, Gibbs free energy) change during the reaction ($\Delta_r G$), shortly reaction Gibbs energy (i.e., energy change in isothermal, isobaric, reversible conditions without a change in composition so that the amount of substances corresponding to the stoichiometric numbers in the equation reacts), i.e., the maximal useful (nonmechanical

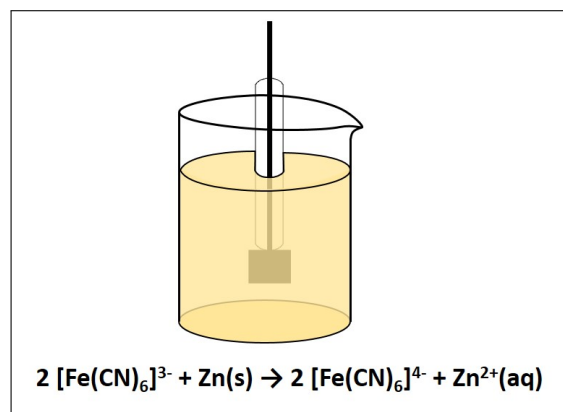


Figure 1: The reaction as a "simple" heterogeneous redox process.

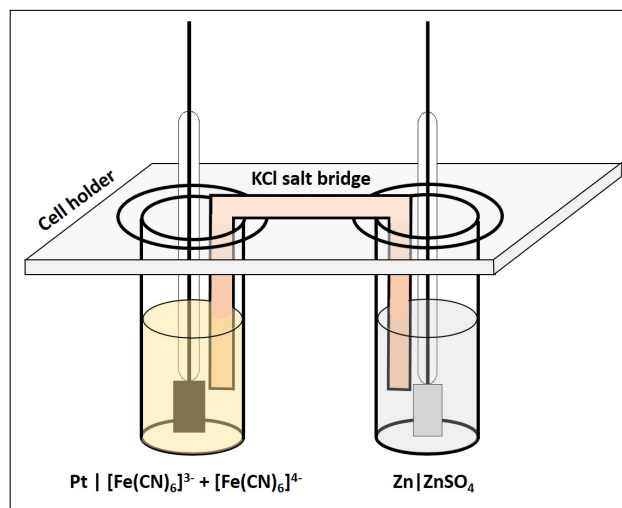


Figure 2: The reaction as an electrochemical process.

pressure-volume) work (w_{\max}) can be given as the derivative of the Gibbs energy with respect to the reaction coordinate (ξ). By definition, the reaction coordinate is

$$d\xi = \frac{dn_i}{\nu_i}, \quad (1)$$

where dn_i is the change in the amount of substance of the i -th component and ν_i is the stoichiometric coefficient of this component in the reaction equation. Based on these,

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_{i=1}^n \nu_i \cdot \mu_i, \quad (2)$$

where μ_i is the chemical potential of the component, i.e., its partial molar Gibbs energy,

$$\mu_i = \left(\frac{\partial G_i}{\partial n_i} \right)_{p,T,n_{j \neq i}}. \quad (3)$$

The chemical potential depends on the composition,

$$\mu_i = \mu_i^0 + RT \ln a_i, \quad (4)$$

where μ_i^0 is the standard chemical potential of the i -th component and a_i is the activity. Summarizing the above,

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_{i=1}^n \nu_i \cdot \mu_i = \sum_{i=1}^n \nu_i \cdot \mu_i^0 + RT \ln \prod_{i=1}^n a_i^{\nu_i} = \Delta_r G^0 + RT \ln Q, \quad (5)$$

where $\Delta_r G^0$ is the standard Gibbs energy of the reaction and Q is the reaction quotient. Apparently, the Gibbs energy of the reaction depends on the composition, and even if the standard Gibbs energy of the reaction is independent of the temperature, it can also depend on the temperature. The reaction Gibbs energy, can also be electrical work. That is, the transfer of z mol of electron ($-z \cdot F$ charge, where F is the Faraday constant or molar elementary charge) from the anode to the cathode we can assign a potential difference (cell voltage) by which we do the same work. Electrical work can be given as the product of voltage (U) and passed charge (Q_{electron}), i.e.,

$$w = U \cdot Q_{\text{electron}}. \quad (6)$$

In electrochemistry, the calculation of the maximum useful work of a chemical reaction is based on the number of electrons transferred during *one mole reaction*, i.e., when all stoichiometric number is the smallest possible integer.¹ Therefore, the unit of work $w_{r,\max}$ is J/mol just like that of reaction Gibbs energy. Accordingly,

$$\Delta_r G = w_{r,\max} = -z \cdot F \cdot E_{\text{cell}}, \quad (7)$$

where E_{cell} is the maximal potential difference that can develop in the cell. This is the so-called cell reaction potential (in American literature it is often denoted as E_{rxn}). The theoretically defined cell reaction potential and the practically measurable cell voltage (potential difference between the cathode and the anode) can differ from each other for several reasons. If we ensure that no current flows through the cell during the measurement, and the two half-cells are in equilibrium for charge transfer and all other chemical processes, and no other potential difference develops between the half-cells, then the measurable maximum cell voltage (electromotive force, E_{MF}) is equal to the cell reaction potential. Thus,

$$\Delta_r G = -z \cdot F \cdot E_{\text{MF}} \quad (8)$$

¹Formation reactions are exceptions because in these cases one mole reaction means the production of 1 mol product from elements. Therefore, the stoichiometric number of the reactants is not necessarily an integer, e.g., $\frac{1}{2}\text{H}_{2(\text{g})} + \frac{1}{2}\text{Cl}_{2(\text{g})} \longrightarrow \text{HCl}_{(\text{g})}$.

The Gibbs energy of the reaction can be easily calculated from the measured electromotive force. The temperature coefficient of Gibbs energy at constant pressure is

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, \quad (9)$$

where S is the entropy. Because this is true for all components,

$$\left(\frac{\partial \Delta_r G}{\partial T}\right)_p = -\Delta_r S, \quad (10)$$

where $\Delta_r S$ is the entropy of the reaction. The entropy of the reaction can thus be given as the temperature partial derivative of the Gibbs energy of the reaction. At any temperature it is true that

$$\Delta_r G = \Delta_r H - T \cdot \Delta_r S, \quad (11)$$

where $\Delta_r H$ is the enthalpy of the reaction. In this expression, the product $T \cdot \Delta_r S$ is the part of the enthalpy change of one mole reaction that cannot be used for work (*may be called the bound enthalpy*), that is, the heat of the reaction (q_r). If the reaction is carried out in such a way that there is no useful work (as it is the case in Fig. 1), this equals to the reaction enthalpy ($\Delta_r H$). Due to the relationship between Gibbs energy and electromotive force,

$$\Delta_r G = -z \cdot F \cdot E_{MF}, \quad (12)$$

$$\Delta_r S = z \cdot F \cdot \frac{dE_{MF}}{dT} \quad (13)$$

$$\Delta_r H = -z \cdot F \cdot E_{MF} + z \cdot F \cdot T \cdot \frac{dE_{MF}}{dT} \quad (14)$$

$$q_r = z \cdot F \cdot T \cdot \frac{dE_{MF}}{dT}. \quad (15)$$

Thus, the thermodynamic parameters of the reaction can be determined from the temperature dependence of E_{MF} . Notice the “trick”: parameters can be determined without a reaction occurring. During the experiments, electromotive force is measured, no current flows in the system, i.e., there is no change, no reaction. We only measure the possibility (potential) of the reaction!

Also observe, that the Gibbs energy of the reaction expressed by eq. (5) (i.e., the maximum useful work under isothermal, isobaric, and reversible conditions) arises from the difference between the equilibrium (*final*) state of the system and that described by the reaction quotient (non-equilibrium, initial state) at the given temperature, since

$$\Delta_r G = -RT \ln K - (-RT \ln Q) = \Delta_r G^0 + RT \ln Q, \quad (16)$$

where K is the equilibrium constant at the given temperature.

2 Experimental

For the measurements assemble the cell as illustrated in Figs. 2–3.

The anodic solution is $c_{\text{anode}} \text{ZnSO}_4$, and the solution of the cathodic half-cell should contain c_1 of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and c_2 of $\text{K}_4[\text{Fe}(\text{CN})_6]$, respectively. 50 cm^3 should be prepared from both solution, and the actual concentration will be given by the instructor in the range of $c_{\text{anode}} = 0.1 - 0.4 \text{ M}$, $c_1 = 0.01 - 0.05 \text{ M}$ and $c_2 = 0.01 - 0.05 \text{ M}$. *If it is not specified otherwise*, $c_{\text{anode}} = 0.2 \text{ M}$, $c_1 = 0.03 \text{ M}$, and $c_2 = 0.02 \text{ M}$. To control the temperature, place the cell in a thermostat. Also put a thermometer in one of the half cells, because it is not the thermostat but the cell temperature that you need to know exactly. Connect the electrodes to a high input resistance voltmeter. Measure the cell voltage from 15°C to 50°C , raising the thermostat temperature in increments of 2°C . If the thermostat is not appropriate for cooling, add ice into the water bath. Make sure that the voltage is only read when the thermal equilibrium has been reached. Thermal equilibrium can be established faster by gently stirring the solutions in the half-cells with a glass rod (using separate glass rods).

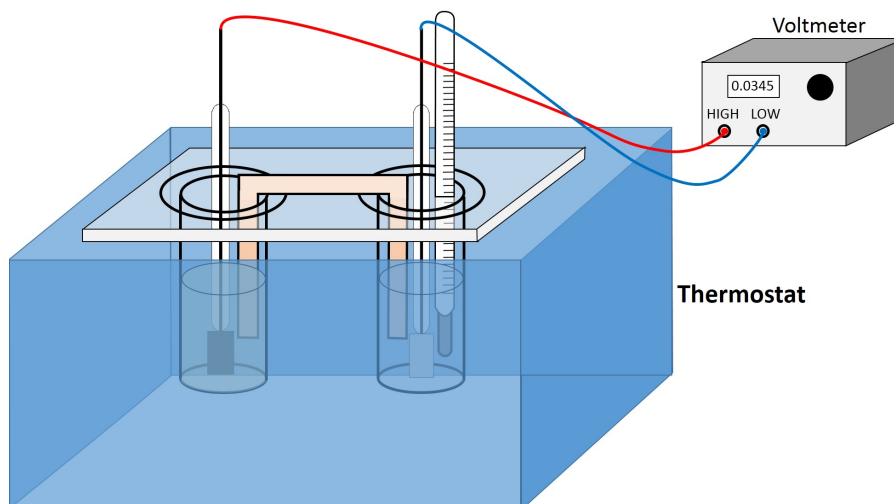


Figure 3: Schematic of the apparatus used for the measurements.

3 Evaluation

- The measured data and the calculations should be summarized according to Table 1.

Table 1: Measured and calculated values.

$$c_{\text{anód}} = \dots M, \quad c_1 = \dots M, \quad c_2 = \dots M$$

t (°C)	T (K)	E_{MF} (V)	$\frac{dE_{\text{MF}}}{dT}$ (V/K)	$\Delta_r G$ (kJ/mol)	$\Delta_r S$ (kJ/(K mol))	$\Delta_r H$ (kJ/mol)	q (kJ/mol)	η (%)

- To obtain $\frac{dE_{\text{MF}}}{dT}$ values, calculate the derivatives (numerically) for the function $E_{\text{MF}} - T$ (see Fig. 4). Be aware that one incorrect measurement affects several calculated values during numerical derivation. If $\frac{dE_{\text{MF}}}{dT}$ can be taken as constant within the given temperature range, i.e., if the average of $\frac{dE_{\text{MF}}}{dT}$ values agrees within experimental error (i.e., standard deviation) with the slope of the linear fitted through the $E_{\text{MF}} - T$ data, then use this value for further calculations otherwise use the separate values. See Appendix for the determination of the standard deviation of the slope.
- According to Eqs. (12)–(15) determine the thermodynamic parameters at each temperature.
- For each temperature, calculate what percentage (η) of the energy potentially released by the reaction can be taken as useful work, i.e., what is the proportion of the maximum useful work and the reaction enthalpy? Plot $\eta - T$ function and explain the observations in a few sentence.
- Plot the $\Delta_r G - T$, $\Delta_r S - T$, $\Delta_r H - T$ and $q_r - T$ functions.
- Interpret the change and possible constancy of the parameters with the help of previous studies on thermodynamics. Although the chemical reaction practically does not take place during the measurement, the temperature dependence of E_{MF} is related to what would happen if it was indeed taking place. Therefore, during the interpretation, consider what could happen in the separate half cells on a molecular scale (e.g., dissolution of metal sheet, formation of hydration sphere, change of oxidation state of complex, etc.), and how strongly these processes depend on temperature (even recall equation from previous studies). Finally, also consider which of them could be potentially dominant for the determination of reaction enthalpy and reaction entropy.

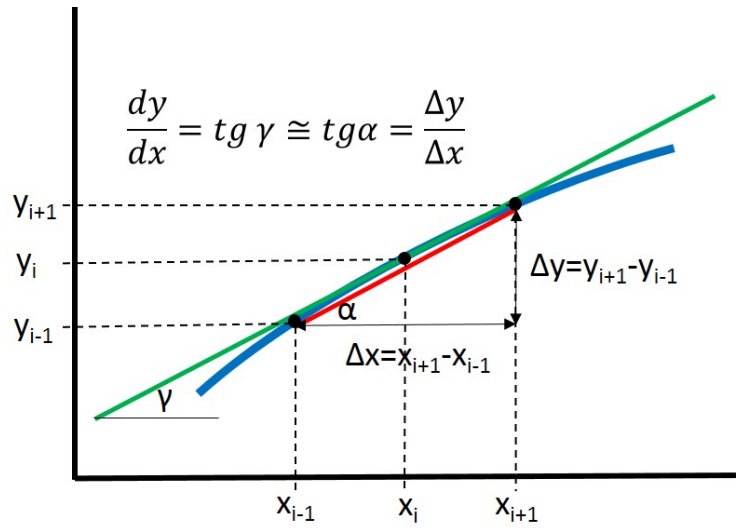


Figure 4: Three-point numerical differentiation: Use two neighbors to find the derivative at a given point (x_i).

Questions

1. What reaction will you study and what parameters of the reaction should be determined?
 2. Draw a schematic of the electrochemical cell to be used.
 3. What kind of electrodes are the distinct half-cells? Prove your statement.
 4. Give the relationship between the free enthalpy of the reaction and the measurable maximal cell voltage.
 5. Give the definition equation for the free enthalpy of the reaction.
 6. Derive the entropy of the reaction using the free enthalpy of the reaction or the electromotive force.
 7. Derive the enthalpy of reaction by the electromotive force.
 8. Derive the reaction heat by the electromotive force.
 9. A solution to be prepared must be 0.03 M for $[\text{Fe}(\text{CN})_6]^{3-}$ and 0.02 M for $[\text{Fe}(\text{CN})_6]^{4-}$. How do you make 100 cm³ of this solution?
 $M_r(\text{K}_3[\text{Fe}(\text{CN})_6]) = 329.27$ and $M_r(\text{K}_4[\text{Fe}(\text{CN})_6] \times 3\text{H}_2\text{O}) = 422.43$.
 10. At 34.5 °C, E_{MF} is 1.1956 V. What is the maximal electric work of the reaction tested at this temperature?
 11. Upon investigating the temperature dependence of E_{MF} we obtained the data summarized in the table below. By applying numerical differentiation, calculate the slope of the $E_{\text{MF}}-T$ function (where T stands for absolute temperature) a) either for the first or for the last point of the data set (two-point formula), and b) for an arbitrarily selected temperature excluding the two above (three-point formula).
- | | | | | | | | | | |
|--------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| t/°C | 21.4 | 23.2 | 25.3 | 27.3 | 29.2 | 31.1 | 33.0 | 34.8 | 36.7 |
| E_{MF}/V | 1.2526 | 1.2479 | 1.2437 | 1.2394 | 1.2360 | 1.2317 | 1.2274 | 1.2235 | 1.2194 |
12. At 32 °C, $E_{\text{MF}} = 1.1956 \text{ V}$, at 34 °C, $E_{\text{MF}} = 1.1931 \text{ V}$ and at 36 °C, $E_{\text{MF}} = 1.1906 \text{ V}$. Calculate $\Delta_r G$, $\Delta_r S$, $\Delta_r H$, and q_r at 34 °C.