

# Determining thermodynamic parameters of a reaction by electrochemical measurements

Theoretical background: Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods*, Ch. 2.

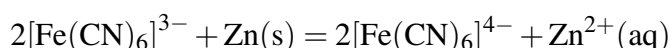
(Novák Mihály, Szűcs Árpád, *Elektrokémia*, Ch. 9 (Hungarian))

Type of the practice: individual

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

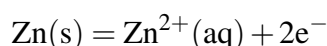
## 1 Introduction

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

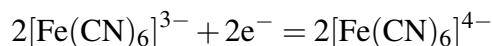


You will determine the Gibbs energy ( $\Delta G_r$ ), the entropy ( $\Delta S_r$ ), the enthalpy ( $\Delta H_r$ ), and the heat of the reaction ( $q$ ) as the function of temperature.

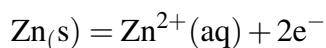
The simplest way to carry out the above reaction is to put a piece of zinc into hexacyanoferrate(III) solution (Fig. 1). Then the oxidation half reaction is



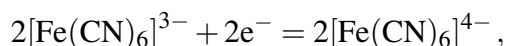
and the reduction half reaction is



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) is



while the reduction half reaction (cathodic process) is



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 ensures the electric connection between the two electrolyte solutions without mixing them, and 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.  $\text{K}^+$  and  $\text{Cl}^-$  ions have about the same electric mobility (diffusion coefficient).

Gibbs energy (earlier it was called free enthalpy, Gibbs free energy) change during the reaction ( $\Delta G_r$ ), shortly reaction Gibbs energy (i.e., energy change in isothermal, isobaric, reversible conditions without a

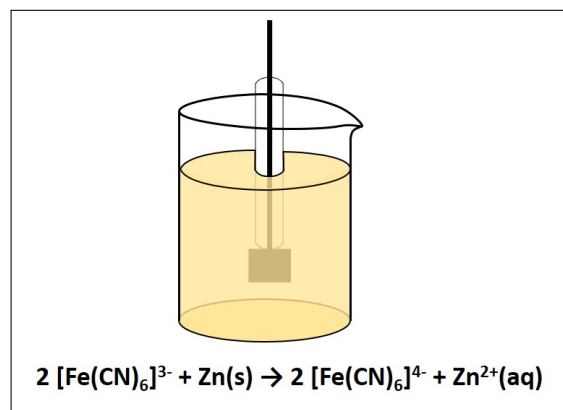


Figure 1: The reaction as a "simple" heterogeneous redox process.

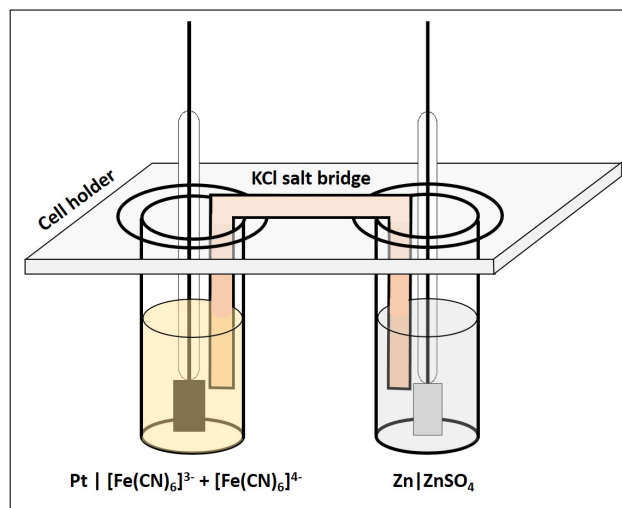


Figure 2: The reaction as an electrochemical process.

change in composition so that the amount of substances corresponding to the stoichiometric numbers in the equation reacts), i.e., the maximal useful (nonmechanical pressure-volume) work ( $w_{\max}$ ) can be given as the derivative of the Gibbs energy with respect to the reaction coordinate ( $\xi$ ). By definition, the reaction coordinate is

$$d\xi = \frac{dn_i}{\nu_i}$$

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

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

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

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

The chemical potential depends on the composition,

$$\mu_i = \mu_i^0 + RT \ln a_i$$

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

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

where  $\Delta G_r^0$  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 ( $Q_{\text{electron}}$ ), i.e.,

$$w = U \cdot Q_{\text{electron}}$$

Accordingly,

$$\Delta G_r = w_{\max} = -z \cdot F \cdot E_{\text{cell}}$$

where  $E_{\text{cell}}$  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  $E_{\text{rxn}}$ ). 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,  $E_{\text{MF}}$ ) is equal to the cell reaction potential. Thus,

$$\Delta G_r = -z \cdot F \cdot E_{\text{MF}}$$

The Gibbs energy of the reaction can be easily calculated from the measured electromotive force. The temperature coefficient of Gibbs energy (at constant pressure, if there is no work done when the temperature changes) is

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

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

$$\left( \frac{\partial \Delta G_r}{\partial T} \right)_p = -\Delta S_r$$

where  $\Delta S_r$  is the entropy of the reaction. The entropy of the reaction can thus be given as the temperature (partial) derivative of the free enthalpy of the reaction. At any temperature it is true that

$$\Delta G_r = \Delta H_r - T \cdot \Delta S_r$$

where  $\Delta H_r$  is the enthalpy of the reaction. In this expression, the product  $T \cdot \Delta S_r$  is the part of the enthalpy change (*may be called the bound enthalpy or the isothermally unavailable enthalpy*) that cannot be used for work, that is, the heat of reaction ( $q$ ). Due to the relationship between free enthalpy and electromotive force,

$$\Delta G_r = -z \cdot F \cdot E_{MF}, \quad (1)$$

$$\Delta S_r = z \cdot F \cdot \frac{dE_{MF}}{dT} \quad (2)$$

$$\Delta H_r = -z \cdot F \cdot E_{MF} + z \cdot F \cdot T \cdot \frac{dE_{MF}}{dT} \quad (3)$$

$$q = z \cdot F \cdot T \cdot \frac{dE_{MF}}{dT} \quad (4)$$

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!

## 2 Experimental

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

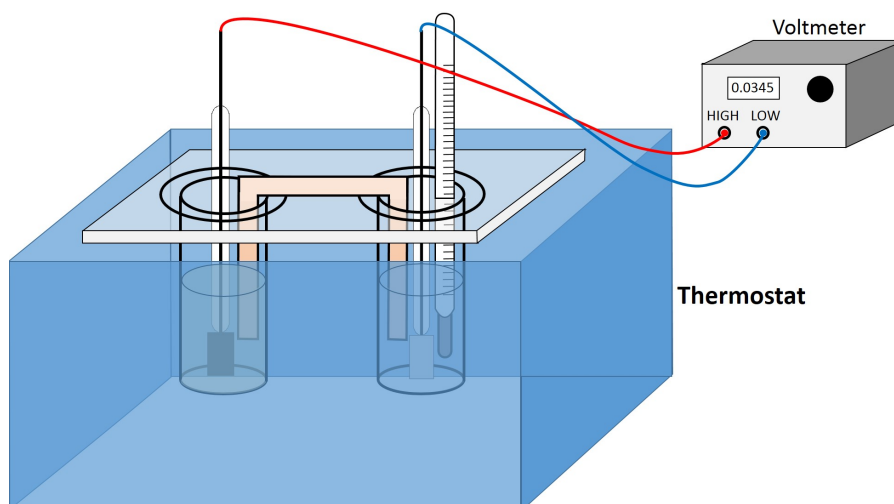


Figure 3: Schematic of the apparatus used for the measurements.

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.  $100 \text{ cm}^3$  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 M and  $c_2 = 0.01 - 0.05$  M. If it is not specified otherwise,  $c_{\text{anode}} = 0.2$  M,  $c_1 = 0.03$  M, and  $c_2 = 0.02$  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 5 °C to 45 °C, raising the thermostat temperature in increments of 2 °C. 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).

### 3 Evaluation

- The measured data and the calculations should be summarized according to Table 1.
- To obtain  $\frac{dE_{\text{MF}}}{dT}$  values, calculate the derivatives (numerically) for the function  $E_{\text{MF}} - T$  (see Fig. 4).
- According to EqS. 1–4, determine the thermodynamic parameters at each temperature.
- Plot the  $E_{\text{MF}} - T$ ,  $\Delta G_r - T$ ,  $\Delta S_r - T$ ,  $\Delta H_r - T$  and  $q - T$  functions.
- Interpret the change and possible constancy of the parameters.

Table 1: Measured and calculated values.

| $c_{\text{anode}} = \dots\dots \text{M}, \quad c_1 = \dots \text{M}, \quad c_2 = \dots \text{M}$ |         |                     |                           |                       |                           |                       |              |
|--------------------------------------------------------------------------------------------------|---------|---------------------|---------------------------|-----------------------|---------------------------|-----------------------|--------------|
| $t$ (°C)                                                                                         | $T$ (K) | $E_{\text{MF}}$ (V) | $dE_{\text{MF}}/dT$ (V/K) | $\Delta G_r$ (kJ/mol) | $\Delta S_r$ (kJ/(K mol)) | $\Delta H_r$ (kJ/mol) | $q$ (kJ/mol) |
|                                                                                                  |         |                     |                           |                       |                           |                       |              |

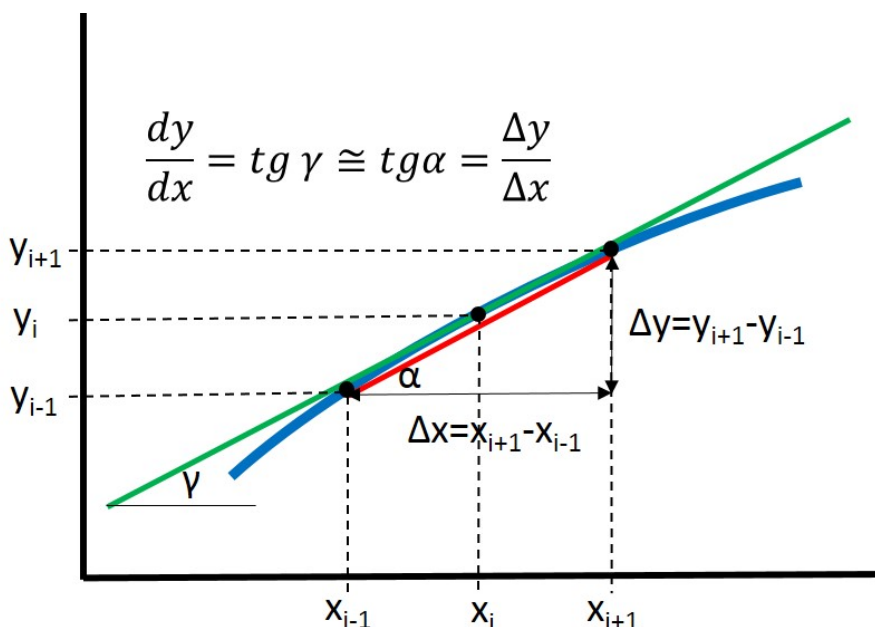


Figure 4: Numerical differentiation.

## Control 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. Give the relationship between the free enthalpy of the reaction and the measurable maximal cell voltage.
4. Give the definition equation for the free enthalpy of the reaction.
5. Derive the entropy of the reaction using the free enthalpy of the reaction or the electromotive force.
6. Derive the enthalpy of reaction by the electromotive force.
7. Derive the reaction heat by the electromotive force.
8. 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 cm<sup>3</sup> of this solution?  
 $M_r(\text{K}_3[\text{Fe}(\text{CN})_6]) = 329.27$  and  $M_r(\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}) = 422.43$ .
9. At 34.5 °C,  $E_{\text{MF}}$  is 1.1956 V. What is the maximal electric work of the reaction tested at this temperature?
10. At 32 °C,  $E_{\text{MF}} = 1.1956$  V, at 34 °C,  $E_{\text{MF}} = 1.1931$  V and at 36 °C,  $E_{\text{MF}} = 1.1906$  V. Calculate  $\Delta G_r$ ,  $\Delta S_r$ ,  $\Delta H_r$ , and  $q$  at 34 °C.