

3. Thermochemical measurement

3.a. Excerpt from Chapter 3a



The total amount of the released heat Q during reaction in the calorimeter is determined by the temperature rise in the calorimeter according to the formula:

$$Q = C \cdot \Delta T = -\Delta H \quad (3.1.)$$

where ΔT is the temperature rise during neutralization, C is the heat capacity of the calorimeter, which indicates the amount of heat required to heat the calorimetric vessel with its content of 1°C . In the case of an aqueous solution experiment, the C constant depends mainly on the amount of water ($c_{\text{H}_2\text{O}}^p(25^\circ\text{C}, 1\text{Atm}) = 4,1796 \text{ J K}^{-1} \text{ kg}^{-1}$).

We calibrate the heat capacity of the calorimeter C by measuring the temperature rise $\Delta T'$ in the calorimeter after releasing heat Q_E , which is produced by the passage of the current I through the electrical resistor immersed in the calorimeter filling. The heat capacity is given by eqn

$$C = \frac{Q_E}{\Delta T'} = \frac{E \cdot I \cdot t}{\Delta T'} \quad (3.2.)$$

where E is the voltage at the resistance heater terminals and t is the flow time of the electric current I .

3.b. Determination of thermodynamic functions of galvanic cell



Chemical reactions associated with electron transfer can be realized in electrochemical cells. For example reaction:



where equilibrium is shifted to the benefit of substances on the right side of the equation, can be done in the so-called Daniel's cell:



The cell potential of the Daniel's cell is standard cell potential $\Delta E^0 = 1,097 \text{ V}$ if the pressure is 1Atm , $t=25^\circ\text{C}$, and the cationic activities Cu^{+2} a Zn^{+2} are equal to "1". The cation activities usually differ from "standard" conditions, then the cell gives electromotive voltage:

$$\Delta E = \Delta E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Cu}^{2+}}}{a_{\text{Zn}^{2+}}} \quad (3.5.)$$

where R is the universal gas constant, T is the temperature in Kelvin, n is the number of electrons transferred in the overall cell reaction (3.3), $F=96485 \text{ C/mol}$ is the Faraday constant and a_i is the activity of cation i .

The activities of the Cu^{+2} and Zn^{+2} cations can be calculated according to the relation $a_i = c_i \gamma_i^\pm$. The tabulated mean ion activity coefficients are $\gamma_{\text{Cu}^{2+}}^\pm = 0,154$ and $\gamma_{\text{Zn}^{2+}}^\pm = 0,150$ for the cationic concentrations of $0,1\text{M}$ (see cell note (3.4.)).

Electrical work W_e usable from a galvanic cell of voltage ΔE is equal to the change in the molar Gibbs energy ΔG that accompanies the electrochemical processes in the cell:

$$W_e = -\Delta G = nF\Delta E \quad (3.6.)$$

If the article provides a standard electromotive voltage ΔE^0 , then this relationship applies:

$$-\Delta G^0 = nF\Delta E^0 \quad (3.7.)$$

where $-\Delta G^0$ is standard change of molar reaction Gibbs energy (3.3.), which is related to the equilibrium thermodynamic constant K of the reaction (3.3) as follows:

$$\ln K = \frac{nF \cdot \Delta E^0}{RT} = \frac{-\Delta G^0}{RT} \quad (3.8.)$$

Changes in both the molar enthalpy ΔH and the molar entropy ΔS of the reaction in the cell are linked to the change in molar Gibbs energy ΔG by:

$$\Delta G = \Delta H - T\Delta S \quad (3.9.)$$

The enthalpy change ΔH can be experimentally determined, for example from the thermal effect of the reaction (3.3) in the calorimeter. The reaction entropy change in the galvanic cells is given by relation:

$$\Delta S = -\left(\frac{\delta \Delta G}{\delta T}\right)_p \quad (3.10.)$$

Considering the expression (3.6.), we can make an adjustment and to obtain:

$$\Delta S = nF \cdot \left(\frac{\delta \Delta E}{\delta T}\right)_p \quad (3.11.)$$

This relationship can be used to theoretically calculate the change in the molar entropy of the reaction in the cell if we evaluate its dependence on temperature (ie, the sensitivity of voltage ΔE to change of T).

The voltage sensitivity to the temperature for the Daniel cell under standard pressure has a table value:

$$\left(\frac{\delta \Delta E}{\delta T}\right)_p = -4,29 \cdot 10^{-4} \text{ V / K} \quad (3.12.)$$

? **TASK:** Determine the change of the thermodynamic functions and the equilibrium constant K for the Daniel cell using the calorimetric and potentiometric measurements of the reaction inside. Compare the theoretical and experimental values of the reaction entropy (eqns (3.11.) and (3.12.)).



LABORATORY AIDS AND CHEMICALS: zinc and copper electrodes, salt bridge, 2 beakers (150 ml), millivolt meter, calorimeter with accessories according to exercise 3a, powder zinc, weighting bottle (25 g), pipettes (25 a 50 ml), graduated cylinder (100 ml), spoon, 0,1M $ZnSO_4$, 0,1M $CuSO_4$, saturated KCl .



INSTRUCTIONS: The aim is to obtain a change in the molar reaction enthalpy by calorimetric experiment at room temperature and to determine the standard reaction Gibbs energy of the same reaction that occurs in Daniel's cell.

- 1. Calorimetric measurement.** Proceed similarly to the neutralization heat experiment according to exercise **3a** with the following differences: pipette $50\text{ ml } 0,1\text{ M CuSO}_4$ into the calorimeter vessel and dilute with 150 ml of water. Insert the cup holder for powder zinc into the calorimeter stopper instead of the dosing capillary. Put an over-stoichiometric amount (about 3 g) of powdered zinc to the cup. Close the vessel with the stopper and make sure that the cup involving zinc powder is placed above the solution and that no zinc fell in solution. The recommended times of temperature data collection are: initial relaxation $5\text{-}7\text{ min}$, after inserting all zinc in the solution stir gently few times with the cup holder, and collect temperature data for 10 min . Switch on the heater element for a time sufficient to increase the temperature by approx. $0,7^\circ\text{C}$. Write down the exact time you switch on and off the heating element on your computer monitor! Watch the final thermal relaxation for about 10 minutes. In this way, we get finally a record similar to the dependency on **FIGURE 2, EXERCISE 3.A.** Visually inspect the course of the reaction (discoloration of the solution) after the experiment. Empty the calorimeter vessel and rinse it with distilled water.
- 2. MEASUREMENT OF CELL VOLTAGE.** Clean the electrodes with emery paper and rinse them. Assemble Daniel's cell according to the record (3.4.) and measure its voltage using a millivolt meter. Check the voltage after 5 min .



REPORT: Graph 1: the time dependent record of the temperature inside the calorimeter. **NEXT:** Daniel's cell voltage, electric current and voltage on heating element used in eqn (3.2.), thermal capacity of the calorimeter C , enthalpy change ΔH , molar amount of substance Cu_{2+} reacted in calorimeter vessel, change of molar enthalpy, cell temperature, electromotive voltage ΔE and standard cell potential ΔE_0 , changes in molar Gibbs energy: ΔG a ΔG_0 , equilibrium reaction constant K . Comparison of the value ΔS calculated according to eqn (3.9.) with the theoretical value calculated from the temperature coefficient (eqns (3.11.), (3.12.)).