TEMPERATURE DEPENDENCE OF THE EQUILIBRIUM CONSTANT

INTRODUCTION

For reversible reactions:

$$aA + bB \rightleftarrows cC + dD \tag{1}$$

the ratio of the quotient of the concentrations of products and substrates, once equilibrium has been reached, is a constant value and is called the equilibrium constant:

$$K = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} \tag{2}$$

The dependence of the equilibrium constant of a reaction *K* on the temperature is described by the ***van't Hoff equation:***

$$\left(\frac{\delta \ln K}{\delta T}\right)_p = \frac{\Delta H^0}{RT^2} \tag{3}$$

The integration of equation (3) leads to equation (4):

$$logK = \frac{-\Delta H^o}{2{,}303\ RT} + const. \tag{4}$$

From equation (4) a linear dependence of the logarithm of the reaction equilibrium constant on the inverse of the temperature is obtained.

The above indications apply to all chemical reactions, including the dissolution reactions investigated in this exercise.

In the case of a dissolution reaction in a saturated solution, the equilibrium constant can be replaced by the *solubility product* $\boldsymbol{K_{sp}}$.

For the dissolution reaction:

$$AB \rightleftarrows A^+ + B^- \tag{5}$$

the equilibrium constant is:

$$K = \frac{[A^+][B^-]}{[AB]} \tag{6}$$

Due to the fact that the concentration of the undissolved part [AB] is higher than the concentration of the dissolved salt, it can be treated as a constant value [AB] = const. This value can be included in the equilibrium constant of the reaction:

$$K \cdot [AB] = [A^+][B^-] \tag{7}$$

OBJECTIVE OF THE EXERCISE

The aim of this exercise is to analyze the dependence of the equilibrium constant in the salt dissolution reaction:

$$CaCO_3 \Leftrightarrow Ca_{aq}^{+2} + CO_{3aq}^{-2} \quad (8)$$

or

$$BaCO_3 \Leftrightarrow Ba_{aq}^{+2} + CO_{3aq}^{-2} \quad (9)$$

i.e. the reaction of dissolving calcium (or barium) carbonate in aqueous solution.

LABORATORY EQUIPMENT, LABORATORY GLASSWARE

1. Thermostat.
2. Conductometer CC 551.
3. Thermostatic reaction vessel.
4. Magnetic stirrer.
5. Beakers 100 cm^3 - 2 pieces.
6. Volumetric flask 100 cm^3.
7. Pincete.

CHEMICALS

1. Calcium carbonate $CaCO_3$ (solid).
2. Barium carbonate $BaCO_3$ (solid).

EXPERIMENT PROCEDURES

1. Pour approx. 2 g salt indicated by the instructor into a 100 cm^3 flask. Fill up with distilled water. Shake for 5 minutes. Then put it aside.

2. Measure the values of conductivity of distilled water at the following temperatures: 25, 35, 45, 55, 65 and 75 $^{\circ}C$.

3. The solution should be stirred during temperature adjustment.

4. Measure the conductivity of the solution of the salt to be tested at the temperatures indicated for water.

The specific conductivity is indicated by the letter κ (kappa).

ATTENTION! Immediately after mixing, transfer the solution with the sediment to the thermostatic vessel!

CALCULATIONS:

1. To eliminate the contribution of the conductivity associated with the solvent (water), the value of the conductivity κ_s of the water (for each temperature measured) should be subtracted from the value of the measured conductivity κ_{aq} of the salt solution.

$$\kappa_s = \kappa - \kappa_{aq} \quad (9)$$

2. Calculate the ion concentrations in solution C_+ or C_- from the recorded conductivity values κ_s based on equation (10):

$$\kappa_s = F(\nu_+ + \nu_-)\alpha\, z\, C \quad (10)$$

Knowing that in the case of the salts tested:

$$C_+ = C_- = C \quad (11)$$

where:
C_+ - cation concentration,
C_- - anion concentration,
C - concentration of solution,
F - Faraday constant,
ν_+ - cation mobility,
ν_- - anion mobility,
α - stoichiometric coefficient in the chemical equation,
z - ionic valence.

The mobility values of the individual ions are as follows:

Ca^{2+} = 5,3 · 10^{-8} [$m^2s^{-1}V^{-1}$]

Ba^{2+} = 5,7 · 10^{-8} [$m^2s^{-1}V^{-1}$]

CO_3^{2-} = 7,2 · 10^{-8} [$m^2s^{-1}V^{-1}$]

3. Calculate the product of salt solubility K_{sp} at given temperatures from the determined values of anion and cation concentrations.

$$K_{sp} = C_+ \cdot C_- = C^2 \quad (12)$$

4. Plot the graph of the dependence $logK_{sp} = f(T^{-1})$. Use linear regression to find the coefficients describing this dependence.
5. Determine the standard enthalpy of the reaction (from the equation (4)) (remember that in a saturated solution the equilibrium constant can be replaced by the concept of *solubility product* K_{sp}).

ATTENTION!

The CC-551 conductometer is equipped with a probe of known conductivity coefficient, so the values obtained are specific conductance values and are expressed in S/cm.

Template of the table and draft of the study

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

…………………………….. *Wydział* ……………………………….. *Kierunek* *Studia stacjonarne/niestacjonarne*	……………………………………………… *Imię i Nazwisko studenta*	……………………………………... *Data wykonywania ćwiczenia:*
Nr grupy: …………………... *Nr zespołu:* …………………..	………..…………… *Nr ćwiczenia:*	……………………………………. *Nazwisko Prowadzącego:*

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: