9. HETEROGENEOUS IONIC EQUILIBRIA

$$C_{\nu_C}A_{\nu_A} = \nu_C\, C^{z_C} + \nu_A\, A^{z_A} \qquad \text{(C … cation, A … anion)}$$

$$a_{\pm} = (a_C^{\nu_C} \cdot a_A^{\nu_A})^{1/(\nu_C+\nu_A)}$$

$$\gamma_{\pm} = (\gamma_C^{\nu_C} \cdot \gamma_A^{\nu_A})^{1/(\nu_C+\nu_A)}$$

$$K_S = \gamma_{\pm}^{(\nu_C+\nu_A)} \cdot (\nu_C^{\nu_C} \cdot \nu_A^{\nu_A}) \cdot \left(\frac{c}{c^{st}}\right)^{(\nu_C+\nu_A)}$$

$I < 0.001$ mol dm^{-3}: $\quad \ln\gamma_{\pm} = -z_C \cdot z_A \cdot A \cdot \sqrt{I} \quad , \quad I = \frac{1}{2}\sum_i (c_i \cdot z_i^2)$

$I < 0.1$ mol mol^{-3} $\quad \ln\gamma_{\pm} = -\dfrac{z_C \cdot z_A \cdot A \cdot \sqrt{I}}{1 + a \cdot \sqrt{I}} \quad , \quad a \approx 1$ mol$^{-1/2}$ dm$^{3/2}$

Problem 9-01 Heterogeneous ionic equilibria

The solubility product of silver chloride at 20 °C has the value of $1.26 \cdot 10^{-10}$ and that of calcium fluoride at the same temperature is $3.4 \cdot 10^{-11}$ (both for the standard state of infinite dilution, c^{st} = 1 mol dm^{-3}). Which of the previously mentioned substances is more soluble in water? Suppose that activities can be put equal to concentration.

[$c_{AgCl} = 1.122 \cdot 10^{-5}$ mol dm^{-3}, $c_{CaF2} = 2.041 \cdot 10^{-4}$ mol dm^{-3}]

Problem 9-02 Heterogeneous ionic equilibria – mean activity coefficient

The concentration of the saturated solution at 20 °C was found to be $2.45 \cdot 10^{-4}$ mol dm^{-3}. Calculate the mean activity coefficient of CaF_2 in the saturated solution. Compare the result with the previous problem and find out if the assumption, that the mean activity coefficient is equal to one, made there, was justified.

[$\gamma_{\pm} = 0.833 \neq 1$; the assumption was not justified]

Problem 9-03 Heterogeneous ionic equilibria – solubility of sparingly soluble salts

The solubility product of lanthanum oxalate (standard state of infinite dilution, c^{st} = 1 mol dm^{-3}) at 25 °C is $2 \cdot 10^{-28}$. Lanthanum oxalate precipitate was four times decanted always with 50 cm^3 of distilled water (it is supposed that each time the equilibrium between the solid phase and the solution was established). Calculate total weight loss of the precipitate. Assume that the mean activity coefficient is equal to one. $M_{La_2(C_2O_4)_3}$ = 541.9 g mol^{-1}.

[$\Delta m = 1.226 \cdot 10^{-4}$ g]

Problem 9-04 Heterogeneous ionic equilibria – solubility product, mean activity coefficient, Debye-Hückel equation

In 1300 cm^3 of saturated lead iodide solution at 26 °C was found 0.905 g of PbI_2 (M = 461 g mol^{-1}). Calculate the solubility product of lead iodide (standard state of infinite dilution, c^{st} = 1 mol dm^{-3}). To determine the mean activity coefficient use the Debye-Hückel relation (A = 1.175 dm$^{3/2}$ mol$^{-1/2}$).

[$K_S = 8.84 \cdot 10^{-9}$]

Problem 9-05 Heterogeneous ionic equilibria – precipitation from solution

Acid mine water contains 0.001 mol Fe^{3+}/dm^3. Determine the pH at which begins the precipitation of $Fe(OH)_3$. The solubility product of $Fe(OH)_3$ at the temperature of 18 °C is $3.8 \cdot 10^{-38}$, the ionic product of water $5.78 \cdot 10^{-15}$ (both for the standard state of infinite dilution, c^{st} = 1 mol dm^{-3}). Assume that activities can be replaced by relative concentrations.

[pH = 2.8]

Problem 9-06 Heterogeneous ionic equilibria – solubility in the presence of other ions

The solubility product of lead chloride at 25 °C has the value of $2 \cdot 10^{-5}$ (standard state of infinite dilution, c^{st} = 1 mol dm^{-3}). Calculate the solubility of $PbCl_2$ in pure water and compare it with its solubility in NaCl solution (0.1 mol dm^{-3}).

[solubility in water: 0.017 mol dm^{-3}, solubility in NaCl is by one order lower, 0.002 mol dm^{-3}]

Problem 9-07 Heterogeneous ionic equilibria – solubility in the presence of other ions

5 grams of silver molybdate was stirred in 500 cm^3

(a) of distilled water,

(b) of silver nitrate solution with concentration of 0.02 mol dm^{-3}

(c) of sodium molybdate with concentration of 0.02 mol dm^{-3}

Calculate what percentage of the original amount of Ag_2MoO_4 will be dissolved in each experiment. The solubility product of Ag_2MoO_4 (standard state of infinite dilution, c^{st} = 1 mol dm^{-3}) has the value of $3.1 \cdot 10^{-11}$. Assume that activities can be replaced by relative concentrations.

[(a) 0.744 % , (b) 0.0029 % , (c) 0.074 %]