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 $3.1\cdot10^{-11}$. Assume that activities can be replaced by relative concentrations.

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

Solution:

$K_S = 3.1\cdot10^{-11}$

$M = 375.7$ g mol^{-1}

(a) $Ag_2MoO_4\,(s) = 2\,Ag^+ + MoO_4^{2-}$

$c_0 = c_{Ag_2MoO_4}$ – solubility in pure water

$c_{Ag^+} = 2\,c_0$

$c_{MoO_4^{2-}} = c_0$

$$K_S = a^2_{Ag^+}\cdot a_{MoO_4^{2-}} = \left(\gamma_+\cdot\frac{c_{Ag^+}}{c^{st}}\right)^2\cdot\gamma_-\cdot\frac{c_{MoO_4^{2-}}}{c^{st}} = \gamma^3_\pm\cdot\left(\frac{2\,c_0}{c^{st}}\right)^2\cdot\frac{c_0}{c^{st}} = \gamma^3_\pm\cdot 4\cdot\left(\frac{c_0}{c^{st}}\right)^3$$

$\gamma_+^2\cdot\gamma_- = \gamma_\pm^3 = 1$, $c^{st} = 1$ mol dm^{-3}

$$c_0 = \left(\frac{K_S}{4}\right)^{1/3} = \left(\frac{3.1\cdot10^{-11}}{4}\right)^{1/3} = 1.98\cdot10^{-4}\ \text{mol dm}^{-3}$$

The mass of the molybdate dissolved in the volume V = 500 cm^3 of saturated solution

$\Delta m_0 = c_0\cdot V\cdot M = 1.98\cdot10^{-4}\cdot 500\cdot10^{-3}\cdot 375.7 = 0.037194$ g,

i.e. $100\cdot\dfrac{0.03719}{5}$ = 0.744 % of initial amount of 5 g

(b) In the presence of $AgNO_3$

$Ag_2MoO_4\,(s) = 2\,Ag^+ + MoO_4^{2-}$

$AgNO_3 = Ag^+ + NO_3^-$

$c_1 = c_{Ag_2MoO_4}$ .... concentration of Ag_2MoO_4 in $AgNO_3$ solution

$c_{Ag^+} = 2\,c_1 + c_{AgNO3}$

$c_{MoO_4^{2-}} = c_1$

$$K_S = c^2_{Ag^+}\cdot c_{MoO_4^{2-}} = (2\,c_1 + c_{AgNO_3})^2\cdot c_1 \doteq c^2_{AgNO_3}\cdot c_1$$

(approximately: $2\,c_1 \ll c_{AgNO3}$)

$$c_1 = \frac{K_S}{c^2_{AgNO_3}} = \frac{3.1\cdot10^{-11}}{0.02^2} = 7.75\cdot10^{-8}\ \text{mol dm}^{-3}$$ (the assumption $2\,c_1 \ll c_{AgNO3}$ was justified)

$\Delta m_1 = c_1\cdot V\cdot M = 7.75\cdot10^{-8}\cdot 500\cdot10^{-3}\cdot 375.7 = 1.45\cdot10^{-5}$ g,

i.e. $100\cdot\dfrac{1.45\cdot10^{-5}}{5}$ = 0.0029 % of initial amount of 5 g

(c) In the presence of Na_2MoO_4

$Ag_2MoO_4\,(s) = 2\,Ag^+ + MoO_4^{2-}$

$Na_2MoO_4\,(s) = 2\,Na^+ + MoO_4^{2-}$

$c_2 = c_{Ag_2MoO_4}$ .... concentration of Ag_2MoO_4 in Na_2MoO_4 solution

$c_{Ag^+} = 2\,c_2$

$c_{MoO_4{}^{2-}} = c_2$

$$K_S = c_{Ag^+}^2 \cdot c_{MoO_4^{2-}} = (2\,c_2)^2 \cdot (c_2 + c_{Na_2MoO_4}) \doteq 4\,c_2^2 \cdot c_{Na_2MoO_4}$$

(approximately: $c_2 << c_{Na_2MoO_4}$)

$$c_2 = \sqrt{\frac{K_S}{4\,c_{Na_2MoO_4}}} = \sqrt{\frac{3.1\cdot 10^{-11}}{4\cdot 0.02}} = 1.97\cdot 10^{-5}\ \text{mol dm}^{-3}$$

$\Delta m_1 = c_1 \cdot V \cdot M = 1.97 \cdot 10^{-5} \cdot 500 \cdot 10^{-3} \cdot 375.7 = 3.698\cdot 10^{-3}$ g,

i.e. $100 \cdot \dfrac{3.698\cdot 10^{-3}}{5} =$ 0.074 % of initial amount of 5 g