

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

5 grams of silver molybdate was stirred in 500 cm<sup>3</sup>

(a) of distilled water,

(b) of silver nitrate solution with concentration of 0.02 mol dm<sup>-3</sup>

(c) of sodium molybdate with concentration of 0.02 mol dm<sup>-3</sup>

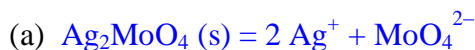
Calculate what percentage of the original amount of Ag<sub>2</sub>MoO<sub>4</sub> will be dissolved in each experiment. The solubility product of Ag<sub>2</sub>MoO<sub>4</sub> (standard state of infinite dilution,  $c^{\text{st}} = 1 \text{ mol dm}^{-3}$ ) has the value of  $3.1 \cdot 10^{-11}$ . Assume that activities can be replaced by relative concentrations.

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

**Solution:**

$$K_S = 3.1 \cdot 10^{-11}$$

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



$c_0 = c_{\text{Ag}_2\text{MoO}_4}$  – solubility in pure water

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

$$c_{\text{MoO}_4^{2-}} = c_0$$

$$K_S = a_{\text{Ag}^+}^2 \cdot a_{\text{MoO}_4^{2-}} = \left( \gamma_+ \cdot \frac{c_{\text{Ag}^+}}{c^{\text{st}}} \right)^2 \cdot \gamma_- \cdot \frac{c_{\text{MoO}_4^{2-}}}{c^{\text{st}}} = \gamma_{\pm}^3 \cdot \left( \frac{2 c_0}{c^{\text{st}}} \right)^2 \cdot \frac{c_0}{c^{\text{st}}} = \gamma_{\pm}^3 \cdot 4 \cdot \left( \frac{c_0}{c^{\text{st}}} \right)^3$$

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

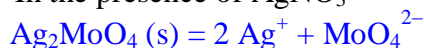
$$c_0 = \left( \frac{K_S}{4} \right)^{1/3} = \left( \frac{3.1 \cdot 10^{-11}}{4} \right)^{1/3} = 1.98 \cdot 10^{-4} \text{ mol dm}^{-3}$$

The mass of the molybdate dissolved in the volume  $V = 500 \text{ cm}^3$  of saturated solution

$$\Delta m_0 = c_0 \cdot V \cdot M = 1.98 \cdot 10^{-4} \cdot 500 \cdot 10^{-3} \cdot 375.7 = 0.037194 \text{ g},$$

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

(b) In the presence of AgNO<sub>3</sub>



$c_1 = c_{\text{Ag}_2\text{MoO}_4}$  .... concentration of Ag<sub>2</sub>MoO<sub>4</sub> in AgNO<sub>3</sub> solution

$$c_{\text{Ag}^+} = 2 c_1 + c_{\text{AgNO}_3}$$

$$c_{\text{MoO}_4^{2-}} = c_1$$

$$K_S = c_{\text{Ag}^+}^2 \cdot c_{\text{MoO}_4^{2-}} = (2 c_1 + c_{\text{AgNO}_3})^2 \cdot c_1 \doteq c_{\text{AgNO}_3}^2 \cdot c_1$$

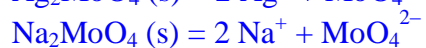
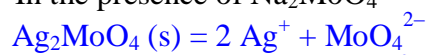
(approximately:  $2 c_1 \ll c_{\text{AgNO}_3}$ )

$$c_1 = \frac{K_S}{c_{\text{AgNO}_3}^2} = \frac{3.1 \cdot 10^{-11}}{0.02^2} = 7.75 \cdot 10^{-8} \text{ mol dm}^{-3} \text{ (the assumption } 2 c_1 \ll c_{\text{AgNO}_3} \text{ was justified)}$$

$$\Delta m_1 = c_1 \cdot V \cdot M = 7.75 \cdot 10^{-8} \cdot 500 \cdot 10^{-3} \cdot 375.7 = 1.45 \cdot 10^{-5} \text{ g},$$

$$\text{i.e. } 100 \cdot \frac{1.45 \cdot 10^{-5}}{5} = 0.0029 \% \text{ of initial amount of 5 g}$$

(c) In the presence of  $\text{Na}_2\text{MoO}_4$



$c_2 = c_{\text{Ag}_2\text{MoO}_4}$  .... concentration of  $\text{Ag}_2\text{MoO}_4$  in  $\text{Na}_2\text{MoO}_4$  solution

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

$$c_{\text{MoO}_4^{2-}} = c_2$$

$$K_S = c_{\text{Ag}^+}^2 \cdot c_{\text{MoO}_4^{2-}} = (2 c_2)^2 \cdot (c_2 + c_{\text{Na}_2\text{MoO}_4}) \doteq 4 c_2^2 \cdot c_{\text{Na}_2\text{MoO}_4}$$

(approximately:  $c_2 \ll c_{\text{Na}_2\text{MoO}_4}$ )

$$c_2 = \sqrt{\frac{K_S}{4 c_{\text{Na}_2\text{MoO}_4}}} = \sqrt{\frac{3.1 \cdot 10^{-11}}{4 \cdot 0.02}} = 1.97 \cdot 10^{-5} \text{ mol dm}^{-3}$$

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

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