PRINCIPLES OF GEOCHEMISTRY
GEOL 423
PROBLEM SET 5
FALL 2009
ANSWERS

Problem 1:

$$MgF_2(s) \leftrightarrow Mg^{2+} + 2F^- \qquad K_{SP} = 10^{-8.2}$$

Let x = number of moles of $MgF_2(s)$ dissolved. Then by stoichiometry:

$$[Mg^{2+}] = x; [F^-] = 2x$$

$$K_{SP} = [Mg^{2+}][F^-]^2$$
$$10^{-8.2} = (x)(2x)^2$$
$$4x^3 = 6.31x10^{-9}$$
$$x = 1.16x10^{-3} \text{ mol L}^{-1}$$

$$[Mg^{2+}] = 1.16x10^{-3} \text{ mol L}^{-1}; [F^-] = 2.33x10^{-3} \text{ mol L}^{-1}$$

$$\text{solubility} = (1.16x10^{-3} \text{ mol L}^{-1})(62.3018 \text{ g mol}^{-1}) = 0.0723 \text{ g L}^{-1}$$
$$= 7.23x10^{-3} \text{ g/100 mL}$$

Problem 2:

A quantity of 0.1 g of solid Na_2SO_4 in one liter of water corresponds to a concentration of

$$0.1 \text{ g L}^{-1}/(142.043 \text{ g mol}^{-1}) = 7.04\times10^{-4} \text{ mol L}^{-1}$$

Because Na_2SO_4 completely dissolves, and in so doing dissociates to 2 Na^+ and 1 SO_4^{2-}, the initial $[SO_4^{2-}] = 7.04\times10^{-4}$ mol L^{-1}.

To demonstrate that the solution is supersaturated with respect to $PbSO_4$, we need to first calculate the IAP.

$$IAP = [Pb^{2+}]_{act}[SO_4^{2-}]_{act} = (3\times10^{-2} \text{ mol L}^{-1})(7.04\times10^{-4} \text{ mol L}^{-1}) = 2.112\times10^{-5} \text{ mol}^2 \text{ L}^{-2}$$
$$\Omega = IAP/K_{SP} = (2.112\times10^{-5} \text{ mol}^2 \text{ L}^{-2})/(10^{-7.8} \text{ mol}^2 \text{ L}^{-2}) = 1.333\times10^3$$

so the solution is supersaturated greatly with respect to $PbSO_4$, and the latter should precipitate. Now we must calculate how much will precipitate.

$$[Pb^{2+}]_{act} = (3\times10^{-2} \text{ mol L}^{-1}) - x$$
$$[SO_4^{2-}]_{eq} = (7.04x10^{-4} \text{ mol L}^{-1}) - x$$

$$K_{SP} = 10^{-7.8} = [(3\times10^{-2} \text{ mol L}^{-1}) - x][(7.04\times10^{-4} \text{ mol L}^{-1}) - x]$$

Because $10^{-7.8}$ is quite small relative to 3×10^{-2} or 7.04×10^{-4}, we can neglect it and set

$$[(3\times10^{-2}\text{ mol L}^{-1}) - x][(7.04\times10^{-4}\text{ mol L}^{-1}) - x] \approx 0$$

The right hand side can be zero if either

$$[(3\times10^{-2}\text{ mol L}^{-1}) - x] = 0 \text{ or } [(7.04\times10^{-4}\text{ mol L}^{-1}) - x] = 0$$

The two roots of this equation are therefore $x \approx 3\times10^{-2}$ and $x \approx 7.04\times10^{-4}$. However, the first root is not physically realistic because it implies that more $PbSO_4$ would precipitate than the sulfate available (in other words, substituting the root $x \approx 7.04\times10^{-4}$ would make $[SO_4^{2-}]_{eq} = (7.04\times10^{-4}$ mol $L^{-1}) - (3\times10^{-2}$ mol $L^{-1}) = -2.93\times10^{-2}$, and a negative concentration makes no physical sense). In other words, sulfate is the limiting reagent here. Thus, the second root is the only realistic root so:

$$\text{mass } PbSO_4 \text{ precipitated} \approx (7.04\times10^{-4}\text{ mol})(303.264\text{ g mol}^{-1}) = 0.213\text{ g } PbSO_4$$

Problem 3:

$$PbS \leftrightarrow Pb^{2+} + S^{2-} \qquad K_{SP} = 10^{-27.5}$$
$$ZnS \leftrightarrow Zn^{2+} + S^{2-} \qquad K_{SP} = 10^{-24.7}$$

$$[Pb^{2+}] = \frac{10^{-27.5}}{[S^{2-}]}$$

$$[Zn^{2+}] = \frac{10^{-24.7}}{[S^{2-}]}$$

$$\frac{[Pb^{2+}]}{[Zn^{2+}]} = \frac{10^{-27.5}}{10^{-24.7}} = 10^{-2.80} = 1.58\times10^{-3}$$

$$\frac{[Zn^{2+}]}{[Pb^{2+}]} = 631$$

Problem 4:

We must first calculate what the equilibrium ratio will be. We find from the text that K_{SP} (CdS) = $10^{-27.0}$ and K_{SP} (PbS) = $10^{-27.5}$. Thus,

$$[Cd^{2+}] = \frac{10^{-27.0}}{[S^{2-}]}$$

$$[Pb^{2+}] = \frac{10^{-27.5}}{[S^{2-}]}$$

$$\frac{[Cd^{2+}]}{[Pb^{2+}]} = \frac{10^{-27.0}}{10^{-27.5}} = 10^{0.5} = 3.16$$

The actual ratio $\frac{[Cd^{2+}]}{[Pb^{2+}]} = 25$ is greater than the equilibrium ratio, so CdS will precipitate and PbS will dissolve until the ratio attains the equilibrium value of $10^{0.5}$. We would thus expect that CdS will replace PbS.

Problem 5:

Species: Pb^{2+}, MoO_4^{2-}, Ca^{2+}, H^+, OH^-

Mass-action Expressions:

$$PbMoO_4 \leftrightarrow Pb^{2+} + MoO_4^{2-} \qquad K_{SP,1} = 10^{-16.0}$$
$$CaMoO_4 \leftrightarrow Ca^{2+} + MoO_4^{2-} \qquad K_{SP,2} = 10^{-7.94}$$
$$H_2O(l) \leftrightarrow OH^- + H^+ \qquad K_w = 10^{-14}$$

Stoichiometric constraint: $[Pb^{2+}] + [Ca^{2+}] = [MoO_4^{2-}]$

Charge-balance constraint: $2[Pb^{2+}] + 2[Ca^{2+}] + [H^+] = 2[MoO_4^{2-}] + [OH^-]$

Substituting the mass-action expressions $[Pb^{2+}] = \frac{10^{-16.0}}{[MoO_4^{2-}]}$ and $[Ca^{2+}] = \frac{10^{-7.94}}{[MoO_4^{2-}]}$

into the stoichiometric constraint we obtain:

$$\frac{10^{-16.0}}{[MoO_4^{2-}]} + \frac{10^{-7.94}}{[MoO_4^{2-}]} = [MoO_4^{2-}]$$

The first term is negligible, so we get:

$$10^{-7.94} = [MoO_4^{2-}]^2$$
$$[MoO_4^{2-}] = 10^{-3.97} \text{ mol L}^{-1}$$
$$[Pb^{2+}] = \frac{10^{-16.0}}{10^{-3.97}} = 10^{-12.03} = 9.33\times10^{-13} \text{ mol L}^{-1}$$
$$[Ca^{2+}] = \frac{10^{-7.94}}{10^{-3.97}} = 10^{-3.97} = 1.07\times10^{-4} \text{ mol L}^{-1}$$

Problem 6:

First, convert ppm = mg L^{-1} to mol L^{-1}:

Al: $(353\ \text{mg L}^{-1})/[(26.982\ \text{g mol}^{-1})(1000\ \text{mg g}^{-1})] = 0.0131\ \text{mol L}^{-1}$

K: $(586\ \text{mg L}^{-1})/[(39.098\ \text{g mol}^{-1})(1000\ \text{mg g}^{-1})] = 0.0150\ \text{mol L}^{-1}$

SO_4^{2-}: $(68280\ \text{mg L}^{-1})/[(96.064\ \text{g mol}^{-1})(1000\ \text{mg g}^{-1})] = 0.7108\ \text{mol L}^{-1}$

The solubility reaction of interest is:

$$KAl_3(SO_4)_2(OH)_6 \leftrightarrow K^+ + 3Al^{3+} + 2SO_4^{2-} + 6OH^-$$

$$K = 10^{-80.95} = [K^+][Al^{3+}]^3[SO_4^{2-}]^2[OH^-]^6$$

To calculate the IAP we will need the concentration of hydroxide ion:

$$[OH^-] = \frac{10^{-14}}{10^{-2.4}} = 10^{-11.6} = 2.512 \times 10^{-12}$$

$$IAP = (0.0150)(0.0131)^3(0.7108)^2(2.512\times10^{-12})^6 = 4.28\times10^{-78}$$

$$\Omega = IAP/K_{SP} = 4.28\times10^{-78}/10^{-80.95} = 3814$$

So the solution is supersaturated and alunite should precipitate. However, if activity coefficient effects and hydrolysis/complexation were taken into account, the IAP would be lowered somewhat.