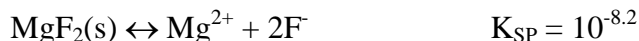


PRINCIPLES OF GEOCHEMISTRY
GEOL 423
PROBLEM SET 5
FALL 2009
ANSWERS

Problem 1:



Let x = number of moles of $\text{MgF}_2(\text{s})$ dissolved. Then by stoichiometry:

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

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

$$[\text{Mg}^{2+}] = 1.16 \times 10^{-3} \text{ mol L}^{-1}; [\text{F}^-] = 2.33 \times 10^{-3} \text{ mol L}^{-1}$$

$$\begin{aligned} \text{solubility} &= (1.16 \times 10^{-3} \text{ mol L}^{-1})(62.3018 \text{ g mol}^{-1}) = 0.0723 \text{ g L}^{-1} \\ &= 7.23 \times 10^{-3} \text{ g/100 mL} \end{aligned}$$

Problem 2:

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

$$0.1 \text{ g L}^{-1} / (142.043 \text{ g mol}^{-1}) = 7.04 \times 10^{-4} \text{ mol L}^{-1}$$

Because Na_2SO_4 completely dissolves, and in so doing dissociates to 2Na^+ and 1SO_4^{2-} , the initial $[\text{SO}_4^{2-}] = 7.04 \times 10^{-4} \text{ mol L}^{-1}$.

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

$$\begin{aligned} \text{IAP} &= [\text{Pb}^{2+}]_{\text{act}}[\text{SO}_4^{2-}]_{\text{act}} = (3 \times 10^{-2} \text{ mol L}^{-1})(7.04 \times 10^{-4} \text{ mol L}^{-1}) = 2.112 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2} \\ \Omega &= \text{IAP}/K_{\text{SP}} = (2.112 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2}) / (10^{-7.8} \text{ mol}^2 \text{ L}^{-2}) = 1.333 \times 10^3 \end{aligned}$$

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

$$\begin{aligned} [\text{Pb}^{2+}]_{\text{act}} &= (3 \times 10^{-2} \text{ mol L}^{-1}) - x \\ [\text{SO}_4^{2-}]_{\text{eq}} &= (7.04 \times 10^{-4} \text{ mol L}^{-1}) - x \end{aligned}$$

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

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

$$[(3 \times 10^{-2} \text{ mol L}^{-1}) - x][(7.04 \times 10^{-4} \text{ mol L}^{-1}) - x] \approx 0$$

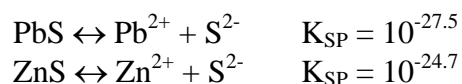
The right hand side can be zero if either

$$[(3 \times 10^{-2} \text{ mol L}^{-1}) - x] = 0 \text{ or } [(7.04 \times 10^{-4} \text{ mol L}^{-1}) - x] = 0$$

The two roots of this equation are therefore $x \approx 3 \times 10^{-2}$ and $x \approx 7.04 \times 10^{-4}$. 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 $x \approx 7.04 \times 10^{-4}$ would make $[\text{SO}_4^{2-}]_{\text{eq}} = (7.04 \times 10^{-4} \text{ mol L}^{-1}) - (3 \times 10^{-2} \text{ mol L}^{-1}) = -2.93 \times 10^{-2}$, 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:

$$\text{mass PbSO}_4 \text{ precipitated} \approx (7.04 \times 10^{-4} \text{ mol})(303.264 \text{ g mol}^{-1}) = 0.213 \text{ g PbSO}_4$$

Problem 3:



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

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

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

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

Problem 4:

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

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

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

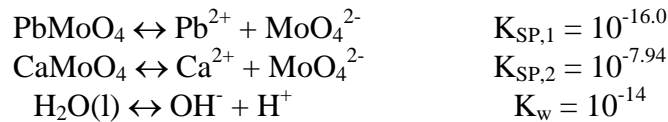
$$\frac{[Cd^{2+}]}{[Pb^{2+}]} = \frac{10^{-27.0}}{10^{-27.5}} = 10^{0.5} = 3.16$$

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:



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:

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

Problem 6:

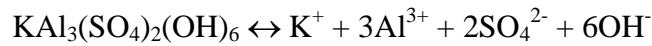
First, convert ppm = mg L⁻¹ to mol L⁻¹:

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

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

$$\text{SO}_4^{2-}: \quad (68280 \text{ mg L}^{-1}) / [(96.064 \text{ g mol}^{-1})(1000 \text{ mg g}^{-1})] = 0.7108 \text{ mol L}^{-1}$$

The solubility reaction of interest is:



$$K = 10^{-80.95} = [\text{K}^+][\text{Al}^{3+}]^3[\text{SO}_4^{2-}]^2[\text{OH}^-]^6$$

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

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

$$\text{IAP} = (0.0150)(0.0131)^3(0.7108)^2(2.512 \times 10^{-12})^6 = 4.28 \times 10^{-78}$$

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

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.