

Chemistry 2000B Spring 2002 Assignment 4 Solutions

1. The required data are in Tables 11 and 12 of Appendix D (p A-18). We can break the calculation up into several pieces:

- Heat to melt solid:

$$(28.53 \text{ g})(11 \text{ J/g}) = 0.31 \text{ kJ}$$

- Heat to warm liquid from melting (-38.8°C) to boiling point (357°C):

$$(28.53 \text{ g})(0.138 \text{ J K}^{-1} \text{ g}^{-1}) [357 - (-38.8) \text{ K}] = 1.56 \text{ kJ}$$

- Heat to vaporize liquid:

$$(28.53 \text{ g})(294 \text{ J/g}) = 8.39 \text{ kJ}$$

- The specific heat capacity of the vapor is given on a molar basis. The number of moles of mercury is

$$n_{\text{Hg}} = \frac{28.53 \text{ g}}{200.59 \text{ g/mol}} = 0.1422 \text{ mol.}$$

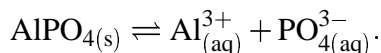
∴ heat required to warm vapor to final temperature:

$$(0.1422 \text{ mol})(20.77 \text{ J K}^{-1} \text{ mol}^{-1}) (500 - 357 \text{ K}) = 0.422 \text{ kJ}$$

The total heat required is therefore

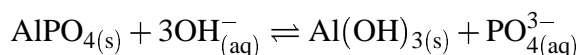
$$0.31 + 1.56 + 8.39 + 0.422 \text{ kJ} = 10.68 \text{ kJ.}$$

2. The solubility equilibrium for aluminium phosphate is

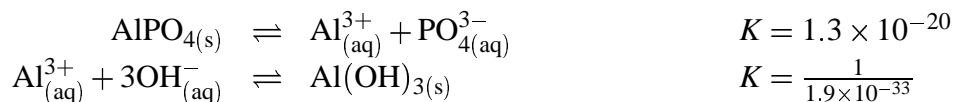


The pK_a of HPO_4^{2-} , the conjugate acid of phosphate, is 12.44 (calculated from data in table 17.4, p 799). If the pH is well above 12.44, phosphate is the dominant species and the solubility should be low (but see below). As the pH approaches the pK_a , there will be less free phosphate in solution and more HPO_4^{2-} . This will tend to increase the solubility. Well below the pK_a , there will be very little free phosphate in solution and aluminium phosphate should be very soluble.

There's are additional complicating factors: Aluminium hydroxide isn't very soluble either so at high pH , precipitation of this salt might remove aluminium from solution and therefore increase the amount of aluminium phosphate which will dissolve. Whether this will occur will depend on whether the reaction



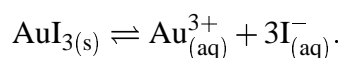
is spontaneous or not under the given conditions. This reaction can be broken down into



so that the equilibrium constant for the overall reaction is $1.3 \times 10^{-20} / 1.9 \times 10^{-33} = 6.8 \times 10^{12}$. This is huge, so this reaction will be spontaneous under any reasonable conditions of high pH (high hydroxide ion concentration). In other words, we can “dissolve” aluminium phosphate at high pH , too, at least in the limited sense that $\text{AlPO}_4(s)$ will disappear to be replaced by $\text{Al}(\text{OH})_3(s)$, leaving phosphate in solution.

I will admit that I had not thought of this second possibility when I framed this question. It just goes to show that you have to think about the chemistry of these things all the time.

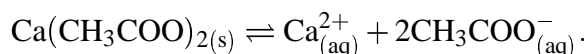
3. The solubility equilibrium is



Since $a_{\text{I}^{-}} = 3a_{\text{Au}^{3+}}$,

$$\begin{aligned} K_{\text{sp}} &= (a_{\text{Au}^{3+}})(a_{\text{I}^{-}})^3 = (a_{\text{Au}^{3+}})(3a_{\text{Au}^{3+}})^3 = 27(a_{\text{Au}^{3+}})^4. \\ \therefore (a_{\text{Au}^{3+}})^4 &= \frac{1.0 \times 10^{-46}}{27} = 3.7 \times 10^{-48}. \\ \therefore a_{\text{Au}^{3+}} &= 1.4 \times 10^{-12}. \\ \therefore \text{solubility} &= (1.4 \times 10^{-12} \text{ mol/L})(577.6800 \text{ g/mol}) = 8.0 \times 10^{-10} \text{ g/L}. \end{aligned}$$

4. (a) The solubility equilibrium is



The concentration of calcium acetate is

$$[\text{Ca}(\text{CH}_3\text{COO})_2] = \frac{374 \text{ g/L}}{158.167 \text{ g/mol}} = 2.36 \text{ mol/L}.$$

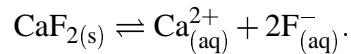
The activity of calcium ions in solution is therefore¹ $a_{\text{Ca}^{2+}} = 2.36$ while the activity of acetate ions is $a_{\text{CH}_3\text{COO}^{-}} = 2(2.36) = 4.73$. The K_{sp} is therefore

$$K_{\text{sp}} = (a_{\text{Ca}^{2+}})(a_{\text{CH}_3\text{COO}^{-}})^2 = (2.36)(4.73)^2 = 52.9.$$

(b) The solubility of calcium acetate is so high that under normal conditions we would not expect to exceed its solubility.

¹Neglecting nonideal behavior.

5. This is based on the solubility equilibrium



For this reaction,

$$K_{\text{sp}} = 3.9 \times 10^{-11} = (a_{\text{Ca}^{2+}})(a_{\text{F}^{-}})^2$$

We want $a_{\text{F}^{-}} = 10^{-6}$ at the end of the reaction. This means that the activity due to the excess calcium must be

$$a_{\text{Ca}^{2+}} = \frac{3.9 \times 10^{-11}}{(10^{-6})^2} = 39.$$

This is an excessively high (almost certainly unrealizable) concentration of calcium in solution. In other words, you probably can't remove all of that fluoride by this reaction. However, assuming that you can actually get this much calcium dissolved in water, the number of moles of calcium ions in 50 L would be

$$n_{\text{Ca}^{2+}, \text{aq}} = (39 \text{ mol/L})(50 \text{ L}) = 1950 \text{ mol}.$$

The number of moles of fluoride removed from solution is

$$n_{\text{F}^{-}, \text{precip}} = (0.025 - 10^{-6} \text{ mol/L})(50 \text{ L}) = 1.25 \text{ mol}.$$

By stoichiometry, the number of moles of calcium ions required to precipitate this much fluoride is

$$n_{\text{Ca}^{2+}, \text{precip}} = \frac{1}{2}(1.25 \text{ mol}) = 0.625 \text{ mol}.$$

The total number of moles of calcium ions which we must add is therefore

$$n_{\text{Ca}^{2+}, \text{total}} = 0.625 + 1950 \text{ mol} = 1951 \text{ mol}.$$

The calcium ions are added in the form of a nitrate with a molar mass of 164.0878 g/mol. The mass of calcium nitrate required is therefore

$$m_{\text{Ca}(\text{NO}_3)_2} = (1951 \text{ mol})(164.0878 \text{ g/mol}) = 320 \text{ kg},$$

again, clearly an absurd number.

6. The Henry's law constant for oxygen in water is $1.66 \times 10^{-6} \text{ mol L}^{-1} \text{ mmHg}^{-1}$ (table 14.2, p 653). The partial pressure of oxygen in air at sea level is 0.2095 atm (table 12.2, p 559). The concentration of oxygen in water which is in equilibrium with the atmosphere at sea level is therefore

$$[\text{O}_{2(\text{aq})}] = (1.66 \times 10^{-6} \text{ mol L}^{-1} \text{ mmHg}^{-1})(0.2095 \text{ atm})(760 \text{ mmHg/atm}) = 2.64 \times 10^{-4} \text{ mol/L}.$$

(The conversion factor from atm to mmHg came from the back cover of the book.) 1 L of water therefore contains $2.64 \times 10^{-4} \text{ mol}$ of oxygen. If we transfer this many moles of oxygen into a 1 L (0.001 m^3) container, it would exert a pressure of

$$P = \frac{nRT}{V} = \frac{(2.64 \times 10^{-4} \text{ mol})(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{0.001 \text{ m}^3} = 655 \text{ Pa}.$$