Chapter 6
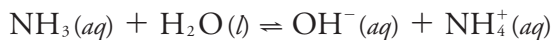
1. (a) The equilibrium constant expression is

$$K = \frac{[NH_4^+]}{[NH_3][H_3O^+]}$$

To find the equilibrium constant's value, we note that the overall re-action is the sum of two reactions, each with a standard equilibrium constant; thus

$$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

$$K = K_{b,NH_3} \times (K_w)^{-1} = \frac{K_w}{K_{a,NH_4^+}} \times \frac{1}{K_w} = \frac{1}{K_{a,NH_4^+}}$$

$$K = \frac{1}{5.70 \times 10^{-10}} = 1.75 \times 10^9$$

By "standard equilibrium constant," we mean one of the following: an acid disso-ciation constant, a base dissociation con-stant, a solubility product, a stepwise or an overall formation constant, or a solvent dissociation constant.

(b) The equilibrium constant expression is

$$K = \frac{[I^-]^2}{[S^{2-}]}$$

To find the equilibrium constant's value, we note that the overall re-action is the sum of two reactions, each with a standard equilibrium constant; thus
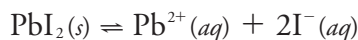
$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

$$Pb^{2+}(aq) + S^{2-}(aq) \rightleftharpoons PbS(s)$$
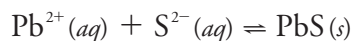
$$K = K_{sp,PbI_2} \times (K_{sp,PbS})^{-1}$$

$$K = (7.9 \times 10^{-9}) \times \frac{1}{3 \times 10^{-28}} = 3 \times 10^{19}$$

(c) The equilibrium constant expression is

$$K = \frac{[Cd(CN)_4^{2-}][Y^{4-}]}{[CdY^{2-}][CN^-]^4}$$

To find the equilibrium constant's value, we note that the overall re-action is the sum of two reactions, each with a standard equilibrium constant; thus
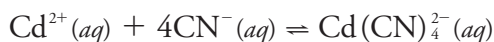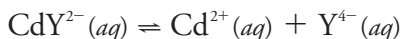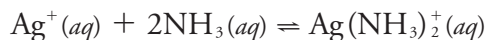
$$CdY^{2-}(aq) \rightleftharpoons Cd^{2+}(aq) + Y^{4-}(aq)$$

$$Cd^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Cd(CN)_4^{2-}(aq)$$

$$K = (K_{f,CdY^{2-}})^{-1} \times \beta_{4,Cd(CN)_4^{2-}}$$

$$= \frac{1}{2.88 \times 10^{16}} \times (8.32 \times 10^{17}) = 28.9$$

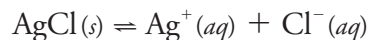where β_4 is equal to $K_1 \times K_2 \times K_3 \times K_4$.

From Appendix 12, we have $\log K_1 = 6.01$, $\log K_2 = 5.11$, $\log K_3 = 4.53$, and $\log K_4 = 2.27$. Adding together these four values gives $\log \beta_4$ as 17.92 and β_4 as 8.32×10^{17}.

(d) The equilibrium constant expression is

$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2}$$

To find the equilibrium constant's value, we note that the overall reaction is the sum of two reactions, each with a standard equilibrium constant; thus

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

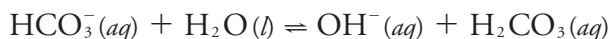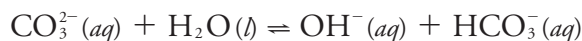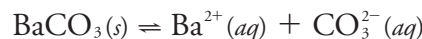$$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$$

$$K = K_{\text{sp,AgCl}} \times \beta_{2,\text{Ag}(\text{NH}_3)_2^+}$$

$$K = (1.8 \times 10^{-10}) \times (1.66 \times 10^7) = 3.0 \times 10^{-3}$$

(e) The equilibrium constant expression is

$$K = \frac{[\text{Ba}^{2+}][\text{H}_2\text{CO}_3]}{[\text{H}_3\text{O}^+]^2}$$

To find the equilibrium constant's value, we note that the overall reaction is the sum of five reactions, each with a standard equilibrium constant; thus
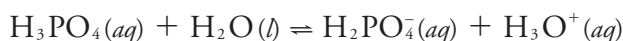
$$\text{BaCO}_3(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{CO}_3^{2-}(aq)$$

$$\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HCO}_3^-(aq)$$

$$\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{H}_2\text{CO}_3(aq)$$

$$\text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \rightleftharpoons 2\text{H}_2\text{O}(l)$$

$$\text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \rightleftharpoons 2\text{H}_2\text{O}(l)$$

$$K = K_{\text{sp,BaCO}_3} \times K_{\text{b,CO}_3^{2-}} \times K_{\text{b,HCO}_3^-} \times (K_\text{w})^{-2}$$

$$K = K_{\text{sp,BaCO}_3} \times \frac{K_\text{w}}{K_{\text{a,HCO}_3^-}} \times \frac{K_\text{w}}{K_{\text{a,H}_2\text{CO}_3}} \times \frac{1}{(K_\text{w})^2}$$

$$K = (5.0 \times 10^{-9}) \times \frac{1}{4.69 \times 10^{-11}} \times \frac{1}{4.45 \times 10^{-7}} = 2.4 \times 10^8$$

From Appendix 12, we have $\log K_1 = 3.31$ and $\log K_2 = 3.91$. Adding together these four values gives $\log \beta_2$ as 7.22 and β_2 as 1.66×10^7.
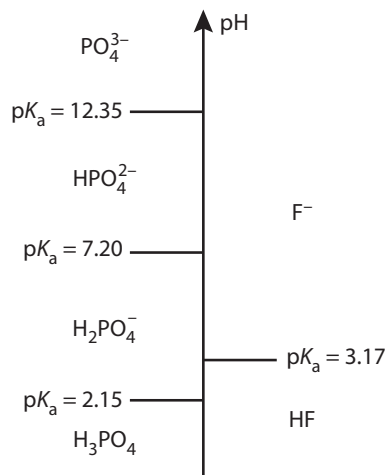
2. Figure SM6.1 shows the ladder diagram for H_3PO_4 and for HF. From the ladder diagram, we predict that a reaction between H_3PO_4 and F^- is favorable because their respective areas of predominance do not overlap. On the other hand, a reaction between H_2PO_4^- and F^-, which must take place if the final product is to include HPO_4^{2-}, is unfavorable because the areas of predominance for H_2PO_4^- and F^-, overlap.

To find the equilibrium constant for the first reaction, we note that it is the sum of three reactions, each with a standard equilibrium constant; thus

$$\text{H}_3\text{PO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{PO}_4^-(aq) + \text{H}_3\text{O}^+(aq)$$
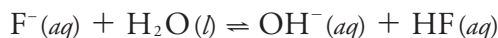

Figure SM6.1 Ladder diagram showing the areas of predominance for H_3PO_4 on the left and the areas of predominance for HF on the right.
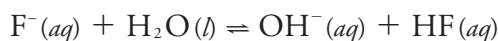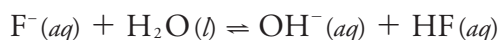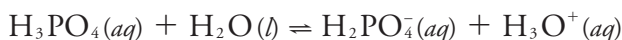
$$F^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HF(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

$$K = K_{a,H_3PO_4} \times K_{b,F^-} \times (K_w)^{-1} = K_{a,H_3PO_4} \times \frac{K_w}{K_{a,HF}} \times \frac{1}{K_w}$$

$$K = \frac{7.11 \times 10^{-3}}{6.8 \times 10^{-4}} = 10.5$$

Because K is greater than 1, we know that the reaction is favorable.

To find the equilibrium constant for the second reaction, we note that it is the sum of six reactions, each with a standard equilibrium constant; thus

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

$$F^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HF(aq)$$

$$F^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HF(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

$$K = K_{a,H_3PO_4} \times K_{a,H_2PO_4^-} \times (K_{b,F^-})^2 \times (K_w)^{-2}$$

$$K = K_{a,H_3PO_4} \times K_{a,H_2PO_4^-} \times \left(\frac{K_w}{K_{a,HF}}\right)^2 \times \left(\frac{1}{K_w}\right)^2$$

$$K = (7.11 \times 10^{-3}) \times (6.32 \times 10^{-8}) \times \left(\frac{1}{6.8 \times 10^{-4}}\right)^2 = 9.7 \times 10^{-4}$$
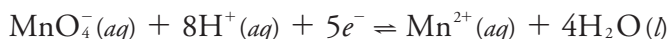
Because K is less than 1, we know that the reaction is unfavorable.

3. To calculate the potential we use the Nernst equation; thus

$$E = (E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Sn^{4+}/Sn^{2+}}) - \frac{0.05916}{2} \log \frac{[Sn^{4+}][Fe^{2+}]^2}{[Sn^{2+}][Fe^{3+}]^2}$$

$$= (0.771 - 0.154) - \frac{0.05916}{2} \log \frac{(0.020)(0.030)^2}{(0.015)(0.050)^2}$$

$$= +0.626 \text{ V}$$

4. We can balance these reactions in a variety of ways; here we will identify the balanced half-reactions from Appendix 13 and add them together after adjusting the stoichiometric coefficients so that all electrons released in the oxidation reaction are consumed in the reduction reaction.

    (a) The two half-reactions are

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$

$$H_2SO_3(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$

which combine to give an overall reaction of

Within the context of this problem, we do not need to balance the reactions; instead, we simply need to identify the two half-reactions and subtract their standard state reduction potentials to arrive at the reaction's standard state potential. Nevertheless, it is useful to be able to write the balanced overall reaction from the half-reactions as this information is needed if, as in Problem 3, we seek the reaction's potential under non-standard state conditions.
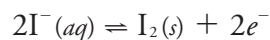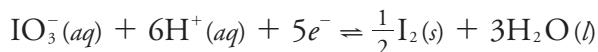
$$2MnO_4^{2-}(aq) + 5H_2SO_3(aq) \rightleftharpoons$$
$$2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 4H^+(aq) + 3H_2O(l)$$
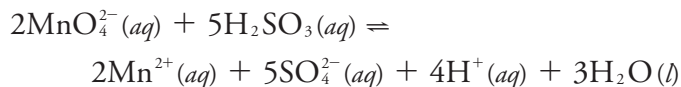
Using the Nernst equation, the standard state potential is

$$E^\circ = (E^\circ_{MnO_4^-/Mn^{2+}} - E^\circ_{SO_4^{2-}/H_2SO_3}) = 1.51 - 0.172$$
$$= 1.338\ V \approx 1.34\ V$$

and an equilibrium constant of

$$K = 10^{nE^\circ/0.05916} = 10^{(10)(1.338)/0.05916} = 1.47 \times 10^{226}$$

(b) The two half-reactions are

$$IO_3^-(aq) + 6H^+(aq) + 5e^- \rightleftharpoons \frac{1}{2}I_2(s) + 3H_2O(l)$$

$$2I^-(aq) \rightleftharpoons I_2(s) + 2e^-$$

which combine to give an overall reaction of

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightleftharpoons 3I_2(s) + 3H_2O(l)$$

Using the Nernst equation, the standard state potential is

$$E^\circ = (E^\circ_{IO_3^-/I_2} - E^\circ_{I_2/I^-}) = 1.195 - 0.5355$$
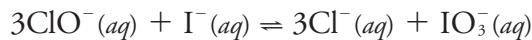$$= 0.6595\ V \approx 0.660\ V$$

and an equilibrium constant of

$$K = 10^{nE^\circ/0.05916} = 10^{(5)(0.6595)/0.05916} = 5.48 \times 10^{55}$$

(c) The two half-reactions are
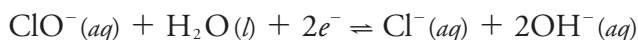
$$ClO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons Cl^-(aq) + 2OH^-(aq)$$

$$I^-(aq) + 6OH^-(aq) \rightleftharpoons IO_3^-(aq) + 3H_2O(l) + 6e^-$$

which combine to give an overall reaction of

$$3ClO^-(aq) + I^-(aq) \rightleftharpoons 3Cl^-(aq) + IO_3^-(aq)$$

Using the Nernst equation, the standard state potential is

$$E^\circ = (E^\circ_{ClO^-/Cl^-} - E^\circ_{IO_3^-/I^-}) = 0.890 - 0.257 = 0.633\ V$$

and an equilibrium constant of

$$K = 10^{nE^\circ/0.05916} = 10^{(6)(0.633)/0.05916} = 1.58 \times 10^{64}$$

5. (a) Because SO_4^{2-} is a weak base, decreasing the solution's pH, which makes the solution more acidic, converts some of the SO_4^{2-} to HSO_4^-. Decreasing the concentration of SO_4^{2-} shifts the solubility reaction to the right, increasing the solubility of $BaSO_4$.

(b) Adding $BaCl_2$, which is a soluble salt, increases the concentration of Ba^{2+} in solution, pushing the solubility reaction to the left and decreasing the solubility of $BaSO_4$.

(c) Increasing the solution's volume by adding water decreases the concentration of both Ba^{2+} and of SO_4^{2-}, which, in turn, pushes the solubility reaction to the right, increasing the solubility of $BaSO_4$.

6. (a) A solution of NaCl contains the following species: Na^+, Cl^-, H_3O^+, and OH^-. The charge balance equation is

$$[H_3O^+] + [Na^+] = [Cl^-] + [OH^-]$$

and the mass balance equations are

$$0.10 \text{ M} = [Na^+]$$
$$0.10 \text{ M} = [Cl^-]$$

(b) A solution of HCl contains the following species: Cl^-, H_3O^+, and OH^-. The charge balance equation is

$$[H_3O^+] = [Cl^-] + [OH^-]$$

and the mass balance equation is

$$0.10 \text{ M} = [Cl^-]$$

A solution of HCl will contain some un-dissociated HCl(*aq*); however, because HCl is a strong acid, the concentration of HCl(*aq*) is so small that we can safely ignore it when writing the mass balance equation for chlorine.

(c) A solution of HF contains the following species: HF, F^-, H_3O^+, and OH^-. The charge balance equation is

$$[H_3O^+] = [F^-] + [OH^-]$$

and the mass balance equation is

$$0.10 \text{ M} = [HF] + [F^-]$$

(d) A solution of NaH_2PO_4 contains the following species: Na^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H_3O^+, and OH^-. The charge balance equation is

$$[Na^+] + [H_3O^+] = [OH^-] + [H_2PO_4^-] +$$
$$2 \times [HPO_4^{2-}] + 3 \times [PO_4^{3-}]$$

and the mass balance equations are

$$0.10 \text{ M} = [Na^+]$$
$$0.10 \text{ M} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

(e) A saturated solution of $MgCO_3$ contains the following species: Mg^{2+}, CO_3^{2-}, HCO_3^-, H_2CO_3, H_3O^+, and OH^-. The charge balance equation is

$$2 \times [Mg^{2+}] + [H_3O^+] = [OH^-] + [HCO_3^-] + 2 \times [CO_3^{2-}]$$

and the mass balance equation is

$$[Mg^{2+}] = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

For a saturated solution of $MgCO_3$, we know that the concentration of Mg^{2+} must equal the combined concentration of carbonate in all three of its forms.

(f) A solution of $Ag(CN)_2^-$ prepared using $AgNO_3$ and KCN contains the following ions: Ag^+, NO_3^-, K^+, CN^-, $Ag(CN)_2^-$, HCN, H_3O^+, and OH^-. The charge balance equation is

$$[Ag^+] + [K^+] + [H_3O^+] =$$
$$[OH^-] + [NO_3^-] + [CN^-] + [Ag(CN)_2^-]$$

and the mass balance equations are

$$[NO_3^-] = [Ag^+] + [Ag(CN)_2^-]$$

$$[K^+] = [CN^-] + [HCN] + 2 \times [Ag(CN)_2^-]$$

(g) A solution of HCl and $NaNO_2$ contains the following ions: H_3O^+, OH^-, Cl^-, Na^+, NO_2^-, and HNO_2. The charge balance equation is

$$[Na^+] + [H_3O^+] = [OH^-] + [NO_2^-] + [Cl^-]$$

and the mass balance equations are

$$0.10\ M = [Cl^-]$$

$$0.050\ M = [Na^+]$$

$$0.050\ M = [NO_2^-] + [HNO_2]$$

7. (a) Perchloric acid, $HClO_4$, is a strong acid, a solution of which contains the following species: H_3O^+, OH^-, and ClO_4^-. The composition of the solution is defined by a charge balance equation and a mass balance equation for ClO_4^-

$$[H_3O^+] = [OH^-] + [ClO_4^-]$$

$$[ClO_4^-] = 0.050\ M$$

and by the K_w expression for water.

$$[H_3O^+][OH^-] = K_w$$

Because $HClO_4$ is a strong acid and its concentration of 0.050 M is relatively large, we can assume that

$$[OH^-] \ll [ClO_4^-]$$

and that

$$[H_3O^+] = [ClO_4^-] = 0.050\ M$$

The pH, therefore is, 1.30. To check our assumption, we note that a pH of 1.30 corresponds to a pOH of 12.70 and to a $[OH^-]$ of 2.0×10^{-13} M. As this is less than 5% of 0.050 M, our assumption that

$$[OH^-] \ll [ClO_4^-]$$

is reasonable.

(b) Hydrochloric acid, HCl, is a strong acid, a solution of which contains the following species: H_3O^+, OH^-, and Cl^-. The composition of the solution is defined by a charge balance equation and a mass balance equation for Cl^-

$$[H_3O^+] = [OH^-] + [Cl^-]$$

$$[Cl^-] = 1.00 \times 10^{-7} \text{ M}$$

and by the K_w expression for water.

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

Although HCl is a strong acid, its concentration of 1.00×10^{-7} M is relatively small such that we likely cannot assume that

$$[OH^-] \ll [Cl^-]$$

To find the pH, therefore, we substitute the mass balance equation for Cl^- into the charge balance equation and rearrange to solve for the concentration of OH^-

$$[OH^-] = [H_3O^+] - 1.00 \times 10^{-7}$$

and then substitute this into the K_w expression for the dissociation of water

$$[H_3O^+]\{[H_3O^+] - 1.00 \times 10^{-7}\} = 1.00 \times 10^{-14}$$

$$[H_3O^+]^2 + (1.00 \times 10^{-7})[H_3O^+] + 1.00 \times 10^{-14} = 0$$

Solving the quadratic equation gives $[H_3O^+]$ as 1.62×10^{-7} and the pH as 6.79.

(c) Hypochlorous acid, HOCl, is a weak acid, a solution of which contains the following species: H_3O^+, OH^-, HOCl, and ClO^-. The composition of the solution is defined by a charge balance equation and a mass balance equation for HOCl

$$[H_3O^+] = [OH^-] + [OCl^-]$$

$$[HOCl] + [ClO^-] = 0.025 \text{ M}$$

and by the K_a and K_w expressions for HOCl and water, respectively

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = 3.0 \times 10^{-8}$$

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

Because the solution is acidic, let's assume that

$$[OH^-] \ll [H_3O^+]$$

which reduces the charge balance equation to

$$[H_3O^+] = [ClO^-] = x$$

Next, we substitute this equation for $[ClO^-]$ into the mass balance equation and solve for [HOCl]

$$[HOCl] = 0.025 - x$$

Here, and elsewhere in this textbook, we assume that you have access to a calculator or other tool that can solve the quadratic equation. Be sure that you examine both roots to the equation and that you choose the root that makes chemical sense.

Having defined the concentrations of all three species in terms of a single variable, we substitute them back into the K_a expression for HOCl

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = \frac{x^2}{0.025 - x} = 3.0 \times 10^{-8}$$

which we can solve using the quadratic equation. Alternatively, we can simplify further by recognizing that because HOCl is a weak acid, x likely is significantly smaller than 0.025 and $0.025 - x \approx 0.025$

$$\frac{x^2}{0.025} = 3.0 \times 10^{-8}$$

which gives x as 2.74×10^{-5} and the pH as 4.56. Checking our assumptions, we note that both are reasonable: 2.74×10^{-5} is less than 5% of 0.025 and [OH⁻], which is 3.6×10^{-10} is less than 5% of [H_3O^+, which is 2.74×10^{-5}.

(d) Formic acid, HCOOH, is a weak acid, a solution of which contains the following species: H_3O^+, OH⁻, HCOOH, and HCOO⁻. The composition of the solution is defined by a charge balance equation and a mass balance equation for HCOOH

$$[H_3O^+] = [OH^-] + [HCOO^-]$$

$$[HCOOH] + [HCOO^-] = 0.010 \text{ M}$$

and the K_a and K_w expressions for HCOOH and water, respectively

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = 1.80 \times 10^{-4}$$

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

Because the solution is acidic, let's assume that

$$[OH^-] << [H_3O^+]$$

which reduces the charge balance equation to

$$[H_3O^+] = [HCOO^-] = x$$

Next, we substitute this equation for [HCOO⁻] into the mass balance equation and solve for [HCOOH]

$$[HCOOH] = 0.010 - x$$

Having defined the concentrations of all three species in terms of a single variable, we substitute them back into the K_a expression for HCOOH

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = \frac{x^2}{0.010 - x} = 1.80 \times 10^{-4}$$

and solve for x. In Problem 8b we simplified this equation further by assuming that x is significantly smaller than the initial concentration

of the weak acid; this likely is not the case here because HCOOH is a stronger weak acid than HOCl and, therefore, more likely to dissociate. Solving for x using the quadratic equation gives its value as 1.25×10^{-3} and the pH as 2.90. Checking our one assumption, we note that it is reasonable: the $[OH^-]$, which is 8.00×10^{-12}, is less than 5% of $[H_3O^+]$, which is 1.25×10^{-3}.

(e) Barium hydroxide, $Ba(OH)_2$, is a strong base, a solution of which contains the following species: H_3O^+, OH^-, and Ba^{2+}. The composition of the solution is defined by a charge balance equation and a mass balance equation for Ba^{2+}

$$2 \times [Ba^{2+}] + [H_3O^+] = [OH^-]$$

$$[Ba^{2+}] = 0.050 \text{ M}$$

and by the K_w expression for water.

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

Because $Ba(OH)_2$ is a strong base and its concentration of 0.050 M is relatively large, we can assume that

$$[H_3O^+] \ll [OH^-]$$

and that

$$[OH^-] = 2 \times [Ba^{2+}] = 2 \times (0.050 \text{ M}) = 0.10 \text{ M}$$

The pOH, therefore is, 1.00 and the pH is 13.00. To check our assumption, we note that a pH of 13.00 corresponds to a $[H_3O^+]$ of 1.0×10^{-13} M. As this is less than 5% of 0.10 M, our assumption that

$$[H_3O^+] \ll [OH^-]$$

is reasonable.

(f) Pyridine, C_5H_5N, is a weak base, a solution of which contains the following species: H_3O^+, OH^-, C_5H_5N, and $C_5H_5NH^+$. The composition of the solution is defined by a charge balance equation and a mass balance equation for C_5H_5N

$$[H_3O^+] + [C_5H_5NH^+] = [OH^-]$$

$$[C_5H_5N] + [C_5H_5NH^+] = 0.010 \text{ M}$$

and the K_b and K_w expressions for C_5H_5N and water, respectively

$$K_b = \frac{[OH^-][C_5H_5NH^+]}{[C_5H_5N]} = 1.69 \times 10^{-9}$$

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

Because the solution is basic, let's assume that

$$[H_3O^+] << [OH^-]$$

which reduces the charge balance equation to

$$[C_5H_5N^+] = [OH^-] = x$$

Next, we substitute this equation for $[C_5H_5NH^+]$ into the mass balance equation and solve for $[C_5H_5N]$

$$[C_5H_5N] = 0.010 - x$$

Having defined the concentrations of all three species in terms of a single variable, we substitute them back into the K_b expression for C_5H_5NH

$$K_b = \frac{[OH^-][C_5H_5NH^+]}{[C_5H_5N]} = \frac{x^2}{0.010 - x} = 1.69 \times 10^{-9}$$

which we can solve using the quadratic equation. Alternatively, we can simplify further by recognizing that because C_5H_5N is a weak base, x likely is significantly smaller than 0.010 and $0.010 - x \approx 0.010$

$$\frac{x^2}{0.010} = 1.69 \times 10^{-9}$$

which gives x as 4.11×10^{-6}, the pOH as 5.39, and the pH as 8.61. Checking our assumptions, we note that both are reasonable: 4.11×10^{-6} is less than 5% of 0.010 and $[H_3O^+]$, which is 2.43×10^{-9} is less than 5% of $[OH^-]$, which is 4.11×10^{-6}.

8. (a) Figure SM6.2 shows a ladder diagram for maleic acid. A solution of 0.10 M H_2A will contain more H_2A than HA^-, and have a pH of less than 1.910. Maleic acid is a relatively strong weak acid (K_{a1} is 0.0123) and is likely to dissociate to an appreciable extent; thus, a reasonable estimate is that the solution's pH falls in the acidic portion of maleic acid's buffer region, perhaps between 1.4 and 1.6.

A solution of 0.10 M NaHA will contain more HA^- than H_2A or A^{2-}, and have a pH between 1.910 and 6.332. A reasonable estimate is that the pH is near the middle of the predominance region for HL^-, or approximately 4.1.

A solution of 0.10 M Na_2A will contain more A^{2-} than H_2A or HA^-, and, because A^{2-} is a weak base, will have a pH greater than 7. Although more difficult to estimate, a pH between 9 and 10 is a reasonable guess.

(b) Figure SM6.3 shows a ladder diagram for malonic acid. A solution of 0.10 M H_2A will contain more H_2A than HA^-, and have a pH of less than 2.847. Malonic acid is a relatively strong weak acid (K_{a1} is 1.42×10^{-3}) and is likely to dissociate to an appreciable extent, but less than for maleic acid; thus, a reasonable estimate is that the solution's
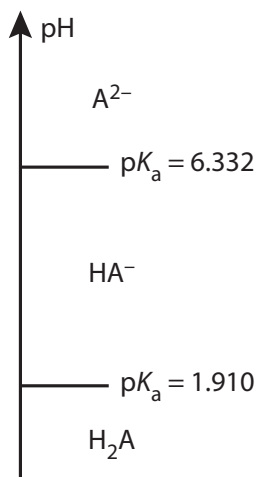

Figure SM6.2 Ladder diagram for maleic acid showing the pH values for which H_2A, HA^-, and A^{2-} are the predominate species.
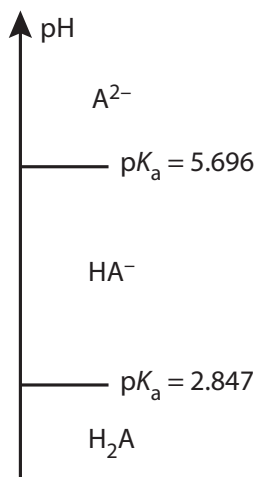

Figure SM6.3 Ladder diagram for malonic acid showing the pH values for which H_2A, HA^-, and A^{2-} are the predominate species.

pH falls close to the bottom of the acidic portion of malonic acid's buffer region, perhaps between 1.8 and 2.0.

A solution of 0.10 M NaHA will contain more HA^- than H_2A or A^{2-}, and have a pH between 2.847 and 5.696. A reasonable estimate is that the pH is near the middle of the predominance region for HA^-, or approximately 4.3.

A solution of 0.10 M Na_2A will contain more A^{2-} than H_2A or HA^-, and, because A^{2-} is a weak base, will have a pH greater than 7. Although more difficult to estimate, a pH between 9 and 10 is a reasonable guess.

(c) Figure SM6.4 shows a ladder diagram for succinic acid. A solution of 0.10 M H_2A will contain more H_2A than HA^-, and have a pH of less than 4.207. Maleic acid is not a relatively strong weak acid (K_{a1} is 6.21×10^{-5}); thus, a reasonable estimate is that the solution's pH falls below maleic acid's buffer region, perhaps between 2.5 and 3.0.

A solution of 0.10 M NaHA will contain more HA^- than H_2A or A^{2-}, and have a pH between 4.207 and 5.636. A reasonable estimate is that the pH is near the middle of the predominance region for HA^-, or approximately 4.9.

A solution of 0.10 M Na_2A will contain more A^{2-} than H_2A or HA^-, and, because A^{2-} is a weak base, will have a pH greater than 7. Although more difficult to estimate, a pH between 9 and 10 is a reasonable guess.

Figure SM6.4 Ladder diagram for succinic acid showing the pH values for which H_2A, HA^-, and A^{2-} are the predominate species.

9. (a) Malonic acid, H_2A, is a diprotic weak acid, a solution of which contains the following species: H_3O^+, OH^-, H_2A, HA^-, and A^{2-}. From its ladder diagram (see Figure SM6.3), we assume that

$$[A^{2-}] << [HA^-]$$

which means we can treat a solution of H_2L as if it is a monoprotic weak acid. Assuming that

$$[OH^-] << [H_3O^+]$$

then we know that

$$K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]} = \frac{x^2}{0.10 - x} = 1.42 \times 10^{-3}$$

which we solve using the quadratic equation, finding that x is 0.0112 and that the pH is 1.95, which is within our estimated range of 1.8–2.0 from Problem 8. Checking our assumptions, we note that the concentration of OH^-, which is 8.93×10^{-13}, is less than 5% of $[H_3O^+]$; thus, this assumption is reasonable. To evaluate the assumption that we can ignore A^{2-}, we use K_{a2} to determine its concentration

$$K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = \frac{(0.0112)[A^{2-}]}{(0.0112)} = [A^{2-}] = 2.01 \times 10^{-6}$$

finding that it is less than 5% of [HA⁻]; thus, this assumption is reasonable as well.

(b) A solution of monohydrogen malonate, NaHA, contains the following species: H_3O^+, OH^-, H_2A, and HA^-, and A^{2-}. From its ladder diagram (see Figure SM6.3), we assume that

$$[H_2A] << [HA^-] \quad \text{and} \quad [A^{2-}] << [HA^-]$$

Under these conditions, the $[H_3O^+]$ is given by the equation

$$[H_3O^+] = \sqrt{\frac{K_{a1} K_{a2} C_{NaHA} + K_{a1} K_w}{C_{NaHA} + K_{a1}}}$$

Substituting in values for K_{a1}, K_{a2}, K_w, and C_{NaHA} gives $[H_3O^+]$ as 5.30×10^{-5}, or a pH of 4.28, which is very close to our estimate of 4.3 from Problem 8. To evaluate the assumption that we can ignore H_2A, we use K_{a1} to calculate its concentration

$$[H_2A] = \frac{[H_3O^+][HA^-]}{K_{a1}} = \frac{(5.30 \times 10^{-5})(0.10)}{1.42 \times 10^{-3}} = 3.73 \times 10^{-3}$$

finding that it is less than 5% of $[HA^-] \approx C_{NaHA} = 0.10$ M. To evaluate the assumption that we can ignore A^{2-}, we use K_{a2} to determine its concentration

$$[A^{2-}] = \frac{K_{a2}[HA^-]}{[H_3O^+]} = \frac{(2.01 \times 10^{-6})(0.10)}{5.30 \times 10^{-5}} = 3.79 \times 10^{-3}$$

finding that it, too, is less than 5% of $[HA^-] \approx C_{NaHA} = 0.10$ M.

(c) Sodium malonate, Na_2A, is a diprotic weak base, a solution of which contains the following species: H_3O^+, OH^-, Na^+, H_2A, HA^-, and A^{2-}. From its ladder diagram (see Figure SM6.3), we assume that

$$[H_2A] << [HA^-]$$

which means we can treat a solution of A^{2-} as if it is a monoprotic weak base. Assuming that

$$[H_3O^+] << [OH^-]$$

then we know that

$$K_{b1} = \frac{[OH^-][HA^-]}{[A^{2-}]} = \frac{x^2}{0.10 - x} = 4.98 \times 10^{-9}$$

which we solve using the quadratic equation, finding that x is 2.23×10^{-5}, that the pOH is 4.65, and that the pH is 9.35, which is within our estimated range of 9–10 from Problem 8. Checking our assumptions, we note that the concentration of H_3O^+, which is 4.48×10^{-10}, is less than 5% of $[OH^-]$; thus, this assumption is reasonable. To evaluate the assumption that we can ignore H_2A, we use K_{b2} to determine its concentration

$$[H_2A] = \frac{K_{b2}[HA^-]}{[OH^-]} =$$

$$\frac{(7.04 \times 10^{-12})(2.23 \times 10^{-5})}{(2.23 \times 10^{-5})} = 7.04 \times 10^{-12}$$

finding that it is less than 5% of $[HA^-]$; thus, this assumption is reasonable as well.

10. For a simple solubility reaction without any complications from acid–base chemistry or from complexation chemistry, the composition of the system at equilibrium is determined by the solubility reaction

$$Hg_2Br_2\,(s) \rightleftharpoons Hg_2^{2+}\,(aq) + 2Br^-\,(aq)$$
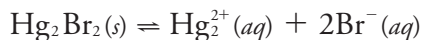
its corresponding solubility product

$$K_{sp} = [Hg_2^{2+}][Br^-]^2 = 5.6 \times 10^{-23}$$

and the stoichiometry of the solubility reaction.

(a) For a simple saturated solution of Hg_2Br_2, the following table defines the equilibrium concentrations of Hg_2^{2+} and Br^- in terms of their concentrations in the solution prior to adding Hg_2Br_2 and the change in their concentrations due to the solubility reaction.

	$Hg_2Br_2\,(s)$ $\rightleftharpoons$	$Hg_2^{2+}\,(aq)$ +	$2Br^-\,(aq)$
intial	—	0	0
change	—	$+x$	$+2x$
equilibrium	—	x	$2x$

Substituting the equilibrium concentrations into the K_{sp} expression

$$K_{sp} = [Hg_2^{2+}][Br^-]^2 = (x)(2x)^2 = 4x^3 = 5.6 \times 10^{-23}$$

and solving gives x as 2.4×10^{-8}. The molar solubility of Hg_2Br_2 is the concentration of Hg_2^{2+}, which is x or 2.4×10^{-8} M.

(b) For a saturated solution of Hg_2Br_2 in 0.025 M $Hg_2(NO_3)_2$, the following table defines the equilibrium concentrations of Hg_2^{2+} and Br^- in terms of their concentrations in the solution prior to adding Hg_2Br_2, and the change in their concentrations due to the solubility reaction.

	$Hg_2Br_2\,(s)$ $\rightleftharpoons$	$Hg_2^{2+}\,(aq)$ +	$2Br^-\,(aq)$
I	—	0.025	0
C	—	$+x$	$+2x$
E	—	$0.025 + x$	$2x$

Substituting the equilibrium concentrations into the K_{sp} expression

$$K_{sp} = [Hg_2^{2+}][Br^-]^2 = (0.025 + x)(2x)^2 = 5.6 \times 10^{-23}$$

leaves us with a cubic equation that is difficult to solve. We can simplify the problem if we assume that x is small relative to 0.025 M, an

Although perhaps not obvious, the approach we are taking here is equivalent to the systematic approach to solving equilibrium problems described in Section 6G.3 that combines a charge balance equation and/or a mass balance equation with equilibrium constant expressions. For part (a), a charge balance equation requires that

$$2 \times [Hg_2^{2+}] = [Cl^-]$$

If we define the concentration of Hg_2^{2+} as x, then the concentration of Cl^- is $2x$, which is the stoichiometric relationship shown in the table and leads to the same equation

$$K_{sp} = 4x^3 = 5.6 \times 10^{-23}$$

Note that we ignore the presence of H_3O^+ and OH^- when writing this charge balance equation because the solution has a neutral pH and the concentrations of H_3O^+ and OH^- are identical.

The same argument holds true for parts (b) and (c), although you may need to do a little work to convince yourself of this.

To save space, we use "I" to label the row of initial concentrations, "C" to label the row showing changes in concentration, and "E" to label the row of equilibrium concentrations. For obvious reasons, these tables sometimes are called ICE tables.

assumption that seems reasonable given that the molar solubility of Hg_2Br_2 in water is just 2.4×10^{-8} M; thus

$$K_{sp} = (0.025 + x)(2x)^2 \approx (0.025)(2x)^2 = 5.6 \times 10^{-23}$$

Solving gives x as 2.4×10^{-11}, a result that clearly is significantly less than 0.025. The molar solubility of Hg_2Br_2 is the concentration of Hg_2^{2+} from the Hg_2Br_2, which is x or 2.4×10^{-11} M.

(c) For a saturated solution of Hg_2Br_2 in 0.050 M NaBr, the following table defines the equilibrium concentrations of Hg_2^{2+} and Br^- in terms of their concentrations in the solution prior to adding Hg_2Br_2 and the change in their concentrations due to the solubility reaction.

$Hg_2Br_2(s)$	$\rightleftharpoons$	$Hg_2^{2+}(aq)$	+	$2Br^-(aq)$
I	—	0		0.050
C	—	$+x$		$+2x$
E	—	x		$0.050 + 2x$

Substituting the equilibrium concentrations into the K_{sp} expression

$$K_{sp} = [Hg_2^{2+}][Br^-]^2 = (x)(0.050 + 2x)^2 = 5.6 \times 10^{-23}$$

leaves us with a cubic equation that is difficult to solve. We can simplify the problem if we assume that $2x$ is small relative to 0.050 M, an assumption that seems reasonable given that the molar solubility of Hg_2Br_2 in water is just 2.4×10^{-8} M; thus

$$K_{sp} = (x)(0.050 + 2x)^2 \approx (x)(0.050)^2 = 5.6 \times 10^{-23}$$

Solving gives x as 2.2×10^{-20}, a result that clearly makes $2x$ significantly less than 0.050. The molar solubility of Hg_2Br_2 is the concentration of Hg_2^{2+}, which is x or 2.2×10^{-20} M.

11. Because F^- is a weak base, the molar solubility of CaF_2 depends on the solution's pH and whether fluorine is present as F^- or as HF. The ladder diagram for HF, which is included in Figure SM6.1, shows that F^- is the only significant form of fluorine at a pH of 7.00, which means the solubility of CaF_2 is determined by the reaction

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$
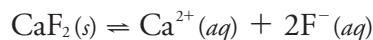
for which the equilibrium constant expression is

$$K_{sp} = [Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$$

The following table defines the equilibrium concentrations of Ca^{2+} and F^- in terms of their concentrations in the solution prior to adding CaF_2, and the change in their concentrations due to the solubility reaction.

$$\frac{CaF_2\,(s) \;\rightleftharpoons\; Ca^{2+}\,(aq) \;+\; 2F^-\,(aq)}{}$$

	CaF₂(s)	Ca²⁺(aq)	2F⁻(aq)
I	—	0	0
C	—	$+x$	$+2x$
E	—	x	$2x$

<div style="float:right">Note that the molar solubility of CaF_2 is independent of pH for any pH level greater than approximately $pK_{a,HF} + 1 \approx 4.2$. This is because at these pH levels the solubility reaction does not include any acid-base chemistry.</div>

Substituting the equilibrium concentrations into the K_{sp} expression
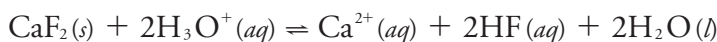
$$K_{sp} = [Ca^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3 = 3.9 \times 10^{-11}$$

and solving gives x as 2.1×10^{-4}. The molar solubility of CaF_2 at a pH of 7.00 is the concentration of Ca^{2+}, which is x or 2.1×10^{-4} M. Our solution here assumes that we can ignore the presence of HF; as a check on this assumption, we note that
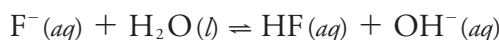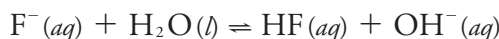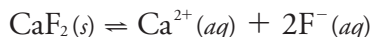
$$[HF] = \frac{[H_3O^+][F^-]}{K_{a,HF}} = \frac{(1.0 \times 10^{-7})(2.1 \times 10^{-4})}{6.8 \times 10^{-4}} = 3.1 \times 10^{-8}$$

a concentration that is negligible when compared to the concentration of F^-.

At a pH of 2.00, the only significant form of fluorine is HF, which means we must write the solubility reaction for CaF_2 in terms of HF instead of F^-; thus

$$CaF_2\,(s) + 2H_3O^+\,(aq) \rightleftharpoons Ca^{2+}\,(aq) + 2HF\,(aq) + 2H_2O\,(l)$$

<div style="float:right">We also can write this reaction as
$$CaF_2\,(s) + 2H_2O\,(l) \rightleftharpoons$$
$$Ca^{2+}\,(aq) + 2F^-\,(aq) + 2OH^-\,(aq)$$
and then make appropriate changes to the equations that follow. The final answer is the same.</div>

To determine the equilibrium constant for this reaction, we note that it is the sum of five reactions, each with a standard equilibrium constant; thus
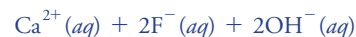
$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2F^-\,(aq)$$

$$F^-\,(aq) + H_2O\,(l) \rightleftharpoons HF\,(aq) + OH^-\,(aq)$$

$$F^-\,(aq) + H_2O\,(l) \rightleftharpoons HF\,(aq) + OH^-\,(aq)$$

$$H_3O^+\,(aq) + OH^-\,(aq) \rightleftharpoons 2H_2O\,(l)$$

$$H_3O^+\,(aq) + OH^-\,(aq) \rightleftharpoons 2H_2O\,(l)$$

$$K = K_{sp,CaF_2} \times (K_{b,F^-})^2 \times (K_w)^{-2}$$
$$= K_{sp,CaF_2} \times \left(\frac{K_w}{K_{a,HF}}\right)^2 \times \left(\frac{1}{K_w}\right)^2$$
$$= \frac{K_{sp,CaF_2}}{(K_{a,HF})^2} = \frac{3.9 \times 10^{-11}}{(6.8 \times 10^{-4})^2} = 8.4 \times 10^{-5}$$

The following table defines the equilibrium concentrations of Ca^{2+}, HF, and H_3O^+ in terms of their concentrations in the solution prior to adding CaF_2, and the change in their concentrations due to the solubility reaction; for H_3O^+, note that its concentration does not change because the solution is buffered.

		$CaF_2 (s)$	$+$	$2H_3O^+$	$\rightleftharpoons$	Ca^{2+}	$+$	$2HF$	$+$	$2H_2O (l)$
I		—		0.010		0		0		—
C		—		—		$+x$		$+2x$		—
E		—		0.010		x		$2x$		—

Substituting the equilibrium concentrations into the reaction's equilibrium constant expression

$$K = \frac{[Ca^{2+}][HF]^2}{[H_3O^+]^2} = \frac{(x)(2x)^2}{(0.010)^2} = \frac{4x^3}{(0.010)^2} = 8.4 \times 10^{-5}$$

and solving gives x as 1.3×10^{-3}. The molar solubility of CaF_2 at a pH of 2.00 is the concentration of Ca^{2+}, which is x or 1.3×10^{-3} M. Our solution here assumes that we can ignore the presence of F^-; as a check on this assumption, we note that

$$[F^-] = \frac{K_{a,HF}[HF]}{[H_3O^+]} = \frac{(6.8 \times 10^{-4})(1.3 \times 10^{-3})}{0.01} = 8.8 \times 10^{-5}$$

a concentration that is negligible when compared to the concentration of HF.

12. The solubility of $Mg(OH)_2$ is determined by the following reaction

$$Mg(OH)_2 (s) \rightleftharpoons Mg^{2+} (aq) + 2OH^- (aq)$$
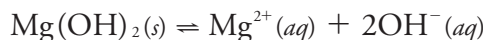
for which the equilibrium constant expression is

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 7.1 \times 10^{-12}$$

The following table defines the equilibrium concentrations of Mg^{2+} and OH^- in terms of their concentrations in the solution prior to adding CaF_2 and the change in their concentrations due to the solubility reaction; note that the concentration of OH^- is fixed by the buffer.

		$Mg(OH)_2 (s)$	$\rightleftharpoons$	$Mg^{2+} (aq)$	$+$	$2OH^- (aq)$
I		—		0		1.0×10^{-7}
C		—		$+x$		—
E		—		x		1.0×10^{-7}

Substituting the equilibrium concentrations into the K_{sp} expression

$$K_{sp} = [Mg^{2+}][OH^-]^2 = (x)(1.0 \times 10^{-7})^2 = 7.1 \times 10^{-12}$$

and solving gives x as 710. The molar solubility of $Mg(OH)_2$ at a pH of 7.00 is the concentration of Mg^{2+}, which is x or 710 M; clearly, $Mg(OH)_2$ is very soluble in a pH 7.00 buffer.

If the solution is not buffered, then we have

	$Mg(OH)_2(s)$	$\rightleftharpoons$	$Mg^{2+}(aq)$	+	$2OH^-(aq)$
I	—		0		1.0×10^{-7}
C	—		$+x$		$+2x$
E	—		x		$(1.0 \times 10^{-7}) + 2x$

and substituting into the equilibrium constant expression

$$K_{sp} = [Mg^{2+}][OH^-]^2 = (x)\{(1.0 \times 10^{-7}) + 2x)\}^2 = 7.1 \times 10^{-12}$$

leaves us with an equation that is not easy to solve exactly. To simplify the problem, lets assume that x is sufficiently large that

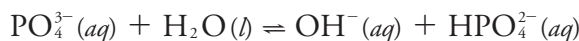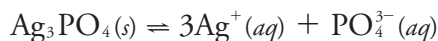$$(1.0 \times 10^{-7}) + 2x \approx 2x$$

Substituting back

$$K_{sp} = [Mg^{2+}][OH^-]^2 = (x)(2x)^2 = 4x^3 = 7.1 \times 10^{-12}$$

and solving gives x as 1.2×10^{-4}. Checking our one assumption, we note that it is reasonable: 1.0×10^{-7} is less than 5% of $2x$. The molar solubility of $Mg(OH)_2$ is the concentration of Mg^{2+}, which is x or 1.2×10^{-4} M; clearly, $Mg(OH)_2$ is much less soluble in the unbuffered solution.

13. Because PO_4^{3-} is a weak base, the molar solubility of Ag_3PO_4 depends on the solution's pH and the specific form of phosphate present. The ladder diagram for H_3PO_4, which is included in Figure SM6.1, shows that HPO_4^{2-} is the only significant form of phosphate at a pH of 9.00, which means the solubility of Ag_3PO_4 is determined by the reaction
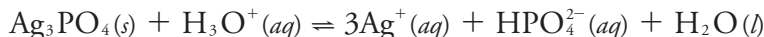
$$Ag_3PO_4(s) + H_3O^+(aq) \rightleftharpoons 3Ag^+(aq) + HPO_4^{2-}(aq) + H_2O(l)$$

To determine the equilibrium constant for this reaction, we note that it is the sum of three reactions, each with a standard equilibrium constant; thus

$$Ag_3PO_4(s) \rightleftharpoons 3Ag^+(aq) + PO_4^{3-}(aq)$$

$$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HPO_4^{2-}(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

$$K = K_{sp,Ag_3PO_4} \times K_{b,PO_4^{3-}} \times (K_w)^{-1} = K_{sp,Ag_3PO_4} \times \frac{K_w}{K_{a,HPO_4^{2-}}} \times \frac{1}{K_w}$$

$$= \frac{K_{sp,Ag_3PO_4}}{K_{a,HPO_4^{2-}}} = \frac{2.8 \times 10^{-18}}{4.5 \times 10^{-13}} = 6.2 \times 10^{-6}$$

The following table defines the equilibrium concentrations of Ag^+, HPO_4^{2-}, and H_3O^+ in terms of their concentrations in the solution prior to adding Ag_3PO_4, and the change in their concentrations due to the solubility reaction; for H_3O^+, note that its concentration does not change because the solution is buffered.

$$\begin{array}{c|ccccc} & Ag_3PO_4(s) & + & H_3O^+ & \rightleftharpoons & 3Ag^+ & + & HPO_4^{2-} & + & H_2O(l) \\ \hline I & - & & 1.0 \times 10^{-9} & & 0 & & 0 & & - \\ C & - & & - & & +3x & & +x & & - \\ E & - & & 1.0 \times 10^{-9} & & 3x & & x & & - \end{array}$$

Substituting the equilibrium concentrations into the reaction's equilibrium constant expression

$$K = \frac{[Ag^+]^3 [HPO_4^{2-}]}{[H_3O^+]} = \frac{(3x)^3(x)}{1.0 \times 10^{-9}} = \frac{27x^4}{1.0 \times 10^{-9}} = 6.2 \times 10^{-6}$$

and solving gives x as 1.2×10^{-4}. The molar solubility of Ag_3PO_4 at a pH of 2.00 is the concentration of HPO_4^{2-}, which is x or 1.2×10^{-4} M. Our solution here assumes that we can ignore the presence of other phosphate species; as a check on this assumption, we note that

$$[PO_4^{3-}] = \frac{K_{a,HPO_4^{2-}}[HPO_4^{2-}]}{[H_3O^+]} =$$
$$\frac{(4.5 \times 10^{-13})(1.2 \times 10^{-4})}{1.0 \times 10^{-9}} = 5.4 \times 10^{-8}$$

and that

$$[H_2PO_4^-] = \frac{[HPO_4^{2-}][H_3O^+]}{K_{a,H_2PO_4^-}} =$$
$$\frac{(1.2 \times 10^{-4})(1.0 \times 10^{-9})}{6.32 \times 10^{-8}} = 1.9 \times 10^{-6}$$

Both concentrations are less than 5% of the concentration of HPO_4^{2-}, so our assumptions are reasonable. Note that we do not need to check the assumption that the concentration of H_3PO_4 is negligible as it must be smaller than the concentration of $H_2PO_4^-$.

14. The equilibrium constants for the three reactions are

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

$$K_1 = \frac{[AgCl(aq)]}{[Ag^+][Cl^-]} = 5.01 \times 10^3$$

$$K_2 = \frac{[AgCl_2^-]}{[AgCl(aq)][Cl^-]} = 83.2$$

The concentration of AgCl(aq) is easy to determine because the denominator of K_1 is simply K_{sp}; thus

$$[AgCl(aq)] = K_1 K_{sp} = (5.01 \times 10^3)(1.8 \times 10^{-10}) = 9.0 \times 10^{-7} \text{ M}$$

To determine the concentration of the remaining species, we note that a charge balance equation requires that

$$[Ag^+] = [Cl^-] + [AgCl_2^-]$$

You may wonder why our approach to this problem does not involve setting up an ICE table. We can use an ICE table to organize our work if there is one and only one reaction that describes the equilibrium system. This is the case, for example, in Problem 10 where the solubility reaction for Hg_2Br_2 is the only reaction in solution, and the case in Problem 11 because only one reaction contributes significantly to the equilibrium condition. For more complicated systems, such as Problem 14 and several that follow, we must work with multiple equations, often solving them simultaneously.

Given that the concentration of AgCl(aq) is 9.0×10^{-7}, it seems reasonable to assume that the concentration of $AgCl_2^-$ is less than this and that we can simplify the charge balance equation to

$$[Ag^+] = [Cl^-] = x$$

Substituting into the K_{sp} equation

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.8 \times 10^{-10}$$

and solving gives x as 1.3×10^{-5}; thus, both the $[Ag^+]$ and the $[Cl^-]$ are 1.3×10^{-5} M. To check our assumption, we note that

$$[AgCl_2^-] = K_2[AgCl(aq)][Cl^-]$$
$$= (83.2)(9.0 \times 10^{-7})(1.3 \times 10^{-5}) = 9.7 \times 10^{-10}$$

the concentration of $AgCl_2^-$ is 9.7×10^{-10} M; thus, our assumption that we can ignore the concentration of $AgCl_2^-$ is reasonable.

15. (a) A solution of 0.050 M NaCl is 0.050 M in Na^+ and 0.050 M in Cl^-; thus

$$\mu = \frac{1}{2}\{(0.050)(+1)^2 + (0.050)(-1)^2\} = 0.050 \text{ M}$$

(b) A solution of 0.025 M $CuCl_2$ is 0.025 M in Cu^{2+} and 0.050 M in Cl^-; thus

$$\mu = \frac{1}{2}\{(0.025)(+2)^2 + (0.050)(-1)^2\} = 0.075 \text{ M}$$

(c) A solution of 0.10 M Na_2SO_4 is 0.20 M in Na^+ and 0.10 M in SO_4^{2-}; thus

$$\mu = \frac{1}{2}\{(0.20)(+1)^2 + (0.10)(-2)^2\} = 0.30 \text{ M}$$

16. (a) From Problem 10a, we know that the molar solubility of Hg_2Br_2 is sufficiently small that the solution's ionic strength is not altered significantly by the limited number of Hg_2^{2+} and Br^- ions in solution. The molar solubility remains 2.4×10^{-8} M.

(b) From Problem 10b we know that the molar solubility of Hg_2Br_2 is sufficiently small that the solution's ionic strength is not altered significantly by the limited number of Br^- ions or Hg_2^{2+} ions arising from the solubility reaction; however, we cannot ignore the contribution of $Hg_2(NO_3)_2$ to the solution's ionic strength, which is

$$\mu = \frac{1}{2}\{(0.025)(+2)^2 + (0.050)(-1)^2\} = 0.075 \text{ M}$$

Given the ionic strength, we next find the activity coefficients for Hg_2^{2+} and for Br^-; thus

$$-\log\gamma_{Hg_2^{2+}} = \frac{(0.51)(+2)^2\sqrt{0.075}}{1 + (3.3)(0.40)\sqrt{0.075}} = 0.410$$
$$\gamma_{Hg_2^{2+}} = 0.389$$

As we must form AgCl(aq) before we can form $AgCl_2^-$, the concentration of $AgCl_2^-$ will be less than [AgCl(aq)] unless there is a large excess of Cl^-.

Note that we did not include H_3O^+ and OH^- when calculating the ionic strength of these solutions because their concentrations are sufficiently small that they will not affect the ionic strength within the limit of our significant figures.

The same reasoning explains why we did not consider the acid-base chemistry of SO_4^{2-} in part (c) as the concentrations of H_3O^+, OH^-, and HSO_4^- are sufficiently small that we can safely ignore them.

$$-\log \gamma_{Br^-} = \frac{(0.51)(-1)^2 \sqrt{0.075}}{1 + (3.3)(0.30)\sqrt{0.075}} = 0.110$$

$$\gamma_{Br^-} = 0.776$$

where values of alpha are from Table 6.2. The ionic strength-adjusted K_{sp} for the solubility of Hg_2Br_2 is

$$K_{sp} = [Hg_2^{2+}][Br^-]^2 \gamma_{Hg_2^{2+}} \gamma_{Br^-}^2 = 5.6 \times 10^{-23}$$

From here, we proceed as in Problem 10b; thus

$$K_{sp} = (0.025 + x)(2x)^2(0.389)(0.776)^2 = 5.6 \times 10^{-23}$$

$$\approx (0.025)(2x)^2(0.389)(0.776)^2 = 5.6 \times 10^{-23}$$

finding that x is 4.9×10^{-11} and that the molar solubility of Hg_2Br_2 of 4.9×10^{-11} M is greater than the value of 2.4×10^{-11} M that we calculated when we ignored the affect on solubility of ionic strength.

(c) From Problem 10c we know that the molar solubility of Hg_2Br_2 is sufficiently small that the solution's ionic strength is not altered significantly by the limited number of Br^- ions or Hg_2^{2+} ions arising from the solubility reaction; however, we cannot ignore the contribution of NaBr to the solution's ionic strength, which is

$$\mu = \frac{1}{2}\{(0.050)(+1)^2 + (0.050)(-1)^2\} = 0.050 \text{ M}$$

Given the ionic strength, we next find the activity coefficients for Hg_2^{2+} and for Br^-; thus

$$-\log \gamma_{Hg_2^{2+}} = \frac{(0.51)(+2)^2 \sqrt{0.050}}{1 + (3.3)(0.40)\sqrt{0.050}} = 0.352$$

$$\gamma_{Hg_2^{2+}} = 0.444$$

$$-\log \gamma_{Br^-} = \frac{(0.51)(-1)^2 \sqrt{0.050}}{1 + (3.3)(0.30)\sqrt{0.050}} = 0.0934$$

$$\gamma_{Br^-} = 0.807$$

where values of alpha are from Table 6.2. The ionic strength-adjusted K_{sp} for the solubility of Hg_2Br_2 is

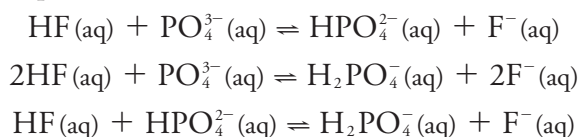$$K_{sp} = [Hg_2^{2+}][Br^-]^2 \gamma_{Hg_2^{2+}} \gamma_{Br^-}^2 = 5.6 \times 10^{-23}$$

From here, we proceed as in Problem 10c; thus

$$K_{sp} = (x)(0.050 + 2x)^2(0.444)(0.807)^2 = 5.6 \times 10^{-23}$$

$$K_{sp} \approx (x)(0.050)^2(0.444)(0.807)^2 = 5.6 \times 10^{-23}$$

finding that x is 7.7×10^{-20} and that the molar solubility of Hg_2Br_2 of 7.7×10^{-20} M is greater than the value of 2.2×10^{-20} M that we calculated when we ignored the affect on solubility of ionic strength.

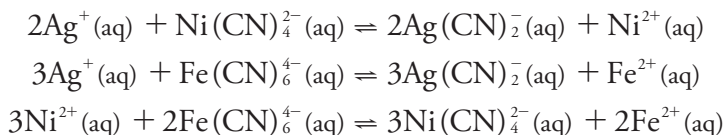17. Because phosphate is a weak base, the solubility of $Ca_3(PO_4)_2$ will increase at lower pH levels as the predominate phosphate species transitions from PO_4^{3-} to HPO_4^{2-} to $H_2PO_4^-$ to H_3PO_4. A ladder diagram for phosphate is included in Figure SM6.1 and shows that PO_4^{3-} is the predominate species for pH levels greater than 12.35; thus, to minimize the solubility of $Ca_3(PO_4)_2$ we need to maintain the pH above 12.35.

18. (a) Figure SM6.1 shows a ladder diagram for HF and H_3PO_4. Based on this ladder diagram, we expect that the weak acid HF will react with the weak bases PO_4^{3-} and HPO_4^{2-} as their areas of predominance do not overlap with HF; thus

$$HF\,(aq) + PO_4^{3-}\,(aq) \rightleftharpoons HPO_4^{2-}\,(aq) + F^-\,(aq)$$

$$2HF\,(aq) + PO_4^{3-}\,(aq) \rightleftharpoons H_2PO_4^-\,(aq) + 2F^-\,(aq)$$

$$HF\,(aq) + HPO_4^{2-}\,(aq) \rightleftharpoons H_2PO_4^-\,(aq) + F^-\,(aq)$$

We also expect that the weak base F^- will react with the weak acid H_3PO_4; thus

$$F^-\,(aq) + H_3PO_4\,(aq) \rightleftharpoons H_2PO_4^{2-}\,(aq) + HF\,(aq)$$
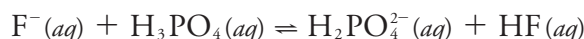
(b) Figure SM6.5 shows a ladder diagram for the cyano complexes of Ag^+, Ni^{2+}, and Fe^{2+}. Based on this ladder diagram, we expect that Ag^+ will displace Ni^{2+} from the $Ni(CN)_4^{2-}$ complex, that Ag^+ will displace Fe^{2+} from the $Fe(CN)_6^{4-}$ complex, and that Ni^{2+} will displace Fe^{2+} from the $Fe(CN)_6^{4-}$; thus

$$2Ag^+\,(aq) + Ni(CN)_4^{2-}\,(aq) \rightleftharpoons 2Ag(CN)_2^-\,(aq) + Ni^{2+}\,(aq)$$

$$3Ag^+\,(aq) + Fe(CN)_6^{4-}\,(aq) \rightleftharpoons 3Ag(CN)_2^-\,(aq) + Fe^{2+}\,(aq)$$

$$3Ni^{2+}\,(aq) + 2Fe(CN)_6^{4-}\,(aq) \rightleftharpoons 3Ni(CN)_4^{2-}\,(aq) + 2Fe^{2+}\,(aq)$$

(c) Figure SM6.6 shows a ladder diagram for the $Cr_2O_7^{2-}/Cr^{3+}$ and the Fe^{3+}/Fe^{2+} redox half-reactions. Based on this ladder diagram, we expect that Fe^{2+} will reduce $Cr_2O_7^{2-}$ to Cr^{3+}; thus

$$Cr_2O_7^{2-}\,(aq) + 6Fe^{2+}\,(aq) + 14H^+\,(aq) \rightleftharpoons$$
$$2Cr^{3+}\,(aq) + 6Fe^{3+}\,(aq) + 7H_2O\,(l)$$
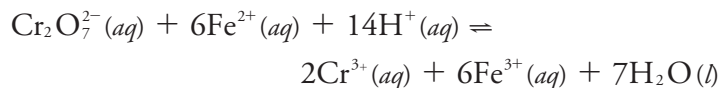
19. The pH of a buffer that contains a weak acid, HA, and its conjugate weak base, A^-, is given by equation 6.60

$$pH = pK_a + \log\frac{C_{A^-}}{C_{HA}}$$

which holds if the concentrations of OH^- and of H_3O^+ are significantly smaller than the concentrations of HA, C_{HA}, and of A^-, C_{A^-}.

(a) The pH of the buffer is
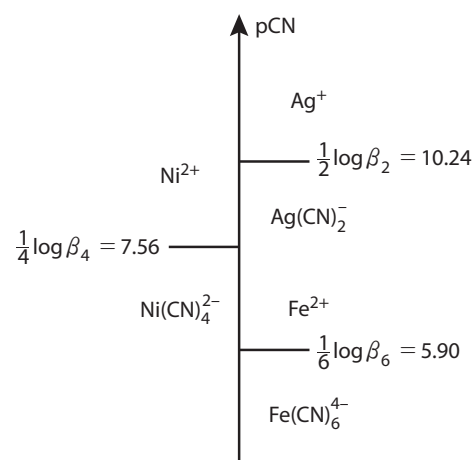
$$pH = 3.745 + \log\frac{0.015}{0.025} = 3.52$$

Figure SM6.5 Ladder diagram for Problem 18b showing the areas of predominance for Ag^+, Ni^{2+}, and Fe^{3+} and their cyano complexes.
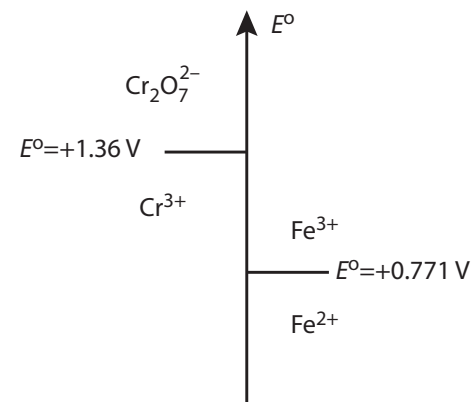

Figure SM6.6 Ladder diagram for Problem 18c showing the $Cr_2O_7^{2-}/Cr^{3+}$ and the Fe^{3+}/Fe^{2+} redox half-reactions.

With a pH of 3.52, the $[H_3O^+]$ is 3.0×10^{-4} and the $[OH^-]$ is 3.3×10^{-11}); thus, the assumptions inherent in equation 6.60 hold.

(b) A mixture consisting of an excess of a weak base, NH_3, and a limiting amount of a strong acid, HCl, will react to convert some of the NH_3 to its conjugate weak acid form, NH_4^+; thus

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$
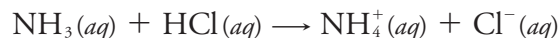
The moles of NH_4^+ formed are

$$mol\ NH_4^+ = M_{HCl}\ V_{HCl} = (1.0\ M)(0.00350\ L) = 3.50 \times 10^{-3}$$

which leaves the moles of NH_3 as

$$mol\ NH_3 = M_{NH_3} V_{NH_3} - M_{HCl} V_{HCl}$$
$$= (0.12\ M)(0.05000\ L) - (1.0\ M)(0.00350\ L)$$
$$= 2.50 \times 10^{-3}$$

The total volume is 53.50 mL, which gives the concentrations of NH_4^+ and of NH_3 as

$$[NH_4^+] = \frac{3.50 \times 10^{-3}\ mol}{0.0535\ L} = 0.0654\ M$$

$$[NH_3] = \frac{2.50 \times 10^{-3}\ mol}{0.0535\ L} = 0.0467\ M$$

and a pH of

$$pH = 9.244 + \log\frac{0.0467}{0.0654} = 9.10$$

With a pH of 9.10, the $[H_3O^+]$ is 8.0×10^{-10} and the $[OH^-]$ is 1.3×10^{-5}); thus, the assumptions inherent in equation 6.60 hold.

(c) To calculate the pH we first determine the concentration of the weak acid, HCO_3^-, and the weak base, CO_3^{2-}

$$[HCO_3^-] = \frac{5.00\ g\ NaHCO_3 \times \dfrac{1\ mol\ HCO_3^-}{84.007\ g\ NaHCO_3}}{0.100\ L} = 0.595\ M$$

$$[CO_3^{2-}] = \frac{5.00\ g\ Na_2CO_3 \times \dfrac{1\ mol\ CO_3^{2-}}{105.99\ g\ Na_2CO_3}}{0.100\ L} = 0.472\ M$$

and then the pH

$$pH = 10.329 + \log\frac{0.472}{0.595} = 10.23$$

With a pH of 10.23, the $[H_3O^+]$ is 5.9×10^{-11} and the $[OH^-]$ is 1.7×10^{-4}); thus, the assumptions inherent in equation 6.60 hold.

20. Adding 5.0×10^{-4} mol of HCl converts 5.0×10^{-4} mol of the buffer's conjugate weak base, A^-, to its conjugate weak acid, HA. To simplify the calculations, we note that we can replace the concentrations of HA and of A^- in equation 6.60 with their respective moles as both

HA and A⁻ are in the same solution and, therefore, share the same volume.

(a) The pH after adding 5.0×10^{-4} mol of HCl is

$$pH = 3.745 + \log\frac{(0.015)(0.100) - 5.00 \times 10^{-4}}{(0.025)(0.100) + 5.00 \times 10^{-4}} = 3.27$$

As expected, adding HCl makes the solution more acidic, with the pH decreasing from 3.52 to 3.27.

With a pH of 3.27, the $[H_3O^+]$ is 5.4×10^{-4} and the $[OH^-]$ is 1.9×10^{-11}); thus, the assumptions inherent in equation 6.60 hold.

(b) The pH after adding 5.0×10^{-4} mol of HCl is

$$pH = 9.244 + \log\frac{(0.0467)(0.0535) - 5.00 \times 10^{-4}}{(0.0654)(0.0535) + 5.00 \times 10^{-4}} = 8.94$$

As expected, adding HCl makes the solution more acidic, with the pH decreasing from 9.01 to 8.94.

With a pH of 8.94, the $[H_3O^+]$ is 1.1×10^{-9} and the $[OH^-]$ is 9.1×10^{-6}); thus, the assumptions inherent in equation 6.60 hold.

(c) The pH after adding 5.0×10^{-4} mol of HCl is

$$pH = 10.329 + \log\frac{(0.472)(0.100) - 5.00 \times 10^{-4}}{(0.595)(0.100) + 5.00 \times 10^{-4}} = 10.22$$

As expected, adding HCl makes the solution more acidic, with the pH decreasing from 10.23 to 10.22; the change in pH is smaller here because the concentration of the buffering agents is larger.

With a pH of 10.22, the $[H_3O^+]$ is 6.0×10^{-11} and the $[OH^-]$ is 1.7×10^{-4}); thus, the assumptions inherent in equation 6.60 hold.

21. Adding 5.0×10^{-4} mol of NaOH converts 5.0×10^{-4} mol of the buffer's conjugate weak base, HA, to its conjugate weak acid, A⁻. To simplify the calculations, we note that we can replace the concentrations of HA and of A⁻ in equation 6.60 with their respective moles as both HA and A⁻ are in the same solution and, therefore, share the same volume.

(a) The pH after adding 5.0×10^{-4} mol of NaOH is

$$pH = 3.745 + \log\frac{(0.015)(0.100) + 5.00 \times 10^{-4}}{(0.025)(0.100) - 5.00 \times 10^{-4}} = 3.74$$

As expected, adding NaOH makes the solution more basic, with the pH increasing from 3.52 to 3.74.

With a pH of 3.74, the $[H_3O^+]$ is 1.8×10^{-4} and the $[OH^-]$ is 5.5×10^{-11}); thus, the assumptions inherent in equation 6.60 hold.

(b) The pH after adding 5.0×10^{-4} mol of NaOH is

$$pH = 9.244 + \log\frac{(0.0467)(0.0535) + 5.00 \times 10^{-4}}{(0.0654)(0.0535) - 5.00 \times 10^{-4}} = 9.24$$

As expected, adding NaOH makes the solution more basic, with the pH increasing from 9.01 to 9.24.

With a pH of 9.24, the $[H_3O^+]$ is 5.8×10^{-10} and the $[OH^-]$ is 1.7×10^{-5}); thus, the assumptions inherent in equation 6.60 hold.

(c) The pH after adding 5.0×10^{-4} mol of NaOH is

$$pH = 10.329 + \log\frac{(0.472)(0.100) + 5.00 \times 10^{-4}}{(0.595)(0.100) - 5.00 \times 10^{-4}} = 10.24$$

As expected, adding NaOH makes the solution more basic, with the pH increasing from 10.23 to 10.22; the change in pH is smaller here because the concentration of the buffering agents is larger.

With a pH of 10.24, the $[H_3O^+]$ is 5.8×10^{-11} and the $[OH^-]$ is 1.7×10^{-4}); thus, the assumptions inherent in equation 6.60 hold.

22. (a) The equilibrium constant for the reaction is

$$K_1 = \frac{[ML]}{[M][L]}$$

Taking the log of both sides of this equation gives

$$\log K_1 = \log\frac{[ML]}{[L]} - \log[M] = \log\frac{[ML]}{[L]} + pM$$

which, upon rearranging, gives the desired equation

$$pM = \log K_1 - \log\frac{[ML]}{[L]}$$

For the case where K_1 is 1.5×10^8 we have

$$pM = \log(1.5 \times 10^8) - \log\frac{[ML]}{[L]} = 8.18 - \log\frac{[ML]}{[L]}$$

(b) Because the reaction between M and L is very favorable, we expect that all of M, which is the limiting reagent, is converted to ML, consuming an equivalent amount of L. Once equilibrium is reached, 0.010 mol of L remain and 0.010 mol of ML are formed, which gives

$$pM = 8.18 - \log\frac{0.010}{0.010} = 8.18$$

(c) Adding an additional 0.002 mol M converts an additional 0.002 mol of L to ML; thus, we now have 0.012 mol ML and 0.008 mol L, and pM is

$$pM = 8.18 - \log\frac{0.012}{0.008} = 8.00$$

23. The potential of a redox buffer is given by the Nernst equation

$$E = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Because Fe^{2+} and Fe^{3+} are in the same solution, we can replace their concentrations in the Nernst equation with moles; thus
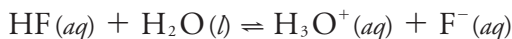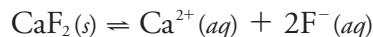
$$E = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{mol\ Fe^{2+}}{mol\ Fe^{3+}} =$$

$$0.771 - 0.05916\log\frac{0.015}{0.010} = 0.761\ V$$

After converting 0.002 mol Fe^{2+} to Fe^{3+}, the solution contains 0.013 mol Fe^{2+} and 0.012 mol Fe^{3+}; the potential, therefore, is

$$E = 0.771 - 0.05916\log\frac{0.013}{0.012} = 0.769\ V$$

24. A general approach to each problem is provided here, but more specific details of setting up an Excel spreadsheet or writing a function in R are left to you; see Section 6J for more details.

(a) To find the solubility of CaF_2 we first write down all relevant equilibrium reactions; these are

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2F^-\,(aq)$$

$$HF\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + F^-\,(aq)$$

$$2H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

There are five species whose concentrations define this system (Ca^{2+}, F^-, HF, H_3O^+, and OH^-), which means we need five equations that relate the concentrations of these species to each other; these are the three equilibrium constant expressions

$$K_{sp} = [Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.8 \times 10^{-4}$$

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

a charge balance equation

$$2[Ca^{2+}] + [H_3O^+] = [OH^-] + [F^-]$$

and a mass balance equation

$$2 \times [Ca^{2+}] = [HF] + [F^-]$$

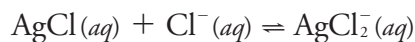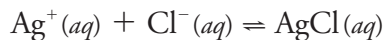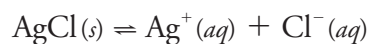Be sure you understand why the concentration of Ca^{2+} is multiplied by 2.

To solve this system of five equations, we make a guess for $[Ca^{2+}]$, and then use K_{sp} to calculate $[F^-]$, the mass balance equation to calculate $[HF]$, K_a to calculate $[H_3O^+]$, and K_w to calculate $[OH^-]$. We evaluate each guess by rewriting the charge balance equation as an error function

$$error = 2 \times [Ca^{2+}] + [H_3O^+] - [OH^-] - [F^-]$$

searching for a $[Ca^{2+}]$ that gives an error sufficiently close to zero. Successive iterations over a narrower range of concentrations for Ca^{2+} will lead you to a equilibrium molar solubility of 2.1×10^{-4} M.

(b) To find the solubility of AgCl we first write down all relevant equilibrium reactions; these are

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(aq)$$

$$AgCl(aq) + Cl^-(aq) \rightleftharpoons AgCl_2^-(aq)$$

$$AgCl_2^-(aq) + Cl^-(aq) \rightleftharpoons AgCl_3^-(aq)$$

$$AgCl_3^-(aq) + Cl^-(aq) \rightleftharpoons AgCl_4^-(aq)$$
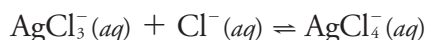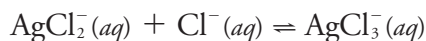
There are six species whose concentrations define this system (Ag^+, Cl^-, AgCl(aq), $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$), which means we need six equations that relate the concentrations of these species to each other; these are the five equilibrium constant expressions

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

$$K_1 = \frac{[AgCl(aq)]}{[Ag^+][Cl^-]} = 5.01 \times 10^3$$

$$K_2 = \frac{[AgCl_2^-]}{[AgCl\,(aq)]\,[Cl^-]} = 83.2$$

$$K_3 = \frac{[AgCl_3^{2-}]}{[AgCl_2^-]\,[Cl^-]} = 6.03$$

$$K_4 = \frac{[AgCl_4^{3-}]}{[AgCl_3^{2-}]\,[Cl^-]} = 0.501$$

and a charge balance equation
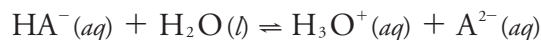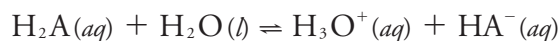
$$[Ag^+] = [Cl^-] + [AgCl_2^-] + 2 \times [AgCl_3^{2-}] + 3 \times [AgCl_4^{3-}]$$

To solve this system of five equations, we make a guess for $[Ag^+]$, and then use K_{sp} to calculate $[Cl^-]$, K_1 to calculate $[AgCl(aq)]$, K_2 to calculate $[AgCl_2^-]$, K_3 to calculate $[AgCl_3^{2-}]$, and K_4 to calculate $[AgCl_4^{3-}]$. We evaluate each guess by rewriting the charge balance equation as an error function

$$\text{error} = [Ag^+] - [Cl^-] - [AgCl_2^-] - 2 \times [AgCl_3^{2-}] - 3 \times [AgCl_4^{3-}]$$

searching for a $[Ag^+]$ that gives an error sufficiently close to zero. Successive iterations over a narrower range of concentrations for Ag^+ will lead you to a equilibrium molar solubility of 1.3×10^{-5} M.

(c) To find the pH of 0.10 M fumaric acid we first write down all relevant equilibrium reactions; letting H_2A represent fumaric acid, these are

$$H_2A\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HA^-\,(aq)$$

$$HA^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^{2-}\,(aq)$$

$$2H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

There are five species whose concentrations define this system (H_2A, HA^-, A^{2-}, H_3O^+, and OH^-), which means we need five equations that relate the concentrations of these species to each other; these are the three equilibrium constant expressions

$$K_{a1} = \frac{[H_3O^+]\,[HA^-]}{[H_2A]} = 8.85 \times 10^{-4}$$

$$K_{a2} = \frac{[H_3O^+]\,[A^{2-}]}{[HA^-]} = 3.21 \times 10^{-5}$$

$$K_w = [H_3O^+]\,[OH^-] = 1.00 \times 10^{-14}$$

a charge balance equation

$$[H_3O^+] = [OH^-] + [HA^-] + 2 \times [A^{2-}]$$

and a mass balance equation

$$0.10\,M = [H_2A] + [HA^-] + [A^{2-}]$$

To solve this system of five equations, we make a guess for the pH, calculate $[H_3O^+]$ and use K_w to calculate $[OH^-]$. Because each of the remaining equations include at least two of the remaining species, we must combine one or more of these equations to isolate a single species. There are several ways to accomplish this, one of which is to use K_{a1} to express $[HA^-]$ in terms of $[H_2A]$, and to use K_{a1} and K_{a2} to express $[A^{2-}]$ in terms of $[H_2A]$

$$[HA^-] = \frac{K_{a1}[H_2A]}{[H_3O^+]}$$

$$[A^{2-}] = \frac{K_{a2}[HA^-]}{[H_3O^+]} = \frac{K_{a1}K_{a2}[H_2A]}{[H_3O^+]^2}$$

and then substitute both into the mass balance equation

$$0.10\,M = [H_2A] + \frac{K_{a1}[H_2A]}{[H_3O^+]} + \frac{K_{a1}K_{a2}[H_2A]}{[H_3O^+]^2}$$

$$= [H_2A] \times \left\{ 1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2} \right\}$$

which we use to calculate $[H_2A]$. Finally, we calculate $[HA^-]$ using K_{a1} and $[A^{2-}]$ using K_{a2}. We evaluate each guess by rewriting the charge balance equation as an error function

$$\text{error} = [H_3O^+] - [OH^-] - [HA^-] - 2 \times [A^{2-}]$$

searching for a pH that gives an error sufficiently close to zero. Successive iterations over a narrower range of pH values will lead you to a equilibrium pH of 2.05.

25. The four equations that describe the composition of an equilibrium solution of HF are the K_a and K_w equilibrium constant expressions

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$K_w = [H_3O^+][OH^-]$$

a charge balance equation

$$[H_3O^+] = [OH^-] + [F^-]$$

and a mass balance equation

$$C_{HF} = [HF] + [F^-]$$

To combine the equations, we first use the mass balance equation to express [HF] in terms of C_{HF} and $[F^-]$

$$[HF] = C_{HF} - [F^-]$$

and then substitute this into the K_a expression

$$K_a = \frac{[H_3O^+][F^-]}{C_{HF} - [F^-]}$$

which we then solve for $[F^-]$

$$K_a C_{HF} - K_a[F^-] = [H_3O^+][F^-]$$

$$K_a C_{HF} = [H_3O^+][F^-] + K_a[F^-]$$

$$[F^-]\{[H_3O^+] + K_a\} = K_a C_{HF}$$

$$[F^-] = \frac{K_a C_{HFa}}{[H_3O^+] + K_a}$$

Next, we solve K_w for $[OH^-]$

$$[OH^-] = \frac{K_w}{[H_3O^+]}$$

and then substitute this and the equation for $[F^-]$ into the charge balance equation

$$[H_3O^+] = \frac{K_w}{[H_3O^+]} + \frac{K_a C_{HF}}{[H_3O^+] + K_a}$$

Rearranging this equation

$$[H_3O^+] - \frac{K_w}{[H_3O^+]} - \frac{K_a C_{HFa}}{[H_3O^+] + K_a} = 0$$

multiplying through by $[H_3O^+]$

$$[H_3O^+]^2 - K_w - \frac{K_a C_{HF}[H_3O^+]}{[H_3O^+] + K_a} = 0$$

multiplying through by $[H_3O^+] + K_a$

$$[H_3O^+]^3 + K_a[H_3O^+]^2 - K_w[H_3O^+] -$$
$$K_a K_w - K_a C_{HF}[H_3O^+] = 0$$

and gathering terms leaves us with the final equation

$$[H_3O^+]^3 + K_a[H_3O^+]^2 - (K_a C_{HF} + K_w)[H_3O^+] - K_a K_w = 0$$