

17 Additional Aspects of Aqueous Equilibria

Visualizing Concepts

- 17.1 *Analyze.* Given diagrams showing equilibrium mixtures of HX and X^- with different compositions, decide which has the highest pH. HX is a weak acid and X^- is its conjugate base. *Plan.* Evaluate the contents of the boxes. Use acid-base equilibrium principles to relate $[H^+]$ to box composition. *Solve.*

Use the following acid ionization equilibrium to describe the mixtures:

$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$. Each box has 4 HX molecules, but differing amounts of X^- ions. The greater the amount of X^- (conjugate base), for the same amount of HX (weak acid), the lower the amount of H^+ and the higher the pH. The middle box, with most X^- , has least H^+ and highest pH.

- 17.2 (a) According to Figure 16.7, methyl orange is yellow above pH 4.5 and red (really pink) below pH 3.5. The beaker on the left has a pH greater than 4.5, and the one on the right has pH less than 3.5. (By calculation, pH of left beaker = 4.7, pH of right beaker = 2.9.) The right beaker, with lower pH and greater $[H^+]$, is pure acetic acid. The left beaker contains equal amounts of the weak acid and its conjugate base, acetic acid and acetate ion. Adding the "common-ion" acetate (in the form of sodium acetate) shifts the acid ionization equilibrium to the left, decreases $[H^+]$, and raises pH.
- (b) When small amounts of NaOH are added, the left beaker is better able to maintain its pH. For solutions of the same weak acid, pH depends on the ratio of conjugate base to conjugate acid. Small additions of base (or acid) have the least effect when this ratio is close to one. The left beaker is a buffer because it contains a weak conjugate acid-conjugate base pair and resists rapid pH change upon addition of small amounts of strong base or acid.
- 17.3 $[HX] > [X^-]$. Buffers prepared from weak acids (HX) and their conjugate bases (X^- , usually in the form of a salt) have pH values in a range of approximately 2 pH units, centered around pK_a for the weak acid. If concentration of the weak acid is greater than concentration of the conjugate base, $pH < pK_a$. If concentration of the conjugate base is greater than concentration of the weak acid, $pH > pK_a$. This is generally true for buffers containing a weak conjugate acid (CA) and conjugate base (CB) pair.

$[CA] > [CB]$, pH of buffer $< pK_a$ of CA

$[CA] < [CB]$, pH of buffer $> pK_a$ of CA

- 17.4 *Analyze/Plan.* When strong acid is added to a buffer, it reacts with conjugate base (CB) to produce conjugate acid (CA). [CA] increases and [CB] decreases. The opposite happens when strong base is added to a buffer, [CB] increases and [CA] decreases. Match these situations to the drawings. *Solve.*

The buffer begins with equal concentrations of HX and X^- .

- After addition of strong acid, [HX] will increase and $[X^-]$ will decrease. Drawing (3) fits this description.
- Adding of strong base causes [HX] to decrease and $[X^-]$ to increase. Drawing (1) matches the description.
- Drawing (2) shows both [HX] and $[X^-]$ to be smaller than the initial concentrations shown on the left. This situation cannot be achieved by adding strong acid or strong base to the original buffer.

- 17.5 *Analyze/Plan.* Consider the reaction $HA + OH^- \rightarrow A^- + H_2O$. What are the major species present in solution at the listed stages of the titration? Which diagram represents these species? *Solve.*

- Before addition of NaOH, the solution is mostly HA. The only A^- is produced by the ionization equilibrium of HA and is too small to appear in the diagram. This situation is shown in diagram (iii), which contains only HA.
- After addition of NaOH but before the equivalence point, some, but not all, HA has been converted to A^- . The solution contains a mixture of HA and A^- ; this is shown in diagram (i).
- At the equivalence point, all HA has been converted to A^- , with no excess HA or OH^- present. This is shown in diagram (iv).
- After the equivalence point, the same amount of A^- is present as at the equivalence point, plus some excess OH^- . This is diagram (ii).

- 17.6 *Analyze/Plan.* In each case, the first substance is in the buret, and the second is in the flask. If acid is in the flask, the initial pH is low; with base in the flask, the pH starts high. Strong acids have lower pH than weak acids; strong bases have higher pH than weak bases. Polyprotic acids and bases have more than one "jump" in pH.

- Strong base in flask, pH starts high, ends low as acid is added. Only diagram (ii) fits this description.
- Weak acid in flask, pH starts low, but not extremely low. Diagrams (i), (iii), and (iv) all start at low pH and get higher. Diagram (i) has very low initial pH, and likely has strong acid in the flask. Diagram (iv) has two pH jumps, so it has a polyprotic acid in the flask. Diagram (iii) best fits the profile of adding a strong base to a weak acid.
- Strong acid in the flask, pH starts very low, diagram (i).
- Polyprotic acid, more than one pH jump, diagram (iv).

17.7 *Analyze.* Given two titration curves where 0.10 M NaOH is the titrant, decide which represents the more concentrated acid, and which the stronger acid.

Plan. For equal volumes of acid, concentration is related to volume of titrant (0.10 M NaOH) at the equivalence points. To determine K_a , $\text{pH} = \text{p}K_a$ half-way to the equivalence point.

Solve.

(a) Both acids have one ionizable hydrogen, because there is one "jump" in each titration curve. For equal volumes of acid, and the same titrant, the more concentrated acid requires a greater volume of titrant to reach equivalence. The equivalence point of the blue curve is at 25 mL NaOH, the red curve at 35 mL NaOH. The red acid is more concentrated.

(b) According to the Henderson-Hasselbach equation, $\text{pH} = \text{p}K_a + \log \frac{[\text{conj. base}]}{[\text{conj. acid}]}$. At half-way to the equivalence point, $[\text{conj. acid}] = [\text{conj. base}]$ and $\text{pH} = \text{p}K_a$ of the conjugate acid. For the blue curve, half-way is 12.5 mL NaOH. The pH at this volume is approximately 7.0. For the red curve, half-way is 17.5 mL NaOH. The pH at this volume is approximately 4.2. A $\text{p}K_a$ of 7 corresponds to K_a of 1×10^{-7} , while $\text{p}K_a$ of 4.2 corresponds to K_a of 6×10^{-5} . The red acid has the larger K_a value.

Note that the stronger acid, the one with the larger K_a value, has a larger change in pH (jump) at the equivalence point. Also note that initial acid pH was not a definitive measure of acid strength, because the acids have different starting concentrations. Both K_a values and concentration contribute to solution pH.

17.8 *Analyze/Plan.* The product of the ion concentrations in a saturated solution equals K_{sp} . Use numbers of anions and cations as a measure of concentration to calculate relative " K_{sp} " values. Counting cations is not adequate, because excess anions in some of the boxes drive down the cation concentrations. Ion-products must be considered.

Solve.



AgY has the smallest K_{sp} .

17.9 *Analyze/Plan.* Consider the solubility equilibrium $\text{MX(s)} \rightleftharpoons \text{M}^{2+}(\text{aq}) + \text{X}^{2-}(\text{aq})$, as well as the effects of common ions and competing equilibria.

(a) In pure water, the dissociation of MX is the only source of M^{2+} and X^{2-} , so the numbers of each ion are equal (ignoring any hydrolysis of X^{2-}). This describes figure (b).

(b) If MX(s) is dissolved in $\text{Na}_2\text{X(aq)}$, $\text{X}^{2-}(\text{aq})$ is a common ion. There are two sources of X^{2-} dissociation of MX(s) and $\text{Na}_2\text{X(aq)}$. There will be more X^{2-} than M^{2+} in the resulting solution. This describes figure (c).

- (c) If X^{2-} is a basic anion, it will combine with $2H^+(aq)$ to form H_2X molecules, which are not shown in the figures. This will reduce the number of free X^{2-} ions, and the solution will contain more M^{2+} than X^{2-} . This describes figure (a).
- (d) K_{sp} will have the same value in each of the three scenarios. While the presence of a common ion or hydrolysis of an anion changes the solubility of MX , the value of K_{sp} is constant at a specified temperature.

17.10 *Analyze/Plan.* Common anions or cations decrease the solubility of salts. Ions that participate in acid-base or complex ion equilibria increase solubility. *Solve.*

- (a) CO_2^{3-} from $BaCO_3$ reacts with H^+ from HNO_3 , causing solubility of $BaCO_3$ to increase with increasing HNO_3 concentration. This behavior matches the right diagram.
- (b) Extra CO_2^{3-} from Na_2CO_3 decreases the solubility of $BaCO_3$. Solubility of $BaCO_3$ decreases as $[Na_2CO_3]$ increases. This behavior matches the left diagram.
- (c) $NaNO_3$ has no common ions, nor does it enter into acid-base or complex ion equilibria with Ba^{2+} or CO_3^{2-} ; it does not affect the solubility of $BaCO_3$. This behavior is shown in the center diagram.

17.11 A metal hydroxide that is soluble at very low and very high pH's, that is, in strong acid or strong base, is called amphoteric.

17.12 According to Figure 17.22, the two precipitating agents are 6 M HCl (first) and H_2S in 0.2 M HCl (second).

Cation A = Ag^+ (precipitates as $AgCl$)

Cation B = Cu^+ (precipitates as Cu_2S , acid insoluble)

Cation C = Ni^{2+} (remains in acidic solution)

Common-Ion Effect

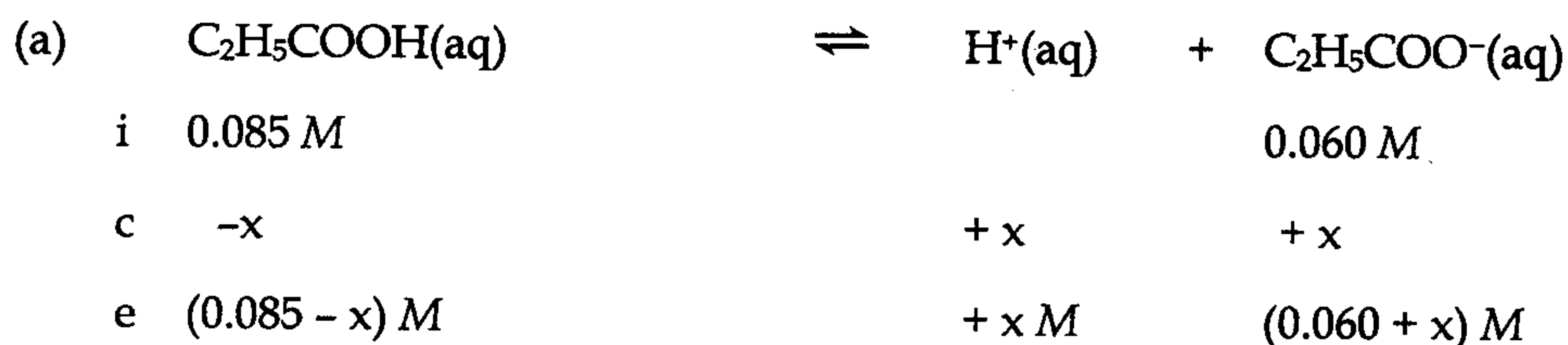
17.13 (a) The extent of ionization of a weak electrolyte is decreased when a strong electrolyte containing an ion in common with the weak electrolyte is added to it.

(b) $NaNO_2$

17.14 (a) For a generic weak base B, $K_b = \frac{[HB^+][OH^-]}{[B]}$. If an external source of HB^+ such as HB^+Cl^- is added to a solution of $B(aq)$, $[HB^+]$ increases, decreasing $[OH^-]$ and increasing $[B]$, effectively suppressing the ionization (hydrolysis) of B.

(b) NH_4Cl

17.15 *Analyze/Plan.* Follow the logic in Sample Exercise 17.1.

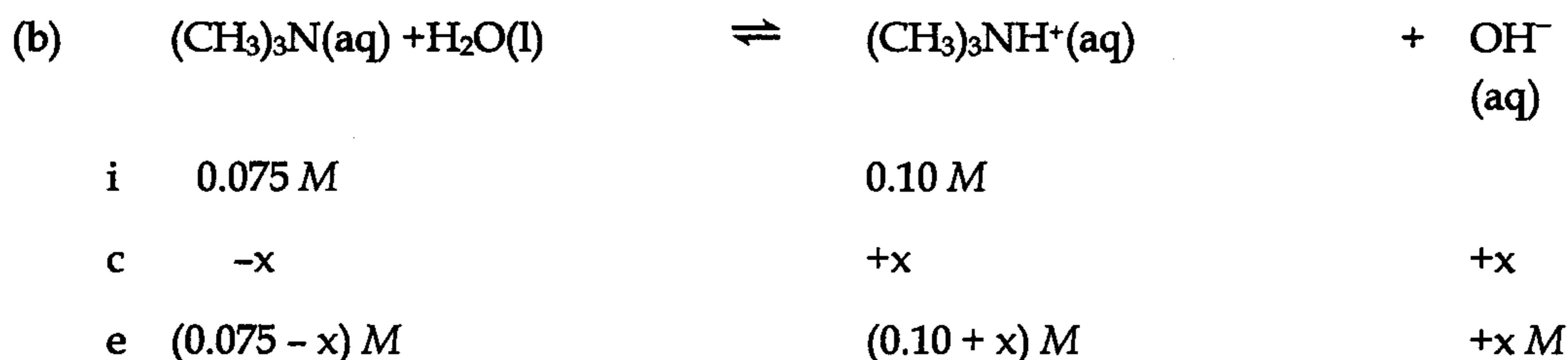


$$K_a = 1.3 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]} = \frac{(x)(0.060+x)}{(0.085-x)}$$

Assume x is small compared to 0.060 and 0.085.

$$1.3 \times 10^{-5} = \frac{0.060x}{0.085}; x = 1.8 \times 10^{-5} = [\text{H}^+], \text{pH} = 4.73$$

Check. Since the extent of ionization of a weak acid or base is suppressed by the presence of a conjugate salt, the 5% rule usually holds true in buffer solutions.



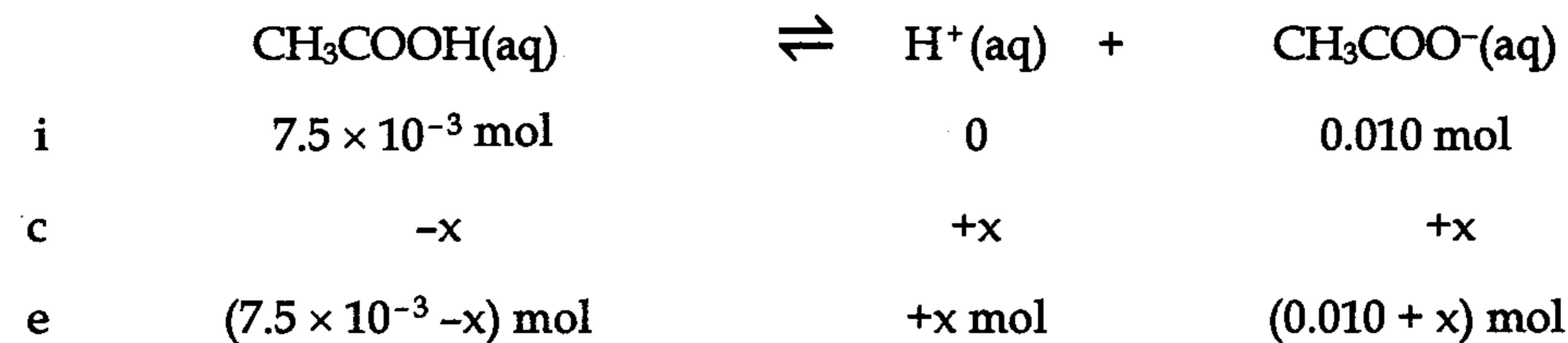
$$K_b = 6.4 \times 10^{-5} = \frac{[\text{OH}^-][(\text{CH}_3)_3\text{NH}^+]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(0.10+x)}{(0.075-x)} \approx \frac{0.10x}{0.075}$$

$$x = 4.8 \times 10^{-5} = [\text{OH}^-], \text{pOH} = 4.32, \text{pH} = 14.00 - 4.32 = 9.68$$

Check. In a buffer, if [conj. acid] > [conj. base], $\text{pH} < \text{pK}_a$ of the conj. acid. If [conj. acid] < [conj. base], $\text{pH} > \text{pK}_a$ of the conj. acid. In this buffer, pK_a of $(\text{CH}_3)_3\text{NH}^+$ is 9.81. $[(\text{CH}_3)_3\text{NH}^+] > [(\text{CH}_3)_3\text{N}]$ and $\text{pH} = 9.68$, less than 9.81.

(c) $\text{mol} = M \times L$; $\text{mol CH}_3\text{COOH} = 0.15 \text{ M} \times 0.0500 \text{ L} = 7.5 \times 10^{-3} \text{ mol}$

$\text{mol CH}_3\text{COO}^- = 0.20 \text{ M} \times 0.0500 \text{ L} = 0.010 \text{ mol}$



$[\text{CH}_3\text{COOH}(\text{aq})] = (7.5 \times 10^{-3} - x) \text{ mol} / 0.1000 \text{ L}$;

$[\text{CH}_3\text{COO}^-(\text{aq})] = (0.010 + x) \text{ mol} / 0.1000 \text{ L}$

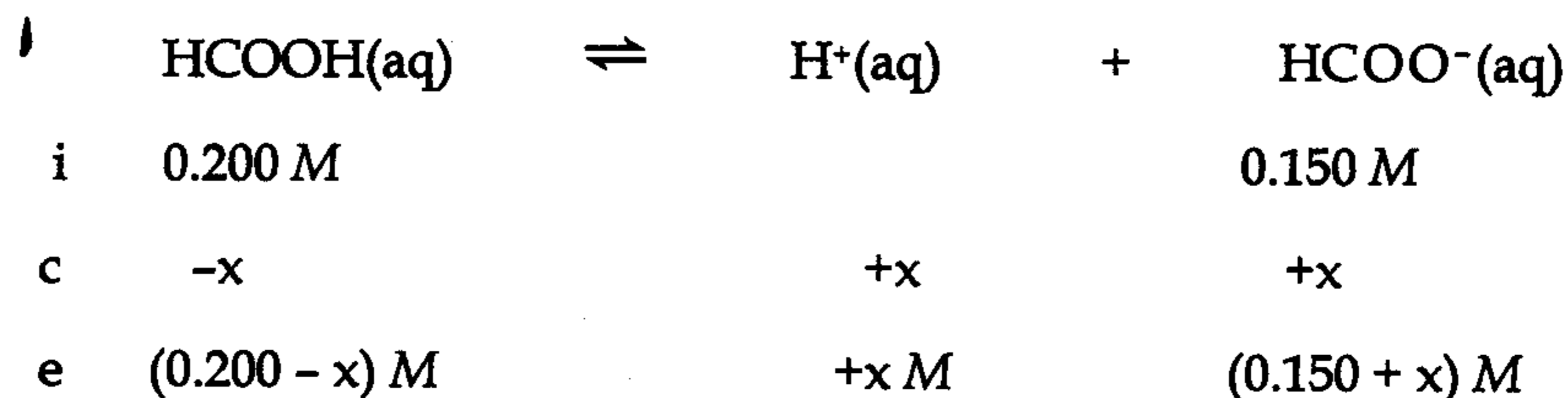
$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(0.010+x)/0.1000 \text{ L}}{(0.0075-x)/0.1000 \text{ L}} \approx \frac{x(0.010)}{0.0075}$$

$$x = 1.35 \times 10^{-5} \text{ M} = 1.4 \times 10^{-5} \text{ M H}^+; \text{pH} = 4.87$$

Check. pK_a for $\text{CH}_3\text{COOH} = 4.74$. $[\text{CH}_3\text{COO}^-] > [\text{CH}_3\text{COOH}]$, pH of buffer = 4.87, greater than 4.74.

17.16 *Analyze/Plan.* Follow the logic in Sample Exercise 17.1. *Solve.*

(a) HCOOH is a weak acid, and HCOONa contains the common ion HCOO^- , the conjugate base of HCOOH . Solve the common-ion equilibrium problem.

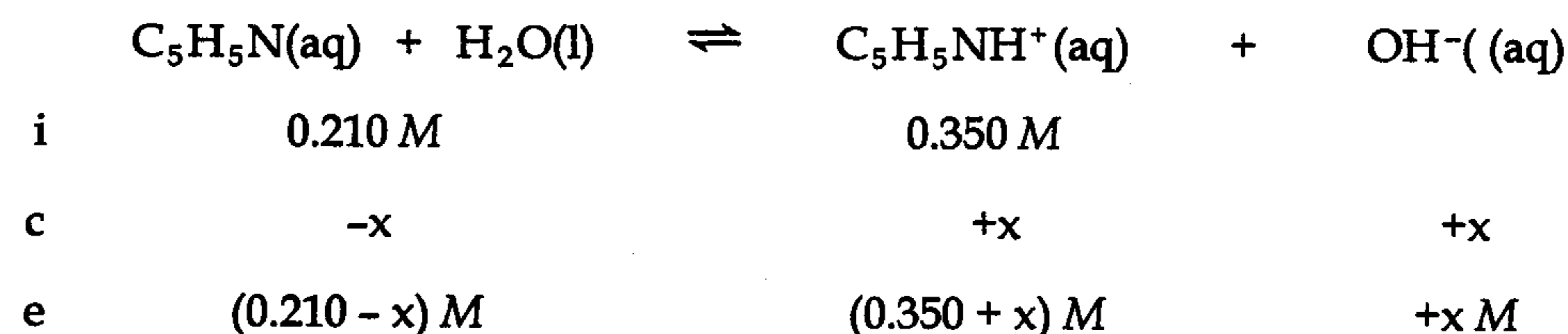


$$K_a = 1.8 \times 10^{-4} = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{(x)(0.150+x)}{(0.200-x)} \approx \frac{0.150x}{0.200}$$

$$x = 2.40 \times 10^{-4} = 2.4 \times 10^{-4} \text{ M} = [\text{H}^+], \text{pH} = 3.62$$

Check. Since the extent of ionization of a weak acid or base is suppressed by the presence of a conjugate salt, the 5% rule usually holds true in buffer solutions.

- (b) $\text{C}_5\text{H}_5\text{N}$ is a weak base, and $\text{C}_5\text{H}_5\text{NHCl}$ contains the common ion $\text{C}_5\text{H}_5\text{NH}^+$, which is the conjugate acid of $\text{C}_5\text{H}_5\text{N}$. Solve the common ion equilibrium problem.

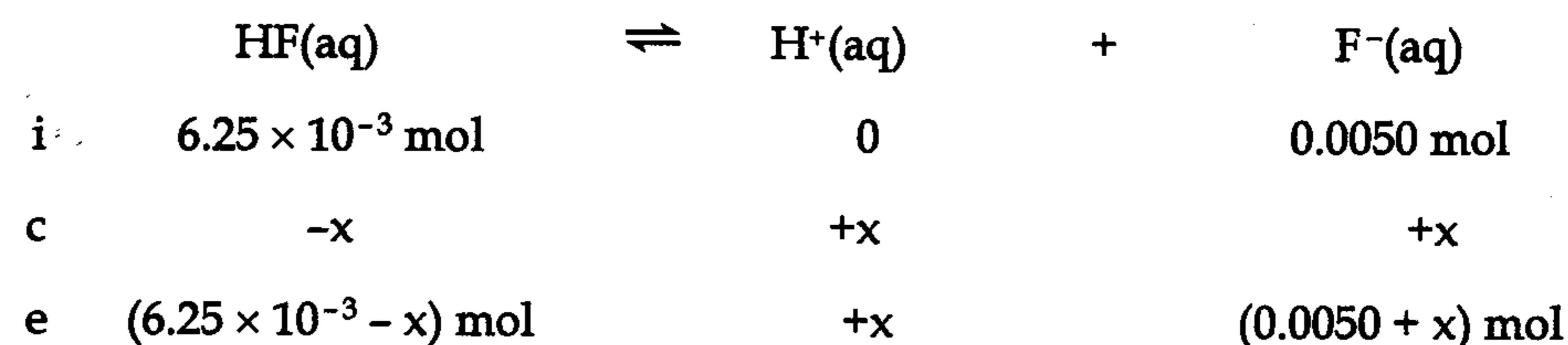


$$K_b = 1.7 \times 10^{-9} = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]} = \frac{(0.350+x)(x)}{(0.210-x)} \approx \frac{0.350x}{0.210}$$

$$x = 1.02 \times 10^{-9} = 1.0 \times 10^{-9} \text{ M} = [\text{OH}^-], \text{pOH} = 8.991, \text{pH} = 14.00 - 8.991 = 5.01$$

Check. In a buffer, if [conj. acid] > [conj. base], $\text{pH} < \text{pK}_a$ of the conj. acid. If [conj. acid] < [conj. base], $\text{pH} > \text{pK}_a$ of the conj. acid. In this buffer, pK_a of $\text{C}_5\text{H}_5\text{NH}^+$ is 5.23. $[\text{C}_5\text{H}_5\text{NH}^+] > [\text{C}_5\text{H}_5\text{N}]$ and $\text{pH} = 5.01$, less than 5.23.

- (c) $\text{mol} = M \times L$; $\text{mol HF} = 0.050 \text{ M} \times 0.125 \text{ L} = 6.25 \times 10^{-3} = 6.3 \times 10^{-3} \text{ mol}$;
 $\text{mol F}^- = 0.10 \text{ M} \times 0.0500 \text{ L} = 0.0050 \text{ mol}$



$$[\text{HF}] = (6.25 \times 10^{-3} + x)/0.175 \text{ L}; [\text{F}^-] = (0.0050 + x)/0.175 \text{ L}$$

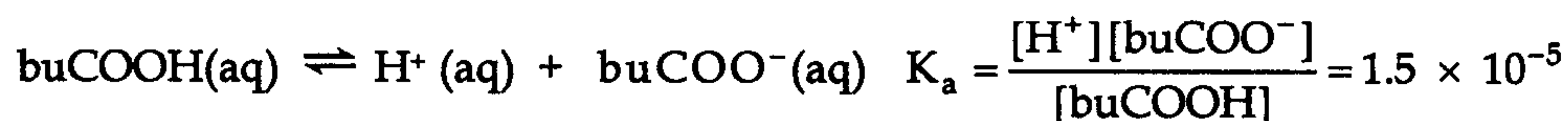
Note that the volumes will cancel when substituted into the K_a expression.

$$K_a = 6.8 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{x(0.0050+x)/0.175}{(6.25 \times 10^{-3} - x)/0.175} \approx \frac{x(0.0050)}{0.00625}$$

$$x = 8.50 \times 10^{-4} = 8.5 \times 10^{-4} \text{ M H}^+; \text{ pH} = 3.07$$

Check. $\text{p}K_a$ for HF = 3.17. $[\text{HF}] > [\text{F}^-]$, pH of buffer = 3.07, less than 3.17.

17.17 *Analyze/Plan.* We are asked to calculate % ionization of (a) a weak acid and (b) a weak acid in a solution containing a common ion, its conjugate base. Calculate % ionization as in Sample Exercise 16.13. In part (b), the concentration of the common ion is 0.085 M, not x , as in part (a). *Solve.*



$$\text{equil (a)} \quad 0.0075 - x \text{ M} \quad x \text{ M} \quad x \text{ M}$$

$$\text{equil (b)} \quad 0.0075 - x \text{ M} \quad x \text{ M} \quad 0.085 + x \text{ M}$$

$$(a) \quad K_a = 1.5 \times 10^{-5} = \frac{x^2}{0.0075 - x} \approx \frac{x^2}{0.0075}; x = [\text{H}^+] = 3.354 \times 10^{-4} = 3.4 \times 10^{-4} \text{ M H}^+$$

$$\% \text{ ionization} = \frac{3.4 \times 10^{-4} \text{ M H}^+}{0.0075 \text{ M buCOOH}} \times 100 = 4.5\% \text{ ionization}$$

$$(b) \quad K_a = 1.5 \times 10^{-5} = \frac{(x)(0.085+x)}{0.0075-x} \approx \frac{0.085x}{0.0075}; x = 1.3 \times 10^{-6} \text{ M H}^+$$

$$\% \text{ ionization} = \frac{1.3 \times 10^{-6} \text{ M H}^+}{0.0075 \text{ M buCOOH}} \times 100 = 0.018\% \text{ ionization}$$

Check. Percent ionization is much smaller when the "common ion" is present.



$$\text{equil (a)} \quad 0.085 - x \text{ M} \quad x \text{ M} \quad x \text{ M}$$

$$\text{equil (b)} \quad 0.095 - x \text{ M} \quad x \text{ M} \quad 0.0075 + x \text{ M}$$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CH(OH)COO}^-]}{[\text{CH}_3\text{CH(OH)COOH}]} = 1.4 \times 10^{-4}$$

$$(a) \quad K_a = 1.4 \times 10^{-4} = \frac{x^2}{0.085 - x} \approx \frac{x^2}{0.085}; x = [\text{H}^+] = 3.45 \times 10^{-3} \text{ M} = 3.5 \times 10^{-3} \text{ M H}^+$$

$$\% \text{ ionization} = \frac{3.5 \times 10^{-3} \text{ M H}^+}{0.085 \text{ M CH}_3\text{CH(OH)COOH}} \times 100 = 4.1\% \text{ ionization}$$

$$(b) \quad K_a = 1.4 \times 10^{-4} = \frac{(x)(0.0075+x)}{0.095-x} \approx \frac{0.0075x}{0.095}; x = 1.8 \times 10^{-3} \text{ M H}^+$$

$$\% \text{ ionization} = \frac{1.8 \times 10^{-3} \text{ M H}^+}{0.095 \text{ M CH}_3\text{CH(OH)COOH}} \times 100 = 1.9\% \text{ ionization}$$

Buffers

17.19 CH_3COOH and CH_3COONa are a weak conjugate acid/conjugate base pair which acts as a buffer because unionized CH_3COOH reacts with added base, while CH_3COO^- combines with added acid, leaving $[\text{H}^+]$ relatively unchanged. Although HCl and NaCl are a conjugate acid/conjugate base pair, Cl^- is a negligible base. That is, it has no tendency to combine with added acid to form molecular HCl . Any added acid simply increases $[\text{H}^+]$ in an HCl/NaCl mixture. In general, the conjugate bases of strong acids are negligible and mixtures of strong acids and their conjugate salts do not act as buffers.

17.20 NaOH is a strong base and will react with CH_3COOH to form CH_3COONa . As long as CH_3COOH is present in excess, the resulting solution will contain both the conjugate acid $\text{CH}_3\text{COOH}(\text{aq})$ and the conjugate base $\text{CH}_3\text{COO}^-(\text{aq})$, the requirements for a buffer.

$$\text{mmol} = M \times \text{mL}; \text{mmol } \text{CH}_3\text{COOH} = 1.00 \text{ M} \times 100 \text{ mL} = 10.0 \text{ mmol}$$

$$\text{mmol } \text{NaOH} = 0.100 \text{ M} \times 50 \text{ mL} = 5.0 \text{ mmol}$$

	$\text{CH}_3\text{COOH}(\text{aq})$	+	$\text{NaOH}(\text{aq})$	\rightarrow	$\text{CH}_3\text{COONa}(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$
initial	10.0 mmol		5.0 mmol				
after rx	5.0 mmol		0		5.0 mmol		

Mixing these two solutions has created a buffer by partial neutralization of the weak acid CH_3COOH .

17.21 *Analyze/Plan.* Follow the logic in Sample Exercise 17.3. Assume that % ionization is small in these buffers (Solutions 17.17 and 17.18). *Solve.*

$$(a) \quad K_a = \frac{[\text{H}^+][\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}; [\text{H}^+] = \frac{[K_a][\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]}$$

$$[\text{H}^+] = \frac{1.4 \times 10^{-4} (0.12)}{(0.11)}; [\text{H}^+] = 1.53 \times 10^{-4} = 1.5 \times 10^{-4} \text{ M}; \text{pH} = 3.82$$

(b) $\text{mol} = M \times L$; total volume = 85 mL + 95 mL = 180 mL

$$[\text{H}^+] = \frac{K_a[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]} = \frac{1.4 \times 10^{-4} (0.13 \text{ M} \times 0.085 \text{ L})/0.180 \text{ L}}{(0.15 \text{ M} \times 0.095 \text{ L})/0.180 \text{ L}}$$

$$[\text{H}^+] = \frac{1.4 \times 10^{-4} (0.13 \times 0.085)}{(0.15 \times 0.095)}; [\text{H}^+] = 1.086 \times 10^{-4} = 1.1 \times 10^{-4} \text{ M}; \text{pH} = 3.96$$

17.22 Assume that % ionization is small in these buffers (Solutions 17.17 and 17.18).

(a) The conjugate acid in this buffer is HCO_3^- , so use K_{a2} for H_2CO_3 , 5.6×10^{-11}

$$K_a = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}; [\text{H}^+] = \frac{K_a[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{5.6 \times 10^{-11} (0.105)}{(0.125)}$$

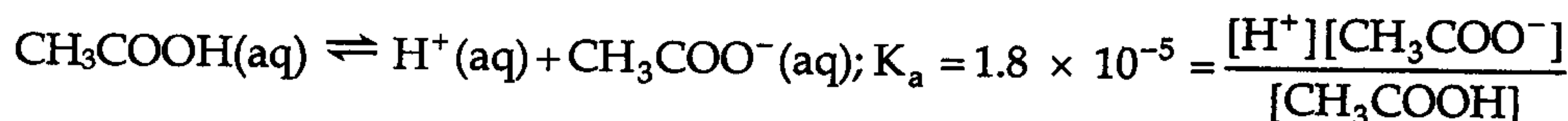
$$[\text{H}^+] = 4.70 \times 10^{-11} = 4.7 \times 10^{-11} \text{ M}; \text{pH} = 10.33$$

(b) $\text{mol} = M \times L$; total volume = 140 mL = 0.140 L

$$[\text{H}^+] = \frac{K_a (0.20 \text{ M} \times 0.065 \text{ L})/0.140 \text{ L}}{(0.15 \text{ M} \times 0.075 \text{ L})/0.140 \text{ L}} = \frac{5.6 \times 10^{-11} (0.20 \times 0.065)}{(0.15 \times 0.075)}$$

$$[\text{H}^+] = 6.47 \times 10^{-11} = 6.5 \times 10^{-11} \text{ M}; \text{pH} = 10.19$$

- 17.23 (a) *Analyze/Plan.* Follow the logic in Sample Exercises 17.1 and 17.3. As in Sample Exercise 17.1, start by calculating concentrations of the components. *Solve.*



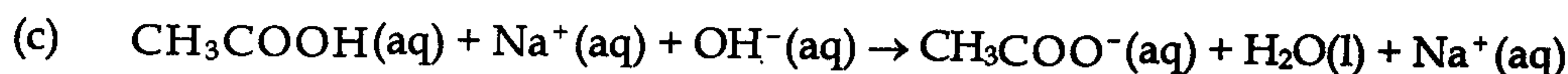
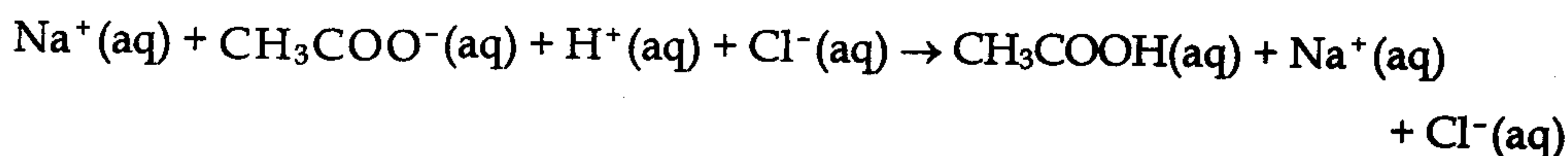
$$[\text{CH}_3\text{COOH}] = \frac{20.0 \text{ g CH}_3\text{COOH}}{2.00 \text{ L soln}} \times \frac{1 \text{ mol CH}_3\text{COOH}}{60.05 \text{ g CH}_3\text{COOH}} = 0.167 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{20.0 \text{ g CH}_3\text{COONa}}{2.00 \text{ L soln}} \times \frac{1 \text{ mol CH}_3\text{COONa}}{82.04 \text{ g CH}_3\text{COONa}} = 0.122 \text{ M}$$

$$[\text{H}^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{1.8 \times 10^{-5} (0.167 - x)}{(0.122 + x)} \approx \frac{1.8 \times 10^{-5} (0.167)}{(0.122)}$$

$$[\text{H}^+] = 2.4639 \times 10^{-5} = 2.5 \times 10^{-5} \text{ M}, \text{pH} = 4.61$$

- (b) *Plan.* On the left side of the equation, write all ions present in solution after HCl or NaOH is added to the buffer. Using acid-base properties and relative strengths, decide which ions will combine to form new products. *Solve.*



- 17.24 $\text{NH}_4^+/\text{NH}_3$ is a basic buffer. Either the hydrolysis of NH_3 or the dissociation of NH_4^+ can be used to determine the pH of the buffer. Using the dissociation of NH_4^+ leads directly to $[\text{H}^+]$ and facilitates use of the Henderson-Hasselbach relationship.



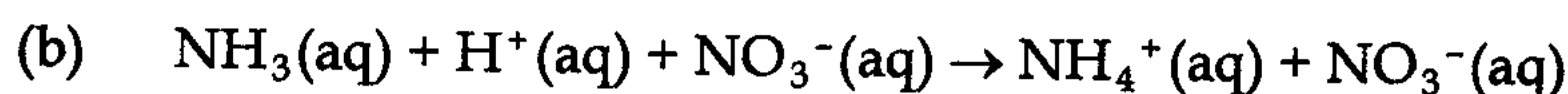
$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = 5.6 \times 10^{-10}$$

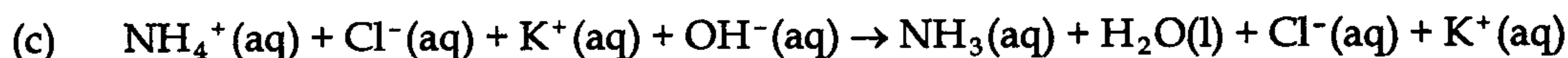
$$[\text{NH}_3] = \frac{7.0 \text{ g NH}_3}{2.50 \text{ L soln}} \times \frac{1 \text{ mol NH}_3}{17.0 \text{ g NH}_3} = 0.1647 = 0.16 \text{ M NH}_3$$

$$[\text{NH}_4^+] = \frac{20.0 \text{ g NH}_4\text{Cl}}{2.50 \text{ L}} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.50 \text{ g NH}_4\text{Cl}} = 0.1495 = 0.15 \text{ M NH}_4^+$$

$$K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]}; [\text{H}^+] = \frac{K_a[\text{NH}_4^+]}{[\text{NH}_3]} = \frac{5.56 \times 10^{-10} (0.1495 - x)}{(0.1647 + x)} \approx \frac{5.56 \times 10^{-10} (0.1495)}{(0.1647)}$$

$$[\text{H}^+] = 5.047 \times 10^{-10} = 5.0 \times 10^{-10} \text{ M}, \text{pH} = 9.30$$





17.25 *Analyze/Plan.* Follow the logic in Sample Exercise 17.4. *Solve.*

In this problem, $[\text{BrO}^-]$ is the unknown.

$$\text{pH} = 9.15, [\text{H}^+] = 10^{-9.15} = 7.0795 \times 10^{-10} = 7.1 \times 10^{-10} \text{ M}$$

$$[\text{HBrO}] = 0.050 - 7.1 \times 10^{-10} \approx 0.050 \text{ M}$$

$$K_a = 2.5 \times 10^{-9} = \frac{7.0795 \times 10^{-10} [\text{BrO}^-]}{0.050}; [\text{BrO}^-] = 0.1766 = 0.18 \text{ M}$$

For 1.00 L, 0.18 mol NaBrO are needed.



$$[\text{H}^+] = \frac{K_a [\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]}; [\text{H}^+] = 10^{-4.00} = 1.0 \times 10^{-4}$$

$$[\text{CH}_3\text{CH}(\text{OH})\text{COOH}] = 0.150 \text{ M}; \text{ calculate } [\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]$$

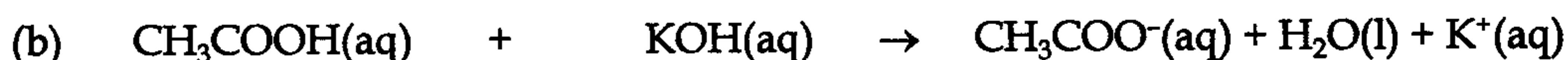
$$[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-] = \frac{K_a [\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}{[\text{H}^+]} = \frac{1.4 \times 10^{-4} (0.150)}{1.0 \times 10^{-4}} = 0.2100 = 0.21 \text{ M}$$

$$\frac{0.210 \text{ mol CH}_3\text{CH}(\text{OH})\text{COONa}}{1.00 \text{ L}} \times \frac{112.1 \text{ g CH}_3\text{CH}(\text{OH})\text{COONa}}{1 \text{ mol CH}_3\text{CH}(\text{OH})\text{COONa}} = 23.54 = 24 \text{ g CH}_3\text{CH}(\text{OH})\text{COONa}$$

17.27 *Analyze/Plan.* Follow the logic in Sample Exercise 17.3 and 17.5. *Solve.*

$$(a) \quad K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}; [\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$[\text{H}^+] \approx \frac{1.8 \times 10^{-5} (0.10)}{(0.13)} = 1.385 \times 10^{-5} = 1.4 \times 10^{-5} \text{ M}; \text{ pH} = 4.86$$

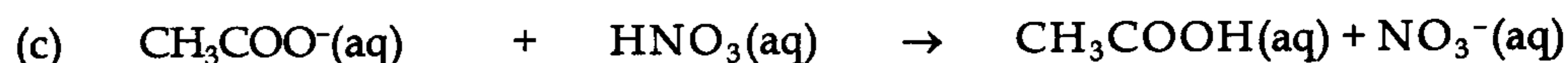


$$0.10 \text{ mol} \qquad \qquad 0.02 \text{ mol} \qquad \qquad 0.13 \text{ mol}$$

$$-0.02 \text{ mol} \qquad \qquad -0.02 \text{ mol} \qquad \qquad +0.02 \text{ mol}$$

$$0.08 \text{ mol} \qquad \qquad 0 \text{ mol} \qquad \qquad 0.15 \text{ mol}$$

$$[\text{H}^+] = \frac{1.8 \times 10^{-5} (0.08 \text{ mol}/1.00 \text{ L})}{(0.15 \text{ mol}/1.00 \text{ L})} = 9.60 \times 10^{-6} = 1 \times 10^{-5} \text{ M}; \text{ pH} = 5.02 = 5.0$$



$$0.13 \text{ mol} \qquad \qquad 0.02 \text{ mol} \qquad \qquad 0.10 \text{ mol}$$

$$-0.02 \text{ mol} \qquad \qquad -0.02 \text{ mol} \qquad \qquad +0.02 \text{ mol}$$

$$0.11 \text{ mol} \qquad \qquad 0 \text{ mol} \qquad \qquad 0.12 \text{ mol}$$

$$[\text{H}^+] = \frac{1.8 \times 10^{-5} (0.12 \text{ mol}/1.00 \text{ L})}{(0.11 \text{ mol}/1.00 \text{ L})} = 1.96 \times 10^{-5} = 2.0 \times 10^{-5} \text{ M}; \text{ pH} = 4.71$$

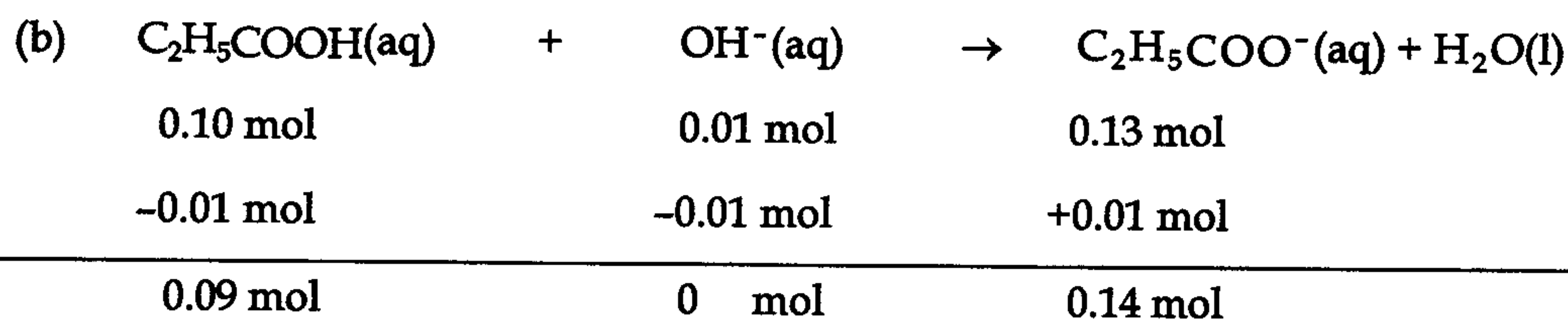
17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

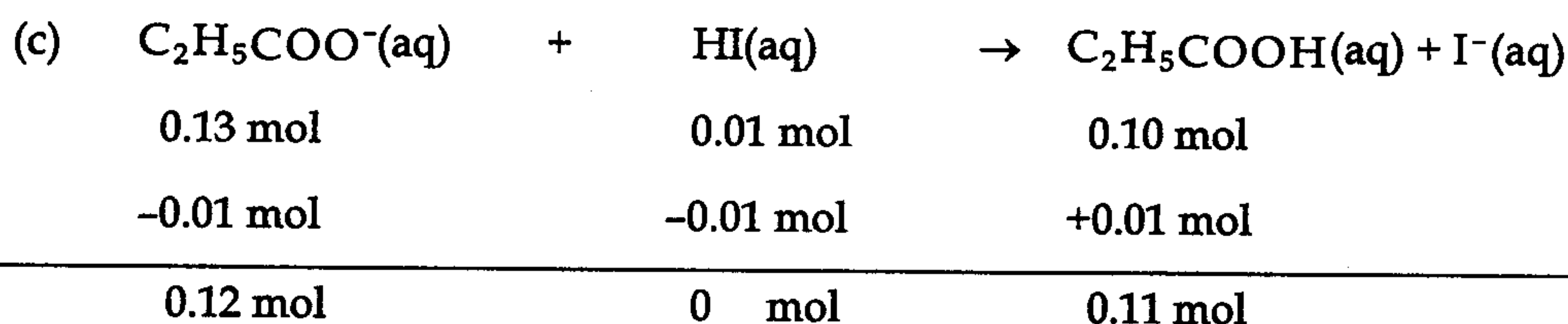
$$17.28 \quad (a) \quad K_a = \frac{[H^+][C_2H_5COO^-]}{[C_2H_5COOH]}; [H^+] = \frac{K_a[C_2H_5COOH]}{[C_2H_5COO^-]}$$

Since this expression contains a ratio of concentrations, we can ignore total volume and work directly with moles.

$$[H^+] = \frac{1.3 \times 10^{-5} (0.10 - x)}{(0.13 + x)} \approx \frac{1.3 \times 10^{-5} (0.10)}{0.13} = 1.00 \times 10^{-5} = 1.0 \times 10^{-5} M, \text{pH} = 5.00$$

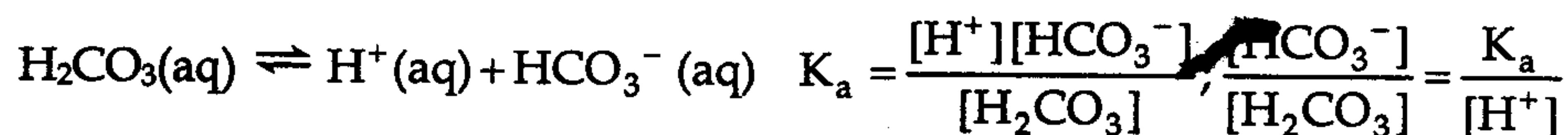


$$[H^+] \approx \frac{1.3 \times 10^{-5} (0.09)}{(0.14)} = 8.357 \times 10^{-6} = 8 \times 10^{-6} M; \text{pH} = 5.1$$



$$[H^+] \approx \frac{1.3 \times 10^{-5} (0.11)}{(0.12)} = 1.192 \times 10^{-5} = 1.19 \times 10^{-5} M; \text{pH} = 4.92$$

17.29 *Analyze/Plan.* Calculate the [conj. base]/[conj. acid] ratio in the H_2CO_3/HCO_3^- blood buffer. Write the acid dissociation equilibrium and K_a expression. Find K_a for H_2CO_3 in Appendix D. Calculate $[H^+]$ from the pH and solve for the ratio. *Solve.*



$$(a) \quad \text{at pH} = 7.4, [H^+] = 10^{-7.4} = 4.0 \times 10^{-8} M; \frac{[HCO_3^-]}{[H_2CO_3]} = \frac{4.3 \times 10^{-7}}{4.0 \times 10^{-8}} = 11$$

$$(b) \quad \text{at pH} = 7.1, [H^+] = 7.9 \times 10^{-8} M; \frac{[HCO_3^-]}{[H_2CO_3]} = 5.4$$

$$17.30 \quad \frac{6.5 \text{ g NaH}_2\text{PO}_4}{0.355 \text{ L soln}} \times \frac{1 \text{ mol NaH}_2\text{PO}_4}{120 \text{ g NaH}_2\text{PO}_4} = 0.153 = 0.15 M$$

$$\frac{8.0 \text{ g Na}_2\text{HPO}_4}{0.355 \text{ L soln}} \times \frac{1 \text{ mol Na}_2\text{HPO}_4}{142 \text{ g Na}_2\text{HPO}_4} = 0.159 = 0.16 M$$

Use Equation [17.9] to find the pH of the buffer. K_a for $H_2PO_4^-$ is K_{a2} for H_3PO_4 , 6.2×10^{-8}

$$\text{pH} = -\log(6.2 \times 10^{-8}) + \log \frac{0.159}{0.153} = 7.2076 + 0.0167 = 7.22$$

17.31 *Analyze.* Given six solutions, decide which two should be used to prepare a pH 3.50 buffer. Calculate the volumes of the two 0.10 M solutions needed to make approximately 1 L of buffer.

Plan. A buffer must contain a conjugate acid/conjugate base (CA/CB) pair. By examining the chemical formulas, decide which pairs of solutions could be used to make a buffer. If there is more than one possible pair, calculate pK_a for the acids. A buffer is most effective when its pH is within 1 pH unit of pK_a for the conjugate acid component. Select the pair with pK_a nearest to 3.50. Use Equation [17.9] to calculate the $[CB]/[CA]$ ratio and the volumes of 0.10 M solutions needed to prepare 1 L of buffer.

Solve.

There are three CA/CB pairs:



The most appropriate solutions are HCOOH/HCOONa, because pK_a for HCOOH is nearest to 3.50.

$$\text{pH} = pK_a + \log \frac{[\text{CB}]}{[\text{CA}]}; \quad 3.50 = 3.7447 + \log \frac{[\text{HCOONa}]}{[\text{HCOOH}]}$$

$$\log \frac{[\text{HCOONa}]}{[\text{HCOOH}]} = -0.2447; \quad \frac{[\text{HCOONa}]}{[\text{HCOOH}]} = 0.5692 = 0.57$$

Since we are making a total of 1 L of buffer,

let y = vol HCOONa and $(1 - y)$ = vol HCOOH.

$$0.5692 = \frac{[\text{HCOONa}]}{[\text{HCOOH}]} = \frac{(0.10 \text{ M} \times y)/1\text{L}}{[0.10 \text{ M} \times (1 - y)]/1 \text{ L}}; \quad 0.5692[0.10(1 - y)] = 0.10 y;$$

$$0.05692 = 0.15692 y; \quad y = 0.3627 = 0.36 \text{ L}$$

360 mL of 0.10 M HCOONa, 640 mL of 0.10 M HCOOH.

Check. The pH of the buffer is less than pK_a for the conjugate acid, indicating that the amount of CA in the buffer is greater than the amount of CB. This agrees with our result.

17.32 The solutes listed contain three possible conjugate acid/conjugate base (CA/CB) pairs.

These are:



For maximum buffer capacity, pK_a should be within 1 pH unit of the buffer. The propionic acid/propionate pair are most appropriate for a buffer with pH 4.80.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CB}]}{[\text{CA}]}; 4.80 = 4.886 + \log \frac{[\text{C}_2\text{H}_5\text{COONa}]}{[\text{C}_2\text{H}_5\text{COOH}]}$$

$$\log \frac{[\text{C}_2\text{H}_5\text{COONa}]}{[\text{C}_2\text{H}_5\text{COOH}]} = -0.0861; \frac{[\text{C}_2\text{H}_5\text{COONa}]}{[\text{C}_2\text{H}_5\text{COOH}]} = 0.8202 = 0.82$$

Since we are making a total of 1 L of buffer, let $y = \text{vol C}_2\text{H}_5\text{COONa}$ and

$$(1 - y) = \text{vol C}_2\text{H}_5\text{COOH}.$$

$$0.8202 = \frac{[\text{C}_2\text{H}_5\text{COONa}]}{[\text{C}_2\text{H}_5\text{COOH}]} = \frac{(0.10 \text{ M} \times y)/1.0 \text{ L}}{[0.10 \text{ M} \times (1 - y)]/1.0 \text{ L}} = \frac{0.10 y}{0.10 - 0.10 y}$$

$$0.8202(0.10 - 0.10 y) = 0.10 y; 0.08202 = 0.18202 y; y = 0.4506 = 0.45 \text{ L}$$

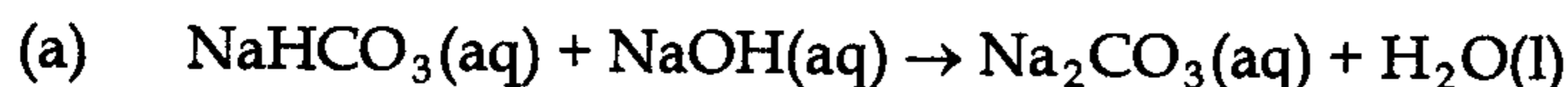
450 mL of 0.10 M $\text{C}_2\text{H}_5\text{COONa}$, 550 mL $\text{C}_2\text{H}_5\text{COOH}$

Check. $\text{pH}(\text{buffer}) < \text{pK}_a(\text{CA})$ and the calculated amount of CA in the buffer is greater than the amount of CB.

Acid-Base Titrations

- 17.33 (a) Curve B. The initial pH is lower and the equivalence point region is steeper.
 (b) pH at the approximate equivalence point of curve A = 8.0
 pH at the approximate equivalence point of curve B = 7.0
 (c) Volume of base required to reach the equivalence point depends only on moles of acid present; it is independent of acid strength. Since acid B requires 40 mL and acid A requires only 30 mL, more moles of acid B are being titrated. For equal volumes of A and B, the concentration of acid B is greater.
- 17.34 (a) The quantity of base required to reach the equivalence point is the same in the two titrations, assuming both sample solutions contain equal moles of acid.
 (b) The pH is higher initially in the titration of a weak acid.
 (c) The pH is higher at the equivalence point in the titration of a weak acid.
 (d) The pH in excess base is essentially the same for the two cases.
 (e) In titrating a weak acid, one needs an indicator that changes at a higher pH than for the strong acid titration. The choice is more critical because the change in pH close to the equivalence point is smaller for the weak acid titration.
- 17.35 *Analyze.* Given reactants, predict whether pH at the equivalence point of a titration is less than, equal to or greater than 7.

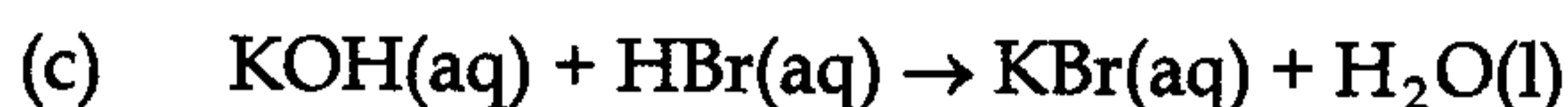
Plan. At the equivalence point of a titration, only product is present in solution; there is no excess of either reactant. Determine the product of each reaction and whether a solution of it is acidic, basic or neutral. *Solve.*



At the equivalence point, the major species in solution are Na^+ and CO_3^{2-} . Na^+ is negligible and CO_3^{2-} is the CB of HCO_3^- . The solution is basic, above pH 7.



At the equivalence point, the major species are NH_4^+ and Cl^- . Cl^- is negligible, NH_4^+ is the CA of NH_3 . The solution is acidic, below pH 7.



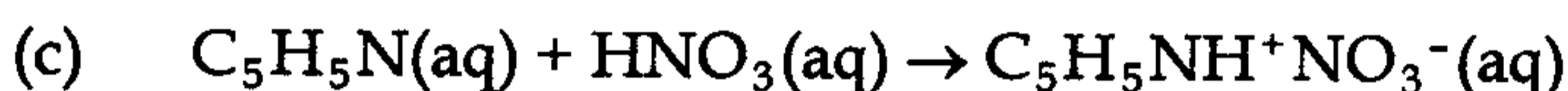
At the equivalence point, the major species are K^+ and Br^- ; both are negligible. The solution is at pH 7.



At the equivalence point, the major species are Na^+ and HCOO^- . Na^+ is negligible and HCOO^- is the CB of HCOOH . The solution is basic, above pH 7.



At the equivalence point, the major species are Ca^{2+} and ClO_4^- ; both are negligible. The solution is at pH 7.



At the equivalence point, the major species are $\text{C}_5\text{H}_5\text{NH}^+$ and NO_3^- . NO_3^- is negligible and $\text{C}_5\text{H}_5\text{NH}^+$ is the CA of $\text{C}_5\text{H}_5\text{N}$. The solution is acidic, below pH 7.

17.37 (a) HX is weaker. The pH at the equivalence point is determined by the identity and concentration of the conjugate base, X^- or Y^- . The higher the pH at the equivalence point, the stronger the conjugate base (X^-) and the weaker the conjugate acid (HX).

(b) Phenolphthalein, which changes color in the pH 8-10 range, is perfect for HX and probably appropriate for HY. Bromthymol blue changes from 6-7.5, and thymol blue between from 8-9.5, but these are two-color indicators. One-color indicators such as phenolphthalein are preferred because detection of the color change is more reproducible.

17.38 (a) At the equivalence point, moles HX added = moles B initially present = $0.10 \text{ M} \times 0.0300 \text{ L} = 0.0030$ moles HX added.



(c) Both K_a for BH^+ and concentration BH^+ determine pH at the equivalence point.

(d) Because the pH at the equivalence point will be less than 7, methyl red would be more appropriate.

17.39 *Analyze/Plan.* We are asked to calculate the volume of 0.0850 M NaOH required to titrate various acid solutions to their equivalence point. At the equivalence point, moles base added equals moles acid initially present. Solve the stoichiometry problem, recalling that $\text{mol} = M \times L$. In part (c) calculate molarity of HCl from g/L and proceed as outlined above. *Solve.*

$$\begin{aligned} \text{(a)} \quad 40.0 \text{ mL HNO}_3 &\times \frac{0.0900 \text{ mol HNO}_3}{1000 \text{ mL soln}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HNO}_3} \times \frac{1000 \text{ mL soln}}{0.0850 \text{ mol NaOH}} \\ &= 42.353 = 42.4 \text{ mL NaOH soln} \end{aligned}$$

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

$$(b) \quad 35.0 \text{ mL CH}_3\text{COOH} \times \frac{0.0850 \text{ M CH}_3\text{COOH}}{1000 \text{ mL soln}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol CH}_3\text{COOH}} \times \frac{1000 \text{ mL soln}}{0.0850 \text{ mol NaOH}} = 35.0 \text{ mL NaOH soln}$$

$$(c) \quad \frac{1.85 \text{ g HCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} = 0.05074 = 0.0507 \text{ M HCl}$$

$$50.0 \text{ mL HCl} \times \frac{0.05074 \text{ mol HCl}}{1000 \text{ mL}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} \times \frac{1000 \text{ mL soln}}{0.0850 \text{ mol NaOH}} = 29.847 = 29.8 \text{ mL NaOH soln}$$

$$17.40 \quad (a) \quad 45.0 \text{ mL NaOH} \times \frac{0.0950 \text{ mol NaOH}}{1000 \text{ mL soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1000 \text{ mL soln}}{0.105 \text{ mol HCl}} = 40.7 \text{ mL HCl soln}$$

$$(b) \quad 22.5 \text{ mL NH}_3 \times \frac{0.118 \text{ mol NH}_3}{1000 \text{ mL soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NH}_3} \times \frac{1000 \text{ mL soln}}{0.105 \text{ mol HCl}} = 25.3 \text{ mL HCl soln}$$

$$(c) \quad 125.0 \text{ mL} \times \frac{1.35 \text{ g NaOH}}{1000 \text{ mL}} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1000 \text{ mL soln}}{0.105 \text{ mol HCl}} = 40.2 \text{ mL HCl soln}$$

17.41 *Analyze/Plan.* Follow the logic in Sample Exercise 17.6 for the titration of a strong acid with a strong base. *Solve.*

$$\text{moles H}^+ = M_{\text{HBr}} \times L_{\text{HBr}} = 0.200 \text{ M} \times 0.0200 \text{ L} = 4.00 \times 10^{-3} \text{ mol}$$

$$\text{moles OH}^- = M_{\text{NaOH}} \times L_{\text{NaOH}} = 0.200 \text{ M} \times L_{\text{NaOH}}$$

	mL _{HBr}	mL _{NaOH}	Total Volume	Moles H ⁺	Moles OH ⁻	Molarity Excess Ion	pH
(a)	20.0	15.0	35.0	4.00 × 10 ⁻³	3.00 × 10 ⁻³	0.0286(H ⁺)	1.544
(b)	20.0	19.9	39.9	4.00 × 10 ⁻³	3.98 × 10 ⁻³	5 × 10 ⁻⁴ (H ⁺)	3.3
(c)	20.0	20.0	40.0	4.00 × 10 ⁻³	4.00 × 10 ⁻³	1 × 10 ⁻⁷ (H ⁺)	7.0
(d)	20.0	20.1	40.1	4.00 × 10 ⁻³	4.02 × 10 ⁻³	5 × 10 ⁻⁴ (OH ⁻)	10.7
(e)	20.0	35.0	55.0	4.00 × 10 ⁻³	7.00 × 10 ⁻³	0.0545(OH ⁻)	12.737

molarity of excess ion = moles ion / total vol in L

$$(a) \quad \frac{4.00 \times 10^{-3} \text{ mol H}^+ - 3.00 \times 10^{-3} \text{ mol OH}^-}{0.0350 \text{ L}} = 0.0286 \text{ M H}^+$$

$$(b) \quad \frac{4.00 \times 10^{-3} \text{ mol H}^+ - 3.98 \times 10^{-3} \text{ mol OH}^-}{0.0339 \text{ L}} = 5.01 \times 10^{-4} = 5 \times 10^{-4} \text{ M H}^+$$

(c) equivalence point, mol H⁺ = mol OH⁻

NaBr does not hydrolyze, so [H⁺] = [OH⁻] = 1 × 10⁻⁷ M

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

$$(d) \quad \frac{4.02 \times 10^{-3} \text{ mol H}^+ - 4.00 \times 10^{-3} \text{ mol OH}^-}{0.0401 \text{ L}} = 4.99 \times 10^{-4} = 5 \times 10^{-4} \text{ M OH}^-$$

$$(e) \quad \frac{7.00 \times 10^{-3} \text{ mol H}^+ - 4.00 \times 10^{-3} \text{ mol OH}^-}{0.0550 \text{ L}} = 0.054545 = 0.0545 \text{ M OH}^-$$

17.42 moles OH⁻ = M_{KOH} × L_{KOH} = 0.150 M × 0.0300 L = 4.50 × 10⁻³ mol

moles H⁺ = M_{HClO₄} × L_{HClO₄} = 0.125 M × L_{HClO₄}

	mL _{KOH}	mL _{HClO₄}	Total Volum e	Moles OH ⁻	Moles H ⁺	Molarity Excess Ion	pH
(a)	30.0	30.0	60.0	4.50 × 10 ⁻³	3.75 × 10 ⁻³	0.0125(OH ⁻)	12.10
(b)	30.0	35.0	65.0	4.50 × 10 ⁻³	4.38 × 10 ⁻³	1.9 × 10 ⁻³ (OH ⁻)	11.28
(c)	30.0	36.0	66.0	4.50 × 10 ⁻³	4.50 × 10 ⁻³	1.0 × 10 ⁻⁷ (OH ⁻)	7.00
(d)	30.0	37.0	67.0	4.50 × 10 ⁻³	4.63 × 10 ⁻³	1.9 × 10 ⁻³ (H ⁺)	2.73
(e)	30.0	40.0	70.0	4.50 × 10 ⁻³	5.00 × 10 ⁻³	7.1 × 10 ⁻³ (H ⁺)	2.15

$$\text{molarity of excess ion} = \frac{\text{moles ion}}{\text{total vol in L}}$$

$$(a) \quad \frac{4.50 \times 10^{-3} \text{ mol OH}^- - 3.75 \times 10^{-3} \text{ mol H}^+}{0.0600 \text{ L}} = 0.0125 = 0.013 \text{ M OH}^-$$

$$(b) \quad \frac{4.50 \times 10^{-3} \text{ mol OH}^- - 4.38 \times 10^{-3} \text{ mol H}^+}{0.0650 \text{ L}} = 1.92 \times 10^{-3} = 1.9 \times 10^{-3} \text{ M OH}^-$$

(c) equivalence point, mol H⁺ = mol OH⁻

KClO₄ does not hydrolyze, so [H⁺] = [OH⁻] = 1 × 10⁻⁷

$$(d) \quad \frac{4.63 \times 10^{-3} \text{ mol H}^+ - 4.50 \times 10^{-3} \text{ mol OH}^-}{0.0670 \text{ L}} = 1.87 \times 10^{-3} = 1.9 \times 10^{-3} \text{ M H}^+$$

$$(e) \quad \frac{5.00 \times 10^{-3} \text{ mol H}^+ - 4.50 \times 10^{-3} \text{ mol OH}^-}{0.0700 \text{ L}} = 7.14 \times 10^{-3} = 7.1 \times 10^{-3} \text{ M H}^+$$

17.43 *Analyze/Plan.* Follow the logic in Sample Exercise 17.7 for the titration of a weak acid with a strong base. *Solve.*

(a) At 0 mL, only weak acid, CH₃COOH, is present in solution. Using the acid ionization equilibrium

	CH ₃ COOH(aq)	⇌	H ⁺ (aq)	+	CH ₃ COO ⁻ (aq)
Initial	0.150 M		0		0
equil	0.150 - x M		x M		x M

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5} \text{ (Appendix D)}$$

$$1.8 \times 10^{-5} = \frac{x^2}{(0.150 - x)} \approx \frac{x^2}{0.150}; x^2 = 2.7 \times 10^{-6}; x = [\text{H}^+] = 0.001643$$

$$= 1.6 \times 10^{-3} \text{ M}; \text{pH} = 2.78$$

- (b)-(f) Calculate the moles of each component after the acid-base reaction takes place.
 Moles CH_3COOH originally present = $M \times L = 0.150 \text{ M} \times 0.0350 \text{ L} = 5.25 \times 10^{-3} \text{ mol}$.
 Moles NaOH added = $M \times L = 0.150 \text{ M} \times y \text{ mL}$.

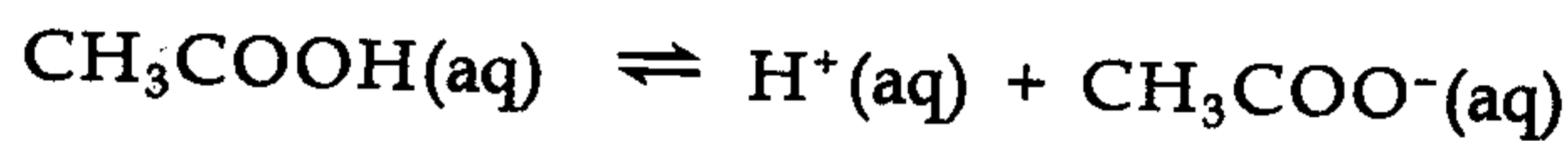
		NaOH(aq)	+	$\text{CH}_3\text{COOH (aq)}$	\rightarrow	$\text{CH}_3\text{COONa(aq)}$	+ $\text{H}_2\text{O(l)}$
		$(0.150 \text{ M} \times 0.0175 \text{ L}) =$					
(b)	before rx	$2.625 \times 10^{-3} \text{ mol}$		$5.25 \times 10^{-3} \text{ mol}$			
	after rx	0		$2.625 \times 10^{-3} \text{ mol}$		$2.63 \times 10^{-3} \text{ mol}$	
		$(0.150 \text{ M} \times 0.0345 \text{ L}) =$					
(c)	before rx	$5.175 \times 10^{-3} \text{ mol}$		$5.25 \times 10^{-3} \text{ mol}$			
	after rx	0		$0.075 \times 10^{-3} \text{ mol}$		$5.18 \times 10^{-3} \text{ mol}$	
		$(0.150 \text{ M} \times 0.0350 \text{ L}) =$					
(d)	before rx	$5.25 \times 10^{-3} \text{ mol}$		$5.25 \times 10^{-3} \text{ mol}$			
	after rx	0		0		$5.25 \times 10^{-3} \text{ mol}$	
		$(0.150 \text{ M} \times 0.0355 \text{ L}) =$					
(e)	before rx	$5.325 \times 10^{-3} \text{ mol}$		$5.25 \times 10^{-3} \text{ mol}$			
	after rx	$0.075 \times 10^{-3} \text{ mol}$		0		$5.25 \times 10^{-3} \text{ mol}$	
		$(0.150 \text{ M} \times 0.0500 \text{ L}) =$					
(f)	before rx	$7.50 \times 10^{-3} \text{ mol}$		$5.25 \times 10^{-3} \text{ mol}$			
	after rx	$2.25 \times 10^{-3} \text{ mol}$		0		$5.25 \times 10^{-3} \text{ mol}$	

Calculate the molarity of each species ($M = \text{mol/L}$) and solve the appropriate equilibrium problem in each part.

(b) $V_T = 35.0 \text{ mL CH}_3\text{COOH} + 17.5 \text{ mL NaOH} = 52.5 \text{ mL} = 0.0525 \text{ L}$

$$[\text{CH}_3\text{COOH}] = \frac{2.625 \times 10^{-3} \text{ mol}}{0.0525} = 0.0500 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{2.625 \times 10^{-3} \text{ mol}}{0.0525} = 0.0500 \text{ M}$$



equil $0.0500 - x \text{ M}$ $x \text{ M}$ $0.0500 + x \text{ M}$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}; [\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$[\text{H}^+] = \frac{1.8 \times 10^{-5} (0.0500 - x)}{(0.0500 + x)} = 1.8 \times 10^{-5} \text{ M H}^+; \text{pH} = 4.74$$

(c) $[\text{CH}_3\text{COOH}] = \frac{7.5 \times 10^{-5} \text{ mol}}{0.0695 \text{ L}} = 0.001079 = 1.1 \times 10^{-3} \text{ M}$

$$[\text{CH}_3\text{COO}^-] = \frac{5.175 \times 10^{-3} \text{ mol}}{0.0695 \text{ L}} = 0.07446 = 0.074 \text{ M}$$

$$[\text{H}^+] = \frac{1.8 \times 10^{-5} (1.079 \times 10^{-3} - x)}{(0.07446 + x)} \approx 2.6 \times 10^{-7} \text{ M H}^+; \text{pH} = 6.58$$

(d) At the equivalence point, only CH_3COO^- is present.

$$[\text{CH}_3\text{COO}^-] = \frac{5.25 \times 10^{-3} \text{ mol}}{0.0700 \text{ L}} = 0.0750 \text{ M}$$

The pertinent equilibrium is the base hydrolysis of CH_3COO^- .

	$\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{CH}_3\text{COOH}(\text{aq}) +$	$\text{OH}^-(\text{aq})$
initial	0.0750 M		0	0
equil	$0.0750 - x \text{ M}$		x	x

$$K_b = \frac{K_w}{K_a \text{ for } \text{CH}_3\text{COOH}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = 5.6 \times 10^{-10} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$5.56 \times 10^{-10} = \frac{x^2}{0.0750 - x}; x^2 \approx 5.56 \times 10^{-10} (0.0750); x = 6.458 \times 10^{-6}$$

$$= 6.5 \times 10^{-6} \text{ M OH}^-$$

$$\text{pOH} = -\log(6.458 \times 10^{-6}) = 5.19; \text{pH} = 14.00 - \text{pOH} = 8.81$$

(e) After the equivalence point, the excess strong base determines the pOH and pH. The $[\text{OH}^-]$ from the hydrolysis of CH_3COO^- is small and can be ignored.

$$[\text{OH}^-] = \frac{0.075 \times 10^{-3} \text{ mol}}{0.0705 \text{ L}} = 1.064 \times 10^{-3} = 1.1 \times 10^{-3} \text{ M}; \text{pOH} = 2.97$$

$$\text{pH} = 14.00 - 2.97 = 11.03$$

(f) $[\text{OH}^-] = \frac{2.25 \times 10^{-3} \text{ mol}}{0.0850 \text{ L}} = 0.0265 \text{ M OH}^-; \text{pOH} = 1.577; \text{pH} = 14.00 - 1.577 = 12.423$

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

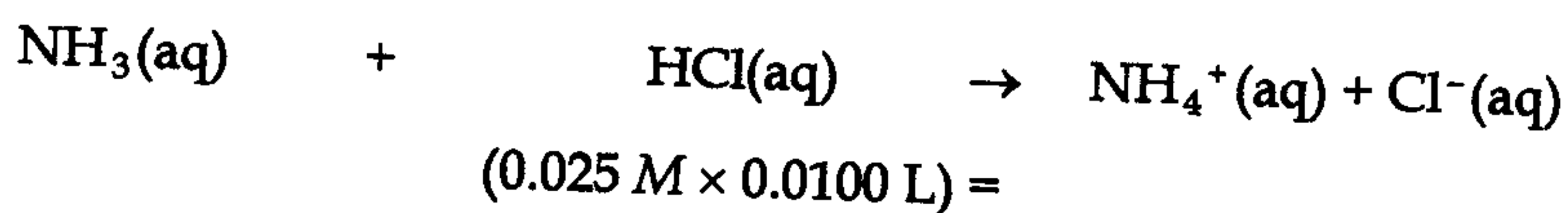
17.44 (a) Weak base problem: $K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$

At equilibrium, $[\text{OH}^-] = x$, $[\text{NH}_3] = (0.030 - x)$; $[\text{NH}_4^+] = x$

$$1.8 \times 10^{-5} = \frac{x^2}{(0.030 - x)} \approx \frac{x^2}{0.030}; x = [\text{OH}^-] = 7.348 \times 10^{-4} = 7.3 \times 10^{-4} \text{ M}$$

$$\text{pH} = 14.00 - 3.13 = 10.87$$

(b-f) Calculate mol NH_3 and mol NH_4^+ after the acid-base reaction takes place. $0.030 \text{ M NH}_3 \times 0.0300 \text{ L} = 9.0 \times 10^{-4} \text{ mol NH}_3$ present initially.



(b)	before rx	$9.0 \times 10^{-4} \text{ mol}$	$2.5 \times 10^{-4} \text{ mol}$	0 mol
	after rx	$6.5 \times 10^{-4} \text{ mol}$	0 mol	$2.5 \times 10^{-4} \text{ mol}$

(0.025 M × 0.0200 L) =

(c)	before rx	$9.0 \times 10^{-4} \text{ mol}$	$5.0 \times 10^{-4} \text{ mol}$	0 mol
	after rx	$4.0 \times 10^{-4} \text{ mol}$	0 mol	$5.0 \times 10^{-4} \text{ mol}$

(0.025 M × 0.0350 L) =

(d)	before rx	$9.0 \times 10^{-4} \text{ mol}$	$8.75 \times 10^{-4} \text{ mol}$	0 mol
	after rx	$0.25 \times 10^{-4} \text{ mol}$	0 mol	$8.75 \times 10^{-4} \text{ mol}$

(0.025 M × 0.0360 L) =

(e)	before rx	$9.0 \times 10^{-4} \text{ mol}$	$9.0 \times 10^{-4} \text{ mol}$	0 mol
	after rx	0 mol	0 mol	$9.0 \times 10^{-4} \text{ mol}$

(0.025 M × 0.0370 L) =

(f)	before rx	$9.0 \times 10^{-4} \text{ mol}$	$9.25 \times 10^{-4} \text{ mol}$	0 mol
	after rx	0 mol	$0.25 \times 10^{-4} \text{ mol}$	$9.0 \times 10^{-4} \text{ mol}$

(b) Using the acid dissociation equilibrium for NH_4^+ (so that we calculate $[\text{H}^+]$ directly), $\text{NH}_4^+(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NH}_3(\text{aq})$

$$K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{K_w}{K_b \text{ for NH}_3} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = 5.6 \times 10^{-10}$$

$$[\text{NH}_3] = \frac{6.5 \times 10^{-4} \text{ mol}}{0.0400 \text{ L}} = 0.01625 \text{ M}; [\text{NH}_4^+] = \frac{2.50 \times 10^{-4} \text{ mol}}{0.0400 \text{ L}} = 6.25 \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = \frac{5.56 \times 10^{-10} [\text{NH}_4^+]}{[\text{NH}_3]} \approx \frac{5.56 \times 10^{-10} (6.25 \times 10^{-3})}{(0.01625)} = 2.14 \times 10^{-10}; \text{pH} = 9.67$$

(We will assume $[\text{H}^+]$ is small compared to $[\text{NH}_3]$ and $[\text{NH}_4^+]$.)

$$(c) \quad [\text{NH}_3] = \frac{4.0 \times 10^{-4} \text{ mol}}{0.0500 \text{ L}} = 0.0080 \text{ M}; [\text{NH}_4^+] = \frac{5.0 \times 10^{-4} \text{ mol}}{0.0500 \text{ L}} = 0.010 \text{ M}$$

$$[\text{H}^+] = \frac{5.56 \times 10^{-10} (0.010)}{(0.0080)} = 6.94 \times 10^{-10} = 6.9 \times 10^{-10} \text{ M}; \text{pH} = 9.16$$

$$(d) \quad [\text{NH}_3] = \frac{0.25 \times 10^{-4} \text{ mol}}{0.0650 \text{ L}} = 3.846 \times 10^{-4} = 4 \times 10^{-4} \text{ M}; [\text{NH}_4^+] = \frac{8.75 \times 10^{-4} \text{ mol}}{0.0650 \text{ L}} \\ = 0.01346 = 0.013 \text{ M}$$

$$[\text{H}^+] = \frac{5.56 \times 10^{-10} (0.01346)}{3.846 \times 10^{-4}} = 1.946 \times 10^{-8} = 2 \times 10^{-8} \text{ M}; \text{pH} = 7.7$$

(e) At the equivalence point, $[\text{H}^+] = [\text{NH}_3] = x$

$$[\text{NH}_4^+] = \frac{9.0 \times 10^{-4} \text{ M}}{0.0660 \text{ L}} = 0.01364 = 0.014 \text{ M}$$

$$5.56 \times 10^{-10} = \frac{x^2}{0.01364}; x = [\text{H}^+] = 2.754 \times 10^{-6} = 2.8 \times 10^{-6}; \text{pH} = 5.56$$

(f) Past the equivalence point, $[\text{H}^+]$ from the excess HCl determines the pH.

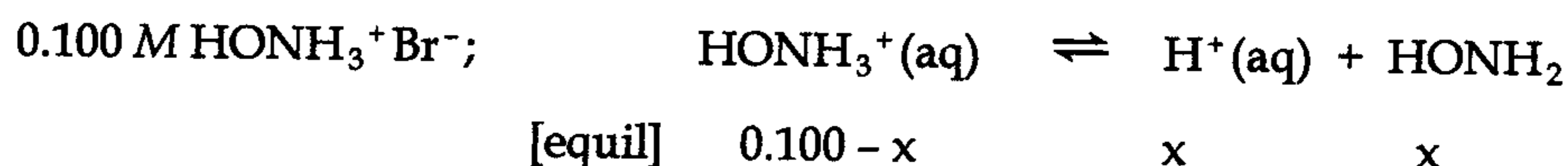
$$[\text{H}^+] = \frac{0.25 \times 10^{-4} \text{ mol}}{0.0670 \text{ L}} = 3.731 \times 10^{-4} = 4 \times 10^{-4} \text{ M}; \text{pH} = 3.4$$

17.45 *Analyze/Plan.* Calculate the pH at the equivalence point for the titration of several bases with 0.200 M HBr. The volume of 0.200 M HBr required in all cases equals the volume of base and the final volume = $2V_{\text{base}}$. The concentration of the salt produced at the equivalence point is $\frac{0.200 \text{ M} \times V_{\text{base}}}{2V_{\text{base}}} = 0.100 \text{ M}$.

In each case, identify the salt present at the equivalence point, determine its acid-base properties (Section 16.9), and solve the pH problem. *Solve.*

(a) NaOH is a strong base; the salt present at the equivalence point, NaBr, does not affect the pH of the solution. 0.100 M NaBr, pH = 7.00

(b) HONH_2 is a weak base, so the salt present at the equivalence point is $\text{HONH}_3^+ \text{Br}^-$. This is the salt of a strong acid and a weak base, so it produces an acidic solution.



$$K_a = \frac{[\text{H}^+][\text{HONH}_2]}{[\text{HONH}_3^+]} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.09 \times 10^{-7} = 9.1 \times 10^{-7}$$

Assume x is small with respect to [salt].

$$K_a = x^2 / 0.100; x = [\text{H}^+] = 3.02 \times 10^{-4} = 3.0 \times 10^{-4} \text{ M}, \text{pH} = 3.52$$

- (c) $\text{C}_6\text{H}_5\text{NH}_2$ is a weak base and $\text{C}_6\text{H}_5\text{NH}_3^+\text{Br}^-$ is an acidic salt.

0.100 M $\text{C}_6\text{H}_5\text{NH}_3^+\text{Br}^-$. Proceeding as in (b):

$$K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{NH}_2]}{[\text{C}_6\text{H}_5\text{NH}_3^+]} = \frac{K_w}{K_b} = 2.33 \times 10^{-5} = 2.3 \times 10^{-5}$$

$$[\text{H}^+]^2 = 0.100(2.33 \times 10^{-5}); [\text{H}^+] = 1.52 \times 10^{-3} = 1.5 \times 10^{-3} \text{ M}, \text{pH} = 2.82$$

- 17.46 The volume of NaOH solution required in all cases is

$$V_{\text{base}} = \frac{V_{\text{acid}} \times M_{\text{acid}}}{M_{\text{base}}} = \frac{(0.100) V_{\text{acid}}}{(0.080)} = 1.25 V_{\text{acid}}$$

The total volume at the equivalence point is $V_{\text{base}} + V_{\text{acid}} = 2.25 V_{\text{acid}}$.

The concentration of the salt at the equivalence point is $\frac{M_{\text{acid}} V_{\text{acid}}}{2.25 V_{\text{acid}}} = \frac{0.100}{2.25} = 0.0444 \text{ M}$

- (a) 0.0444 M NaBr, pH = 7.00

- (b) 0.0444 M $\text{Na}^+ \text{C}_3\text{H}_5\text{O}_3^-$; $\text{C}_3\text{H}_5\text{O}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HC}_3\text{H}_5\text{O}_3(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_b = \frac{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-4}} = 7.14 \times 10^{-11} = 7.1 \times 10^{-11}$$

$$[\text{CH}_3\text{CH}(\text{OH})\text{COOH}] = [\text{OH}^-]; [\text{CH}_3\text{CH}(\text{OH})\text{COO}^-] \approx 0.0444$$

$$[\text{OH}^-]^2 \approx 0.0444(7.14 \times 10^{-11}); [\text{OH}^-] = 1.78 \times 10^{-6} = 1.8 \times 10^{-6} \text{ M}, \text{pOH} = 5.75;$$

$$\text{pH} = 8.25$$

- (c) $\text{CrO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCrO}_4^-(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_b = \frac{[\text{HCrO}_4^-][\text{OH}^-]}{[\text{CrO}_4^{2-}]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-7}} = 3.33 \times 10^{-8} = 3.3 \times 10^{-8}$$

$$[\text{OH}^-]^2 \approx 0.0444(3.33 \times 10^{-8}); [\text{OH}^-] = 3.849 \times 10^{-5} = 3.8 \times 10^{-5}, \text{pH} = 9.59$$

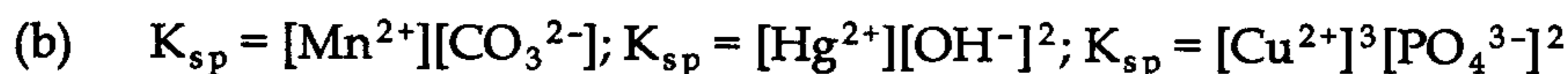
Solubility Equilibria and Factors Affecting Solubility

- 17.47 (a) The concentration of undissolved solid does not appear in the solubility product expression because it is constant as long as there is solid present. Concentration is a ratio of moles solid to volume of the solid; solids occupy a specific volume not dependent on the solution volume. As the amount (moles) of solid changes, the volume changes proportionally, so that the ratio of moles solid to volume solid is constant.

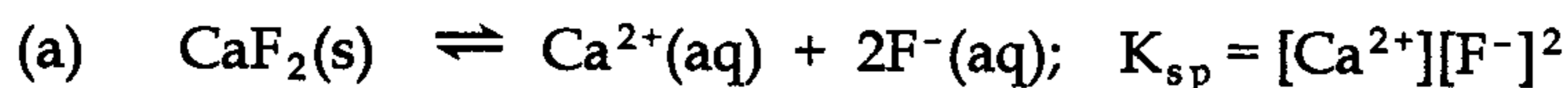
- (b) *Analyze/Plan.* Follow the example in Sample Exercise 17.9. *Solve.*

$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]; K_{\text{sp}} = [\text{Sr}^{2+}][\text{SO}_4^{2-}]; K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^-]^2; K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Br}^-]^2$$

- 17.48 (a) Solubility is the amount (grams, moles) of solute that will dissolve in a certain volume of solution. Solubility-product constant is an equilibrium constant, the product of the molar concentrations of all the dissolved ions in solution.



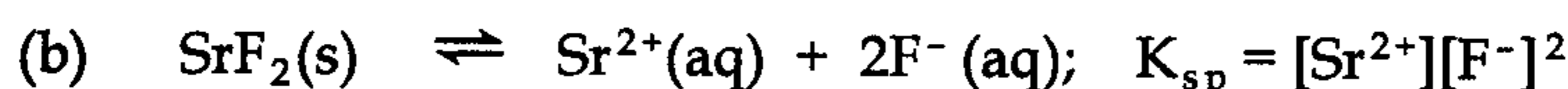
17.49 *Analyze/Plan.* Follow the logic in Sample Exercise 17.10. *Solve.*



The molar solubility is the moles of CaF_2 that dissolve per liter of solution. Each mole of CaF_2 produces 1 mol $\text{Ca}^{2+}(aq)$ and 2 mol $\text{F}^-(aq)$.

$$[\text{Ca}^{2+}] = 1.24 \times 10^{-3} \text{ M}; [\text{F}^-] = 2 \times 1.24 \times 10^{-3} \text{ M} = 2.48 \times 10^{-3} \text{ M}$$

$$K_{sp} = (1.24 \times 10^{-3})(2.48 \times 10^{-3})^2 = 7.63 \times 10^{-9}$$

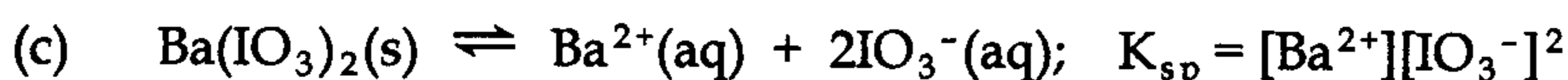


Transform the gram solubility to molar solubility.

$$\frac{1.1 \times 10^{-2} \text{ g SrF}_2}{0.100 \text{ L}} \times \frac{1 \text{ mol SrF}_2}{125.6 \text{ g SrF}_2} = 8.76 \times 10^{-4} = 8.8 \times 10^{-4} \text{ mol SrF}_2 / \text{L}$$

$$[\text{Sr}^{2+}] = 8.76 \times 10^{-4} \text{ M}; [\text{F}^-] = 2(8.76 \times 10^{-4} \text{ M})$$

$$K_{sp} = (8.76 \times 10^{-4})(2(8.76 \times 10^{-4}))^2 = 2.7 \times 10^{-9}$$

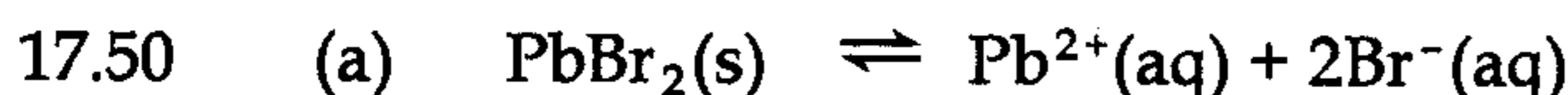


Since 1 mole of dissolved $\text{Ba}(\text{IO}_3)_2$ produces 1 mole of Ba^{2+} , the molar solubility of

$$\text{Ba}(\text{IO}_3)_2 = [\text{Ba}^{2+}]. \text{ Let } x = [\text{Ba}^{2+}]; [\text{IO}_3^-] = 2x$$

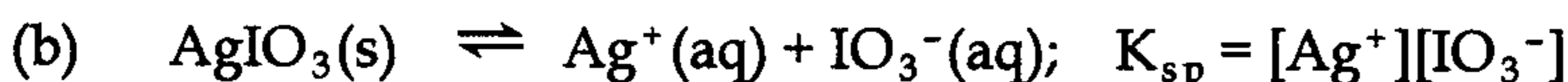
$$K_{sp} = 6.0 \times 10^{-10} = (x)(2x)^2; 4x^3 = 6.0 \times 10^{-10}; x^3 = 1.5 \times 10^{-10}; x = 5.3 \times 10^{-4} \text{ M}$$

The molar solubility of $\text{Ba}(\text{IO}_3)_2$ is $5.3 \times 10^{-4} \text{ mol/L}$.



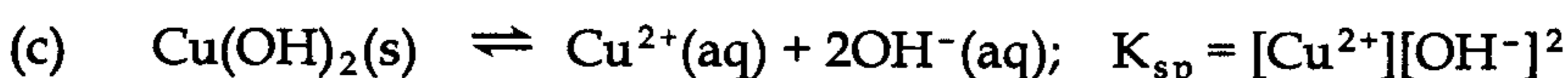
$$K_{sp} = [\text{Pb}^{2+}][\text{Br}^-]^2; [\text{Pb}^{2+}] = 1.0 \times 10^{-2} \text{ M}, [\text{Br}^-] = 2.0 \times 10^{-2} \text{ M}$$

$$K_{sp} = (1.0 \times 10^{-2} \text{ M})(2.0 \times 10^{-2} \text{ M})^2 = 4.0 \times 10^{-6}$$



$$[\text{Ag}^+] = [\text{IO}_3^-] = \frac{0.0490 \text{ g AgIO}_3}{1.00 \text{ L soln}} \times \frac{1 \text{ mol AgIO}_3}{282.8 \text{ g AgIO}_3} = 1.733 \times 10^{-4} = 1.73 \times 10^{-4} \text{ M}$$

$$K_{sp} = (1.733 \times 10^{-4} \text{ M})(1.733 \times 10^{-4} \text{ M}) = 3.00 \times 10^{-8}$$



$$[\text{Cu}^{2+}] = x, [\text{OH}^-] = 2x; K_{sp} = 4.8 \times 10^{-20} = (x)(2x)^2$$

$$4.8 \times 10^{-20} = 4x^3; x = [\text{Cu}^{2+}] = 2.290 \times 10^{-7} = 2.3 \times 10^{-7} \text{ M}$$

$$\frac{2.290 \times 10^{-7} \text{ mol Cu}(\text{OH})_2}{1 \text{ L}} \times \frac{97.56 \text{ g Cu}(\text{OH})_2}{1 \text{ mol Cu}(\text{OH})_2} = 2.2 \times 10^{-5} \text{ g Cu}(\text{OH})_2$$

However, $[\text{OH}^-]$ from $\text{Cu}(\text{OH})_2 = 4.58 \times 10^{-7} \text{ M}$; this is similar to $[\text{OH}^-]$ from the autoionization of water.

$$K_w = [\text{H}^+][\text{OH}^-]; [\text{H}^+] = y, [\text{OH}^-] = (4.58 \times 10^{-7} + y)$$

$$1.0 \times 10^{-14} = y(4.58 \times 10^{-7} + y); y^2 + 4.58 \times 10^{-7}y - 1.0 \times 10^{-14}$$

$$y = \frac{-4.58 \times 10^{-7} \pm \sqrt{(4.58 \times 10^{-7})^2 - 4(1)(-1.0 \times 10^{-14})}}{2}; y = 2.09 \times 10^{-8}$$

$$[\text{OH}^-]_{\text{total}} = 4.58 \times 10^{-7} \text{ M} + 0.209 \times 10^{-7} \text{ M} = 4.79 \times 10^{-7} \text{ M}$$

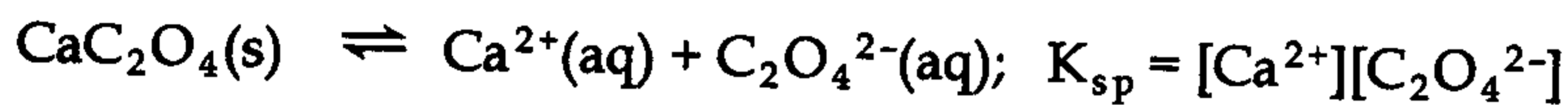
Recalculating $[\text{Cu}^{2+}]$ and thus molar solubility of $\text{Cu}(\text{OH})_2(\text{s})$:

$$4.8 \times 10^{-20} = x(4.79 \times 10^{-7})^2; x = 2.09 \times 10^{-7} \text{ M Cu}^{2+}$$

$$\frac{2.09 \times 10^{-7} \text{ mol Cu}(\text{OH})_2(\text{s})}{1 \text{ L}} \times \frac{97.56 \text{ g Cu}(\text{OH})_2}{1 \text{ mol Cu}(\text{OH})_2} = 2.0 \times 10^{-5} \text{ g Cu}(\text{OH})_2$$

Note that the presence of OH^- as a common ion decreases the water solubility of $\text{Cu}(\text{OH})_2$.

- 17.51 *Analyze/Plan.* Given gram solubility of a compound, calculate K_{sp} . Write the dissociation equilibrium and K_{sp} expression. Change gram solubility to molarity of the individual ions, taking the stoichiometry of the compound into account. Calculate K_{sp} . *Solve.*



$$[\text{Ca}^{2+}] = [\text{C}_2\text{O}_4^{2-}] = \frac{0.0061 \text{ g CaC}_2\text{O}_4}{1.00 \text{ L soln}} \times \frac{1 \text{ mol CaC}_2\text{O}_4}{128.1 \text{ g CaC}_2\text{O}_4} = 4.76 \times 10^{-5} = 4.8 \times 10^{-5} \text{ M}$$

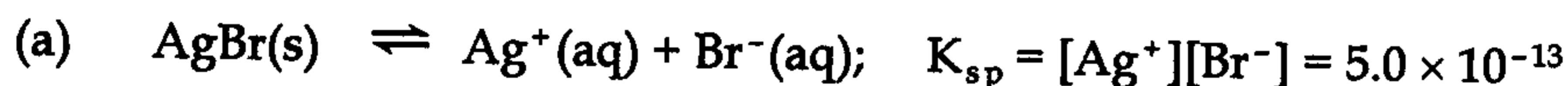
$$K_{\text{sp}} = (4.76 \times 10^{-5} \text{ M})(4.76 \times 10^{-5} \text{ M}) = 2.3 \times 10^{-9}$$

- 17.52 $\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}); K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2$

$$[\text{Pb}^{2+}] = \frac{0.54 \text{ g PbI}_2}{1.00 \text{ L soln}} \times \frac{1 \text{ mol PbI}_2}{461.0 \text{ g PbI}_2} = 1.17 \times 10^{-3} = 1.2 \times 10^{-3} \text{ M}$$

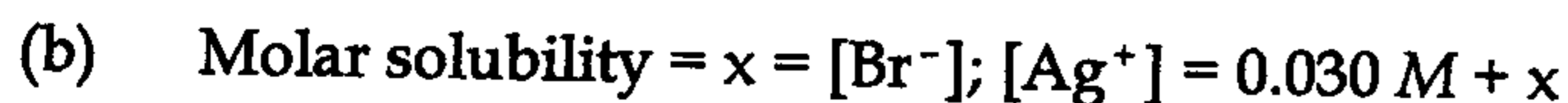
$$[\text{I}^-] = 2[\text{Pb}^{2+}]; K_{\text{sp}} = [\text{Pb}^{2+}](2[\text{Pb}^{2+}])^2 = 4[\text{Pb}^{2+}]^3 = 4(1.17 \times 10^{-3})^3 = 6.4 \times 10^{-9}$$

- 17.53 *Analyze/Plan.* Follow the logic in Sample Exercises 17.11 and 17.12. *Solve.*



$$\text{molar solubility} = x = [\text{Ag}^+] = [\text{Br}^-]; K_{\text{sp}} = x^2$$

$$x = (5.0 \times 10^{-13})^{1/2}; x = 7.1 \times 10^{-7} \text{ mol AgBr/L}$$



$$K_{\text{sp}} = (0.030 + x)(x) \approx 0.030(x)$$

$$5.0 \times 10^{-13} = 0.030(x); x = 1.7 \times 10^{-11} \text{ mol AgBr/L}$$

(c) Molar solubility = $x = [\text{Ag}^+]$

There are two sources of Br^- : $\text{NaBr}(0.10 \text{ M})$ and $\text{AgBr}(x \text{ M})$

$K_{\text{sp}} = (x)(0.10 + x)$; Assuming x is small compared to 0.10 M

$$5.0 \times 10^{-13} = 0.10(x); x \approx 5.0 \times 10^{-12} \text{ mol AgBr/L}$$

17.54 $\text{LaF}_3(\text{s}) \rightleftharpoons \text{La}^{3+}(\text{aq}) + 3\text{F}^-(\text{aq}); K_{\text{sp}} = [\text{La}^{3+}][\text{F}^-]^3$

(a) molar solubility = $x = [\text{La}^{3+}]; [\text{F}^-] = 3x$

$$K_{\text{sp}} = 2 \times 10^{-19} = (x)(3x)^3; 2 \times 10^{-19} = 27x^4; x = (7.41 \times 10^{-21})^{1/4}, x = 9.28 \times 10^{-6} \\ = 9 \times 10^{-6} \text{ M La}^{3+}$$

$$\frac{9.28 \times 10^{-6} \text{ mol LaF}_3}{1 \text{ L}} \times \frac{195.9 \text{ g LaF}_3}{1 \text{ mol}} = 1.82 \times 10^{-3} = 2 \times 10^{-3} \text{ g LaF}_3/\text{L}$$

(b) molar solubility = $x = [\text{La}^{3+}]$

There are two sources of F^- : $\text{KF}(0.010 \text{ M})$ and $\text{LaF}_3(3x \text{ M})$

$K_{\text{sp}} = (x)(0.010 + 3x)^3$; assume x is small compared to 0.010 M .

$$2 \times 10^{-19} = (0.010)^3 x; x = 2 \times 10^{-19} / 1.0 \times 10^{-6} = 2 \times 10^{-13} \text{ M La}^{3+}$$

$$\frac{2 \times 10^{-13} \text{ mol LaF}_3}{1 \text{ L}} \times \frac{195.9 \text{ g LaF}_3}{1 \text{ mol}} = 3.92 \times 10^{-11} = 4 \times 10^{-11} \text{ g LaF}_3/\text{L}$$

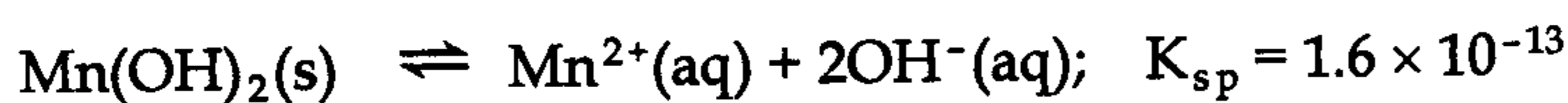
(c) molar solubility = $x, [\text{F}^-] = 3x, [\text{La}^{3+}] = 0.050 \text{ M} + x$

$K_{\text{sp}} = (0.050 + x)(3x)^3$; assume x is small compared to 0.050 M .

$$2 \times 10^{-19} = (0.050)(27x^3) = 1.35x^3; x = (1.48 \times 10^{-19})^{1/3} = 5.29 \times 10^{-7} = 5 \times 10^{-7} \text{ M}$$

$$\frac{5.29 \times 10^{-7} \text{ mol LaF}_3}{1 \text{ L}} \times \frac{195.9 \text{ g LaF}_3}{1 \text{ mol}} = 1.04 \times 10^{-4} = 1 \times 10^{-4} \text{ g LaF}_3/\text{L}$$

17.55 *Analyze/Plan.* We are asked to calculate the solubility of a slightly-soluble hydroxide salt at various pH values. This is a common ion problem; pH tells us not only $[\text{H}^+]$ but also $[\text{OH}^-]$, which is an ion common to the salt. Use pH to calculate $[\text{OH}^-]$, then proceed as in Sample Exercise 17.12. *Solve.*



Since $[\text{OH}^-]$ is set by the pH of the solution, the solubility of $\text{Mn}(\text{OH})_2$ is just $[\text{Mn}^{2+}]$.

(a) $\text{pH} = 7.0, \text{pOH} = 14 - \text{pH} = 7.0, [\text{OH}^-] = 10^{-\text{pOH}} = 1.0 \times 10^{-7} \text{ M}$

$$K_{\text{sp}} = 1.6 \times 10^{-13} = [\text{Mn}^{2+}](1.0 \times 10^{-7})^2; [\text{Mn}^{2+}] = \frac{1.6 \times 10^{-13}}{1.0 \times 10^{-14}} = 16 \text{ M}$$

$$\frac{16 \text{ mol Mn}(\text{OH})_2}{1 \text{ L}} \times \frac{88.95 \text{ g Mn}(\text{OH})_2}{1 \text{ mol Mn}(\text{OH})_2} = 1423 = 1.4 \times 10^3 \text{ g Mn}(\text{OH})_2/\text{L}$$

Check. Note that the solubility of $\text{Mn}(\text{OH})_2$ in pure water is $3.6 \times 10^{-5} \text{ M}$, and the pH of the resulting solution is 9.0. The relatively low pH of a solution buffered to pH 7.0 actually increases the solubility of $\text{Mn}(\text{OH})_2$.

(b) $\text{pH} = 9.5, \text{pOH} = 4.5, [\text{OH}^-] = 3.16 \times 10^{-5} = 3.2 \times 10^{-5} \text{ M}$

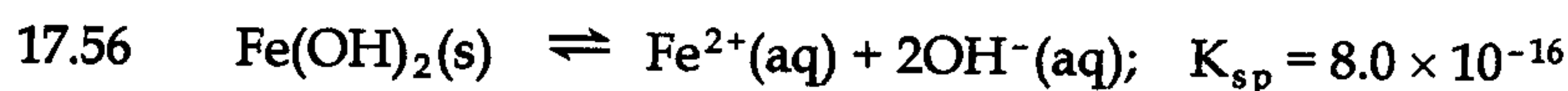
$$K_{\text{sp}} = 1.6 \times 10^{-13} = [\text{Mn}^{2+}](3.16 \times 10^{-5})^2; [\text{Mn}^{2+}] = \frac{1.6 \times 10^{-13}}{1.0 \times 10^{-9}} = 1.6 \times 10^{-4} \text{ M}$$

$$1.6 \times 10^{-4} \text{ M Mn(OH)}_2 \times 88.95 \text{ g/mol} = 0.0142 = 0.014 \text{ g/L}$$

(c) $\text{pH} = 11.8, \text{pOH} = 2.2, [\text{OH}^-] = 6.31 \times 10^{-3} = 6.3 \times 10^{-3} \text{ M}$

$$K_{\text{sp}} = 1.6 \times 10^{-13} = [\text{Mn}^{2+}](6.31 \times 10^{-3})^2; [\text{Mn}^{2+}] = \frac{1.6 \times 10^{-13}}{3.98 \times 10^{-5}} = 4.0 \times 10^{-9} \text{ M}$$

$$4.02 \times 10^{-9} \text{ M Mn(OH)}_2 \times 88.95 \text{ g/mol} = 3.575 \times 10^{-7} = 3.6 \times 10^{-7} \text{ g/L}$$



Since the $[\text{OH}^-]$ is set by the pH of the solution, the solubility of Fe(OH)_2 is just $[\text{Fe}^{2+}]$.

(a) $\text{pH} = 8.0, \text{pOH} = 14 - \text{pH} = 6.0, [\text{OH}^-] = 10^{-\text{pOH}} = 1 \times 10^{-6} \text{ M}$

$$K_{\text{sp}} = 7.9 \times 10^{-16} = [\text{Fe}^{2+}](1.0 \times 10^{-6})^2; [\text{Fe}^{2+}] = \frac{7.9 \times 10^{-16}}{1.0 \times 10^{-12}} = 7.9 \times 10^{-4} = 8 \times 10^{-4} \text{ M}$$

(b) $\text{pH} = 10.0, \text{pOH} = 4.0, [\text{OH}^-] = 1.0 \times 10^{-4} = 1 \times 10^{-4} \text{ M}$

$$K_{\text{sp}} = 7.9 \times 10^{-16} = [\text{Fe}^{2+}][1.0 \times 10^{-4}]^2; [\text{Fe}^{2+}] = \frac{7.9 \times 10^{-16}}{1.0 \times 10^{-8}} = 7.9 \times 10^{-8} = 8 \times 10^{-8} \text{ M}$$

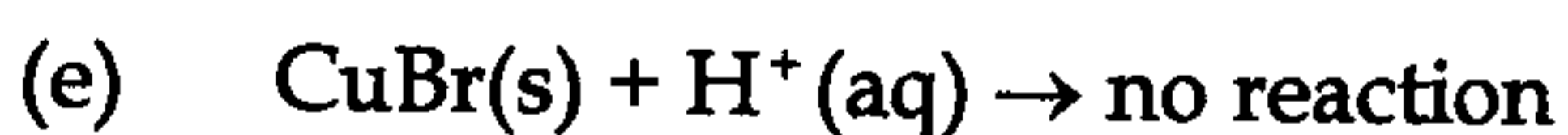
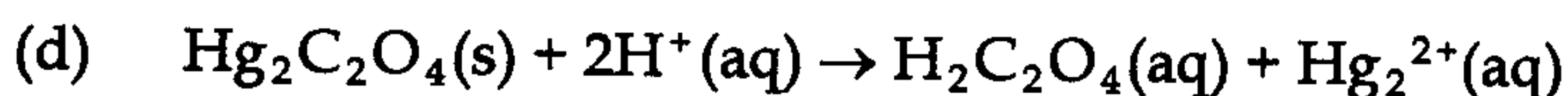
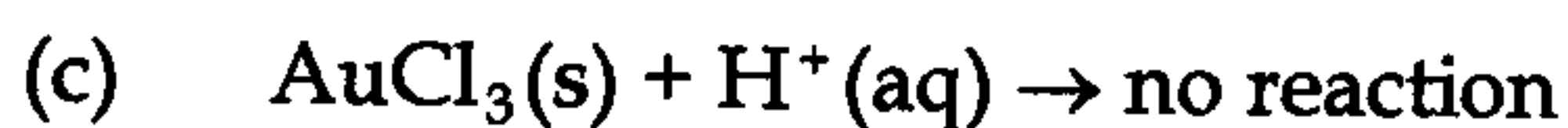
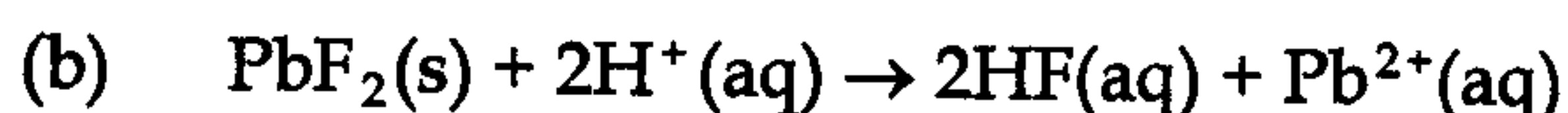
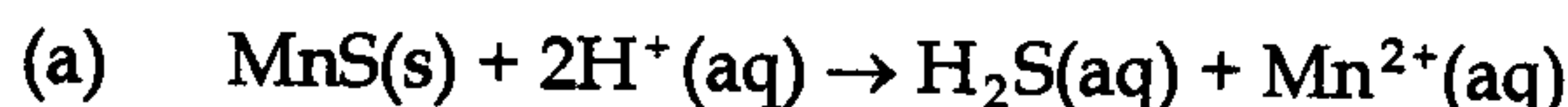
(c) $\text{pH} = 12.0, \text{pOH} = 2.0, [\text{OH}^-] = 1.0 \times 10^{-2} = 1 \times 10^{-2} \text{ M}$

$$K_{\text{sp}} = 7.9 \times 10^{-16} = [\text{Fe}^{2+}][1.0 \times 10^{-2}]^2; [\text{Fe}^{2+}] = \frac{7.9 \times 10^{-16}}{1.0 \times 10^{-4}} = 7.9 \times 10^{-12} = 8 \times 10^{-12} \text{ M}$$

17.57 *Analyze/Plan.* Follow the logic in Sample Exercise 17.13. *Solve.*

If the anion of the salt is the conjugate base of a weak acid, it will combine with H^+ , reducing the concentration of the free anion in solution, thereby causing more salt to dissolve. More soluble in acid: (a) ZnCO_3 , (b) ZnS , (d) AgCN , (e) $\text{Ba}_3(\text{PO}_4)_2$

17.58 If the anion in the slightly soluble salt is the conjugate base of a strong acid, there will be no reaction.

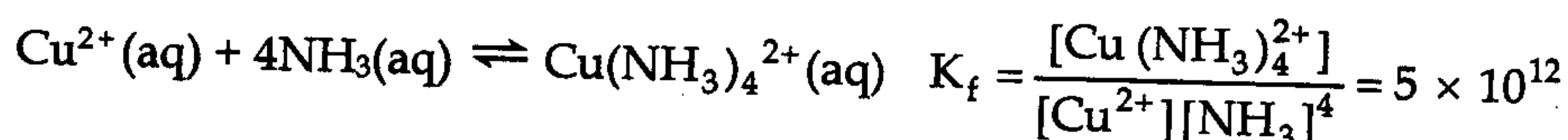


17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

17.59 *Analyze/Plan.* Follow the logic in Sample Exercise 17.14. *Solve.*

The formation equilibrium is



Assuming that nearly all the Cu^{2+} is in the form $\text{Cu}(\text{NH}_3)_4^{2+}$,

$$[\text{Cu}(\text{NH}_3)_4^{2+}] = 1 \times 10^{-3} \text{ M}; [\text{Cu}^{2+}] = x; [\text{NH}_3] = 0.10 \text{ M}$$

$$5 \times 10^{12} = \frac{(1 \times 10^{-3})}{x(0.10)^4}; x = 2 \times 10^{-12} \text{ M} = [\text{Cu}^{2+}]$$

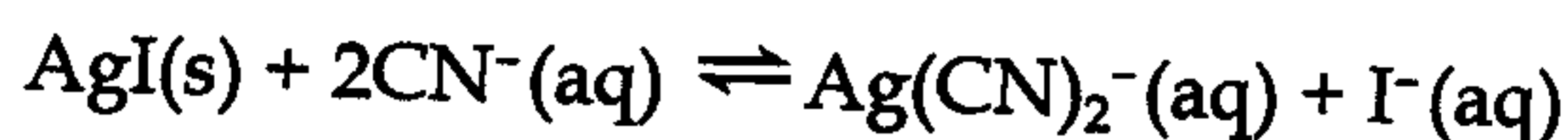
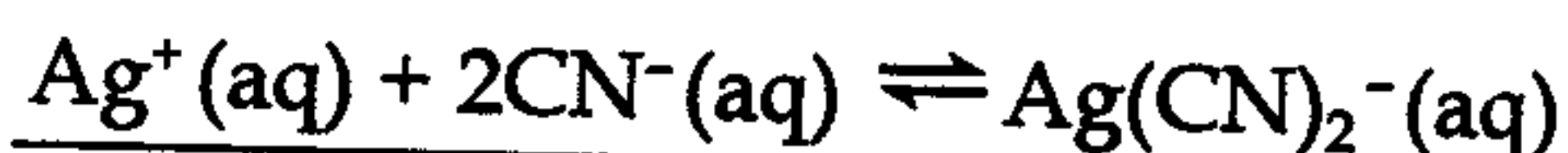
17.60 $\text{NiC}_2\text{O}_4(\text{s}) \rightleftharpoons \text{Ni}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}); \quad K_{sp} = [\text{Ni}^{2+}][\text{C}_2\text{O}_4^{2-}] = 4 \times 10^{-10}$

When the salt has just dissolved, $[\text{C}_2\text{O}_4^{2-}]$ will be 0.020 M. Thus $[\text{Ni}^{2+}]$ must be less than $4 \times 10^{-10} / 0.020 = 2 \times 10^{-8} \text{ M}$. To achieve this low $[\text{Ni}^{2+}]$ we must complex the Ni^{2+} ion with NH_3 : $\text{Ni}^{2+}(\text{aq}) + 6\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(\text{aq})$. Essentially all Ni(II) is in the form of the complex, so $[\text{Ni}(\text{NH}_3)_6^{2+}] = 0.020$. Find K_f for $\text{Ni}(\text{NH}_3)_6^{2+}$ in Table 17.1.

$$K_f = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}]}{[\text{Ni}^{2+}][\text{NH}_3]^6} = \frac{(0.020)}{(2 \times 10^{-8})[\text{NH}_3]^6} = 1.2 \times 10^9; [\text{NH}_3]^6 = 8.33 \times 10^{-4};$$

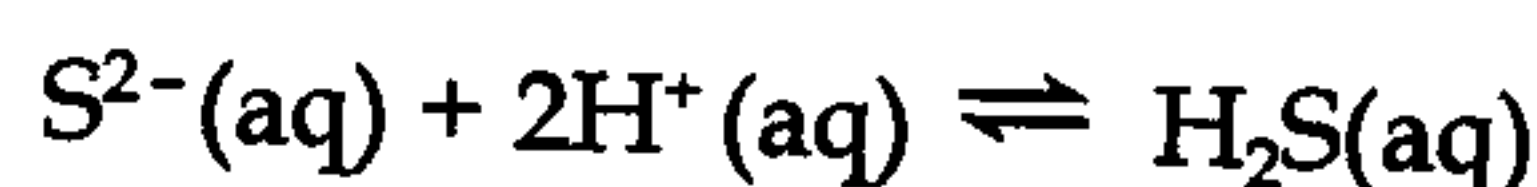
$$[\text{NH}_3] = 0.307 = 0.3 \text{ M}$$

17.61 *Analyze/Plan.* We are asked to calculate K_{eq} for a particular reaction, making use of pertinent K_{sp} and K_f values from Appendix D and Table 17.1. Write the dissociation equilibrium for AgI and the formation reaction for $\text{Ag}(\text{CN})_2^-$. Use algebra to manipulate these equations and their associated equilibrium constants to obtain the desired reaction and its equilibrium constant. *Solve.*

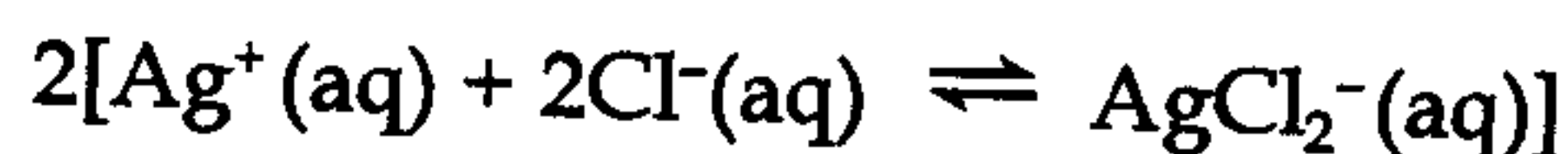


$$K = K_{sp} \times K_f = [\text{Ag}^+][\text{I}^-] \times \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = (8.3 \times 10^{-17})(1 \times 10^{21}) = 8 \times 10^4$$

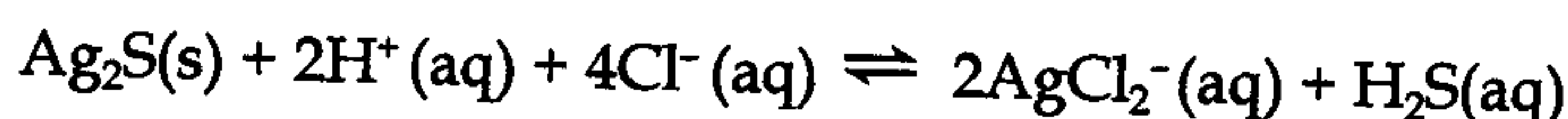
17.62 $\text{Ag}_2\text{S}(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{S}^{2-}(\text{aq})$ K_{sp}



$$1/(K_{a1} \times K_{a2})$$



$$K_f^2$$



$$K = \frac{K_{sp} \times K_f^2}{K_{a1} \times K_{a2}} = \frac{(6 \times 10^{-51})(1.1 \times 10^5)^2}{(9.5 \times 10^{-8})(1 \times 10^{-19})} = 7.64 \times 10^{-15} = 8 \times 10^{-15}$$

Precipitation; Qualitative Analysis

17.63 *Analyze/Plan.* Follow the logic in Sample Exercise 17.15. Precipitation conditions: will Q (see Chapter 15) exceed K_{sp} for the compound? *Solve.*

(a) In base, Ca^{2+} can form $\text{Ca}(\text{OH})_2(\text{s})$.



$$Q = [\text{Ca}^{2+}][\text{OH}^{-}]^2; [\text{Ca}^{2+}] = 0.050 \text{ M}; \text{pOH} = 14 - 8.0 = 6.0; [\text{OH}^{-}] = 1.0 \times 10^{-6} \text{ M}$$

$$Q = (0.050)(1.0 \times 10^{-6})^2 = 5.0 \times 10^{-14}; K_{sp} = 6.5 \times 10^{-6} \text{ (Appendix D)}$$

$Q < K_{sp}$, no $\text{Ca}(\text{OH})_2$ precipitates.

(b) $\text{Ag}_2\text{SO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^{+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}); K_{sp} = [\text{Ag}^{+}]^2[\text{SO}_4^{2-}]$

$$[\text{Ag}^{+}] = \frac{0.050 \text{ M} \times 100 \text{ mL}}{110 \text{ mL}} = 4.545 \times 10^{-2} = 4.5 \times 10^{-2} \text{ M}$$

$$[\text{SO}_4^{2-}] = \frac{0.050 \text{ M} \times 10 \text{ mL}}{110 \text{ mL}} = 4.545 \times 10^{-3} = 4.5 \times 10^{-3} \text{ M}$$

$$Q = (4.545 \times 10^{-2})^2 (4.545 \times 10^{-3}) = 9.4 \times 10^{-6}; K_{sp} = 1.5 \times 10^{-5}$$

$Q < K_{sp}$, no Ag_2SO_4 precipitates.

17.64 (a) $\text{Co}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Co}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}); K_{sp} = [\text{Co}^{2+}][\text{OH}^{-}]^2 = 1.3 \times 10^{-15}$

$$\text{pH} = 8.5; \text{pOH} = 14 - 8.5 = 5.5; [\text{OH}^{-}] = 10^{-5.5} = 3.16 \times 10^{-6} = 3 \times 10^{-6} \text{ M}$$

$$Q = (0.020)(3.16 \times 10^{-6})^2 = 2 \times 10^{-13}; Q > K_{sp}, \text{Co}(\text{OH})_2 \text{ will precipitate}$$

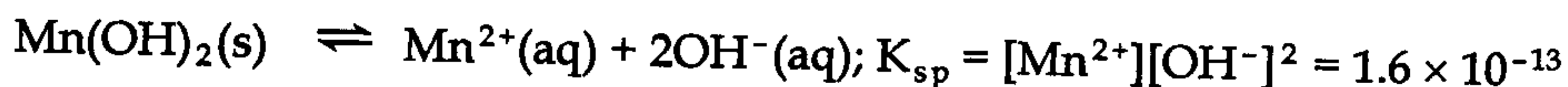
(b) $\text{AgIO}_3(\text{s}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{IO}_3^{-}(\text{aq}); K_{sp} = [\text{Ag}^{+}][\text{IO}_3^{-}] = 3.1 \times 10^{-8}$

$$[\text{Ag}^{+}] = \frac{0.010 \text{ M Ag}^{+} \times 0.020 \text{ L}}{0.030 \text{ L}} = 6.667 \times 10^{-3} = 6.7 \times 10^{-3} \text{ M}$$

$$[\text{IO}_3^{-}] = \frac{0.015 \text{ M IO}_3^{-} \times 0.010 \text{ L}}{0.030 \text{ L}} = 5.000 \times 10^{-3} = 5.0 \times 10^{-3} \text{ M}$$

$$Q = (6.667 \times 10^{-3})(5.00 \times 10^{-3}) = 3.3 \times 10^{-5}; Q > K_{sp}, \text{AgIO}_3 \text{ will precipitate}$$

17.65 *Analyze/Plan.* We are asked to calculate pH necessary to precipitate $\text{Mn}(\text{OH})_2(\text{s})$ if the resulting Mn^{2+} concentration is $\leq 1 \mu\text{g/L}$.



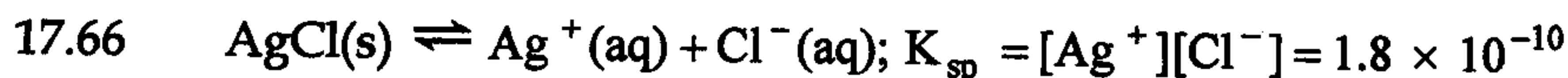
At equilibrium, $[\text{Mn}^{2+}][\text{OH}^{-}]^2 = 1.6 \times 10^{-13}$. Change concentration $\text{Mn}^{2+}(\text{aq})$ to mol/L and solve for $[\text{OH}^{-}]$. *Solve.*

$$\frac{1 \mu\text{g Mn}^{2+}}{1 \text{ L}} \times \frac{1 \times 10^{-6} \text{ g}}{1 \mu\text{g}} \times \frac{1 \text{ mol Mn}^{2+}}{54.94 \text{ g Mn}^{2+}} = 1.82 \times 10^{-8} = 2 \times 10^{-8} \text{ M Mn}^{2+}$$

$$1.6 \times 10^{-13} = (1.82 \times 10^{-8})[\text{OH}^{-}]^2; [\text{OH}^{-}]^2 = 8.79 \times 10^{-6}; [\text{OH}^{-}] = 2.96 \times 10^{-3} = 3 \times 10^{-3} \text{ M}$$

$$\text{pOH} = 2.53; \text{pH} = 14 - 2.53 = 11.47 = 11.5$$

Aqueous Equilibria



$$[\text{Ag}^+] = \frac{0.10 \text{ M} \times 0.2 \text{ mL}}{10.2 \text{ mL}} = 2 \times 10^{-3} \text{ M}; \quad [\text{Cl}^-] = \frac{1.8 \times 10^{-10}}{2 \times 10^{-3} \text{ M}} = 9 \times 10^{-8} \text{ M}$$

$$\frac{9 \times 10^{-8} \text{ mol Cl}^-}{1 \text{ L}} \times \frac{35.45 \text{ g Cl}^-}{1 \text{ mol Cl}^-} \times 0.0102 \text{ L} = 3.25 \times 10^{-8} \text{ g Cl}^- = 3 \times 10^{-8} \text{ g Cl}^-$$

17.67 *Analyze/Plan.* We are asked which ion will precipitate first from a solution containing $\text{Pb}^{2+}(aq)$ and $\text{Ag}^+(aq)$ when $\text{I}^-(aq)$ is added. Follow the logic in Sample Exercise 17.16. Calculate $[\text{I}^-]$ needed to initiate precipitation of each ion. The cation that requires lower $[\text{I}^-]$ will precipitate first. *Solve.*

$$\text{Ag}^+: K_{sp} = [\text{Ag}^+][\text{I}^-]; 8.3 \times 10^{-17} = (2.0 \times 10^{-4})[\text{I}^-]; [\text{I}^-] = \frac{8.3 \times 10^{-17}}{2.0 \times 10^{-4}} = 4.2 \times 10^{-13} \text{ M I}^-$$

$$\text{Pb}^{2+}: K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2; 7.9 \times 10^{-9} = (1.5 \times 10^{-3})[\text{I}^-]^2; [\text{I}^-] = \left(\frac{7.9 \times 10^{-9}}{1.5 \times 10^{-3}} \right)^{1/2} = 2.3 \times 10^{-3} \text{ M I}^-$$

AgI will precipitate first, at $[\text{I}^-] = 4.2 \times 10^{-13} \text{ M}$.

17.68 (a) Precipitation will begin when $Q = K_{sp}$.

$$\text{BaSO}_4: K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$$

$$1.1 \times 10^{-10} = (0.010)[\text{SO}_4^{2-}]; [\text{SO}_4^{2-}] = 1.1 \times 10^{-8} \text{ M}$$

$$\text{SrSO}_4: K_{sp} = [\text{Sr}^{2+}][\text{SO}_4^{2-}] = 3.2 \times 10^{-7}$$

$$3.2 \times 10^{-7} = (0.010)[\text{SO}_4^{2-}]; [\text{SO}_4^{2-}] = 3.2 \times 10^{-5} \text{ M}$$

The $[\text{SO}_4^{2-}]$ necessary to begin precipitation is the smaller of the two values, $1.1 \times 10^{-8} \text{ M SO}_4^{2-}$.

(b) Ba^{2+} precipitates first, because it requires the smaller $[\text{SO}_4^{2-}]$.

(c) Sr^{2+} will begin to precipitate when $[\text{SO}_4^{2-}]$ in solution (not bound in BaSO_4) reaches $3.2 \times 10^{-5} \text{ M}$.

17.69 *Analyze/Plan.* Use Figure 17.22 and the description of the five qualitative analysis "groups" in Section 17.7 to analyze the given data. *Solve.*

The first two experiments eliminate Group 1 and 2 ions (Figure 17.22). The fact that no insoluble phosphates form in the filtrate from the third experiment rules out Group 4 ions. The ions which might be in the sample are those of Group 3, that is, Al^{3+} , Fe^{3+} , Zn^{2+} , Cr^{3+} , Ni^{2+} , Co^{2+} , or Mn^{2+} , and those of Group 5, NH_4^+ , Na^+ or K^+ .

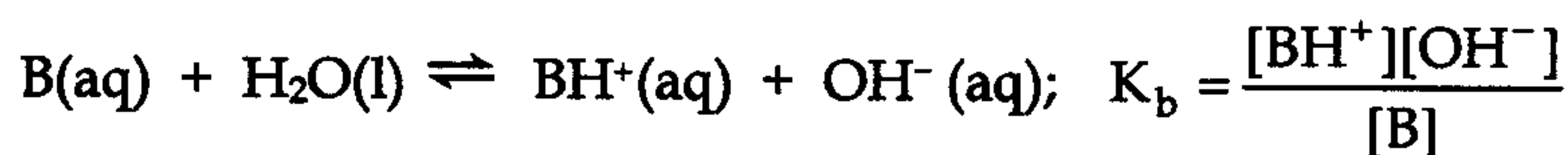
17.70 Initial solubility in water rules out CdS and HgO . Formation of a precipitate on addition of HCl indicates the presence of $\text{Pb}(\text{NO}_3)_2$ (formation of PbCl_2). Formation of a precipitate on addition of H_2S at pH 1 probably indicates $\text{Cd}(\text{NO}_3)_2$ (formation of CdS). (This test can be misleading because enough Pb^{2+} can remain in solution after filtering PbCl_2 to lead to visible precipitation of PbS .) Absence of a precipitate on

addition of H_2S at pH 8 indicates that ZnSO_4 is not present. The yellow flame test indicates presence of Na^+ . In summary, $\text{Pb}(\text{NO}_3)_2$ and Na_2SO_4 are definitely present, $\text{Cd}(\text{NO}_3)_2$ is probably present, and CdS , HgO and ZnSO_4 are definitely absent.

- 17.71 *Analyze/Plan.* We are asked to devise a procedure to separate various pairs of ions in aqueous solutions. In each case, refer to Figure 17.22 to find a set of conditions where the solubility of the two ions differs. Construct a procedure to generate these conditions. *Solve.*
- Cd^{2+} is in Gp. 2, but Zn^{2+} is not. Make the solution acidic using 0.5 M HCl; saturate with H_2S . CdS will precipitate, ZnS will not.
 - $\text{Cr}(\text{OH})_3$ is amphoteric but $\text{Fe}(\text{OH})_3$ is not. Add excess base; $\text{Fe}(\text{OH})_3(\text{s})$ precipitates, but Cr^{3+} forms the soluble complex $\text{Cr}(\text{OH})_4^-$.
 - Mg^{2+} is a member of Gp. 4, but K^+ is not. Add $(\text{NH}_4)_2\text{HPO}_4$ to a basic solution; Mg^{2+} precipitates as MgNH_4PO_4 , K^+ remains in solution.
 - Ag^+ is a member of Gp. 1, but Mn^{2+} is not. Add 6 M HCl, precipitate Ag^+ as $\text{AgCl}(\text{s})$.
- 17.72
- Make the solution slightly acidic and saturate with H_2S ; CdS will precipitate, Na^+ remains in solution.
 - Make the solution acidic, saturate with H_2S ; CuS will precipitate, Mg^{2+} remains in solution.
 - Add HCl, PbCl_2 precipitates. (It is best to carry out the reaction in an ice-water bath to reduce the solubility of PbCl_2 .)
 - Add dilute HCl; AgCl precipitates, Hg^{2+} remains in solution.
- 17.73
- Because phosphoric acid is a weak acid, the concentration of free $\text{PO}_4^{3-}(\text{aq})$ in an aqueous phosphate solution is low except in strongly basic media. In less basic media, the solubility product of the phosphates that one wishes to precipitate is not exceeded.
 - K_{sp} for those cations in Group 3 is much larger. Thus, to exceed K_{sp} a higher $[\text{S}^{2-}]$ is required. This is achieved by making the solution more basic.
 - They should all redissolve in strongly acidic solution, e.g., in 12 M HCl (all the chlorides of Group 3 metals are soluble).
- 17.74 The addition of $(\text{NH}_4)_2\text{HPO}_4$ could result in precipitation of salts from metal ions of the other groups. The $(\text{NH}_4)_2\text{HPO}_4$ will render the solution basic, so metal hydroxides could form as well as insoluble phosphates. It is essential to separate the metal ions of a group from other metal ions before carrying out the specific tests for that group.

Additional Exercises

- 17.75 *Analyze/Plan.* Follow the approach for deriving the Henderson-Hasselbach (H-H) equation from the K_a expression shown in Section 17.2. Begin with a general K_b expression. *Solve.*



$\text{pOH} = -\log[\text{OH}^-]$; rearrange K_b to solve for $[\text{OH}^-]$.

$$[\text{OH}^-] = \frac{K_b[\text{B}]}{[\text{BH}^+]}; \text{ take the } -\log \text{ of both sides}$$

$$-\log[\text{OH}^-] = -\log K_b + (-\log[\text{B}] - (-\log[\text{BH}^+]))$$

$$\text{pOH} = \text{p}K_b + \log[\text{BH}^+] - \log[\text{B}]$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{BH}^+]}{[\text{B}]}$$

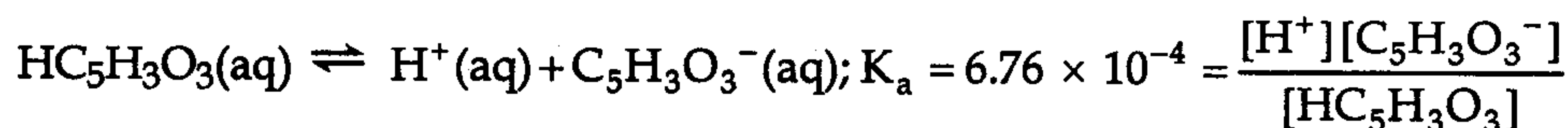
17.76 Benzene sulfonic acid = BSOH, sodium benzene sulfonate = BSONa

Use Equation 17.9, $\text{pH} = \text{p}K_a + \log [\text{CB}]/[\text{CA}]$.

$$\text{pH} = 2.25 + \log(0.125 \text{ M BSONa}/0.150 \text{ M BSOH})$$

$$\text{pH} = 2.25 + \log(0.8333) = 2.25 + (-0.0792) = 2.17$$

17.77 The equilibrium of interest is



Begin by calculating $[\text{HC}_5\text{H}_3\text{O}_3]$ and $[\text{C}_5\text{H}_3\text{O}_3^-]$ for each case.

$$(a) \quad \frac{25.0 \text{ g HC}_5\text{H}_3\text{O}_3}{0.250 \text{ L soln}} \times \frac{1 \text{ mol HC}_5\text{H}_3\text{O}_3}{112.1 \text{ g HC}_5\text{H}_3\text{O}_3} = 0.8921 = 0.892 \text{ M HC}_5\text{H}_3\text{O}_3$$

$$\frac{30.0 \text{ g NaC}_5\text{H}_3\text{O}_3}{0.250 \text{ L soln}} \times \frac{1 \text{ mol NaC}_5\text{H}_3\text{O}_3}{134.1 \text{ g NaC}_5\text{H}_3\text{O}_3} = 0.8949 = 0.895 \text{ M C}_5\text{H}_3\text{O}_3^-$$

$$[\text{H}^+] = \frac{K_a[\text{HC}_5\text{H}_3\text{O}_3]}{[\text{C}_5\text{H}_3\text{O}_3^-]} = \frac{6.76 \times 10^{-4} (0.8921 - x)}{(0.8949 + x)} \approx \frac{6.76 \times 10^{-4} (0.8921)}{(0.8949)}$$

$$[\text{H}^+] = 6.74 \times 10^{-4} \text{ M}, \text{ pH} = 3.171$$

(b) For dilution, $M_1 V_1 = M_2 V_2$

$$[\text{HC}_5\text{H}_3\text{O}_3] = \frac{0.250 \text{ M} \times 30.0 \text{ mL}}{125 \text{ mL}} = 0.0600 \text{ M}$$

$$[\text{C}_5\text{H}_3\text{O}_3^-] = \frac{0.220 \text{ M} \times 20.0 \text{ mL}}{125 \text{ mL}} = 0.0352 \text{ M}$$

$$[\text{H}^+] \approx \frac{6.76 \times 10^{-4} (0.0600)}{0.0352} = 1.15 \times 10^{-3} \text{ M}, \text{ pH} = 2.938$$

(yes, $[\text{H}^+]$ is $< 5\%$ of 0.0352 M)

(c) $0.0850 \text{ M} \times 0.500 \text{ L} = 0.0425 \text{ mol HC}_5\text{H}_3\text{O}_3$

$$1.65 \text{ M} \times 0.0500 \text{ L} = 0.0825 \text{ mol NaOH}$$

	$\text{HC}_5\text{H}_3\text{O}_3(\text{aq})$	+	$\text{NaOH}(\text{aq})$	\rightarrow	$\text{NaC}_5\text{H}_3\text{O}_3(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$
initial	0.0425 mol		0.0825 mol				
reaction	-0.0425 mol		-0.0425 mol		+0.0425 mol		
after	0 mol		0.0400 mol		0.0425 mol		

The strong base NaOH dominates the pH; the contribution of $\text{C}_5\text{H}_3\text{O}_3^-$ is negligible. This combination would be "after the equivalence point" of a titration. The total volume is 0.550 L.

$$[\text{OH}^-] = \frac{0.0400 \text{ mol}}{0.550 \text{ L}} = 0.0727 \text{ M}; \text{pOH} = 1.138, \text{pH} = 12.862$$

17.78 $K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$; at pH = 4.68, $[\text{HIn}] = [\text{In}^-]$; $[\text{H}^+] = K_a$; pH = pK_a = 4.68

17.79 (a) $\text{HA}(\text{aq}) + \text{B}(\text{aq}) \rightleftharpoons \text{HB}^+(\text{aq}) + \text{A}^-(\text{aq})$ $K_{\text{eq}} = \frac{[\text{HB}^+][\text{A}^-]}{[\text{HA}][\text{B}]}$

(b) Note that the solution is slightly basic because B is a stronger base than HA is an acid. (Or, equivalently, that A⁻ is a stronger base than HB⁺ is an acid.) Thus, a little of the A⁻ is used up in reaction: $\text{A}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HA}(\text{aq}) + \text{OH}^-(\text{aq})$. Since pH is not very far from neutral, it is reasonable to assume that the reaction in part (a) has gone far to the right, and that $[\text{A}^-] \approx [\text{HB}^+]$ and $[\text{HA}] \approx [\text{B}]$. Then

$$K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} = 8.0 \times 10^{-5}; \text{ when pH} = 9.2, [\text{H}^+] = 6.31 \times 10^{-10} = 6 \times 10^{-10} \text{ M}$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 8.0 \times 10^{-5} / 6.31 \times 10^{-10} = 1.268 \times 10^5 = 1 \times 10^5$$

From the assumptions above, $\frac{[\text{A}^-]}{[\text{HA}]} = \frac{[\text{HB}^+]}{[\text{B}]}$, so $K_{\text{eq}} \approx \frac{[\text{A}^-]^2}{[\text{HA}]^2} = 1.608 \times 10^{10} = 2 \times 10^{10}$

(c) K_b for the reaction $\text{B}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{BH}^+(\text{aq}) + \text{OH}^-(\text{aq})$ can be calculated by noting that the equilibrium constant for the reaction in part (a) can be written as $K = K_a(\text{HA}) \times K_b(\text{B}) / K_w$. (You should prove this to yourself.) Then,

$$K_b(\text{B}) = \frac{K \times K_w}{K_a(\text{HA})} = \frac{(1.608 \times 10^{10})(1.0 \times 10^{-14})}{8.0 \times 10^{-5}} = 2.010 = 2$$

K_b(B) is larger than K_a(HA), as it must be if the solution is basic.

17.80 (a) $K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$; $[\text{H}^+] = \frac{K_a[\text{HCOOH}]}{[\text{HCOO}^-]}$

Buffer A: $[\text{HCOOH}] = [\text{HCOO}^-] = \frac{1.00 \text{ mol}}{1.00 \text{ L}} = 1.00 \text{ M}$

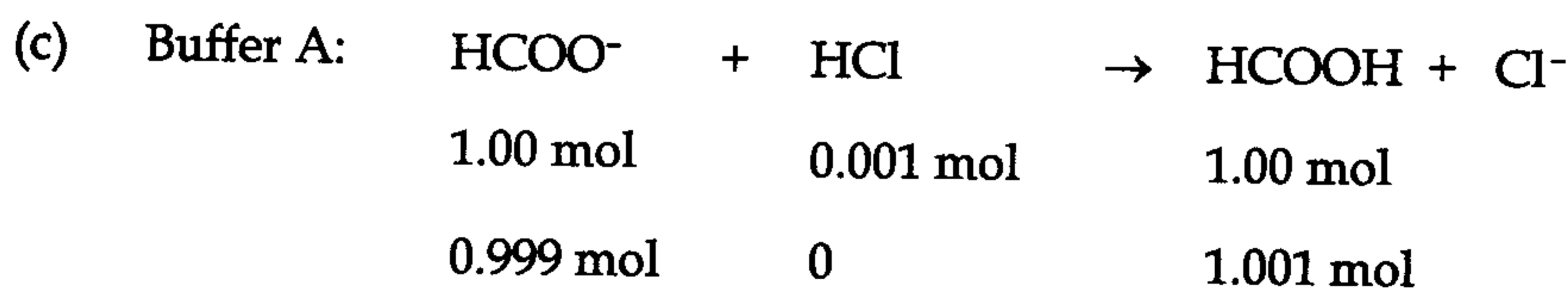
$$[\text{H}^+] = \frac{1.8 \times 10^{-4} (1.00 \text{ M})}{(1.00 \text{ M})} = 1.8 \times 10^{-4} \text{ M}, \text{pH} = 3.74$$

$$\text{Buffer B: } [\text{HCOOH}] = [\text{HCOO}^-] = \frac{0.010 \text{ mol}}{1.00 \text{ L}} = 0.010 \text{ M}$$

$$[\text{H}^+] = \frac{1.8 \times 10^{-4} (0.010 \text{ M})}{(0.010 \text{ M})} = 1.8 \times 10^{-4} \text{ M}, \text{ pH} = 3.74$$

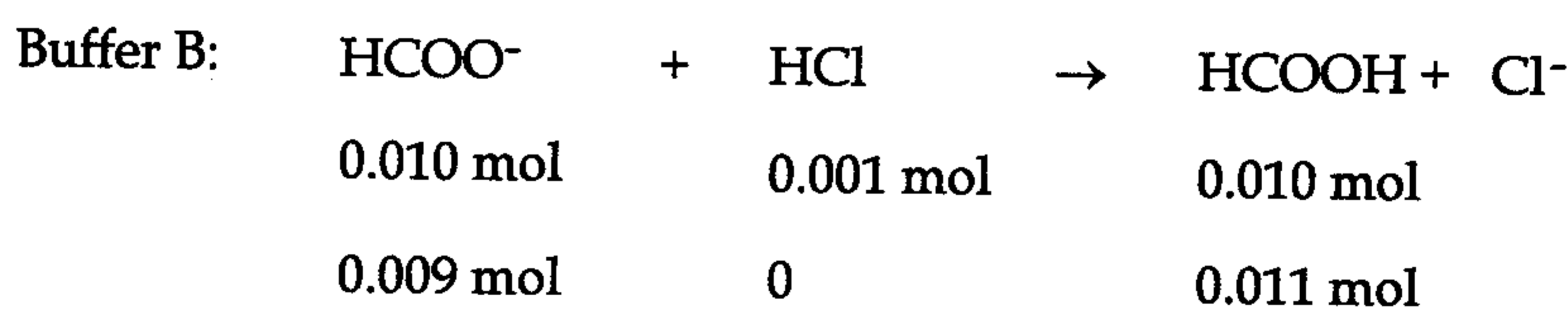
The pH of a buffer is determined by the identity of the conjugate acid/conjugate base pair (that is, the relevant K_a value) and the ratio of concentrations of the conjugate acid and conjugate base. The absolute concentrations of the components is not relevant. The pH values of the two buffers are equal because they both contain HCOOH and HCOONa and the $[\text{HCOOH}] / [\text{HCOO}^-]$ ratio is the same in both solutions.

- (b) Buffer capacity is determined by the absolute amount of conjugate acid and conjugate base available to absorb strong acid (H^+) or strong base (OH^-) that is added to the buffer. Buffer A has the greater capacity because it contains the greater absolute concentrations of HCOOH and HCOO^- .



$$[\text{H}^+] = \frac{1.8 \times 10^{-4} (1.001)}{(0.999)} = 1.8 \times 10^{-4} \text{ M}, \text{ pH} = 3.74$$

(In a buffer calculation, volumes cancel and we can substitute moles directly into the K_a expression.)



$$[\text{H}^+] = \frac{1.8 \times 10^{-4} (0.011)}{(0.009)} = 2.2 \times 10^{-4} \text{ M}, \text{ pH} = 3.66$$

- (d) Buffer A: $1.00 \text{ M HCl} \times 0.010 \text{ L} = 0.010 \text{ mol H}^+$ added

$$\text{mol HCOOH} = 1.00 + 0.010 = 1.01 \text{ mol}$$

$$\text{mol HCOO}^- = 1.00 - 0.010 = 0.99 \text{ mol}$$

$$[\text{H}^+] = \frac{1.8 \times 10^{-4} (1.01)}{(0.99)} = 1.8 \times 10^{-4} \text{ M}, \text{ pH} = 3.74$$

$$\text{Buffer B: mol HCOOH} = 0.010 + 0.010 = 0.020 \text{ mol} = 0.020 \text{ M}$$

$$\text{mol HCOO}^- = 0.010 - 0.010 = 0.000 \text{ mol}$$

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

The solution is no longer a buffer; the only source of HCOO^- is the dissociation of HCOOH .

$$K_a = \frac{[\text{H}^+][\text{COO}^-]}{[\text{HCOOH}]} = \frac{x^2}{(0.020 - x) M}$$

The extent of ionization is greater than 5%; from the quadratic formula, $x = [\text{H}^+] = 1.8 \times 10^{-3}$, $\text{pH} = 2.74$.

- (e) Adding 10 mL of 1.00 M HCl to buffer B exceeded its capacity, while the pH of buffer A was unaffected. This is quantitative confirmation that buffer A has a significantly greater capacity than buffer B. In fact, 1.0 L of 1.0 M HCl would be required to exceed the capacity of buffer A. Buffer A, with 100 times more HCOOH and HCOO^- has 100 times the capacity of buffer B.

$$17.81 \quad \frac{0.15 \text{ mol CH}_3\text{COOH}}{1 \text{ L soln}} \times 0.750 \text{ L} = 0.1125 = 0.11 \text{ mol CH}_3\text{COOH}$$

$$0.1125 \text{ mol CH}_3\text{COOH} \times \frac{60.05 \text{ g CH}_3\text{COOH}}{1 \text{ mol CH}_3\text{COOH}} \times \frac{1 \text{ g gl acetic acid}}{0.99 \text{ g CH}_3\text{COOH}} \times \frac{1.00 \text{ mL gl acetic acid}}{1.05 \text{ g gl acetic acid}} = 6.5 \text{ mL glacial acetic acid}$$

At pH 4.50, $[\text{H}^+] = 10^{-4.50} = 3.16 \times 10^{-5} = 3.2 \times 10^{-5} \text{ M}$; this is small compared to 0.15 M CH_3COOH .

$$K_a = \frac{(3.16 \times 10^{-5})[\text{CH}_3\text{COO}^-]}{0.15} = 1.8 \times 10^{-5}; [\text{CH}_3\text{COO}^-] = 0.0854 = 0.085 \text{ M}$$

$$\frac{0.0854 \text{ mol CH}_3\text{COONa}}{1 \text{ L soln}} \times 0.750 \text{ L} \times \frac{82.03 \text{ g CH}_3\text{COONa}}{1 \text{ mol CH}_3\text{COONa}} = 5.253 = 5.25 \text{ g CH}_3\text{COONa}$$

- 17.82 (a) For a monoprotic acid (one H^+ per mole of acid), at the equivalence point moles OH^- added = moles H^+ originally present

$$M_B \times V_B = \text{g acid} / \text{molar mass}$$

$$\text{MM} = \frac{\text{g acid}}{M_B \times V_B} = \frac{0.2140 \text{ g}}{0.0950 \text{ M} \times 0.0274 \text{ L}} = 82.21 = 82.2 \text{ g/mol}$$

(b) initial mol HA = $\frac{0.2140 \text{ g}}{82.21 \text{ g/mol}} = 2.603 \times 10^{-3} = 2.60 \times 10^{-3} \text{ mol HA}$

$$\text{mol OH}^- \text{ added to pH 6.50} = 0.0950 \text{ M} \times 0.0150 \text{ L} = 1.425 \times 10^{-3} = 1.43 \times 10^{-3} \text{ mol OH}^-$$

	HA(aq)	+	NaOH(aq)	→	NaA(aq) + H ₂ O
before rx	$2.603 \times 10^{-3} \text{ mol}$		$1.425 \times 10^{-3} \text{ mol}$		0
change	$-1.425 \times 10^{-3} \text{ mol}$		$-1.425 \times 10^{-3} \text{ mol}$		$+1.425 \times 10^{-3} \text{ mol}$
after rx	$1.178 \times 10^{-3} \text{ mol}$		0		$1.425 \times 10^{-3} \text{ mol}$

$$[\text{HA}] = \frac{1.178 \times 10^{-3} \text{ mol}}{0.0400 \text{ L}} = 0.02945 = 0.0295 \text{ M}$$

$$[\text{A}^-] = \frac{1.425 \times 10^{-3} \text{ mol}}{0.0400 \text{ L}} = 0.03563 = 0.0356 \text{ M}; [\text{H}^+] = 10^{-6.50} = 3.162 \times 10^{-7} \\ = 3.2 \times 10^{-7} \text{ M}$$

The mixture after reaction (a buffer) can be described by the acid dissociation equilibrium.

	HA(aq)	⇌	H ⁺ (aq)	+	A ⁻ (aq)
initial	0.0295 M		0		0.0356 M
equil	(0.0295 - 3.2 × 10 ⁻⁷ M)		3.2 × 10 ⁻⁷ M		(0.0356 + 3.2 × 10 ⁻⁷) M

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \approx \frac{(3.162 \times 10^{-7})(0.03563)}{(0.02945)} = 3.8 \times 10^{-7}$$

(Although we have carried 3 figures through the calculation to avoid rounding errors, the data dictate an answer with 2 significant figures.)

- 17.83 At the equivalence point of a titration, moles strong base added equals moles weak acid initially present. $M_B \times V_B = \text{mol base added} = \text{mol acid initial}$

At the half-way point, the volume of base is one-half of the volume required to reach the equivalence point, and the moles base delivered equals one-half of the mol acid initially present. This means that one-half of the weak acid HA is converted to the conjugate base A⁻. If exactly half of the acid reacts, mol HA = mol A⁻ and [HA] = [A⁻] at the half-way point.

From Equation [17.9], $\text{pH} = \text{p}K_a + \log \frac{[\text{conj. base}]}{[\text{conj. acid}]} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}^-]}$.

If [A⁻]/[HA] = 1, log(1) = 0 and pH = pK_a of the weak acid being titrated.

- 17.84 (a) $\frac{0.4885 \text{ g KHP}}{0.100 \text{ L}} \times \frac{1 \text{ mol KHP}}{204.2 \text{ g KHP}} = 0.02392 = 0.0239 \text{ M P}^{2-}$ at the equivalence point

The pH at the equivalence point is determined by the hydrolysis of P²⁻.



$$K_b = \frac{[\text{HP}^-][\text{OH}^-]}{[\text{P}^{2-}]} = \frac{K_w}{K_a \text{ for HP}^-} = \frac{1.0 \times 10^{-14}}{3.1 \times 10^{-6}} = 3.23 \times 10^{-9} = 3.2 \times 10^{-9}$$

$$3.23 \times 10^{-9} = \frac{x^2}{(0.02392 - x)} \approx \frac{x^2}{0.02392}; X = [\text{OH}^-] = 8.8 \times 10^{-6} \text{ M}$$

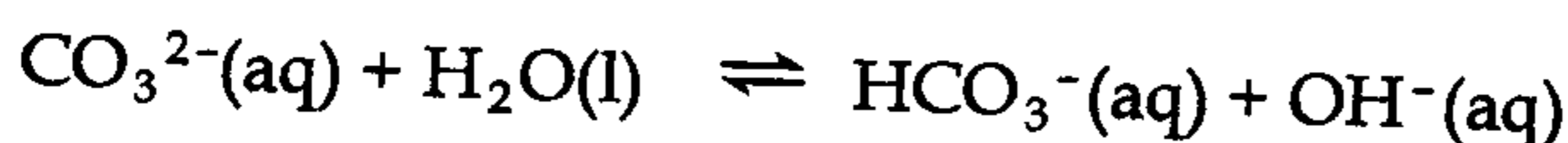
pH = 14 - 5.06 = 8.94. From Figure 16.7, either phenolphthalein (pH 8.2 - 10.0) or thymol blue (pH 8.0 - 9.6) could be used to detect the equivalence point. Phenolphthalein is usually the indicator of choice because the colorless to pink change is easier to see.

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

$$(b) \quad 0.4885 \text{ g KHP} \times \frac{1 \text{ mol KHP}}{204.2 \text{ g KHP}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol KHP}} \times \frac{1}{0.03855 \text{ L NaOH}} = 0.06206 \text{ M NaOH}$$

17.85 (a) Initially, the solution is 0.100 M in CO_3^{2-} .



$$K_b = \frac{[\text{HCO}_3^{-}][\text{OH}^{-}]}{[\text{CO}_3^{2-}]} = \frac{K_w}{K_a[\text{HCO}_3^{-}]} = 1.79 \times 10^{-4} = 1.8 \times 10^{-4}$$

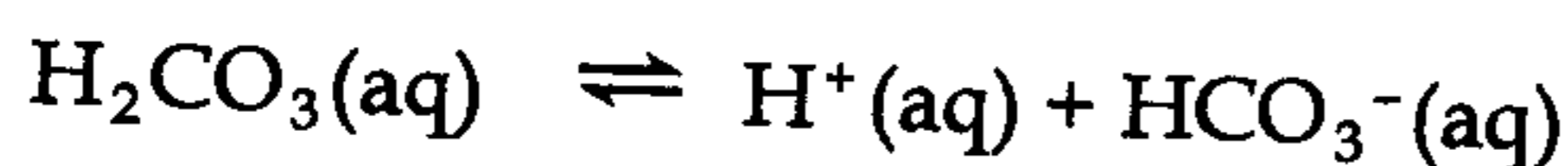
Proceeding in the usual way for a weak base,

calculate $[\text{OH}^{-}] = 4.23 \times 10^{-3} = 4.2 \times 10^{-3} \text{ M}$, $\text{pH} = 11.63$.

(b) It will require 40.00 mL of 0.100 M HCl to reach the first equivalence point, at which point HCO_3^{-} is the predominant species.

(c) An additional 40.00 mL are required to react with HCO_3^{-} to form H_2CO_3 , the predominant species at the second equivalence point.

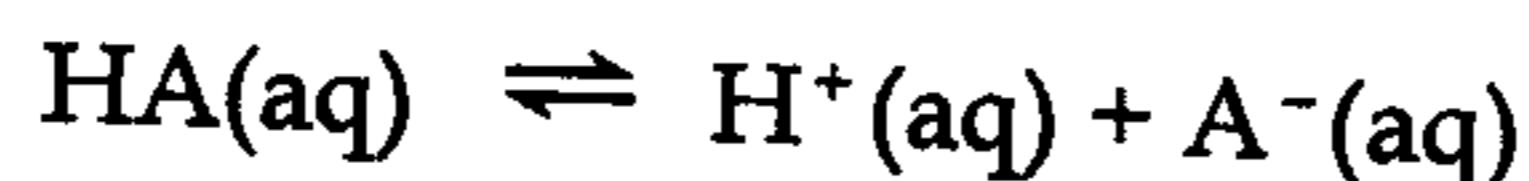
(d) At the second equivalence point there is a 0.0333 M solution of H_2CO_3 . By the usual procedure for a weak acid:



$$K_a = \frac{[\text{H}^{+}][\text{HCO}_3^{-}]}{[\text{H}_2\text{CO}_3]} = 4.3 \times 10^{-7}; \frac{(x)^2}{(0.0333-x)} \approx \frac{x^2}{0.0333} \approx 4.3 \times 10^{-7}$$

$$x = 1.20 \times 10^{-4} = 1.2 \times 10^{-4} \text{ M H}^{+}; \text{pH} = 3.92$$

17.86 The reaction involved is $\text{HA}(\text{aq}) + \text{OH}^{-}(\text{aq}) \rightleftharpoons \text{A}^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$. We thus have 0.080 mol A^{-} and 0.12 mol HA in a total volume of 1.0 L, so the "initial" molarities of A^{-} and HA are 0.080 M and 0.12 M, respectively. The weak acid equilibrium of interest is



$$(a) \quad K_a = \frac{[\text{H}^{+}][\text{A}^{-}]}{[\text{HA}]}; [\text{H}^{+}] = 10^{-4.80} = 1.58 \times 10^{-5} = 1.6 \times 10^{-5} \text{ M}$$

Assuming $[\text{H}^{+}]$ is small compared to $[\text{HA}]$ and $[\text{A}^{-}]$,

$$K_a \approx \frac{(1.58 \times 10^{-5})(0.080)}{(0.12)} = 1.06 \times 10^{-5} = 1.1 \times 10^{-5}, \text{p}K_a = 4.98$$

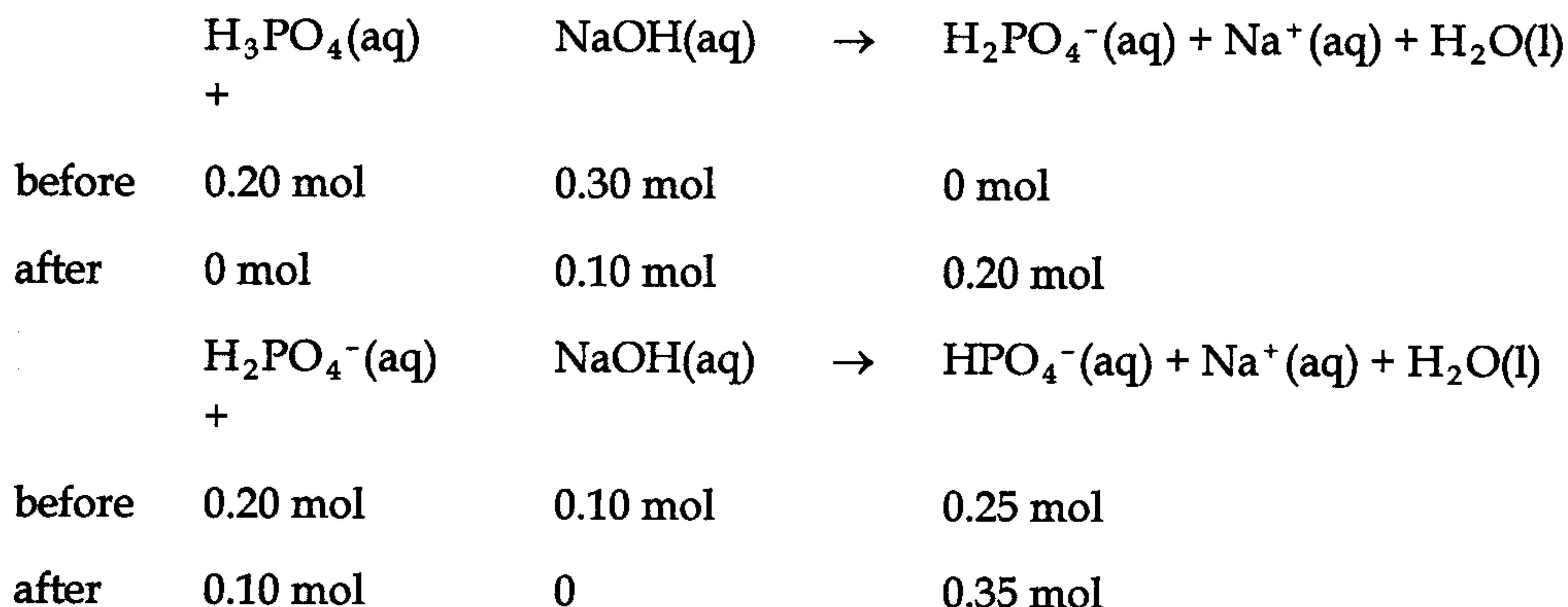
(b) At $\text{pH} = 5.00$, $[\text{H}^{+}] = 1.0 \times 10^{-5} \text{ M}$. Let b = extra moles NaOH.

$$[\text{HA}] = 0.12 - b, [\text{A}^{-}] = 0.080 + b$$

$$1.06 \times 10^{-5} \approx \frac{(1.0 \times 10^{-5})(0.080 + b)}{(0.12 - b)}; 2.06 \times 10^{-5} b = 4.72 \times 10^{-7};$$

$$b = 0.023 \text{ mol NaOH}$$

- 17.87 Assume that H_3PO_4 will react with NaOH in a stepwise fashion: (This is not unreasonable, since the three K_a values for H_3PO_4 are significantly different.)

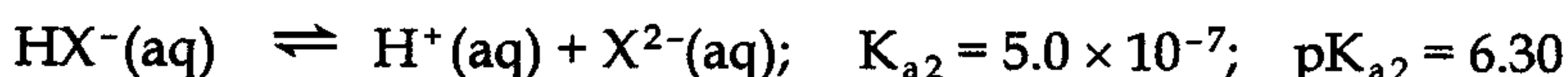
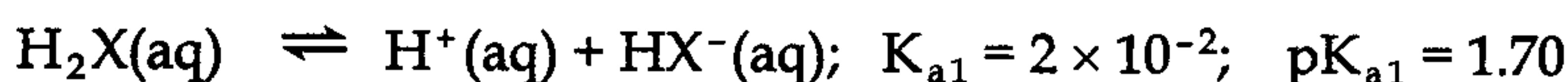


Thus, after all NaOH has reacted, the resulting 1.00 L solution is a buffer containing 0.10 mol H_2PO_4^- and 0.35 mol HPO_4^{2-} . $\text{H}_2\text{PO}_4^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$

$$K_a = 6.2 \times 10^{-8} = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{[\text{H}_2\text{PO}_4^-]}; [\text{H}^+] = \frac{6.2 \times 10^{-8} (0.10 \text{ M})}{0.35 \text{ M}} = 1.77 \times 10^{-8} = 1.8 \times 10^{-8} \text{ M};$$

pH = 7.75

- 17.88 The pH of a buffer system is centered around $\text{p}K_a$ for the conjugate acid component. For a diprotic acid, two conjugate acid/conjugate base pairs are possible.



Clearly $\text{HX}^- / \text{X}^{2-}$ is the more appropriate combination for preparing a buffer with pH = 6.50. The $[\text{H}^+]$ in this buffer = $10^{-6.50} = 3.16 \times 10^{-7} = 3.2 \times 10^{-7} \text{ M}$. Using the K_{a2} expression to calculate the $[\text{X}^{2-}] / [\text{HX}^-]$ ratio:

$$K_{a2} = \frac{[\text{H}^+][\text{X}^{2-}]}{[\text{HX}^-]}; \frac{K_{a2}}{[\text{H}^+]} = \frac{[\text{X}^{2-}]}{[\text{HX}^-]} = \frac{5.0 \times 10^{-7}}{3.16 \times 10^{-7}} = 1.58 = 1.6$$

Since X^{2-} and HX^- are present in the same solution, the ratio of concentrations is also a ratio of moles.

$$\frac{[\text{X}^{2-}]}{[\text{HX}^-]} = \left(\frac{\text{mol X}^{2-} / \text{L soln}}{\text{mol HX}^- / \text{L soln}} \right) = \frac{\text{mol X}^{2-}}{\text{mol HX}^-} = 1.58; \text{mol X}^{2-} = (1.58) \text{ mol HX}^-$$

In the 1.0 L of 1.0 M H_2X , there is 1.0 mol of X^{2-} containing material.

Thus, $\text{mol HX}^- + 1.58 (\text{mol HX}^-) = 1.0 \text{ mol}$. $2.58 (\text{mol HX}^-) = 1.0$;

$\text{mol HX}^- = 1.0 / 2.58 = 0.39 \text{ mol HX}^-$; $\text{mol X}^{2-} = 1.0 - 0.39 = 0.61 \text{ mol X}^{2-}$.

Thus enough 1.0 M NaOH must be added to produce 0.39 mol HX^- and 0.61 mol X^{2-} .

Considering the neutralization in a step-wise fashion (see discussion of titrations of polyprotic acids in Section 17.3).

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

	$\text{H}_2\text{X}(\text{aq})$	+	$\text{NaOH}(\text{aq})$	\rightarrow	$\text{HX}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
before	1.0 mol		1 mol		0
after	0		0		1.0 mol
	$\text{HX}^-(\text{aq})$	+	$\text{NaOH}(\text{aq})$	\rightarrow	$\text{X}^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
before	1.0				0.61
change	-0.61		-0.61		+0.61
after	0.39		0		0.61

Starting with 1.0 mol of H_2X , 1.0 mol of NaOH is added to completely convert it to 1.0 mol of HX^- . Of that 1.0 mol of HX^- , 0.61 mol must be converted to 0.61 mol X^{2-} . The total moles of NaOH added is $(1.00 + 0.61) = 1.61$ mol NaOH .

$$\text{L NaOH} = \frac{\text{mol NaOH}}{\text{M NaOH}} = \frac{1.61 \text{ mol}}{1.0 \text{ M}} = 1.6 \text{ L of } 1.0 \text{ M NaOH}$$

- 17.89 $\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$ will be formed by reaction $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ with NaOH .
 $0.1000 \text{ M} \times 0.02500 \text{ L} = 2.500 \times 10^{-3} \text{ mol CH}_3\text{CH}(\text{OH})\text{COOH}$; $b = \text{mol NaOH}$ needed

	$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	+	NaOH	\rightarrow	$\text{CH}_3\text{CH}(\text{OH})\text{COO}^- + \text{H}_2\text{O} + \text{Na}^+$
initial	$2.500 \times 10^{-3} \text{ mol}$		$b \text{ mol}$		
rx	$-b \text{ mol}$		$-b \text{ mol}$		$+b \text{ mol}$
after rx	$(2.500 \times 10^{-3} - b) \text{ mol}$		0		$b \text{ mol}$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}; K_a = 1.4 \times 10^{-4}; [\text{H}^+] = 10^{-\text{pH}} = 10^{-3.75} = 1.778 \times 10^{-4} = 1.8 \times 10^{-4} \text{ M}$$

Since solution volume is the same for reaction $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ and $\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$, we can use moles in the equation for $[\text{H}^+]$.

$$K_a = 1.4 \times 10^{-4} = \frac{1.778 \times 10^{-4} (b)}{(2.500 \times 10^{-3} - b)}; 0.7874 (2.500 \times 10^{-3} - b) = b, 1.969 \times 10^{-3} = 1.7874 b,$$

$$b = 1.10 \times 10^{-3} = 1.1 \times 10^{-3} \text{ mol OH}^-$$

(The precision of K_a dictates that the result has 2 sig figs.)

Substituting this result into the K_a expression gives $[\text{H}^+] = 1.8 \times 10^{-4}$. This checks and confirms our result. Calculate volume NaOH required from $M = \text{mol/L}$.

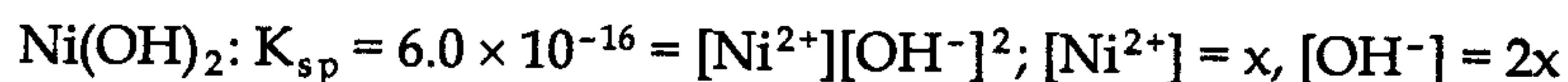
$$1.10 \times 10^{-3} \text{ mol OH}^- \times \frac{1 \text{ L}}{1.000 \text{ mol}} \times \frac{1 \mu\text{L}}{1 \times 10^{-6} \text{ L}} = 1.1 \times 10^3 \mu\text{L} (1.1 \text{ mL})$$

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

A person breathing normally exhales $\text{CO}_2(\text{g})$. Rapid breathing causes excess $\text{CO}_2(\text{g})$ to be removed from the blood. By LeChatelier's principle, this causes both equilibria above to shift right, reducing $[\text{H}^+]$ in the blood and raising blood pH.

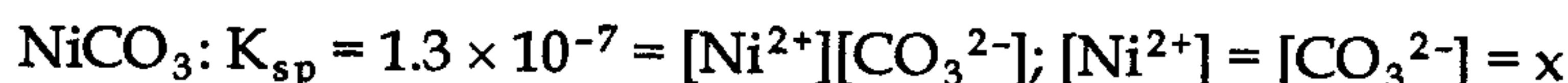
- (b) Breathing in a paper bag traps the exhaled CO_2 ; the gas in the bag contains more CO_2 than ambient air. When a person inhales gas from the bag, a greater amount (partial pressure) of $\text{CO}_2(\text{g})$ in the lungs shifts the equilibria left, increasing $[\text{H}^+]$ and lowering blood pH.

- 17.91 (a) CdS: 8.0×10^{-28} ; CuS: 6×10^{-37} CdS has greater molar solubility.
 (b) PbCO_3 : 7.4×10^{-14} ; BaCrO_4 : 2.1×10^{-10} BaCrO_4 has greater molar solubility.
 (c) Since the stoichiometry of the two complexes is not the same, K_{sp} values can't be compared directly; molar solubilities must be calculated from K_{sp} values.



$$6.0 \times 10^{-16} = (x)(2x)^2 = 4x^3; x = 5.3 \times 10^{-6} \text{ M Ni}^{2+}$$

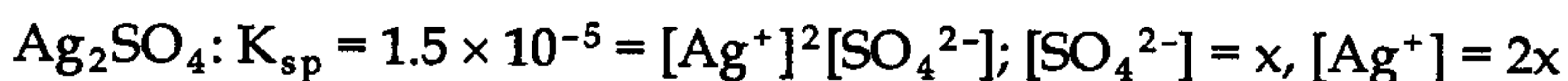
Note that $[\text{OH}^-]$ from the autoionization of water is less than 1% of $[\text{OH}^-]$ from Ni(OH)_2 and can be neglected.



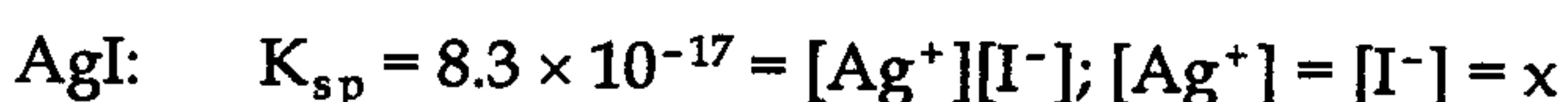
$$1.3 \times 10^{-7} = x^2; x = 3.6 \times 10^{-4} \text{ M Ni}^{2+}$$

NiCO_3 has greater molar solubility than Ni(OH)_2 , but the values are much closer than expected from inspection of K_{sp} values alone.

- (d) Again, molar solubilities must be calculated for comparison.



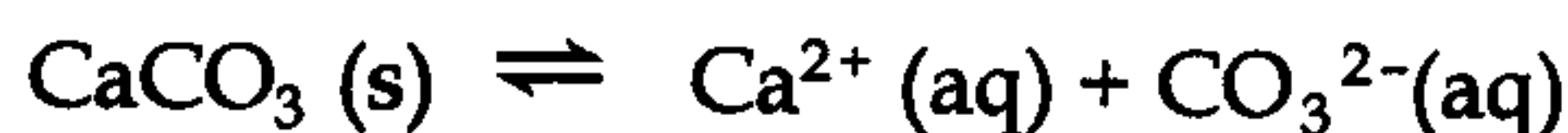
$$1.5 \times 10^{-5} = (2x)^2(x) = 4x^3; x = 1.6 \times 10^{-2} \text{ M SO}_4^{2-}$$



$$8.3 \times 10^{-17} = x^2; x = 9.1 \times 10^{-9} \text{ M Ag}^+$$

Ag_2SO_4 has greater molar solubility than AgI.

- 17.92 Consider the effects of common ions and competing equilibria on the solubility equilibrium.



- (a) 0.10 M NaCl, same. Neither Na^+ nor Cl^- are ions common to CaCO_3 . To a first approximation, the solubility of CaCO_3 is the same in 0.10 M NaCl as in water. (Ionic strength, an expression of the total number of ions in a solution, does influence solubility somewhat.)
 (b) 0.10 M $\text{Ca(NO}_3)_2$, less soluble. Ca^{2+} is common to CaCO_3 . The $\text{Ca}^{2+}(\text{aq})$ shifts the solubility equilibrium to the left and decreases the solubility of CaCO_3 relative to its solubility in water.
 (c) 0.10 M Na_2CO_3 , less soluble. CO_3^{2-} is common to CaCO_3 . The $\text{CO}_3^{2-}(\text{aq})$ shifts the solubility equilibrium to the left and decreases the solubility of CaCO_3 relative to pure water.
 (d) 0.10 M HCl, more soluble. H^+ reacts with CO_3^{2-} , removing it from solution and shifting the solubility equilibrium to the right. CaCO_3 is more soluble in 0.10 M HCl (or any acid) than in water.

- 17.93 (a) Hydroxyapatite: $K_{sp} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{OH}^-]$
 Fluoroapatite: $K_{sp} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{F}^-]$

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

- (b) For each mole of apatite dissolved, one mole of OH⁻ or F⁻ is formed. Express molar solubility, *s*, in terms of [OH⁻] and [F⁻].

Hydroxyapatite: [OH⁻] = *s*, [Ca²⁺] = 5*s*, [PO₄³⁻] = 3*s*

$$K_{sp} = 6.8 \times 10^{-27} = (5s)^5(3s)^3 (s) = 84,375 s^9$$

$$s^9 = 8.059 \times 10^{-32} = 8.1 \times 10^{-32}$$

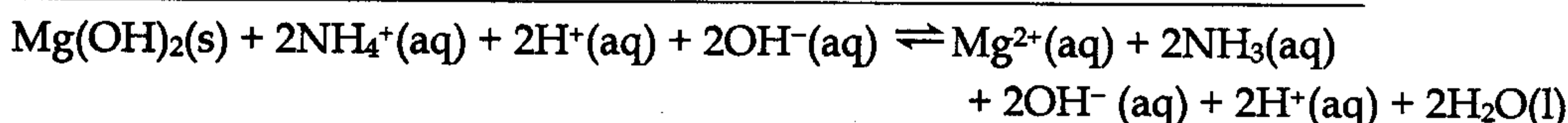
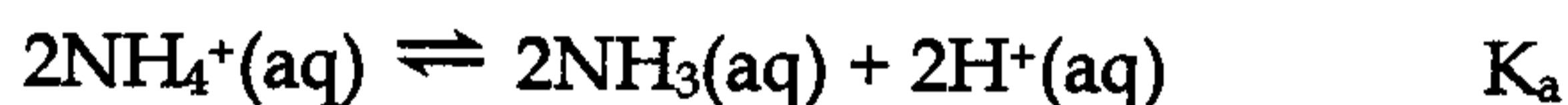
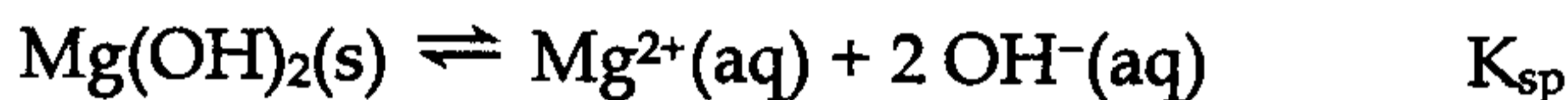
Use logs to find *s*. $s = 3.509 \times 10^{-4} = 3.5 \times 10^{-4} \text{ M Ca}_5(\text{PO}_4)_3\text{OH}$.

Fluoroapatite: [F⁻] = *s*, [Ca²⁺] = 5*s*, [PO₄³⁻] = 3*s*

$$K_{sp} = 1.0 \times 10^{-60} = (5s)^5(3s)^3 (s) = 84,375 s^9$$

$$s^9 = 1.185 \times 10^{-65} = 1.2 \times 10^{-65}; s = 6.109 \times 10^{-8} = 6.1 \times 10^{-8} \text{ M Ca}_5(\text{PO}_4)_3\text{F}$$

- 17.94 *Analyze/Plan.* Calculate the solubility of Mg(OH)₂ in 0.50 M NH₄Cl. Find *K_{sp}* for Mg(OH)₂ in Appendix D. NH₄⁺ is a weak acid, which will increase the solubility of Mg(OH)₂. Combine the various interacting equilibria to obtain an overall reaction. Calculate *K* for this reaction and use it to calculate solubility (*s*) for Mg(OH)₂ in 0.50 M NH₄Cl. *Solve.*



$$K = \frac{[\text{Mg}^{2+}][\text{NH}_3]^2}{[\text{NH}_4^{+}]^2} = \frac{K_{sp} \times K_a^2}{K_w^2}$$

$$K_a \text{ for } \text{NH}_4^{+} = \frac{K_w}{K_b \text{ for } \text{NH}_3}; \frac{K_a}{K_w} = \frac{1}{K_b}$$

$$K = \frac{K_{sp} \times K_a^2}{K_w^2} = \frac{K_{sp}}{K_b^2} = \frac{1.8 \times 10^{-11}}{(1.8 \times 10^{-5})^2} = 5.556 \times 10^{-2} = 5.6 \times 10^{-2}$$

Let [Mg²⁺] = *s*, [NH₃] = 2*s*, [NH₄⁺] = 0.50 - 2*s*

$$K = 5.6 \times 10^{-2} = \frac{[\text{Mg}^{2+}][\text{NH}_3]^2}{[\text{NH}_4^{+}]^2} = \frac{s(2s)^2}{(0.5 - 2s)^2} = \frac{4s^3}{0.25 - 2s + 4s^2}$$

$$5.6 \times 10^{-2}(0.25 - 2s + 4s^2) = 4s^3; 4s^3 - 0.222s^2 + 0.111s - 1.39 \times 10^{-2} = 0$$

Clearly, 2*s* is not small relative to 0.50. Solving the third-order equation, *s* = 0.1054 = 0.11 M. The solubility of Mg(OH)₂ in 0.50 M NH₄Cl is 0.11 mol/L.

Check. Substitute *s* = 0.1054 into the *K* expression.

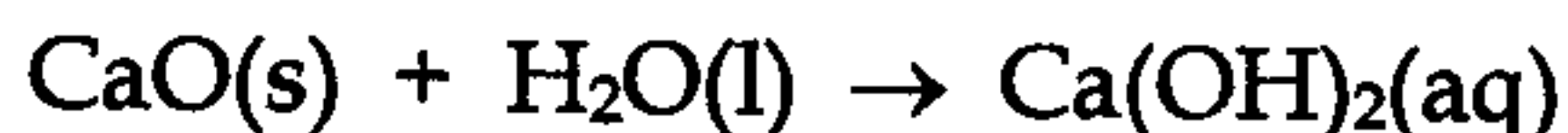
17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

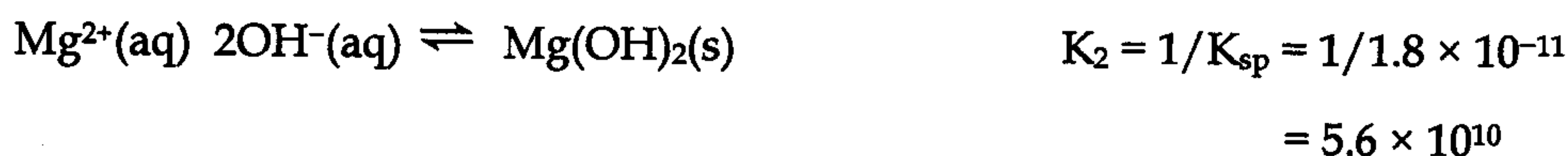
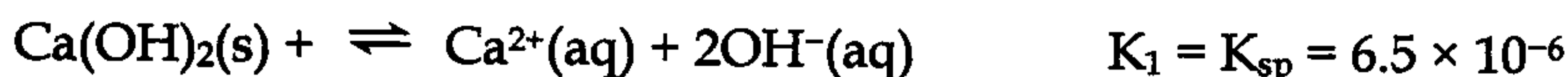
$$K = \frac{4(0.1054)^3}{[0.50 - 2(0.1054)]^2} = 5.6 \times 10^{-2}$$

The solubility and K value are consistent, to the precision of the K_{sp} and K_b values.

- 17.95 Calcium oxide dissolves in and reacts with water to form calcium hydroxide.



Ca(OH)_2 provides OH^- (aq) to precipitate Mg(OH)_2 (s), removing Mg^{2+} (aq) from seawater. Consider this reaction in two steps.



$$K = \frac{[\text{Ca}^{2+}]}{[\text{Mg}^{2+}]} = 3.6 \times 10^5$$

The reaction goes to completion. A stoichiometric amount of CaO quantitatively removes Mg^{2+} (aq) from seawater.

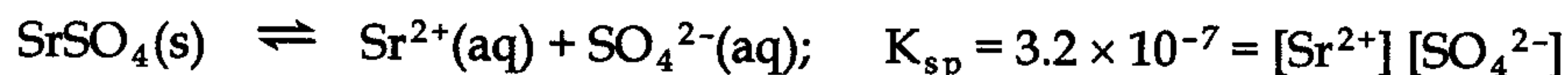
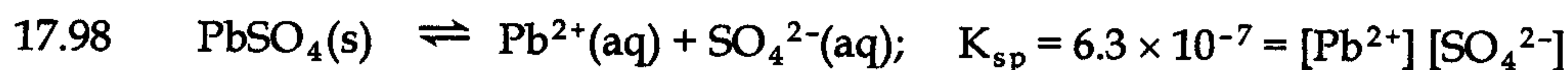
17.96 $K_{sp} = [\text{Ba}^{2+}][\text{MnO}_4^-]^2 = 2.5 \times 10^{-10}$

$$[\text{MnO}_4^-]^2 = 2.5 \times 10^{-10} / 2.0 \times 10^{-8} = 0.0125; \quad [\text{MnO}_4^-] = \sqrt{0.0125} = 0.11 \text{ M}$$

17.97 $[\text{Ca}^{2+}][\text{CO}_3^{2-}] = 4.5 \times 10^{-9}$; $[\text{Fe}^{2+}][\text{CO}_3^{2-}] = 2.1 \times 10^{-11}$

Since $[\text{CO}_3^{2-}]$ is the same for both equilibria:

$$[\text{CO}_3^{2-}] = \frac{4.5 \times 10^{-9}}{[\text{Ca}^{2+}]} = \frac{2.1 \times 10^{-11}}{[\text{Fe}^{2+}]}; \text{ rearranging } \frac{[\text{Ca}^{2+}]}{[\text{Fe}^{2+}]} = \frac{4.5 \times 10^{-9}}{2.1 \times 10^{-11}} = 214 = 2.1 \times 10^2$$



$$\text{Let } x = [\text{Pb}^{2+}], y = [\text{Sr}^{2+}], x + y = [\text{SO}_4^{2-}]$$

$$\frac{x(x+y)}{y(x+y)} = \frac{6.3 \times 10^{-7}}{3.2 \times 10^{-7}}; \quad \frac{x}{y} = 1.9688 = 2.0; \quad x = 1.969 y = 2.0 y$$

$$y(1.969 y + y) = 3.2 \times 10^{-7}; \quad 2.969 y^2 = 3.2 \times 10^{-7}; \quad y = 3.283 \times 10^{-4} = 3.3 \times 10^{-4}$$

$$x = 1.969 y; \quad x = 1.969(3.283 \times 10^{-4}) = 6.464 \times 10^{-4} = 6.5 \times 10^{-4}$$

$$[\text{Pb}^{2+}] = 6.5 \times 10^{-4} \text{ M}, \quad [\text{Sr}^{2+}] = 3.3 \times 10^{-4} \text{ M}, \quad [\text{SO}_4^{2-}] = (3.283 + 6.464) \times 10^{-4} = 9.7 \times 10^{-4} \text{ M}$$

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises



$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{C}_2\text{O}_4^{2-}] = 8.6 \times 10^{-5}$$

If $[\text{Mg}^{2+}]$ is to be $3.0 \times 10^{-2} \text{ M}$, $[\text{C}_2\text{O}_4^{2-}] = 8.6 \times 10^{-5} / 3.0 \times 10^{-2} = 2.87 \times 10^{-3} = 2.9 \times 10^{-3} \text{ M}$

The oxalate ion undergoes hydrolysis:



$$K_{\text{b}} = \frac{[\text{HC}_2\text{O}_4^{-}][\text{OH}^{-}]}{[\text{C}_2\text{O}_4^{2-}]} = 1.0 \times 10^{-14} / 6.4 \times 10^{-5} = 1.56 \times 10^{-10} = 1.6 \times 10^{-10}$$

$$[\text{Mg}^{2+}] = 3.0 \times 10^{-2} \text{ M}, [\text{C}_2\text{O}_4^{2-}] = 2.87 \times 10^{-3} = 2.9 \times 10^{-3} \text{ M}$$

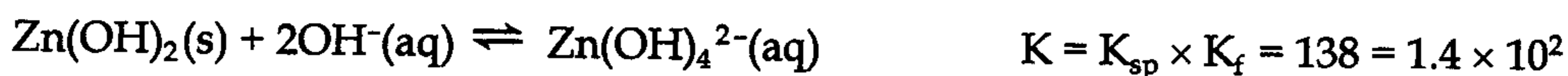
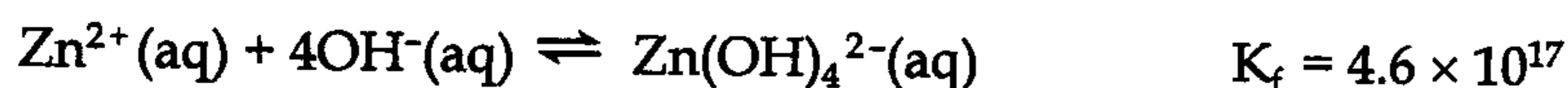
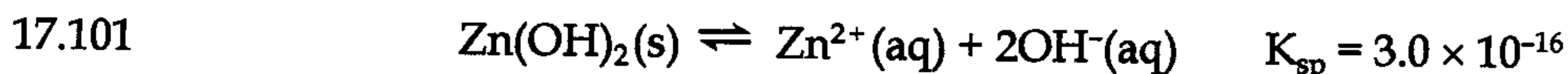
$$[\text{HC}_2\text{O}_4^{-}] = (3.0 \times 10^{-2} - 2.87 \times 10^{-3}) \text{ M} = 2.71 \times 10^{-2} = 2.7 \times 10^{-2} \text{ M}$$

$$[\text{OH}^{-}] = 1.56 \times 10^{-10} \times \frac{[\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^{-}]} = 1.56 \times 10^{-10} \times \frac{(2.87 \times 10^{-3})}{(2.71 \times 10^{-2})} = 1.652 \times 10^{-11}$$

$$[\text{OH}^{-}] = 1.7 \times 10^{-11}; \text{pOH} = 10.78, \text{pH} = 3.22$$

17.100 The student failed to account for the hydrolysis of the AsO_4^{3-} ion. If there were no hydrolysis, $[\text{Mg}^{2+}]$ would indeed be 1.5 times that of $[\text{AsO}_4^{3-}]$. However, as the reaction $\text{AsO}_4^{3-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HAsO}_4^{2-}(\text{aq}) + \text{OH}^{-}(\text{aq})$ proceeds, the ion product $[\text{Mg}^{2+}]^3[\text{AsO}_4^{3-}]^2$ falls below the value for K_{sp} . More $\text{Mg}_3(\text{AsO}_4)_2$ dissolves, more hydrolysis occurs, and so on, until an equilibrium is reached. At this point $[\text{Mg}^{2+}]$ in solution is much greater than 1.5 times free $[\text{AsO}_4^{3-}]$. However, it is exactly 1.5 times the total concentration of all arsenic-containing species. That is,

$$[\text{Mg}^{2+}] = 1.5 ([\text{AsO}_4^{3-}] + [\text{HAsO}_4^{2-}] + [\text{H}_2\text{AsO}_4^{-}] + [\text{H}_3\text{AsO}_4])$$



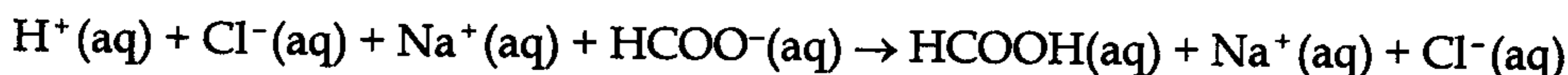
$$K = 138 = 1.4 \times 10^2 = \frac{[\text{Zn}(\text{OH})_4^{2-}]}{[\text{OH}^{-}]^2}$$

If 0.015 mol $\text{Zn}(\text{OH})_2$ dissolves, 0.015 mol $\text{Zn}(\text{OH})_4^{2-}$ should be present at equilibrium.

$$[\text{OH}^{-}]^2 = \frac{(0.015)}{138}; [\text{OH}^{-}] = 1.043 \times 10^{-2} \text{ M}; [\text{OH}^{-}] \geq 1.0 \times 10^{-2} \text{ M or pH} \geq 12.02$$

Integrative Exercises

17.102 (a) Complete ionic ($\text{CHO}_2^{-} = \text{HCOO}^{-}$)



Na^{+} and Cl^{-} are spectator ions.



- (b) The net ionic equation in part (a) is the reverse of the dissociation of HCOOH.

$$K = \frac{1}{K_a} = \frac{1}{1.8 \times 10^{-4}} = 5.55 \times 10^3 = 5.6 \times 10^3$$

- (c) For Na⁺ and Cl⁻, this is just a dilution problem.

$$M_1 V_1 = M_2 V_2; V_2 \text{ is } 50.0 \text{ mL} + 50.0 \text{ mL} = 100.0 \text{ mL}$$

$$\text{Cl}^-: \frac{0.15 \text{ M} \times 50.0 \text{ mL}}{100.0 \text{ mL}} = 0.075 \text{ M}; \text{Na}^+: \frac{0.15 \text{ M} \times 50.0 \text{ mL}}{100.0 \text{ mL}} = 0.075 \text{ M}$$

H⁺ and HCOO⁻ react to form HCOOH. Since $K \gg 1$, the reaction essentially goes to completion.

$$0.15 \text{ M} \times 0.0500 \text{ mL} = 7.5 \times 10^{-3} \text{ mol H}^+$$

$$\frac{0.15 \text{ M} \times 0.0500 \text{ mL} = 7.5 \times 10^{-3} \text{ mol HCOO}^-}{= 7.5 \times 10^{-3} \text{ mol HCOOH}}$$

Solve the weak acid problem to determine [H⁺], [HCOO⁻] and [HCOOH] at equilibrium.

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}; [\text{H}^+] = [\text{HCOO}^-] = x \text{ M}; [\text{HCOOH}] = \frac{(7.5 \times 10^{-3} - x) \text{ mol}}{0.100 \text{ L}} = (0.075 - x) \text{ M}$$

$$1.8 \times 10^{-4} = \frac{x^2}{(0.075 - x)} \approx \frac{x^2}{0.075}; x = 3.7 \times 10^{-3} \text{ M H}^+ \text{ and HCOO}^-$$

$$[\text{HCOOH}] = (0.075 - 0.0037) = 0.071 \text{ M}$$

$$\frac{[\text{H}^+]}{[\text{HCOOH}]} \times 100 = \frac{3.7 \times 10^{-3}}{0.075} \times 100 = 4.9\% \text{ dissociation}$$

In summary:

$$[\text{Na}^+] = [\text{Cl}^-] = 0.075 \text{ M}, [\text{HCOOH}] = 0.071 \text{ M}, [\text{H}^+] = [\text{HCOO}^-] = 0.0037 \text{ M}$$

- 17.103 (a) For a monoprotic acid (one H⁺ per mole of acid), at the equivalence point moles OH⁻ added = moles H⁺ originally present

$$M_B \times V_B = \text{g acid} / \text{molar mass}$$

$$\text{MM} = \frac{\text{g acid}}{M_B \times V_B} = \frac{0.1044 \text{ g}}{0.0500 \text{ M} \times 0.02210 \text{ L}} = 94.48 = 94.5 \text{ g/mol}$$

- (b) 11.05 mL is exactly half-way to the equivalence point (22.10 mL). When half of the unknown acid is neutralized, [HA] = [A⁻], [H⁺] = K_a and pH = pK_a.

$$K_a = 10^{-4.89} = 1.3 \times 10^{-5}$$

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

(c) From Appendix D, Table D.1, acids with K_a values close to 1.3×10^{-5} are

name	K_a	formula	molar mass
propionic	1.3×10^{-5}	C_2H_5COOH	74.1
butanoic	1.5×10^{-5}	C_3H_7COOH	88.1
acetic	1.8×10^{-5}	CH_3COOH	60.1
hydroazoic	1.9×10^{-5}	HN_3	43.0

Of these, butanoic has the closest match for K_a and molar mass, but the agreement is not good.

$$17.104 \quad n = \frac{PV}{RT} = 735 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{7.5 \text{ L}}{295 \text{ K}} \times \frac{K - \text{mol}}{0.08206 \text{ L} \cdot \text{atm}} = 0.300 = 0.30 \text{ mol NH}_3$$

$$0.40 \text{ M} \times 0.50 \text{ L} = 0.20 \text{ mol HCl}$$

	HCl(aq)	+	NH ₃ (g)	→	NH ₄ ⁺ (aq)	+	Cl ⁻ (aq)
Before	0.20 mol		0.30 mol				
after	0		0.10 mol		0.20 mol		0.20 mol

The solution will be a buffer because of the substantial concentrations of NH₃ and NH₄⁺ present. Use K_a for NH₄⁺ to describe the equilibrium.



$$\text{equil. } 0.20 - x \quad 0.10 + x \quad x$$

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = 5.6 \times 10^{-10}; K_a = \frac{[NH_3][H^+]}{[NH_4^+]}; [H^+] = \frac{K_a[NH_4^+]}{[NH_3]}$$

Since this expression contains a ratio of concentrations, volume will cancel and we can substitute moles directly. Assume x is small compared to 0.10 and 0.20.

$$[H^+] = \frac{5.56 \times 10^{-10} (0.20)}{(0.10)} = 1.111 \times 10^{-9} = 1.1 \times 10^{-9} \text{ M}, \text{pH} = 8.95$$

17.105 Calculate the initial M of aspirin in the stomach and solve the equilibrium problem to find equilibrium concentrations of $C_8H_7O_2COOH$ and $C_8H_7O_2COO^-$. At $\text{pH} = 2$, $[H^+] = 1 \times 10^{-2}$.

$$\frac{325 \text{ mg}}{\text{tablet}} \times 2 \text{ tablets} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol } C_8H_7O_2COOH}{180.2 \text{ g } C_8H_7O_2COOH} \times \frac{1}{1 \text{ L}} = 3.61 \times 10^{-3} = 4 \times 10^{-3} \text{ M}$$

	$C_8H_7O_2COOH(aq)$	\rightleftharpoons	$C_8H_7O_2COO^-$	+	$H^+(aq)$
initial	$3.61 \times 10^{-3} \text{ M}$		0		$1 \times 10^{-2} \text{ M}$
equil	$(3.61 \times 10^{-3} - x) \text{ M}$		$x \text{ M}$		$(1 \times 10^{-2} + x) \text{ M}$

$$K_a = 3 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_8\text{H}_7\text{O}_2\text{COO}^-]}{[\text{C}_8\text{H}_7\text{O}_2\text{COOH}]} = \frac{(0.01+x)(x)}{(3.61 \times 10^{-3} - x)} \approx \frac{0.01x}{3.61 \times 10^{-3}}$$

$$x = [\text{C}_8\text{H}_7\text{O}_2\text{COO}^-] = 1.08 \times 10^{-5} = 1 \times 10^{-5} \text{ M}$$

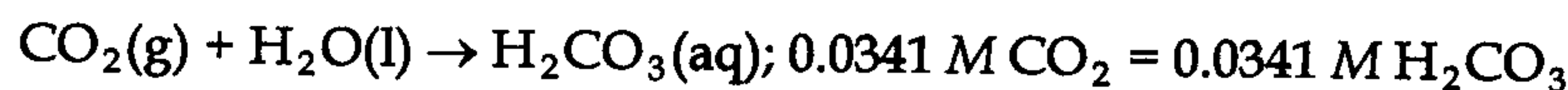
$$\% \text{ ionization} = \frac{1.08 \times 10^{-5} \text{ M C}_8\text{H}_7\text{O}_2\text{COO}^-}{3.61 \times 10^{-3} \text{ M C}_8\text{H}_7\text{O}_2\text{COOH}} \times 100 = 0.3\%$$

(% ionization is small, so the assumption was valid.)

$$\% \text{ aspirin molecules} = 100.0\% - 0.3\% = 99.7\% \text{ molecules}$$

17.106 According to Equation [13.4], $S_g = kP_g$

$$S_{\text{CO}_2} = 3.1 \times 10^{-2} \frac{\text{mol}}{\text{L-atm}} \times 1.10 \text{ atm} = 0.0341 = \frac{0.034 \text{ mol}}{\text{L}} = 0.034 \text{ M CO}_2$$



Consider the stepwise dissociation of $\text{H}_2\text{CO}_3(\text{aq})$.

	$\text{H}_2\text{CO}_3(\text{aq})$	\rightleftharpoons	$\text{H}^+(\text{aq})$	+	$\text{HCO}_3^-(\text{aq})$
initial	0.0341 M		0		0
equil.	(0.0341-x) M		x		x

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{(0.0341-x)} \approx \frac{x^2}{0.0341} \approx 4.3 \times 10^{-7}$$

$$x^2 = 1.47 \times 10^{-8}; x = 1.2 \times 10^{-4} \text{ M H}^+; \text{pH} = 3.92$$

$K_{a2} = 5.6 \times 10^{-11}$; assume the second ionization does not contribute significantly to $[\text{H}^+]$.

17.107 $\text{Ca}(\text{OH})_2(\text{aq}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + 2\text{H}_2\text{O}$

$$\text{mmol HCl} = M \times \text{mL} = 0.0983 \text{ M} \times 11.23 \text{ mL} = 1.1039 = 1.10 \text{ mmol HCl}$$

$$\text{mmol Ca}(\text{OH})_2 = \text{mmol HCl}/2 = 1.1039/2 = 0.55195 = 0.552 \text{ mmol Ca}(\text{OH})_2$$

$$[\text{Ca}^{2+}] = \frac{0.55195 \text{ mmol}}{50.00 \text{ mL}} = 0.01104 = 0.0110 \text{ M}$$

$$[\text{OH}^-] = 2[\text{Ca}^{2+}] = 0.02208 = 0.0221 \text{ M}$$

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = (0.01104)(0.02208)^2 = 5.38 \times 10^{-6}$$

The value in Appendix D is 6.5×10^{-6} , a difference of 17%. Since a change in temperature does change the value of an equilibrium constant, the solution may not have been kept at 25 °C. It is also possible that experimental errors led to the difference in K_{sp} values.

17 Additional Aspects of Aqueous Equilibria

Solutions to Exercises

$$17.108 \quad \Pi = MRT, M = \frac{\Pi}{RT} = \frac{21 \text{ torr}}{298 \text{ K}} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{\text{K} \cdot \text{mol}}{0.08206 \text{ L} \cdot \text{atm}} = 1.13 \times 10^{-3} = 1.1 \times 10^{-3} \text{ M}$$



The total particle concentration is $1.13 \times 10^{-3} \text{ M}$. Each mole of SrSO_4 that dissolves produces 2 mol of ions, so $[\text{Sr}^{2+}] = [\text{SO}_4^{2-}] = 1.13 \times 10^{-3} \text{ M}/2 = 5.65 \times 10^{-4} = 5.7 \times 10^{-4} \text{ M}$.

$$K_{\text{sp}} = (5.65 \times 10^{-4})^2 = 3.2 \times 10^{-7}$$

17.109 For very dilute aqueous solutions, assume the solution density is 1 g/mL.

$$\text{ppb} = \frac{\text{g solute}}{10^9 \text{ g solution}} = \frac{1 \times 10^{-6} \text{ g solute}}{1 \times 10^3 \text{ g solution}} = \frac{\mu\text{g solute}}{\text{L solution}}$$

$$(a) \quad K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}; [\text{Ag}^+] = (1.8 \times 10^{-10})^{1/2} = 1.34 \times 10^{-5} = 1.3 \times 10^{-5} \text{ M}$$

$$\frac{1.34 \times 10^{-5} \text{ mol Ag}^+}{\text{L}} \times \frac{107.9 \text{ g Ag}^+}{1 \text{ mol Ag}^+} \times \frac{1 \mu\text{g}}{1 \times 10^{-6} \text{ g}} = \frac{1.4 \times 10^3 \mu\text{g Ag}^+}{\text{L}} = 1.4 \times 10^3 \text{ ppb} = 1.4 \text{ ppm}$$

$$(b) \quad K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = 5.0 \times 10^{-13}; [\text{Ag}^+] = (5.0 \times 10^{-13})^{1/2} = 7.07 \times 10^{-7} = 7.1 \times 10^{-7} \text{ M}$$

$$\frac{7.07 \times 10^{-7} \text{ mol Ag}^+}{\text{L}} \times \frac{107.9 \text{ g Ag}^+}{1 \text{ mol Ag}^+} \times \frac{1 \mu\text{g}}{1 \times 10^{-6} \text{ g}} = 76 \text{ ppb}$$

$$(c) \quad K_{\text{sp}} = [\text{Ag}^+][\text{I}^-] = 8.3 \times 10^{-17}; [\text{Ag}^+] = (8.3 \times 10^{-17})^{1/2} = 9.11 \times 10^{-9} = 9.1 \times 10^{-9} \text{ M}$$

$$\frac{9.11 \times 10^{-9} \text{ mol Ag}^+}{\text{L}} \times \frac{107.9 \text{ g Ag}^+}{1 \text{ mol Ag}^+} \times \frac{1 \mu\text{g}}{1 \times 10^{-6} \text{ g}} = 0.98 \text{ ppb}$$

$\text{AgBr}(\text{s})$ would maintain $[\text{Ag}^+]$ in the correct range.

17.110 To determine precipitation conditions, we must know K_{sp} for $\text{CaF}_2(\text{s})$ and calculate Q under the specified conditions. $K_{\text{sp}} = 3.9 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2$

$[\text{Ca}^{2+}]$ and $[\text{F}^-]$: The term 1 ppb means 1 part per billion or 1 g solute per billion g solution. Assuming that the density of this very dilute solution is the density of water:

$$1 \text{ ppb} = \frac{1 \text{ g solute}}{1 \times 10^9 \text{ g solution}} \times \frac{1 \text{ g solution}}{1 \text{ mL solution}} \times \frac{1 \times 10^3 \text{ mL}}{1 \text{ L}} = \frac{1 \times 10^{-6} \text{ g solute}}{1 \text{ L solution}}$$

$$\frac{1 \times 10^{-6} \text{ g solute}}{1 \text{ L solution}} \times \frac{1 \mu\text{g}}{1 \times 10^{-6} \text{ g}} = 1 \mu\text{g}/1 \text{ L}$$

$$8 \text{ ppb Ca}^{2+} \times \frac{1 \mu\text{g}}{1 \text{ L}} = \frac{8 \mu\text{g Ca}^{2+}}{1 \text{ L}} = \frac{8 \times 10^{-6} \text{ g Ca}^{2+}}{1 \text{ L}} \times \frac{1 \text{ mol Ca}^{2+}}{40 \text{ g}} = 2 \times 10^{-7} \text{ M Ca}^{2+}$$

$$1 \text{ ppb F}^- \times \frac{1 \mu\text{g}}{1 \text{ L}} = \frac{1 \mu\text{g F}^-}{1 \text{ L}} = \frac{1 \times 10^{-6} \text{ g F}^-}{1 \text{ L}} \times \frac{1 \text{ mol F}^-}{19.0 \text{ g}} = 5 \times 10^{-8} \text{ M F}^-$$

$$Q = [\text{Ca}^{2+}][\text{F}^-]^2 = (2 \times 10^{-7})(5 \times 10^{-8})^2 = 5 \times 10^{-22}$$

$5 \times 10^{-22} < 3.9 \times 10^{-11}$, $Q < K_{\text{sp}}$, no CaF_2 will precipitate