

# 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 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

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  $X^-$ .

- (a) After addition of strong acid, [HX] will increase and  $[X^-]$  will decrease. Drawing (3) fits this description.
- (b) Adding of strong base causes [HX] to decrease and  $[X^-]$  to increase. Drawing (1) matches the description.
- (c) 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.*

- (a) *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.
- (b) *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).
- (c) *At the equivalence point*, all HA has been converted to  $A^-$ , with no excess HA or  $OH^-$  present. This is shown in diagram (iv).
- (d) *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.

- (a) Strong base in flask, pH starts high, ends low as acid is added. Only diagram (ii) fits this description.
- (b) 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.
- (c) Strong acid in the flask, pH starts very low, diagram (i).
- (d) 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  $1 \times 10^{-7}$ , while  $\text{p}K_a$  of 4.2 corresponds to  $K_a$  of  $6 \times 10^{-5}$ . 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 beaker of saturated  $\text{Cd}(\text{OH})_2(\text{aq})$  contains undissolved  $\text{Cd}(\text{OH})_2(\text{s})$ ,  $\text{Cd}^{2+}(\text{aq})$ , and  $\text{OH}^{-}(\text{aq})$ . Decide how amounts of each of these three components change when  $\text{HCl}(\text{aq})$  is added. *Solve.*

When  $\text{HCl}(\text{aq})$  is added, it reacts with  $\text{OH}^{-}(\text{aq})$  to form  $\text{H}_2\text{O}(\text{l})$  and  $\text{Cl}^{-}(\text{aq})$ . (Both have been omitted from the figure.) When  $\text{OH}^{-}(\text{aq})$  is removed from solution, more  $\text{Cd}(\text{OH})_2(\text{s})$  dissolves to replace it;  $[\text{Cd}^{2+}(\text{aq})]$  increases,  $[\text{OH}^{-}(\text{aq})]$  decreases and the amount of undissolved  $\text{Cd}(\text{OH})_2(\text{s})$  decreases. In the resulting solution,  $[\text{Cd}^{2+}(\text{aq})]$  is greater than  $[\text{OH}^{-}(\text{aq})]$  and there is less undissolved solid on the bottom of the beaker. Beaker A accurately represents the solution after equilibrium is reestablished.

17.9 *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)  $\text{CO}_2^{3-}$  from  $\text{BaCO}_3$  reacts with  $\text{H}^+$  from  $\text{HNO}_3$ , causing solubility of  $\text{BaCO}_3$  to increase with increasing  $\text{HNO}_3$  concentration. This behavior matches the right diagram.

(b) Extra  $\text{CO}_2^{3-}$  from  $\text{Na}_2\text{CO}_3$  decreases the solubility of  $\text{BaCO}_3$ . Solubility of  $\text{BaCO}_3$  decreases as  $[\text{Na}_2\text{CO}_3]$  increases. This behavior matches the left diagram.

- (c)  $\text{NaNO}_3$  has no common ions, nor does it enter into acid-base or complex ion equilibria with  $\text{Ba}^{2+}$  or  $\text{CO}_3^{2-}$ ; it does not affect the solubility of  $\text{BaCO}_3$ . This behavior is shown in the center diagram.
- 17.10 *Analyze/Plan.* Calculate the molarity of the solution assuming all  $\text{Ca(OH)}_2(\text{s})$  dissolves. Use this concentration along with the  $K_{\text{sp}}$  expression for  $\text{Ca(OH)}_2$  to answer the questions.
- (a) 
$$[\text{Ca(OH)}_2] = \frac{0.370 \text{ g Ca(OH)}_2}{0.500 \text{ L soln}} \times \frac{1 \text{ mol Ca(OH)}_2}{74.093 \text{ g Ca(OH)}_2} = 0.00998745 = 0.00999 \text{ M}$$
$$[\text{Ca}^{2+}] = 0.00999 \text{ M}; [\text{OH}^-] = 2(0.00998745) = 0.0199749 = 0.0200 \text{ M};$$
$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2. \text{ Calculate the reaction quotient using the calculated molarities. If it is equal to or greater than } K_{\text{sp}}, \text{ the resulting solution is saturated.}$$
$$Q = (0.0098745)(0.0199749)^2 = 3.99 \times 10^{-6}.$$
$$Q < K_{\text{sp}} (6.5 \times 10^{-6}) \text{ and the solution is not saturated.}$$
- (b) Consider the beakers individually.
- (i) The 50 mL of 1.0 M HCl is more than enough to neutralize 50 mL of 0.0200 M  $\text{OH}^-$  (aq). No precipitate forms.
- (ii) NaCl does not react with  $\text{Ca(OH)}_2$  and the two compounds contain no common ions. No precipitate forms.
- (iii)  $\text{CaCl}_2$  does contain a common ion. Calculate  $Q$  for the resulting solution to see if  $\text{Ca(OH)}_2$  precipitates.  $[\text{OH}^-]$  in the new solution is 0.00999 M, because it is diluted by a factor of 2.  $[\text{Ca}^{2+}] = (1.0 + 0.00999)/2 = 0.5050 \text{ M}$ .  
 $Q = (0.5050)(0.00999)^2 = 5.04 \times 10^{-5}$ .  
 $Q > K_{\text{sp}} (6.5 \times 10^{-6})$  and  $\text{Ca(OH)}_2$  precipitates.
- (iv) A common ion with a different concentration;  $[\text{Ca}^{2+}] = (0.10 + 0.00999)/2 = 0.0550 = 0.055 \text{ M}$ .  $Q = (0.0550)(0.00999)^2 = 5.49 \times 10^{-6}$ .  $Q \approx K_{\text{sp}} (6.5 \times 10^{-6})$ ; the solution is very nearly saturated, but no precipitate forms.
- 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 17.23, the two precipitating agents are 6 M HCl (first) and  $\text{H}_2\text{S}$  in 0.2 M HCl (second).
- Cation A =  $\text{Ag}^+$  (precipitates as AgCl)  
Cation B =  $\text{Cu}^+$  (precipitates as CuS, acid insoluble)  
Cation C =  $\text{Ni}^{2+}$  (remains in acidic solution)

**Common-Ion Effect (section 17.1)**

- 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)  $\text{NaNO}_2$

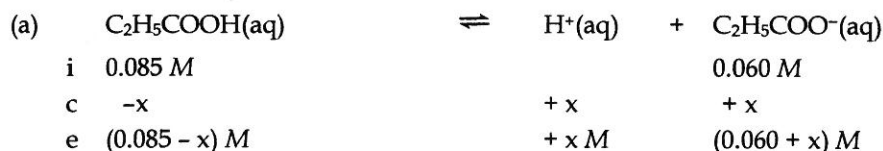
# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

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

(b)  $\text{NH}_4\text{Cl}$

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

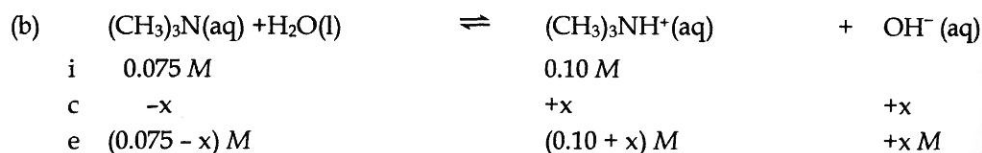


$$K_a = 1.3 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]} = \frac{(x)(0.060 + x)}{(0.085 - x)}$$

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.

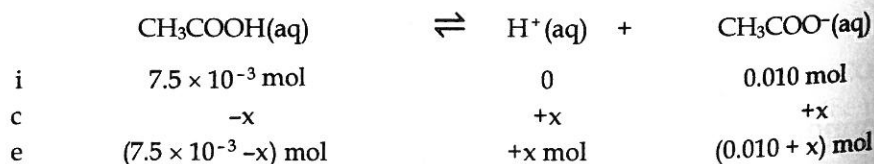


$$K_b = 6.4 \times 10^{-5} = \frac{[\text{OH}^-][(\text{CH}_3)_3\text{NH}^+]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(0.10 + x)}{(0.075 - x)} \approx \frac{0.10x}{0.075}$$

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

*Check.* In a buffer, if  $[\text{conj. acid}] > [\text{conj. base}]$ ,  $\text{pH} < \text{p}K_a$  of the conj. acid. If  $[\text{conj. acid}] < [\text{conj. base}]$ ,  $\text{pH} > \text{p}K_a$  of the conj. acid. In this buffer,  $\text{p}K_a$  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)  $\text{mol} = M \times L$ ;  $\text{mol CH}_3\text{COOH} = 0.15 \text{ M} \times 0.0500 \text{ L} = 7.5 \times 10^{-3} \text{ mol}$   
 $\text{mol CH}_3\text{COO}^- = 0.20 \text{ M} \times 0.0500 \text{ L} = 0.010 \text{ mol}$



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

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

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## Solutions to Exercises

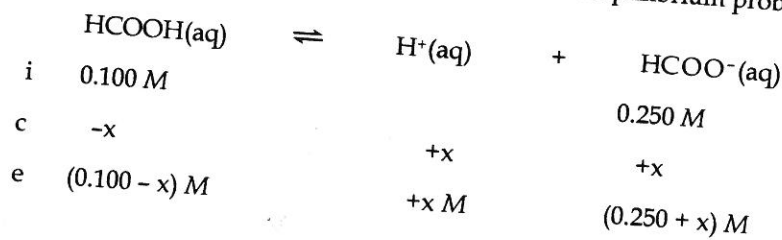
$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(0.010+x)/0.1000 \text{ L}}{(0.0075-x)/0.1000 \text{ L}} \approx \frac{x(0.010)}{0.0075}$$

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

Check.  $\text{p}K_a$  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)  $\text{HCOOH}$  is a weak acid, and  $\text{HCOONa}$  contains the common ion  $\text{HCOO}^-$ , the conjugate base of  $\text{HCOOH}$ . Solve the common-ion equilibrium problem.

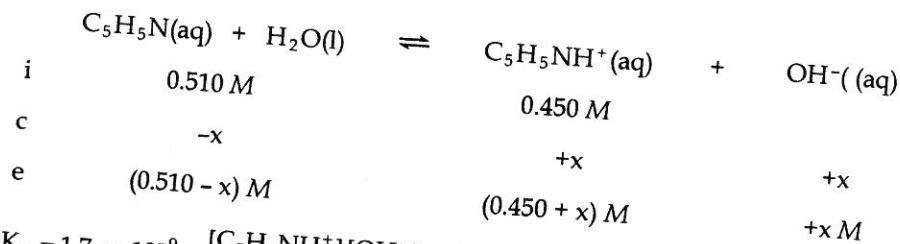


$$K_a = 1.8 \times 10^{-4} = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{(x)(0.250+x)}{(0.100-x)} \approx \frac{0.250x}{0.100}$$

$$x = 7.20 \times 10^{-5} = 7.2 \times 10^{-5} \text{ M} = [\text{H}^+], \text{pH} = 4.14$$

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.



$$K_b = 1.7 \times 10^{-9} = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]} = \frac{(0.450+x)(x)}{(0.510-x)} \approx \frac{0.450x}{0.510}$$

$$x = 1.927 \times 10^{-9} = 1.9 \times 10^{-9} \text{ M} = [\text{OH}^-], \text{pOH} = 8.715, \text{pH} = 14.00 - 8.715 = 5.29$$

Check. In a buffer, if  $[\text{conj. acid}] > [\text{conj. base}]$ ,  $\text{pH} < \text{p}K_a$  of the conj. acid. If  $[\text{conj. acid}] < [\text{conj. base}]$ ,  $\text{pH} > \text{p}K_a$  of the conj. acid. In this buffer,  $\text{p}K_a$  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  $\text{pH} = 5.29$ , greater than 5.23.

- (c)  $\text{mol} = \text{M} \times \text{L}$ ;  $\text{mol HF} = 0.050 \text{ M} \times 0.055 \text{ L} = 2.75 \times 10^{-3} = 2.8 \times 10^{-3} \text{ mol}$ ;  
 $\text{mol F}^- = 0.10 \text{ M} \times 0.125 \text{ L} = 0.0125 = 0.013 \text{ mol}$

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

	$\text{HF(aq)}$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	$+$	$\text{F}^-(\text{aq})$
i	$2.75 \times 10^{-3} \text{ mol}$		0		0.0125 mol
c	$-x$		$+x$		$+x$
e	$(2.75 \times 10^{-3} - x) \text{ mol}$		$+x$		$(0.0125 + x) \text{ mol}$

$$[\text{HF}] = (2.75 \times 10^{-3} + x)/0.180 \text{ L}; [\text{F}^-] = (0.0125 + x)/0.180 \text{ L}$$

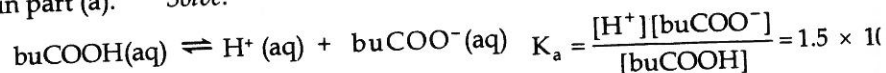
Note that the volumes will cancel when substituted into the  $K_a$  expression.

$$K_a = 6.8 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{x(0.0125 + x)/0.180}{(2.75 \times 10^{-3} - x)/0.180} \approx \frac{x(0.0125)}{0.00275}$$

$$x = 1.50 \times 10^{-4} = 1.5 \times 10^{-4} \text{ M H}^+; \text{pH} = 3.83$$

Check.  $\text{p}K_a$  for HF = 3.17.  $[\text{HF}] < [\text{F}^-]$ , pH of buffer = 3.83, greater 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.*



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

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

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

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

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

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



equil (a)	$0.125 - x \text{ M}$	$x \text{ M}$	$x \text{ M}$
equil (b)	$0.125 - x \text{ M}$	$x \text{ M}$	$0.0075 + x \text{ M}$

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

$$(a) \quad K_a = 1.4 \times 10^{-4} = \frac{x^2}{0.125 - x} \approx \frac{x^2}{0.125}; x = [\text{H}^+] = 4.18 \times 10^{-3} \text{ M} = 4.2 \times 10^{-3} \text{ M H}^+$$

$$\% \text{ ionization} = \frac{4.2 \times 10^{-3} \text{ M H}^+}{0.125 \text{ M CH}_3\text{CH}(\text{OH})\text{COOH}} \times 100 = 3.4\% \text{ ionization}$$

$$(b) \quad K_a = 1.4 \times 10^{-4} = \frac{(x)(0.0075 + x)}{0.125 - x} \approx \frac{0.0075x}{0.125}; \quad x = 2.3 \times 10^{-3} \text{ M H}^+$$

$$\% \text{ ionization} = \frac{2.3 \times 10^{-3} \text{ M H}^+}{0.125 \text{ M CH}_3\text{CH(OH)COOH}} \times 100 = 1.9\% \text{ ionization}$$

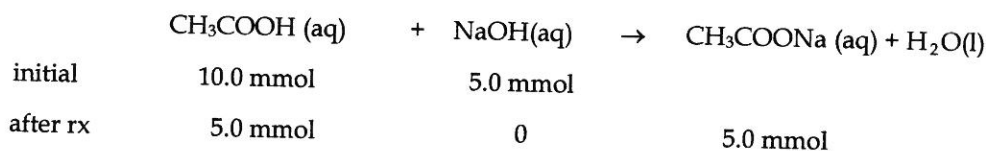
### Buffered Solutions (section 17.2)

17.19  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  are a weak conjugate acid/conjugate base pair which acts as a buffer because unionized  $\text{CH}_3\text{COOH}$  reacts with added base, while  $\text{CH}_3\text{COO}^-$  combines with added acid, leaving  $[\text{H}^+]$  relatively unchanged. Although  $\text{HCl}$  and  $\text{NaCl}$  are a conjugate acid/conjugate base pair,  $\text{Cl}^-$  is a negligible base. That is, it has no tendency to combine with added acid to form molecular  $\text{HCl}$ . Any added acid simply increases  $[\text{H}^+]$  in an  $\text{HCl}/\text{NaCl}$  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  $\text{NaOH}$  is a strong base and will react with  $\text{CH}_3\text{COOH}$  to form  $\text{CH}_3\text{COONa}$ . As long as  $\text{CH}_3\text{COOH}$  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.

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

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



Mixing these two solutions has created a buffer by partial neutralization of the weak acid  $\text{CH}_3\text{COOH}$ .

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.*

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

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

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

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

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



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

(a) The conjugate acid in this buffer is  $\text{HCO}_3^-$ , so use  $K_{a2}$  for  $\text{H}_2\text{CO}_3$ ,  $5.6 \times 10^{-11}$

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

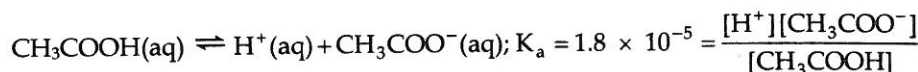
$$[\text{H}^+] = 4.70 \times 10^{-11} = 4.7 \times 10^{-11} \text{ M}; \text{pH} = 10.33$$

(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.*



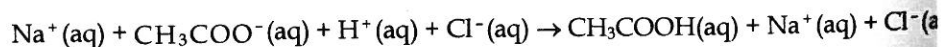
$$[\text{CH}_3\text{COOH}] = 0.150 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{20.0 \text{ g CH}_3\text{COONa}}{0.500 \text{ L soln}} \times \frac{1 \text{ mol CH}_3\text{COONa}}{82.04 \text{ g CH}_3\text{COONa}} = 0.488 \text{ M}$$

$$[\text{H}^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{1.8 \times 10^{-5} (0.150 - x)}{(0.488 + x)} \approx \frac{1.8 \times 10^{-5} (0.150)}{(0.488)}$$

$$[\text{H}^+] = 5.533 \times 10^{-6} = 5.5 \times 10^{-6} \text{ M}, \text{pH} = 5.26$$

(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.*



(c)  $\text{CH}_3\text{COOH}(\text{aq}) + \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{Na}^+(\text{aq})$

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

(a)  $\text{NH}_4^+(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NH}_3(\text{aq})$

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

$$[\text{NH}_3] = 1.00 \text{ M NH}_3$$

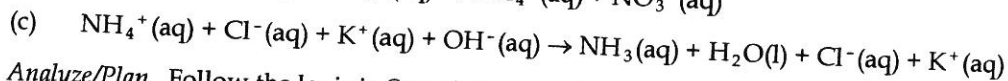
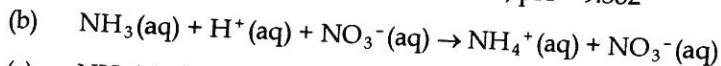
$$[\text{NH}_4^+] = \frac{10.0 \text{ g NH}_4\text{Cl}}{0.250 \text{ L}} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.50 \text{ g NH}_4\text{Cl}} = 0.74766 = 0.748 \text{ M NH}_4^+$$

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

$$K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]}; [\text{H}^+] = \frac{K_a[\text{NH}_4^+]}{[\text{NH}_3]} = \frac{5.56 \times 10^{-10} (0.74766 - x)}{(1.00 + x)} \approx \frac{5.56 \times 10^{-10} (0.74766)}{(1.00)}$$

$$[\text{H}^+] = 4.1537 \times 10^{-10} = 4.15 \times 10^{-10} \text{ M}, \text{ pH} = 9.382$$



17.25 *Analyze/Plan.* Follow the logic in Sample Exercise 16.12 and 17.4. *Solve.*

(a)  $K_a = 6.8 \times 10^{-4} = \frac{x^2}{1.00 - x} = \frac{x^2}{1.00}; x = [\text{H}^+] = 0.02608 = 0.026 \text{ M}; \text{ pH} = 1.58$

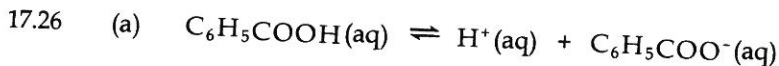
There is 2.6% ionization, so the approximation is valid.

(b) In this problem,  $[\text{F}^-]$  is the unknown.

$$\text{pH} = 3.00, [\text{H}^+] = 10^{-3.00} = 1.0 \times 10^{-3}; [\text{HF}] = 1.00 - 0.0010 = 0.999 \text{ M}$$

$$K_a = 6.8 \times 10^{-4} = \frac{1.0 \times 10^{-3} [\text{F}^-]}{0.999}; [\text{F}^-] = 0.6793 = 0.68 \text{ M}$$

$$\frac{0.6793 \text{ mol NaF}}{1 \text{ L}} \times \frac{41.990 \text{ g NaF}}{1 \text{ mol NaF}} \times 1.25 \text{ L} = 35.654 = 36 \text{ g NaF}$$



$$K_a = 6.3 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}; [\text{C}_6\text{H}_5\text{COOH}] = 0.0200 \text{ M};$$

$$[\text{H}^+] = [\text{C}_6\text{H}_5\text{COO}^-] = x$$

$$K_a = 6.3 \times 10^{-5} \approx \frac{x^2}{0.02000}; x = [\text{H}^+] = 1.123 \times 10^{-3} = 1.1 \times 10^{-3} \text{ M}; \text{ pH} = 2.95$$

Note that  $\text{C}_6\text{H}_5\text{COOH}$  is 5.6% ionized. Solving the quadratic for  $[\text{H}^+]$  yields  $(1.0914 \times 10^{-3} \Rightarrow) 1.1 \times 10^{-3} \text{ M H}^+$ ,  $\text{pH} = 2.96$ ; this is not a significant difference.

(b)  $[\text{H}^+] = \frac{K_a[\text{C}_6\text{H}_5\text{COOH}]}{[\text{C}_6\text{H}_5\text{COO}^-]}; [\text{H}^+] = 10^{-4.00} = 1.0 \times 10^{-4} \text{ M}$

$[\text{C}_6\text{H}_5\text{COOH}] = 0.0200 \text{ M}$ ; calculate  $[\text{C}_6\text{H}_5\text{COO}^-]$ . Because the common ion  $\text{C}_6\text{H}_5\text{COO}^-$  reduces % ionization, we assume the 5% approximation is valid.

$$[\text{C}_6\text{H}_5\text{COO}^-] = \frac{K_a[\text{C}_6\text{H}_5\text{COOH}]}{[\text{H}^+]} = \frac{6.3 \times 10^{-5} (0.0200)}{1.0 \times 10^{-4}} = 0.01260 = 0.013 \text{ M}$$

$$\frac{0.0126 \text{ mol C}_6\text{H}_5\text{COONa}}{\text{L}} \times 1.50 \text{ L} \times \frac{144.11 \text{ g C}_6\text{H}_5\text{COONa}}{1 \text{ mol C}_6\text{H}_5\text{COONa}}$$

$$= 2.724 = 2.7 \text{ g C}_6\text{H}_5\text{COONa}$$

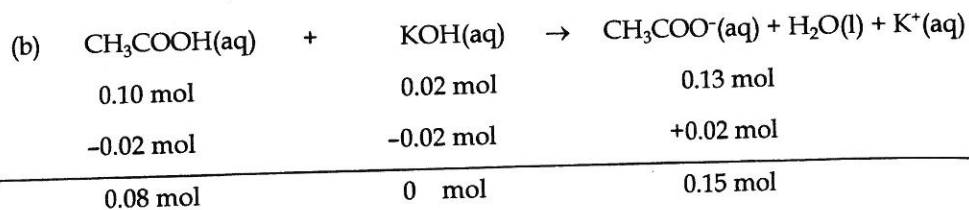
17.27 *Analyze/Plan.* Follow the logic in Sample Exercise 17.3 and 17.5. *Solve.*

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

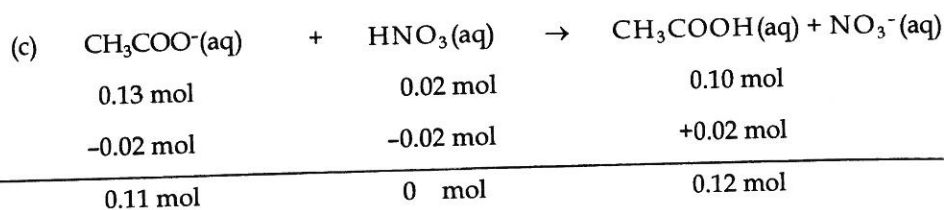
# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

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



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

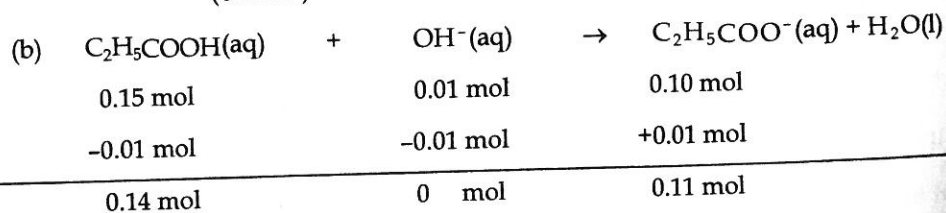


$$[\text{H}^+] = \frac{1.8 \times 10^{-5} (0.12 \text{ mol}/1.00 \text{ L})}{(0.11 \text{ mol}/1.00 \text{ L})} = 1.96 \times 10^{-5} = 2.0 \times 10^{-5} \text{ M}; \text{pH} = 4.71$$

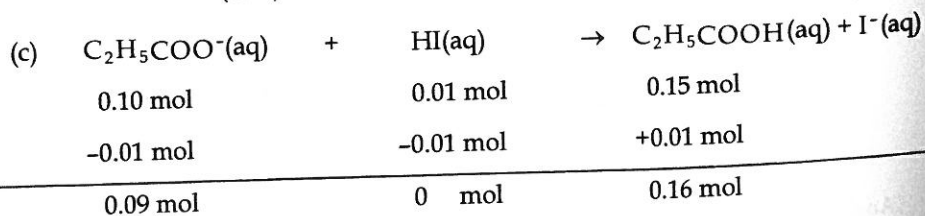
17.28 (a)  $K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]}; [\text{H}^+] = \frac{K_a[\text{C}_2\text{H}_5\text{COOH}]}{[\text{C}_2\text{H}_5\text{COO}^-]}$

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

$$[\text{H}^+] = \frac{1.3 \times 10^{-5} (0.15 - x)}{(0.10 + x)} \approx \frac{1.3 \times 10^{-5} (0.15)}{0.10} = 1.950 \times 10^{-5} = 2.0 \times 10^{-5} \text{ M}, \text{pH} = 4.71$$



$$[\text{H}^+] \approx \frac{1.3 \times 10^{-5} (0.14)}{(0.11)} = 1.6545 \times 10^{-5} = 1.7 \times 10^{-5} \text{ M}; \text{pH} = 4.78$$

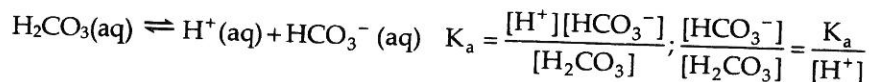


$$[\text{H}^+] \approx \frac{1.3 \times 10^{-5} (0.16)}{(0.09)} = 2.3111 \times 10^{-5} = 2 \times 10^{-5} \text{ M}; \text{pH} = 4.6$$

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

- 17.29 *Analyze/Plan.* Calculate the [conj. base]/[conj. acid] ratio in the  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$  blood buffer. Write the acid dissociation equilibrium and  $K_a$  expression. Find  $K_a$  for  $\text{H}_2\text{CO}_3$  in Appendix D. Calculate  $[\text{H}^+]$  from the pH and solve for the ratio. *Solve.*



(a) at pH = 7.4,  $[\text{H}^+] = 10^{-7.4} = 4.0 \times 10^{-8} \text{ M}$ ;  $\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{4.3 \times 10^{-7}}{4.0 \times 10^{-8}} = 11$

(b) at pH = 7.1,  $[\text{H}^+] = 7.9 \times 10^{-8} \text{ M}$ ;  $\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 5.4$

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

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

Use Equation [17.9] to find the pH of the buffer.  $K_a$  for  $\text{H}_2\text{PO}_4^-$  is  $K_{a2}$  for  $\text{H}_3\text{PO}_4$ ,  $6.2 \times 10^{-8}$

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

- 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  $\text{p}K_a$  for the acids. A buffer is most effective when its pH is within 1 pH unit of  $\text{p}K_a$  for the conjugate acid component. Select the pair with  $\text{p}K_a$  nearest to 3.50. Use Equation [17.9] to calculate the  $[\text{CB}]/[\text{CA}]$  ratio and the volumes of 0.10 M solutions needed to prepare 1 L of buffer. *Solve.*

There are three CA/CB pairs:

$\text{HCOOH}/\text{HCOONa}$ ,  $\text{p}K_a = 3.74$

$\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ ,  $\text{p}K_a = 4.74$

$\text{H}_3\text{PO}_4/\text{NaH}_2\text{PO}_4$ ,  $\text{p}K_a = 2.12$

The most appropriate solutions are  $\text{HCOOH}/\text{HCOONa}$ , because  $\text{p}K_a$  for  $\text{HCOOH}$  is nearest to 3.50.

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

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

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

let  $y = \text{vol HCOONa}$  and  $(1 - y) = \text{vol HCOOH}$ .

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

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

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

*Check.* The pH of the buffer is less than  $\text{pK}_a$  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:

HCOOH/HCOONa,  $\text{pK}_a = 3.74$

$\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ ,  $\text{pK}_a = 4.74$

HCN/NaCN,  $\text{pK}_a = 9.31$

For maximum buffer capacity,  $\text{pK}_a$  should be within 1 pH unit of the buffer. The acetic acid/acetate pair are most appropriate for a buffer with pH 5.00.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CB}]}{[\text{CA}]}; 5.00 = 4.745 + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$\log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} = 0.2553; \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} = 1.800 = 1.8$$

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

let  $y = \text{vol CH}_3\text{COONa}$  and  $(1 - y) = \text{vol CH}_3\text{COOH}$ .

$$1.800 = \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} = \frac{(0.10 \text{ M} \times y)/1.0 \text{ L}}{[0.10 \text{ M} \times (1-y)]/1.0 \text{ L}} = \frac{0.10 y}{0.10 - 0.10 y}$$

$$1.800(0.10 - 0.10 y) = 0.10 y; 0.1800 = 0.2800 y; y = 0.6429 = 0.64 \text{ L}$$

640 mL of 0.10 M  $\text{CH}_3\text{COONa}$ , 360 mL  $\text{CH}_3\text{COOH}$

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

### Acid-Base Titrations (section 17.3)

- 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 (a) False. The same volume of NaOH(aq) is required to reach the equivalence point of both titrations, because moles of acid to be titrated are the same in both flasks.
- (b) True. CH<sub>3</sub>COONa, the salt formed in the titration of CH<sub>3</sub>COOH, produces a basic solution, while NaNO<sub>3</sub>, formed in the titration of HNO<sub>3</sub> produces a neutral solution.
- (c) True. Even though the pH values at the equivalence points of the two titrations are different, phenolphthalein changes color over a wide range of pH values and is appropriate for both titrations.
- 17.36 (a) False. The pH at the beginning of the titration of the weaker acid, CH<sub>3</sub>COOH, will be higher.
- (b) True. Past the equivalence point, the titration curves are very similar (but not identical).
- (c) False. According to Figures 17.13 and 17.14, methyl red is suitable for the titration of the strong acid HNO<sub>3</sub>, but not for the titration of the weak acid CH<sub>3</sub>COOH.
- 17.37 *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.*
- (a)  $\text{NaHCO}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
At the equivalence point, the major species in solution are Na<sup>+</sup> and CO<sub>3</sub><sup>2-</sup>. Na<sup>+</sup> is negligible and CO<sub>3</sub><sup>2-</sup> is the CB of HCO<sub>3</sub><sup>-</sup>. The solution is basic, above pH 7.
- (b)  $\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{aq})$   
At the equivalence point, the major species are NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>. Cl<sup>-</sup> is negligible, NH<sub>4</sub><sup>+</sup> is the CA of NH<sub>3</sub>. The solution is acidic, below pH 7.
- (c)  $\text{KOH}(\text{aq}) + \text{HBr}(\text{aq}) \rightarrow \text{KBr}(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
At the equivalence point, the major species are K<sup>+</sup> and Br<sup>-</sup>; both are negligible. The solution is at pH 7.
- 17.38 (a)  $\text{HCOOH}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{HCOONa}(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
At the equivalence point, the major species are Na<sup>+</sup> and HCOO<sup>-</sup>. Na<sup>+</sup> is negligible and HCOO<sup>-</sup> is the CB of HCOOH. The solution is basic, above pH 7.

- (b)  $\text{Ca}(\text{OH})_2(\text{aq}) + 2\text{HClO}_4(\text{aq}) \rightarrow \text{Ca}(\text{ClO}_4)_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$   
At the equivalence point, the major species are  $\text{Ca}^{2+}$  and  $\text{ClO}_4^-$ ; both are negligible. The solution is at pH 7.
- (c)  $\text{C}_5\text{H}_5\text{N}(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{C}_5\text{H}_5\text{NH}^+\text{NO}_3^-(\text{aq})$   
At the equivalence point, the major species are  $\text{C}_5\text{H}_5\text{NH}^+$  and  $\text{NO}_3^-$ .  $\text{NO}_3^-$  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.
- 17.39 The second color change, from yellow to blue near pH = 8.5, is more suitable for the titration of a weak acid with a strong base. The salt present at the equivalence point of this type of titration produces a slightly basic solution. The second color change of Thymol blue is in the correct pH range to show (indicate) the equivalence point.
- 17.40 (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.
- (b)  $\text{BH}^+(\text{aq})$
- (c) Both  $K_a$  for  $\text{BH}^+$  and concentration  $\text{BH}^+$  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.
- 17.41 *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.*
- (a) 
$$40.0 \text{ mL HNO}_3 \times \frac{0.0900 \text{ mol HNO}_3}{1000 \text{ mL soln}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HNO}_3} \times \frac{1000 \text{ mL soln}}{0.0850 \text{ mol NaOH}}$$

$$= 42.353 = 42.4 \text{ mL NaOH soln}$$
- (b) 
$$35.0 \text{ mL CH}_3\text{COOH} \times \frac{0.0850 \text{ M CH}_3\text{COOH}}{1000 \text{ mL soln}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol CH}_3\text{COOH}} \times \frac{1000 \text{ mL soln}}{0.0850 \text{ mol NaOH}}$$

$$= 35.0 \text{ mL NaOH soln}$$
- (c) 
$$\frac{1.85 \text{ g HCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} = 0.05074 = 0.0507 \text{ M HCl}$$

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

$$= 29.847 = 29.8 \text{ mL NaOH soln}$$
- 17.42 (a) 
$$45.0 \text{ mL NaOH} \times \frac{0.0950 \text{ mol NaOH}}{1000 \text{ mL soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1000 \text{ mL soln}}{0.105 \text{ mol HCl}}$$

$$= 40.7 \text{ mL HCl soln}$$

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

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

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

17.43 *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 <sub>HBr</sub>	mL <sub>NaOH</sub>	Total Volume	Moles H <sup>+</sup>	Moles OH <sup>-</sup>	Molarity Excess Ion	pH
(a)	20.0	15.0	35.0	4.00 × 10 <sup>-3</sup>	3.00 × 10 <sup>-3</sup>	0.0286(H <sup>+</sup> )	1.544
(b)	20.0	19.9	39.9	4.00 × 10 <sup>-3</sup>	3.98 × 10 <sup>-3</sup>	5 × 10 <sup>-4</sup> (H <sup>+</sup> )	3.3
(c)	20.0	20.0	40.0	4.00 × 10 <sup>-3</sup>	4.00 × 10 <sup>-3</sup>	1 × 10 <sup>-7</sup> (H <sup>+</sup> )	7.0
(d)	20.0	20.1	40.1	4.00 × 10 <sup>-3</sup>	4.02 × 10 <sup>-3</sup>	5 × 10 <sup>-4</sup> (OH <sup>-</sup> )	10.7
(e)	20.0	35.0	55.0	4.00 × 10 <sup>-3</sup>	7.00 × 10 <sup>-3</sup>	0.0545(OH <sup>-</sup> )	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<sup>+</sup> = mol OH<sup>-</sup>

NaBr does not hydrolyze, so [H<sup>+</sup>] = [OH<sup>-</sup>] = 1 × 10<sup>-7</sup> M

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

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

17.44 moles OH<sup>-</sup> = M<sub>KOH</sub> × L<sub>KOH</sub> = 0.150 M × 0.0200 L = 3.00 × 10<sup>-3</sup> mol

moles H<sup>+</sup> = M<sub>HClO<sub>4</sub></sub> × L<sub>HClO<sub>4</sub></sub> = 0.125 M × L<sub>HClO<sub>4</sub></sub>



# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

	mL <sub>KOH</sub>	mL <sub>HClO<sub>4</sub></sub>	Total Volume	Moles OH <sup>-</sup>	Moles H <sup>+</sup>	Molarity Excess Ion	pH
(a)	20.0	20.0	40.0	$3.00 \times 10^{-3}$	$2.50 \times 10^{-3}$	0.013(OH <sup>-</sup> )	12.10
(b)	20.0	23.0	43.0	$3.00 \times 10^{-3}$	$2.88 \times 10^{-3}$	$2.9 \times 10^{-3}$ (OH <sup>-</sup> )	11.46
(c)	20.0	24.0	44.0	$3.00 \times 10^{-3}$	$3.00 \times 10^{-3}$	$1.0 \times 10^{-7}$ (OH <sup>-</sup> )	7.00
(d)	20.0	25.0	45.0	$3.00 \times 10^{-3}$	$3.13 \times 10^{-3}$	$2.8 \times 10^{-3}$ (H <sup>+</sup> )	2.56
(e)	20.0	30.0	50.0	$3.00 \times 10^{-3}$	$3.75 \times 10^{-3}$	0.015(H <sup>+</sup> )	1.82

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

$$(a) \quad \frac{3.00 \times 10^{-3} \text{ mol OH}^- - 2.50 \times 10^{-3} \text{ mol H}^+}{0.0400 \text{ L}} = 0.0125 = 0.013 \text{ M OH}^-$$

$$(b) \quad \frac{3.00 \times 10^{-3} \text{ mol OH}^- - 2.875 \times 10^{-3} \text{ mol H}^+}{0.0430 \text{ L}} = 2.91 \times 10^{-3} = 2.9 \times 10^{-3} \text{ M OH}^-$$

(c) equivalence point, mol H<sup>+</sup> = mol OH<sup>-</sup>

KClO<sub>4</sub> does not hydrolyze, so [H<sup>+</sup>] = [OH<sup>-</sup>] =  $1 \times 10^{-7} \text{ M}$

$$(d) \quad \frac{3.125 \times 10^{-3} \text{ mol H}^+ - 3.00 \times 10^{-3} \text{ mol OH}^-}{0.0450 \text{ L}} = 2.78 \times 10^{-3} = 2.8 \times 10^{-3} \text{ M H}^+$$

$$(e) \quad \frac{3.75 \times 10^{-3} \text{ mol H}^+ - 3.00 \times 10^{-3} \text{ mol OH}^-}{0.0500 \text{ L}} = 0.0150 = 0.015 \text{ M H}^+$$

17.45 *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, CH<sub>3</sub>COOH, is present in solution. Using the acid ionization equilibrium



Initial	0.150 M	0	0
equil	0.150 - x M	x M	x M

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

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

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

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

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

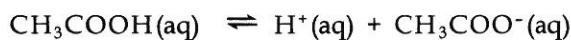
	NaOH(aq)	+	CH <sub>3</sub> COOH (aq)	→	CH <sub>3</sub> COONa(aq) + H <sub>2</sub> O(l)
	(0.150 M × 0.0175 L) =				
(b) before rx	2.625 × 10 <sup>-3</sup> mol		5.25 × 10 <sup>-3</sup> mol		
after rx	0		<b>2.625 × 10<sup>-3</sup> mol</b>		<b>2.63 × 10<sup>-3</sup> mol</b>
	(0.150 M × 0.0345 L) =				
(c) before rx	5.175 × 10 <sup>-3</sup> mol		5.25 × 10 <sup>-3</sup> mol		
after rx	0		<b>0.075 × 10<sup>-3</sup> mol</b>		<b>5.18 × 10<sup>-3</sup> mol</b>
	(0.150 M × 0.0350 L) =				
(d) before rx	5.25 × 10 <sup>-3</sup> mol		5.25 × 10 <sup>-3</sup> mol		
after rx	0		0		<b>5.25 × 10<sup>-3</sup> mol</b>
	(0.150 M × 0.0355 L) =				
(e) before rx	5.325 × 10 <sup>-3</sup> mol		5.25 × 10 <sup>-3</sup> mol		
after rx	<b>0.075 × 10<sup>-3</sup> mol</b>		0		<b>5.25 × 10<sup>-3</sup> mol</b>
	(0.150 M × 0.0500 L) =				
(f) before rx	7.50 × 10 <sup>-3</sup> mol		5.25 × 10 <sup>-3</sup> mol		
after rx	<b>2.25 × 10<sup>-3</sup> mol</b>		0		<b>5.25 × 10<sup>-3</sup> mol</b>

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

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

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

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



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

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

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

(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  $\text{CH}_3\text{COO}^-$  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  $\text{CH}_3\text{COO}^-$ .

	$\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	$\text{CH}_3\text{COOH}(\text{aq}) +$	$\text{OH}^-(\text{aq})$
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  $\text{CH}_3\text{COO}^-$  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)  $[\text{OH}^-] = \frac{2.25 \times 10^{-3} \text{ mol}}{0.0850 \text{ L}} = 0.0265 \text{ M OH}^-; \text{pOH} = 1.577; \text{pH} = 14.00 - 1.577 = 12.423$

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

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

$$1.8 \times 10^{-5} = \frac{x^2}{(0.030 - x)} \approx \frac{x^2}{0.030}; x = [\text{OH}^-] = 9.487 \times 10^{-4} = 9.5 \times 10^{-4} \text{ M}$$

$$\text{pH} = 14.00 - 3.02 = 10.98$$

- (b-f) Calculate mol  $\text{NH}_3$  and mol  $\text{NH}_4^+$  after the acid-base reaction takes place.  
 $0.050 \text{ M NH}_3 \times 0.0300 \text{ L} = 1.5 \times 10^{-3} \text{ mol NH}_3$  present initially.

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

	$\text{NH}_3(\text{aq})$	+	$\text{HCl}(\text{aq})$	$\rightarrow$	$\text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$
			$(0.025 \text{ M} \times 0.0200 \text{ L}) =$		
(b) before rx	$1.5 \times 10^{-3} \text{ mol}$		$0.50 \times 10^{-3} \text{ mol}$		0 mol
after rx	<b><math>1.0 \times 10^{-3} \text{ mol}</math></b>		<b>0 mol</b>		<b><math>5.0 \times 10^{-4} \text{ mol}</math></b>
			$(0.025 \text{ M} \times 0.0590 \text{ L}) =$		
(c) before rx	$1.5 \times 10^{-3} \text{ mol}$		$1.475 \times 10^{-3} \text{ mol}$		0 mol
after rx	<b><math>2.5 \times 10^{-5} \text{ mol}</math></b>		<b>0 mol</b>		<b><math>1.475 \times 10^{-3} \text{ mol}</math></b>
			$(0.025 \text{ M} \times 0.0600 \text{ L}) =$		
(d) before rx	$1.5 \times 10^{-3} \text{ mol}$		$1.5 \times 10^{-3} \text{ mol}$		0 mol
after rx	<b>0 mol</b>		<b>0 mol</b>		<b><math>1.5 \times 10^{-3} \text{ mol}</math></b>
			$(0.025 \text{ M} \times 0.0610 \text{ L}) =$		
(e) before rx	$1.5 \times 10^{-3} \text{ mol}$		$1.525 \times 10^{-3} \text{ mol}$		0 mol
after rx	<b>0 mol</b>		<b><math>2.5 \times 10^{-5} \text{ mol}</math></b>		<b><math>1.5 \times 10^{-3} \text{ mol}</math></b>
			$(0.025 \text{ M} \times 0.0650 \text{ L}) =$		
(f) before rx	$1.5 \times 10^{-3} \text{ mol}$		$1.625 \times 10^{-3} \text{ mol}$		0 mol
after rx	<b>0 mol</b>		<b><math>1.25 \times 10^{-4} \text{ mol}</math></b>		<b><math>1.5 \times 10^{-3} \text{ mol}</math></b>

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

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

$$[\text{NH}_3] = \frac{1.0 \times 10^{-3} \text{ mol}}{0.0500 \text{ L}} = 0.020 \text{ M}; [\text{NH}_4^+] = \frac{5.0 \times 10^{-4} \text{ mol}}{0.0500 \text{ L}} = 0.010 \text{ M}$$

$$[\text{H}^+] = \frac{5.56 \times 10^{-10} [\text{NH}_4^+]}{[\text{NH}_3]} \approx \frac{5.56 \times 10^{-10} (0.010)}{(0.020)} = 2.78 \times 10^{-10}; \text{pH} = 9.56$$

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

(c)  $[\text{NH}_3] = \frac{2.5 \times 10^{-5} \text{ mol}}{0.0890 \text{ L}} = 2.8 \times 10^{-4} \text{ M}; [\text{NH}_4^+] = \frac{1.475 \times 10^{-3} \text{ mol}}{0.0890 \text{ L}} = 0.017 \text{ M}$

$$[\text{H}^+] = \frac{5.56 \times 10^{-10} (0.017)}{(2.8 \times 10^{-4})} = 3.38 \times 10^{-8} = 3.4 \times 10^{-8} \text{ M}; \text{pH} = 7.47$$

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

$$[\text{NH}_4^+] = \frac{1.5 \times 10^{-3} \text{ M}}{0.0900 \text{ L}} = 0.01667 = 0.017 \text{ M}$$

$$5.56 \times 10^{-10} = \frac{x^2}{0.01667}; x = [\text{H}^+] = 3.043 \times 10^{-6} = 3.0 \times 10^{-6} \text{ M}; \text{pH} = 5.52$$

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

$$[\text{H}^+] = \frac{2.5 \times 10^{-5} \text{ mol}}{0.0910 \text{ L}} = 2.747 \times 10^{-4} = 2.7 \times 10^{-4} \text{ M}; \text{pH} = 3.56$$

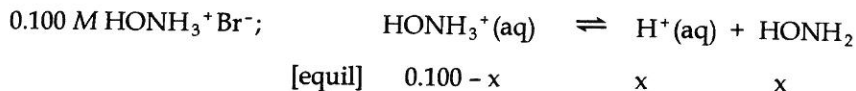
- (f) Past the equivalence point,  $[\text{H}^+]$  from the excess HCl determines the pH.

$$[\text{H}^+] = \frac{1.25 \times 10^{-4} \text{ mol}}{0.0950 \text{ L}} = 1.316 \times 10^{-3} = 1.3 \times 10^{-3} \text{ M}; \text{pH} = 2.88$$

17.47 *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)  $\text{HONH}_2$  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):

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

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

17.48 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)  $0.0444 \text{ M NaBr}$ ,  $\text{pH} = 7.00$

(b)  $0.0444 \text{ M NaClO}_2$ ;  $\text{ClO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HClO}_2(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_b = \frac{[\text{HClO}_2][\text{OH}^-]}{[\text{ClO}_2^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.09 \times 10^{-13} = 9.1 \times 10^{-13}$$

$$[\text{HClO}_2] = [\text{OH}^-]; [\text{ClO}_2^-] \approx 0.0444 \text{ M}$$

$$[\text{OH}^-]^2 \approx 0.0444(9.09 \times 10^{-13}); [\text{OH}^-] = 2.01 \times 10^{-7} = 2.0 \times 10^{-7} \text{ M}, \text{pOH} = 6.70;$$

$$\text{pH} = 7.30$$

Note that  $\text{HClO}_2$  is a relatively strong acid (large  $K_a$  value), so the pH at the equivalence point is not much greater than 7.0. Since  $[\text{OH}^-]$  from the hydrolysis of  $\text{ClO}_2^-$  is very small, the autoionization equilibrium should be considered for a more accurate value of the equivalence point pH.

$$\text{Let } [\text{H}^+] = x, [\text{OH}^-] = (2.0 \times 10^{-7} \text{ M} + x); 1.0 \times 10^{-14} = (x)(2.0 \times 10^{-7} \text{ M} + x)$$

Solving the quadratic equation gives a pH of 7.38.

(c)  $\text{C}_6\text{H}_5\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_6\text{H}_5\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_b = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.59 \times 10^{-10} = 1.6 \times 10^{-10}$$

$$[\text{OH}^-]^2 \approx 0.0444(1.59 \times 10^{-8}); [\text{OH}^-] = 2.655 \times 10^{-6} = 2.7 \times 10^{-6}, \text{pH} = 8.42$$

### Solubility Equilibria and Factors Affecting Solubility (sections 17.4 and 17.5)

17.49 (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.*

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

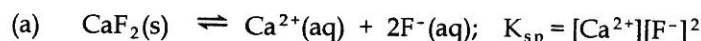
17.50 (a) Solubility is the amount (grams, moles) of solute that will dissolve in a certain volume of solution. Solubility-product constant is an equilibrium constant, the product of the molar concentrations of all the dissolved ions in solution.

(b)  $K_{\text{sp}} = [\text{Mn}^{2+}][\text{CO}_3^{2-}]; K_{\text{sp}} = [\text{Hg}^{2+}][\text{OH}^-]^2; K_{\text{sp}} = [\text{Cu}^{2+}]^3[\text{PO}_4^{3-}]^2$

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

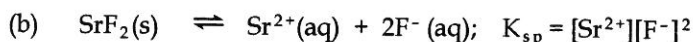
17.51 *Analyze/Plan.* Follow the logic in Sample Exercise 17.10. *Solve.*



The molar solubility is the moles of  $\text{CaF}_2$  that dissolve per liter of solution. Each mole of  $\text{CaF}_2$  produces 1 mol  $\text{Ca}^{2+}(\text{aq})$  and 2 mol  $\text{F}^{-}(\text{aq})$ .

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

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

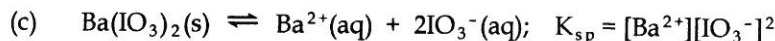


Transform the gram solubility to molar solubility.

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

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

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

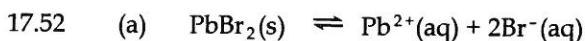


Since 1 mole of dissolved  $\text{Ba}(\text{IO}_3)_2$  produces 1 mole of  $\text{Ba}^{2+}$ , the molar solubility of

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

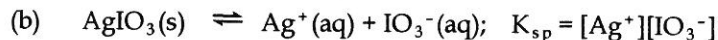
$$K_{\text{sp}} = 6.0 \times 10^{-10} = (x)(2x)^2; 4x^3 = 6.0 \times 10^{-10}; x^3 = 1.5 \times 10^{-10}; x = 5.3 \times 10^{-4} \text{ M}$$

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



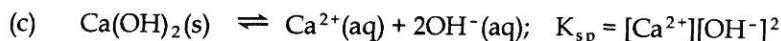
$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Br}^{-}]^2; [\text{Pb}^{2+}] = 1.0 \times 10^{-2} \text{ M}, [\text{Br}^{-}] = 2.0 \times 10^{-2} \text{ M}$$

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



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

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



$$[\text{Ca}^{2+}] = x, [\text{OH}^{-}] = 2x; K_{\text{sp}} = 6.5 \times 10^{-6} = (x)(2x)^2$$

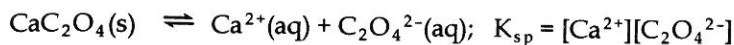
$$6.5 \times 10^{-6} = 4x^3; x = [\text{Ca}^{2+}] = 0.01176 = 0.012 \text{ M}; [\text{OH}^{-}] = 0.02351 = 0.024 \text{ M}$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.629 = 12.37$$

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

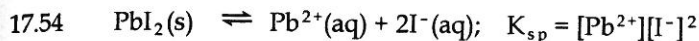
# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises



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

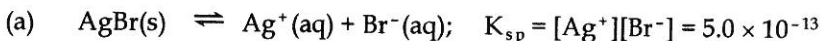
$$K_{\text{sp}} = (4.76 \times 10^{-5} \text{ M})(4.76 \times 10^{-5} \text{ M}) = 2.3 \times 10^{-9}$$



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

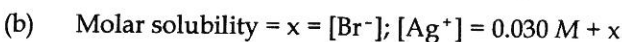
$$[\text{I}^{-}] = 2[\text{Pb}^{2+}]; K_{\text{sp}} = [\text{Pb}^{2+}](2[\text{Pb}^{2+}])^2 = 4[\text{Pb}^{2+}]^3 = 4(1.17 \times 10^{-3})^3 = 6.4 \times 10^{-9}$$

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



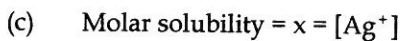
$$\text{molar solubility} = x = [\text{Ag}^{+}] = [\text{Br}^{-}]; K_{\text{sp}} = x^2$$

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



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

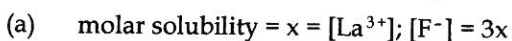
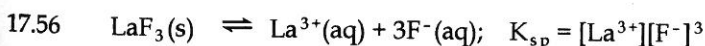
$$5.0 \times 10^{-13} = 0.030(x); x = 1.7 \times 10^{-11} \text{ mol AgBr/L}$$



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

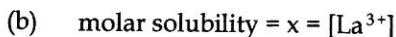
$$K_{\text{sp}} = (x)(0.10 + x); \text{Assuming } x \text{ is small compared to } 0.10 \text{ M}$$

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



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

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



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

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

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

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



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

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

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

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

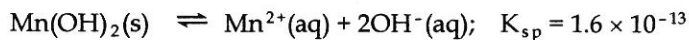
17.57 *Analyze/Plan.* Given a saturated solution of  $CaF_2$  in contact with undissolved  $CaF_2(s)$ , consider the effect of adding  $CaCl_2(s)$ . The two salts have the  $Ca^{2+}$  ion in common. *Solve.* As  $CaCl_2$  is added,  $[Ca^{2+}]$  increases,  $K_{sp}$  is exceeded, and additional  $CaF_2$  precipitates until equilibrium is reestablished. At the new equilibrium position:

- (a) The amount of  $CaF_2(s)$  on the bottom of the beaker increases because the added  $Ca^{2+}$  from  $CaCl_2$  decreases the solubility of  $CaF_2$ .
- (b) The  $[Ca^{2+}]$  in solution increases because of the added  $CaCl_2$ .
- (c) The  $[F^-]$  in solution decreases because  $CaF_2(s)$  precipitates upon addition of  $CaCl_2$ . The product of  $[Ca^{2+}]$  and  $[F^-]$ , the  $K_{sp}$ , is the same.

17.58 As  $KI$  is added,  $[I^-]$  increases,  $K_{sp}$  is exceeded, and additional  $PbI_2$  precipitates until equilibrium is reestablished. At the new equilibrium position:

- (a) The amount of  $PbI_2(s)$  on the bottom of the beaker increases because the added  $I^-$  from  $KI$  decreases the solubility of  $PbI_2$ .
- (b) The  $[Pb^{2+}]$  in solution decreases because  $PbI_2(s)$  precipitates upon addition of  $KI$ .
- (c) The  $[I^-]$  in solution increases because of the added  $KI$ . The product of  $[Pb^{2+}]$  and  $[I^-]$ , the  $K_{sp}$ , is the same.

17.59 *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  $[H^+]$  but also  $[OH^-]$ , which is an ion common to the salt. Use pH to calculate  $[OH^-]$ , then proceed as in Sample Exercise 17.12. *Solve.*



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

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

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

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

*Check.* Note that the solubility of  $Mn(OH)_2$  in pure water is  $3.6 \times 10^{-5} M$ , 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  $Mn(OH)_2$ .

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

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

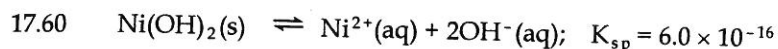
$$K_{\text{sp}} = 1.6 \times 10^{-13} = [\text{Mn}^{2+}](3.16 \times 10^{-5})^2; [\text{Mn}^{2+}] = \frac{1.6 \times 10^{-13}}{1.0 \times 10^{-9}} = 1.6 \times 10^{-4} \text{ M}$$

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

(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  $\text{Ni(OH)}_2$  is just  $[\text{Ni}^{2+}]$ .

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

$$K_{\text{sp}} = 6.0 \times 10^{-16} = [\text{Ni}^{2+}](1.0 \times 10^{-6})^2; [\text{Ni}^{2+}] = \frac{6.0 \times 10^{-16}}{1.0 \times 10^{-12}} = 6.0 \times 10^{-4} = 6 \times 10^{-4} \text{ M}$$

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

$$K_{\text{sp}} = 6.0 \times 10^{-16} = [\text{Ni}^{2+}](1.0 \times 10^{-4})^2; [\text{Ni}^{2+}] = \frac{6.0 \times 10^{-16}}{1.0 \times 10^{-8}} = 6.0 \times 10^{-8} = 6 \times 10^{-8} \text{ M}$$

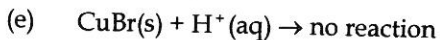
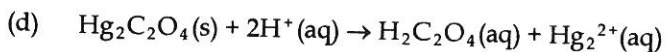
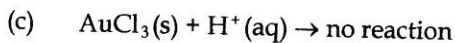
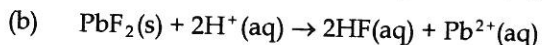
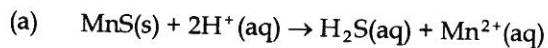
(c)  $\text{pH} = 12.0, \text{pOH} = 2.0, [\text{OH}^-] = 1.0 \times 10^{-2} = 1 \times 10^{-2} \text{ M}$

$$K_{\text{sp}} = 6.0 \times 10^{-16} = [\text{Ni}^{2+}](1.0 \times 10^{-2})^2; [\text{Ni}^{2+}] = \frac{6.0 \times 10^{-16}}{1.0 \times 10^{-4}} = 6.0 \times 10^{-12} = 6 \times 10^{-12} \text{ M}$$

17.61 *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  $\text{H}^+$ , reducing the concentration of the free anion in solution, thereby causing more salt to dissolve. More soluble in acid: (a)  $\text{ZnCO}_3$ , (b)  $\text{ZnS}$ , (d)  $\text{AgCN}$ , (e)  $\text{Ba}_3(\text{PO}_4)_2$

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

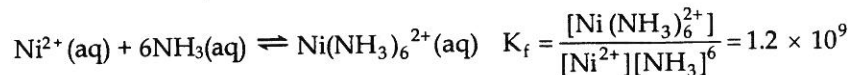


# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

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

The formation equilibrium is



Assuming that nearly all the  $\text{Ni}^{2+}$  is in the form  $\text{Ni}(\text{NH}_3)_6^{2+}$ ,

$$[\text{Ni}(\text{NH}_3)_6^{2+}] = 1 \times 10^{-3} \text{ M}; [\text{Ni}^{2+}] = x; [\text{NH}_3] = 0.20 \text{ M}$$

$$1.2 \times 10^9 = \frac{(1 \times 10^{-3})}{x(0.20)^6}; x = 1.30 \times 10^{-8} = 1 \times 10^{-8} \text{ M} = [\text{Ni}^{2+}]$$

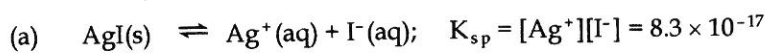
- 17.64  $\text{NiC}_2\text{O}_4(\text{s}) \rightleftharpoons \text{Ni}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}); K_{sp} = [\text{Ni}^{2+}][\text{C}_2\text{O}_4^{2-}] = 4 \times 10^{-10}$

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  $\text{Ni}^{2+}$  ion with  $\text{NH}_3$ :  $\text{Ni}^{2+}(\text{aq}) + 6\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(\text{aq})$ . 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.

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

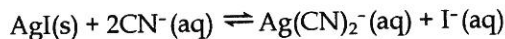
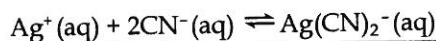
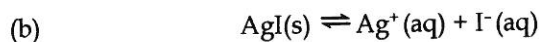
$$[\text{NH}_3] = 0.307 = 0.3 \text{ M}$$

- 17.65 *Analyze/Plan.* Calculate the solubility of AgI in pure water according to the method in Sample Exercise 17.11. Obtain  $K_{eq}$  for the complexation 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. Finally, use this  $K_{eq}$  value to calculate the solubility of AgI in 0.100 M NaCN solution. *Solve.*



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

$$x = (8.3 \times 10^{-17})^{1/2}; x = 9.1 \times 10^{-9} \text{ mol AgI/L}$$



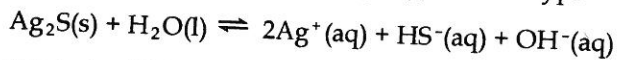
$$K = K_{sp} \times K_f = [\text{Ag}^+][\text{I}^-] \times \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = (8.3 \times 10^{-17})(1 \times 10^{21}) = 8 \times 10^4$$

- (c)  $K$  is much greater than one for the reaction of  $\text{AgI}(\text{s})$  with  $\text{CN}^-$ . This means that the reaction goes to completion. For a  $\text{AgI}(\text{s})$  in 0.100 M NaCN solution,  $\text{CN}^-$  is the limiting reactant. Two moles of  $\text{CN}^-$  react with one mole of  $\text{AgI}$ , so the solubility of AgI in 0.100 M NaCN is  $(0.100/2) = 0.0500 \text{ M}$ .

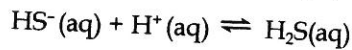
# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

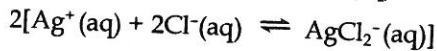
17.66 According to Table D-3,  $K_{sp}$  for  $\text{Ag}_2\text{S}(s)$  is of the type



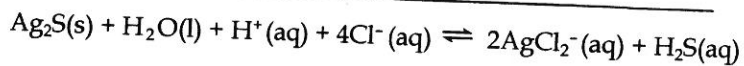
$K_{sp}$



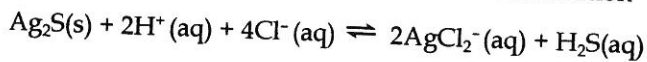
$1/K_{a1}$



$K_f^2$



Add  $\text{H}^+(\text{aq})$  to each side to obtain the overall reaction

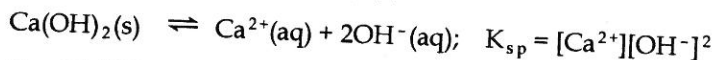


$$K = \frac{K_{sp} \times K_f^2}{K_{a1}} = \frac{(6 \times 10^{-51})(1.1 \times 10^5)^2}{(9.5 \times 10^{-8})} = 7.64 \times 10^{-34} = 8 \times 10^{-34}$$

### Precipitation and Separation of Ions (section 17.6)

17.67 *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,  $\text{Ca}^{2+}$  can form  $\text{Ca}(\text{OH})_2(s)$ .



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

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

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

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

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

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

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

$Q < K_{sp}$ , no  $\text{Ag}_2\text{SO}_4$  precipitates.

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

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

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

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

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

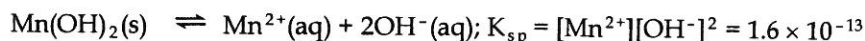
# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

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

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

- 17.69 *Analyze/Plan.* We are asked to calculate pH necessary to precipitate  $\text{Mn(OH)}_2(\text{s})$  if the resulting  $\text{Mn}^{2+}$  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.*

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

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

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

- 17.70  $\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}); K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 = 8.49 \times 10^{-9}$

(This  $K_{sp}$  value is taken from *CRC Handbook of Chemistry and Physics*, 74<sup>th</sup> Edition.)

$$[\text{Pb}^{2+}] = \frac{0.10 \text{ M} \times 0.2 \text{ mL}}{10.2 \text{ mL}} = 1.96 \times 10^{-3} = 2 \times 10^{-3} \text{ M}; [\text{I}^-] = \left( \frac{8.49 \times 10^{-9}}{1.96 \times 10^{-3} \text{ M}} \right)^{1/2} = 2.08 \times 10^{-3} = 2 \times 10^{-3} \text{ M}$$

$$\frac{2.08 \times 10^{-3} \text{ mol I}^-}{1 \text{ L}} \times \frac{126.90 \text{ g I}^-}{1 \text{ mol I}^-} \times 0.0102 \text{ L} = 2.69 \times 10^{-3} \text{ g I}^- = 3 \times 10^{-3} \text{ g I}^-$$

- 17.71 *Analyze/Plan.* We are asked which ion will precipitate first from a solution containing  $\text{Pb}^{2+}(\text{aq})$  and  $\text{Ag}^+(\text{aq})$  when  $\text{I}^-(\text{aq})$  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.*

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

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

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

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

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

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

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

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

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Exercises

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)  $\text{Ba}^{2+}$  precipitates first, because it requires the smaller  $[\text{SO}_4^{2-}]$ .  
 (c)  $\text{Sr}^{2+}$  will begin to precipitate when  $[\text{SO}_4^{2-}]$  in solution (not bound in  $\text{BaSO}_4$ ) reaches  $3.2 \times 10^{-5} \text{ M}$ .

17.73 *Analyze/Plan.* We are asked which ion will precipitate first when dilute  $\text{Ag}^+(\text{aq})$  is added to a solution containing  $0.20 \text{ M CrO}_4^{2-}$ ,  $0.10 \text{ M CO}_3^{2-}$  and  $0.10 \text{ M Cl}^-$ . The anions are present at different concentrations and their silver compounds have different stoichiometry, so we cannot directly compare  $K_{sp}$  values. Follow the logic in Sample Exercise 17.16. Calculate  $[\text{Ag}^+]$  needed to initiate precipitation of each ion. The anion that requires lowest  $[\text{Ag}^+]$  will precipitate first, and so on. *Solve.*

$$\text{Ag}_2\text{CrO}_4: K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 1.2 \times 10^{-12}$$

$$1.2 \times 10^{-12} = [\text{Ag}^+]^2(0.20); [\text{Ag}^+]^2 = 6.0 \times 10^{-12}; [\text{Ag}^+] = 2.4 \times 10^{-6} \text{ M}$$

$$\text{Ag}_2\text{CO}_3: K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = 8.1 \times 10^{-12}$$

$$8.1 \times 10^{-12} = [\text{Ag}^+]^2(0.10); [\text{Ag}^+]^2 = 8.1 \times 10^{-11}; [\text{Ag}^+] = 9.0 \times 10^{-6} \text{ M}$$

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

$$1.8 \times 10^{-10} = [\text{Ag}^+](0.10); [\text{Ag}^+] = 1.8 \times 10^{-9}$$

$\text{AgCl}$  requires the smallest  $[\text{Ag}^+]$  for precipitation and it will precipitate first. The other two will precipitate almost simultaneously.

17.74 It is not appropriate to compare  $K_{sp}$  values directly, because the stoichiometries of the two precipitates are different.

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

$$\text{CaSO}_4: K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 2.4 \times 10^{-5}$$

$$2.4 \times 10^{-5} = (0.20)[\text{SO}_4^{2-}]; [\text{SO}_4^{2-}] = 1.2 \times 10^{-4} \text{ M}$$

$$\text{Ag}_2\text{SO}_4: K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = 1.5 \times 10^{-5}$$

$$1.5 \times 10^{-5} = (0.30)^2[\text{SO}_4^{2-}]; [\text{SO}_4^{2-}] = 1.7 \times 10^{-4} \text{ M}$$

$\text{CaSO}_4$  requires the smaller  $[\text{SO}_4^{2-}]$  for precipitation and it will precipitate first.

- (b) The  $[\text{SO}_4^{2-}]$  necessary to begin precipitation is the smaller of the two values,  $1.2 \times 10^{-4} \text{ M SO}_4^{2-}$ .

$$1.2 \times 10^{-4} \text{ M} = \frac{1.0 \text{ M SO}_4^{2-} \times x \text{ L}}{(0.010 + x \text{ L})}; x = (0.010)1.2 \times 10^{-4} = 1.2 \times 10^{-6} \text{ L}$$

We assume  $x$  is small compared to  $0.010 \text{ L}$ . The required volume is then  $1.2 \times 10^{-6} \text{ L}$  or  $0.0012 \text{ mL}$  or  $1.2 \mu\text{L}$ . If one drop is approximately  $0.2 \text{ mL}$ , precipitation will begin as the first drop of  $1.0 \text{ M Na}_2\text{SO}_4$  solution is added.

## Qualitative Analysis for Metallic Elements (section 17.7)

- 17.75 *Analyze/Plan.* Use Figure 17.23 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 17.23). 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,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ , or  $\text{Co}^{2+}$ , and those of Group 5,  $\text{NH}_4^+$ ,  $\text{Na}^+$  or  $\text{K}^+$ .
- 17.76 Initial solubility in water rules out  $\text{CdS}$  and  $\text{HgO}$ . Formation of a precipitate on addition of  $\text{HCl}$  indicates the presence of  $\text{Pb}(\text{NO}_3)_2$  (formation of  $\text{PbCl}_2$ ). Formation of a precipitate on addition of  $\text{H}_2\text{S}$  at pH 1 probably indicates  $\text{Cd}(\text{NO}_3)_2$  (formation of  $\text{CdS}$ ). (This test can be misleading because enough  $\text{Pb}^{2+}$  can remain in solution after filtering  $\text{PbCl}_2$  to lead to visible precipitation of  $\text{PbS}$ .) Absence of a precipitate on addition of  $\text{H}_2\text{S}$  at pH 8 indicates that  $\text{ZnSO}_4$  is not present. The yellow flame test indicates presence of  $\text{Na}^+$ . In summary,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Na}_2\text{SO}_4$  are definitely present,  $\text{Cd}(\text{NO}_3)_2$  is probably present, and  $\text{CdS}$ ,  $\text{HgO}$  and  $\text{ZnSO}_4$  are definitely absent.
- 17.77 *Analyze/Plan.* We are asked to devise a procedure to separate various pairs of ions in aqueous solutions. In each case, refer to Figure 17.23 to find a set of conditions where the solubility of the two ions differs. Construct a procedure to generate these conditions. *Solve.*
- $\text{Cd}^{2+}$  is in Gp. 2, but  $\text{Zn}^{2+}$  is not. Make the solution acidic using 0.2 M  $\text{HCl}$ ; saturate with  $\text{H}_2\text{S}$ .  $\text{CdS}$  will precipitate,  $\text{ZnS}$  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  $\text{Cr}^{3+}$  forms the soluble complex  $\text{Cr}(\text{OH})_4^-$ .
  - $\text{Mg}^{2+}$  is a member of Gp. 4, but  $\text{K}^+$  is not. Add  $(\text{NH}_4)_2\text{HPO}_4$  to a basic solution;  $\text{Mg}^{2+}$  precipitates as  $\text{MgNH}_4\text{PO}_4$ ,  $\text{K}^+$  remains in solution.
  - $\text{Ag}^+$  is a member of Gp. 1, but  $\text{Mn}^{2+}$  is not. Add 6 M  $\text{HCl}$ , precipitate  $\text{Ag}^+$  as  $\text{AgCl}(\text{s})$ .
- 17.78
- Make the solution slightly acidic and saturate with  $\text{H}_2\text{S}$ ;  $\text{CdS}$  will precipitate,  $\text{Na}^+$  remains in solution.
  - Make the solution acidic, saturate with  $\text{H}_2\text{S}$ ;  $\text{CuS}$  will precipitate,  $\text{Mg}^{2+}$  remains in solution.
  - Add  $\text{HCl}$ ,  $\text{PbCl}_2$  precipitates. (It is best to carry out the reaction in an ice-water bath to reduce the solubility of  $\text{PbCl}_2$ .)
  - Add dilute  $\text{HCl}$ ;  $\text{AgCl}$  precipitates,  $\text{Hg}^{2+}$  remains in solution.
- 17.79
- 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 of interest is not exceeded.
  - $K_{\text{sp}}$  for those cations in Group 3 is much larger. Thus, to exceed  $K_{\text{sp}}$ , a higher  $[\text{S}^{2-}]$  is required. This is achieved by making the solution more basic.

# 17 Additional Aspects of Aqueous Equilibria

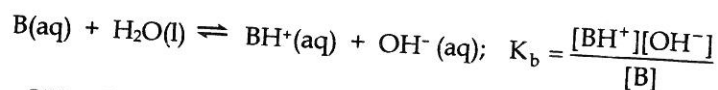
## Solutions to Exercises

(c) They should all redissolve in strongly acidic solution, e.g., in 12 M HCl (the chlorides of all Group 3 metals are soluble).

17.80 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

17.81 *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  $[\text{OH}^-]$ .

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

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

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

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

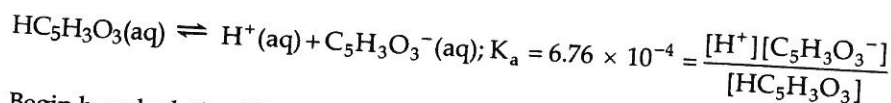
17.82 Benzene sulfonic acid = BSOH, sodium benzene sulfonate = BSONa

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

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

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

17.83 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.

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

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

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

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