

# CHAPTER 16

## ACID-BASE EQUILIBRIA AND SOLUBILITY EQUILIBRIA

- 16.5 (a) This is a weak acid problem. Setting up the standard equilibrium table:

	$\text{CH}_3\text{COOH}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CH}_3\text{COO}^-(aq)$
Initial ( <i>M</i> ):	0.40		0.00		0.00
Change ( <i>M</i> ):	- <i>x</i>		+ <i>x</i>		+ <i>x</i>
Equilibrium ( <i>M</i> ):	(0.40 - <i>x</i> )		<i>x</i>		<i>x</i>

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

$$1.8 \times 10^{-5} = \frac{x^2}{(0.40 - x)} \approx \frac{x^2}{0.40}$$

$$x = [\text{H}^+] = 2.7 \times 10^{-3} M$$

$$\text{pH} = 2.57$$

- (b) In addition to the acetate ion formed from the ionization of acetic acid, we also have acetate ion formed from the sodium acetate dissolving.



Dissolving 0.20 *M* sodium acetate initially produces 0.20 *M*  $\text{CH}_3\text{COO}^-$  and 0.20 *M*  $\text{Na}^+$ . The sodium ions are not involved in any further equilibrium (why?), but the acetate ions must be added to the equilibrium in part (a).

	$\text{CH}_3\text{COOH}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CH}_3\text{COO}^-(aq)$
Initial ( <i>M</i> ):	0.40		0.00		0.20
Change ( <i>M</i> ):	- <i>x</i>		+ <i>x</i>		+ <i>x</i>
Equilibrium ( <i>M</i> ):	(0.40 - <i>x</i> )		<i>x</i>		(0.20 + <i>x</i> )

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

$$1.8 \times 10^{-5} = \frac{(x)(0.20 + x)}{(0.40 - x)} \approx \frac{x(0.20)}{0.40}$$

$$x = [\text{H}^+] = 3.6 \times 10^{-5} M$$

$$\text{pH} = 4.44$$

Could you have predicted whether the pH should have increased or decreased after the addition of the sodium acetate to the pure 0.40 *M* acetic acid in part (a)?

An alternate way to work part (b) of this problem is to use the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log \frac{0.20 \text{ M}}{0.40 \text{ M}} = 4.74 - 0.30 = \mathbf{4.44}$$

**16.6 (a)** This is a weak base calculation.

	$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$		
Initial (M):	0.20	0	0
Change (M):	-x	+x	+x
Equilibrium (M):	0.20 - x	x	x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{0.20 - x} \approx \frac{x^2}{0.20}$$

$$x = 1.9 \times 10^{-3} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = 2.72$$

$$\text{pH} = \mathbf{11.28}$$

**(b)** The initial concentration of  $\text{NH}_4^+$  is 0.30 M from the salt  $\text{NH}_4\text{Cl}$ . We set up a table as in part (a).

	$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$		
Initial (M):	0.20	0.30	0
Change (M):	-x	+x	+x
Equilibrium (M):	0.20 - x	0.30 + x	x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{(x)(0.30 + x)}{0.20 - x} \approx \frac{x(0.30)}{0.20}$$

$$x = 1.2 \times 10^{-5} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = 4.92$$

$$\text{pH} = \mathbf{9.08}$$

Alternatively, we could use the Henderson-Hasselbalch equation to solve this problem. Table 15.4 gives the value of  $K_a$  for the ammonium ion. Substituting into the Henderson-Hasselbalch equation gives:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} = -\log(5.6 \times 10^{-10}) + \log \frac{(0.20)}{(0.30)}$$

$$\text{pH} = 9.25 - 0.18 = \mathbf{9.07}$$

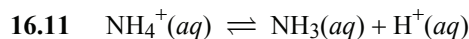
Is there any difference in the Henderson-Hasselbalch equation in the cases of a weak acid and its conjugate base and a weak base and its conjugate acid?

- 16.9**
- (a) HCl (hydrochloric acid) is a strong acid. A buffer is a solution containing both a weak acid and a weak base. Therefore, this is *not* a buffer system.
  - (b) H<sub>2</sub>SO<sub>4</sub> (sulfuric acid) is a strong acid. A buffer is a solution containing both a weak acid and a weak base. Therefore, this is *not* a buffer system.
  - (c) This solution contains both a weak acid, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and its conjugate base, HPO<sub>4</sub><sup>2-</sup>. Therefore, this is a buffer system.
  - (d) HNO<sub>2</sub> (nitrous acid) is a weak acid, and its conjugate base, NO<sub>2</sub><sup>-</sup> (nitrite ion, the anion of the salt KNO<sub>2</sub>), is a weak base. Therefore, this is a buffer system.

**16.10 Strategy:** What constitutes a buffer system? Which of the preceding solutions contains a weak acid and its salt (containing the weak conjugate base)? Which of the preceding solutions contains a weak base and its salt (containing the weak conjugate acid)? Why is the conjugate base of a strong acid not able to neutralize an added acid?

**Solution:** The criteria for a buffer system are that we must have a weak acid and its salt (containing the weak conjugate base) or a weak base and its salt (containing the weak conjugate acid).

- (a) HCN is a weak acid, and its conjugate base, CN<sup>-</sup>, is a weak base. Therefore, this is a buffer system.
- (b) HSO<sub>4</sub><sup>-</sup> is a weak acid, and its conjugate base, SO<sub>4</sub><sup>2-</sup> is a weak base (see Table 15.5 of the text). Therefore, this is a buffer system.
- (c) NH<sub>3</sub> (ammonia) is a weak base, and its conjugate acid, NH<sub>4</sub><sup>+</sup> is a weak acid. Therefore, this is a buffer system.
- (d) Because HI is a strong acid, its conjugate base, I<sup>-</sup>, is an extremely weak base. This means that the I<sup>-</sup> ion will not combine with a H<sup>+</sup> ion in solution to form HI. Thus, this system cannot act as a buffer system.



$$K_a = 5.6 \times 10^{-10}$$

$$\text{p}K_a = 9.25$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.25 + \log \frac{0.15 \text{ M}}{0.35 \text{ M}} = \mathbf{8.88}$$

**16.12 Strategy:** The pH of a buffer system can be calculated in a similar manner to a weak acid equilibrium problem. The difference is that a common-ion is present in solution. The  $K_a$  of CH<sub>3</sub>COOH is  $1.8 \times 10^{-5}$  (see Table 15.3 of the text).

**Solution:**

- (a) We summarize the concentrations of the species at equilibrium as follows:

	$\text{CH}_3\text{COOH}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	$+$	$\text{CH}_3\text{COO}^-(aq)$
Initial ( <i>M</i> ):	2.0		0		2.0
Change ( <i>M</i> ):	- <i>x</i>		+ <i>x</i>		+ <i>x</i>
Equilibrium ( <i>M</i> ):	$2.0 - x$		<i>x</i>		$2.0 + x$

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

$$K_a = \frac{[\text{H}^+](2.0 + x)}{(2.0 - x)} \approx \frac{[\text{H}^+](2.0)}{2.0}$$

$$K_a = [\text{H}^+]$$

Taking the  $-\log$  of both sides,

$$\text{p}K_a = \text{pH}$$

Thus, for a buffer system in which the [weak acid] = [weak base],

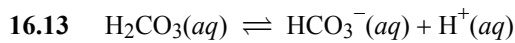
$$\text{pH} = \text{p}K_a$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) = \mathbf{4.74}$$

(b) Similar to part (a),

$$\text{pH} = \text{p}K_a = \mathbf{4.74}$$

**Buffer (a)** will be a more effective buffer because the concentrations of acid and base components are ten times higher than those in (b). Thus, buffer (a) can neutralize 10 times more added acid or base compared to buffer (b).



$$K_{a_1} = 4.2 \times 10^{-7}$$

$$\text{p}K_{a_1} = 6.38$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$8.00 = 6.38 + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$\log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 1.62$$

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 41.7$$

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = \mathbf{0.024}$$

- 16.14** *Step 1:* Write the equilibrium that occurs between  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ . Set up a table relating the initial concentrations, the change in concentration to reach equilibrium, and the equilibrium concentrations.

$$\text{H}_2\text{PO}_4^-(aq) \rightleftharpoons \text{H}^+(aq) + \text{HPO}_4^{2-}(aq)$$

Initial (M):	0.15	0	0.10
Change (M):	-x	+x	+x
Equilibrium (M):	0.15 - x	x	0.10 + x

- Step 2:* Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant ( $K_a$ ), solve for  $x$ .

$$K_a = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

You can look up the  $K_a$  value for dihydrogen phosphate in Table 15.5 of your text.

$$6.2 \times 10^{-8} = \frac{(x)(0.10 + x)}{(0.15 - x)}$$

$$6.2 \times 10^{-8} \approx \frac{(x)(0.10)}{(0.15)}$$

$$x = [\text{H}^+] = 9.3 \times 10^{-8} M$$

- Step 3:* Having solved for the  $[\text{H}^+]$ , calculate the pH of the solution.

$$\text{pH} = -\log[\text{H}^+] = -\log(9.3 \times 10^{-8}) = 7.03$$

- 16.15** Using the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$4.50 = 4.74 + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Thus,

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 0.58$$

- 16.16** We can use the Henderson-Hasselbalch equation to calculate the ratio  $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$ . The Henderson-Hasselbalch equation is:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

For the buffer system of interest,  $\text{HCO}_3^-$  is the conjugate base of the acid,  $\text{H}_2\text{CO}_3$ . We can write:

$$\text{pH} = 7.40 = -\log(4.2 \times 10^{-7}) + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$7.40 = 6.38 + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

The [conjugate base]/[acid] ratio is:

$$\log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 7.40 - 6.38 = 1.02$$

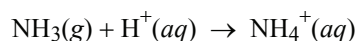
$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{1.02} = \mathbf{1.0 \times 10^1}$$

The buffer should be more effective against an added acid because ten times more base is present compared to acid. Note that a pH of 7.40 is only a two significant figure number (Why?); the final result should only have two significant figures.

**16.17** For the first part we use  $K_a$  for ammonium ion. (Why?) The Henderson–Hasselbalch equation is

$$\mathbf{pH} = -\log(5.6 \times 10^{-10}) + \log \frac{(0.20 \text{ M})}{(0.20 \text{ M})} = \mathbf{9.25}$$

For the second part, the acid–base reaction is



We find the number of moles of HCl added

$$10.0 \text{ mL} \times \frac{0.10 \text{ mol HCl}}{1000 \text{ mL soln}} = 0.0010 \text{ mol HCl}$$

The number of moles of  $\text{NH}_3$  and  $\text{NH}_4^+$  originally present are

$$65.0 \text{ mL} \times \frac{0.20 \text{ mol}}{1000 \text{ mL soln}} = 0.013 \text{ mol}$$

Using the acid–base reaction, we find the number of moles of  $\text{NH}_3$  and  $\text{NH}_4^+$  after addition of the HCl.

	$\text{NH}_3(\text{aq})$	$+ \text{H}^+(\text{aq})$	$\rightarrow$	$\text{NH}_4^+(\text{aq})$
Initial (mol):	0.013	0.0010		0.013
Change (mol):	-0.0010	-0.0010		+0.0010
Final (mol):	0.012	0		0.014

We find the new pH:

$$\mathbf{pH} = 9.25 + \log \frac{(0.012)}{(0.014)} = \mathbf{9.18}$$

**16.18** As calculated in Problem 16.12, the pH of this buffer system is equal to  $\text{p}K_a$ .

$$\text{pH} = \text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

**(a)** The added NaOH will react completely with the acid component of the buffer,  $\text{CH}_3\text{COOH}$ . NaOH ionizes completely; therefore, 0.080 mol of  $\text{OH}^-$  are added to the buffer.

**Step 1:** The neutralization reaction is:

	$\text{CH}_3\text{COOH}(aq)$	+	$\text{OH}^-(aq)$	$\longrightarrow$	$\text{CH}_3\text{COO}^-(aq)$	+	$\text{H}_2\text{O}(l)$
Initial (mol):	1.00		0.080		1.00		
Change (mol):	-0.080		-0.080		+0.080		
Final (mol):	0.92		0		1.08		

**Step 2:** Now, the acetic acid equilibrium is reestablished. Since the volume of the solution is 1.00 L, we can convert directly from moles to molar concentration.

	$\text{CH}_3\text{COOH}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CH}_3\text{COO}^-(aq)$
Initial (M):	0.92		0		1.08
Change (M):	-x		+x		+x
Equilibrium (M):	$0.92 - x$		x		$1.08 + x$

Write the  $K_a$  expression, then solve for  $x$ .

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

$$1.8 \times 10^{-5} = \frac{(x)(1.08 + x)}{(0.92 - x)} \approx \frac{x(1.08)}{0.92}$$

$$x = [\text{H}^+] = 1.5 \times 10^{-5} M$$

**Step 3:** Having solved for the  $[\text{H}^+]$ , calculate the pH of the solution.

$$\text{pH} = -\log[\text{H}^+] = -\log(1.5 \times 10^{-5}) = 4.82$$

The pH of the buffer increased from 4.74 to 4.82 upon addition of 0.080 mol of strong base.

(b) The added acid will react completely with the base component of the buffer,  $\text{CH}_3\text{COO}^-$ . HCl ionizes completely; therefore, 0.12 mol of  $\text{H}^+$  ion are added to the buffer

**Step 1:** The neutralization reaction is:

	$\text{CH}_3\text{COO}^-(aq)$	+	$\text{H}^+(aq)$	$\longrightarrow$	$\text{CH}_3\text{COOH}(aq)$
Initial (mol):	1.00		0.12		1.00
Change (mol):	-0.12		-0.12		+0.12
Final (mol):	0.88		0		1.12

**Step 2:** Now, the acetic acid equilibrium is reestablished. Since the volume of the solution is 1.00 L, we can convert directly from moles to molar concentration.

	$\text{CH}_3\text{COOH}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CH}_3\text{COO}^-(aq)$
Initial (M):	1.12		0		0.88
Change (M):	-x		+x		+x
Equilibrium (M):	$1.12 - x$		x		$0.88 + x$

Write the  $K_a$  expression, then solve for  $x$ .

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

$$1.8 \times 10^{-5} = \frac{(x)(0.88 + x)}{(1.12 - x)} \approx \frac{x(0.88)}{1.12}$$

$$x = [\text{H}^+] = 2.3 \times 10^{-5} \text{ M}$$

**Step 3:** Having solved for the  $[\text{H}^+]$ , calculate the pH of the solution.

$$\text{pH} = -\log[\text{H}^+] = -\log(2.3 \times 10^{-5}) = 4.64$$

The pH of the buffer decreased from 4.74 to 4.64 upon addition of 0.12 mol of strong acid.

**16.19** We write

$$K_{a_1} = 1.1 \times 10^{-3} \quad \text{p}K_{a_1} = 2.96$$

$$K_{a_2} = 2.5 \times 10^{-6} \quad \text{p}K_{a_2} = 5.60$$

In order for the buffer solution to behave effectively, the  $\text{p}K_a$  of the acid component must be close to the desired pH. Therefore, the proper buffer system is **Na<sub>2</sub>A/NaHA**.

**16.20 Strategy:** For a buffer to function effectively, the concentration of the acid component must be roughly equal to the conjugate base component. According to Equation (16.4) of the text, when the desired pH is close to the  $\text{p}K_a$  of the acid, that is, when  $\text{pH} \approx \text{p}K_a$ ,

$$\log \frac{[\text{conjugate base}]}{[\text{acid}]} \approx 0$$

or

$$\frac{[\text{conjugate base}]}{[\text{acid}]} \approx 1$$

**Solution:** To prepare a solution of a desired pH, we should choose a weak acid with a  $\text{p}K_a$  value close to the desired pH. Calculating the  $\text{p}K_a$  for each acid:

$$\text{For HA,} \quad \text{p}K_a = -\log(2.7 \times 10^{-3}) = 2.57$$

$$\text{For HB,} \quad \text{p}K_a = -\log(4.4 \times 10^{-6}) = 5.36$$

$$\text{For HC,} \quad \text{p}K_a = -\log(2.6 \times 10^{-9}) = 8.59$$

The buffer solution with a  $\text{p}K_a$  closest to the desired pH is HC. Thus, **HC** is the best choice to prepare a buffer solution with  $\text{pH} = 8.60$ .

**16.23** Since the acid is monoprotic, the number of moles of KOH is equal to the number of moles of acid.

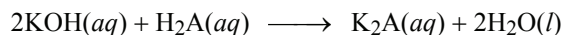
$$\text{Moles acid} = 16.4 \text{ mL} \times \frac{0.08133 \text{ mol}}{1000 \text{ mL}} = 0.00133 \text{ mol}$$

$$\text{Molar mass} = \frac{0.2688 \text{ g}}{0.00133 \text{ mol}} = 202 \text{ g/mol}$$

- 16.24** We want to calculate the molar mass of the diprotic acid. The mass of the acid is given in the problem, so we need to find moles of acid in order to calculate its molar mass.

$$\begin{array}{ccc} \text{want to calculate} & & \text{given} \\ \downarrow & & \downarrow \\ \text{molar mass of H}_2\text{A} = & \frac{\text{g H}_2\text{A}}{\text{mol H}_2\text{A}} & \\ & \uparrow & \\ & \text{need to find} & \end{array}$$

The neutralization reaction is:



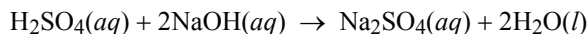
From the volume and molarity of the base needed to neutralize the acid, we can calculate the number of moles of  $\text{H}_2\text{A}$  reacted.

$$11.1 \text{ mL KOH} \times \frac{1.00 \text{ mol KOH}}{1000 \text{ mL}} \times \frac{1 \text{ mol H}_2\text{A}}{2 \text{ mol KOH}} = 5.55 \times 10^{-3} \text{ mol H}_2\text{A}$$

We know that 0.500 g of the diprotic acid were reacted (1/10 of the 250 mL was tested). Divide the number of grams by the number of moles to calculate the molar mass.

$$\mathcal{M}(\text{H}_2\text{A}) = \frac{0.500 \text{ g H}_2\text{A}}{5.55 \times 10^{-3} \text{ mol H}_2\text{A}} = \mathbf{90.1 \text{ g/mol}}$$

- 16.25** The neutralization reaction is:



Since one mole of sulfuric acid combines with two moles of sodium hydroxide, we write:

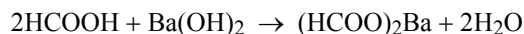
$$\text{mol NaOH} = 12.5 \text{ mL H}_2\text{SO}_4 \times \frac{0.500 \text{ mol H}_2\text{SO}_4}{1000 \text{ mL soln}} \times \frac{2 \text{ mol NaOH}}{1 \text{ mol H}_2\text{SO}_4} = 0.0125 \text{ mol NaOH}$$

$$\text{concentration of NaOH} = \frac{0.0125 \text{ mol NaOH}}{50.0 \times 10^{-3} \text{ L soln}} = \mathbf{0.25 \text{ M}}$$

- 16.26** We want to calculate the molarity of the  $\text{Ba}(\text{OH})_2$  solution. The volume of the solution is given (19.3 mL), so we need to find the moles of  $\text{Ba}(\text{OH})_2$  to calculate the molarity.

$$\begin{array}{ccc} \text{want to calculate} & & \text{need to find} \\ \downarrow & & \downarrow \\ M \text{ of Ba(OH)}_2 = & \frac{\text{mol Ba(OH)}_2}{\text{L of Ba(OH)}_2 \text{ soln}} & \\ & \uparrow & \\ & \text{given} & \end{array}$$

The neutralization reaction is:



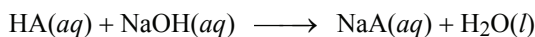
From the volume and molarity of HCOOH needed to neutralize Ba(OH)<sub>2</sub>, we can determine the moles of Ba(OH)<sub>2</sub> reacted.

$$20.4 \text{ mL HCOOH} \times \frac{0.883 \text{ mol HCOOH}}{1000 \text{ mL}} \times \frac{1 \text{ mol Ba}(\text{OH})_2}{2 \text{ mol HCOOH}} = 9.01 \times 10^{-3} \text{ mol Ba}(\text{OH})_2$$

The molarity of the Ba(OH)<sub>2</sub> solution is:

$$\frac{9.01 \times 10^{-3} \text{ mol Ba}(\text{OH})_2}{19.3 \times 10^{-3} \text{ L}} = \mathbf{0.467 \text{ M}}$$

- 16.27 (a)** Since the acid is monoprotic, the moles of acid equals the moles of base added.



$$\text{Moles acid} = 18.4 \text{ mL} \times \frac{0.0633 \text{ mol}}{1000 \text{ mL soln}} = 0.00116 \text{ mol}$$

We know the mass of the unknown acid in grams and the number of moles of the unknown acid.

$$\mathbf{\text{Molar mass}} = \frac{0.1276 \text{ g}}{0.00116 \text{ mol}} = \mathbf{1.10 \times 10^2 \text{ g/mol}}$$

- (b)** The number of moles of NaOH in 10.0 mL of solution is

$$10.0 \text{ mL} \times \frac{0.0633 \text{ mol}}{1000 \text{ mL soln}} = 6.33 \times 10^{-4} \text{ mol}$$

The neutralization reaction is:

	$\text{HA}(aq)$	+	$\text{NaOH}(aq)$	$\longrightarrow$	$\text{NaA}(aq)$	+	$\text{H}_2\text{O}(l)$
Initial (mol):	0.00116		$6.33 \times 10^{-4}$		0		
Change (mol):	$-6.33 \times 10^{-4}$		$-6.33 \times 10^{-4}$		$+6.33 \times 10^{-4}$		
Final (mol):	$5.3 \times 10^{-4}$		0		$6.33 \times 10^{-4}$		

Now, the weak acid equilibrium will be reestablished. The total volume of solution is 35.0 mL.

$$[\text{HA}] = \frac{5.3 \times 10^{-4} \text{ mol}}{0.035 \text{ L}} = 0.015 \text{ M}$$

$$[\text{A}^-] = \frac{6.33 \times 10^{-4} \text{ mol}}{0.035 \text{ L}} = 0.0181 \text{ M}$$

We can calculate the [H<sup>+</sup>] from the pH.

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-5.87} = 1.35 \times 10^{-6} \text{ M}$$

	$\text{HA}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	$+$	$\text{A}^-(aq)$
Initial ( <i>M</i> ):	0.015		0		0.0181
Change ( <i>M</i> ):	$-1.35 \times 10^{-6}$		$+1.35 \times 10^{-6}$		$+1.35 \times 10^{-6}$
Equilibrium ( <i>M</i> ):	0.015		$1.35 \times 10^{-6}$		0.0181

Substitute the equilibrium concentrations into the equilibrium constant expression to solve for  $K_a$ .

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(1.35 \times 10^{-6})(0.0181)}{0.015} = 1.6 \times 10^{-6}$$

- 16.28** The resulting solution is not a buffer system. There is excess NaOH and the neutralization is well past the equivalence point.

$$\text{Moles NaOH} = 0.500 \text{ L} \times \frac{0.167 \text{ mol}}{1 \text{ L}} = 0.0835 \text{ mol}$$

$$\text{Moles CH}_3\text{COOH} = 0.500 \text{ L} \times \frac{0.100 \text{ mol}}{1 \text{ L}} = 0.0500 \text{ mol}$$

	$\text{CH}_3\text{COOH}(aq)$	$+$	$\text{NaOH}(aq)$	$\rightarrow$	$\text{CH}_3\text{COONa}(aq)$	$+$	$\text{H}_2\text{O}(l)$
Initial (mol):	0.0500		0.0835		0		
Change (mol):	$-0.0500$		$-0.0500$		$+0.0500$		
Final (mol):	0		0.0335		0.0500		

The volume of the resulting solution is 1.00 L (500 mL + 500 mL = 1000 mL).

$$[\text{OH}^-] = \frac{0.0335 \text{ mol}}{1.00 \text{ L}} = 0.0335 \text{ M}$$

$$[\text{Na}^+] = \frac{(0.0335 + 0.0500) \text{ mol}}{1.00 \text{ L}} = 0.0835 \text{ M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0335} = 3.0 \times 10^{-13} \text{ M}$$

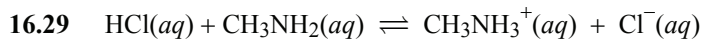
$$[\text{CH}_3\text{COO}^-] = \frac{0.0500 \text{ mol}}{1.00 \text{ L}} = 0.0500 \text{ M}$$

	$\text{CH}_3\text{COO}^-(aq)$	$+$	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{CH}_3\text{COOH}(aq)$	$+$	$\text{OH}^-(aq)$
Initial ( <i>M</i> ):	0.0500				0		0.0335
Change ( <i>M</i> ):	$-x$				$+x$		$+x$
Equilibrium ( <i>M</i> ):	$0.0500 - x$				$x$		$0.0335 + x$

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$5.6 \times 10^{-10} = \frac{(x)(0.0335 + x)}{(0.0500 - x)} \approx \frac{(x)(0.0335)}{(0.0500)}$$

$$x = [\text{CH}_3\text{COOH}] = 8.4 \times 10^{-10} \text{ M}$$



Since the concentrations of acid and base are equal, equal volumes of each solution will need to be added to reach the equivalence point. Therefore, the solution volume is doubled at the equivalence point, and the concentration of the conjugate acid from the salt,  $\text{CH}_3\text{NH}_3^+$ , is:

$$\frac{0.20 \text{ M}}{2} = 0.10 \text{ M}$$

The conjugate acid undergoes hydrolysis.

	$\text{CH}_3\text{NH}_3^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{NH}_2(aq)$		
Initial ( <i>M</i> ):	0.10	0	0
Change ( <i>M</i> ):	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
Equilibrium ( <i>M</i> ):	$0.10 - x$	<i>x</i>	<i>x</i>

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]}$$

$$2.3 \times 10^{-11} = \frac{x^2}{0.10 - x}$$

Assuming that,  $0.10 - x \approx 0.10$

$$x = [\text{H}_3\text{O}^+] = 1.5 \times 10^{-6} \text{ M}$$

$$\text{pH} = 5.82$$

**16.30** Let's assume we react 1 L of  $\text{HCOOH}$  with 1 L of  $\text{NaOH}$ .

	$\text{HCOOH}(aq) + \text{NaOH}(aq) \rightarrow \text{HCOONa}(aq) + \text{H}_2\text{O}(l)$		
Initial (mol):	0.10	0.10	0
Change (mol):	-0.10	-0.10	+0.10
Final (mol):	0	0	0.10

The solution volume has doubled (1 L + 1 L = 2 L). The concentration of  $\text{HCOONa}$  is:

$$M(\text{HCOONa}) = \frac{0.10 \text{ mol}}{2 \text{ L}} = 0.050 \text{ M}$$

$\text{HCOO}^-(aq)$  is a weak base. The hydrolysis is:

	$\text{HCOO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCOOH}(aq) + \text{OH}^-(aq)$		
Initial ( <i>M</i> ):	0.050	0	0
Change ( <i>M</i> ):	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
Equilibrium ( <i>M</i> ):	$0.050 - x$	<i>x</i>	<i>x</i>

$$K_b = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]}$$

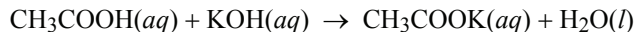
$$5.9 \times 10^{-11} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$$x = 1.7 \times 10^{-6} M = [\text{OH}^-]$$

$$\text{pOH} = 5.77$$

$$\text{pH} = 8.23$$

**16.31** The reaction between  $\text{CH}_3\text{COOH}$  and  $\text{KOH}$  is:



We see that 1 mole  $\text{CH}_3\text{COOH} \simeq 1$  mol  $\text{KOH}$ . Therefore, at every stage of titration, we can calculate the number of moles of acid reacting with base, and the pH of the solution is determined by the excess acid or base left over. At the equivalence point, however, the neutralization is complete, and the pH of the solution will depend on the extent of the hydrolysis of the salt formed, which is  $\text{CH}_3\text{COOK}$ .

(a) No  $\text{KOH}$  has been added. This is a weak acid calculation.

	$\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)$		
Initial (M):	0.100	0	0
Change (M):	-x	+x	+x
Equilibrium (M):	0.100 - x	x	x

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

$$1.8 \times 10^{-5} = \frac{(x)(x)}{0.100 - x} \approx \frac{x^2}{0.100}$$

$$x = 1.34 \times 10^{-3} M = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 2.87$$

(b) The number of moles of  $\text{CH}_3\text{COOH}$  originally present in 25.0 mL of solution is:

$$25.0 \text{ mL} \times \frac{0.100 \text{ mol CH}_3\text{COOH}}{1000 \text{ mL CH}_3\text{COOH soln}} = 2.50 \times 10^{-3} \text{ mol}$$

The number of moles of  $\text{KOH}$  in 5.0 mL is:

$$5.0 \text{ mL} \times \frac{0.200 \text{ mol KOH}}{1000 \text{ mL KOH soln}} = 1.00 \times 10^{-3} \text{ mol}$$

We work with moles at this point because when two solutions are mixed, the solution volume increases. As the solution volume increases, molarity will change, but the number of moles will remain the same. The changes in number of moles are summarized.

	$\text{CH}_3\text{COOH}(aq)$	+	$\text{KOH}(aq)$	$\rightarrow$	$\text{CH}_3\text{COOK}(aq) + \text{H}_2\text{O}(l)$
Initial (mol):	$2.50 \times 10^{-3}$		$1.00 \times 10^{-3}$		0
Change (mol):	$-1.00 \times 10^{-3}$		$-1.00 \times 10^{-3}$		$+1.00 \times 10^{-3}$
Final (mol):	$1.50 \times 10^{-3}$		0		$1.00 \times 10^{-3}$

At this stage, we have a buffer system made up of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  (from the salt,  $\text{CH}_3\text{COOK}$ ). We use the Henderson-Hasselbalch equation to calculate the pH.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log \left( \frac{1.00 \times 10^{-3}}{1.50 \times 10^{-3}} \right)$$

$$\text{pH} = 4.56$$

- (c) This part is solved similarly to part (b).

The number of moles of KOH in 10.0 mL is:

$$10.0 \text{ mL} \times \frac{0.200 \text{ mol KOH}}{1000 \text{ mL KOH soln}} = 2.00 \times 10^{-3} \text{ mol}$$

The changes in number of moles are summarized.

	$\text{CH}_3\text{COOH}(aq)$	+	$\text{KOH}(aq)$	$\rightarrow$	$\text{CH}_3\text{COOK}(aq) + \text{H}_2\text{O}(l)$
Initial (mol):	$2.50 \times 10^{-3}$		$2.00 \times 10^{-3}$		0
Change (mol):	$-2.00 \times 10^{-3}$		$-2.00 \times 10^{-3}$		$+2.00 \times 10^{-3}$
Final (mol):	$0.50 \times 10^{-3}$		0		$2.00 \times 10^{-3}$

At this stage, we have a buffer system made up of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  (from the salt,  $\text{CH}_3\text{COOK}$ ). We use the Henderson-Hasselbalch equation to calculate the pH.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log \left( \frac{2.00 \times 10^{-3}}{0.50 \times 10^{-3}} \right)$$

$$\text{pH} = 5.34$$

- (d) We have reached the equivalence point of the titration.  $2.50 \times 10^{-3}$  mole of  $\text{CH}_3\text{COOH}$  reacts with  $2.50 \times 10^{-3}$  mole KOH to produce  $2.50 \times 10^{-3}$  mole of  $\text{CH}_3\text{COOK}$ . The only major species present in solution at the equivalence point is the salt,  $\text{CH}_3\text{COOK}$ , which contains the conjugate base,  $\text{CH}_3\text{COO}^-$ . Let's calculate the molarity of  $\text{CH}_3\text{COO}^-$ . The volume of the solution is:  $(25.0 \text{ mL} + 12.5 \text{ mL} = 37.5 \text{ mL} = 0.0375 \text{ L})$ .

$$M(\text{CH}_3\text{COO}^-) = \frac{2.50 \times 10^{-3} \text{ mol}}{0.0375 \text{ L}} = 0.0667 \text{ M}$$

We set up the hydrolysis of  $\text{CH}_3\text{COO}^-$ , which is a weak base.

	$\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq)$
Initial (M):	0.0667		0      0
Change (M):	$-x$		$+x$ $+x$
Equilibrium (M):	$0.0667 - x$		$x$ $x$

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$5.6 \times 10^{-10} = \frac{(x)(x)}{0.0667 - x} \approx \frac{x^2}{0.0667}$$

$$x = 6.1 \times 10^{-6} M = [\text{OH}^-]$$

$$\text{pOH} = 5.21$$

$$\text{pH} = 8.79$$

- (e) We have passed the equivalence point of the titration. The excess strong base, KOH, will determine the pH at this point. The moles of KOH in 15.0 mL are:

$$15.0 \text{ mL} \times \frac{0.200 \text{ mol KOH}}{1000 \text{ mL KOH soln}} = 3.00 \times 10^{-3} \text{ mol}$$

The changes in number of moles are summarized.

	$\text{CH}_3\text{COOH}(aq)$	+	$\text{KOH}(aq)$	$\rightarrow$	$\text{CH}_3\text{COOK}(aq) + \text{H}_2\text{O}(l)$
Initial (mol):	$2.50 \times 10^{-3}$		$3.00 \times 10^{-3}$		0
Change (mol):	$-2.50 \times 10^{-3}$		$-2.50 \times 10^{-3}$		$+2.50 \times 10^{-3}$
Final (mol):	0		$0.50 \times 10^{-3}$		$2.50 \times 10^{-3}$

Let's calculate the molarity of the KOH in solution. The volume of the solution is now 40.0 mL = 0.0400 L.

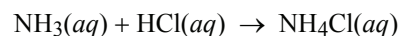
$$M(\text{KOH}) = \frac{0.50 \times 10^{-3} \text{ mol}}{0.0400 \text{ L}} = 0.0125 M$$

KOH is a strong base. The pOH is:

$$\text{pOH} = -\log(0.0125) = 1.90$$

$$\text{pH} = 12.10$$

- 16.32** The reaction between  $\text{NH}_3$  and HCl is:



We see that 1 mole  $\text{NH}_3 \cong 1$  mol HCl. Therefore, at every stage of titration, we can calculate the number of moles of base reacting with acid, and the pH of the solution is determined by the excess base or acid left over. At the equivalence point, however, the neutralization is complete, and the pH of the solution will depend on the extent of the hydrolysis of the salt formed, which is  $\text{NH}_4\text{Cl}$ .

- (a) No HCl has been added. This is a weak base calculation.

	$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$
Initial (M):	0.300                      0                      0
Change (M):	$-x$ $+x$ $+x$
Equilibrium (M):	$0.300 - x$ $x$ $x$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{0.300 - x} \approx \frac{x^2}{0.300}$$

$$x = 2.3 \times 10^{-3} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = 2.64$$

$$\text{pH} = 11.36$$

- (b) The number of moles of  $\text{NH}_3$  originally present in 10.0 mL of solution is:

$$10.0 \text{ mL} \times \frac{0.300 \text{ mol NH}_3}{1000 \text{ mL NH}_3 \text{ soln}} = 3.00 \times 10^{-3} \text{ mol}$$

The number of moles of HCl in 10.0 mL is:

$$10.0 \text{ mL} \times \frac{0.100 \text{ mol HCl}}{1000 \text{ mL HCl soln}} = 1.00 \times 10^{-3} \text{ mol}$$

We work with moles at this point because when two solutions are mixed, the solution volume increases. As the solution volume increases, molarity will change, but the number of moles will remain the same. The changes in number of moles are summarized.

	$\text{NH}_3(aq)$	+	$\text{HCl}(aq)$	$\rightarrow$	$\text{NH}_4\text{Cl}(aq)$
Initial (mol):	$3.00 \times 10^{-3}$		$1.00 \times 10^{-3}$		0
Change (mol):	$-1.00 \times 10^{-3}$		$-1.00 \times 10^{-3}$		$+1.00 \times 10^{-3}$
Final (mol):	$2.00 \times 10^{-3}$		0		$1.00 \times 10^{-3}$

At this stage, we have a buffer system made up of  $\text{NH}_3$  and  $\text{NH}_4^+$  (from the salt,  $\text{NH}_4\text{Cl}$ ). We use the Henderson-Hasselbalch equation to calculate the pH.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = -\log(5.6 \times 10^{-10}) + \log \left( \frac{2.00 \times 10^{-3}}{1.00 \times 10^{-3}} \right)$$

$$\text{pH} = 9.55$$

- (c) This part is solved similarly to part (b).

The number of moles of HCl in 20.0 mL is:

$$20.0 \text{ mL} \times \frac{0.100 \text{ mol HCl}}{1000 \text{ mL HCl soln}} = 2.00 \times 10^{-3} \text{ mol}$$

The changes in number of moles are summarized.

	$\text{NH}_3(aq)$	+	$\text{HCl}(aq)$	$\rightarrow$	$\text{NH}_4\text{Cl}(aq)$
Initial (mol):	$3.00 \times 10^{-3}$		$2.00 \times 10^{-3}$		0
Change (mol):	$-2.00 \times 10^{-3}$		$-2.00 \times 10^{-3}$		$+2.00 \times 10^{-3}$
Final (mol):	$1.00 \times 10^{-3}$		0		$2.00 \times 10^{-3}$

At this stage, we have a buffer system made up of  $\text{NH}_3$  and  $\text{NH}_4^+$  (from the salt,  $\text{NH}_4\text{Cl}$ ). We use the Henderson-Hasselbalch equation to calculate the pH.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = -\log(5.6 \times 10^{-10}) + \log \left( \frac{1.00 \times 10^{-3}}{2.00 \times 10^{-3}} \right)$$

$$\text{pH} = 8.95$$

- (d) We have reached the equivalence point of the titration.  $3.00 \times 10^{-3}$  mole of  $\text{NH}_3$  reacts with  $3.00 \times 10^{-3}$  mole  $\text{HCl}$  to produce  $3.00 \times 10^{-3}$  mole of  $\text{NH}_4\text{Cl}$ . The only major species present in solution at the equivalence point is the salt,  $\text{NH}_4\text{Cl}$ , which contains the conjugate acid,  $\text{NH}_4^+$ . Let's calculate the molarity of  $\text{NH}_4^+$ . The volume of the solution is:  $(10.0 \text{ mL} + 30.0 \text{ mL} = 40.0 \text{ mL} = 0.0400 \text{ L})$ .

$$M(\text{NH}_4^+) = \frac{3.00 \times 10^{-3} \text{ mol}}{0.0400 \text{ L}} = 0.0750 \text{ M}$$

We set up the hydrolysis of  $\text{NH}_4^+$ , which is a weak acid.

	$\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NH}_3(aq)$		
Initial (M):	0.0750	0	0
Change (M):	-x	+x	+x
Equilibrium (M):	$0.0750 - x$	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

$$5.6 \times 10^{-10} = \frac{(x)(x)}{0.0750 - x} \approx \frac{x^2}{0.0750}$$

$$x = 6.5 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 5.19$$

- (e) We have passed the equivalence point of the titration. The excess strong acid,  $\text{HCl}$ , will determine the pH at this point. The moles of  $\text{HCl}$  in 40.0 mL are:

$$40.0 \text{ mL} \times \frac{0.100 \text{ mol HCl}}{1000 \text{ mL HCl soln}} = 4.00 \times 10^{-3} \text{ mol}$$

The changes in number of moles are summarized.

	$\text{NH}_3(aq)$	+	$\text{HCl}(aq)$	$\rightarrow$	$\text{NH}_4\text{Cl}(aq)$
Initial (mol):	$3.00 \times 10^{-3}$		$4.00 \times 10^{-3}$		0
Change (mol):	$-3.00 \times 10^{-3}$		$-3.00 \times 10^{-3}$		$+3.00 \times 10^{-3}$
Final (mol):	0		$1.00 \times 10^{-3}$		$3.00 \times 10^{-3}$

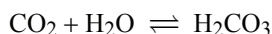
Let's calculate the molarity of the HCl in solution. The volume of the solution is now 50.0 mL = 0.0500 L.

$$M(\text{HCl}) = \frac{1.00 \times 10^{-3} \text{ mol}}{0.0500 \text{ L}} = 0.0200 \text{ M}$$

HCl is a strong acid. The pH is:

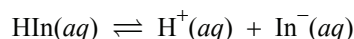
$$\text{pH} = -\log(0.0200) = 1.70$$

- 16.35** (a) HCOOH is a weak acid and NaOH is a strong base. Suitable indicators are cresol red and phenolphthalein.
- (b) HCl is a strong acid and KOH is a strong base. Suitable indicators are all those listed with the exceptions of thymol blue, bromophenol blue, and methyl orange.
- (c) HNO<sub>3</sub> is a strong acid and CH<sub>3</sub>NH<sub>2</sub> is a weak base. Suitable indicators are bromophenol blue, methyl orange, methyl red, and chlorophenol blue.
- 16.36** CO<sub>2</sub> in the air dissolves in the solution:



The carbonic acid neutralizes the NaOH.

- 16.37** The weak acid equilibrium is



We can write a  $K_a$  expression for this equilibrium.

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

Rearranging,

$$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{[\text{H}^+]}{K_a}$$

From the pH, we can calculate the H<sup>+</sup> concentration.

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-4} = 1.0 \times 10^{-4} \text{ M}$$

$$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{[\text{H}^+]}{K_a} = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-6}} = 100$$

Since the concentration of HIn is 100 times greater than the concentration of In<sup>-</sup>, the color of the solution will be that of HIn, the nonionized form. The color of the solution will be **red**.

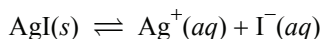
- 16.38** According to Section 16.5 of the text, when  $[\text{HIn}] \approx [\text{In}^-]$  the indicator color is a mixture of the colors of HIn and In<sup>-</sup>. In other words, the indicator color changes at this point. When  $[\text{HIn}] \approx [\text{In}^-]$  we can write:

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_a}{[\text{H}^+]} = 1$$

$$[\text{H}^+] = K_a = 2.0 \times 10^{-6}$$

$$\text{pH} = 5.70$$

- 16.45 (a) The solubility equilibrium is given by the equation



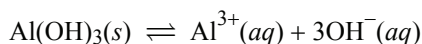
The expression for  $K_{\text{sp}}$  is given by

$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$$

The value of  $K_{\text{sp}}$  can be found in Table 16.2 of the text. If the equilibrium concentration of silver ion is the value given, the concentration of iodide ion must be

$$[\text{I}^-] = \frac{K_{\text{sp}}}{[\text{Ag}^+]} = \frac{8.3 \times 10^{-17}}{9.1 \times 10^{-9}} = 9.1 \times 10^{-9} \text{ M}$$

- (b) The value of  $K_{\text{sp}}$  for aluminum hydroxide can be found in Table 16.2 of the text. The equilibrium expressions are:



$$K_{\text{sp}} = [\text{Al}^{3+}][\text{OH}^-]^3$$

Using the given value of the hydroxide ion concentration, the equilibrium concentration of aluminum ion is:

$$[\text{Al}^{3+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^3} = \frac{1.8 \times 10^{-33}}{(2.9 \times 10^{-9})^3} = 7.4 \times 10^{-8} \text{ M}$$

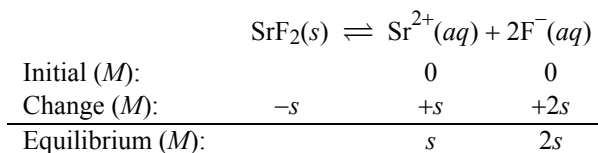
What is the pH of this solution? Will the aluminum concentration change if the pH is altered?

- 16.46 **Strategy:** In each part, we can calculate the number of moles of compound dissolved in one liter of solution (the molar solubility). Then, from the molar solubility,  $s$ , we can determine  $K_{\text{sp}}$ .

**Solution:**

$$(a) \frac{7.3 \times 10^{-2} \text{ g SrF}_2}{1 \text{ L soln}} \times \frac{1 \text{ mol SrF}_2}{125.6 \text{ g SrF}_2} = 5.8 \times 10^{-4} \text{ mol/L} = s$$

Consider the dissociation of  $\text{SrF}_2$  in water. Let  $s$  be the molar solubility of  $\text{SrF}_2$ .



$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{F}^-]^2 = (s)(2s)^2 = 4s^3$$

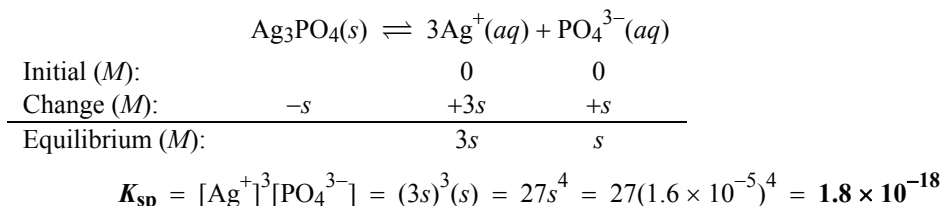
The molar solubility ( $s$ ) was calculated above. Substitute into the equilibrium constant expression to solve for  $K_{\text{sp}}$ .

$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{F}^-]^2 = 4s^3 = 4(5.8 \times 10^{-4})^3 = 7.8 \times 10^{-10}$$

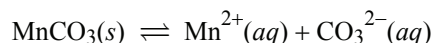
$$(b) \frac{6.7 \times 10^{-3} \text{ g Ag}_3\text{PO}_4}{1 \text{ L soln}} \times \frac{1 \text{ mol Ag}_3\text{PO}_4}{418.7 \text{ g Ag}_3\text{PO}_4} = 1.6 \times 10^{-5} \text{ mol/L} = s$$

(b) is solved in a similar manner to (a)

The equilibrium equation is:



**16.47** For  $\text{MnCO}_3$  dissolving, we write



For every mole of  $\text{MnCO}_3$  that dissolves, one mole of  $\text{Mn}^{2+}$  will be produced and one mole of  $\text{CO}_3^{2-}$  will be produced. If the molar solubility of  $\text{MnCO}_3$  is  $s$  mol/L, then the concentrations of  $\text{Mn}^{2+}$  and  $\text{CO}_3^{2-}$  are:

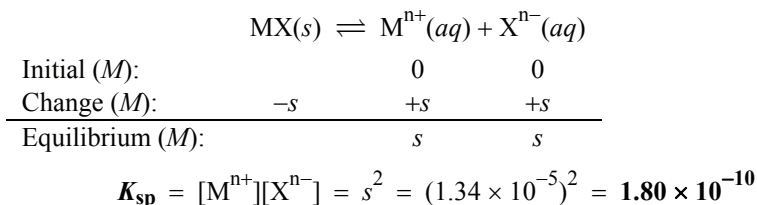
$$[\text{Mn}^{2+}] = [\text{CO}_3^{2-}] = s = 4.2 \times 10^{-6} \text{ M}$$

$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{CO}_3^{2-}] = s^2 = (4.2 \times 10^{-6})^2 = \mathbf{1.8 \times 10^{-11}}$$

**16.48** First, we can convert the solubility of  $\text{MX}$  in g/L to mol/L.

$$\frac{4.63 \times 10^{-3} \text{ g MX}}{1 \text{ L soln}} \times \frac{1 \text{ mol MX}}{346 \text{ g MX}} = 1.34 \times 10^{-5} \text{ mol/L} = s \text{ (molar solubility)}$$

The equilibrium reaction is:



**16.49** The charges of the M and X ions are +3 and -2, respectively (are other values possible?). We first calculate the number of moles of  $\text{M}_2\text{X}_3$  that dissolve in 1.0 L of water. We carry an additional significant figure throughout this calculation to minimize rounding errors.

$$\text{Moles M}_2\text{X}_3 = (3.6 \times 10^{-17} \text{ g}) \times \frac{1 \text{ mol}}{288 \text{ g}} = 1.25 \times 10^{-19} \text{ mol}$$

The molar solubility,  $s$ , of the compound is therefore  $1.3 \times 10^{-19} \text{ M}$ . At equilibrium the concentration of  $\text{M}^{3+}$  must be  $2s$  and that of  $\text{X}^{2-}$  must be  $3s$ . (See Table 16.3 of the text.)

$$K_{\text{sp}} = [\text{M}^{3+}]^2[\text{X}^{2-}]^3 = [2s]^2[3s]^3 = 108s^5$$

Since these are equilibrium concentrations, the value of  $K_{sp}$  can be found by simple substitution

$$K_{sp} = 108s^5 = 108(1.25 \times 10^{-19})^5 = 3.3 \times 10^{-93}$$

**16.50 Strategy:** We can look up the  $K_{sp}$  value of  $\text{CaF}_2$  in Table 16.2 of the text. Then, setting up the dissociation equilibrium of  $\text{CaF}_2$  in water, we can solve for the molar solubility,  $s$ .

**Solution:** Consider the dissociation of  $\text{CaF}_2$  in water.

	$\text{CaF}_2(s)$	$\rightleftharpoons$	$\text{Ca}^{2+}(aq)$	$+$	$2\text{F}^{-}(aq)$
Initial ( $M$ ):			0		0
Change ( $M$ ):	- $s$		+ $s$		+ $2s$
Equilibrium ( $M$ ):			$s$		$2s$

Recall, that the concentration of a pure solid does not enter into an equilibrium constant expression. Therefore, the concentration of  $\text{CaF}_2$  is not important.

Substitute the value of  $K_{sp}$  and the concentrations of  $\text{Ca}^{2+}$  and  $\text{F}^{-}$  in terms of  $s$  into the solubility product expression to solve for  $s$ , the molar solubility.

$$\begin{aligned} K_{sp} &= [\text{Ca}^{2+}][\text{F}^{-}]^2 \\ 4.0 \times 10^{-11} &= (s)(2s)^2 \\ 4.0 \times 10^{-11} &= 4s^3 \\ s &= \text{molar solubility} = 2.2 \times 10^{-4} \text{ mol/L} \end{aligned}$$

The molar solubility indicates that  $2.2 \times 10^{-4}$  mol of  $\text{CaF}_2$  will dissolve in 1 L of an aqueous solution.

**16.51** Let  $s$  be the molar solubility of  $\text{Zn}(\text{OH})_2$ . The equilibrium concentrations of the ions are then

$$\begin{aligned} [\text{Zn}^{2+}] &= s \text{ and } [\text{OH}^{-}] = 2s \\ K_{sp} &= [\text{Zn}^{2+}][\text{OH}^{-}]^2 = (s)(2s)^2 = 4s^3 = 1.8 \times 10^{-14} \\ s &= \left( \frac{1.8 \times 10^{-14}}{4} \right)^{\frac{1}{3}} = 1.7 \times 10^{-5} \end{aligned}$$

$$[\text{OH}^{-}] = 2s = 3.4 \times 10^{-5} \text{ M and pOH} = 4.47$$

$$\text{pH} = 14.00 - 4.47 = 9.53$$

If the  $K_{sp}$  of  $\text{Zn}(\text{OH})_2$  were smaller by many more powers of ten, would  $2s$  still be the hydroxide ion concentration in the solution?

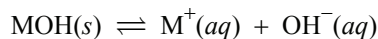
**16.52** First we can calculate the  $\text{OH}^{-}$  concentration from the pH.

$$\text{pOH} = 14.00 - \text{pH}$$

$$\text{pOH} = 14.00 - 9.68 = 4.32$$

$$[\text{OH}^{-}] = 10^{-\text{pOH}} = 10^{-4.32} = 4.8 \times 10^{-5} \text{ M}$$

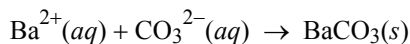
The equilibrium equation is:



From the balanced equation we know that  $[\text{M}^+] = [\text{OH}^-]$

$$K_{\text{sp}} = [\text{M}^+][\text{OH}^-] = (4.8 \times 10^{-5})^2 = 2.3 \times 10^{-9}$$

**16.53** According to the solubility rules, the only precipitate that might form is  $\text{BaCO}_3$ .



The number of moles of  $\text{Ba}^{2+}$  present in the original 20.0 mL of  $\text{Ba}(\text{NO}_3)_2$  solution is

$$20.0 \text{ mL} \times \frac{0.10 \text{ mol Ba}^{2+}}{1000 \text{ mL soln}} = 2.0 \times 10^{-3} \text{ mol Ba}^{2+}$$

The total volume after combining the two solutions is 70.0 mL. The concentration of  $\text{Ba}^{2+}$  in 70 mL is

$$[\text{Ba}^{2+}] = \frac{2.0 \times 10^{-3} \text{ mol Ba}^{2+}}{70.0 \times 10^{-3} \text{ L}} = 2.9 \times 10^{-2} \text{ M}$$

The number of moles of  $\text{CO}_3^{2-}$  present in the original 50.0 mL  $\text{Na}_2\text{CO}_3$  solution is

$$50.0 \text{ mL} \times \frac{0.10 \text{ mol CO}_3^{2-}}{1000 \text{ mL soln}} = 5.0 \times 10^{-3} \text{ mol CO}_3^{2-}$$

The concentration of  $\text{CO}_3^{2-}$  in the 70.0 mL of combined solution is

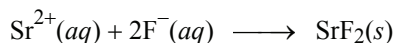
$$[\text{CO}_3^{2-}] = \frac{5.0 \times 10^{-3} \text{ mol CO}_3^{2-}}{70.0 \times 10^{-3} \text{ L}} = 7.1 \times 10^{-2} \text{ M}$$

Now we must compare  $Q$  and  $K_{\text{sp}}$ . From Table 16.2 of the text, the  $K_{\text{sp}}$  for  $\text{BaCO}_3$  is  $8.1 \times 10^{-9}$ . As for  $Q$ ,

$$Q = [\text{Ba}^{2+}]_0[\text{CO}_3^{2-}]_0 = (2.9 \times 10^{-2})(7.1 \times 10^{-2}) = 2.1 \times 10^{-3}$$

Since  $(2.1 \times 10^{-3}) > (8.1 \times 10^{-9})$ , then  $Q > K_{\text{sp}}$ . Therefore,  $\text{BaCO}_3$  will precipitate.

**16.54** The net ionic equation is:



Let's find the limiting reagent in the precipitation reaction.

$$\text{Moles F}^- = 75 \text{ mL} \times \frac{0.060 \text{ mol}}{1000 \text{ mL soln}} = 0.0045 \text{ mol}$$

$$\text{Moles Sr}^{2+} = 25 \text{ mL} \times \frac{0.15 \text{ mol}}{1000 \text{ mL soln}} = 0.0038 \text{ mol}$$

From the stoichiometry of the balanced equation, twice as many moles of  $F^-$  are required to react with  $Sr^{2+}$ . This would require 0.0076 mol of  $F^-$ , but we only have 0.0045 mol. Thus,  $F^-$  is the limiting reagent.

Let's assume that the above reaction goes to completion. Then, we will consider the equilibrium that is established when  $SrF_2$  partially dissociates into ions.

	$Sr^{2+}(aq)$	$+ 2 F^-(aq)$	$\longrightarrow$	$SrF_2(s)$
Initial (mol):	0.0038	0.0045		0
Change (mol):	-0.00225	-0.0045		+0.00225
Final (mol):	0.00155	0		0.00225

Now, let's establish the equilibrium reaction. The total volume of the solution is 100 mL = 0.100 L. Divide the above moles by 0.100 L to convert to molar concentration.

	$SrF_2(s)$	$\rightleftharpoons$	$Sr^{2+}(aq)$	$+ 2F^-(aq)$
Initial (M):	0.0225		0.0155	0
Change (M):	-s		+s	+2s
Equilibrium (M):	$0.0225 - s$		$0.0155 + s$	$2s$

Write the solubility product expression, then solve for  $s$ .

$$K_{sp} = [Sr^{2+}][F^-]^2$$

$$2.0 \times 10^{-10} = (0.0155 + s)(2s)^2 \approx (0.0155)(2s)^2$$

$$s = 5.7 \times 10^{-5} M$$

$$[F^-] = 2s = \mathbf{1.1 \times 10^{-4} M}$$

$$[Sr^{2+}] = 0.0155 + s = \mathbf{0.016 M}$$

Both sodium ions and nitrate ions are spectator ions and therefore do not enter into the precipitation reaction.

$$[NO_3^-] = \frac{2(0.0038) \text{ mol}}{0.10 \text{ L}} = \mathbf{0.076 M}$$

$$[Na^+] = \frac{0.0045 \text{ mol}}{0.10 \text{ L}} = \mathbf{0.045 M}$$

- 16.55** (a) The solubility product expressions for both substances have exactly the same mathematical form and are therefore directly comparable. The substance having the smaller  $K_{sp}$  (**AgI**) will precipitate first. (Why?)
- (b) When  $CuI$  just begins to precipitate the solubility product expression will just equal  $K_{sp}$  (saturated solution). The concentration of  $Cu^+$  at this point is 0.010 M (given in the problem), so the concentration of iodide ion must be:

$$K_{sp} = [Cu^+][I^-] = (0.010)[I^-] = 5.1 \times 10^{-12}$$

$$[I^-] = \frac{5.1 \times 10^{-12}}{0.010} = 5.1 \times 10^{-10} M$$

Using this value of  $[I^-]$ , we find the silver ion concentration

$$[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.3 \times 10^{-17}}{5.1 \times 10^{-10}} = \mathbf{1.6 \times 10^{-7} M}$$

(c) The percent of silver ion remaining in solution is:

$$\% \text{Ag}^+(aq) = \frac{1.6 \times 10^{-7} M}{0.010 M} \times 100\% = \mathbf{0.0016\%} \text{ or } \mathbf{1.6 \times 10^{-3}\%}$$

Is this an effective way to separate silver from copper?

**16.56** For  $\text{Fe}(\text{OH})_3$ ,  $K_{\text{sp}} = 1.1 \times 10^{-36}$ . When  $[\text{Fe}^{3+}] = 0.010 M$ , the  $[\text{OH}^-]$  value is:

$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3$$

or

$$[\text{OH}^-] = \left( \frac{K_{\text{sp}}}{[\text{Fe}^{3+}]} \right)^{\frac{1}{3}}$$

$$[\text{OH}^-] = \left( \frac{1.1 \times 10^{-36}}{0.010} \right)^{\frac{1}{3}} = 4.8 \times 10^{-12} M$$

This  $[\text{OH}^-]$  corresponds to a pH of 2.68. In other words,  $\text{Fe}(\text{OH})_3$  will begin to precipitate from this solution at pH of 2.68.

For  $\text{Zn}(\text{OH})_2$ ,  $K_{\text{sp}} = 1.8 \times 10^{-14}$ . When  $[\text{Zn}^{2+}] = 0.010 M$ , the  $[\text{OH}^-]$  value is:

$$[\text{OH}^-] = \left( \frac{K_{\text{sp}}}{[\text{Zn}^{2+}]} \right)^{\frac{1}{2}}$$

$$[\text{OH}^-] = \left( \frac{1.8 \times 10^{-14}}{0.010} \right)^{\frac{1}{2}} = 1.3 \times 10^{-6} M$$

This corresponds to a pH of 8.11. In other words  $\text{Zn}(\text{OH})_2$  will begin to precipitate from the solution at pH = 8.11. These results show that  $\text{Fe}(\text{OH})_3$  will precipitate when the pH just exceeds 2.68 and that  $\text{Zn}(\text{OH})_2$  will precipitate when the pH just exceeds 8.11. Therefore, to selectively remove iron as  $\text{Fe}(\text{OH})_3$ , the pH must be *greater than 2.68* but *less than 8.11*.

**16.59** First let  $s$  be the molar solubility of  $\text{CaCO}_3$  in this solution.

	$\text{CaCO}_3(s)$	$\rightleftharpoons$	$\text{Ca}^{2+}(aq)$	$+$	$\text{CO}_3^{2-}(aq)$
Initial (M):			0.050		0
Change (M):	-s		+s		+s
Equilibrium (M):			(0.050 + s)		s

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = (0.050 + s)s = 8.7 \times 10^{-9}$$

We can assume  $0.050 + s \approx 0.050$ , then

$$s = \frac{8.7 \times 10^{-9}}{0.050} = 1.7 \times 10^{-7} M$$

The mass of  $\text{CaCO}_3$  can then be found.

$$(3.0 \times 10^2 \text{ mL}) \times \frac{1.7 \times 10^{-7} \text{ mol}}{1000 \text{ mL soln}} \times \frac{100.1 \text{ g CaCO}_3}{1 \text{ mol}} = 5.1 \times 10^{-6} \text{ g CaCO}_3$$

- 16.60 Strategy:** In parts (b) and (c), this is a common-ion problem. In part (b), the common ion is  $\text{Br}^-$ , which is supplied by both  $\text{PbBr}_2$  and  $\text{KBr}$ . Remember that the presence of a common ion will affect only the solubility of  $\text{PbBr}_2$ , but not the  $K_{\text{sp}}$  value because it is an equilibrium constant. In part (c), the common ion is  $\text{Pb}^{2+}$ , which is supplied by both  $\text{PbBr}_2$  and  $\text{Pb}(\text{NO}_3)_2$ .

**Solution:**

- (a) Set up a table to find the equilibrium concentrations in pure water.

	$\text{PbBr}_2(s)$	$\rightleftharpoons$	$\text{Pb}^{2+}(aq)$	$+$	$2\text{Br}^-(aq)$
Initial ( <i>M</i> )			0		0
Change ( <i>M</i> )	$-s$		$+s$		$+2s$
Equilibrium ( <i>M</i> )			$s$		$2s$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Br}^-]^2$$

$$8.9 \times 10^{-6} = (s)(2s)^2$$

$$s = \text{molar solubility} = \mathbf{0.013 \text{ M}}$$

- (b) Set up a table to find the equilibrium concentrations in 0.20 *M*  $\text{KBr}$ .  $\text{KBr}$  is a soluble salt that ionizes completely giving an initial concentration of  $\text{Br}^- = 0.20 \text{ M}$ .

	$\text{PbBr}_2(s)$	$\rightleftharpoons$	$\text{Pb}^{2+}(aq)$	$+$	$2\text{Br}^-(aq)$
Initial ( <i>M</i> )			0		0.20
Change ( <i>M</i> )	$-s$		$+s$		$+2s$
Equilibrium ( <i>M</i> )			$s$		$0.20 + 2s$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Br}^-]^2$$

$$8.9 \times 10^{-6} = (s)(0.20 + 2s)^2$$

$$8.9 \times 10^{-6} \approx (s)(0.20)^2$$

$$s = \text{molar solubility} = \mathbf{2.2 \times 10^{-4} \text{ M}}$$

Thus, the molar solubility of  $\text{PbBr}_2$  is reduced from 0.013 *M* to  $2.2 \times 10^{-4} \text{ M}$  as a result of the common ion ( $\text{Br}^-$ ) effect.

- (c) Set up a table to find the equilibrium concentrations in 0.20 *M*  $\text{Pb}(\text{NO}_3)_2$ .  $\text{Pb}(\text{NO}_3)_2$  is a soluble salt that dissociates completely giving an initial concentration of  $[\text{Pb}^{2+}] = 0.20 \text{ M}$ .

	$\text{PbBr}_2(s)$	$\rightleftharpoons$	$\text{Pb}^{2+}(aq)$	$+$	$2\text{Br}^-(aq)$
Initial ( <i>M</i> ):	0.20		0		
Change ( <i>M</i> ):	$-s$		$+s$		$+2s$
Equilibrium ( <i>M</i> ):			$0.20 + s$		$2s$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Br}^{-}]^2$$

$$8.9 \times 10^{-6} = (0.20 + s)(2s)^2$$

$$8.9 \times 10^{-6} \approx (0.20)(2s)^2$$

$$s = \text{molar solubility} = 3.3 \times 10^{-3} M$$

Thus, the molar solubility of  $\text{PbBr}_2$  is reduced from  $0.013 M$  to  $3.3 \times 10^{-3} M$  as a result of the common ion ( $\text{Pb}^{2+}$ ) effect.

**Check:** You should also be able to predict the decrease in solubility due to a common-ion using Le Châtelier's principle. Adding  $\text{Br}^{-}$  or  $\text{Pb}^{2+}$  ions shifts the system to the left, thus decreasing the solubility of  $\text{PbBr}_2$ .

**16.61** We first calculate the concentration of chloride ion in the solution.

$$[\text{Cl}^{-}] = \frac{10.0 \text{ g CaCl}_2}{1 \text{ L soln}} \times \frac{1 \text{ mol CaCl}_2}{111.0 \text{ g CaCl}_2} \times \frac{2 \text{ mol Cl}^{-}}{1 \text{ mol CaCl}_2} = 0.180 M$$

	$\text{AgCl}(s)$	$\rightleftharpoons$	$\text{Ag}^{+}(aq)$	$+$	$\text{Cl}^{-}(aq)$
Initial ( $M$ ):			0.000		0.180
Change ( $M$ ):	$-s$		$+s$		$+s$
Equilibrium ( $M$ ):			$s$		$(0.180 + s)$

If we assume that  $(0.180 + s) \approx 0.180$ , then

$$K_{\text{sp}} = [\text{Ag}^{+}][\text{Cl}^{-}] = 1.6 \times 10^{-10}$$

$$[\text{Ag}^{+}] = \frac{K_{\text{sp}}}{[\text{Cl}^{-}]} = \frac{1.6 \times 10^{-10}}{0.180} = 8.9 \times 10^{-10} M = s$$

The molar solubility of  $\text{AgCl}$  is  $8.9 \times 10^{-10} M$ .

**16.62 (a)** The equilibrium reaction is:

	$\text{BaSO}_4(s)$	$\rightleftharpoons$	$\text{Ba}^{2+}(aq)$	$+$	$\text{SO}_4^{2-}(aq)$
Initial ( $M$ ):			0		0
Change ( $M$ ):	$-s$		$+s$		$+s$
Equilibrium ( $M$ ):			$s$		$s$

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$1.1 \times 10^{-10} = s^2$$

$$s = 1.0 \times 10^{-5} M$$

The molar solubility of  $\text{BaSO}_4$  in pure water is  $1.0 \times 10^{-5} \text{ mol/L}$ .

- (b) The initial concentration of  $\text{SO}_4^{2-}$  is 1.0 M.

	$\text{BaSO}_4(s)$	$\rightleftharpoons$	$\text{Ba}^{2+}(aq)$	$+$	$\text{SO}_4^{2-}(aq)$
Initial (M):			0		1.0
Change (M):	-s		+s		+s
Equilibrium (M):			s		1.0 + s

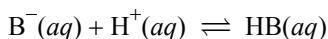
$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$1.1 \times 10^{-10} = (s)(1.0 + s) \approx (s)(1.0)$$

$$s = 1.1 \times 10^{-10} \text{ M}$$

Due to the common ion effect, the molar solubility of  $\text{BaSO}_4$  decreases to  $1.1 \times 10^{-10}$  mol/L in 1.0 M  $\text{SO}_4^{2-}(aq)$  compared to  $1.0 \times 10^{-5}$  mol/L in pure water.

- 16.63** When the anion of a salt is a base, the salt will be more soluble in acidic solution because the hydrogen ion decreases the concentration of the anion (Le Chatelier's principle):

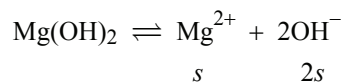


- (a)  $\text{BaSO}_4$  will be slightly more soluble because  $\text{SO}_4^{2-}$  is a base (although a weak one).  
 (b) The solubility of  $\text{PbCl}_2$  in acid is unchanged over the solubility in pure water because  $\text{HCl}$  is a strong acid, and therefore  $\text{Cl}^-$  is a negligibly weak base.  
 (c)  $\text{Fe}(\text{OH})_3$  will be more soluble in acid because  $\text{OH}^-$  is a base.  
 (d)  $\text{CaCO}_3$  will be more soluble in acidic solution because the  $\text{CO}_3^{2-}$  ions react with  $\text{H}^+$  ions to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The  $\text{CO}_2$  escapes from the solution, shifting the equilibrium. Although it is not important in this case, the carbonate ion is also a base.

- 16.64** (b)  $\text{SO}_4^{2-}(aq)$  is a weak base  
 (c)  $\text{OH}^-(aq)$  is a strong base  
 (d)  $\text{C}_2\text{O}_4^{2-}(aq)$  is a weak base  
 (e)  $\text{PO}_4^{3-}(aq)$  is a weak base.

The solubilities of the above will increase in acidic solution. Only (a), which contains an extremely weak base ( $\text{I}^-$  is the conjugate base of the strong acid  $\text{HI}$ ) is unaffected by the acid solution.

- 16.65** In water:



$$K_{\text{sp}} = 4s^3 = 1.2 \times 10^{-11}$$

$$s = 1.4 \times 10^{-4} \text{ M}$$

In a buffer at  $\text{pH} = 9.0$

$$[\text{H}^+] = 1.0 \times 10^{-9}$$

$$[\text{OH}^-] = 1.0 \times 10^{-5}$$

$$1.2 \times 10^{-11} = (s)(1.0 \times 10^{-5})^2$$

$$s = \mathbf{0.12 M}$$

**16.66** From Table 16.2, the value of  $K_{\text{sp}}$  for iron(II) is  $1.6 \times 10^{-14}$ .

(a) At pH = 8.00, pOH = 14.00 – 8.00 = 6.00, and  $[\text{OH}^-] = 1.0 \times 10^{-6} M$

$$[\text{Fe}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} = \frac{1.6 \times 10^{-14}}{(1.0 \times 10^{-6})^2} = 0.016 M$$

The *molar solubility* of iron(II) hydroxide at pH = 8.00 is **0.016 M**

(b) At pH = 10.00, pOH = 14.00 – 10.00 = 4.00, and  $[\text{OH}^-] = 1.0 \times 10^{-4} M$

$$[\text{Fe}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} = \frac{1.6 \times 10^{-14}}{(1.0 \times 10^{-4})^2} = 1.6 \times 10^{-6} M$$

The *molar solubility* of iron(II) hydroxide at pH = 10.00 is  **$1.6 \times 10^{-6} M$** .

**16.67** The solubility product expression for magnesium hydroxide is

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.2 \times 10^{-11}$$

We find the hydroxide ion concentration when  $[\text{Mg}^{2+}]$  is  $1.0 \times 10^{-10} M$

$$[\text{OH}^-] = \left( \frac{1.2 \times 10^{-11}}{1.0 \times 10^{-10}} \right)^{\frac{1}{2}} = \mathbf{0.35 M}$$

Therefore the concentration of  $\text{OH}^-$  must be slightly greater than 0.35 M.

**16.68** We first determine the effect of the added ammonia. Let's calculate the concentration of  $\text{NH}_3$ . This is a dilution problem.

$$\begin{aligned} M_i V_i &= M_f V_f \\ (0.60 M)(2.00 \text{ mL}) &= M_f(1002 \text{ mL}) \\ M_f &= 0.0012 M \text{ NH}_3 \end{aligned}$$

Ammonia is a weak base ( $K_{\text{b}} = 1.8 \times 10^{-5}$ ).

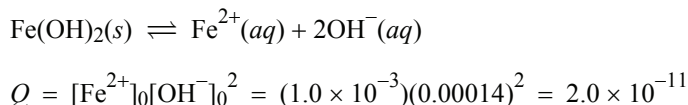
	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$		
Initial (M):	0.0012	0	0
Change (M):	-x	+x	+x
Equil. (M):	$0.0012 - x$	x	x

$$K_{\text{b}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{(0.0012 - x)}$$

Solving the resulting quadratic equation gives  $x = 0.00014$ , or  $[\text{OH}^-] = 0.00014 \text{ M}$

This is a solution of iron(II) sulfate, which contains  $\text{Fe}^{2+}$  ions. These  $\text{Fe}^{2+}$  ions could combine with  $\text{OH}^-$  to precipitate  $\text{Fe}(\text{OH})_2$ . Therefore, we must use  $K_{\text{sp}}$  for iron(II) hydroxide. We compute the value of  $Q_c$  for this solution.



Note that when adding 2.00 mL of  $\text{NH}_3$  to 1.0 L of  $\text{FeSO}_4$ , the concentration of  $\text{FeSO}_4$  will decrease slightly. However, rounding off to 2 significant figures, the concentration of  $1.0 \times 10^{-3} \text{ M}$  does not change.  $Q$  is larger than  $K_{\text{sp}} [\text{Fe}(\text{OH})_2] = 1.6 \times 10^{-14}$ . The concentrations of the ions in solution are greater than the equilibrium concentrations; the solution is saturated. The system will shift left to reestablish equilibrium; therefore, **a precipitate of  $\text{Fe}(\text{OH})_2$  will form.**

**16.71** First find the molarity of the copper(II) ion

$$\text{Moles CuSO}_4 = 2.50 \text{ g} \times \frac{1 \text{ mol}}{159.6 \text{ g}} = 0.0157 \text{ mol}$$

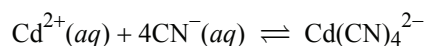
$$[\text{Cu}^{2+}] = \frac{0.0157 \text{ mol}}{0.90 \text{ L}} = 0.0174 \text{ M}$$

As in Example 16.15 of the text, the position of equilibrium will be far to the right. We assume essentially all the copper ion is complexed with  $\text{NH}_3$ . The  $\text{NH}_3$  consumed is  $4 \times 0.0174 \text{ M} = 0.0696 \text{ M}$ . The uncombined  $\text{NH}_3$  remaining is  $(0.30 - 0.0696) \text{ M}$ , or  $0.23 \text{ M}$ . The equilibrium concentrations of  $\text{Cu}(\text{NH}_3)_4^{2+}$  and  $\text{NH}_3$  are therefore **0.0174 M** and **0.23 M**, respectively. We find  $[\text{Cu}^{2+}]$  from the formation constant expression.

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 5.0 \times 10^{13} = \frac{0.0174}{[\text{Cu}^{2+}](0.23)^4}$$

$$[\text{Cu}^{2+}] = 1.2 \times 10^{-13} \text{ M}$$

**16.72 Strategy:** The addition of  $\text{Cd}(\text{NO}_3)_2$  to the  $\text{NaCN}$  solution results in complex ion formation. In solution,  $\text{Cd}^{2+}$  ions will complex with  $\text{CN}^-$  ions. The concentration of  $\text{Cd}^{2+}$  will be determined by the following equilibrium

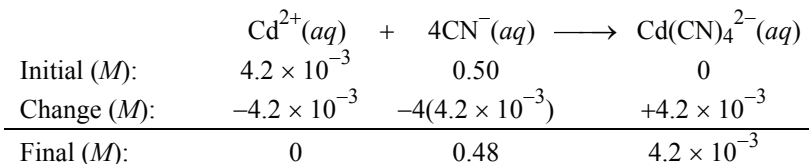


From Table 16.4 of the text, we see that the formation constant ( $K_f$ ) for this reaction is very large ( $K_f = 7.1 \times 10^{16}$ ). Because  $K_f$  is so large, the reaction lies mostly to the right. At equilibrium, the concentration of  $\text{Cd}^{2+}$  will be very small. As a good approximation, we can assume that essentially all the dissolved  $\text{Cd}^{2+}$  ions end up as  $\text{Cd}(\text{CN})_4^{2-}$  ions. What is the initial concentration of  $\text{Cd}^{2+}$  ions? A very small amount of  $\text{Cd}^{2+}$  will be present at equilibrium. Set up the  $K_f$  expression for the above equilibrium to solve for  $[\text{Cd}^{2+}]$ .

**Solution:** Calculate the initial concentration of  $\text{Cd}^{2+}$  ions.

$$[\text{Cd}^{2+}]_0 = \frac{0.50 \text{ g} \times \frac{1 \text{ mol Cd(NO}_3)_2}{236.42 \text{ g Cd(NO}_3)_2} \times \frac{1 \text{ mol Cd}^{2+}}{1 \text{ mol Cd(NO}_3)_2}}{0.50 \text{ L}} = 4.2 \times 10^{-3} \text{ M}$$

If we assume that the above equilibrium goes to completion, we can write



To find the concentration of free  $\text{Cd}^{2+}$  at equilibrium, use the formation constant expression.

$$K_f = \frac{[\text{Cd(CN)}_4^{2-}]}{[\text{Cd}^{2+}][\text{CN}^{-}]^4}$$

Rearranging,

$$[\text{Cd}^{2+}] = \frac{[\text{Cd(CN)}_4^{2-}]}{K_f[\text{CN}^{-}]^4}$$

Substitute the equilibrium concentrations calculated above into the formation constant expression to calculate the equilibrium concentration of  $\text{Cd}^{2+}$ .

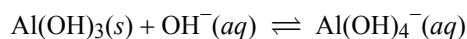
$$[\text{Cd}^{2+}] = \frac{[\text{Cd(CN)}_4^{2-}]}{K_f[\text{CN}^{-}]^4} = \frac{4.2 \times 10^{-3}}{(7.1 \times 10^{16})(0.48)^4} = 1.1 \times 10^{-18} \text{ M}$$

$$[\text{CN}^{-}] = 0.48 \text{ M} + 4(1.1 \times 10^{-18} \text{ M}) = 0.48 \text{ M}$$

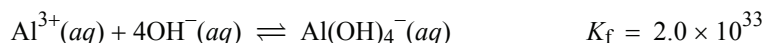
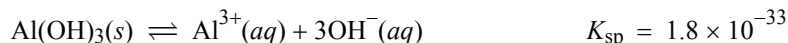
$$[\text{Cd(CN)}_4^{2-}] = (4.2 \times 10^{-3} \text{ M}) - (1.1 \times 10^{-18}) = 4.2 \times 10^{-3} \text{ M}$$

**Check:** Substitute the equilibrium concentrations calculated into the formation constant expression to calculate  $K_f$ . Also, the small value of  $[\text{Cd}^{2+}]$  at equilibrium, compared to its initial concentration of  $4.2 \times 10^{-3} \text{ M}$ , certainly justifies our approximation that almost all the  $\text{Cd}^{2+}$  ions react.

### 16.73 The reaction



is the sum of the two known reactions



The equilibrium constant is

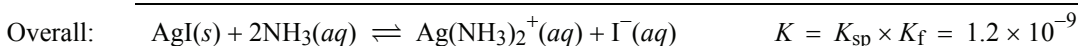
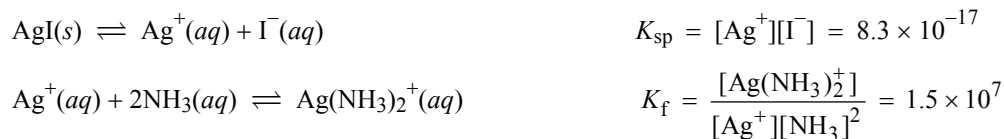
$$K = K_{\text{sp}}K_f = (1.8 \times 10^{-33})(2.0 \times 10^{33}) = 3.6 = \frac{[\text{Al(OH)}_4^{-}]}{[\text{OH}^{-}]}$$

When  $\text{pH} = 14.00$ ,  $[\text{OH}^-] = 1.0 \text{ M}$ , therefore

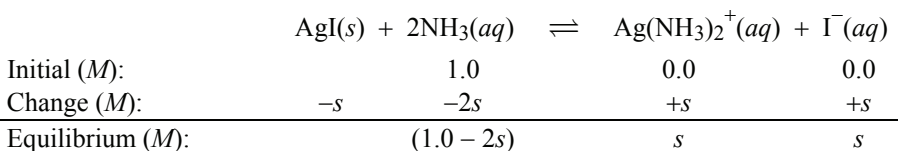
$$[\text{Al}(\text{OH})_4^-] = K[\text{OH}^-] = (3.6)(1 \text{ M}) = 3.6 \text{ M}$$

This represents the maximum possible concentration of the complex ion at  $\text{pH} 14.00$ . Since this is much larger than the initial  $0.010 \text{ M}$ , the complex ion will be the predominant species.

- 16.74** Silver iodide is only slightly soluble. It dissociates to form a small amount of  $\text{Ag}^+$  and  $\text{I}^-$  ions. The  $\text{Ag}^+$  ions then complex with  $\text{NH}_3$  in solution to form the complex ion  $\text{Ag}(\text{NH}_3)_2^+$ . The balanced equations are:



If  $s$  is the molar solubility of  $\text{AgI}$  then,



Because  $K_{\text{f}}$  is large, we can assume all of the silver ions exist as  $\text{Ag}(\text{NH}_3)_2^+$ . Thus,

$$[\text{Ag}(\text{NH}_3)_2^+] = [\text{I}^-] = s$$

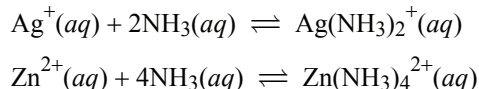
We can write the equilibrium constant expression for the above reaction, then solve for  $s$ .

$$K = 1.2 \times 10^{-9} = \frac{(s)(s)}{(1.0 - 2s)^2} \approx \frac{(s)(s)}{(1.0)^2}$$

$$s = 3.5 \times 10^{-5} \text{ M}$$

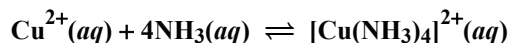
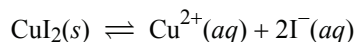
At equilibrium,  $3.5 \times 10^{-5}$  moles of  $\text{AgI}$  dissolves in 1 L of  $1.0 \text{ M}$   $\text{NH}_3$  solution.

- 16.75** The balanced equations are:



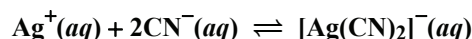
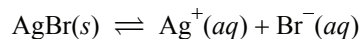
Zinc hydroxide forms a complex ion with excess  $\text{OH}^-$  and silver hydroxide does not; therefore, zinc hydroxide is soluble in  $6 \text{ M}$   $\text{NaOH}$ .

- 16.76 (a)** The equations are as follows:

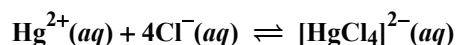
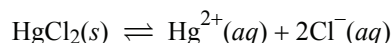


The ammonia combines with the  $\text{Cu}^{2+}$  ions formed in the first step to form the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , effectively removing the  $\text{Cu}^{2+}$  ions, causing the first equilibrium to shift to the right (resulting in more  $\text{CuI}_2$  dissolving).

(b) Similar to part (a):

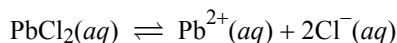


(c) Similar to parts (a) and (b).



**16.79** Silver chloride will dissolve in aqueous ammonia because of the formation of a complex ion. Lead chloride will not dissolve; it doesn't form an ammonia complex.

**16.80** Since some  $\text{PbCl}_2$  precipitates, the solution is saturated. From Table 16.2, the value of  $K_{\text{sp}}$  for lead(II) chloride is  $2.4 \times 10^{-4}$ . The equilibrium is:



We can write the solubility product expression for the equilibrium.

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$K_{\text{sp}}$  and  $[\text{Cl}^-]$  are known. Solving for the  $\text{Pb}^{2+}$  concentration,

$$[\text{Pb}^{2+}] = \frac{K_{\text{sp}}}{[\text{Cl}^-]^2} = \frac{2.4 \times 10^{-4}}{(0.15)^2} = \mathbf{0.011 \text{ M}}$$

**16.81** Ammonium chloride is the salt of a weak base (ammonia). It will react with strong aqueous hydroxide to form ammonia (Le Châtelier's principle).



The human nose is an excellent ammonia detector. Nothing happens between  $\text{KCl}$  and strong aqueous  $\text{NaOH}$ .

**16.82** Chloride ion will precipitate  $\text{Ag}^+$  but not  $\text{Cu}^{2+}$ . So, dissolve some solid in  $\text{H}_2\text{O}$  and add  $\text{HCl}$ . If a precipitate forms, the salt was  $\text{AgNO}_3$ . A flame test will also work.  $\text{Cu}^{2+}$  gives a green flame test.

**16.83** According to the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

If:  $\frac{[\text{conjugate base}]}{[\text{acid}]} = 10$ , then:

$$\text{pH} = \text{p}K_a + 1$$

If:  $\frac{[\text{conjugate base}]}{[\text{acid}]} = 0.1$ , then:

$$\text{pH} = \text{p}K_a - 1$$

Therefore, the range of the ratio is:

$$0.1 < \frac{[\text{conjugate base}]}{[\text{acid}]} < 10$$

**16.84** We can use the Henderson-Hasselbalch equation to solve for the pH when the indicator is 90% acid / 10% conjugate base and when the indicator is 10% acid / 90% conjugate base.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Solving for the pH with 90% of the indicator in the HIn form:

$$\text{pH} = 3.46 + \log \frac{[10]}{[90]} = 3.46 - 0.95 = 2.51$$

Next, solving for the pH with 90% of the indicator in the In<sup>-</sup> form:

$$\text{pH} = 3.46 + \log \frac{[90]}{[10]} = 3.46 + 0.95 = 4.41$$

Thus the pH range varies from **2.51 to 4.41** as the [HIn] varies from 90% to 10%.

**16.85** Referring to Figure 16.5, at the half-equivalence point, [weak acid] = [conjugate base]. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

so,

$$\text{pH} = \text{p}K_a$$

**16.86** First, calculate the pH of the 2.00 M weak acid (HNO<sub>2</sub>) solution before any NaOH is added.

	$\text{HNO}_2(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	$+$	$\text{NO}_2^-(aq)$
Initial (M):	2.00		0		0
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$2.00 - x$		$x$		$x$

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

$$4.5 \times 10^{-4} = \frac{x^2}{2.00 - x} \approx \frac{x^2}{2.00}$$

$$x = [\text{H}^+] = 0.030 \text{ M}$$

$$\text{pH} = -\log(0.030) = 1.52$$

Since the pH after the addition is 1.5 pH units greater, the new  $\text{pH} = 1.52 + 1.50 = 3.02$ .

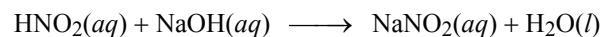
From this new pH, we can calculate the  $[\text{H}^+]$  in solution.

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-3.02} = 9.55 \times 10^{-4} \text{ M}$$

When the NaOH is added, we dilute our original 2.00 M  $\text{HNO}_2$  solution to:

$$\begin{aligned} M_i V_i &= M_f V_f \\ (2.00 \text{ M})(400 \text{ mL}) &= M_f (600 \text{ mL}) \\ M_f &= 1.33 \text{ M} \end{aligned}$$

Since we have not reached the equivalence point, we have a buffer solution. The reaction between  $\text{HNO}_2$  and NaOH is:



Since the mole ratio between  $\text{HNO}_2$  and NaOH is 1:1, the decrease in  $[\text{HNO}_2]$  is the same as the decrease in  $[\text{NaOH}]$ .

We can calculate the decrease in  $[\text{HNO}_2]$  by setting up the weak acid equilibrium. From the pH of the solution, we know that the  $[\text{H}^+]$  at equilibrium is  $9.55 \times 10^{-4} \text{ M}$ .

	$\text{HNO}_2(\text{aq})$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	$+$	$\text{NO}_2^-(\text{aq})$
Initial (M):	1.33		0		0
Change (M):	-x				+x
Equilibrium (M):	$1.33 - x$		$9.55 \times 10^{-4}$		x

We can calculate  $x$  from the equilibrium constant expression.

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} \\ 4.5 \times 10^{-4} &= \frac{(9.55 \times 10^{-4})(x)}{1.33 - x} \\ x &= 0.426 \text{ M} \end{aligned}$$

Thus,  $x$  is the decrease in  $[\text{HNO}_2]$  which equals the concentration of added  $\text{OH}^-$ . However, this is the concentration of NaOH after it has been diluted to 600 mL. We need to correct for the dilution from 200 mL to 600 mL to calculate the concentration of the original NaOH solution.

$$\begin{aligned} M_i V_i &= M_f V_f \\ M_i (200 \text{ mL}) &= (0.426 \text{ M})(600 \text{ mL}) \\ [\text{NaOH}] = M_i &= 1.28 \text{ M} \end{aligned}$$

**16.87** The  $K_a$  of butyric acid is obtained by taking the antilog of 4.7 ( $10^{-4.7}$ ) which is  $2 \times 10^{-5}$ . The value of  $K_b$  is:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2 \times 10^{-5}} = 5 \times 10^{-10}$$

**16.88** The resulting solution is not a buffer system. There is excess NaOH and the neutralization is well past the equivalence point.

$$\text{Moles NaOH} = 0.500 \text{ L} \times \frac{0.167 \text{ mol}}{1 \text{ L}} = 0.0835 \text{ mol}$$

$$\text{Moles HCOOH} = 0.500 \text{ L} \times \frac{0.100 \text{ mol}}{1 \text{ L}} = 0.0500 \text{ mol}$$

	$\text{HCOOH}(aq) + \text{NaOH}(aq) \rightarrow \text{HCOONa}(aq) + \text{H}_2\text{O}(l)$		
Initial (mol):	0.0500	0.0835	0
Change (mol):	-0.0500	-0.0500	+0.0500
Final (mol):	0	0.0335	0.0500

The volume of the resulting solution is 1.00 L (500 mL + 500 mL = 1000 mL).

$$[\text{OH}^-] = \frac{0.0335 \text{ mol}}{1.00 \text{ L}} = 0.0335 \text{ M}$$

$$[\text{Na}^+] = \frac{(0.0335 + 0.0500) \text{ mol}}{1.00 \text{ L}} = 0.0835 \text{ M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0335} = 3.0 \times 10^{-13} \text{ M}$$

$$[\text{HCOO}^-] = \frac{0.0500 \text{ mol}}{1.00 \text{ L}} = 0.0500 \text{ M}$$

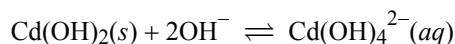
	$\text{HCOO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCOOH}(aq) + \text{OH}^-(aq)$		
Initial (M):	0.0500	0	0.0335
Change (M):	-x	+x	+x
Equilibrium (M):	0.0500 - x	x	0.0335 + x

$$K_b = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]}$$

$$5.9 \times 10^{-11} = \frac{(x)(0.0335 + x)}{(0.0500 - x)} \approx \frac{(x)(0.0335)}{(0.0500)}$$

$$x = [\text{HCOOH}] = 8.8 \times 10^{-11} \text{ M}$$

**16.89** Most likely the increase in solubility is due to complex ion formation:



This is a Lewis acid-base reaction.

**16.90** The number of moles of  $\text{Ba}(\text{OH})_2$  present in the original 50.0 mL of solution is:

$$50.0 \text{ mL} \times \frac{1.00 \text{ mol Ba}(\text{OH})_2}{1000 \text{ mL soln}} = 0.0500 \text{ mol Ba}(\text{OH})_2$$

The number of moles of  $\text{H}_2\text{SO}_4$  present in the original 86.4 mL of solution, assuming complete dissociation, is:

$$86.4 \text{ mL} \times \frac{0.494 \text{ mol H}_2\text{SO}_4}{1000 \text{ mL soln}} = 0.0427 \text{ mol H}_2\text{SO}_4$$

The reaction is:

	$\text{Ba}(\text{OH})_2(\text{aq})$	$+$	$\text{H}_2\text{SO}_4(\text{aq})$	$\rightarrow$	$\text{BaSO}_4(\text{s})$	$+$	$2\text{H}_2\text{O}(\text{l})$
Initial (mol):	0.0500		0.0427		0		
Change (mol):	-0.0427		-0.0427		+0.0427		
Final (mol):	0.0073		0		0.0427		

Thus the mass of  $\text{BaSO}_4$  formed is:

$$0.0427 \text{ mol BaSO}_4 \times \frac{233.4 \text{ g BaSO}_4}{1 \text{ mol BaSO}_4} = \mathbf{9.97 \text{ g BaSO}_4}$$

The pH can be calculated from the excess  $\text{OH}^-$  in solution. First, calculate the molar concentration of  $\text{OH}^-$ . The total volume of solution is  $136.4 \text{ mL} = 0.1364 \text{ L}$ .

$$[\text{OH}^-] = \frac{0.0073 \text{ mol Ba}(\text{OH})_2 \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba}(\text{OH})_2}}{0.1364 \text{ L}} = 0.11 \text{ M}$$

$$\text{pOH} = -\log(0.11) = 0.96$$

$$\mathbf{\text{pH} = 14.00 - \text{pOH} = 14.00 - 0.96 = 13.04}$$

**16.91** A solubility equilibrium is an equilibrium between a solid (reactant) and its components (products: ions, neutral molecules, etc.) in solution. Only (d) represents a solubility equilibrium.

Consider part (b). Can you write the equilibrium constant for this reaction in terms of  $K_{\text{sp}}$  for calcium phosphate?

**16.92** First, we calculate the molar solubility of  $\text{CaCO}_3$ .

	$\text{CaCO}_3(\text{s})$	$\rightleftharpoons$	$\text{Ca}^{2+}(\text{aq})$	$+$	$\text{CO}_3^{2-}(\text{aq})$
Initial (M):	0		0		0
Change (M):	-s		+s		+s
Equil. (M):	s		s		s

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = s^2 = 8.7 \times 10^{-9}$$

$$s = 9.3 \times 10^{-5} \text{ M} = 9.3 \times 10^{-5} \text{ mol/L}$$

The moles of  $\text{CaCO}_3$  in the kettle are:

$$116 \text{ g} \times \frac{1 \text{ mol CaCO}_3}{100.1 \text{ g CaCO}_3} = 1.16 \text{ mol CaCO}_3$$

The volume of distilled water needed to dissolve 1.16 moles of  $\text{CaCO}_3$  is:

$$1.16 \text{ mol CaCO}_3 \times \frac{1 \text{ L}}{9.3 \times 10^{-5} \text{ mol CaCO}_3} = 1.2 \times 10^4 \text{ L}$$

The number of times the kettle would have to be filled is:

$$(1.2 \times 10^4 \text{ L}) \times \frac{1 \text{ filling}}{2.0 \text{ L}} = \mathbf{6.0 \times 10^3 \text{ fillings}}$$

Note that the very important assumption is made that each time the kettle is filled, the calcium carbonate is allowed to reach equilibrium before the kettle is emptied.

**16.93** Since equal volumes of the two solutions were used, the initial molar concentrations will be halved.

$$[\text{Ag}^+] = \frac{0.12 \text{ M}}{2} = 0.060 \text{ M}$$

$$[\text{Cl}^-] = \frac{2(0.14 \text{ M})}{2} = 0.14 \text{ M}$$

Let's assume that the  $\text{Ag}^+$  ions and  $\text{Cl}^-$  ions react completely to form  $\text{AgCl}(s)$ . Then, we will reestablish the equilibrium between  $\text{AgCl}$ ,  $\text{Ag}^+$ , and  $\text{Cl}^-$ .

	$\text{Ag}^+(aq)$	$+ \text{Cl}^-(aq)$	$\longrightarrow$	$\text{AgCl}(s)$
Initial (M):	0.060	0.14		0
Change (M):	-0.060	-0.060		+0.060
Final (M):	0	0.080		0.060

Now, setting up the equilibrium,

	$\text{AgCl}(s)$	$\rightleftharpoons$	$\text{Ag}^+(aq)$	$+ \text{Cl}^-(aq)$
Initial (M):	0.060		0	0.080
Change (M):	-s		+s	+s
Equilibrium (M):	$0.060 - s$		s	$0.080 + s$

Set up the  $K_{\text{sp}}$  expression to solve for  $s$ .

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

$$1.6 \times 10^{-10} = (s)(0.080 + s)$$

$$s = 2.0 \times 10^{-9} \text{ M}$$

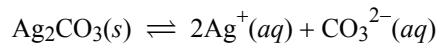
$$[\text{Ag}^+] = s = \mathbf{2.0 \times 10^{-9} \text{ M}}$$

$$[\text{Cl}^-] = 0.080 \text{ M} + s = \mathbf{0.080 \text{ M}}$$

$$[\text{Zn}^{2+}] = \frac{0.14 \text{ M}}{2} = \mathbf{0.070 \text{ M}}$$

$$[\text{NO}_3^-] = \frac{0.12 \text{ M}}{2} = \mathbf{0.060 \text{ M}}$$

- 16.94** First we find the molar solubility and then convert moles to grams. The solubility equilibrium for silver carbonate is:



Initial ( <i>M</i> ):	0	0
Change ( <i>M</i> ):	- <i>s</i>	+2 <i>s</i>
Equilibrium ( <i>M</i> ):	2 <i>s</i>	<i>s</i>

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = (2s)^2(s) = 4s^3 = 8.1 \times 10^{-12}$$

$$s = \left( \frac{8.1 \times 10^{-12}}{4} \right)^{\frac{1}{3}} = 1.3 \times 10^{-4} \text{ M}$$

Converting from mol/L to g/L:

$$\frac{1.3 \times 10^{-4} \text{ mol}}{1 \text{ L soln}} \times \frac{275.8 \text{ g}}{1 \text{ mol}} = \mathbf{0.036 \text{ g/L}}$$

- 16.95** For  $\text{Mg}(\text{OH})_2$ ,  $K_{\text{sp}} = 1.2 \times 10^{-11}$ . When  $[\text{Mg}^{2+}] = 0.010 \text{ M}$ , the  $[\text{OH}^-]$  value is

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

or

$$[\text{OH}^-] = \left( \frac{K_{\text{sp}}}{[\text{Mg}^{2+}]} \right)^{\frac{1}{2}}$$

$$[\text{OH}^-] = \left( \frac{1.2 \times 10^{-11}}{0.010} \right)^{\frac{1}{2}} = 3.5 \times 10^{-5} \text{ M}$$

This  $[\text{OH}^-]$  corresponds to a pH of 9.54. In other words,  $\text{Mg}(\text{OH})_2$  will begin to precipitate from this solution at pH of 9.54.

For  $\text{Zn}(\text{OH})_2$ ,  $K_{\text{sp}} = 1.8 \times 10^{-14}$ . When  $[\text{Zn}^{2+}] = 0.010 \text{ M}$ , the  $[\text{OH}^-]$  value is

$$[\text{OH}^-] = \left( \frac{K_{\text{sp}}}{[\text{Zn}^{2+}]} \right)^{\frac{1}{2}}$$

$$[\text{OH}^-] = \left( \frac{1.8 \times 10^{-14}}{0.010} \right)^{\frac{1}{2}} = 1.3 \times 10^{-6} \text{ M}$$

This corresponds to a pH of 8.11. In other words  $\text{Zn}(\text{OH})_2$  will begin to precipitate from the solution at pH = 8.11. These results show that  $\text{Zn}(\text{OH})_2$  will precipitate when the pH just exceeds 8.11 and that  $\text{Mg}(\text{OH})_2$  will precipitate when the pH just exceeds 9.54. Therefore, to selectively remove zinc as  $\text{Zn}(\text{OH})_2$ , the pH must be greater than 8.11 but less than 9.54.

- 16.96 (a)** To  $2.50 \times 10^{-3}$  mole HCl (that is, 0.0250 L of 0.100 M solution) is added  $1.00 \times 10^{-3}$  mole  $\text{CH}_3\text{NH}_2$  (that is, 0.0100 L of 0.100 M solution).

	$\text{HCl}(aq)$	+	$\text{CH}_3\text{NH}_2(aq)$	$\rightarrow$	$\text{CH}_3\text{NH}_3\text{Cl}(aq)$
Initial (mol):	$2.50 \times 10^{-3}$		$1.00 \times 10^{-3}$		0
Change (mol):	$-1.00 \times 10^{-3}$		$-1.00 \times 10^{-3}$		$+1.00 \times 10^{-3}$
Equilibrium (mol):	$1.50 \times 10^{-3}$		0		$1.00 \times 10^{-3}$

After the acid-base reaction, we have  $1.50 \times 10^{-3}$  mol of HCl remaining. Since HCl is a strong acid, the  $[\text{H}^+]$  will come from the HCl. The total solution volume is 35.0 mL = 0.0350 L.

$$[\text{H}^+] = \frac{1.50 \times 10^{-3} \text{ mol}}{0.0350 \text{ L}} = 0.0429 \text{ M}$$

$$\text{pH} = 1.37$$

- (b)** When a total of 25.0 mL of  $\text{CH}_3\text{NH}_2$  is added, we reach the equivalence point. That is,  $2.50 \times 10^{-3}$  mol HCl reacts with  $2.50 \times 10^{-3}$  mol  $\text{CH}_3\text{NH}_2$  to form  $2.50 \times 10^{-3}$  mol  $\text{CH}_3\text{NH}_3\text{Cl}$ . Since there is a total of 50.0 mL of solution, the concentration of  $\text{CH}_3\text{NH}_3^+$  is:

$$[\text{CH}_3\text{NH}_3^+] = \frac{2.50 \times 10^{-3} \text{ mol}}{0.0500 \text{ L}} = 5.00 \times 10^{-2} \text{ M}$$

This is a problem involving the hydrolysis of the weak acid  $\text{CH}_3\text{NH}_3^+$ .

	$\text{CH}_3\text{NH}_3^+(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CH}_3\text{NH}_2(aq)$
Initial (M):	$5.00 \times 10^{-2}$		0		0
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$(5.00 \times 10^{-2}) - x$		$x$		$x$

$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}^+]}{[\text{CH}_3\text{NH}_3^+]}$$

$$2.3 \times 10^{-11} = \frac{x^2}{(5.00 \times 10^{-2}) - x} \approx \frac{x^2}{5.00 \times 10^{-2}}$$

$$1.15 \times 10^{-12} = x^2$$

$$x = 1.07 \times 10^{-6} \text{ M} = [\text{H}^+]$$

$$\text{pH} = 5.97$$

- (c)** 35.0 mL of 0.100 M  $\text{CH}_3\text{NH}_2$  ( $3.50 \times 10^{-3}$  mol) is added to the 25 mL of 0.100 M HCl ( $2.50 \times 10^{-3}$  mol).

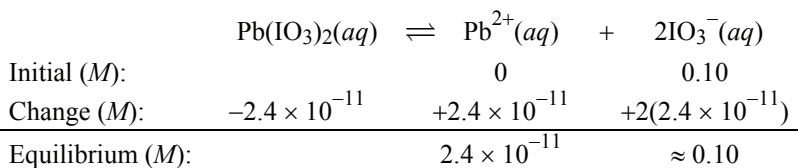
	$\text{HCl}(aq)$	+	$\text{CH}_3\text{NH}_2(aq)$	$\rightarrow$	$\text{CH}_3\text{NH}_3\text{Cl}(aq)$
Initial (mol):	$2.50 \times 10^{-3}$		$3.50 \times 10^{-3}$		0
Change (mol):	$-2.50 \times 10^{-3}$		$-2.50 \times 10^{-3}$		$+2.50 \times 10^{-3}$
Equilibrium (mol):	0		$1.00 \times 10^{-3}$		$2.50 \times 10^{-3}$

This is a buffer solution. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = -\log(2.3 \times 10^{-11}) + \log \frac{(1.00 \times 10^{-3})}{(2.50 \times 10^{-3})} = \mathbf{10.24}$$

**16.97** The equilibrium reaction is:

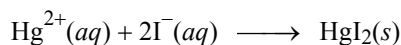


Substitute the equilibrium concentrations into the solubility product expression to calculate  $K_{\text{sp}}$ .

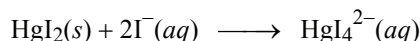
$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{IO}_3^{-}]^2$$

$$K_{\text{sp}} = (2.4 \times 10^{-11})(0.10)^2 = \mathbf{2.4 \times 10^{-13}}$$

**16.98** The precipitate is  $\text{HgI}_2$ .



With further addition of  $\text{I}^{-}$ , a soluble complex ion is formed and the precipitate redissolves.



**16.99**  $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

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

$$[\text{Ba}^{2+}] = 1.0 \times 10^{-5} \text{ M}$$

In 5.0 L, the number of moles of  $\text{Ba}^{2+}$  is

$$(5.0 \text{ L})(1.0 \times 10^{-5} \text{ mol/L}) = 5.0 \times 10^{-5} \text{ mol Ba}^{2+} = 5.0 \times 10^{-5} \text{ mol BaSO}_4$$

The number of grams of  $\text{BaSO}_4$  dissolved is

$$(5.0 \times 10^{-5} \text{ mol BaSO}_4) \times \frac{233.4 \text{ g BaSO}_4}{1 \text{ mol BaSO}_4} = 0.012 \text{ g BaSO}_4$$

In practice, even less  $\text{BaSO}_4$  will dissolve because the  $\text{BaSO}_4$  is not in contact with the entire volume of blood.  $\text{Ba}(\text{NO}_3)_2$  is too soluble to be used for this purpose.

**16.100** We can use the Henderson-Hasselbalch equation to solve for the pH when the indicator is 95% acid / 5% conjugate base and when the indicator is 5% acid / 95% conjugate base.

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Solving for the pH with 95% of the indicator in the HIn form:

$$\text{pH} = 9.10 + \log \frac{[5]}{[95]} = 9.10 - 1.28 = 7.82$$

Next, solving for the pH with 95% of the indicator in the In<sup>-</sup> form:

$$\text{pH} = 9.10 + \log \frac{[95]}{[5]} = 9.10 + 1.28 = 10.38$$

Thus the pH range varies from **7.82 to 10.38** as the [HIn] varies from 95% to 5%.

- 16.101 (a)** The solubility product expressions for both substances have exactly the same mathematical form and are therefore directly comparable. The substance having the smaller  $K_{\text{sp}}$  (**AgBr**) will precipitate first. (Why?)
- (b)** When CuBr just begins to precipitate the solubility product expression will just equal  $K_{\text{sp}}$  (saturated solution). The concentration of Cu<sup>+</sup> at this point is 0.010 M (given in the problem), so the concentration of bromide ion must be:

$$K_{\text{sp}} = [\text{Cu}^+][\text{Br}^-] = (0.010)[\text{Br}^-] = 4.2 \times 10^{-8}$$

$$[\text{Br}^-] = \frac{4.2 \times 10^{-8}}{0.010} = 4.2 \times 10^{-6} \text{ M}$$

Using this value of [Br<sup>-</sup>], we find the silver ion concentration

$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Br}^-]} = \frac{7.7 \times 10^{-13}}{4.2 \times 10^{-6}} = \mathbf{1.8 \times 10^{-7} \text{ M}}$$

- (c)** The percent of silver ion remaining in solution is:

$$\% \text{Ag}^+(\text{aq}) = \frac{1.8 \times 10^{-7} \text{ M}}{0.010 \text{ M}} \times 100\% = \mathbf{0.0018\% \text{ or } 1.8 \times 10^{-3}\%}$$

Is this an effective way to separate silver from copper?

- 16.102 (a)** We abbreviate the name of cacodylic acid to CacH. We set up the usual table.

	$\text{CacH}(\text{aq}) \rightleftharpoons \text{Cac}^-(\text{aq}) + \text{H}^+(\text{aq})$
Initial (M):	0.10          0          0
Change (M):	-x            +x          +x
Equilibrium (M):	0.10 - x      x          x

$$K_{\text{a}} = \frac{[\text{H}^+][\text{Cac}^-]}{[\text{CacH}]}$$

$$6.4 \times 10^{-7} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x = 2.5 \times 10^{-4} \text{ M} = [\text{H}^+]$$

$$\mathbf{\text{pH} = -\log(2.5 \times 10^{-4}) = 3.60}$$

(b) We set up a table for the hydrolysis of the anion:

	$\text{Cac}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CacH}(aq) + \text{OH}^-(aq)$		
Initial ( <i>M</i> ):	0.15	0	0
Change ( <i>M</i> ):	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
Equilibrium ( <i>M</i> ):	$0.15 - x$	<i>x</i>	<i>x</i>

The ionization constant,  $K_b$ , for  $\text{Cac}^-$  is:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-7}} = 1.6 \times 10^{-8}$$

$$K_b = \frac{[\text{CacH}][\text{OH}^-]}{[\text{Cac}^-]}$$

$$1.6 \times 10^{-8} = \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$x = 4.9 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(4.9 \times 10^{-5}) = 4.31$$

$$\text{pH} = 14.00 - 4.31 = \mathbf{9.69}$$

(c) Number of moles of  $\text{CacH}$  from (a) is:

$$50.0 \text{ mL CacH} \times \frac{0.10 \text{ mol CacH}}{1000 \text{ mL}} = 5.0 \times 10^{-3} \text{ mol CacH}$$

Number of moles of  $\text{Cac}^-$  from (b) is:

$$25.0 \text{ mL CacNa} \times \frac{0.15 \text{ mol CacNa}}{1000 \text{ mL}} = 3.8 \times 10^{-3} \text{ mol CacNa}$$

At this point we have a buffer solution.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Cac}^-]}{[\text{CacH}]} = -\log(6.4 \times 10^{-7}) + \log \frac{3.8 \times 10^{-3}}{5.0 \times 10^{-3}} = \mathbf{6.07}$$

**16.103** The initial number of moles of  $\text{Ag}^+$  is

$$\text{mol Ag}^+ = 50.0 \text{ mL} \times \frac{0.010 \text{ mol Ag}^+}{1000 \text{ mL soln}} = 5.0 \times 10^{-4} \text{ mol Ag}^+$$

We can use the counts of radioactivity as being proportional to concentration. Thus, we can use the ratio to determine the quantity of  $\text{Ag}^+$  still in solution. However, since our original 50 mL of solution has been diluted to 500 mL, the counts per mL will be reduced by ten. Our diluted solution would then produce 7402.5 counts per minute if no removal of  $\text{Ag}^+$  had occurred.

The number of moles of  $\text{Ag}^+$  that correspond to 44.4 counts are:

$$44.4 \text{ counts} \times \frac{5.0 \times 10^{-4} \text{ mol Ag}^+}{7402.5 \text{ counts}} = 3.0 \times 10^{-6} \text{ mol Ag}^+$$

$$\text{Original mol of IO}_3^- = 100 \text{ mL} \times \frac{0.030 \text{ mol IO}_3^-}{1000 \text{ mL soln}} = 3.0 \times 10^{-3} \text{ mol}$$

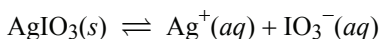
The quantity of  $\text{IO}_3^-$  remaining after reaction with  $\text{Ag}^+$ :

$$\begin{aligned} (\text{original moles} - \text{moles reacted with Ag}^+) &= (3.0 \times 10^{-3} \text{ mol}) - [(5.0 \times 10^{-4} \text{ mol}) - (3.0 \times 10^{-6} \text{ mol})] \\ &= 2.5 \times 10^{-3} \text{ mol IO}_3^- \end{aligned}$$

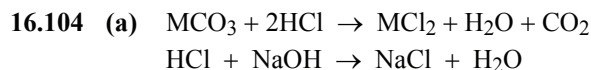
The total final volume is 500 mL or 0.50 L.

$$[\text{Ag}^+] = \frac{3.0 \times 10^{-6} \text{ mol Ag}^+}{0.50 \text{ L}} = 6.0 \times 10^{-6} \text{ M}$$

$$[\text{IO}_3^-] = \frac{2.5 \times 10^{-3} \text{ mol IO}_3^-}{0.50 \text{ L}} = 5.0 \times 10^{-3} \text{ M}$$



$$K_{\text{sp}} = [\text{Ag}^+][\text{IO}_3^-] = (6.0 \times 10^{-6})(5.0 \times 10^{-3}) = 3.0 \times 10^{-8}$$



**(b)** We are given the mass of the metal carbonate, so we need to find moles of the metal carbonate to calculate its molar mass. We can find moles of  $\text{MCO}_3$  from the moles of HCl reacted.

Moles of HCl reacted with  $\text{MCO}_3$  = Total moles of HCl – Moles of excess HCl

$$\text{Total moles of HCl} = 20.00 \text{ mL} \times \frac{0.0800 \text{ mol}}{1000 \text{ mL soln}} = 1.60 \times 10^{-3} \text{ mol HCl}$$

$$\text{Moles of excess HCl} = 5.64 \text{ mL} \times \frac{0.1000 \text{ mol}}{1000 \text{ mL soln}} = 5.64 \times 10^{-4} \text{ mol HCl}$$

$$\text{Moles of HCl reacted with MCO}_3 = (1.60 \times 10^{-3} \text{ mol}) - (5.64 \times 10^{-4} \text{ mol}) = 1.04 \times 10^{-3} \text{ mol HCl}$$

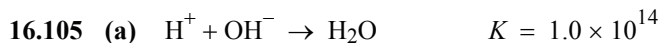
$$\text{Moles of MCO}_3 \text{ reacted} = (1.04 \times 10^{-3} \text{ mol HCl}) \times \frac{1 \text{ mol MCO}_3}{2 \text{ mol HCl}} = 5.20 \times 10^{-4} \text{ mol MCO}_3$$

$$\text{Molar mass of MCO}_3 = \frac{0.1022 \text{ g}}{5.20 \times 10^{-4} \text{ mol}} = 197 \text{ g/mol}$$

$$\text{Molar mass of CO}_3 = 60.01 \text{ g}$$

$$\text{Molar mass of M} = 197 \text{ g/mol} - 60.01 \text{ g/mol} = 137 \text{ g/mol}$$

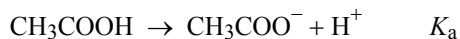
The metal, M, is **Ba**!



$$K = \frac{1}{K_a} = \frac{1}{5.6 \times 10^{-10}} = 1.8 \times 10^9$$



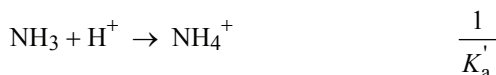
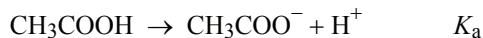
Broken into 2 equations:



$$K = \frac{K_a}{K_w} = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-14}} = 1.8 \times 10^9$$



Broken into 2 equations:



$$K = \frac{K_a}{K'_a} = \frac{1.8 \times 10^{-5}}{5.6 \times 10^{-10}} = 3.2 \times 10^4$$

**16.106** The number of moles of NaOH reacted is:

$$15.9 \text{ mL NaOH} \times \frac{0.500 \text{ mol NaOH}}{1000 \text{ mL soln}} = 7.95 \times 10^{-3} \text{ mol NaOH}$$

Since two moles of NaOH combine with one mole of oxalic acid, the number of moles of oxalic acid reacted is  $3.98 \times 10^{-3}$  mol. This is the number of moles of oxalic acid hydrate in 25.0 mL of solution. In 250 mL, the number of moles present is  $3.98 \times 10^{-2}$  mol. Thus the molar mass is:

$$\frac{5.00 \text{ g}}{3.98 \times 10^{-2} \text{ mol}} = 126 \text{ g/mol}$$

From the molecular formula we can write:

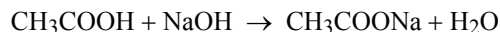
$$2(1.008)\text{g} + 2(12.01)\text{g} + 4(16.00)\text{g} + x(18.02)\text{g} = 126 \text{ g}$$

Solving for  $x$ :

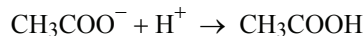
$$x = 2$$

**16.107 (a)** Mix 500 mL of 0.40 M  $\text{CH}_3\text{COOH}$  with 500 mL of 0.40 M  $\text{CH}_3\text{COONa}$ . Since the final volume is 1.00 L, then the concentrations of the two solutions that were mixed must be one-half of their initial concentrations.

- (b) Mix 500 mL of 0.80 *M* CH<sub>3</sub>COOH with 500 mL of 0.40 *M* NaOH. (Note: half of the acid reacts with all of the base to make a solution identical to that in part (a) above.)



- (c) Mix 500 mL of 0.80 *M* CH<sub>3</sub>COONa with 500 mL of 0.40 *M* HCl. (Note: half of the salt reacts with all of the acid to make a solution identical to that in part (a) above.)



**16.108 (a)**  $\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$

$$8.00 = 9.10 + \log \frac{[\text{ionized}]}{[\text{un-ionized}]}$$

$$\frac{[\text{un-ionized}]}{[\text{ionized}]} = 12.6 \quad (1)$$

- (b) First, let's calculate the total concentration of the indicator. 2 drops of the indicator are added and each drop is 0.050 mL.

$$2 \text{ drops} \times \frac{0.050 \text{ mL phenolphthalein}}{1 \text{ drop}} = 0.10 \text{ mL phenolphthalein}$$

This 0.10 mL of phenolphthalein of concentration 0.060 *M* is diluted to 50.0 mL.

$$\begin{aligned} M_i V_i &= M_f V_f \\ (0.060 \text{ M})(0.10 \text{ mL}) &= M_f (50.0 \text{ mL}) \\ M_f &= 1.2 \times 10^{-4} \text{ M} \end{aligned}$$

Using equation (1) above and letting  $y = [\text{ionized}]$ , then  $[\text{un-ionized}] = (1.2 \times 10^{-4}) - y$ .

$$\begin{aligned} \frac{(1.2 \times 10^{-4}) - y}{y} &= 12.6 \\ y &= 8.8 \times 10^{-6} \text{ M} \end{aligned}$$

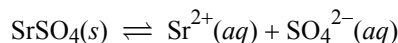
- 16.109** The sulfur-containing air-pollutants (like H<sub>2</sub>S) reacts with Pb<sup>2+</sup> to form PbS, which gives paintings a darkened look.

**16.110 (a)** Add sulfate. Na<sub>2</sub>SO<sub>4</sub> is soluble, BaSO<sub>4</sub> is not.

(b) Add sulfide. K<sub>2</sub>S is soluble, PbS is not

(c) Add iodide. ZnI<sub>2</sub> is soluble, HgI<sub>2</sub> is not.

- 16.111** Strontium sulfate is the more soluble of the two compounds. Therefore, we can assume that all of the SO<sub>4</sub><sup>2-</sup> ions come from SrSO<sub>4</sub>.



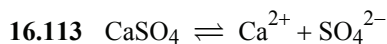
$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{SO}_4^{2-}] = s^2 = 3.8 \times 10^{-7}$$

$$s = [\text{Sr}^{2+}] = [\text{SO}_4^{2-}] = \sqrt{3.8 \times 10^{-7}} = 6.2 \times 10^{-4} \text{ M}$$

For BaSO<sub>4</sub>:

$$[\text{Ba}^{2+}] = \frac{K_{\text{sp}}}{[\text{SO}_4^{2-}]} = \frac{1.1 \times 10^{-10}}{6.2 \times 10^{-4}} = 1.8 \times 10^{-7} \text{ M}$$

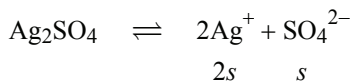
**16.112** The amphoteric oxides cannot be used to prepare buffer solutions because they are insoluble in water.



$$s^2 = 2.4 \times 10^{-5}$$

$$s = 4.9 \times 10^{-3} \text{ M}$$

$$\text{Solubility} = \frac{4.9 \times 10^{-3} \text{ mol}}{1 \text{ L}} \times \frac{136.2 \text{ g}}{1 \text{ mol}} = 0.67 \text{ g/L}$$



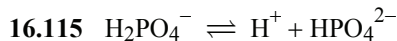
$$1.4 \times 10^{-5} = 4s^3$$

$$s = 0.015 \text{ M}$$

$$\text{Solubility} = \frac{0.015 \text{ mol}}{1 \text{ L}} \times \frac{311.1 \text{ g}}{1 \text{ mol}} = 4.7 \text{ g/L}$$

**Note:** Ag<sub>2</sub>SO<sub>4</sub> has a larger solubility.

**16.114** The ionized polyphenols have a dark color. In the presence of citric acid from lemon juice, the anions are converted to the lighter-colored acids.



$$K_{\text{a}} = 6.2 \times 10^{-8}$$

$$\text{p}K_{\text{a}} = 7.20$$

$$7.50 = 7.20 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 2.0$$

We need to add enough NaOH so that

$$[\text{HPO}_4^{2-}] = 2[\text{H}_2\text{PO}_4^-]$$

Initially there was

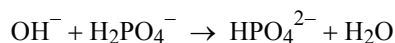
$$0.200 \text{ L} \times 0.10 \text{ mol/L} = 0.020 \text{ mol NaH}_2\text{PO}_4 \text{ present.}$$

For  $[\text{HPO}_4^{2-}] = 2[\text{H}_2\text{PO}_4^-]$ , we must add enough NaOH to react with  $2/3$  of the  $\text{H}_2\text{PO}_4^-$ . After reaction with NaOH, we have:

$$\frac{0.020}{3} \text{ mol H}_2\text{PO}_4^- = 0.0067 \text{ mol H}_2\text{PO}_4^-$$

$$\text{mol HPO}_4^{2-} = 2 \times 0.0067 \text{ mol} = 0.013 \text{ mol HPO}_4^{2-}$$

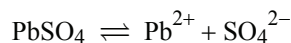
The moles of NaOH reacted is equal to the moles of  $\text{HPO}_4^{2-}$  produced because the mole ratio between  $\text{OH}^-$  and  $\text{HPO}_4^{2-}$  is 1:1.



$$V_{\text{NaOH}} = \frac{\text{mol}_{\text{NaOH}}}{M_{\text{NaOH}}} = \frac{0.013 \text{ mol}}{1.0 \text{ mol/L}} = 0.013 \text{ L} = \mathbf{13 \text{ mL}}$$

**16.116** Assuming the density of water to be 1.00 g/mL, 0.05 g  $\text{Pb}^{2+}$  per  $10^6$  g water is equivalent to  $5 \times 10^{-5}$  g  $\text{Pb}^{2+}/\text{L}$

$$\frac{0.05 \text{ g Pb}^{2+}}{1 \times 10^6 \text{ g H}_2\text{O}} \times \frac{1 \text{ g H}_2\text{O}}{1 \text{ mL H}_2\text{O}} \times \frac{1000 \text{ mL H}_2\text{O}}{1 \text{ L H}_2\text{O}} = 5 \times 10^{-5} \text{ g Pb}^{2+}/\text{L}$$



Initial (M):		0	0
Change (M):	-s	+s	+s
Equilibrium (M):		s	s

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

$$1.6 \times 10^{-8} = s^2$$

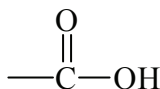
$$s = 1.3 \times 10^{-4} \text{ M}$$

The solubility of  $\text{PbSO}_4$  in g/L is:

$$\frac{1.3 \times 10^{-4} \text{ mol}}{1 \text{ L}} \times \frac{303.3 \text{ g}}{1 \text{ mol}} = 4.0 \times 10^{-2} \text{ g/L}$$

**Yes.** The  $[\text{Pb}^{2+}]$  exceeds the safety limit of  $5 \times 10^{-5}$  g  $\text{Pb}^{2+}/\text{L}$ .

**16.117 (a)** The acidic hydrogen is from the carboxyl group.



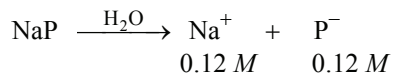
**(b)** At pH 6.50, Equation (16.4) of the text can be written as:

$$6.50 = -\log(1.64 \times 10^{-3}) + \log \frac{[\text{P}^-]}{[\text{HP}]}$$

$$\frac{[\text{P}^-]}{[\text{HP}]} = 5.2 \times 10^3$$

Thus, nearly all of the penicillin G will be in the ionized form. The ionized form is more soluble in water because it bears a net charge; penicillin G is largely nonpolar and therefore much less soluble in water. (Both penicillin G and its salt are effective antibiotics.)

(c) First, the dissolved NaP salt completely dissociates in water as follows:



We need to concentrate only on the hydrolysis of the  $\text{P}^-$  ion.

**Step 1:** Let  $x$  be the equilibrium concentrations of HP and  $\text{OH}^-$  due to the hydrolysis of  $\text{P}^-$  ions. We summarize the changes:

	$\text{P}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HP}(aq) + \text{OH}^-(aq)$		
Initial (M):	0.12	0	0
Change (M):	- $x$	+ $x$	+ $x$
Equilibrium (M):	$0.12 - x$	$x$	$x$

$$\text{Step 2: } K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.64 \times 10^{-3}} = 6.10 \times 10^{-12}$$

$$K_b = \frac{[\text{HP}][\text{OH}^-]}{[\text{P}^-]}$$

$$6.10 \times 10^{-12} = \frac{x^2}{0.12 - x}$$

Assuming that  $0.12 - x \approx 0.12$ , we write:

$$6.10 \times 10^{-12} = \frac{x^2}{0.12}$$

$$x = 8.6 \times 10^{-7} \text{ M}$$

**Step 3:** At equilibrium:

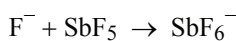
$$[\text{OH}^-] = 8.6 \times 10^{-7} \text{ M}$$

$$\text{pOH} = -\log(8.6 \times 10^{-7}) = 6.07$$

$$\text{pH} = 14.00 - 6.07 = \mathbf{7.93}$$

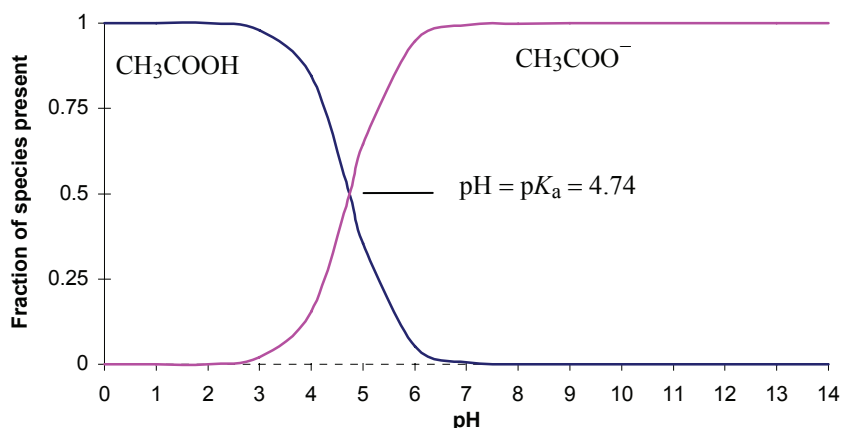
Because HP is a relatively strong acid,  $\text{P}^-$  is a weak base. Consequently, only a small fraction of  $\text{P}^-$  undergoes hydrolysis and the solution is slightly basic.

**16.118 (c)** has the highest  $[\text{H}^+]$



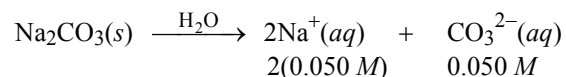
Removal of  $\text{F}^-$  promotes further ionization of HF.

## 16.119



16.120 (a) This is a common ion ( $\text{CO}_3^{2-}$ ) problem.

The dissociation of  $\text{Na}_2\text{CO}_3$  is:



Let  $s$  be the molar solubility of  $\text{CaCO}_3$  in  $\text{Na}_2\text{CO}_3$  solution. We summarize the changes as:

	$\text{CaCO}_3(s)$	$\rightleftharpoons$	$\text{Ca}^{2+}(aq)$	$+$	$\text{CO}_3^{2-}(aq)$
Initial (M):	0.00		0.00		0.050
Change (M):	+s		+s		+s
Equil. (M):	+s		+s		$0.050 + s$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

$$8.7 \times 10^{-9} = s(0.050 + s)$$

Since  $s$  is small, we can assume that  $0.050 + s \approx 0.050$

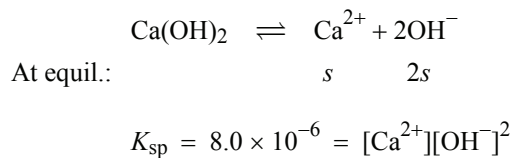
$$8.7 \times 10^{-9} = 0.050s$$

$$s = 1.7 \times 10^{-7}\text{ M}$$

Thus, the addition of washing soda to permanent hard water removes most of the  $\text{Ca}^{2+}$  ions as a result of the common ion effect.

(b)  $\text{Mg}^{2+}$  is not removed by this procedure, because  $\text{MgCO}_3$  is fairly soluble ( $K_{\text{sp}} = 4.0 \times 10^{-5}$ ).

(c) The  $K_{\text{sp}}$  for  $\text{Ca}(\text{OH})_2$  is  $8.0 \times 10^{-6}$ .



$$4s^3 = 8.0 \times 10^{-6}$$

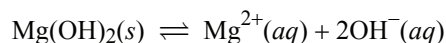
$$s = 0.0126 M$$

$$[\text{OH}^-] = 2s = 0.0252 M$$

$$\text{pOH} = -\log(0.0252) = 1.60$$

$$\text{pH} = 12.40$$

- (d) The  $[\text{OH}^-]$  calculated above is  $0.0252 M$ . At this rather high concentration of  $\text{OH}^-$ , most of the  $\text{Mg}^{2+}$  will be removed as  $\text{Mg}(\text{OH})_2$ . The small amount of  $\text{Mg}^{2+}$  remaining in solution is due to the following equilibrium:



$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$1.2 \times 10^{-11} = [\text{Mg}^{2+}](0.0252)^2$$

$$[\text{Mg}^{2+}] = 1.9 \times 10^{-8} M$$

- (e) Remove  $\text{Ca}^{2+}$  first because it is present in larger amounts.

$$16.121 \quad \text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

For acid color:

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{1}{10}$$

$$\text{pH} = \text{p}K_{\text{a}} - \log 10$$

$$\text{pH} = \text{p}K_{\text{a}} - 1$$

For base color:

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{10}{1}$$

$$\text{pH} = \text{p}K_{\text{a}} + 1$$

Combining these two equations:

$$\text{pH} = \text{p}K_{\text{a}} \pm 1$$

$$16.122 \quad \text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

At  $\text{pH} = 1.0$ ,

$$-\text{COOH} \quad 1.0 = 2.3 + \log \frac{[-\text{COO}^-]}{[-\text{COOH}]}$$

$$\frac{[-\text{COOH}]}{[-\text{COO}^-]} = 20$$

$$-\text{NH}_3^+ \quad 1.0 = 9.6 + \log \frac{[-\text{NH}_2]}{[-\text{NH}_3^+]}$$

$$\frac{[-\text{NH}_3^+]}{[-\text{NH}_2]} = 4 \times 10^8$$

Therefore the **predominant species** is:  $^+\text{NH}_3 - \text{CH}_2 - \text{COOH}$

**At pH = 7.0,**

$$-\text{COOH} \quad 7.0 = 2.3 + \log \frac{[-\text{COO}^-]}{[-\text{COOH}]}$$

$$\frac{[-\text{COO}^-]}{[-\text{COOH}]} = 5 \times 10^4$$

$$-\text{NH}_3^+ \quad 7.0 = 9.6 + \log \frac{[-\text{NH}_2]}{[-\text{NH}_3^+]}$$

$$\frac{[-\text{NH}_3^+]}{[-\text{NH}_2]} = 4 \times 10^2$$

**Predominant species:**  $^+\text{NH}_3 - \text{CH}_2 - \text{COO}^-$

**At pH = 12.0,**

$$-\text{COOH} \quad 12.0 = 2.3 + \log \frac{[-\text{COO}^-]}{[-\text{COOH}]}$$

$$\frac{[-\text{COO}^-]}{[-\text{COOH}]} = 5 \times 10^9$$

$$-\text{NH}_3^+ \quad 12.0 = 9.6 + \log \frac{[-\text{NH}_2]}{[-\text{NH}_3^+]}$$

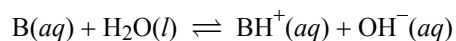
$$\frac{[-\text{NH}_2]}{[-\text{NH}_3^+]} = 2.5 \times 10^2$$

**Predominant species:**  $\text{NH}_2 - \text{CH}_2 - \text{COO}^-$

- 16.123 (a)** The  $pK_b$  value can be determined at the half-equivalence point of the titration (half the volume of added acid needed to reach the equivalence point). At this point in the titration  $\text{pH} = pK_a$ , where  $K_a$  refers to the acid ionization constant of the conjugate acid of the weak base. The Henderson-Hasselbalch equation reduces to  $\text{pH} = pK_a$  when  $[\text{acid}] = [\text{conjugate base}]$ . Once the  $pK_a$  value is determined, the  $pK_b$  value can be calculated as follows:

$$pK_a + pK_b = 14.00$$

- (b) Let B represent the base, and  $\text{BH}^+$  represents its conjugate acid.



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

$$[\text{OH}^-] = \frac{K_b[\text{B}]}{[\text{BH}^+]}$$

Taking the negative logarithm of both sides of the equation gives:

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

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

The titration curve would look very much like Figure 16.5 of the text, except the  $y$ -axis would be pOH and the  $x$ -axis would be volume of strong acid added. The  $\text{p}K_b$  value can be determined at the half-equivalence point of the titration (half the volume of added acid needed to reach the equivalence point). At this point in the titration, the concentrations of the buffer components, [B] and  $[\text{BH}^+]$ , are equal, and hence  $\text{pOH} = \text{p}K_b$ .

- 16.124 (a) Before dilution:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\text{pH} = 4.74 + \log \frac{[0.500]}{[0.500]} = 4.74$$

After a 10-fold dilution:

$$\text{pH} = 4.74 + \log \frac{[0.0500]}{[0.0500]} = 4.74$$

There is no change in the pH of a buffer upon dilution.

- (b) Before dilution:

	$\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)$		
Initial (M):	0.500	0	0
Change (M):	-x	+x	+x
Equilibrium (M):	$0.500 - x$	x	x

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

$$1.8 \times 10^{-5} = \frac{x^2}{0.500 - x} \approx \frac{x^2}{0.500}$$

$$x = 3.0 \times 10^{-3} M = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(3.0 \times 10^{-3}) = 2.52$$

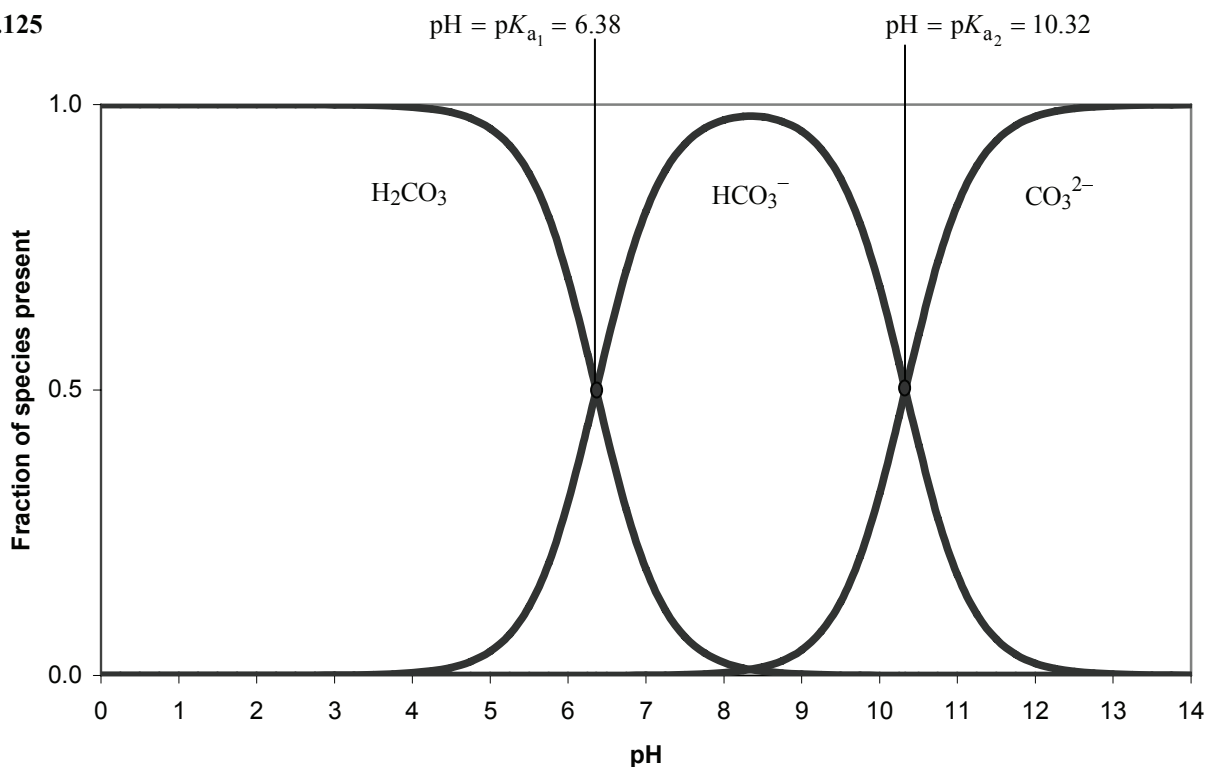
After dilution:

$$1.8 \times 10^{-5} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}$$

$$x = 9.5 \times 10^{-4} M = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(9.5 \times 10^{-4}) = 3.02$$

16.125



Main features: At low pH's,  $\text{H}_2\text{CO}_3$  predominates and  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$  are the only important species. At high pH's,  $\text{CO}_3^{2-}$  predominates and  $\text{HCO}_3^-/\text{CO}_3^{2-}$  are the only important species. Also, at fraction 0.5, we have  $[\text{H}_2\text{CO}_3] = [\text{HCO}_3^-]$  so  $\text{pH} = \text{p}K_{a1}$  and  $[\text{HCO}_3^-] = [\text{CO}_3^{2-}]$  so  $\text{pH} = \text{p}K_{a2}$ .

16.126 The reaction is:



First, we calculate moles of HCl and  $\text{NH}_3$ .

$$n_{\text{HCl}} = \frac{PV}{RT} = \frac{\left(372 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)(0.96 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(295 \text{ K})} = 0.0194 \text{ mol}$$

$$n_{\text{NH}_3} = \frac{0.57 \text{ mol NH}_3}{1 \text{ L soln}} \times 0.034 \text{ L} = 0.0194 \text{ mol}$$

The mole ratio between  $\text{NH}_3$  and  $\text{HCl}$  is 1:1, so we have complete neutralization.

	$\text{NH}_3$	+	$\text{HCl}$	$\rightarrow$	$\text{NH}_4\text{Cl}$
Initial (mol):	0.0194		0.0194		0
Change (mol):	-0.0194		-0.0194		+0.0194
Final (mol):	0		0		0.0194

$\text{NH}_4^+$  is a weak acid. We set up the reaction representing the hydrolysis of  $\text{NH}_4^+$ .

	$\text{NH}_4^+(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{H}_3\text{O}^+(aq)$	+	$\text{NH}_3(aq)$
Initial (M):	0.0194 mol/0.034 L				0		0
Change (M):	-x				+x		+x
Equilibrium (M):	0.57 - x				x		x

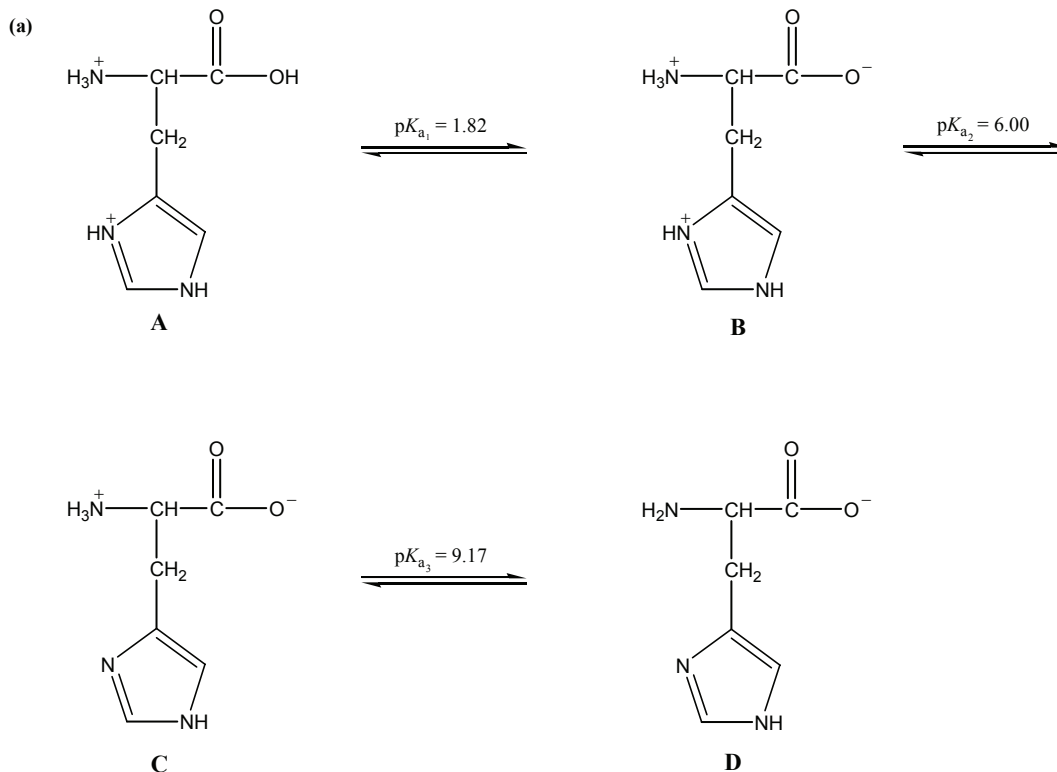
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.57 - x} \approx \frac{x^2}{0.57}$$

$$x = 1.79 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(1.79 \times 10^{-5}) = 4.75$$

## 16.127

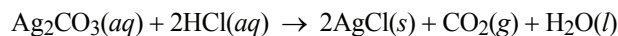


(b) The species labeled **C** is the dipolar ion because it has an equal number of + and – charges.

$$(c) \text{pI} = \frac{\text{p}K_{\text{a}_2} + \text{p}K_{\text{a}_3}}{2} = \frac{6.00 + 9.17}{2} = 7.59$$

(d) Because the pH of blood is close to 7, the conjugate acid-base pair most suited to buffer blood is **B** (acid) and **C** (base), because  $\text{p}K_{\text{a}_2}$  is closest to 7.

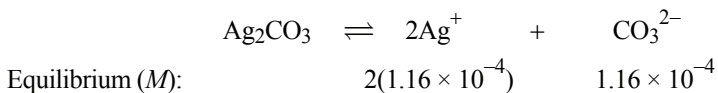
**16.128** The reaction is:



The moles of  $\text{CO}_2(g)$  produced will equal the moles of  $\text{CO}_3^{2-}$  in  $\text{Ag}_2\text{CO}_3$  due to the stoichiometry of the reaction.

$$n_{\text{CO}_2} = \frac{PV}{RT} = \frac{\left(114 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)(0.019 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})} = 1.16 \times 10^{-4} \text{ mol}$$

Because the solution volume is 1.0 L,  $[\text{CO}_3^{2-}] = 1.16 \times 10^{-4} \text{ M}$ . We set up a table representing the dissociation of  $\text{Ag}_2\text{CO}_3$  to solve for  $K_{\text{sp}}$ .



$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$$

$$K_{\text{sp}} = (2.32 \times 10^{-4})^2(1.16 \times 10^{-4})$$

$$K_{\text{sp}} = \mathbf{6.2 \times 10^{-12}} \text{ (at } 5^\circ\text{C)}$$