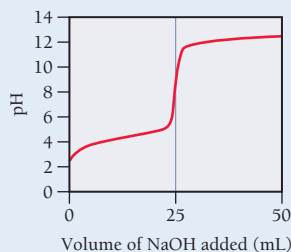


Continued—

- Q9.** A 20.0-mL sample of 0.150 M ethylamine is titrated with 0.0981 M HCl. What is the pH after the addition of 5.0 mL of HCl? For ethylamine,  $pK_b = 3.25$ .  
**MISSED THIS?** Read Section 18.4; Watch KCV 18.4B, IWE 18.7  
a) 10.75    b) 11.04    c) 2.96    d) 11.46
- Q10.** Three 15.0-mL acid samples—0.10 M HA, 0.10 M HB, and 0.10 M  $H_2C$ —are all titrated with 0.100 M NaOH. If HA is a weak acid, HB is a strong acid, and  $H_2C$  is a diprotic acid, which statement is true of all three titrations?  
**MISSED THIS?** Read Section 18.4; Watch KCV 18.4A, KCV 18.4B  
a) All three titrations have the same pH at the first equivalence point.  
b) All three titrations have the same initial pH.  
c) All three titrations have the same final pH.  
d) All three titrations require the same volume of NaOH to reach the first equivalence point.
- Q11.** A weak unknown monoprotic acid is titrated with a strong base. The titration curve is shown. Find  $K_a$  for the unknown acid.  
**MISSED THIS?** Read Section 18.4; Watch KCV 18.4B, IWE 18.7



- a)  $2.5 \times 10^{-3}$     b)  $3.2 \times 10^{-5}$   
c)  $3.2 \times 10^{-7}$     d)  $2.5 \times 10^{-9}$

- Q12.** Calculate the molar solubility of lead(II) bromide ( $PbBr_2$ ). For lead(II) bromide,  $K_{sp} = 4.67 \times 10^{-6}$ .  
**MISSED THIS?** Read Section 18.5; Watch IWE 18.8  
a) 0.00153 M  
b) 0.0105 M  
c) 0.0167 M  
d) 0.0211 M
- Q13.** Calculate the molar solubility of magnesium fluoride ( $MgF_2$ ) in a solution that is 0.250 M in NaF. For magnesium fluoride,  $K_{sp} = 5.16 \times 10^{-11}$ .  
**MISSED THIS?** Read Section 18.5  
a)  $2.35 \times 10^{-4}$  M  
b)  $2.06 \times 10^{-10}$  M  
c)  $2.87 \times 10^{-5}$  M  
d)  $8.26 \times 10^{-10}$  M
- Q14.** A solution is 0.0250 M in  $Pb^{2+}$ . What minimum concentration of  $Cl^-$  is required to begin to precipitate  $PbCl_2$ ? For  $PbCl_2$ ,  $K_{sp} = 1.17 \times 10^{-5}$ .  
**MISSED THIS?** Read Section 18.6; Watch IWE 18.12  
a)  $1.17 \times 10^{-5}$  M  
b) 0.0108 M  
c) 0.0216 M  
d)  $5.41 \times 10^{-4}$  M
- Q15.** Which compound is more soluble in an acidic solution than in a neutral solution?  
**MISSED THIS?** Read Section 18.5  
a)  $PbBr_2$   
b) CuCl  
c) AgI  
d)  $BaF_2$

Answers: 1. (c) 2. (b) 3. (b) 4. (d) 5. (b) 6. (a) 7. (a) 8. (d) 9. (d) 10. (d) 11. (b) 12. (b) 13. (d) 14. (c) 15. (d)

## CHAPTER 18 IN REVIEW

### TERMS

#### Section 18.2

buffer (788)  
common ion effect (790)  
Henderson–Hasselbalch equation (792)

#### Section 18.3

buffer capacity (802)

#### Section 18.4

acid–base titration (803)  
indicator (803)  
equivalence point (803)  
endpoint (814)

#### Section 18.5

solubility product constant ( $K_{sp}$ ) (817)

molar solubility (817)

#### Section 18.6

selective precipitation (824)

#### Section 18.7

qualitative analysis (826)  
quantitative analysis (826)

#### Section 18.8

complex ion (829)  
ligand (829)  
formation constant ( $K_f$ ) (829)

### CONCEPTS

#### The Danger of Antifreeze (18.1)

- Although buffers closely regulate the pH of mammalian blood, the capacity of these buffers to neutralize can be overwhelmed.
- Ethylene glycol, the main component of antifreeze, is metabolized by the liver into glycolic acid. The resulting acidity can exceed the buffering capacity of blood and cause acidosis, a serious condition that results in oxygen deprivation.

#### Buffers: Solutions That Resist pH Change (18.2)

- Buffers contain significant amounts of both a weak acid and its conjugate base (or a weak base and its conjugate acid), enabling the buffer to neutralize added acid or added base.
- Adding a small amount of acid to a buffer converts a stoichiometric amount of base to the conjugate acid. Adding a small amount of base to a buffer converts a stoichiometric amount of the acid to the conjugate base.

- We can determine the pH of a buffer solution by solving an equilibrium problem, focusing on the common ion effect, or by using the Henderson–Hasselbalch equation.

### Buffer Range and Buffer Capacity (18.3)

- A buffer works best when the amounts of acid and conjugate base it contains are large and approximately equal.
- If the relative amounts of acid and base in a buffer differ by more than a factor of 10, the ability of the buffer to neutralize added acid and added base diminishes. The maximum pH range at which a buffer is effective is one pH unit on either side of the acid's  $pK_a$ .

### Titration and pH Curves (18.4)

- A titration curve is a graph of the change in pH versus added volume of acid or base during a titration.
- This chapter examines three types of titration curves, representing three types of acid–base reactions: a strong acid with a strong base, a weak acid with a strong base (or vice versa), and a polyprotic acid with a strong base.
- The equivalence point of a titration can be made visible by an indicator, a compound that changes color over a specific pH range.

### Solubility Equilibria and the Solubility Product Constant (18.5)

- The solubility product constant ( $K_{sp}$ ) is an equilibrium constant for the dissolution of an ionic compound in water.
- We can determine the molar solubility of an ionic compound from  $K_{sp}$  and vice versa. Although the value of  $K_{sp}$  is constant at a given temperature, the solubility of an ionic substance can depend on other factors such as the presence of common ions and the pH of the solution.

### Precipitation (18.6)

- We can compare the magnitude of  $K_{sp}$  to the reaction quotient,  $Q$ , in order to determine the relative saturation of a solution.
- Substances with cations that have sufficiently different values of  $K_{sp}$  can be separated by selective precipitation, in which an added reagent forms a precipitate with one of the dissolved cations but not others.

### Qualitative Chemical Analysis (18.7)

- Qualitative analysis operates on the principle that a mixture of cations can be separated and analyzed based on the differences in the solubilities of their salts.
- In a classic qualitative analysis scheme, an unknown mixture of cations is sequentially treated with different reagents, each of which precipitates a known subgroup of cations.

### Complex Ion Equilibria (18.8)

- A complex ion contains a central metal ion coordinated to two or more ligands.
- The equilibrium constant for the formation of a complex ion is called a formation constant and is usually quite large.
- The solubility of an ionic compound containing a metal cation that forms complex ions increases in the presence of Lewis bases that complex with the cation because the formation of the complex ion drives the dissolution reaction to the right.
- All metal hydroxides become more soluble in the presence of acids, but amphoteric metal hydroxides also become more soluble in the presence of bases.

## EQUATIONS AND RELATIONSHIPS

The Henderson–Hasselbalch Equation (18.2)

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

Effective Buffer Range (18.3)

$$\text{pH range} = \text{p}K_a \pm 1$$

The Relation between  $Q$  and  $K_{sp}$  (18.6)

If  $Q < K_{sp}$ , the solution is unsaturated. More of the solid ionic compound can dissolve in the solution.

If  $Q = K_{sp}$ , the solution is saturated. The solution is holding the equilibrium amount of the dissolved ions, and additional solid will not dissolve in the solution.

If  $Q > K_{sp}$ , the solution is supersaturated. Under most circumstances, the solid will precipitate out of a supersaturated solution.

## LEARNING OUTCOMES

Chapter Objectives	Assessment
Perform pH calculations for buffer solutions containing a common ion (18.2)	Example 18.1 For Practice 18.1 For More Practice 18.1 Exercises 27–34
Perform pH calculations for buffer solutions using the Henderson–Hasselbalch equation (18.2)	Example 18.2 For Practice 18.2 Exercises 35–46
Perform pH calculations for buffer solutions after the addition of a small amount of strong acid or strong base (18.2)	Example 18.3 For Practice 18.3 For More Practice 18.3 Exercises 47–50
Perform pH calculations for buffer solutions containing a weak base and its conjugate acid before and after the addition of an acid or base (18.2)	Example 18.4 For Practice 18.4 For More Practice 18.4 Exercises 51–52
Describe the preparation of an effective buffer solution (18.3)	Example 18.5 For Practice 18.5 Exercises 53–60
Perform pH calculations for the titration of a strong acid with a strong base (18.4)	Example 18.6 For Practice 18.6 Exercise 61

Perform calculations for the titration of a weak acid with a strong base (18.4)	Example 18.7 For Practice 18.7 Exercises 62–77
Identify specific points along the titration curve for a diprotic acid with a strong base (18.4)	Exercises 78–80
Predict properties of indicators in solutions (18.4)	Exercises 81–84
Perform $K_{sp}$ calculations for ionic compounds in pure water (18.5)	Examples 18.8, 18.9 For Practice 18.8, 18.9 Exercises 85–94
Perform $K_{sp}$ calculations involving the common ion effect (18.5)	Example 18.10 For Practice 18.10 Exercises 95–96
Determine the effect of pH on solubility (18.5)	Example 18.11 For Practice 18.11 Exercises 97–100
Predict precipitation reactions by comparing $Q$ to $K_{sp}$ (18.6)	Example 18.12 For Practice 18.12 Exercises 101–106
Perform calculations involving selective precipitation (18.6)	Examples 18.13, 18.14 For Practice 18.13, 18.14 Exercises 107–108
Perform calculations involving complex ion equilibria (18.8)	Example 18.15 For Practice 18.15 Exercises 109–111

## EXERCISES

**Mastering Chemistry** provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

## REVIEW QUESTIONS

- What is the pH range of human blood? How is human blood maintained in this pH range?
- What is a buffer? How does a buffer work? How does it neutralize added acid? Added base?
- What is the common ion effect?
- What is the Henderson–Hasselbalch equation, and why is it useful?
- What is the pH of a buffer solution when the concentrations of both buffer components (the weak acid and its conjugate base) are equal? What happens to the pH when the buffer contains more of the weak acid than the conjugate base? More of the conjugate base than the weak acid?
- Suppose that a buffer contains equal amounts of a weak acid and its conjugate base. What happens to the relative amounts of the weak acid and conjugate base when a small amount of strong acid is added to the buffer? What happens when a small amount of strong base is added?
- How do you use the Henderson–Hasselbalch equation to calculate the pH of a buffer containing a base and its conjugate acid? Specifically, how do you determine the correct value for  $pK_a$ ?
- What factors influence the effectiveness of a buffer? What are the characteristics of an effective buffer?
- What is the effective pH range of a buffer (relative to the  $pK_a$  of the weak acid component)?
- Describe acid–base titration. What is the equivalence point?
- The pH at the equivalence point of the titration of a strong acid with a strong base is 7.0. However, the pH at the equivalence point of the titration of a *weak* acid with a strong base is above 7.0. Explain.
- The volume required to reach the equivalence point of an acid–base titration depends on the volume and concentration of the acid or base to be titrated and on the concentration of the acid or base used to do the titration. It does not, however, depend on whether or not the acid or base being titrated is strong or weak. Explain.
- In the titration of a strong acid with a strong base, how do you calculate these quantities?
  - initial pH
  - pH before the equivalence point
  - pH at the equivalence point
  - pH beyond the equivalence point
- In the titration of a weak acid with a strong base, how do you calculate these quantities?
  - initial pH
  - pH before the equivalence point
  - pH at one-half the equivalence point
  - pH at the equivalence point
  - pH beyond the equivalence point
- The titration of a polyprotic acid with sufficiently different  $pK_a$ s displays two equivalence points. Why?
- In the titration of a polyprotic acid, the volume required to reach the first equivalence point is identical to the volume required to reach the second one. Why?
- What is the difference between the endpoint and the equivalence point in a titration?
- What is an indicator? How can an indicator signal the equivalence point of a titration?
- What is the solubility product constant? Write a general expression for the solubility constant of a compound with the general formula  $A_mX_n$ .
- What is molar solubility? How can you obtain the molar solubility of a compound from  $K_{sp}$ ?
- How does a common ion affect the solubility of a compound? More specifically, how is the solubility of a compound with the general formula  $AX$  different in a solution containing one of the common ions ( $A^+$  or  $X^-$ ) than it is in pure water? Explain.
- How is the solubility of an ionic compound with a basic anion affected by pH? Explain.

23. For a given solution containing an ionic compound, what is the relationship between  $Q$ ,  $K_{sp}$ , and the relative saturation of the solution?
24. What is selective precipitation? Under which conditions does selective precipitation occur?
25. What is qualitative analysis? How does *qualitative* analysis differ from *quantitative* analysis?
26. What are the main groups in the general qualitative analysis scheme described in this chapter? Describe the steps and reagents necessary to identify each group.

## PROBLEMS BY TOPIC

### The Common Ion Effect and Buffers

27. In which of these solutions will  $\text{HNO}_2$  ionize less than it does in pure water? **MISSED THIS?** Read Section 18.2
- 0.10 M NaCl
  - 0.10 M  $\text{KNO}_3$
  - 0.10 M NaOH
  - 0.10 M  $\text{NaNO}_2$
28. A formic acid solution has a pH of 3.25. Which of these substances will raise the pH of the solution upon addition? Explain your answer.
- HCl
  - NaBr
  - $\text{NaCHO}_2$
  - KCl
29. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2A, 18.2B, IWE 18.2
- a solution that is 0.20 M in  $\text{HCHO}_2$  and 0.15 M in  $\text{NaCHO}_2$
  - a solution that is 0.16 M in  $\text{NH}_3$  and 0.22 M in  $\text{NH}_4\text{Cl}$
30. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.
- a solution that is 0.195 M in  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.125 M in  $\text{KC}_2\text{H}_3\text{O}_2$
  - a solution that is 0.255 M in  $\text{CH}_3\text{NH}_2$  and 0.135 M in  $\text{CH}_3\text{NH}_3\text{Br}$
31. Calculate the percent ionization of a 0.15 M benzoic acid solution in pure water and in a solution containing 0.10 M sodium benzoate. Why does the percent ionization differ significantly in the two solutions?
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2A
32. Calculate the percent ionization of a 0.13 M formic acid solution in pure water and also in a solution containing 0.11 M potassium formate. Explain the difference in percent ionization in the two solutions.
33. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2B, IWE 18.2
- 0.15 M HF
  - 0.15 M NaF
  - a mixture that is 0.15 M in HF and 0.15 M in NaF
34. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.
- 0.18 M  $\text{CH}_3\text{NH}_2$
  - 0.18 M  $\text{CH}_3\text{NH}_3\text{Cl}$
  - a mixture that is 0.18 M in  $\text{CH}_3\text{NH}_2$  and 0.18 M in  $\text{CH}_3\text{NH}_3\text{Cl}$
35. A buffer contains significant amounts of acetic acid and sodium acetate. Write equations showing how this buffer neutralizes added acid and added base.
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2A
36. A buffer contains significant amounts of ammonia and ammonium chloride. Write equations showing how this buffer neutralizes added acid and added base.
37. Use the Henderson–Hasselbalch equation to calculate the pH of each solution in Problem 29.
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2B, IWE 18.2
38. Use the Henderson–Hasselbalch equation to calculate the pH of each solution in Problem 30.
39. Use the Henderson–Hasselbalch equation to calculate the pH of each solution.
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2B, IWE 18.2
- a solution that is 0.135 M in HClO and 0.155 M in KClO
  - a solution that contains 1.05%  $\text{C}_2\text{H}_5\text{NH}_2$  by mass and 1.10%  $\text{C}_2\text{H}_5\text{NH}_3\text{Br}$  by mass
  - a solution that contains 10.0 g of  $\text{HC}_2\text{H}_3\text{O}_2$  and 10.0 g of  $\text{NaC}_2\text{H}_3\text{O}_2$  in 150.0 mL of solution
40. Use the Henderson–Hasselbalch equation to calculate the pH of each solution.
- a solution that is 0.145 M in propanoic acid and 0.115 M in potassium propanoate
  - a solution that contains 0.785%  $\text{C}_5\text{H}_5\text{N}$  by mass and 0.985%  $\text{C}_5\text{H}_5\text{NHCl}$  by mass
  - a solution that contains 15.0 g of HF and 25.0 g of NaF in 125 mL of solution
41. Calculate the pH of the solution that results from each mixture.
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2B, IWE 18.2
- 50.0 mL of 0.15 M  $\text{HCHO}_2$  with 75.0 mL of 0.13 M  $\text{NaCHO}_2$
  - 125.0 mL of 0.10 M  $\text{NH}_3$  with 250.0 mL of 0.10 M  $\text{NH}_4\text{Cl}$
42. Calculate the pH of the solution that results from each mixture.
- 150.0 mL of 0.25 M HF with 225.0 mL of 0.30 M NaF
  - 175.0 mL of 0.10 M  $\text{C}_2\text{H}_5\text{NH}_2$  with 275.0 mL of 0.20 M  $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$
43. Calculate the ratio of NaF to HF required to create a buffer with  $\text{pH} = 4.00$ .
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2B, IWE 18.2
44. Calculate the ratio of  $\text{CH}_3\text{NH}_2$  to  $\text{CH}_3\text{NH}_3\text{Cl}$  concentration required to create a buffer with  $\text{pH} = 10.24$ .
45. What mass of sodium benzoate should you add to 150.0 mL of a 0.15 M benzoic acid solution to obtain a buffer with a pH of 4.25? (Assume no volume change.)
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2B, IWE 18.2
46. What mass of ammonium chloride should you add to 2.55 L of a 0.155 M  $\text{NH}_3$  to obtain a buffer with a pH of 9.55? (Assume no volume change.)
47. A 250.0-mL buffer solution is 0.250 M in acetic acid and 0.250 M in sodium acetate.
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2B, IWE 18.2, 18.3
- What is the initial pH of this solution?
  - What is the pH after addition of 0.0050 mol of HCl?
  - What is the pH after addition of 0.0050 mol of NaOH?

48. A 100.0-mL buffer solution is 0.175 M in HClO and 0.150 M in NaClO.
- What is the initial pH of this solution?
  - What is the pH after addition of 150.0 mg of HBr?
  - What is the pH after addition of 85.0 mg of NaOH?
49. For each solution, calculate the initial and final pH after adding 0.010 mol of HCl.
- MISSED THIS?** Read Section 18.2; Watch KCV 18.2B, IWE 18.2, 18.3
- 500.0 mL of pure water
  - 500.0 mL of a buffer solution that is 0.125 M in  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.115 M in  $\text{NaC}_2\text{H}_3\text{O}_2$
  - 500.0 mL of a buffer solution that is 0.155 M in  $\text{C}_2\text{H}_5\text{NH}_2$  and 0.145 M in  $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$
50. For each solution, calculate the initial and final pH after adding 0.010 mol of NaOH.
- 250.0 mL of pure water
  - 250.0 mL of a buffer solution that is 0.195 M in  $\text{HCHO}_2$  and 0.275 M in  $\text{KCHO}_2$
  - 250.0 mL of a buffer solution that is 0.255 M in  $\text{CH}_3\text{CH}_2\text{NH}_2$  and 0.235 M in  $\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$
51. A 350.0-mL buffer solution is 0.150 M in HF and 0.150 M in NaF. What mass of NaOH can this buffer neutralize before the pH rises above 4.00? If the same volume of the buffer were 0.350 M in HF and 0.350 M in NaF, what mass of NaOH could be handled before the pH rises above 4.00? **MISSED THIS?** Read Section 18.3
52. A 100.0-mL buffer solution is 0.100 M in  $\text{NH}_3$  and 0.125 M in  $\text{NH}_4\text{Br}$ . What mass of HCl can this buffer neutralize before the pH falls below 9.00? If the same volume of the buffer were 0.250 M in  $\text{NH}_3$  and 0.400 M in  $\text{NH}_4\text{Br}$ , what mass of HCl could be handled before the pH fell below 9.00?
53. Determine whether or not the mixing of each pair of solutions results in a buffer. **MISSED THIS?** Read Section 18.3
- 100.0 mL of 0.10 M  $\text{NH}_3$ ; 100.0 mL of 0.15 M  $\text{NH}_4\text{Cl}$
  - 50.0 mL of 0.10 M HCl; 35.0 mL of 0.150 M NaOH
  - 50.0 mL of 0.15 M HF; 20.0 mL of 0.15 M NaOH
  - 175.0 mL of 0.10 M  $\text{NH}_3$ ; 150.0 mL of 0.12 M NaOH
  - 125.0 mL of 0.15 M  $\text{NH}_3$ ; 150.0 mL of 0.20 M NaOH
54. Determine whether or not the mixing of each pair of solutions results in a buffer.
- 75.0 mL of 0.10 M HF; 55.0 mL of 0.15 M NaF
  - 150.0 mL of 0.10 M HF; 135.0 mL of 0.175 M HCl
  - 165.0 mL of 0.10 M HF; 135.0 mL of 0.050 M KOH
  - 125.0 mL of 0.15 M  $\text{CH}_3\text{NH}_2$ ; 120.0 mL of 0.25 M  $\text{CH}_3\text{NH}_3\text{Cl}$
  - 105.0 mL of 0.15 M  $\text{CH}_3\text{NH}_2$ ; 95.0 mL of 0.10 M HCl
55. Blood is buffered by carbonic acid and the bicarbonate ion. Normal blood plasma is 0.024 M in  $\text{HCO}_3^-$  and 0.0012 M  $\text{H}_2\text{CO}_3$  ( $\text{p}K_{\text{a}_1}$  for  $\text{H}_2\text{CO}_3$  at body temperature is 6.1).
- MISSED THIS?** Read Sections 18.2, 18.3; Watch KCV 18.2B, IWE 18.2, 18.3
- What is the pH of blood plasma?
  - If the volume of blood in a normal adult is 5.0 L, what mass of HCl can be neutralized by the buffering system in blood before the pH falls below 7.0 (which would result in death)?
  - Given the volume from part (b), what mass of NaOH can be neutralized before the pH rises above 7.8?
56. The fluids within cells are buffered by  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ .
- Calculate the ratio of  $\text{HPO}_4^{2-}$  to  $\text{H}_2\text{PO}_4^-$  required to maintain a pH of 7.1 within a cell.
  - Could a buffer system employing  $\text{H}_3\text{PO}_4$  as the weak acid and  $\text{H}_2\text{PO}_4^-$  as the weak base be used as a buffer system within cells? Explain.

57. Which buffer system is the best choice to create a buffer with  $\text{pH} = 7.20$ ? For the best system, calculate the ratio of the masses of the buffer components required to make the buffer.

**MISSED THIS?** Read Section 18.3



58. Which buffer system is the best choice to create a buffer with  $\text{pH} = 9.00$ ? For the best system, calculate the ratio of the masses of the buffer components required to make the buffer.



59. A 500.0-mL buffer solution is 0.100 M in  $\text{HNO}_2$  and 0.150 M in  $\text{KNO}_2$ . Determine if each addition would exceed the capacity of the buffer to neutralize it. **MISSED THIS?** Read Section 18.3

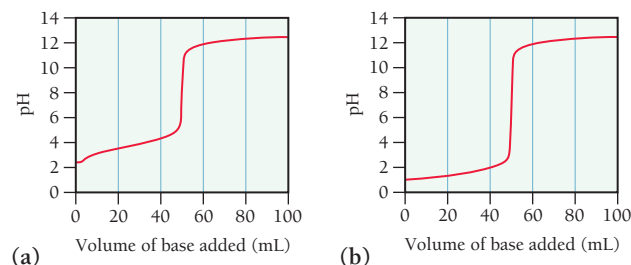
- 250 mg NaOH
- 350 mg KOH
- 1.25 g HBr
- 1.35 g HI

60. A 1.0-L buffer solution is 0.125 M in  $\text{HNO}_2$  and 0.145 M in  $\text{NaNO}_2$ . Determine the concentrations of  $\text{HNO}_2$  and  $\text{NaNO}_2$  after the addition of each substance:

- 1.5 g HCl
- 1.5 g NaOH
- 1.5 g HI

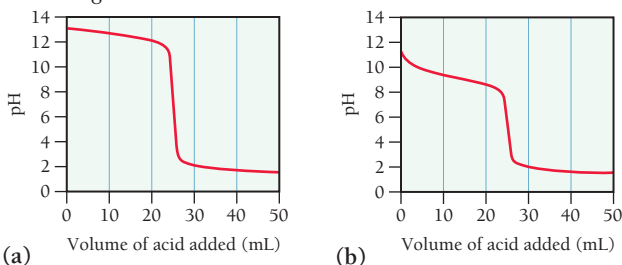
### Titrations, pH Curves, and Indicators

61. The graphs labeled (a) and (b) show the titration curves for two equal-volume samples of monoprotic acids, one weak and one strong. Both titrations were carried out with the same concentration of strong base. **MISSED THIS?** Read Section 18.4



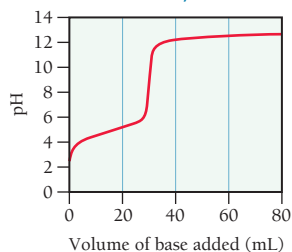
- What is the approximate pH at the equivalence point of each curve?
  - Which graph corresponds to the titration of the strong acid and which one to the titration of the weak acid?
62. Two 25.0-mL samples, one 0.100 M HCl and the other 0.100 M HF, are titrated with 0.200 M KOH.
- What is the volume of added base at the equivalence point for each titration?
  - Is the pH at the equivalence point for each titration acidic, basic, or neutral?
  - Which titration curve has the lower initial pH?
  - Sketch each titration curve.
63. Two 20.0-mL samples, one 0.200 M KOH and the other 0.200 M  $\text{CH}_3\text{NH}_2$ , are titrated with 0.100 M HI.
- MISSED THIS?** Read Section 18.4; Watch KCV 18.4A, 18.4B
- What is the volume of added acid at the equivalence point for each titration?
  - Is the pH at the equivalence point for each titration acidic, basic, or neutral?
  - Which titration curve has the lower initial pH?
  - Sketch each titration curve.

64. The graphs labeled (a) and (b) show the titration curves for two equal-volume samples of bases, one weak and one strong. Both titrations were carried out with the same concentration of strong acid.

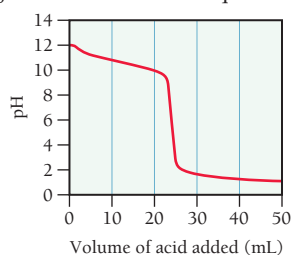


- What is the approximate pH at the equivalence point of each curve?
  - Which graph corresponds to the titration of the strong base and which one to the weak base?
65. Consider the curve shown here for the titration of a weak monoprotic acid with a strong base and answer each question.

**MISSED THIS?** Read Section 18.4; Watch KCV 18.4B



- What is the pH and what is the volume of added base at the equivalence point?
  - At what volume of added base is the pH calculated by working an equilibrium problem based on the initial concentration and  $K_a$  of the weak acid?
  - At what volume of added base does  $\text{pH} = \text{p}K_a$ ?
  - At what volume of added base is the pH calculated by working an equilibrium problem based on the concentration and  $K_b$  of the conjugate base?
  - Beyond what volume of added base is the pH calculated by focusing on the amount of excess strong base added?
66. Consider the curve shown here for the titration of a weak base with a strong acid and answer each question.



- What is the pH and what is the volume of added acid at the equivalence point?
- At what volume of added acid is the pH calculated by working an equilibrium problem based on the initial concentration and  $K_b$  of the weak base?
- At what volume of added acid does  $\text{pH} = 14 - \text{p}K_b$ ?
- At what volume of added acid is the pH calculated by working an equilibrium problem based on the concentration and  $K_a$  of the conjugate acid?
- Beyond what volume of added acid is the pH calculated by focusing on the amount of excess strong acid added?

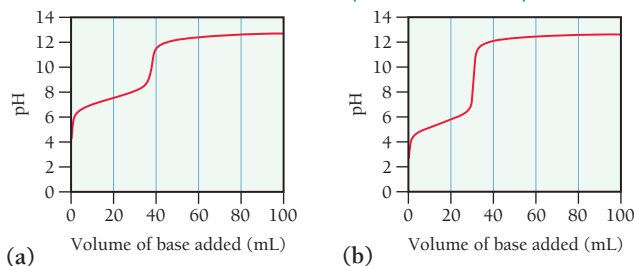
67. Consider the titration of a 35.0-mL sample of 0.175 M HBr with 0.200 M KOH. Determine each quantity.

**MISSED THIS?** Read Section 18.4; Watch KCV 18.4A, IWE 18.6

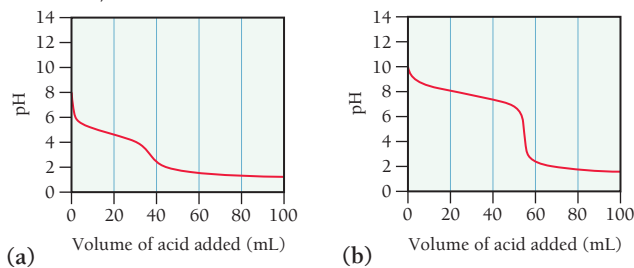
- the initial pH
  - the volume of added base required to reach the equivalence point
  - the pH at 10.0 mL of added base
  - the pH at the equivalence point
  - the pH after adding 5.0 mL of base beyond the equivalence point
68. A 20.0-mL sample of 0.125 M  $\text{HNO}_3$  is titrated with 0.150 M NaOH. Calculate the pH for at least five different points throughout the titration curve and sketch the curve. Indicate the volume at the equivalence point on your graph.
69. Consider the titration of a 25.0-mL sample of 0.115 M RbOH with 0.100 M HCl. Determine each quantity.
- MISSED THIS?** Read Section 18.4; Watch KCV 18.4A, IWE 18.6
- the initial pH
  - the volume of added acid required to reach the equivalence point
  - the pH at 5.0 mL of added acid
  - the pH at the equivalence point
  - the pH after adding 5.0 mL of acid beyond the equivalence point
70. A 15.0-mL sample of 0.100 M  $\text{Ba}(\text{OH})_2$  is titrated with 0.125 M HCl. Calculate the pH for at least five different points throughout the titration curve and sketch the curve. Indicate the volume at the equivalence point on your graph.
71. Consider the titration of a 20.0-mL sample of 0.105 M  $\text{HC}_2\text{H}_3\text{O}_2$  with 0.125 M NaOH. Determine each quantity.
- MISSED THIS?** Read Section 18.4; Watch KCV 18.4B, IWE 18.7
- the initial pH
  - the volume of added base required to reach the equivalence point
  - the pH at 5.0 mL of added base
  - the pH at one-half of the equivalence point
  - the pH at the equivalence point
  - the pH after adding 5.0 mL of base beyond the equivalence point
72. A 30.0-mL sample of 0.165 M propanoic acid is titrated with 0.300 M KOH. Calculate the pH at each volume of added base: 0 mL, 5 mL, 10 mL, equivalence point, one-half equivalence point, 20 mL, 25 mL. Sketch the titration curve.
73. Consider the titration of a 25.0-mL sample of 0.175 M  $\text{CH}_3\text{NH}_2$  with 0.150 M HBr. Determine each quantity.
- MISSED THIS?** Read Section 18.4; Watch KCV 18.4B, IWE 18.7
- the initial pH
  - the volume of added acid required to reach the equivalence point
  - the pH at 5.0 mL of added acid
  - the pH at one-half of the equivalence point
  - the pH at the equivalence point
  - the pH after adding 5.0 mL of acid beyond the equivalence point
74. A 25.0-mL sample of 0.125 M pyridine is titrated with 0.100 M HCl. Calculate the pH at each volume of added acid: 0 mL, 10 mL, 20 mL, equivalence point, one-half equivalence point, 40 mL, 50 mL. Sketch the titration curve.

75. Consider the titration curves (labeled a and b) for two weak acids, both titrated with 0.100 M NaOH.

**MISSED THIS?** Read Section 18.4; Watch KCV 18.4B, IWE 18.7

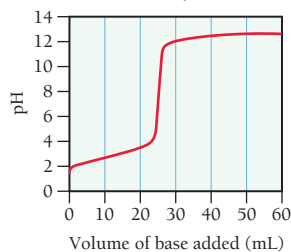


- i. Which acid solution is more concentrated?  
ii. Which acid has the larger  $K_a$ ?
76. Consider the titration curves (labeled a and b) for two weak bases, both titrated with 0.100 M HCl.

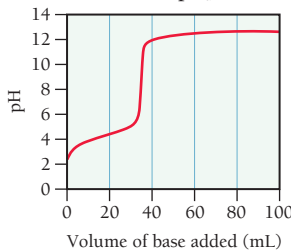


- i. Which base solution is more concentrated?  
ii. Which base has the larger  $K_b$ ?
77. A 0.229-g sample of an unknown monoprotic acid is titrated with 0.112 M NaOH. The resulting titration curve is shown here. Determine the molar mass and  $pK_a$  of the acid.

**MISSED THIS?** Read Section 18.4; Watch KCV 18.4B, IWE 18.7



78. A 0.446-g sample of an unknown monoprotic acid is titrated with 0.105 M KOH. The resulting titration curve is shown here. Determine the molar mass and  $pK_a$  of the acid.



79. A 20.0-mL sample of 0.115 M sulfurous acid ( $H_2SO_3$ ) solution is titrated with 0.1014 M KOH. At what added volume of base solution does each equivalence point occur?

**MISSED THIS?** Read Section 18.4

80. A 20.0-mL sample of a 0.125 M diprotic acid ( $H_2A$ ) solution is titrated with 0.1019 M KOH. The acid ionization constants for the acid are  $K_{a_1} = 5.2 \times 10^{-5}$  and  $K_{a_2} = 3.4 \times 10^{-10}$ . At what added volume of base does each equivalence point occur?

81. Methyl red has a  $pK_a$  of 5.0 and is red in its acid form and yellow in its basic form. If several drops of this indicator are placed in a 25.0-mL sample of 0.100 M HCl, what color will the solution appear? If 0.100 M NaOH is slowly added to the HCl sample, in what pH range will the indicator change color?

**MISSED THIS?** Read Section 18.4

82. Phenolphthalein has a  $pK_a$  of 9.7. It is colorless in its acid form and pink in its basic form. For each of the values of pH, calculate  $[In^-]/[HIn]$  and predict the color of a phenolphthalein solution.
- pH = 2.0
  - pH = 5.0
  - pH = 8.0
  - pH = 11.0
83. Referring to Table 18.1, pick an indicator for use in the titration of each acid with a strong base. **MISSED THIS?** Read Section 18.4
- HF
  - HCl
  - HCN
84. Referring to Table 18.1, pick an indicator for use in the titration of each base with a strong acid.
- $CH_3NH_2$
  - NaOH
  - $C_6H_5NH_2$

## Solubility Equilibria

85. Write balanced equations and expressions for  $K_{sp}$  for the dissolution of each ionic compound. **MISSED THIS?** Read Section 18.5
- $BaSO_4$
  - $PbBr_2$
  - $Ag_2CrO_4$
86. Write balanced equations and expressions for  $K_{sp}$  for the dissolution of each ionic compound.
- $CaCO_3$
  - $PbCl_2$
  - AgI
87. Refer to the  $K_{sp}$  values in Table 18.2 to calculate the molar solubility of each compound in pure water. **MISSED THIS?** Read Section 18.5; Watch IWE 18.8
- AgBr
  - $Mg(OH)_2$
  - $CaF_2$
88. Refer to the  $K_{sp}$  values in Table 18.2 to calculate the molar solubility of each compound in pure water.
- $MX$  ( $K_{sp} = 1.27 \times 10^{-36}$ )
  - $Ag_2CrO_4$
  - $Ca(OH)_2$
89. Use the given molar solubilities in pure water to calculate  $K_{sp}$  for each compound. **MISSED THIS?** Read Section 18.5
- $MX$ ; molar solubility =  $3.27 \times 10^{-11}$  M
  - $PbF_2$ ; molar solubility =  $5.63 \times 10^{-3}$  M
  - $MgF_2$ ; molar solubility =  $2.65 \times 10^{-4}$  M
90. Use the given molar solubilities in pure water to calculate  $K_{sp}$  for each compound.
- $BaCrO_4$ ; molar solubility =  $1.08 \times 10^{-5}$  M
  - $Ag_2SO_3$ ; molar solubility =  $1.55 \times 10^{-5}$  M
  - $Pd(SCN)_2$ ; molar solubility =  $2.22 \times 10^{-8}$  M
91. Two compounds with general formulas  $AX$  and  $AX_2$  have  $K_{sp} = 1.5 \times 10^{-5}$ . Which of the two compounds has the higher molar solubility?

**MISSED THIS?** Read Section 18.5; Watch IWE 18.8

92. Consider the compounds with the generic formulas listed and their corresponding molar solubilities in pure water. Which compound has the smallest value of  $K_{sp}$ ?
- $AX$ ; molar solubility =  $1.35 \times 10^{-4} M$
  - $AX_2$ ; molar solubility =  $2.25 \times 10^{-4} M$
  - $A_2X$ ; molar solubility =  $1.75 \times 10^{-4} M$
93. Refer to the  $K_{sp}$  value from Table 18.2 to calculate the solubility of iron(II) hydroxide in pure water in grams per 100.0 mL of solution. **MISSED THIS?** Read Section 18.5; Watch IWE 18.8
94. The solubility of copper(I) chloride is 3.91 mg per 100.0 mL of solution. Calculate  $K_{sp}$  for  $CuCl$ .
95. Calculate the molar solubility of barium fluoride in each liquid or solution. **MISSED THIS?** Read Section 18.5
- pure water
  - 0.10 M  $Ba(NO_3)_2$
  - 0.15 M  $NaF$
96. Calculate the molar solubility of  $MX$  ( $K_{sp} = 1.27 \times 10^{-36}$ ) in each liquid or solution.
- pure water
  - 0.25 M  $MCl_2$
  - 0.20 M  $Na_2X$
97. Calculate the molar solubility of calcium hydroxide in a solution buffered at each pH. **MISSED THIS?** Read Section 18.5
- pH = 4
  - pH = 7
  - pH = 9
98. Calculate the solubility (in grams per  $1.00 \times 10^2$  mL of solution) of magnesium hydroxide in a solution buffered at pH = 10. How does this compare to the solubility of  $Mg(OH)_2$  in pure water?
99. Determine if each compound is more soluble in acidic solution than it is in pure water. Explain. **MISSED THIS?** Read Section 18.5
- $BaCO_3$
  - $CuS$
  - $AgCl$
  - $PbI_2$
100. Determine if each compound is more soluble in acidic solution than it is in pure water. Explain.
- $Hg_2Br_2$
  - $Mg(OH)_2$
  - $CaCO_3$
  - $AgI$

### Precipitation and Qualitative Analysis

101. A solution containing sodium fluoride is mixed with one containing calcium nitrate to form a solution that is 0.015 M in  $NaF$  and 0.010 M in  $Ca(NO_3)_2$ . Does a precipitate form in the mixed solution? If so, identify the precipitate. **MISSED THIS?** Read Section 18.6; Watch IWE 18.12
102. A solution containing potassium bromide is mixed with one containing lead acetate to form a solution that is 0.013 M in  $KBr$  and 0.0035 M in  $Pb(C_2H_3O_2)_2$ . Does a precipitate form in the mixed solution? If so, identify the precipitate.
103. Predict whether a precipitate will form if you mix 75.0 mL of a  $NaOH$  solution with  $pOH = 2.58$  with 125.0 mL of a 0.018 M  $MgCl_2$  solution. Identify the precipitate, if any. **MISSED THIS?** Read Section 18.6; Watch IWE 18.12
104. Predict whether a precipitate will form if you mix 175.0 mL of a 0.0055 M  $KCl$  solution with 145.0 mL of a 0.0015 M  $AgNO_3$  solution. Identify the precipitate, if any.
105. Potassium hydroxide is used to precipitate each of the cations from their respective solution. Determine the minimum concentration of  $KOH$  required for precipitation to begin in each case. **MISSED THIS?** Read Section 18.6; Watch IWE 18.12
- 0.015 M  $CaCl_2$
  - 0.0025 M  $Fe(NO_3)_2$
  - 0.0018 M  $MgBr_2$
106. Determine the minimum concentration of the precipitating agent on the right to cause precipitation of the cation from the solution on the left.
- 0.035 M  $Ba(NO_3)_2$ ;  $NaF$
  - 0.085 M  $CaI_2$ ;  $K_2SO_4$
  - 0.0018 M  $AgNO_3$ ;  $RbCl$
107. A solution is 0.010 M in  $Ba^{2+}$  and 0.020 M in  $Ca^{2+}$ . **MISSED THIS?** Read Section 18.6; Watch IWE 18.12
- If sodium sulfate is used to selectively precipitate one of the cations while leaving the other cation in solution, which cation will precipitate first? What minimum concentration of  $Na_2SO_4$  will trigger the precipitation of the cation that precipitates first?
  - What is the remaining concentration of the cation that precipitates first, when the other cation begins to precipitate?
108. A solution is 0.022 M in  $Fe^{2+}$  and 0.014 M in  $Mg^{2+}$ .
- If potassium carbonate is used to selectively precipitate one of the cations while leaving the other cation in solution, which cation will precipitate first? What minimum concentration of  $K_2CO_3$  will trigger the precipitation of the cation that precipitates first?
  - What is the remaining concentration of the cation that precipitates first, when the other cation begins to precipitate?

### Complex Ion Equilibria

109. A solution is  $1.1 \times 10^{-3} M$  in  $Zn(NO_3)_2$  and 0.150 M in  $NH_3$ . After the solution reaches equilibrium, what concentration of  $Zn^{2+}(aq)$  remains? **MISSED THIS?** Read Section 18.8
110. A 120.0-mL sample of a solution that is  $2.8 \times 10^{-3} M$  in  $AgNO_3$  is mixed with a 225.0-mL sample of a solution that is 0.10 M in  $NaCN$ . After the solution reaches equilibrium, what concentration of  $Ag^+(aq)$  remains?
111. Use the appropriate values of  $K_{sp}$  and  $K_f$  to find the equilibrium constant for the reaction. **MISSED THIS?** Read Section 18.8
- $$FeS(s) + 6 CN^-(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq) + S^{2-}(aq)$$
112. Use the appropriate values of  $K_{sp}$  and  $K_f$  to find the equilibrium constant for the reaction.
- $$PbCl_2(s) + 3 OH^-(aq) \rightleftharpoons Pb(OH)_3^-(aq) + 2 Cl^-(aq)$$



## CUMULATIVE PROBLEMS

- 113.** A 150.0-mL solution contains 2.05 g of sodium benzoate and 2.47 g of benzoic acid. Calculate the pH of the solution.
- 114.** A solution is made by combining 10.0 mL of 17.5 M acetic acid with 5.54 g of sodium acetate and diluting to a total volume of 1.50 L. Calculate the pH of the solution.
- 115.** A buffer is created by combining 150.0 mL of 0.25 M  $\text{HCHO}_2$  with 75.0 mL of 0.20 M NaOH. Determine the pH of the buffer.
- 116.** A buffer is created by combining 3.55 g of  $\text{NH}_3$  with 4.78 g of HCl and diluting to a total volume of 750.0 mL. Determine the pH of the buffer.
- 117.** A 1.0-L buffer solution initially contains 0.25 mol of  $\text{NH}_3$  and 0.25 mol of  $\text{NH}_4\text{Cl}$ . In order to adjust the buffer pH to 8.75, should you add NaOH or HCl to the buffer mixture? What mass of the correct reagent should you add?
- 118.** A 250.0-mL buffer solution initially contains 0.025 mol of  $\text{HCHO}_2$  and 0.025 mol of  $\text{NaCHO}_2$ . In order to adjust the buffer pH to 4.10, should you add NaOH or HCl to the buffer mixture? What mass of the correct reagent should you add?
- 119.** In analytical chemistry, bases used for titrations must often be standardized; that is, their concentration must be precisely determined. Standardization of sodium hydroxide solutions can be accomplished by titrating potassium hydrogen phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ), also known as KHP, with the NaOH solution to be standardized.
- Write an equation for the reaction between NaOH and KHP.
  - The titration of 0.5527 g of KHP required 25.87 mL of an NaOH solution to reach the equivalence point. What is the concentration of the NaOH solution?
- 120.** A 0.5224-g sample of an unknown monoprotic acid was titrated with 0.0998 M NaOH. The equivalence point of the titration occurred at 23.82 mL. Determine the molar mass of the unknown acid.
- 121.** A 0.25-mol sample of a weak acid with an unknown  $\text{p}K_a$  was combined with 10.0 mL of 3.00 M KOH, and the resulting solution was diluted to 1.500 L. The measured pH of the solution was 3.85. What is the  $\text{p}K_a$  of the weak acid?
- 122.** A 5.55-g sample of a weak acid with  $K_a = 1.3 \times 10^{-4}$  was combined with 5.00 mL of 6.00 M NaOH, and the resulting solution was diluted to 750.0 mL. The measured pH of the solution was 4.25. What is the molar mass of the weak acid?
- 123.** A 0.552-g sample of ascorbic acid (vitamin C) was dissolved in water to a total volume of 20.0 mL and titrated with 0.1103 M KOH. The equivalence point occurred at 28.42 mL. The pH of the solution at 10.0 mL of added base was 3.72. From this data, determine the molar mass and  $K_a$  for vitamin C.
- 124.** Sketch the titration curve from Problem 123 by calculating the pH at the beginning of the titration, at one-half of the equivalence point, at the equivalence point, and at 5.0 mL beyond the equivalence point. Pick a suitable indicator for this titration from Table 18.1.
- 125.** One of the main components of hard water is  $\text{CaCO}_3$ . When hard water evaporates, some of the  $\text{CaCO}_3$  is left behind as a white mineral deposit. If a hard water solution is saturated with calcium carbonate, what volume of the solution has to evaporate to deposit  $1.00 \times 10^2$  g of  $\text{CaCO}_3$ ?
- 126.** Gout—a condition that results in joint swelling and pain—is caused by the formation of sodium urate ( $\text{NaC}_5\text{H}_3\text{N}_4\text{O}_3$ ) crystals within tendons, cartilage, and ligaments. Sodium urate precipitates out of blood plasma when uric acid levels become abnormally high. This sometimes happens as a result of eating too many rich foods and consuming too much alcohol, which is why gout is sometimes referred to as the “disease of kings.” If the sodium concentration in blood plasma is 0.140 M, and  $K_{\text{sp}}$  for sodium urate is  $5.76 \times 10^{-8}$ , what minimum concentration of urate would result in precipitation?
- 127.** Pseudogout, a condition with symptoms similar to those of gout (see Problem 126), is caused by the formation of calcium diphosphate ( $\text{Ca}_2\text{P}_2\text{O}_7$ ) crystals within tendons, cartilage, and ligaments. Calcium diphosphate will precipitate out of blood plasma when diphosphate levels become abnormally high. If the calcium concentration in blood plasma is 9.2 mg/dL, and  $K_{\text{sp}}$  for calcium diphosphate is  $8.64 \times 10^{-13}$ , what minimum concentration of diphosphate results in precipitation?
- 128.** Calculate the solubility of silver chloride in a solution that is 0.100 M in  $\text{NH}_3$ .
- 129.** Calculate the solubility of  $\text{CuX}$  in a solution that is 0.150 M in NaCN.  $K_{\text{sp}}$  for  $\text{CuX}$  is  $1.27 \times 10^{-36}$ .
- 130.** Aniline, abbreviated  $\phi\text{NH}_2$ , where  $\phi$  is  $\text{C}_6\text{H}_5$ , is an important organic base used in the manufacture of dyes. It has  $K_b = 4.3 \times 10^{-10}$ . In a certain manufacturing process, it is necessary to keep the concentration of  $\phi\text{NH}_3^+$  (aniline’s conjugate acid, the anilinium ion) below  $1.0 \times 10^{-9}$  M in a solution that is 0.10 M in aniline. Find the concentration of NaOH required for this process.
- 131.** The  $K_b$  of hydroxylamine,  $\text{NH}_2\text{OH}$ , is  $1.10 \times 10^{-8}$ . A buffer solution is prepared by mixing 100.0 mL of a 0.36 M hydroxylamine solution with 50.0 mL of a 0.26 M HCl solution. Determine the pH of the resulting solution.
- 132.** A 0.867-g sample of an unknown acid requires 32.2 mL of a 0.182 M barium hydroxide solution for neutralization. Assuming the acid is diprotic, calculate the molar mass of the acid.
- 133.** A 25.0-mL volume of a sodium hydroxide solution requires 19.6 mL of a 0.189 M hydrochloric acid for neutralization. A 10.0-mL volume of a phosphoric acid solution requires 34.9 mL of the sodium hydroxide solution for complete neutralization. Calculate the concentration of the phosphoric acid solution.
- 134.** Find the mass of sodium formate that must be dissolved in 250.0  $\text{cm}^3$  of a 1.4 M solution of formic acid to prepare a buffer solution with  $\text{pH} = 3.36$ .
- 135.** What relative masses of dimethyl amine and dimethyl ammonium chloride do you need to prepare a buffer solution of  $\text{pH} = 10.43$ ?
- 136.** You are asked to prepare 2.0 L of a  $\text{HCN}/\text{NaCN}$  buffer that has a pH of 9.8 and an osmotic pressure of 1.35 atm at 298 K. What masses of HCN and NaCN should you use to prepare the buffer? (Assume complete dissociation of NaCN.)
- 137.** What should the molar concentrations of benzoic acid and sodium benzoate be in a solution that is buffered at a pH of 4.55 and has a freezing point of  $-2.0^\circ\text{C}$ ? (Assume complete dissociation of sodium benzoate and a density of 1.01 g/mL for the solution.)

## CHALLENGE PROBLEMS

- 138.** Derive an equation similar to the Henderson–Hasselbalch equation for a buffer composed of a weak base and its conjugate acid. Instead of relating pH to  $pK_a$  and the relative concentrations of an acid and its conjugate base (as the Henderson–Hasselbalch equation does), the equation should relate pOH to  $pK_b$  and the relative concentrations of a base and its conjugate acid.
- 139.** Since soap and detergent action is hindered by hard water, laundry formulations usually include water softeners—called builders—designed to remove hard water ions (especially  $Ca^{2+}$  and  $Mg^{2+}$ ) from the water. A common builder used in North America is sodium carbonate. Suppose that the hard water used to do laundry contains 75 ppm  $Ca^{2+}$  (reported as  $CaCO_3$ ). What mass of  $Na_2CO_3$  is required to remove 90.0% of these ions from 10.0 L of laundry water?
- 140.** A 0.558-g sample of a diprotic acid with a molar mass of 255.8 g/mol is dissolved in water to a total volume of 25.0 mL. The solution is then titrated with a saturated calcium hydroxide solution.
- Assuming that the  $pK_a$  values for each ionization step are sufficiently different to see two equivalence points, determine the volume of added base for the first and second equivalence points.
  - The pH after adding 25.0 mL of the base is 3.82. Find the value of  $K_{a1}$ .
  - The pH after adding 20.0 mL past the first equivalence point is 8.25. Find the value of  $K_{a2}$ .
- 141.** When excess solid  $Mg(OH)_2$  is shaken with 1.00 L of 1.0 M  $NH_4Cl$  solution, the resulting saturated solution has pH = 9.00. Calculate the  $K_{sp}$  of  $Mg(OH)_2$ .
- 142.** What amount of solid NaOH must be added to 1.0 L of a 0.10 M  $H_2CO_3$  solution to produce a solution with  $[H^+] = 3.2 \times 10^{-11}$  M? There is no significant volume change as the result of the addition of the solid.
- 143.** Calculate the solubility of  $Au(OH)_3$  in (a) water and (b) 1.0 M nitric acid solution ( $K_{sp} = 5.5 \times 10^{-46}$ ).
- 144.** Calculate the concentration of  $I^-$  in a solution obtained by shaking 0.10 M KI with an excess of  $AgCl(s)$ .
- 145.** What volume of 0.100 M sodium carbonate solution is required to precipitate 99% of the Mg from 1.00 L of 0.100 M magnesium nitrate solution?
- 146.** Find the solubility of CuI in 0.40 M HCN solution. The  $K_{sp}$  of CuI is  $1.1 \times 10^{-12}$  and the  $K_f$  for the  $Cu(CN)_2^-$  complex ion is  $1 \times 10^{24}$ .
- 147.** Find the pH of a solution prepared from 1.0 L of a 0.10 M solution of  $Ba(OH)_2$  and excess  $Zn(OH)_2(s)$ . The  $K_{sp}$  of  $Zn(OH)_2$  is  $3 \times 10^{-15}$  and the  $K_f$  of  $Zn(OH)_4^{2-}$  is  $2 \times 10^{15}$ .
- 148.** What amount of HCl gas must be added to 1.00 L of a buffer solution that contains [acetic acid] = 2.0 M and [acetate] = 1.0 M in order to produce a solution with pH = 4.00?

## CONCEPTUAL PROBLEMS

- 149.** Without doing any calculations, determine if  $pH = pK_a$ ,  $pH > pK_a$ , or  $pH < pK_a$ . Assume that HA is a weak monoprotic acid.
- 0.10 mol HA and 0.050 mol of  $A^-$  in 1.0 L of solution
  - 0.10 mol HA and 0.150 mol of  $A^-$  in 1.0 L of solution
  - 0.10 mol HA and 0.050 mol of  $OH^-$  in 1.0 L of solution
  - 0.10 mol HA and 0.075 mol of  $OH^-$  in 1.0 L of solution
- 150.** A buffer contains 0.10 mol of a weak acid and 0.20 mol of its conjugate base in 1.0 L of solution. Determine whether or not each addition exceeds the capacity of the buffer.
- adding 0.020 mol of NaOH
  - adding 0.020 mol of HCl
  - adding 0.10 mol of NaOH
  - adding 0.010 mol of HCl
- 151.** Consider three solutions:
- 0.10 M solution of a weak monoprotic acid
  - 0.10 M solution of strong monoprotic acid
  - 0.10 M solution of a weak diprotic acid
- Each solution is titrated with 0.15 M NaOH. Which quantity is the same for all three solutions?
- the volume required to reach the final equivalence point
  - the volume required to reach the first equivalence point
  - the pH at the first equivalence point
  - the pH at one-half the first equivalence point
- 152.** Two monoprotic acid solutions (A and B) are titrated with identical NaOH solutions. The volume to reach the equivalence point for solution A is twice the volume required to reach the equivalence point for solution B, and the pH at the equivalence point of solution A is higher than the pH at the equivalence point for solution B. Which statement is true?
- The acid in solution A is more concentrated than in solution B and is also a stronger acid than that in solution B.
  - The acid in solution A is less concentrated than in solution B and is also a weaker acid than that in solution B.
  - The acid in solution A is more concentrated than in solution B and is also a weaker acid than that in solution B.
  - The acid in solution A is less concentrated than in solution B and is also a stronger acid than that in solution B.
- 153.** Describe the solubility of  $CaF_2$  in each solution compared to its solubility in water.
- in a 0.10 M NaCl solution
  - in a 0.10 M NaF solution
  - in a 0.10 M HCl solution
- 154.** Why does the titration of a weak acid with a strong base always have a basic equivalence point?

## QUESTIONS FOR GROUP WORK

Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

- 155.** Name a compound that you could add to a solution of each of the compounds to make a buffer. Explain your reasoning in complete sentences.
- acetic acid
  - sodium nitrite
  - ammonia
  - potassium formate
  - $\text{Na}_2\text{HPO}_4$  (two possible answers)
- 156.** Derive the Henderson–Hasselbalch equation as a group. Take turns having each group member write and explain the next step in the derivation.
- 157.** With group members acting as atoms or ions, act out the reaction that occurs when HCl is added to a buffer solution composed of  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NaC}_2\text{H}_3\text{O}_2$ . Write out a script for a narrator that describes the processes that occur, including how the buffer keeps the pH approximately the same even though a strong acid is added.
- 158.** A certain town gets its water from an underground aquifer that contains water in equilibrium with calcium carbonate limestone.
- What is the symbol for the equilibrium constant that describes calcium carbonate dissolving in water? What is the numerical value?
  - Calculate the molar solubility of calcium carbonate.
  - If an entire coffee cup of water (about 200 mL) evaporated on your desk over spring break, how many grams of calcium carbonate would be left behind?
  - If you wanted to clean out your coffee cup, would it be better to use an acidic or a basic cleaning solution? Why?
- 159.** Have each group member look up the  $K_{\text{sp}}$  for a different compound. Calculate the molar solubility. Do the numerical values suggest that the compound is soluble or insoluble? Compare answers with the solubility rules from Chapter 5, and have each group member present his or her findings to the group.

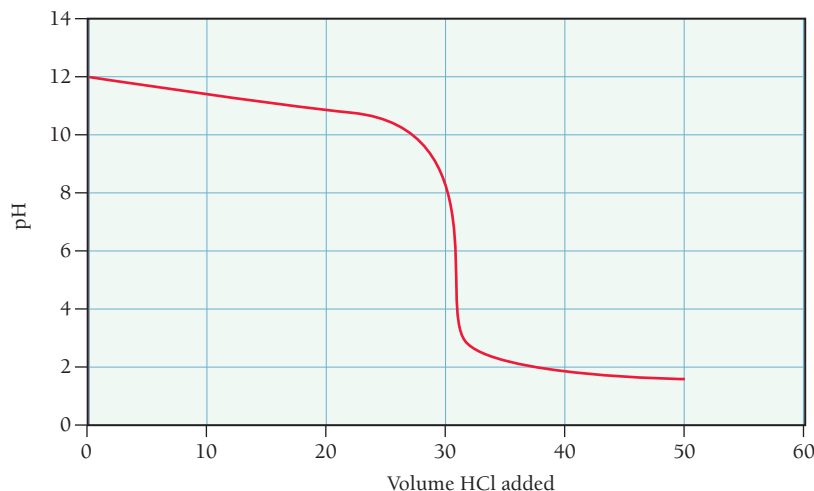
## DATA INTERPRETATION AND ANALYSIS

### Titration of an Unknown Base

- 160.** A base is known to be one of the three listed in the table. You are given a sample of the base and asked to identify it. To do so, you dissolve 0.30 g of the base in enough water to make 25.0 mL of the basic solution. You then titrate the solution with 0.100 M HCl and record the pH as a function of the added acid resulting in the titration curve that follows. Examine the table and the titration curve and answer the questions.

### Possible Bases in Sample

Base	$K_{\text{b}}$
Pyridine ( $\text{C}_5\text{H}_5\text{N}$ )	$1.7 \times 10^{-9}$
Aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ )	$3.9 \times 10^{-10}$
Triethylamine ( $\text{C}_6\text{H}_{15}\text{N}$ )	$5.6 \times 10^{-4}$



Titration Curve for 0.30 g of Unknown Base Dissolved in 25.0 mL of Solution

- What is the volume of added HCl at the equivalence point?
- What is the pH at the half-equivalence point?
- What is the molar mass of the unknown base?
- What are the  $pK_{\text{b}}$  and  $K_{\text{b}}$  of the unknown base?
- What is the most likely identity of the unknown base?

## Cc ANSWERS TO CONCEPTUAL CONNECTIONS

### Buffers

**18.1 (d)** Only this solution contains significant amounts of a weak acid and its conjugate base. (Remember that  $\text{HNO}_3$  is a strong acid, but  $\text{HNO}_2$  is a weak acid.)

### pH of Buffer Solutions

**18.2 (a)** Since the pH of the buffer is less than the  $\text{p}K_a$  of the acid, the buffer must contain more acid than base ( $[\text{HA}] > [\text{A}^-]$ ).

### Buffering Action

**18.3 (a)** Since one HA molecule is converted to one ion of the conjugate base ( $\text{A}^-$  ion), one  $\text{OH}^-$  ion was added to the buffer solution.

### Adding Acid or Base to a Buffer

**18.4 (b)** Since acid is added to the buffer, the pH will become slightly lower (slightly more acidic). Answer **(a)** reflects too large a change in pH for a buffer, and answers **(c)** and **(d)** have the pH changing in the wrong direction.

### Buffer Capacity

**18.5 (a)** Adding 0.050 mol of HCl destroys the buffer because it will react with all of the NaF, leaving no conjugate base in the buffer mixture.

### Titration Equivalence Point

**18.6 (d)** Because the flask contains 7  $\text{H}^+$  ions, the equivalence point is reached when 7  $\text{OH}^-$  ions have been added.

### Weak Acid and Strong Base Titration

**18.7 (c)** Acid A is more concentrated (it took more NaOH to reach the equivalence point), and acid B has the larger  $K_a$  ( $\text{p}K_a$  is smaller so  $K_a$  is larger).

### The Half-Equivalence Point

**18.8 (c)** The pH at the half-equivalence point is the  $\text{p}K_a$  of the conjugate acid, which is equal to  $14.00 - 8.75 = 5.25$ .

### Acid-Base Titrations

**18.9 (c)** Since the volumes and concentrations of all three acids are the same, the volume of NaOH required to reach the first equivalence point (and the only equivalence point for titrations i and iii) is the same for all three titrations.

### Common Ion Effect

**18.10 (c)** The sodium nitrate solution is the only one that has no common ion with barium sulfate. The other two solutions have common ions with barium sulfate; therefore, the solubility of barium sulfate is lower in these solutions.

### Selective Precipitation

**18.11 (a)**  $\text{Ba}^{2+}$  has the smallest solubility product constant and, since the stoichiometry of dissolution is the same for all three ions, it will precipitate first.

### Solubility and Complex Ion Equilibria

**18.12 (c)** Only NaCN contains an anion ( $\text{CN}^-$ ) that forms a complex ion with  $\text{Cu}^{2+}$  [from Table 18.3 we can see that  $K_f = 1.0 \times 10^{25}$  for  $\text{Cu}(\text{CN})_4^{2-}$ ]. Therefore, the presence of  $\text{CN}^-$  will drive the dissolution reaction of CuS.