Pearson

Exercises

Review Questions

1. What is the pH range of human blood? How is human blood maintained in this pH range?
2. What is a buffer? How does a buffer work? How does it neutralize added acid? Added base?
3. What is the common ion effect?
4. What is the Henderson–Hasselbalch equation, and why is it useful?
5. What is the pH of a buffer 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?
6. 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?
7. 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?
8. What factors influence the effectiveness of a buffer? What are the characteristics of an effective buffer?
9. What is the effective pH range of a buffer (relative to the pK_a of the weak acid component)?
10. Describe acid–base titration. What is the equivalence point?
11. 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.
12. 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 the strength or weakness of the acid or base being titrated. Explain.
13. In the titration of a strong acid with a strong base, how do you calculate these quantities?
    - **a.** initial pH
    - **b.** pH before the equivalence point
    - **c.** pH at the equivalence point
    - **d.** pH beyond the equivalence point
14. In the titration of a weak acid with a strong base, how do you calculate these quantities?
    - **a.** initial pH
    - **b.** pH before the equivalence point
    - **c.** pH at one-half the equivalence point
    - **d.** pH at the equivalence point
    - **e.** pH beyond the equivalence point
15. The titration of a diprotic acid with sufficiently different pK_a's displays two equivalence points. Why?
16. 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?
17. What is the difference between the endpoint and the equivalence point in a titration?
18. What is an indicator? How can an indicator signal the equivalence point of a titration?
19. What is the solubility-product constant? Write a general expression for the solubility constant of a compound with the general formula A_mX_n.
20. What is molar solubility? How do you obtain the molar solubility of a compound from K_{sp}?
21. 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 $\left(A^+ \text{or } X^-\right)$ than it is in pure water? Explain.
22. 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?

Problems by Topic

Note: Answers to all odd-numbered Problems can be found in Appendix III. Exercises in the Problems by Topic section are paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.

The Common Ion Effect and Buffers

25. In which of these solutions does HNO_2 ionize less than it does in pure water?

a. 0.10 M NaCl

b. 0.10 M KNO_3

c. 0.10 M NaOH

d. 0.10 M $NaNO_2$

26. A formic acid solution has a pH of 3.25. Which of these substances raises the pH of the solution upon addition? Explain your answer.

a. HCl

b. NaBr

c. $NaCHO_2$

d. KCl

27. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.

a. a solution that is 0.20 M in $HCHO_2$ and 0.15 M in $NaCHO_2$

b. a solution that is 0.16 M in NH_3 and 0.22 M in NH_4Cl

28. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.

a. a solution that is 0.195 M in $HC_2H_3O_2$ and 0.125 M in $KC_2H_3O_2$

b. a solution that is 0.255 M in CH_3NH_2 and 0.135 M in CH_3NH_3Br

29. 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?

30. 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.

31. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.

a. 0.15 M HF

b. 0.15 M NaF

c. a mixture that is 0.15 M in HF and 0.15 M in NaF

32. Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.

a. 0.18 M CH_3NH_2

b. 0.18 M CH_3NH_3Br

c. a mixture that is 0.18 M in CH_3NH_2 and 0.18 M in CH_3NH_3Cl

33. A buffer contains significant amounts of acetic acid and sodium acetate. Write equations that demonstrate how this buffer neutralizes added acid and added base.

34. A buffer contains significant amounts of ammonia and ammonium chloride. Write equations that demonstrate how this buffer neutralizes added acid and added base.

35. Use the Henderson–Hasselbalch equation to calculate the pH of each solution in **Problem 27**.

36. Use the Henderson–Hasselbalch equation to calculate the pH of each solution in **Problem 28**.

37. Use the Henderson–Hasselbalch equation to calculate the pH of each solution.

a. a solution that is 0.135 M in HClO and 0.155 M in KClO

b. a solution that contains 1.05% $C_2H_5NH_2$ by mass and 1.10% $C_2H_5NH_3Br$

c. a solution that contains 10.0 g of $HC_2H_3O_2$ and 10.0 g of $NaC_2H_3O_2$ in 150.0 mL of solution

38. Use the Henderson–Hasselbalch equation to calculate the pH of each solution.

a. a solution that is 0.145 M in propanoic acid and 0.115 M in potassium propanoate

b. a solution that contains 0.785% C_5H_5N by mass and 0.985% C_5H_5NHCl

c. a solution that contains 15.0 g of HF and 25.0 g of NaF in 125 mL of solution

39. Calculate the pH of the solution that results from each mixture.

a. 50.0 mL of 0.15 M $HCHO_2$ with 75.0 mL of 0.13 M $NaCHO_2$

b. 125.0 mL of 0.10 M NH_3 with 250.0 mL of 0.10 M NH_4Cl

40. Calculate the pH of the solution that results from each mixture.

a. 150.0 mL of 0.25 M HF with 225.0 mL of 0.30 M NaF

b. 175.0 mL of 0.10 M $C_5H_5NH_2$ with 275.0 mL of 0.20 M $C_5H_5NH_3Cl$

41. Calculate the ratio of NaF to HF required to create a buffer with pH = 4.00.

42. Calculate the ratio of CH_3NH_2 to CH_3NH_3Cl concentration required to create a buffer with pH = 10.24.

43. 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.)

44. What mass of ammonium chloride should you add to 2.55 L of a 0.155 M NH_3 solution to obtain a buffer with a pH of 9.55? (Assume no volume change.)

45. A 250.0-mL buffer solution is 0.250 M in acetic acid and 0.250 M in sodium acetate.

a. What is the initial pH of this solution?

b. What is the pH after addition of 0.0050 mol of HCl?

c. What is the pH after addition of 0.0050 mol of NaOH?

46. A 100.0-mL buffer solution is 0.175 M in HClO and 0.150 M in NaClO.

a. What is the initial pH of this solution?

b. What is the pH after addition of 150.0 mg of HBr?

c. What is the pH after addition of 85.0 mg of NaOH?

47. For each solution, calculate the initial and final pH after the addition of 0.010 mol of HCl.

a. 500.0 mL of pure water

b. 500.0 mL of a buffer solution that is 0.125 M in $HC_2H_3O_2$ and 0.115 M in $NaC_2H_3O_2$

c. 500.0 mL of a buffer solution that is 0.155 M in $C_2H_5NH_2$ and 0.145 M in $C_2H_5NH_3Cl$

48. For each solution, calculate the initial and final pH after the addition of 0.010 mol of NaOH.

a. 250.0 mL of pure water

b. 250.0 mL of a buffer solution that is 0.195 M in $HCHO_2$ and 0.275 M in $KCHO_2$

c. 250.0 mL of a buffer solution that is 0.255 M in $CH_3CH_2NH_2$ and 0.235 M in $CH_3CH_2NH_3Cl$

49. A 350.0-mL buffer solution is 0.150 M in HF and 0.150 M in NaF. What mass of NaOH does this buffer neutralize before the pH rises above 4.00? If the same volume of the buffer was 0.350 M in HF and 0.350 M in NaF, what mass of NaOH is neutralized before the pH rises above 4.00?

50. A 100.0-mL buffer solution is 0.100 M in NH_3 and 0.125 M in NH_4Br. What mass of HCl does this buffer neutralize before the pH falls below 9.00? If the same volume of the buffer were 0.250 M in NH_3 and 0.400 M in NH_4Br what mass of HCl is neutralized before the pH falls below 9.00?

51. Determine whether the mixing of each pair of solutions results in a buffer.

a. 100.0 mL of 0.10 M NH_3; 100.0 mL of 0.15 M NH_4Cl

b. 50.0 mL of 0.10 M HCl; 35.0 mL of 0.150 M NaOH

c. 50.0 mL of 0.15 M HF; 20.0 mL of 0.15 M NaOH

d. 175.0 mL of 0.10 M NH_3; 150.0 mL of 0.12 M NaOH

e. 125.0 mL of 0.15 M NH_3; 150.0 mL of 0.20 M NaOH

52. Determine whether the mixing of each pair of solutions results in a buffer.

a. 75.0 mL of 0.10 M HF; 55.0 mL of 0.15 M NaF

b. 150.0 mL of 0.10 M HF; 135.0 mL of 0.175 M HCl

c. 165.0 mL of 0.10 M HF; 135.0 mL of 0.050 M KOH

d. 125.0 mL of 0.15 M CH_3NH_2; 120.0 mL of 0.25 M CH_3NH_3Cl

e. 105.0 mL of 0.15 M CH_3NH_2; 95.0 mL of 0.10 M HCl

53. Blood is buffered by carbonic acid and the bicarbonate ion. Normal blood plasma is 0.024 M in HCO_3^- and 0.0012 M H_2CO_3 (pK_{a_1} for H_2CO_3 at body temperature is 6.1).

a. What is the pH of blood plasma?

b. 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)?

c. Given the volume from part b, what mass of NaOH can be neutralized before the pH rises above 7.8?

54. The fluids within cells are buffered by $H_2PO_4^-$ and HPO_4^{2-}.

a. Calculate the ratio of HPO_4^{2-} to $H_2PO_4^-$ required to maintain a pH of 7.1 within a cell.

b. Could a buffer system employing H_3PO_4 as the weak acid and H_2PO_4 as the weak base be used as a buffer system within cells? Explain.

55. Which buffer system is the best choice to create a buffer with pH = 7.20? For the best system, calculate the ratio of the masses of the buffer components required to make the buffer.

$HC_2H_3O_2/KC_2H_3O_2$ $HClO_2/KClO_2$
NH_3/NH_4Cl $HClO/KClO$

56. Which buffer system is the best choice to create a buffer with pH = 9.00? For the best system, calculate the ratio of the masses of the buffer components required to make the buffer.

HF/KF HNO_2/KNO_2
NH_3/NH_4Cl $HClO/KClO$

57. A 500.0-mL buffer solution is 0.100 M in HNO_2 and 0.150 M in KNO_2. Determine whether each addition would exceed the capacity of the buffer to neutralize it.

a. 250.0 mg NaOH

b. 350.0 mg KOH

c. 1.25 g HBr

d. 1.35 g HI

58. A 1.0-L buffer solution is 0.125 M in HNO_2 and 0.145 M in $NaNO_2$. Determine the concentrations of HNO_2 and $NaNO_2$ after the addition of each substance.

a. 1.5 g HCl

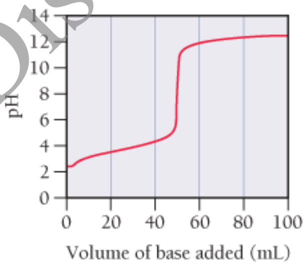
b. 1.5 g NaOH

c. 1.5 g HI

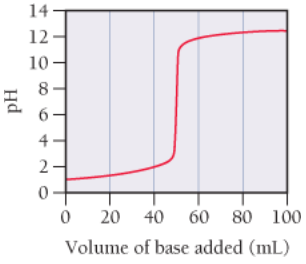
Titrations, pH Curves, and Indicators

59. The graphs labeled (a) and (b) are 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.

a.



b.



i. What is the approximate pH at the equivalence point of each curve?

ii. Which graph corresponds to the titration of the strong acid and which one to the titration of the weak acid?

60. Two 25.0-mL samples, one 0.100 M HCl and the other 0.100 M HF, are titrated with 0.200 M KOH.

a. What is the volume of added base at the equivalence point for each titration?

b. Is the pH at the equivalence point for each titration acidic, basic, or neutral?

c. Which titration curve has the lower initial pH?

d. Sketch each titration curve.

61. Two 20.0-mL samples, one 0.200 M KOH and the other 0.200 M CH_3NH_2, are titrated with 0.100 M HI.

a. What is the volume of added acid at the equivalence point for each titration?

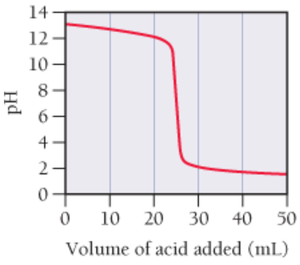
b. Is the pH at the equivalence point for each titration acidic, basic, or neutral?

c. Which titration curve has the lower initial pH?

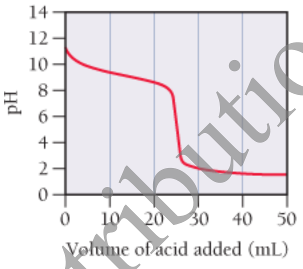
d. Sketch each titration curve.

62. The graphs labeled (a) and (b) are 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.

a.



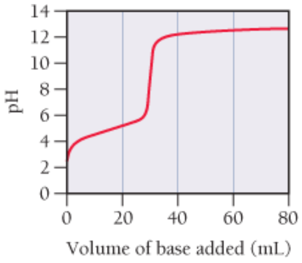
b.



i. What is the approximate pH at the equivalence point of each curve?

ii. Which graph corresponds to the titration of the strong base and which one to the weak base?

63. Consider the curve shown here for the titration of a weak monoprotic acid with a strong base and answer each question.



a. What is the pH, and what is the volume of added base at the equivalence point?

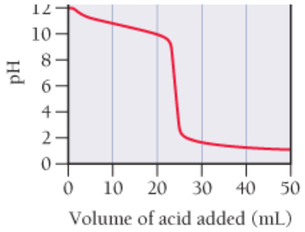
b. At what volume of added base is the pH calculated by working an equilibrium problem based on the initial concentration and K_a of the weak acid?

c. At what volume of added base does $pH = pK_a$?

d. 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?

e. Beyond what volume of added base is the pH calculated by focusing on the amount of excess strong base added?

64. Consider the curve shown here for the titration of a weak base with a strong acid and answer each question.



a. What is the pH, and what is the volume of added acid at the equivalence point?

b. 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?

c. At what volume of added acid does $pH = 14 - pK_b$?

d. 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?

e. Beyond what volume of added acid is the pH calculated by focusing on the amount of excess strong acid added?

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

a. the initial pH

b. the volume of added base required to reach the equivalence point

c. the pH at 10.0 mL of added base

d. the pH at the equivalence point

e. the pH after adding 5.0 mL of base beyond the equivalence point

66. A 20.0-mL sample of 0.125 M HNO_3 is titrated with 0.150 M NaOH. Calculate the pH for at least five different points on the titration curve and sketch the curve. Indicate the volume at the equivalence point on your graph.

67. Consider the titration of a 25.0-mL sample of 0.115 M RbOH with 0.100 M HCl. Determine each quantity.

a. the initial pH

b. the volume of added acid required to reach the equivalence point

c. the pH at 5.0 mL of added acid

d. the pH at the equivalence point

e. the pH after adding 5.0 mL of acid beyond the equivalence point

68. A 15.0-mL sample of 0.100 M $Ba(OH)_2$ is titrated with 0.125 M HCl. Calculate the pH for at least five different points on the titration curve and sketch the curve. Indicate the volume at the equivalence point on your graph.

69. Consider the titration of a 20.0-mL sample of 0.105 M $HC_2H_3O_2$ with 0.125 M NaOH. Determine each quantity.

a. the initial pH

b. the volume of added base required to reach the equivalence point

c. the pH at 5.0 mL of added base

d. the pH at one-half of the equivalence point

e. the pH at the equivalence point

f. the pH after adding 5.0 mL of base beyond the equivalence point

70. 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.

71. Consider the titration of a 25.0-mL sample of 0.175 M CH_3NH_2 with 0.150 M HBr. Determine each quantity.

a. the initial pH

b. the volume of added acid required to reach the equivalence point

c. the pH at 5.0 mL of added acid

d. the pH at one-half of the equivalence point

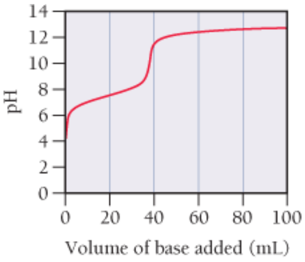
e. the pH at the equivalence point

f. the pH after adding 5.0 mL of acid beyond the equivalence point

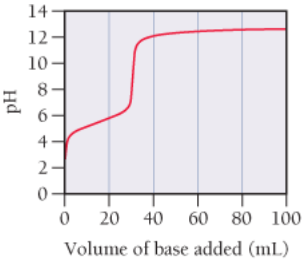
72. A 25.0-mL sample of 0.125 M pyridine is titrated with 0.100 M HCl. Calculate the pH at each volume of added acid: 0 mL, 10 mL, 20 mL, equivalence point, one-half equivalence point, 40 mL, 50 volume of added acid: 0 mL, 10 mL, 20 mL, equivalence point, one-half equivalence point, 40 mL, 50 mL. Sketch the titration curve.

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

a.



b.

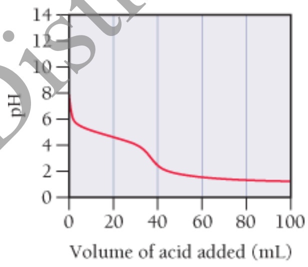


i. Which acid solution is more concentrated?

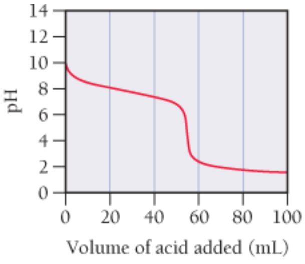
ii. Which acid has the larger K_a

74. Consider the titration curves (labeled a and b) for equal volumes of two weak bases, both titrated with 0.100 M HCl.

a.



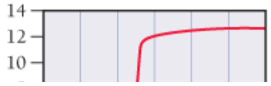
b.

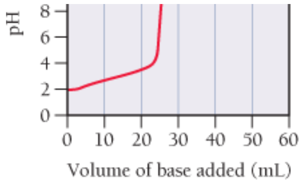


i. Which base solution is more concentrated?

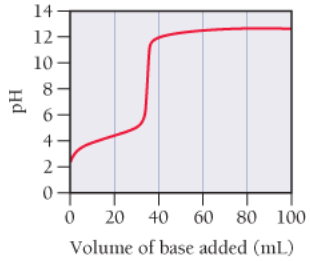
ii. Which base has the larger K_b

75. 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.





76. 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 $\mathrm{p}K_{\mathrm{a}}$ of the acid.



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

78. A 20.0-mL sample of a 0.125 M diprotic acid $\left(H_2A\right)$ 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?

79. Methyl red has a $\mathrm{p}K_{\mathrm{a}}$ 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 does the solution appear? If 0.100 M NaOH is slowly added to the HCl sample, in what pH range will the indicator change color?

80. Phenolphthalein has a $\mathrm{p}K_{\mathrm{a}}$ of 9.7. It is colorless in its acid form and pink in its basic form. For each of the pH values, calculate $\left[\mathrm{In}^-\right]/\left[\mathrm{HIn}\right]$ and predict the color of a phenolphthalein solution.

a. pH = 2.0

b. pH = 5.0

c. pH = 8.0

d. pH = 11.0

81. Referring to **Table 17.1**, pick an indicator for use in the titration of each acid with a strong base.

a. HF

b. HCl

c. HCN

82. Referring to **Table 17.1**, pick an indicator for use in the titration of each base with a strong acid.

a. CH_3NH_2

b. NaOH

c. $C_6H_5NH_2$

Solubility Equilibria

83. Write balanced equations and expressions for K_{sp} for the dissolution of each ionic compound.

a. $BaSO_4$

b. $PbBr_2$

c. Ag_2CrO_4

84. Write balanced equations and expressions for K_{sp} for the dissolution of each ionic compound.

a. $CaCO_3$

b. $PbCl_2$

c. AgI

85. Refer to the K_{sp} values in **Table 17.2** to calculate the molar solubility of each compound in pure water.

a. AgBr

b. $Mg(OH)_2$

c. CaF_2

86. Refer to the K_{sp} values in **Table 17.2** to calculate the molar solubility of each compound in pure water.

a. $MX\left(K_{sp} = 1.27 \times 10^{-36}\right)$

b. Ag_2CrO_4

c. $Ca(OH)_2$

87. Use the given molar solubilities in pure water to calculate K_{sp} for each compound.

a. MX; molar solubility $= 3.27 \times 10^{-11} M$

b. PbF_2; molar solubility $= 5.63 \times 10^{-3} M$

c. MgF_2; molar solubility $= 2.65 \times 10^{-4} M$

88. Use the given molar solubilities in pure water to calculate K_{sp} for each compound.

a. $BaCrO_4$; molar solubility $= 1.08 \times 10^{-5} M$

b. Ag_2SO_3; molar solubility $= 1.55 \times 10^{-5} M$

c. $Pd(SCN)_2$molar solubility $= 2.22 \times 10^{-8} M$

89. 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?

90. 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}

a. AX; molar solubility $= 1.35 \times 10^{-4} M$

b. AX_2; molar solubility $= 2.25 \times 10^{-4} M$

c. A_2X; molar solubility $= 1.75 \times 10^{-4} M$

91. Refer to the K_{sp} value from **Table 17.2** to calculate the solubility of iron(II) hydroxide in pure water in grams per 100.0 mL of solution.

92. The solubility of copper(I) chloride is 3.91 mg per 100.0 mL of solution. Calculate K_{sp} for CuCl.

93. Calculate the molar solubility of barium fluoride in each liquid or solution.

a. pure water

b. $0.10 M Ba\left(NO_3\right)_2$

c. 0.15 M NaF

94. Calculate the molar solubility of MX $\left(K_{sp} = 1.27 \times 10^{-36}\right)$ in each liquid or solution.

a. pure water

b. $0.25 M\ MCl_2$

c. $0.20 M Na_2X$

95. Calculate the molar solubility of calcium hydroxide in a solution buffered at each pH.

a. pH = 4

b. pH = 7

c. pH = 9

96. Calculate the solubility (in grams per 1.00×10^2 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?

97. Is each compound more soluble in acidic solution or in pure water? Explain.

a. $BaCO_3$

b. CuS

c. AgCl

d. PbI_2

98. Is each compound more soluble in acidic solution or in pure water? Explain.

a. Hg_2Br_2

b. $Mg(OH)_2$

c. $CaCO_3$

d. AgI

Precipitation

99. 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 $Ca\left(NO_3\right)_2$. Does a precipitate form in the mixed solution? If so, identify the precipitate.

100. 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 $Pb\left(C_2H_3O_2\right)_2$. Does a precipitate form in the mixed solution? If so, identify the precipitate.

solution? If so, identify the precipitate.

101. Predict whether a precipitate forms 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.

102. Predict whether a precipitate forms 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.

103. 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.

a. $0.015 M CaCl_2$

b. $0.0025 M Fe(NO_3)_2$

c. $0.0018 M\ MgBr_2$

104. Determine the minimum concentration of the precipitating agent on the right you need to cause precipitation of the cation from the solution on the left.

a. $0.035 M\ Ba(NO_3)_2$; NaF

b. $0.085 M\ CaI_2$; K_2SO_4

c. $0.0018 M\ AgNO_3$; RbCl

105. A solution is 0.010 M in Ba^{2+} and 0.020 M in Ca^{2+}.

a. If sodium sulfate is used to selectively precipitate one of the cations while leaving the other cation in solution, which cation precipitates first? What minimum concentration of Na_2SO_4 will trigger the precipitation of the cation that precipitates first?

b. What is the remaining concentration of the cation that precipitates first, when the other cation begins to precipitate?

106. A solution is 0.022 M in Fe^{2+} and 0.014 M in Mg^{2+}.

a. If potassium carbonate is used to selectively precipitate one of the cations while leaving the other cation in solution, which cation precipitates first? What minimum concentration of K_2CO_3 will trigger the precipitation of the cation that precipitates first?

b. What is the remaining concentration of the cation that precipitates first, when the other cation begins to precipitate?

Complex Ion Equilibria

107. A solution is made $1.1 \times 10^{-3} M$ in $Zn(NO_3)_2$ and 0.150 M in NH_3 After the solution reaches equilibrium, what concentration of $Zn^{2+}(aq)$ remains?

108. 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?

109. Use the appropriate values of K_{sp} and K_f to find the equilibrium constant for the reaction:

$$FeS(s) + 6\ CN^{-}(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq) + S^{2-}(aq)$$

110. Use the appropriate values of K_{sp} and K_f to find the equilibrium constant for the reaction:

$$PbCl_2(s) + 3OH^{-}(aq) \rightleftharpoons Pb(OH)_3^{-}(aq) + 2Cl^{-}(aq)$$

Cumulative Problems

111. 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.

112. 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.

113. A buffer is created by combining 150.0 mL of 0.25 M $HCHO_2$ with 75.0 mL of 0.20 M NaOH. Determine the pH of the buffer.

114. A buffer is created by combining 3.55 g of NH_3 with 4.78 g of HCl and diluting to a total volume of 750.0 mL. Determine the pH of the buffer.

115. A 1.0-L buffer solution initially contains 0.25 mol of NH_3 and 0.25 mol of NH_4Cl 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?

116. A 250.0-mL buffer solution initially contains 0.025 mol of $HCHO_2$ and 0.025 mol of $NaCHO_2$. 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?

117. 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 $\left(KHC_8H_4O_4\right)$, also known as KHP, with the NaOH solution to be standardized.

a. Write an equation for the reaction between NaOH and KHP.

b. 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?

118. A 0.5224-g sample of an unknown monoprotic acid was titrated with 0.0998 M NaOH. The equivalence point of the titration occurs at 23.82 mL. Determine the molar mass of the unknown acid.

119. A 0.25-mol sample of a weak acid with an unknown pK_a is combined with 10.0 mL of 3.00 M KOH, and the resulting solution is diluted to 1.500 L. The measured pH of the solution is 3.85. What is the pK_a of the weak acid?

120. A 5.55-g sample of a weak acid with $K_a = 1.3 \times 10^{-4}$ is combined with 5.00 mL of 6.00 M NaOH, and the resulting solution is diluted to 750 mL. The measured pH of the solution is 4.25. What is the molar mass of the weak acid?

121. A 0.552-g sample of ascorbic acid (vitamin C) is dissolved in water to a total volume of 20.0 mL and titrated with 0.1103 M KOH. The equivalence point occurs 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.

122. Sketch the titration curve from **Problem 121** 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 17.1**.

123. One of the main components of hard water is $CaCO_3$ When hard water evaporates, some of the $CaCO_3$ 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 1.00×10^2 mg of $CaCO_3$

124. Gout—a condition that results in joint swelling and pain—is caused by the formation of sodium urate $\left(NaC_5H_3N_4O_3\right)$ crystals within tendons, cartilage, and ligaments. Sodium urate precipitates out of blood plasma when uric acid levels become abnormally high. This can happen 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_{sp} for sodium urate is 5.76×10^{-8}, what minimum concentration of urate results in precipitation?

125. Pseudogout, a condition with symptoms similar to those of gout (see Problem 124), is caused by the formation of calcium diphosphate $\left(Ca_3P_2O_7\right)$ crystals within tendons, cartilage, and ligaments. Calcium diphosphate precipitates out of blood plasma when diphosphate levels become abnormally high. If the calcium concentration in blood plasma is $9.2 mg/dL$ and K_{sp} for calcium diphosphate is 8.64×10^{-13}, what minimum concentration of diphosphate results in precipitation?

126. Calculate the solubility of silver chloride in a solution that is 0.100 M in NH_3.

127. Calculate the solubility of CuX in a solution that is 0.150 M in NaCN. K_{sp} for CuX is 1.27×10^{-36}.

128. Aniline, $C_6H_5NH_2$, 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 $C_6H_5NH_3^+$ (aniline's conjugate acid, the anilinium ion) below 1.0×10^{-9} in a solution that is 0.10 M in aniline. Find the concentration of NaOH required for this process.

129. The K_b of hydroxylamine, NH_2OH is 1.0×10^{-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.

130. 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.

131. 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.

132. Determine the mass of sodium formate that must be dissolved in $250.0 cm^3$ of a 1.4 M solution of formic acid to prepare a buffer solution with $pH = 3.36$.

133. What relative masses of dimethyl amine and dimethyl ammonium chloride do you need to prepare a buffer solution of $pH = 10.43$?

134. You are asked to prepare 2.0 L of a HCN/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.)

135. 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 $-2.0\ °C$? (Assume complete dissociation of sodium benzoate and a density of 1.01 g/mL for the solution.)

Challenge Problems

136. 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.

137. Soap and detergent action is hindered by hard water so that 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 $CaCO_3$ and 55 ppm $MgCO_3$ (by mass). What mass of Na_2CO_3 is required to remove 90.0% of these ions from 10.0 L of laundry water?

138. 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.

a. 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.

b. The pH after adding 25.0 mL of the base is 3.82. Find the value of K_{a_1}.

c. The pH after adding 20.0 mL past the first equivalence point is 8.25. Find the value of K_{a_2}.

139. 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 $Mg(OH)_2$.

140. 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 $\left[H^+\right] = 3.2 \times 10^{-11} M$? There is no significant volume change as the result of adding the solid.

141. Calculate the solubility of $Au(OH)_3$ in (a) water and (b) 1.0 M nitric acid solution $\left(K_{sp} = 5.5 \times 10^{-46}\right)$
.

142. Calculate the concentration of I^- in a solution obtained by shaking 0.10 M KI with an excess of AgCl(s).

143. 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?

144. Find the solubility of CuI in 0.40 M HCN solution. The K_{sp} of CuI is 1.1×10^{-12}, and the K_f for the $Cu(CN)_2^-$ complex ion is 1×10^{24}.

145. 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 3×10^{-15}, and the K_f of $Zn(OH)_4^{2-}$ is 2×10^{15}.

146. 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

147. Without doing any calculations, determine if $pH = pK_a$, $pH > pK_a$, or $pH < pK_a$. Assume that HA is a weak monoprotic acid.

a. 0.10 mol HA and 0.050 mol of A^- in 1.0 L of solution

b. 0.10 mol HA and 0.150 mol of A^- in 1.0 L of solution

c. 0.10 mol HA and 0.050 mol of OH^- in 1.0 L of solution

d. 0.10 mol HA and 0.075 mol of OH^- in 1.0 L of solution

148. 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.

a. adding 0.020 mol of NaOH

b. adding 0.020 mol of HCl
c. adding 0.10 mol of NaOH
d. adding 0.010 mol of HCl

149. Consider three solutions:
i. 0.10 M solution of a weak monoprotic acid
ii. 0.10 M solution of strong monoprotic acid
iii. 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?

a. the volume required to reach the final equivalence point
b. the volume required to reach the first equivalence point
c. the pH at the first equivalence point
d. the pH at one-half the first equivalence point

150. Equal volumes of two monoprotic acid solutions (A and B) are titrated with identical NaOH solutions. The volume needed 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?

a. The acid in solution A is more concentrated than in solution B and is also a stronger acid than that in solution B.
b. The acid in solution A is less concentrated than in solution B and is also a weaker acid than that in solution B.
c. The acid in solution A is more concentrated than in solution B and is also a weaker acid than that in solution B.
d. The acid in solution A is less concentrated than in solution B and is also a stronger acid than that in solution B.

151. Describe the solubility of CaF_2 in each solution compared to its solubility in water.

a. in a 0.10 M NaCl solution
b. in a 0.10 M NaF solution
c. in a 0.10 M HCl solution

Questions for Group Work

Active Classroom Learning

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

152. Name a compound that you could add to a solution of each of the following compounds to make a buffer. Explain your reasoning in complete sentences.

a. acetic acid
b. sodium nitrite
c. ammonia
d. potassium formate
e. Na_2HPO_4 (two possible answers)

153. Derive the Henderson–Hasselbalch equation as a group. Take turns having each group member write and explain the next step in the derivation.

154. With group members acting as atoms or ions, act out the reaction that occurs when HCl is added to a buffer solution composed of $HC_2H_3O_2$ and $NaC_2H_3O_2$. 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.

155. A certain town gets its water from an underground aquifer that contains water in equilibrium with calcium carbonate limestone.

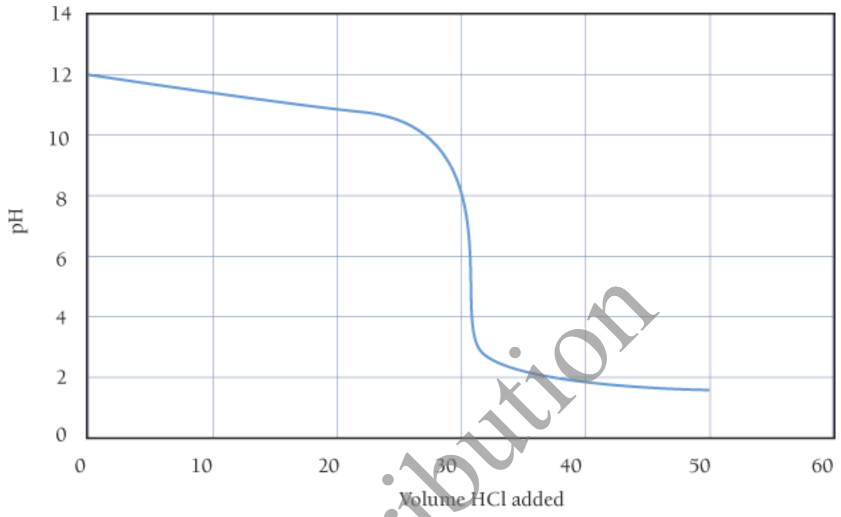
a. What is the symbol for the equilibrium constant that describes calcium carbonate dissolving in water? What is the numerical value?
b. Calculate the molar solubility of calcium carbonate.
c. If you were a resident of this town and an entire coffee cup of water (about 200 mL) evaporated on your desk over spring break, how many grams of calcium carbonate would be left behind?
d. If you wanted to clean out your coffee cup, would it be better to use an acidic or a basic cleaning

solution? Why?

156. Have each group member look up the K_{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 8, and have each group member present his or her findings to the group.

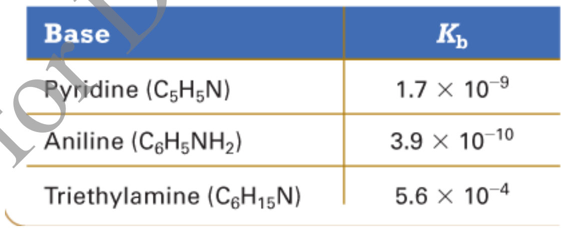
Data Interpretation and Analysis

157. 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.



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

Possible Bases in Sample



Base	K_b
Pyridine (C_5H_5N)	1.7×10^{-9}
Aniline ($C_6H_5NH_2$)	3.9×10^{-10}
Triethylamine ($C_6H_{15}N$)	5.6×10^{-4}

a. What is the volume of added HCl at the equivalence point?
b. What is the pH at the half-equivalence point?
c. What is the molar mass of the unknown base?
d. What are the pK_b and K_b of the unknown base?
e. What is the most likely identity of the unknown base?

Answers to Conceptual Connections

Cc 17.1 **(d)** Only this solution contains significant amounts of a weak acid and its conjugate base. (Remember that HNO_3 is a strong acid, but HNO_2 is a weak acid.)

Cc 17.2 **(a)** Since the pH of the buffer is less than the pK_a of the acid, the buffer must contain more acid than base ($[HA] > [A^-]$). In order to raise the pH of the buffer from 4.25 to 4.72, you must add more of the weak base (adding a base will make the buffer solution more basic).

Cc 17.3 (a) Because one HA molecule is converted to one ion of the conjugate base (A^- ion), one OH^- ion was added to the buffer solution.

Cc 17.4 **(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.

Cc 17.5 **(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.

Cc 17.6 **(d)** Because the flask contains 7 H^+ ions, the equivalence point is reached when 7 OH^- ions have been added.

Cc 17.7 Acid A is more concentrated (it took more NaOH to reach the equivalence point), and acid B has the larger K_a(pK_a is smaller so K_a is larger).

Cc 17.8 **(c)** The pH at the half-equivalence point is the pK_a of the conjugate acid, which is equal to

$14.00 - 8.75 = 5.25$.

Cc 17.9 **(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.

Cc 17.10 **(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.

Cc 17.11 **(c)** Only NaCN contains an anion $\left(CN^-\right)$ that forms a complex ion with Cu^{2+} [from **Table 17.3** we can see that $K_f = 1.0 \times 10^{25}$ for $Cu(CN)_4^{2-}$]. Therefore, the presence of CN^- will drive the dissolution reaction of CuS.