AP

Txt. 75, 81a, 123, 125, 128 and 92

Pyrrolidine

Polyprotic Acids

7. Write out the stepwise K_a reactions for the diprotic acid H_2SO_3.
8. Write out the stepwise K_a reactions for citric acid ($H_3C_6H_5O_7$), a triprotic acid.
9. Using the K_a values in Table 14.4 and only the first dissociation step, calculate the pH of 0.10 M solutions of each of the following polyprotic acids.
   a. H_3PO_4 b. H_2CO_3
10. Arsenic acid (H_3AsO_4) is a triprotic acid with $K_{a_1} = 5 \times 10^{-3}$, $K_{a_2} = 8 \times 10^{-8}$, and $K_{a_3} = 6 \times 10^{-10}$. Calculate $[H^+]$, $[OH^-]$, $[H_3AsO_4]$, $[H_2AsO_4^-]$, $[HAsO_4^{2-}]$, and $[AsO_4^{3-}]$ in a 0.20 M arsenic acid solution.
11. Calculate the pH of a 2.0 M H_2SO_4 solution.
12. Calculate the pH of a 5.0×10^{-3} M solution of H_2SO_4.

Acid-Base Properties of Salts

13. Arrange the following 0.10 M solutions in order of most acidic to most basic.

KOH, KCl, KCN, NH_4Cl, HCl

14. Arrange the following 0.10 M solutions in order of most acidic to most basic.

$Ca(NO_3)_2$, $NaNO_2$, HNO_3, NH_4NO_3, $Ca(OH)_2$

15. Given that the K_a value for acetic acid is 1.8×10^{-5} and the K_a value for hypochlorous acid is 3.5×10^{-8}, which is the stronger base, OCl^- or $C_2H_3O_2^-$?
16. The K_b values for ammonia and methylamine are 1.8×10^{-5} and 4.4×10^{-4}, respectively. Which is the stronger acid, NH_4^+ or $CH_3NH_3^+$?
17. Sodium azide (NaN_3) is sometimes added to water to kill bacteria. Calculate the concentration of all species in a 0.010 M solution of NaN_3. The K_a value for hydrazoic acid (HN_3) is 1.9×10^{-5}.
18. Calculate the concentrations of all species present in a 0.25 M solution of ethylammonium chloride ($C_2H_5NH_3Cl$).
19. Calculate the pH of each of the following solutions.
    a. 0.10 M CH_3NH_3Cl b. 0.050 M NaCN
20. Calculate the pH of each of the following solutions.
    a. 0.12 M KNO_2 c. 0.40 M NH_4ClO_4
    b. 0.45 M NaOCl
21. An unknown salt is either NaCN, $NaC_2H_3O_2$, NaF, NaCl, or NaOCl. When 0.100 mol of the salt is dissolved in 1.00 L of water, the pH of the solution is 8.07. What is the identity of the salt?
22. Consider a solution of an unknown salt having the general formula BHCl, where B is one of the weak bases in Table 14.3. A 0.10 M solution of the unknown salt has a pH of 5.82. What is the actual formula of the salt?
23. Calculate the pH of a 0.050 M $Al(NO_3)_3$ solution. The K_a value for $Al(H_2O)_6^{3+}$ is 1.4×10^{-5}.
24. Calculate the pH of a 0.10 M $CoCl_3$ solution. The K_a value for $Co(H_2O)_6^{3+}$ is 1.0×10^{-5}.
25. Are solutions of the following salts acidic, basic, or neutral? For those that are not neutral, write balanced chemical equations for the reactions causing the solution to be acidic or basic. The relevant K_a and K_b values are found in Tables 14.2 and 14.3.
    a. $NaNO_3$ c. $C_5H_5NHClO_4$ e. KOCl
    b. $NaNO_2$ d. NH_4NO_2 f. NH_4OCl
26. Are solutions of the following salts acidic, basic, or neutral? For those that are not neutral, write balanced equations for the reactions causing the solution to be acidic or basic. The relevant K_a and K_b values are found in Tables 14.2 and 14.3.
    a. KCl c. CH_3NH_3Cl e. NH_4F
    b. $NH_4C_2H_3O_2$ d. KF f. CH_3NH_3CN

Relationships Between Structure and Strengths of Acids and Bases

27. Place the species in each of the following groups in order of increasing acid strength. Explain the order you chose for each group.
    a. HIO_3, $HBrO_3$ c. HOCl, HOI
    b. HNO_2, HNO_3 d. H_3PO_4, H_3PO_3
28. Place the species in each of the following groups in order of increasing base strength. Give your reasoning in each case.
    a. IO_3^-, BrO_3^- b. NO_2^-, NO_3^- c. OCl^-, OI^-
29. Place the species in each of the following groups in order of increasing acid strength.
    a. H_2O, H_2S, H_2Se (bond energies: H—O, 467 kJ/mol; H—S, 363 kJ/mol; H—Se, 276 kJ/mol)
    b. CH_3CO_2H, FCH_2CO_2H, F_2CHCO_2H, F_3CCO_2H
    c. NH_4^+, $HONH_3^+$
    d. NH_4^+, PH_4^+(bond energies: N—H, 391 kJ/mol; P—H, 322 kJ/mol)

    Give reasons for the orders you chose.
30. Using your results from Exercise 119, place the species in each of the following groups in order of increasing base strength.
    a. OH^-, SH^-, SeH^- b. NH_3, PH_3 c. NH_3, $HONH_2$
31. Will the following oxides give acidic, basic, or neutral solutions when dissolved in water? Write reactions to justify your answers.
    a. CaO b. SO_2 c. Cl_2O

32. Will the following oxides give acidic, basic, or neutral solutions when dissolved in water? Write reactions to justify your answers.
    a. Li_2O b. CO_2 c. SrO

Lewis Acids and Bases

33. Identify the Lewis acid and the Lewis base in each of the following reactions.
    a. $B(OH)_3(aq) + H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq)$
    b. $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
    c. $BF_3(g) + F^-(aq) \rightleftharpoons BF_4^-(aq)$
34. Identify the Lewis acid and the Lewis base in each of the following reactions.
    a. $Fe^{3+}(aq) + 6H_2O(l) \rightleftharpoons Fe(H_2O)_6^{3+}(aq)$
    b. $H_2O(l) + CN^-(aq) \rightleftharpoons HCN(aq) + OH^-(aq)$
    c. $HgI_2(s) + 2I^-(aq) \rightleftharpoons HgI_4^{2-}(aq)$
35. Aluminum hydroxide is an amphoteric substance. It can act as either a Brønsted–Lowry base or a Lewis acid. Write a reaction showing $Al(OH)_3$ acting as a base toward H^+ and as an acid toward OH^-.
36. Zinc hydroxide is an amphoteric substance. Write equations that describe $Zn(OH)_2$ acting as a Brønsted–Lowry base toward H^+ and as a Lewis acid toward OH^-.
37. Would you expect Fe^{3+} or Fe^{2+} to be the stronger Lewis acid? Explain.
38. Use the Lewis acid–base model to explain the following reaction.

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$

Additional Exercises

39. A 10.0-mL sample of an HCl solution has a pH of 2.000. What volume of water must be added in order to change the pH to 4.000?
40. Thallium(I) hydroxide is a strong base used in the synthesis of some organic compounds. Calculate the pH of a solution containing 2.48 g TlOH per liter.
41. Derive an expression for the relationship between pK_a and pK_b for a conjugate acid–base pair. ($pK = -\log K$.)
42. At 25°C, a saturated solution of benzoic acid ($K_a = 6.4 \times 10^{-5}$) has a pH of 2.80. Calculate the water solubility of benzoic acid in moles per liter.
43. Quinine ($C_{20}H_{24}N_2O_2$) is an important alkaloid derived from cinchona bark. It is used as an antimalarial drug. For quinine $pK_{b_1} = 5.1$ and $pK_{b_2} = 9.7$ ($pK_b = -\log K_b$). One gram of quinine will dissolve in 1900.0 mL of water. Calculate the pH of a saturated aqueous solution of quinine. Consider only the aqueous reaction $Q + H_2O \rightleftharpoons QH^+ + QH^-$ described by pK_{b_1} where Q = quinine.
44. Phosphoric acid is a common ingredient in traditional cola drinks. It is added to provide the drinks with a pleasantly tart taste. Although phosphoric acid is a triprotic acid, its protons are lost one at a time. Assuming that in cola drinks the concentration of phosphoric acid is 0.007 M, calculate the pH of this solution.
45. Acrylic acid ($CH_2{=}CHCO_2H$) is a precursor for many important plastics. K_a for acrylic acid is 5.6×10^{-5}.
    a. Calculate the pH of a 0.10 M solution of acrylic acid.
    b. Calculate the percent dissociation of a 0.10 M solution of acrylic acid.
    c. Calculate the pH of a 0.050 M solution of sodium acrylate ($NaC_3H_3O_2$).
46. A 0.20 M sodium chlorobenzoate ($NaC_7H_4ClO_2$) solution has a pH of 8.65. Calculate the pH of a 0.20 M chlorobenzoic acid ($HC_7H_4ClO_2$) solution.
47. The equilibrium constant K_a for the reaction

$$Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Fe(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$$

    is 6.0×10^{-3}.
    a. Calculate the pH of a 0.10 M solution of $Fe(H_2O)_6^{3+}$.
    b. Will a 1.0 M solution of iron(II) nitrate have a higher or lower pH than a 1.0 M solution of iron(III) nitrate? Explain.
48. Rank the following 0.10 M solutions in order of increasing pH.
    a. HI, HF, NaF, NaI
    b. NH_4Br, HBr, KBr, NH_3
    c. $C_6H_5NH_3NO_3$, $NaNO_3$, NaOH, HOC_6H_5, KOC$_6$H$_5$, $C_6H_5NH_2$, HNO_3
49. Is an aqueous solution of $NaHSO_4$ acidic, basic, or neutral? What reaction occurs with water? Calculate the pH of a 0.10 M solution of $NaHSO_4$.
50. Calculate $[CO_3^{2-}]$ in a 0.010 M solution of CO_2 in water (H_2CO_3). If all the CO_3^{2-} in this solution comes from the reaction

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

    what percent of the H^+ ions in the solution are a result of the dissociation of HCO_3^-? When acid is added to a solution of sodium hydrogen carbonate ($NaHCO_3$), vigorous bubbling occurs. How is this reaction related to the existence of carbonic acid (H_2CO_3) molecules in aqueous solution?
51. Hemoglobin (abbreviated Hb) is a protein that is responsible for the transport of oxygen in the blood of mammals. A hemoglobin molecule contains four iron atoms that are binding sites for O_2 molecules. The oxygen binding is pH dependent. The relevant equilibrium reaction is

$$HbH_4^{4+}(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq) + 4H^+(aq)$$

    Use Le Châtelier's principle to answer the following.
    a. What form of hemoglobin, HbH_4^{4+} or $Hb(O_2)_4$, is favored in the lungs? What form is favored in the cells?

67. For propanoic acid ($HC_3H_5O_2$, $K_a = 1.3 \times 10^{-5}$), calculate the $[H^+]$, pH, and percent dissociation of a 0.10 *M* solution.
68. Calculate the percent dissociation for a 0.22 *M* solution of chlorous acid ($HClO_2$, $K_a = 1.2 \times 10^{-2}$).

69. A 0.15 *M* solution of a weak acid is 3.0% dissociated. Calculate K_a.
70. In a 0.100 *M* solution of HF, the percent dissociation is 8.1%. Calculate K_a.

71. The pH of a 0.063 *M* solution of hypobromous acid (HOBr but usually written HBrO) is 4.95. Calculate K_a.
72. Trichloroacetic acid (CCl_3CO_2H) is a corrosive acid that is used to precipitate proteins. The pH of a 0.050 *M* solution of trichloroacetic acid is the same as the pH of a 0.040 *M* $HClO_4$ solution. Calculate K_a for trichloroacetic acid.

73. A solution of formic acid (HCOOH, $K_a = 1.8 \times 10^{-4}$) has a pH of 2.70. Calculate the initial concentration of formic acid in this solution.
74. One mole of a weak acid HA was dissolved in 2.0 L of water. After the system had come to equilibrium, the concentration of HA was found to be 0.45 *M*. Calculate K_a for HA.

Solutions of Bases

75. Write the reaction and the corresponding K_b equilibrium expression for each of the following substances acting as bases in water.
a. NH_3 b. C_5H_5N
76. Write the reaction and the corresponding K_b equilibrium expression for each of the following substances acting as bases in water.
a. aniline, $C_6H_5NH_2$ b. dimethylamine, $(CH_3)_2NH$

77. Use Table 14.3 to help order the following bases from strongest to weakest.

$$NO_3^-, \quad H_2O, \quad NH_3, \quad C_5H_5N$$

78. Use Table 14.3 to help order the following acids from strongest to weakest.

$$HNO_3, \quad H_2O, \quad NH_4^+, \quad C_5H_5NH^+$$

79. Use Table 14.3 to help answer the following questions.
a. Which is the stronger base, NO_3^- or NH_3?
b. Which is the stronger base, H_2O or NH_3?
c. Which is the stronger base, OH^- or NH_3?
d. Which is the stronger base, NH_3 or CH_3NH_2?
80. Use Table 14.3 to help answer the following questions.
a. Which is the stronger acid, HNO_3 or NH_4^+?
b. Which is the stronger acid, H_2O or NH_4^+?
c. Which is the stronger acid, NH_4^+ or $CH_3NH_3^+$?

81. Calculate the pH of the following solutions.
a. 0.10 *M* NaOH c. 2.0 *M* NaOH
b. 1.0×10^{-10} *M* NaOH

82. Calculate the pH of the following solutions.
a. 0.0062 *M* $Sr(OH)_2$
b. 0.75 *M* $Sr(OH)_2$
c. 5.0×10^{-10} *M* $Sr(OH)_2$

83. What are the major species present in 0.150 M solution of each of the following bases?
a. KOH b. $Ca(OH)_2$
What is $[OH^-]$ and the pH of each of these solutions?
84. What are the major species present in the following mixtures of bases?
a. 0.050 *M* NaOH and 0.050 *M* LiOH
b. 0.0010 *M* $Ba(OH)_2$ and 0.020 *M* RbOH
What is $[OH^-]$ and the pH of each of these solutions?

85. Calculate the concentration of an aqueous KOH solution that has pH = 10.50.
86. Calculate the concentration of an aqueous $Ba(OH)_2$ that has pH = 10.50.

87. What are the major species present in a 0.150 *M* NH_3 solution? Calculate the $[OH^-]$ and the pH of this solution.
88. For the reaction of hydrazine (N_2H_4) in water,

$$H_2NNH_2(aq) + H_2O(l) \rightleftharpoons H_2NNH_3^+(aq) + OH^-(aq)$$

K_b is 3.0×10^{-6}. Calculate the concentrations of all species and the pH of a 2.0 *M* solution of hydrazine in water.

89. Calculate $[OH^-]$, $[H^+]$, and the pH of 0.20 *M* solutions of each of the following amines.
a. Triethylamine $[(C_2H_5)_3N$, $K_b = 4.0 \times 10^{-4}]$
b. Hydroxylamine ($HONH_2$, $K_b = 1.1 \times 10^{-8}$)
90. Calculate $[OH^-]$, $[H^+]$, and the pH of 0.20 *M* solutions of each of the following amines (the K_b values are found in Table 14.3).
a. Aniline b. Pyridine

91. Calculate the pH of a 0.20 *M* $C_2H_5NH_2$ solution ($K_b = 5.6 \times 10^{-4}$).
92. Calculate the pH of a 0.050 *M* $(C_2H_5)_2NH$ solution ($K_b = 1.3 \times 10^{-3}$).

93. Calculate the percent ionization in each of the following solutions.
a. 0.10 *M* NH_3 b. 0.010 *M* NH_3
94. Calculate the percent ionization in each of the following solutions (see Table 14.3 for K_b values).
a. 0.10 *M* hydroxylamine ($HONH_2$, $K_b = 1.1 \times 10^{-8}$)
b. 0.10 *M* methylamine (CH_3NH_2)

95. Codeine ($C_{18}H_{21}NO_3$) is a derivative of morphine that is used as an analgesic, narcotic, or antitussive. It was once commonly used in cough syrups but is now available only by prescription because of its addictive properties. If the pH of a 1.7×10^{-3} *M* solution of codeine is 9.59, calculate K_b.
96. The pH of a 1.00×10^{-3} *M* solution of pyrrolidine is 10.63. Calculate K_b.