14.9 131 — 141 odd

c. $C_5H_5NHClO_4 \rightarrow C_5H_5NH^+ + ClO_4^-$ acidic; $C_5H_5NH^+$ is a weak acid, and ClO_4^- has no effect on pH.

$$C_5H_5NH^+ \rightleftharpoons H^+ + C_5H_5N \quad K_a = \frac{K_w}{K_{b,\,C_5H_5N}} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}$$

d. $NH_4NO_2 \rightarrow NH_4^+ + NO_2^-$ acidic; NH_4^+ is a weak acid ($K_a = 5.6 \times 10^{-10}$), and NO_2^- is a weak base ($K_b = 2.5 \times 10^{-11}$). Because $K_{a,\,NH_4^+} > K_{b,\,NO_2^-}$, the solution is acidic.

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \quad K_a = 5.6 \times 10^{-10}; \quad NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^- \quad K_b = 2.5 \times 10^{-11}$$

e. $KOCl \rightarrow K^+ + OCl^-$ basic; OCl^- is a weak base, and K^+ has no effect on pH.

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \quad K_b = \frac{K_w}{K_{a,\,HOCl}} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.9 \times 10^{-7}$$

f. $NH_4OCl \rightarrow NH_4^+ + OCl^-$ basic; NH_4^+ is a weak acid, and OCl^- is a weak base. Because $K_{b,\,OCl^-} > K_{a,\,NH_4^+}$, the solution is basic.

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \quad K_a = 5.6 \times 10^{-10}; \quad OCl^- + H_2O \rightleftharpoons HOCl + OH^- \quad K_b = 2.9 \times 10^{-7}$$

Relationships Between Structure and Strengths of Acids and Bases

131. a. $HIO_3 < HBrO_3$; as the electronegativity of the central atom increases, acid strength increases.

b. $HNO_2 < HNO_3$; as the number of oxygen atoms attached to the central nitrogen atom increases, acid strength increases.

c. $HOI < HOCl$; same reasoning as in a.

d. $H_3PO_3 < H_3PO_4$; same reasoning as in b.

133. a. $H_2O < H_2S < H_2Se$; as the strength of the H–X bond decreases, acid strength increases.

b. $CH_3CO_2H < FCH_2CO_2H < F_2CHCO_2H < F_3CCO_2H$; as the electronegativity of neighboring atoms increases, acid strength increases.

c. $NH_4^+ < HONH_3^+$; same reason as in b.

d. $NH_4^+ < PH_4^+$; same reason as in a.

135. In general, metal oxides form basic solutions when dissolved in water, and nonmetal oxides form acidic solutions in water.

a. Basic; $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$; $Ca(OH)_2$ is a strong base.

b. Acidic; $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$; H_2SO_3 is a weak diprotic acid.

c. Acidic; $Cl_2O(g) + H_2O(l) \rightarrow 2\ HOCl(aq)$; HOCl is a weak acid.

Lewis Acids and Bases

137. A Lewis base is an electron pair donor, and a Lewis acid is an electron pair acceptor.

a. $B(OH)_3$, acid; H_2O, base   b. Ag^+, acid; NH_3, base   c. BF_3, acid; F^-, base

139. $Al(OH)_3(s) + 3\ H^+(aq) \rightarrow Al^{3+}(aq) + 3\ H_2O(l)$ (Brønsted-Lowry base, H^+ acceptor)

$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$ (Lewis acid, electron pair acceptor)

141. Fe^{3+} should be the stronger Lewis acid. Fe^{3+} is smaller and has a greater positive charge. Because of this, Fe^{3+} will be more strongly attracted to lone pairs of electrons as compared to Fe^{2+}.

Additional Exercises

143. At pH = 2.000, $[H^+] = 10^{-2.000} = 1.00 \times 10^{-2}\ M$

At pH = 4.000, $[H^+] = 10^{-4.000} = 1.00 \times 10^{-4}\ M$

Moles H^+ present $= 0.0100\ L \times \dfrac{0.0100\ mol\ H^+}{L} = 1.00 \times 10^{-4}\ mol\ H^+$

Let V = total volume of solution at pH = 4.000:

$$1.00 \times 10^{-4}\ mol/L = \frac{1.00 \times 10^{-4}\ mol\ H^+}{V},\ V = 1.00\ L$$

Volume of water added = 1.00 L – 0.0100 L = 0.99 L = 990 mL

145. The light bulb is bright because a strong electrolyte is present; that is, a solute is present that dissolves to produce a lot of ions in solution. The pH meter value of 4.6 indicates that a weak acid is present. (If a strong acid were present, the pH would be close to zero.) Of the possible substances, only HCl (strong acid), NaOH (strong base), and NH_4Cl are strong electrolytes. Of these three substances, only NH_4Cl contains a weak acid (the HCl solution would have a pH close to zero, and the NaOH solution would have a pH close to 14.0). NH_4Cl dissociates into NH_4^+ and Cl^- ions when dissolved in water. Cl^- is the conjugate base of a strong acid, so it has no basic (or acidic properties) in water. NH_4^+, however, is the conjugate acid of the weak base NH_3, so NH_4^+ is a weak acid and would produce a solution with a pH = 4.6 when the concentration is ~1.0 *M*. NH_4Cl is the solute.

147. a. In the lungs there is a lot of O_2, and the equilibrium favors $Hb(O_2)_4$. In the cells there is a lower concentration of O_2, and the equilibrium favors HbH_4^{4+}.

b. CO_2 is a weak acid, $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$. Removing CO_2 essentially decreases H^+, which causes the hemoglobin reaction to shift right. $Hb(O_2)_4$ is then favored, and O_2 is not released by hemoglobin in the cells. Breathing into a paper bag increases CO_2 in the blood, thus increasing $[H^+]$, which shifts the hemoglobin reaction left.