Suggested Problems: Chapter 14

14.1: The easiest reaction to see is NH_3 as the conjugate base of the acid NH_4^+; thus

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

To act as the conjugate acid, NH_3 must have one more proton that its base, which, then, is NH_2^-; thus

$$NH_2^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_3(aq)$$

14.7: A conjugate acid always has one more proton than its conjugate base; thus, the conjugate acids are (a) H_2O, (b) H_3O^+, (c) H_2CO_3, (d) NH_4^+, (e) H_2SO_4, (f) $H_3O_2^+$, (g) H_2S, and (h) $H_6N_2^{2+}$. A conjugate base always has one fewer proton than its conjugate acid; thus the conjugate bases are (a) O^{2-}, (b) OH^-, (c) CO_3^{2-}, (d) NH_2^-, (e) SO_4^{2-}, (f) HO_2^-, (g) S^{2-}, and (h) H_4N_2.

14.9: A Brønsted-Lowry acid is the same thing as a proton donor and a Brønsted-Lowry base is the same thing as a proton acceptor; thus, the two make up a conjugate acid-base pair. Each reaction has two such pairs, each of which we identify below using the general scheme `conjugate acid/conjugate base`; thus

  (a) HNO_3/NO_3^- and H_3O^+/H_2O

  (b) H_2O/OH^- and HCN/CN^-

  (c) H_2SO_4/HSO_4^- and HCl/Cl^-

  (d) HSO_4^-/SO_4^{2-} and H_2O/OH^-

  (e) H_2O/OH^- and OH^-/O^{2-}

  (f) $Al(H_2O)_6^{3+}/Al(H_2O)_5(OH)^{2+}$ and $Cu(H_2O)_4^{2+}/Cu(H_2O)_3(OH)^+$

  (g) H_2S/HS^- and NH_3/NH_2^-
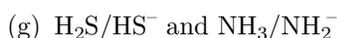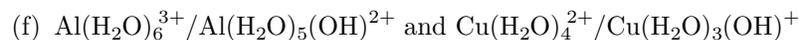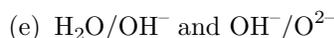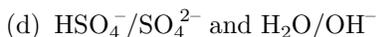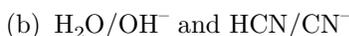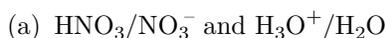
14.17: Regardless of the temperature, the K_w expression for water's dissociation is $K_2 = [H_3O^+][OH^-]$ and, if there is no other source of acid or base, we know that $[H_3O^+] = [OH^-]$; thus

$$[H_3O^+] = [OH^-] = \sqrt{K_w} = \sqrt{2.9 \times 10^{-14}} = 1.7 \times 10^{-7} \text{ M}$$

This means that the pH and the pOH are

$$pH = pOH = \log(1.7 \times 10^{-7}) = 6.77$$

14.19: When a strong acid or a strong base is placed in water it fully ionizes, which means that the concentration of H_3O^+ for a strong acid is the same as the acid's concentration and that the concentration of OH^- for a strong base is the same as the strong base's concentration; thus, for (a) we have

$$pH = -\log[HClO_4] = -\log(0.000259) = 3.587$$

$$pOH = 14 - 3.587 = 10.413$$

For (b) we have

$$pOH = -\log[NaOH] = -\log(0.21) = 0.68$$

$$\text{pH} = 14 - 0.68 = 13.32$$

For (c) we note that each $Ba(OH)_2$ has two hydroxide ions; thus

$$\text{pOH} = -\log(2 \times [Ba(OH)_2]) = -\log(0.000142) = 3.85$$

$$\text{pH} = 14 - 3.85 = 10.15$$

For (d) we have

$$\text{pOH} = -\log[\text{KOH}] = -\log(2.5) = -0.4$$

$$\text{pH} = 14 - (-0.4) = 14.4$$

14.25: We know that $[H_3O^+][OH^-] = K_w$ for any aqueous solution. Solving for H_3O^+ gives its value as

$$H_3O^+ = \frac{K_w}{OH^-} = \frac{1.0 \times 10^{-14}}{3.2 \times 10^{-3}} = 3.1 \times 10^{-12}$$

14.35: For any weak acid/weak base conjugate pair, we know that $K_a \times K_b = K_w$; thus

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.3 \times 10^{-11}$$

14.54: Here we simply substitute the provided equilibrium concentrations into the appropriate equilibrium constant expressions. To determine whether to report K_a or K_b, we make note of whether the concentration of H_3O^+ or of OH^- is reported. thus, for (a) we have

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(3.1 \times 10^{-3})(3.1 \times 10^{-3})}{0.533} = 1.8 \times 10^{-5}$$

For (b) we have

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{(0.0438)(0.011)}{1.07} = 4.5 \times 10^{-4}$$

For (c) we have

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(4.3 \times 10^{-3})(4.3 \times 10^{-3})}{0.25} = 7.4 \times 10^{-5}$$

For (d) we have

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{(7.5 \times 10^{-6})(7.5 \times 10^{-6})}{0.100} = 5.6 \times 10^{-10}$$

14.60: For (a) the reaction is $HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$, which is described by the following K_a expression

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = 3.5 \times 10^{-8}$$

Setting up an ICE table (left to you) gives the equilibrium molar concentrations of the species in the K_a expression as

$$[\text{HClO}] = 0.0092 - x \quad [\text{ClO}^-] = x \quad [\text{H}_3\text{O}^+] = x$$

Substituting these into the K_a expression and assuming that $0.0092 - x \approx 0.0092$ gives

$$K_a = \frac{(x)(x)}{0.0092} = 3.5 \times 10^{-8}$$

Solving gives $x = 1.79 \times 10^{-5}$. The error resulting from the assumption is

$$\frac{\text{calculated} - \text{assumed}}{\text{assumed}} \times 100 = \frac{(0.0092 - 1.79 \times 10^{-5}) - 0.0092}{0.0092} \times 100 = -0.19\%$$

less than 5%. The equlibrium concentrations of the species are

$$[\text{HClO}] = 0.0092 - 1.79 \times 10^{-5} = 0.0092 \text{ M} \quad [\text{ClO}^-] = 1.79 \times 10^{-5} \text{ M} \quad [\text{H}_3\text{O}^+] = 1.79 \times 10^{-5} \text{ M}$$

For (b) the reaction is $\text{C}_6\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{C}_6\text{H}_5\text{NH}_3^+(aq)$, which is described by the following K_b expression

$$K_b = \frac{[\text{OH}^-][\text{C}_6\text{H}_5\text{NH}_3^+]}{[\text{C}_6\text{H}_5\text{NH}_2]} = 4.6 \times 10^{-10}$$

Setting up an ICE table (left to you) gives the equilibrium molar concentrations of the species in the K_b expression as

$$[\text{C}_6\text{H}_5\text{NH}_2] = 0.0784 - x \quad [\text{C}_6\text{H}_5\text{NH}_3^+] = x \quad [\text{OH}^-] = x$$

Substituting these into the K_b expression and assuming that $0.0784 - x \approx 0.0784$ gives

$$K_a = \frac{(x)(x)}{0.0784} = 4.6 \times 10^{-10}$$

Solving gives $x = 6.01 \times 10^{-6}$. The error resulting from the assumption is

$$\frac{\text{calculated} - \text{assumed}}{\text{assumed}} \times 100 = \frac{(0.0784 - 6.01 \times 10^{-6}) - 0.0784}{0.0784} \times 100 = -0.008\%$$

less than 5%. The equlibrium concentrations of the species are

$$[\text{C}_6\text{H}_5\text{NH}_2] = 0.0784 - 6.01 \times 10^{-6} = 0.0784 \text{ M} \quad [\text{C}_6\text{H}_4\text{NH}_3^+] = 6.01 \times 10^{-6} \text{ M} \quad [\text{OH}^-] = 6.01 \times 10^{-6} \text{ M}$$

For (c) the reaction is $\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)$, which is described by the following K_a expression

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = 4 \times 10^{-10}$$

Setting up an ICE table (left to you) gives the equilibrium molar concentrations of the species in the K_a expression as

$$[\text{HCN}] = 0.0810 - x \quad [\text{CN}^-] = x \quad [\text{H}_3\text{O}^+] = x$$

Substituting these into the K_a expression and assuming that $0.0810 - x \approx 0.0810$ gives

$$K_a = \frac{(x)(x)}{0.0810} = 4 \times 10^{-10}$$

Solving gives $x = 5.69 \times 10^{-6}$. The error resulting from the assumption is

$$\frac{\text{calculated} - \text{assumed}}{\text{assumed}} \times 100 = \frac{(0.0810 - 5.69 \times 10^{-6}) - 0.0810}{0.0810} \times 100 = -0.007\%$$

less than 5%. The equlibrium concentrations of the species are

$$[\text{HClO}] = 0.0810 - 5.69 \times 10^{-6} = 0.0810 \text{ M} \quad [\text{ClO}^-] = 5.69 \times 10^{-6} \text{ M} \quad [\text{H}_3\text{O}^+] = 5.69 \times 10^{-6} \text{ M}$$

For (d) the reaction is $(\text{CH}_3)_3\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + (\text{CH}_3)_3\text{NH}^+(aq)$, which is described by the following K_b expression

$$K_b = \frac{[\text{OH}^-][(\text{CH}_3)_3\text{NH}^+]}{[(\text{CH}_3)_3\text{N}]} = 7.4 \times 10^{-5}$$

Setting up an ICE table (left to you) gives the equilibrium molar concentrations of the species in the K_b expression as

$$[(\text{CH}_3)_3\text{N}] = 0.11 - x \quad [(\text{CH}_3)_3\text{NH}^+] = x \quad [\text{OH}^-] = x$$

Substituting these into the K_b expression and assuming that $0.11 - x \approx 0.11$ gives

$$K_a = \frac{(x)(x)}{0.11} = 7.4 \times 10^{-5}$$

Solving gives $x = 2.85 \times 10^{-3}$. The error resulting from the assumption is

$$\frac{\text{calculated} - \text{assumed}}{\text{assumed}} \times 100 = \frac{(0.11 - 2.85 \times 10^{-3}) - 0.11}{0.11} \times 100 = -2.6\%$$

less than 5%. The equlibrium concentrations of the species are

$$[(\text{CH}_3)\text{N}] = 0.11 - 2.85 \times 10^{-3} = 0.107 \text{ M} \quad [(\text{CH}_3)\text{NH}^+] = 2.85 \times 10^{-3} \text{ M} \quad [\text{OH}^-] = 2.85 \times 10^{-3} \text{ M}$$

For (e) the reaction is $\text{Fe}(\text{H}_2\text{O})_6^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+(aq)$, which is described by the following K_a expression

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Fe(H}_2\text{O)}_5(\text{OH})^+]}{[\text{Fe(H}_2\text{O)}_6^{2+}]} = 1.6 \times 10^{-7}$$

Setting up an ICE table (left to you) gives the equilibrium molar concentrations of the species in the K_a expression as

$$[\text{Fe(H}_2\text{O)}_6^{2+}] = 0.120 - x \quad [\text{Fe(H}_2\text{O)}_5(\text{OH})^+] = x \quad [\text{H}_3\text{O}^+] = x$$

Substituting these into the K_a expression and assuming that $0.120 - x \approx 0.120$ gives

$$K_a = \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$$

Solving gives $x = 1.39 \times 10^{-4}$. The error resulting from the assumption is

$$\frac{\text{calculated} - \text{assumed}}{\text{assumed}} \times 100 = \frac{(0.120 - 1.39 \times 10^{-4}) - 0.120}{0.120} \times 100 = -0.12\%$$

less than 5%. The equlibrium concentrations of the species are

$$[\text{Fe(H}_2\text{O)}_6^{2+}] = 0.120 - 1.39 \times 10^{-4} = 0.120 \text{ M} \quad [\text{Fe(H}_2\text{O)}_5(\text{OH})^+] = 1.39 \times 10^{-4} \text{ M} \quad [\text{H}_3\text{O}^+] = 1.39 \times 10^{-4} \text{ M}$$

14.62: The equilibrium reaction is $\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)$ for which the equilibrium constant expression is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

To find the initial concentration of CH_3COOH we note that 1 L of vinegar weighs, given a density of 1.007 g/mL, 1007 g. Of this, 5%, or 50.35 g is CH_3COOH; thus, the initial concentration of CH_3COOH is

$$[\text{CH}_3\text{COOH}] = \frac{50.35 \text{ g} \times \frac{1 \text{ mol}}{60.053 \text{ g}}}{\text{L}} = 0.838 \text{ M}$$

Setting up an ICE table (left to you) gives the equilibrium molar concentrations of the species in the K_a expression as

$$[\text{CH}_3\text{COOH}] = 0.838 - x \quad [\text{CH}_3\text{COO}^-] = x \quad [\text{H}_3\text{O}^+] = x$$

Substituting these into the K_a expression and assuming that $0.838 - x \approx 0.838$ gives

$$K_a = \frac{(x)(x)}{0.838} = 1.8 \times 10^{-5}$$

Solving gives $x = 3.88 \times 10^{-3}$. The error resulting from the assumption is

$$\frac{\text{calculated} - \text{assumed}}{\text{assumed}} \times 100 = \frac{(0.838 - 3.88 \times 10^{-3}) - 0.838}{0.838} \times 100 = -0.46\%$$

less than 5%. The equilibrium concentration of H_3O^+ is 3.88×10^{-3}, which gives the pH as

$$\text{pH} = -\log(3.88 \times 10^{-3}) = 2.41$$

14.78: Adding acid to this buffer converts some $H_2PO_4^-$ to H_3PO_4 and adding base to this buffer converts some H_3PO_4 to $H_2PO_4^-$. The pH of the buffer depends on the ratio of the two species; that is

$$\text{pH} = pK_a + \log\left(\frac{[H_2PO_4^-]}{[H_3PO_4]}\right)$$

Because this ratio is inside a log function, any change in the ratio results in an even smaller change in the ratio's log and pH.

14.80: Because the concentrations of the buffer's conjugate weak acid and conjugate weak base are within a factor of 10 of each other, we know that

$$\text{pH} = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) = 4.74 + \log\left(\frac{0.030}{0.25}\right) = 3.82$$

A pH of 3.82 gives the concentration of H_3O^+ as 1.51×10^{-4}.

14.82: Because the concentrations of the buffer's conjugate weak acaid and conjugate weak base are within a factor of 10 of each other, we know that

$$\text{pH} = pK_a + \log\left(\frac{[CH_3NH_2]}{[CH_3NH_3^+]}\right) = 10.64 + \log\left(\frac{0.125}{0.130}\right) = 10.62$$

A pH of 10.62 corresponds to a pOH of 14 – 10.62, or 3.38; thus, the concentration of OH^- is 4.2×10^{-4} M.

14.86: Because the concentrations of the conjugate weak acid and conjugate weak base are within a factor of 10 of each other, we know that

$$\text{pH} = pK_a + \log\left(\frac{[NH_3]}{[NH_4^+]}\right) = 9.25 + \log\left(\frac{0.20}{0.40}\right) = 8.95$$

14.88: Given that the pK_a for acetic acid is 4.57 and the desired pH of 5.00 is within ± 1 of the pK_a, we know that we are preparing a buffer and that

$$\text{pH} = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) = 4.74 + \log\left(\frac{[CH_3COO^-]}{0.5}\right) = 5.00$$

Solving for the concentration of CH_3COO^- gives

$$0.26 = \log\left(\frac{[CH_3COO^-]}{0.5}\right)$$

$$1.82 = \frac{[CH_3COO^-]}{0.5}$$

and $[CH_3COO^-] = 0.91$ M. This also is the concentration of $NaCH_3COO \cdot 3\,H_2O$; thus, the grams of $NaCH_3COO \cdot 3\,H_2O$ are

$$0.91 \text{ M} \times 0.300 \text{ L} \times 136.080 \text{ g/mol} = 37 \text{ g}$$

14.90: Given that the initial concentrations of CH_3COOH and of $NaCH_3COO$ are within a factor of 10, we know that the solution is a buffer. Mixing equal volumes of the two solutions means that the concentrations of CH_3COOH and of $NaCH_3COO$ are cut in half; thus, we have 0.100 M CH_3COOH and 0.300 M $NaCH_3COO$. For (a) we have

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) = 4.74 + \log\left(\frac{0.3}{0.1}\right) = 5.22$$

and that (b) the solution is acidic. For (c), the moles of $NaCH_3COO$ in 0.200 L of the buffer is

$$0.3 \text{ mol/L} \times 0.200 \text{ L} = 0.0600 \text{ mol}$$

and the moles of CH_3COOH is

$$0.1 \text{ mol/L} \times 0.200 \text{ L} = 0.0200 \text{ mol}$$

Adding $0.034 \text{ mol/L} \times 0.003 \text{ L} = 1.0 \times 10^{-4}$ mol of strong acid converts an equivalent number of moles of $NaCH_3COO$ to CH_3COOH; thus, their moles become

$$0.0600 \text{ mol} - 1.0 \times 10^{-4} \text{ mol} = 0.0599 \text{ mol} NaCH_3COO$$

$$0.0200 \text{mol} + 1.0 \times 10^{-4} \text{ mol} = 0.0201 \text{ mol} CH_3COOH$$

and the buffer's pH shifts to

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{CH_3COOH}\right) = 4.74 + \log\left(\frac{0.0599}{0.0201}\right) = 5.21$$