Answers to Chapter 16 Additional Problems

1. Write net ionic equations for all equilibria that lie more than 50% to the right when the following pairs of solutions are mixed. Assume adequate amounts of each reagent for all possible equilibria.

a. $H_3PO_4(aq) + HCO_2^-(aq) \rightarrow H_2PO_4^-(aq) + HCO_2H(aq)$

b. $H_2C_4H_4O_6(aq) + HCO_3^-(aq) \rightarrow HC_4H_4O_6^-(aq) + H_2CO_3(aq)$ $\{H_2CO_3(aq) = CO_2(g) + H_2O(l)\}$
$HC_4H_4O_6^-(aq) + HCO_3^-(aq) \rightarrow C_4H_4O_6^{2-}(aq) + H_2CO_3(aq)$

c. $H_2S(aq) + SO_3^{2-}(aq) \rightarrow HS^-(aq) + HSO_3^-(aq)$

d. $PO_4^{3-}(aq) + CH_3CO_2H(aq) \rightarrow HPO_4^{2-}(aq) + CH_3O_2^-(aq)$
$HPO_4^{2-}(aq) + CH_3CO_2H(aq) \rightarrow H_2PO_4^-(aq) + CH_3O_2^-(aq)$
$H_2PO_4^-(aq) + CH_3CO_2H(aq) \rightarrow$ no rxn

e. $HC_8H_4O_4^-(aq) + OCl^-(aq) \rightarrow C_8H_4O_4^{2-}(aq) + HOCl(aq)$

2. What is the pH of a 0.10 M $Al(NO_3)_3$ solution?

$Al(NO_3)_3(aq) \rightarrow Al^{3+}(aq) + 3NO_3^-(aq)$

$Al^{3+}(aq)$ is $Al(H_2O)_6^{3+}$, which is a weak acid, HA, with $K_a = 7.9 \times 10^{-6}$:

$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+ \qquad K_a = 7.9 \times 10^{-6}$$

$C_{HA} = 0.10$ M >> $K_a = 7.9 \times 10^{-6}$, so use both Assumptions I and II:

$$[H_3O^+] = \sqrt{(0.10)(7.9 \times 10^{-6})} = 8.9 \times 10^{-4}\,M$$

$$pH = 3.05$$

3. Calculate the concentrations of all species in 0.100 M *o*-phthalic acid, $H_2C_8H_4O_4$. For simplicity, abbreviate the acid H_2Ph.

$$H_2Ph + H_2O \rightleftharpoons HPh^- + H_3O^+ \qquad K_1 = 1.30 \text{ x } 10^{-3}$$
$$HPh^- + H_2O \rightleftharpoons Ph^{2-} + H_3O^+ \qquad K_2 = 3.1 \text{ x } 10^{-6}$$

Assume all hydronium ion comes from hydrolysis step 1, and by Assumption I that $[H_3O^+] = [HPh^-]$. Note that $K_1 = 1.30 \text{ x } 10^{-3}$. $C_{H_2Ph} = 0.100$ M, so we cannot ignore dissociation of the acid (i.e., no Assumption II).

$$K_1 = \frac{[H_3O^+][HPh^-]}{[H_2Ph]} = \frac{[H_3O^+]^2}{0.100 - [H_3O^+]} = 1.30 \times 10^{-3}$$

This yields the following quadratic equation:

$$[H_3O^+]^2 + 1.30 \text{ x } 10^{-3} [H_3O^+] - 1.30 \text{ x } 10^{-4} = 0$$

Taking the positive root gives

$$[H_3O^+] = 0.0107_7 \text{ M} = 0.0108 \text{ M} = [HPh^-]$$

From the exact mass balance expression

$$[H_2Ph] = 0.100 \text{ M} - 0.0108 \text{ M} = 0.089_2 \text{ M} = 0.089 \text{ M}$$

Substituting into K_2 with to find $[Ph^{2-}]$, using the assumption $[H_3O^+] = [HPh^-]$, gives

$$K_2 = \frac{[H_3O^+][Ph^{2-}]}{[HPh^-]} = 3.1 \times 10^{-6} = [Ph^{2-}]$$

(As always in these cases, the second conjugate base concentration equals the value of K_2.)

Finally, solve K_w for $[OH^-]$.

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.0108} = 9.3 \times 10^{-13} \text{ M}$$