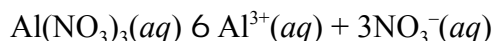


Answers to Chapter 16 Additional Problems

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. $\text{H}_3\text{PO}_4(aq) + \text{HCO}_2^-(aq) \rightleftharpoons \text{H}_2\text{PO}_4^-(aq) + \text{HCO}_2\text{H}(aq)$
- b. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6(aq) + \text{HCO}_3^-(aq) \rightleftharpoons \text{HC}_4\text{H}_4\text{O}_6^-(aq) + \text{H}_2\text{CO}_3(aq)$ $\{\text{H}_2\text{CO}_3(aq) = \text{CO}_2(g) + \text{H}_2\text{O}(l)\}$
 $\text{HC}_4\text{H}_4\text{O}_6^-(aq) + \text{HCO}_3^-(aq) \rightleftharpoons \text{C}_4\text{H}_4\text{O}_6^{2-}(aq) + \text{H}_2\text{CO}_3(aq)$
- c. $\text{H}_2\text{S}(aq) + \text{SO}_3^{2-}(aq) \rightleftharpoons \text{HS}^-(aq) + \text{HSO}_3^-(aq)$
- d. $\text{PO}_4^{3-}(aq) + \text{CH}_3\text{CO}_2\text{H}(aq) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{CH}_3\text{O}_2^-(aq)$
 $\text{HPO}_4^{2-}(aq) + \text{CH}_3\text{CO}_2\text{H}(aq) \rightleftharpoons \text{H}_2\text{PO}_4^-(aq) + \text{CH}_3\text{O}_2^-(aq)$
 $\text{H}_2\text{PO}_4^-(aq) + \text{CH}_3\text{CO}_2\text{H}(aq) \rightleftharpoons \text{no rxn}$
- e. $\text{HC}_8\text{H}_4\text{O}_4^-(aq) + \text{OCl}^-(aq) \rightleftharpoons \text{C}_8\text{H}_4\text{O}_4^{2-}(aq) + \text{HOCl}(aq)$
2. What is the pH of a 0.10 M $\text{Al}(\text{NO}_3)_3$ solution?



$\text{Al}^{3+}(aq)$ is $\text{Al}(\text{H}_2\text{O})_6^{3+}$, which is a weak acid, HA, with $K_a = 7.9 \times 10^{-6}$:

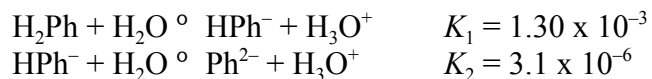


$C_{\text{HA}} = 0.10 \text{ M} \gg K_a = 7.9 \times 10^{-6}$, so use both Assumptions I and II:

$$[\text{H}_3\text{O}^+] = \sqrt{(0.10)(7.9 \times 10^{-6})} = 8.9 \times 10^{-4} \text{ M}$$

$$\text{pH} = 3.05$$

3. Calculate the concentrations of all species in 0.100 M *o*-phthalic acid, $\text{H}_2\text{C}_8\text{H}_4\text{O}_4$. For simplicity, abbreviate the acid H_2Ph .



Assume all hydronium ion comes from hydrolysis step 1, and by Assumption I that $[\text{H}_3\text{O}^+] = [\text{HPh}^-]$. Note that $K_1 = 1.30 \times 10^{-3}$. $C_{\text{H}_2\text{Ph}} = 0.100 \text{ M}$, so we cannot ignore dissociation of the acid (i.e., no Assumption II).

$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{HPh}^-]}{[\text{H}_2\text{Ph}]} = \frac{[\text{H}_3\text{O}^+]^2}{0.100 - [\text{H}_3\text{O}^+]} = 1.30 \times 10^{-3}$$

This yields the following quadratic equation:

$$[\text{H}_3\text{O}^+]^2 + 1.30 \times 10^{-3} [\text{H}_3\text{O}^+] - 1.30 \times 10^{-4} = 0$$

Taking the positive root gives

$$[\text{H}_3\text{O}^+] = 0.01077 \text{ M} = 0.0108 \text{ M} = [\text{HPh}^-]$$

From the exact mass balance expression

$$[\text{H}_2\text{Ph}] = 0.100 \text{ M} - 0.0108 \text{ M} = 0.0892 \text{ M} = 0.089 \text{ M}$$

Substituting into K_2 with to find $[\text{Ph}^{2-}]$, using the assumption $[\text{H}_3\text{O}^+] = [\text{HPh}^-]$, gives

$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{Ph}^{2-}]}{[\text{HPh}^-]} = 3.1 \times 10^{-6} = [\text{Ph}^{2-}]$$

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

Finally, solve K_w for $[\text{OH}^-]$.

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.0108} = 9.3 \times 10^{-13} \text{ M}$$