

*Chemistry 2e*  
**14: Acid-Base Equilibria**  
**14.1: Brønsted-Lowry Acids and Bases**

1. Write equations that show  $\text{NH}_3$  as both a conjugate acid and a conjugate base.

Solution

One example for  $\text{NH}_3$  as a conjugate acid:  $\text{NH}_2^- + \text{H}^+ \longrightarrow \text{NH}_3$ ; as a conjugate base:



2. Write equations that show  $\text{H}_2\text{PO}_4^-$  acting both as an acid and as a base.

Solution

$\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{PO}_4(aq) + \text{OH}^-(aq)$ ; as an acid:



3. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

- (a)  $\text{H}_3\text{O}^+$
- (b)  $\text{HCl}$
- (c)  $\text{NH}_3$
- (d)  $\text{CH}_3\text{CO}_2\text{H}$
- (e)  $\text{NH}_4^+$
- (f)  $\text{HSO}_4^-$

Solution

(a)  $\text{H}_3\text{O}^+(aq) \longrightarrow \text{H}^+(aq) + \text{H}_2\text{O}(l)$ ; (b)  $\text{HCl}(l) \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$ ; (c)  $\text{NH}_3(aq) \longrightarrow \text{H}^+(aq) + \text{NH}_2^-(aq)$ ; (d)  $\text{CH}_3\text{CO}_2\text{H}(aq) \longrightarrow \text{H}^+(aq) + \text{CH}_3\text{CO}_2^-(aq)$ ; (e)  $\text{NH}_4^+(aq) \longrightarrow \text{H}^+(aq) + \text{NH}_3(aq)$ ; (f)  $\text{HSO}_4^-(aq) \longrightarrow \text{H}^+(aq) + \text{SO}_4^{2-}(aq)$

4. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

- (a)  $\text{HNO}_3$
- (b)  $\text{PH}_4^+$
- (c)  $\text{H}_2\text{S}$
- (d)  $\text{CH}_3\text{CH}_2\text{COOH}$
- (e)  $\text{H}_2\text{PO}_4^-$
- (f)  $\text{HS}^-$

Solution

In a Brønsted-Lowry acid, the acid must supply an  $\text{H}^+$ . (a)

$\text{HNO}_3(aq) \longrightarrow \text{H}^+(aq) + \text{NO}_3^-(aq)$ ; (b)  $\text{PH}_4^+(aq) \longrightarrow \text{H}^+(aq) + \text{PH}_3(aq)$ ; (c)  $\text{H}_2\text{S}(aq) \longrightarrow \text{H}^+(aq) + \text{HS}^-(aq)$ ; (d)  $\text{C}_2\text{H}_5\text{CO}_2\text{H}(aq) \longrightarrow \text{H}^+(aq) + \text{C}_2\text{H}_5\text{CO}_2^-(aq)$ ; (e)  $\text{H}_2\text{PO}_4^-(aq) \longrightarrow \text{H}^+(aq) + \text{HPO}_4^{2-}(aq)$ ; (f)  $\text{HS}^-(aq) \longrightarrow \text{H}^+(aq) + \text{S}^{2-}(aq)$

5. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

- (a)  $\text{H}_2\text{O}$

- (b)  $\text{OH}^-$
- (c)  $\text{NH}_3$
- (d)  $\text{CN}^-$
- (e)  $\text{S}^{2-}$
- (f)  $\text{H}_2\text{PO}_4^-$

**Solution**

(a)  $\text{H}_2\text{O}(l) + \text{H}^+(aq) \longrightarrow \text{H}_3\text{O}^+(aq)$ ; (b)  $\text{OH}^-(aq) + \text{H}^+(aq) \longrightarrow \text{H}_2\text{O}(l)$ ; (c)  $\text{NH}_3(aq) + \text{H}^+(aq) \longrightarrow \text{NH}_4^+(aq)$ ; (d)  $\text{CN}^-(aq) + \text{H}^+(aq) \longrightarrow \text{HCN}(aq)$ ; (e)  $\text{S}^{2-}(aq) + \text{H}^+(aq) \longrightarrow \text{HS}^-(aq)$ ; (f)  $\text{H}_2\text{PO}_4^-(aq) + \text{H}^+(aq) \longrightarrow \text{H}_3\text{PO}_4(aq)$

6. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

- (a)  $\text{HS}^-$
- (b)  $\text{PO}_4^{3-}$
- (c)  $\text{NH}_2^-$
- (d)  $\text{C}_2\text{H}_5\text{OH}$
- (e)  $\text{O}^{2-}$
- (f)  $\text{H}_2\text{PO}_4^-$

**Solution**

In a Brønsted-Lowry base, the base must accept an  $\text{H}^+$ .

(a)  $\text{HS}^- + \text{H}^+ \longrightarrow \text{H}_2\text{S}$ ; (b)  $\text{PO}_4^{3-} + \text{H}^+ \longrightarrow \text{HPO}_4^{2-}$ ; (c)  $\text{NH}_2^- + \text{H}^+ \longrightarrow \text{NH}_3$   
 (d)  $\text{C}_2\text{H}_5\text{OH} + \text{H}^+ \longrightarrow \text{C}_2\text{H}_5\text{OH}_2^+$ ; (e)  $\text{O}^{2-} + \text{H}^+ \longrightarrow \text{OH}^-$ ; (f)  
 $\text{HPO}_4^{2-} + \text{H}^+ \longrightarrow \text{H}_2\text{PO}_4^-$

7. What is the conjugate acid of each of the following? What is the conjugate base of each?

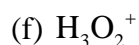
- (a)  $\text{OH}^-$
- (b)  $\text{H}_2\text{O}$
- (c)  $\text{HCO}_3^-$
- (d)  $\text{NH}_3$
- (e)  $\text{HSO}_4^-$
- (f)  $\text{H}_2\text{O}_2$
- (g)  $\text{HS}^-$
- (h)  $\text{H}_5\text{N}_2^+$

**Solution**

(a)  $\text{H}_2\text{O}$ ,  $\text{O}^{2-}$ ; (b)  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ ; (c)  $\text{H}_2\text{CO}_3$ ,  $\text{CO}_3^{2-}$ ; (d)  $\text{NH}_4^+$ ,  $\text{NH}_2^-$ ; (e)  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_4^{2-}$ ; (f)  $\text{H}_3\text{O}_2^+$ ,  $\text{HO}_2^-$ ; (g)  $\text{H}_2\text{S}$ ;  $\text{S}^{2-}$ ; (h)  $\text{H}_6\text{N}_2^{2+}$ ,  $\text{H}_4\text{N}_2$

8. What is the conjugate acid of each of the following? What is the conjugate base of each?

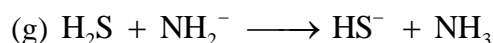
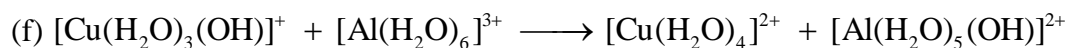
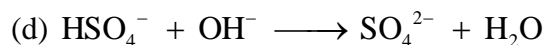
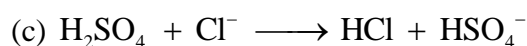
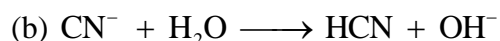
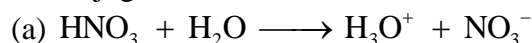
- (a)  $\text{H}_2\text{S}$
- (b)  $\text{H}_2\text{PO}_4^-$
- (c)  $\text{PH}_3$
- (d)  $\text{HS}^-$



Solution

(a)  $\text{H}_3\text{S}^+$ ,  $\text{HS}^-$ ; (b)  $\text{H}_3\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ; (c)  $\text{PH}_4^+$ ,  $\text{PH}_2^-$ ; (d)  $\text{H}_2\text{S}$ ,  $\text{S}^{2-}$ ; (e)  $\text{H}_2\text{SO}_3$ ,  $\text{SO}_3^{2-}$ ; (f)  $\text{H}_4\text{O}_2^{2+}$ ,  $\text{H}_2\text{O}_2$ ; (g)  $\text{H}_5\text{N}_2^+$ ,  $\text{H}_3\text{N}_2^-$ ; (h)  $\text{CH}_3\text{OH}_2^+$ ,  $\text{CH}_3\text{O}^-$

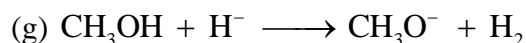
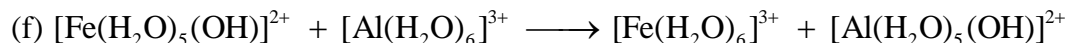
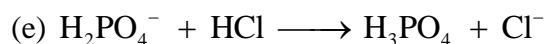
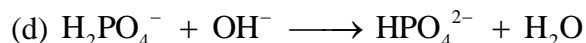
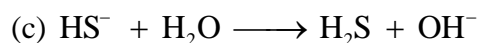
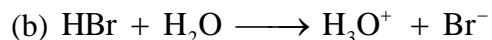
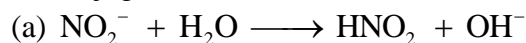
9. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:



Solution

The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. (a)  $\text{HNO}_3$ (BA),  $\text{H}_2\text{O}$ (BB),  $\text{H}_3\text{O}^+$ (CA),  $\text{NO}_3^-$ (CB); (b)  $\text{CN}^-$ (BB),  $\text{H}_2\text{O}$ (BA),  $\text{HCN}$ (CA),  $\text{OH}^-$ (CB); (c)  $\text{H}_2\text{SO}_4$ (BA),  $\text{Cl}^-$ (BB),  $\text{HCl}$ (CA),  $\text{HSO}_4^-$ (CB); (d)  $\text{HSO}_4^-$ (BA),  $\text{OH}^-$ (BB),  $\text{SO}_4^{2-}$ (CB),  $\text{H}_2\text{O}$ (CA); (e)  $\text{O}^{2-}$ (BB),  $\text{H}_2\text{O}$ (BA)  $\text{OH}^-$ (CB and CA); (f)  $[\text{Cu}(\text{H}_2\text{O})_3(\text{OH})]^+$ (BB),  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (BA),  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ (CA),  $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ (CB); (g)  $\text{H}_2\text{S}$ (BA),  $\text{NH}_2^-$ (BB),  $\text{HS}^-$ (CB),  $\text{NH}_3$ (CA)

10. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:



Solution

The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; and its conjugate acid = CA. (a)  $\text{NO}_2^-$ (BB),  $\text{H}_2\text{O}$ (BA),  $\text{HNO}_2$ (CA),  $\text{OH}^-$ (CB); (b)  $\text{HBr}$ (BA),  $\text{H}_2\text{O}$ (BB),  $\text{H}_3\text{O}^+$ (CA),  $\text{Br}^-$ (CB); (c)  $\text{HS}^-$ (BB),  $\text{H}_2\text{O}$ (BA),  $\text{H}_2\text{S}$ (CA),  $\text{OH}^-$ (CB); (d)  $\text{H}_2\text{PO}_4^-$

(BA),  $\text{OH}^-$ (BB),  $\text{HPO}_4^{2-}$  (CB),  $\text{H}_2\text{O}$ (CA); (e)  $\text{H}_2\text{PO}_4^-$  (BB),  $\text{HCl}$ (BA),  $\text{H}_3\text{PO}_4$ (CA),  $\text{Cl}^-$ (CB); (f)  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  (BB),  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  (BA),  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (CA),  $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  (CB); (g)  $\text{CH}_3\text{OH}$ (BA),  $\text{H}^-$ (BB),  $\text{CH}_3\text{O}^-$  (CB),  $\text{H}_2$ (CA)

11. What are amphiprotic species? Illustrate with suitable equations.

**Solution**

Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is  $\text{H}_2\text{O}$ . As an acid:  $\text{H}_2\text{O}(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ .

As a base:  $\text{H}_2\text{O}(\text{aq}) + \text{HCl}(\text{aq}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

12. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

(a)  $\text{H}_2\text{O}$

(b)  $\text{H}_2\text{PO}_4^-$

(c)  $\text{S}^{2-}$

(d)  $\text{CO}_3^{2-}$

(e)  $\text{HSO}_4^-$

**Solution**

amphiprotic:

(a)  $\text{H}_2\text{O}(\text{l}) + \text{HBr}(\text{aq}) \longrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Br}^-(\text{aq})$ ,

$\text{H}_2\text{O}(\text{l}) + \text{CN}^-(\text{aq}) \longrightarrow \text{HCN}(\text{aq}) + \text{OH}^-(\text{aq})$ ;

(b)  $\text{H}_2\text{PO}_4^-(\text{aq}) + \text{HBr}(\text{aq}) \longrightarrow \text{H}_3\text{PO}_4(\text{aq}) + \text{Br}^-(\text{aq})$ ,

$\text{H}_2\text{PO}_4^-(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ ; (e)

$\text{HSO}_4^-(\text{aq}) + \text{HClO}_4(\text{aq}) \longrightarrow \text{H}_2\text{SO}_4(\text{aq}) + \text{ClO}_4^-(\text{aq})$ ,

$\text{HSO}_4^-(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{SO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ ; not amphiprotic: (c)  $\text{S}^{2-}$ , (d)  $\text{CO}_3^{2-}$

13. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

(a)  $\text{NH}_3$

(b)  $\text{HPO}_4^-$

(c)  $\text{Br}^-$

(d)  $\text{NH}_4^+$

(e)  $\text{AsO}_4^{3-}$

**Solution**

(a)  $\text{NH}_3 + \text{H}_3\text{O}^+ \longrightarrow \text{NH}_4\text{OH} + \text{H}_2\text{O}$ ,  $\text{NH}_3 + \text{OCH}_3^- \longrightarrow \text{NH}_2^- + \text{CH}_3\text{OH}$ ; (b)

$\text{HPO}_4^{2-} + \text{OH}^- \longrightarrow \text{PO}_4^{3-} + \text{H}_2\text{O}$ ,  $\text{HPO}_4^{2-} + \text{HClO}_4 \longrightarrow \text{H}_2\text{PO}_4^- + \text{ClO}_4^-$ ;

not amphiprotic: (c)  $\text{Br}^-$ ; (d)  $\text{NH}_4^+$ ; (e)  $\text{AsO}_4^{3-}$

14. Is the self-ionization of water endothermic or exothermic? The ionization constant for water ( $K_w$ ) is  $2.9 \times 10^{-14}$  at  $40^\circ\text{C}$  and  $9.3 \times 10^{-14}$  at  $60^\circ\text{C}$ .

**Solution**

Because  $K_w$  increases with increasing temperature, the reaction is endothermic. When the temperature of the system is increased, the reaction shifts toward the product side, making  $K$  bigger. According to Le Châtelier's principle, the reaction shifts away from the heat term, so the heat term must be on the reactant side of the equation. Therefore, the reaction is endothermic.

*Chemistry 2e*  
14: Acid-Base Equilibria  
14.2: pH and pOH

15. Explain why a sample of pure water at 40 °C is neutral even though  $[\text{H}_3\text{O}^+] = 1.7 \times 10^{-7} \text{ M}$ .  $K_w$  is  $2.910 \times 10^{-14}$  at 40 °C.

**Solution**

In a neutral solution  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ . At 40 °C,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = (2.910 \times 10^{-14})^{1/2} = 1.7 \times 10^{-7}$$

16. The ionization constant for water ( $K_w$ ) is  $2.9 \times 10^{-14}$  at 40 °C. Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH, and pOH for pure water at 40 °C.

**Solution**

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 2.9 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{2.9 \times 10^{-14}} = 1.70 \times 10^{-7} = 1.7 \times 10^{-7} \text{ M}$$

$$\text{pH} = \text{pOH} = -\log(1.70 \times 10^{-7}) = 6.769 = 6.77$$

17. The ionization constant for water ( $K_w$ ) is  $9.311 \times 10^{-14}$  at 60 °C. Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH, and pOH for pure water at 60 °C.

**Solution**

For water,  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = x$ .

$$K_w = 9.311 \times 10^{-14} = x^2$$

$$x = 3.051 \times 10^{-7} \text{ M} = [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

$$\text{pH} = -\log 3.051 \times 10^{-7} = -(-6.5156) = 6.5156$$

$$\text{pOH} = \text{pH} = 6.5156$$

18. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

- (a) 0.200 M HCl
- (b) 0.0143 M NaOH
- (c) 3.0 M HNO<sub>3</sub>
- (d) 0.0031 M Ca(OH)<sub>2</sub>

**Solution**

$\text{pH} = -\log[\text{H}_3\text{O}^+]$ ,  $\text{pOH} = -\log[\text{OH}^-]$ ; (a) Hydrochloric acid is a strong acid; therefore, the hydronium ion concentration is the same as the molar concentration of HCl.  $\text{pH} = -\log(0.200) = -(-0.699) = 0.699$ ;  $\text{pOH} = 14.00 - \text{pH} = 14.00 - 0.699 = 13.30$ ; (b) NaOH is a strong base that is completely ionized in dilute solution. Therefore, since  $[\text{OH}^-] = 0.0143 \text{ M}$ ,  $\text{pOH} = -\log(0.0143) = -(-1.8447) = 1.845$ ;  $\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.845 = 12.16$ ; (c)  $\text{pH} = -\log(3.0) = -(0.477) = -0.48$ ;  $\text{pOH} = 14.00 - \text{pH} = 14.00 - (-0.477) = 14.477 = 14.48$ ; (d)  $[\text{OH}^-] = 2(0.0031) = 0.0062 \text{ M}$ ;  $\text{pOH} = -\log(0.0062) = -(-2.208) = 2.21$ ;  $\text{pH} = 14.00 - 2.208 = 11.792 = 11.79$

19. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

- (a) 0.000259 *M* HClO<sub>4</sub>  
 (b) 0.21 *M* NaOH  
 (c) 0.000071 *M* Ba(OH)<sub>2</sub>  
 (d) 2.5 *M* KOH

Solution

(a)  $\text{pH} = -\log(0.000259) = -(-3.5867) = 3.587$ ;  $\text{pOH} = 14.0000 - 3.5867 = 10.4133 = 10.413$ ; (b)  $\text{pH} = -\log(0.21) = -(-0.678) = 0.68$ ;  $\text{pOH} = 14.000 - 0.678 = 13.322 = 13.32$ ; (c) since  $[\text{OH}^-] = 2(0.000071) = 0.000142 \text{ M}$ ;  $\text{pOH} = -\log(0.000142) = -(-3.848) = 3.85$ ;  $\text{pH} = 14.000 - 3.848 = 10.152 = 10.15$ ; (d)  $\text{pH} = -\log(2.5) = -(0.398) = -0.40$ ;  $\text{pOH} = 14.000 - (-0.398) = 14.398 = 14.4$

20. What are the pH and pOH of a solution of 2.0 *M* HCl, which ionizes completely?

Solution

HCl is a strong acid that undergoes complete ionization in pure water.

$[\text{H}_3\text{O}^+] = \text{molarity of HCl} = 2.0 \text{ M}$

$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(2.0) = -0.30$

$\text{pOH} = 14.00 - \text{pH} = 14.00 - (-0.30) = 14.30$

21. What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

Solution

$[\text{H}_3\text{O}^+] = 10^{-6.52} = 3.0 \times 10^{-7} \text{ M}$ ;  $\text{pOH} = 14.00 - \text{pH}$ ;  $\text{pOH} = 14.00 - 6.52 = 7.48$ ;  $[\text{OH}^-] = 10^{-7.48} = 3.3 \times 10^{-8} \text{ M}$

22. Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See Figure 14.2 for useful information.

Solution

$[\text{H}_3\text{O}^+] = 3 \times 10^{-4}$ ,  $[\text{OH}^-] = 3 \times 10^{-11} \text{ M}$

23. Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure 14.2 for useful information.

Solution

From Figure 14.2 the pH of lime juice is equal to 2. The hydronium ion concentration is  $\text{pH} = 2 = -\log[\text{H}_3\text{O}^+]$ ;  $[\text{H}_3\text{O}^+] = 1 \times 10^{-2} \text{ M}$ ;  $\text{pH} + \text{pOH} = 14$ ;  $\text{pOH} = 14 - 2 = 12$ ;  $[\text{OH}^-] = 1 \times 10^{-12} \text{ M}$

24. The hydronium ion concentration in a sample of rainwater is found to be  $1.7 \times 10^{-6} \text{ M}$  at 25 °C. What is the concentration of hydroxide ions in the rainwater?

Solution

$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ ;  $[1.7 \times 10^{-6}][\text{OH}^-] = 1.0 \times 10^{-14}$ ;

$[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{1.7 \times 10^{-6}} = 5.9 \times 10^{-9} \text{ M}$

25. The hydroxide ion concentration in household ammonia is  $3.2 \times 10^{-3} \text{ M}$  at 25 °C. What is the concentration of hydronium ions in the solution?

Solution

$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ ;  $[\text{H}_3\text{O}^+][3.2 \times 10^{-3}] = 1.0 \times 10^{-14}$ ;

$[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{3.2 \times 10^{-3}} = 3.1 \times 10^{-12} \text{ M}$

## Chemistry 2e

## 14: Acid-Base Equilibria

## 14.3: Relative Strengths of Acids and Bases

26. Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

Solution

The reaction forms the conjugate acid of the weak base. The conjugate acid of a weak base is a weak acid and ionizes to a slight extent giving an acidic solution.

27. Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

Solution

The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms  $\text{OH}^-$ , which causes the solution to be basic. An example is NaCN. The  $\text{CN}^-$  reacts with water as follows:  $\text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq)$

28. Use this list of important industrial compounds (and Figure 14.8) to answer the following questions regarding: CaO,  $\text{Ca}(\text{OH})_2$ ,  $\text{CH}_3\text{CO}_2\text{H}$ ,  $\text{CO}_2$ , HCl,  $\text{H}_2\text{CO}_3$ , HF,  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_3$ , NaOH,  $\text{Na}_2\text{CO}_3$ .

(a) Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.

(b) List those compounds in (a) that can behave as Brønsted-Lowry acids with strengths lying between those of  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$ .

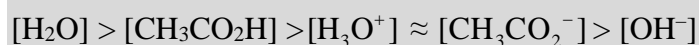
(c) List those compounds in (a) that can behave as Brønsted-Lowry bases with strengths lying between those of  $\text{H}_2\text{O}$  and  $\text{OH}^-$ .

Solution

(a) Brønsted-Lowry acids:  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HNO}_3$ , HCl; Brønsted-Lowry bases: CaO,  $\text{Ca}(\text{OH})_2$ , NaOH; (b)  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ; (c)  $\text{NH}_3$ ,  $\text{Na}_2\text{CO}_3$

29. The odor of vinegar is due to the presence of acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-M aqueous solution of this acid.

Solution



30. Household ammonia is a solution of the weak base  $\text{NH}_3$  in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-M aqueous solution of this base.

Solution



31. Explain why the ionization constant,  $K_a$ , for  $\text{H}_2\text{SO}_4$  is larger than the ionization constant for  $\text{H}_2\text{SO}_3$ .

Solution

The oxidation state of the sulfur in  $\text{H}_2\text{SO}_4$  is greater than the oxidation state of the sulfur in  $\text{H}_2\text{SO}_3$ .

32. Explain why the ionization constant,  $K_a$ , for HI is larger than the ionization constant for HF.

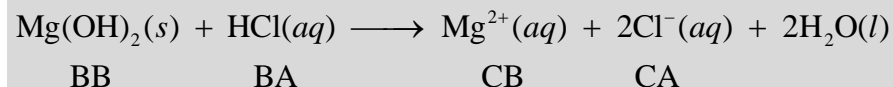
Solution

The radius of I is larger than the radius of F. This is why the H-I bond is weaker than the H-F bond, HI is easier to break than HF, and the  $K_a$  for HI is greater

## 14.1: Brønsted-Lowry Acids and Bases

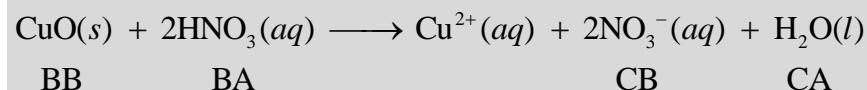
33. Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid  $\text{Mg}(\text{OH})_2$  in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

Solution



34. Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate,  $\text{Cu}(\text{NO}_3)_2$ , a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of  $\text{HNO}_3$  with  $\text{CuO}$ .

Solution



35. What is the ionization constant at 25 °C for the weak acid  $\text{CH}_3\text{NH}_3^+$ , the conjugate acid of the weak base  $\text{CH}_3\text{NH}_2$ ,  $K_b = 4.4 \times 10^{-4}$ .

Solution

$$K_w = K_a \times K_b$$

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

36. What is the ionization constant at 25 °C for the weak acid  $(\text{CH}_3)_2\text{NH}_2^+$ , the conjugate acid of the weak base  $(\text{CH}_3)_2\text{NH}$ ,  $K_b = 5.9 \times 10^{-4}$ ?

Solution

$$K_w = K_a \times K_b$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-4}} = 1.7 \times 10^{-11}$$

37. Which base,  $\text{CH}_3\text{NH}_2$  or  $(\text{CH}_3)_2\text{NH}$ , is the strongest base? Which conjugate acid,  $(\text{CH}_3)_2\text{NH}_2^+$  or  $\text{CH}_3\text{NH}_3^+$ , is the strongest acid?

Solution

The strongest base or strongest acid is the one with the larger  $K_b$  or  $K_a$ , respectively. In these two examples, they are  $(\text{CH}_3)_2\text{NH}$  and  $\text{CH}_3\text{NH}_3^+$ .

38. Which is the stronger acid,  $\text{NH}_4^+$  or  $\text{HBrO}$ ?

Solution

Look up (Appendix H)  $K_a$  for  $\text{HBrO}$ . Using the value of  $K_b$  for  $\text{NH}_3$ , calculate its  $K_a$ . Then compare the values:

$$K_a(\text{HBrO}) = 2.8 \times 10^{-9}$$

$$K_b(\text{NH}_3) = 1.8 \times 10^{-5} = \frac{K_w}{K_a}, K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}$$

39. Which is the stronger base,  $(\text{CH}_3)_3\text{N}$  or  $\text{H}_2\text{BO}_3^-$ ?

Solution

Look up (Appendix I) the value of  $K_b$  for  $(\text{CH}_3)_3\text{N}$  and the value of  $K_a$  for  $\text{H}_3\text{BO}_3$ . From the latter, calculate the value of  $K_b$  for  $\text{H}_2\text{BO}_3^-$ . Then compare values:



$$K_b(\text{CH}_3)_3\text{N} = 6.3 \times 10^{-5}$$

$$K_a(\text{H}_3\text{BO}_3) = 5.4 \times 10^{-10} = \frac{K_w}{K_b}, K_b = \frac{1.0 \times 10^{-14}}{5.4 \times 10^{-10}} = 1.9 \times 10^{-5}$$

A comparison shows that the larger  $K_b$  is that of triethylamine.

40. Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

- (a)  $\text{H}_2\text{O}$  or  $\text{HF}$
- (b)  $\text{B}(\text{OH})_3$  or  $\text{Al}(\text{OH})_3$
- (c)  $\text{HSO}_3^-$  or  $\text{HSO}_4^-$
- (d)  $\text{NH}_3$  or  $\text{H}_2\text{S}$
- (e)  $\text{H}_2\text{O}$  or  $\text{H}_2\text{Te}$

Solution

(a)  $\text{HF}$ ; F is more electronegative than O. (b)  $\text{B}(\text{OH})_3$ ; B is more electronegative than Al. Accordingly  $\text{Al}(\text{OH})_3$  is more basic than  $\text{B}(\text{OH})_3$ . (c)  $\text{HSO}_4^-$ ; S has a +6 oxidation state in  $\text{HSO}_4^-$ , but a +4 oxidation state in  $\text{HSO}_3^-$ . Increasing the oxidation state of the central element in oxyacids increases acidity. (d)  $\text{H}_2\text{S}$ ;  $\text{NH}_3$  is a weak base and  $\text{H}_2\text{S}$  is a very weak acid. Therefore,  $\text{NH}_3$  as an acid is weaker than  $\text{H}_2\text{S}$ . (e)  $\text{H}_2\text{Te}$ ; Te is below O in group 16. Heavier members in acid-forming groups make stronger acids than lighter members of those groups.

41. Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

- (a)  $\text{HSO}_4^-$  or  $\text{HSeO}_4^-$
- (b)  $\text{NH}_3$  or  $\text{H}_2\text{O}$
- (c)  $\text{PH}_3$  or  $\text{HI}$
- (d)  $\text{NH}_3$  or  $\text{PH}_3$
- (e)  $\text{H}_2\text{S}$  or  $\text{HBr}$

Solution

(a)  $\text{HSO}_4^-$ ; higher electronegativity of the central ion. (b)  $\text{H}_2\text{O}$ ;  $\text{NH}_3$  is a base and water is neutral, or decide on the basis of  $K_a$  values. (c)  $\text{HI}$ ;  $\text{PH}_3$  is weaker than  $\text{HCl}$ ;  $\text{HCl}$  is weaker than  $\text{HI}$ . Thus,  $\text{PH}_3$  is weaker than  $\text{HI}$ . (d)  $\text{PH}_3$ ; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group. (e)  $\text{HBr}$ ; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so  $\text{HBr}$  is the stronger acid.

42. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

- (a) acidity:  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$
- (b) basicity:  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{H}^-$ ,  $\text{Cl}^-$
- (c) basicity:  $\text{Mg}(\text{OH})_2$ ,  $\text{Si}(\text{OH})_4$ ,  $\text{ClO}_3(\text{OH})$  (Hint: Formula could also be written as  $\text{HClO}_4$ .)
- (d) acidity:  $\text{HF}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$

Solution

(a)  $\text{HCl} < \text{HBr} < \text{HI}$ ; H-X bond energy decreases going down a group. This consideration is more significant than the decrease in electronegativity. (b)  $\text{Cl}^- < \text{H}_2\text{O} < \text{OH}^- < \text{H}^-$ ;  $\text{Cl}^-$  has no tendency to basic action; water forms  $\text{OH}^-$  in a very low concentration;  $\text{OH}^-$  is very basic; and  $\text{H}^-$  is even more willing to donate a pair of electrons. (c)  $\text{ClO}_3(\text{OH}) < \text{Si}(\text{OH})_4 < \text{Mg}(\text{OH})_2$ ; the more nonmetallic the central atom, the more acidic the substance. As a result, base strength increases

in the opposite direction. (d)  $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$ ; this series can be envisioned in terms of increasing electronegativity of the atom attached to hydrogen. The greater the electronegativity, the stronger a binary acid in the same period of the periodic table.

43. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity:  $\text{NaHSO}_3$ ,  $\text{NaHSeO}_3$ ,  $\text{NaHSO}_4$

(b) basicity:  $\text{BrO}_2^-$ ,  $\text{ClO}_2^-$ ,  $\text{IO}_2^-$

(c) acidity:  $\text{HOCl}$ ,  $\text{HOBr}$ ,  $\text{HOI}$

(d) acidity:  $\text{HOCl}$ ,  $\text{HOClO}$ ,  $\text{HOClO}_2$ ,  $\text{HOClO}_3$

(e) basicity:  $\text{NH}_2^-$ ,  $\text{HS}^-$ ,  $\text{HTe}^-$ ,  $\text{PH}_2^-$

(f) basicity:  $\text{BrO}^-$ ,  $\text{BrO}_2^-$ ,  $\text{BrO}_3^-$ ,  $\text{BrO}_4^-$

#### Solution

(a)  $\text{NaHSeO}_3 < \text{NaHSO}_3 < \text{NaHSO}_4$ ; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner. (b)

$\text{ClO}_2^- < \text{BrO}_2^- < \text{IO}_2^-$ ; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (c)

$\text{HOI} < \text{HOBr} < \text{HOCl}$ ; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (d)  $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$ ; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases). (e)

$\text{HTe}^- < \text{HS}^- \ll \text{PH}_2^- < \text{NH}_2^-$ ;  $\text{PH}_2^-$  and  $\text{NH}_2^-$  are anions of weak bases, so they act as strong bases toward  $\text{H}^+$ .  $\text{HTe}^-$  and  $\text{HS}^-$  are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion. (f)

$\text{BrO}_4^- < \text{BrO}_3^- < \text{BrO}_2^- < \text{BrO}^-$ ; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

44. Both  $\text{HF}$  and  $\text{HCN}$  ionize in water to a limited extent. Which of the conjugate bases,  $\text{F}^-$  or  $\text{CN}^-$ , is the stronger base?

#### Solution

$\text{CN}^-$ ;  $\text{HCN}$  is the weaker acid, so  $\text{CN}^-$  is the stronger base.

45. The active ingredient formed by aspirin in the body is salicylic acid,  $\text{C}_6\text{H}_4\text{OH}(\text{CO}_2\text{H})$ . The carboxyl group ( $-\text{CO}_2\text{H}$ ) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of  $\text{C}_6\text{H}_4\text{OH}(\text{CO}_2\text{H})$ .

#### Solution

$[\text{H}_2\text{O}] > [\text{C}_6\text{H}_4\text{OH}(\text{CO}_2\text{H})] > [\text{H}^+] > [\text{C}_6\text{H}_4\text{OH}(\text{CO}_2)^-] \square [\text{C}_6\text{H}_4\text{O}(\text{CO}_2\text{H})^-] > [\text{OH}^-]$

46. Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

#### Solution

Inversely proportional. The hydronium ion and hydroxide ion are related by the  $K_w$  equilibrium equation

$$K_w = [\text{H}^+][\text{OH}^-]$$

from which we see the inverse relation.

47. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid?

**Solution**

1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration. 2. Assume we can neglect the contribution of water to the equilibrium concentration of  $\text{H}_3\text{O}^+$ .

48. Which of the following will increase the percent of  $\text{NH}_3$  that is converted to the ammonium ion in water?

- (a) addition of NaOH
- (b) addition of HCl
- (c) addition of  $\text{NH}_4\text{Cl}$

**Solution**

The equilibrium is:



(a) The addition of NaOH adds  $\text{OH}^-$  to the system and, according to LeChâtelier's principle, the equilibrium will shift to the left. Thus, the percent of converted  $\text{NH}_3$  will decrease. (b) The addition of HCl will add  $\text{H}_3\text{O}^+$  ions, which will then react with the  $\text{OH}^-$  ions. Thus, the equilibrium will shift to the right, and the percent will increase. (c) The addition of  $\text{NH}_4\text{Cl}$  adds  $\text{NH}_4^+$  ions, shifting the equilibrium to the left. Thus, the percent will decrease.

49. Which of the following will increase the percent of HF that is converted to the fluoride ion in water?

- (a) addition of NaOH
- (b) addition of HCl
- (c) addition of NaF

**Solution**

The equilibrium is:



(a) The addition of NaOH adds  $\text{OH}^-$  to the system, which will then react with the  $\text{H}_3\text{O}^+$  ions. According to LeChâtelier's principle, the equilibrium will shift to the right. Thus, the percent will increase. (b) The addition of HCl will add  $\text{H}_3\text{O}^+$  ions. The equilibrium will shift to the left, and the percent will decrease. (c) The addition of NaF and  $\text{F}^-$  ions, shifting the equilibrium to the left. Thus, the percent will decrease.

50. What is the effect on the concentrations of  $\text{NO}_2^-$ ,  $\text{HNO}_2$ , and  $\text{OH}^-$  when the following are added to a solution of  $\text{KNO}_2$  in water:

- (a) HCl
- (b)  $\text{HNO}_2$
- (c) NaOH
- (d) NaCl

(e) KNO

Solution

(a) Adding HCl will add  $\text{H}_3\text{O}^+$  ions, which will then react with the  $\text{OH}^-$  ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of  $\text{HNO}_2$ , and decreasing the concentration of  $\text{NO}_2^-$  ions. (b) Adding  $\text{HNO}_2$  increases the concentration of  $\text{HNO}_2$  and shifts the equilibrium to the left, increasing the concentration of  $\text{NO}_2^-$  ions and decreasing the concentration of  $\text{OH}^-$  ions. (c) Adding NaOH adds  $\text{OH}^-$  ions, which shifts the equilibrium to the left, increasing the concentration of  $\text{NO}_2^-$  ions and decreasing the concentrations of  $\text{HNO}_2$ . (d) Adding NaCl has no effect on the concentrations of the ions. (e) Adding  $\text{KNO}_2$  adds  $\text{NO}_2^-$  ions and shifts the equilibrium to the right, increasing the  $\text{HNO}_2$  and  $\text{OH}^-$  ion concentrations.

51. What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

- (a) HCl
- (b) KF
- (c) NaCl
- (d) KOH
- (e) HF

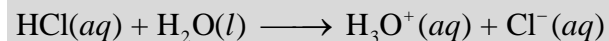
Solution

(a) Adding HCl will add  $\text{H}_3\text{O}^+$  ions. The equilibrium will shift to the left, increasing the concentration of HF and decreasing the concentration of  $\text{F}^-$  ions. (b) Adding KF increases the concentration of  $\text{F}^-$  ions, and shifts the equilibrium to the left, increasing the concentration of HF and decreasing the concentration of  $\text{H}_3\text{O}^+$  ions. (c) Adding NaCl has no effect on the concentrations of  $\text{H}_3\text{O}^+$  ions. (d) Adding KOH adds  $\text{OH}^-$  ions, which will react with the  $\text{H}_3\text{O}^+$  ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of  $\text{F}^-$  ions and decreasing the concentration of HF. (e) Adding HF increases the HF concentration, and shifts the equilibrium to the right, increasing the  $\text{H}_3\text{O}^+$  and  $\text{F}^-$  ion concentrations.

52. Why is the hydronium ion concentration in a solution that is 0.10 M in HCl and 0.10 M in  $\text{HCOOH}$  determined by the concentration of HCl?

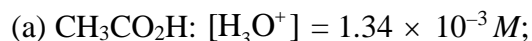
Solution

The equations of the occurring chemical processes are:



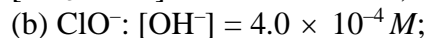
This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the  $\text{HCO}_2\text{H}$  exists primarily as  $\text{HCO}_2\text{H}$  molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the  $\text{HCO}_2\text{H}$  contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the  $[\text{H}_3\text{O}^+]$  produced by the stronger acid.

53. From the equilibrium concentrations given, calculate  $K_a$  for each of the weak acids and  $K_b$  for each of the weak bases.



$$[\text{CH}_3\text{CO}_2^-] = 1.34 \times 10^{-3} \text{ M};$$

$$[\text{CH}_3\text{CO}_2\text{H}] = 9.866 \times 10^{-2} \text{ M};$$



$$[\text{HClO}] = 2.38 \times 10^{-4} \text{ M};$$

$$[\text{ClO}^-] = 0.273 \text{ M};$$



$$[\text{H}_3\text{O}^+] = 9.8 \times 10^{-3} \text{ M};$$

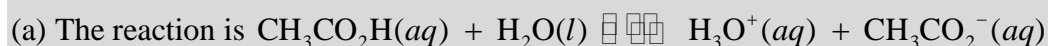
$$[\text{HCO}_2^-] = 9.8 \times 10^{-3} \text{ M};$$



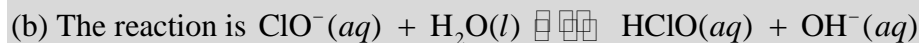
$$[\text{C}_6\text{H}_5\text{NH}_2] = 2.3 \times 10^{-3} \text{ M};$$

$$[\text{H}_3\text{O}^+] = 2.3 \times 10^{-3} \text{ M}$$

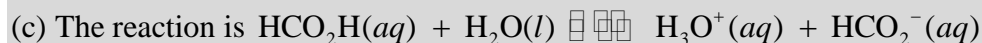
#### Solution



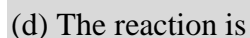
$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(1.34 \times 10^{-3})(1.34 \times 10^{-3})}{(9.866 \times 10^{-2})} = 1.82 \times 10^{-5};$$



$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]} = \frac{(2.38 \times 10^{-4})(4.0 \times 10^{-4})}{(0.273)} = 3.5 \times 10^{-7};$$

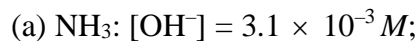


$$K_a = \frac{[\text{HCO}_2^-][\text{H}_3\text{O}^+]}{[\text{HCO}_2\text{H}]} = \frac{(9.8 \times 10^{-3})(9.8 \times 10^{-3})}{(0.524)} = 1.8 \times 10^{-4};$$



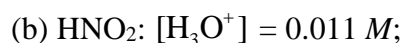
$$K_a = \frac{[\text{C}_6\text{H}_5\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{NH}_3^+]} = \frac{(2.3 \times 10^{-3})(2.3 \times 10^{-3})}{(0.233)} = 2.3 \times 10^{-5}$$

54. From the equilibrium concentrations given, calculate  $K_a$  for each of the weak acids and  $K_b$  for each of the weak bases.



$$[\text{NH}_4^+] = 3.1 \times 10^{-3} \text{ M};$$

$$[\text{NH}_3] = 0.533 \text{ M};$$



$$[\text{NO}_2^-] = 0.0438 \text{ M};$$

$$[\text{HNO}_2] = 1.07 \text{ M};$$



$$[(\text{CH}_3)_3\text{NH}^+] = 4.3 \times 10^{-3} \text{ M};$$

$$[\text{OH}^-] = 3.7 \times 10^{-3} \text{ M};$$

(d)  $\text{NH}_4^+$ :  $[\text{NH}_4^+] = 0.100 \text{ M}$ ;

$[\text{NH}_3] = 7.5 \times 10^{-6} \text{ M}$ ;

$[\text{H}_3\text{O}^+] = 7.5 \times 10^{-6} \text{ M}$

**Solution**

(a) The reaction is  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{NH}_4^+(\text{aq})$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(3.1 \times 10^{-3})(3.1 \times 10^{-3})}{(0.533)} = 1.8 \times 10^{-5};$$

(b) The reaction is  $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_2^-(\text{aq})$

$$K_a = \frac{[\text{NO}_2^-][\text{H}_3\text{O}^+]}{[\text{HNO}_2]} = \frac{(0.0438)(0.011)}{(1.07)} = 4.5 \times 10^{-4};$$

(c) The reaction is  $(\text{CH}_3)_3\text{N}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + (\text{CH}_3)_3\text{NH}^+(\text{aq})$

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(3.7 \times 10^{-3})(4.3 \times 10^{-3})}{(0.25)} = 6.4 \times 10^{-5};$$

(d) The reaction is  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq})$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(7.5 \times 10^{-6})(7.5 \times 10^{-6})}{(0.100)} = 5.6 \times 10^{-10}$$

55. Determine  $K_b$  for the nitrite ion,  $\text{NO}_2^-$ . In a 0.10-M solution this base is 0.0015% ionized.

**Solution**

The reaction is  $\text{NO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HNO}_2(\text{aq}) + \text{OH}^-(\text{aq})$ .

The concentrations at equilibrium are  $[\text{HNO}_2] = [\text{OH}^-] = (1.5 \times 10^{-5})(0.10 \text{ M}) = 1.5 \times 10^{-6} \text{ M}$ .

$[\text{NH}_3] = 0.10 \text{ M} - 1.5 \times 10^{-5} \text{ M} = 0.10 \text{ M}$

$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NH}_3]} = \frac{(1.5 \times 10^{-6})(1.5 \times 10^{-6})}{(0.10)} = 2.3 \times 10^{-11}$$

56. Determine  $K_a$  for hydrogen sulfate ion,  $\text{HSO}_4^-$ . In a 0.10-M solution the acid is 29% ionized.

**Solution**

The reaction is  $\text{HSO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ .

The concentrations at equilibrium are:

$[\text{H}_3\text{O}^+] = [\text{SO}_4^{2-}] = (0.29)(0.10 \text{ M}) = 0.029 \text{ M}$

$[\text{HSO}_4^-] = 0.10 \text{ M} - 0.029 \text{ M} = 0.071 \text{ M}$

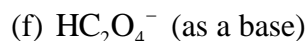
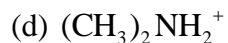
$$K_a = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_4^-]} = \frac{(0.029)(0.029)}{(0.071)} = 1.2 \times 10^{-2}$$

57. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a)  $\text{F}^-$

(b)  $\text{NH}_4^+$

(c)  $\text{AsO}_4^{3-}$

**Solution**

(a) The fluoride ion reacts with water as a base in the following way:



An expression for the equilibrium is written in the usual way:

$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]}$$

This expression is related to the ionization of HF:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.4 \times 10^{-4}$$

Inspection of the expressions for  $K_b$  and for  $K_a$  indicates an inverse relationship between  $K_a$  and  $K_b$  with the substitution of  $[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$  in the expression for  $K_a$

$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{\frac{K_w}{[\text{H}_3\text{O}^+]} \times [\text{HF}]}{[\text{F}^-]} = \frac{K_w[\text{HF}]}{[\text{F}^-][\text{H}_3\text{O}^+]}$$

$$K_b = K_w \times \frac{1}{K_a} = \frac{K_w}{K_a}$$

This final relationship turns out to be the general form for the reaction of an ion from either a weak acid or a weak base.

For the  $\text{F}^-$  ion:

$$K_b = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-4}} = 1.6 \times 10^{-11};$$

(b) This ion is the conjugate acid of the weak base ammonia. Reaction of  $\text{NH}_4^+$  gives:

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b(\text{NH}_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10};$$

$$(c) K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-12}} = 3.3 \times 10^{-3};$$

$$(d) K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-4}} = 1.7 \times 10^{-11};$$

$$(e) K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = 2.2 \times 10^{-11};$$

$$(f) K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.0 \times 10^{-2}} = 1.7 \times 10^{-13}$$

58. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

- (a)  $\text{HTe}^-$  (as a base)
- (b)  $(\text{CH}_3)_3\text{NH}^+$
- (c)  $\text{HAsO}_4^{3-}$  (as a base)
- (d)  $\text{HO}_2^-$  (as a base)
- (e)  $\text{C}_6\text{H}_5\text{NH}_3^+$
- (f)  $\text{HSO}_3^-$  (as a base)

Solution

$$(a) K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{2.3 \times 10^{-3}} = 4.3 \times 10^{-12};$$

$$(b) K_a = \frac{K_w}{K_b} = \frac{(1.00 \times 10^{-14})}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10};$$

$$(c) K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{1.7 \times 10^{-7}} = 5.9 \times 10^{-8};$$

$$(d) K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{2.4 \times 10^{-12}} = 4.2 \times 10^{-3};$$

$$(e) K_a = \frac{K_w}{K_b} = \frac{(1.00 \times 10^{-14})}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5};$$

$$(f) K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{1.6 \times 10^{-2}} = 6.3 \times 10^{-13}$$

59. Using the  $K_a$  values in Appendix H, place  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  in the correct location in Figure 14.7.

Solution

The reaction is:



This is a comparatively weak acid. It lies between hydrofluoric acid at  $K_a \sim 10^{-4}$  and carbonic acid at  $K_a \sim 10^{-6}$ .

60. Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected.

- (a) 0.0092 M  $\text{HClO}$ , a weak acid
- (b) 0.0784 M  $\text{C}_6\text{H}_5\text{NH}_2$ , a weak base
- (c) 0.0810 M  $\text{HCN}$ , a weak acid
- (d) 0.11 M  $(\text{CH}_3)_3\text{N}$ , a weak base
- (e) 0.120 M  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  a weak acid,  $K_a = 1.6 \times 10^{-7}$

Solution



(a) The reaction is:  $\text{HClO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}^-(aq)$

The equilibrium expression is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = 2.9 \times 10^{-8}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HClO]	[H <sub>3</sub> O <sup>+</sup> ]	[ClO <sup>-</sup> ]
Initial concentration (M)	0.0092	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.0092 - x	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that  $(0.0092 - x) \approx 0.0092$  gives:

$$\frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = \frac{(x)(x)}{(0.0092 - x)} \approx \frac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$$

Solving for  $x$  gives  $1.63 \times 10^{-5} M$ . This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{H}_3\text{O}^+] = [\text{ClO}^-] = 1.6 \times 10^{-5} M$$

$$[\text{HClO}] = 0.0092 - 1.63 \times 10^{-5} = 0.00918 = 0.0092 M$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.63 \times 10^{-5}} = 6.1 \times 10^{-10} M ;$$

(b) The reaction is:  $\text{C}_6\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(aq) + \text{OH}^-(aq)$

The equilibrium expression is:

$$K_a = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = 4.3 \times 10^{-10}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> ]	[C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup> ]	[OH <sup>-</sup> ]
Initial concentration (M)	0.0784	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.0784 - x	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that  $(0.0784 - x) \approx 0.0784$  gives:

$$\frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{(x)(x)}{(0.0784 - x)} \approx \frac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$$

Solving for  $x$  gives  $5.81 \times 10^{-6} M$ . This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{CH}_3\text{CO}_2^-] = [\text{OH}^-] = 5.8 \times 10^{-6} M$$

$$[\text{C}_6\text{H}_5\text{NH}_2] = 0.0784 - 5.81 \times 10^{-6} = 0.07839 = 0.0784$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.81 \times 10^{-6}} = 1.7 \times 10^{-9} \text{ M};$$

(c) The reaction is  $\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)$ .

The equilibrium expression is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = 4.9 \times 10^{-10}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HClO]	[H <sub>3</sub> O <sup>+</sup> ]	[CN <sup>-</sup> ]
Initial concentration (M)	0.0810	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.0810 - x	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that  $(0.0810 - x) \approx 0.0810$  gives:

$$\frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4 \times 10^{-10}$$

Solving for  $x$  gives  $6.30 \times 10^{-6} \text{ M}$ . This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{H}_3\text{O}^+] = [\text{CN}^-] = 6.3 \times 10^{-6} \text{ M}$$

$$[\text{HCN}] = 0.0810 - 6.30 \times 10^{-6} = 0.08099 = 0.0810 \text{ M}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{6.30 \times 10^{-6}} = 1.6 \times 10^{-9} \text{ M};$$

(d) The reaction is:



The equilibrium expression is:

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = 6.3 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[(CH <sub>3</sub> ) <sub>3</sub> N]	[(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup> ]	[OH <sup>-</sup> ]
Initial concentration (M)	0.11	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.11 - x	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that  $(0.11 - x) \approx 0.11$  gives:

$$\frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$$

Solving for  $x$  gives  $2.63 \times 10^{-3} M$ . This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[(\text{CH}_3)_3\text{NH}^+] = [\text{OH}^-] = 2.6 \times 10^{-3} M$$

$$[(\text{CH}_3)_3\text{N}] = 0.11 - 2.63 \times 10^{-3} = 0.107 = 0.11 M$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.63 \times 10^{-3}} = 3.8 \times 10^{-12} M ;$$

(e) The reaction is:



The equilibrium expression is:

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

The initial and equilibrium concentrations for this system can be written as follows:

	$[\text{Fe}(\text{H}_2\text{O})_6^{2+}]$	$[\text{H}_3\text{O}^+]$	$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+]$
Initial concentration (M)	0.120	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	$0.120 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that  $(0.120 - x) \approx 0.120$  gives:

$$\frac{[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+][\text{H}_3\text{O}^+]}{[\text{Fe}(\text{H}_2\text{O})_6^{2+}]} = \frac{(x)(x)}{(0.120 - x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$$

Solving for  $x$  gives  $1.39 \times 10^{-4} M$ . This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+] = [\text{H}_3\text{O}^+] = 1.4 \times 10^{-4} M$$

$$[\text{Fe}(\text{H}_2\text{O})_6^{2+}] = 0.120 - 1.39 \times 10^{-4} = 0.1199 = 0.120 M$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.39 \times 10^{-4}} = 7.2 \times 10^{-11} M$$

61. Propionic acid,  $\text{C}_2\text{H}_5\text{CO}_2\text{H}$  ( $K_a = 1.34 \times 10^{-5}$ ), is used in the manufacture of calcium propionate, a food preservative. What is the pH of a 0.698-M solution of  $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ ?

Solution

The reaction is:



The equilibrium expression is:

$$K_a = \frac{[\text{C}_2\text{H}_5\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{C}_2\text{H}_5\text{CO}_2\text{H}]} = 1.34 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[\text{C}_2\text{H}_5\text{CO}_2\text{H}]$	$[\text{H}_3\text{O}^+]$	$[\text{C}_2\text{H}_5\text{CO}_2^-]$
Initial concentration ( $M$ )	0.698	0	0
Change ( $M$ )	$-x$	$+x$	$+x$
Equilibrium ( $M$ )	$0.698 - x$	$x$	$x$

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that  $(0.698 - x) \approx 0.698$  gives:

$$\frac{[\text{C}_2\text{H}_5\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{C}_2\text{H}_5\text{CO}_2\text{H}]} = \frac{(x)(x)}{(0.698 - x)} \approx \frac{(x)(x)}{0.698} = 1.34 \times 10^{-5}$$

Solving for  $x$  gives  $3.058 \times 10^{-3} M$ . Because this value is 5% of 0.698, our assumption is correct. The equilibrium concentration of hydronium ion is therefore:

$$[\text{H}_3\text{O}^+] = 3.058 \times 10^{-3} M$$

$$\text{pH} = -\log(3.058 \times 10^{-3}) = 2.5146 = 2.515$$

62. White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is  $1.007 \text{ g/cm}^3$ , what is the pH?

Solution

First, find the mass of acetic acid.  $d = 1.007 \text{ g/cm}^3$ . Take 1.0 L of solution to have the quantities on a mole basis. Then, since  $1000 \text{ cm}^3 = 1.0 \text{ L}$ ,  $1000 \text{ cm}^3 \times 1.007 \text{ g/cm}^3 = 1007 \text{ g}$  in 1.0 L. Then, 5.00% of this is the mass of acetic acid:

$$\text{Mass (acetic acid)} = 1007 \text{ g} \times \frac{5.0\%}{100\%} = 50.35 \text{ g}$$

Now calculate the number of moles of acetic acid present. The molar mass of acetic acid is  $60.053 \text{ g/mol}$ :

$$\text{mol acetic acid} = \frac{50.35 \text{ g}}{60.053 \text{ g mol}^{-1}} = 0.838 \text{ mol}$$

From the moles of acetic acid and  $K_a$ , calculate  $[\text{H}_3\text{O}^+]$ :

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

	$[\text{CH}_3\text{CO}_2\text{H}]$	$[\text{H}_3\text{O}^+]$	$[\text{CH}_3\text{CO}_2^-]$
Initial concentration ( $M$ )	0.838	0	0
Change ( $M$ )	$-x$	$+x$	$+x$
Equilibrium ( $M$ )	$0.838 - x$	$x$	$x$

Substitution gives:

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.838 - x}$$

Drop  $x$  because it is small in comparison with  $0.838 M$ .

$$x^2 = 0.838(1.8 \times 10^{-5}) = (1.508 \times 10^{-5})^{1/2} = 3.88 \times 10^{-3} M$$

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

63. The ionization constant of lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$ , an acid found in the blood after strenuous exercise, is  $1.36 \times 10^{-4}$ . If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

Solution



$$M \text{ CH}_3\text{CHOHCO}_2\text{H} = 20.0 \text{ g} \times \frac{1 \text{ mol}}{90.0788 \text{ g}} = \frac{0.2220 \text{ mol}}{1.00 \text{ L}} = 0.2220 \text{ M CH}_3\text{CHOHCO}_2\text{H}$$

	$[\text{CH}_3\text{CHOHCO}_2\text{H}]$	$[\text{H}_3\text{O}^+]$	$[\text{CH}_3\text{CHOHCO}_2^-]$
Initial concentration (M)	0.2220	~0	~0
Change (M)	-x	+x	+x
Equilibrium (M)	0.2220 - x	x	x

At equilibrium:

$$\frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CHOHCO}_2^-]}{[\text{CH}_3\text{CHOHCO}_2\text{H}]} = 1.36 \times 10^{-4} = K_a$$

$$\frac{(x)(x)}{(0.2220 - x)} = 4.5 \times 10^{-4}$$

Assume that  $x$  is small:

$$\frac{(x)(x)}{(0.2220)} = 1.36 \times 10^{-4}$$

$$x^2 = (0.2220) \times 1.36 \times 10^{-4} = 3.02 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 0.00549$$

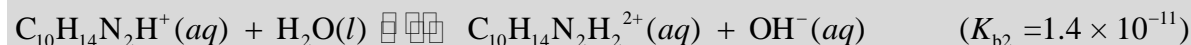
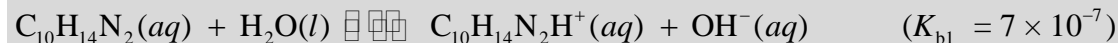
To check our assumption:

$$\frac{0.00549}{0.2220} = 0.0248 \text{ (2.48\%)}$$

Another approximation is not needed.

64. Nicotine,  $\text{C}_{10}\text{H}_{14}\text{N}_2$ , is a base that will accept two protons ( $K_{b1} = 7 \times 10^{-7}$ ,  $K_{b2} = 1.4 \times 10^{-11}$ ). What is the concentration of each species present in a 0.050-M solution of nicotine?

Solution



First set up a concentration table:

	$[\text{C}_{10}\text{H}_{14}\text{N}_2]$	$[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+]$	$[\text{OH}^-]$
Initial concentration (M)	0.050	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.050 - x	x	x

Substituting the equilibrium concentrations into the equilibrium equation and making the assumption that  $(0.050 - x) = 0.050$ , we get:

$$K_{b1} = \frac{[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+][\text{OH}^-]}{[\text{C}_{10}\text{H}_{14}\text{N}_2]} = 7 \times 10^{-7}$$

$$= \frac{(x)(x)}{(0.050 - x)} = \frac{x^2}{0.050} = 7 \times 10^{-7}$$

Solving for  $x$  gives  $1.87 \times 10^{-4} = 2 \times 10^{-4} M = [\text{OH}^-]$

Because  $x$  is less than 5% of 0.050 and  $[\text{OH}^-]$  is greater than  $4.5 \times 10^{-7} M$ , our customary assumptions are justified. We can calculate  $[\text{C}_{10}\text{H}_{14}\text{N}_2] = 0.050 - x = 0.050 - 2 \times 10^{-4} = 0.048 M$ ;  $[\text{OH}^-] = [\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+] = x = 2 \times 10^{-4} M$ . Now calculate the concentration of  $\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}$  in a solution with  $[\text{OH}^-]$  and  $[\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}]$  equal to  $2 \times 10^{-4} M$ . The equilibrium between these species is  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_{10}\text{H}_{14}\text{N}_2\text{H}_2^{2+}(aq) + \text{OH}^-(aq)$ . We know  $[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+]$  and  $[\text{OH}^-]$ , so we can calculate the concentration of  $\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}$  from the equilibrium expression:

$$K_{b2} = \frac{[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}_2^{2+}][\text{OH}^-]}{[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+]} = 1.4 \times 10^{-11}$$

$$= \frac{[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}_2^{2+}][2 \times 10^{-4}]}{[2 \times 10^{-4}]}$$

$$[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}_2^{2+}] = 1.4 \times 10^{-11} M$$

The concentration of  $\text{OH}^-$  produced in this ionization is equal to the concentration of  $\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}$ ,  $1.4 \times 10^{-11} M$ , which is much smaller than the  $2 \times 10^{-4} M$  produced in the first ionization; therefore, we are justified in neglecting the  $\text{OH}^-$  formed from  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+$ .

We can now calculate the concentration of  $\text{H}_3\text{O}^+$  present from the ionization of water:

$$K_a = 1 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{1.9 \times 10^{-4}} = 5.3 \times 10^{-11} M$$

We can now summarize the concentrations of all species in solution as follows:

$$[\text{C}_{10}\text{H}_{14}\text{N}_2] = 0.049 M$$

$$[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+] = 1.9 \times 10^{-4} M$$

$$[\text{C}_{10}\text{H}_2\text{N}_2\text{H}_2^{2+}] = 1.4 \times 10^{-11} M$$

$$[\text{OH}^-] = 1.9 \times 10^{-4} M$$

$$[\text{H}_3\text{O}^+] = 5.3 \times 10^{-11} M$$

65. The pH of a 0.23-M solution of HF is 1.92. Determine  $K_a$  for HF from these data.

**Solution**

The reaction is:



The concentrations at equilibrium are:

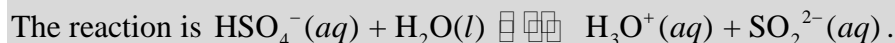
$$[\text{F}^-] = [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-1.92} = 0.0120 M$$

$$[\text{HF}] = 0.23 \text{ M} - 0.0120 \text{ M} = 0.218 \text{ M}$$

$$K_a = \frac{[\text{F}^-][\text{H}_3\text{O}^+]}{[\text{HF}]} = \frac{(0.0120)(0.0120)}{(0.218)} = 6.6 \times 10^{-4}$$

66. The pH of a 0.15-*M* solution of  $\text{HSO}_4^-$  is 1.43. Determine  $K_a$  for  $\text{HSO}_4^-$  from these data.

Solution



The concentrations at equilibrium are  $[\text{SO}_4^{2-}] = [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-1.43} = 0.0372 \text{ M}$

$$[\text{HF}] = 0.15 - 0.0372 \text{ M} = 0.113 \text{ M}$$

$$K_a = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_4^-]} = \frac{(0.0372)(0.0372)}{(0.113)} = 1.2 \times 10^{-2}$$

67. The pH of a 0.10-*M* solution of caffeine is 11.70. Determine  $K_b$  for caffeine from these data:



Solution

The pOH can be determined from  $\text{pOH} = 14.00 - \text{pH} = 14.00 - 11.70 = 2.30$ . Therefore, the concentrations at equilibrium are:

$$[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+] = [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-2.30} = 0.00501 \text{ M}$$

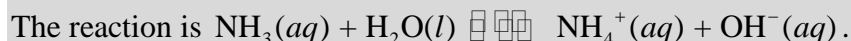
$$[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2] = 0.10 - 0.00501 = 0.095 \text{ M}$$

$$K_b = \frac{[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+][\text{OH}^-]}{[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2]} = \frac{(0.00501)(0.00501)}{(0.095)} = 2.6 \times 10^{-4}$$

68. The pH of a solution of household ammonia, a 0.950 *M* solution of  $\text{NH}_3$ , is 11.612.

Determine  $K_b$  for  $\text{NH}_3$  from these data.

Solution



The pOH can be determined from  $\text{pOH} = 14.000 - \text{pH} = 14.000 - 11.612 = 2.388$ . Therefore, the concentrations at equilibrium are  $[\text{NH}_4^+] = [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-2.388} = 0.004093 \text{ M}$

$$[\text{NH}_3] = 0.950 - 0.004093 = 0.9459 \text{ M}$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.004093)(0.004093)}{(0.9459)} = 1.77 \times 10^{-5}$$

## Chemistry 2e

### 14: Acid-Base Equilibria

#### 14.4: Hydrolysis of Salts

69. Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

- $\text{Al}(\text{NO}_3)_3$
- $\text{RbI}$
- $\text{KHCO}_2$
- $\text{CH}_3\text{NH}_3\text{Br}$

Solution

(a)  $\text{Al}(\text{NO}_3)_3$  dissociates into  $\text{Al}^{3+}$  ions (acidic metal cation) and  $\text{NO}_3^-$  ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic. (b)  $\text{RbI}$

dissociates into  $\text{Rb}^+$  ions (neutral metal cation) and  $\text{I}^-$  ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore neutral. (c)  $\text{KHCO}_2$  dissociates into  $\text{K}^+$  ions (neutral metal cation) and  $\text{HCO}_2^-$  ions (the conjugate base of a weak acid and therefore basic). The aqueous solution is therefore basic. (d)  $\text{CH}_3\text{NH}_3\text{Br}$  dissociates into  $\text{CH}_3\text{NH}_3^+$  ions (a weak acid) and  $\text{Br}^-$  ions (the conjugate base of a strong acid and therefore neutral). The aqueous solution is therefore acidic.

70. Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

- (a)  $\text{FeCl}_3$
- (b)  $\text{K}_2\text{CO}_3$
- (c)  $\text{NH}_4\text{Br}$
- (d)  $\text{KClO}_4$

Solution

(a)  $\text{FeCl}_3$  dissociates into  $\text{Fe}^{3+}$  ions (acidic metal cation) and  $\text{Cl}^-$  ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic. (b)  $\text{K}_2\text{CO}_3$  dissociates into  $\text{K}^+$  ions (neutral metal cation) and  $\text{CO}_3^{2-}$  ions (the conjugate base of a weak acid and therefore basic). The aqueous solution is therefore basic. (c)  $\text{NH}_4\text{Br}$  dissociates into  $\text{NH}_4^+$  ions (a weak acid) and  $\text{Br}^-$  ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic. (d)  $\text{KClO}_4$  dissociates into  $\text{K}^+$  ions (neutral metal cation) and  $\text{ClO}_4^-$  ions (the conjugate base of a strong acid and therefore neutral). The aqueous solution is therefore neutral.

71. Novocaine,  $\text{C}_{13}\text{H}_{21}\text{O}_2\text{N}_2\text{Cl}$ , is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is  $7 \times 10^{-6}$ . Is a solution of novocaine acidic or basic? What are  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

Solution

Using the abbreviation Pc for  $\text{C}_{13}\text{H}_{20}\text{O}_2\text{N}_2$  (procaine), the formula for novocaine is  $\text{PcHCl}$ , which ionizes to form  $\text{PcH}^+$  and  $\text{Cl}^-$ . The molar mass of novocaine is 272.774 g/mol. For convenience, start with 1.00 L of a 2.0% solution by mass:

$$1.00 \times 10^3 \text{ cm}^3 \times 1.0 \text{ g cm}^{-3} = 1.00 \times 10^3 \text{ g}$$

$$\frac{2.0}{100} \times 1.00 \times 10^3 \text{ g} = 20 \text{ g novocaine}$$

$$= \frac{20 \text{ g}}{272.774 \text{ g mol}^{-1}}$$

$$= 0.073 \text{ mol}$$

In exactly 1 L, there is 0.073 M. The cation reacts with water:



$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{7 \times 10^{-6}} = 1.4 \times 10^{-9}$$

It is convenient to set up a table of concentrations:



	$[\text{C}_{13}\text{H}_{21}\text{O}_2\text{N}_2\text{H}^+] \text{ or } [\text{PcH}^+]$	$[\text{H}_3\text{O}^+]$	$[\text{C}_{13}\text{H}_{21}\text{O}_2\text{N}_2] \text{ or } [\text{Pc}]$
Initial concentration ( $M$ )	0.073	0	0
Change ( $M$ )	$-x$	$+x$	$+x$
Equilibrium ( $M$ )	$0.073 - x$	$x$	$x$

$$1.4 \times 10^{-9} = \frac{[\text{Pc}][\text{H}_3\text{O}^+]}{[\text{PcH}^+]} = \frac{x^2}{0.073}$$

The change  $x$  compared with  $0.073 M$  is small and, therefore, neglected:

$$[\text{H}_3\text{O}^+] = x = 1.0 \times 10^{-5} = 1 \times 10^{-5} M$$

The solution is acidic. The hydroxide ion concentration is:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1 \times 10^{-9} M$$

$$\text{pH} = -\log(1.0 \times 10^{-5}) = 5.00 = 5.0$$

### Chemistry 2e 14: Acid-Base Equilibria 14.5: Polyprotic Acids

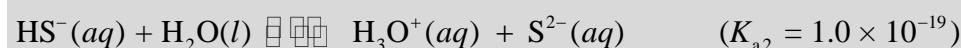
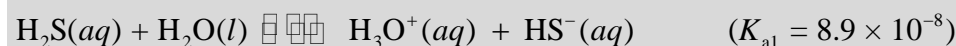
72. Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a  $0.134\text{-}M$  solution of  $\text{H}_2\text{CO}_3$ , a diprotic acid:  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ ,  $[\text{H}_2\text{CO}_3]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ ? No calculations are needed to answer this question.

**Solution**

$[\text{H}_3\text{O}^+]$  and  $[\text{HCO}_3^-]$  are equal in a  $0.134\text{-}M$  solution of  $\text{H}_2\text{CO}_3$ .  $K_a$  of  $\text{H}_2\text{CO}_3$  is significantly larger than  $K_a$  for  $\text{HCO}_3^-$ . Therefore, very little of  $\text{HCO}_3^-$  ionizes to give hydronium ions and  $\text{CO}_3^{2-}$  ions, and the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{HCO}_3^-$  are practically equal in an aqueous solution of  $\text{H}_2\text{CO}_3$ .

73. Calculate the concentration of each species present in a  $0.050\text{-}M$  solution of  $\text{H}_2\text{S}$ .

**Solution**



As indicated by the  $K_a$  values,  $\text{H}_2\text{S}$  is a much stronger acid than  $\text{HS}^-$ , so  $\text{H}_2\text{S}$  is a dominant producer of  $\text{H}_3\text{O}^+$  in solution:

	$[\text{H}_2\text{S}]$	$[\text{H}_3\text{O}^+]$	$[\text{HS}^-]$
Initial concentration ( $M$ )	0.05	$\sim 0$	$\sim 0$
Change ( $M$ )	$-x$	$+x$	$+x$
Equilibrium ( $M$ )	$0.05 - x$	$x$	$x$

Assume that  $(0.05 - x) = 0.05$ . Thus:

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 8.9 \times 10^{-8}$$

$$= \frac{(x)(x)}{0.05} = \frac{x^2}{0.05}$$

$$x^2 = 0.05 \times 8.9 \times 10^{-8}$$

$$x = 6.7 \times 10^{-5}$$

$$[\text{H}_2\text{S}] = 0.050 - x = 0.050 - 6.7 \times 10^{-5} = 0.050 \text{ M}$$

$$[\text{H}_3\text{O}^+] = [\text{HS}^-] = x = 6.7 \times 10^{-5} \text{ M}$$

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{S}^{2-}]}{[\text{HS}^-]} = 1.0 \times 10^{-19}$$

$$= \frac{(6.7 \times 10^{-5})[\text{S}^{2-}]}{6.7 \times 10^{-5}} = 1.0 \times 10^{-19} \text{ M}$$

$$[\text{S}^{2-}] = \frac{(1.0 \times 10^{-19})(6.7 \times 10^{-5})}{6.7 \times 10^{-5}} = 1 \times 10^{-19} \text{ M}$$

The  $[\text{OH}^-]$  can be calculated from  $K_w$  as follows:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{6.7 \times 10^{-5}} = 1.5 \times 10^{-10} \text{ M}$$

In summary, the concentrations of all species present in a 0.050-M solution of  $\text{H}_2\text{S}$  are:

$$[\text{H}_2\text{S}] = 0.050 \text{ M}$$

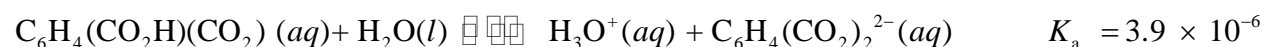
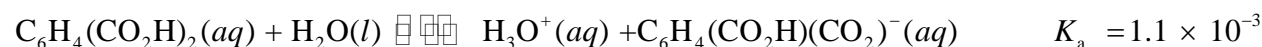
$$[\text{HS}^-] = 6.7 \times 10^{-5} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 6.7 \times 10^{-5} \text{ M}$$

$$[\text{S}^{2-}] = 1 \times 10^{-19} \text{ M}$$

$$[\text{OH}^-] = 1.5 \times 10^{-10} \text{ M}$$

74. Calculate the concentration of each species present in a 0.010-M solution of phthalic acid,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ .



**Solution**

$$[\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2] 7.2 \times 10^{-3} \text{ M}, [\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CO}_2)^-] = [\text{H}_3\text{O}^+] 2.8 \times 10^{-3} \text{ M}, [\text{C}_6\text{H}_4(\text{CO}_2)_2^{2-}] 3.9 \times 10^{-6} \text{ M}, [\text{OH}^-] 3.6 \times 10^{-12} \text{ M}$$

75. Salicylic acid,  $\text{HOC}_6\text{H}_4\text{CO}_2\text{H}$ , and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

(a) Both functional groups of salicylic acid ionize in water, with  $K_a = 1.0 \times 10^{-3}$  for the  $-\text{CO}_2\text{H}$  group and  $4.2 \times 10^{-13}$  for the  $-\text{OH}$  group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).

(b) Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid,  $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ . The  $-\text{CO}_2\text{H}$  functional group is still present, but its acidity is reduced,  $K_a = 3.0 \times 10^{-4}$ . What is

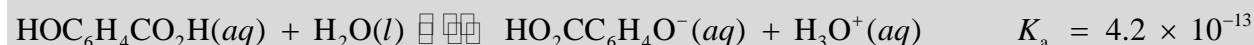
the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

**Solution**

(a) First, find the concentration of the saturated solution. The molar mass of salicylic acid is 138.123 g/mol. This gives:

$$\frac{1.8 \text{ g L}^{-1}}{138.123 \text{ g mol}^{-1}} = 0.0130 \text{ M}$$

The reactions and equilibrium constants are:



Because the equilibrium constant for the first reaction is so much larger than for the second reaction, it will dominate. The equilibrium expression for this reaction is:

$$K_a = \frac{[\text{HOC}_6\text{H}_4\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{HOC}_6\text{H}_4\text{CO}_2\text{H}]} = 1.0 \times 10^{-3}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}]$	$[\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2^-]$	$[\text{H}_3\text{O}^+]$
<b>Initial concentration (M)</b>	0.0130	0	0
<b>Change (M)</b>	-x	+x	+x
<b>Equilibrium (M)</b>	$0.0130 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that  $(0.0130 - x) \approx 0.0130$ , gives:

$$\frac{[\text{HOC}_6\text{H}_4\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{HOC}_6\text{H}_4\text{CO}_2\text{H}]} = \frac{(x)(x)}{(0.0130 - x)} \approx \frac{(x)(x)}{0.0130} = 1.0 \times 10^{-3}$$

Solving for  $x$  gives  $3.61 \times 10^{-3} \text{ M}$ . Because this value is 28% of  $0.0130 \text{ M}$ , our assumption is incorrect. Therefore, use the quadratic formula. Using the provided data gives the quadratic equation:

$$x^2 + 1.0 \times 10^{-3}x - 1.30 \times 10^{-5} = 0$$

Using the quadratic formula gives ( $a = 1$ ,  $b = 1.0 \times 10^{-3}$ , and  $c = -1.30 \times 10^{-5}$ )

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(1.0 \times 10^{-3}) \pm \sqrt{(1.0 \times 10^{-3})^2 - 4(1)(-1.30 \times 10^{-5})}}{2(1)}$$

$$= \frac{-(1.0 \times 10^{-3}) \pm (7.28 \times 10^{-3})}{2} = 3.14 \times 10^{-3} \text{ M} \quad (\text{positive root})$$

Thus,  $[\text{H}^+] = 3.14 \times 10^{-3} \text{ M}$

$$\text{pH} = -\log(3.14 \times 10^{-3}) = 2.503 = 2.50;$$

(b) The reaction and equilibrium constant are:



$$K_a = 3.0 \times 10^{-4}$$

The equilibrium expression for this reaction is:

$$K_a = \frac{[\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}]} = 3.0 \times 10^{-4}$$

For a 0.0130-M initial concentration, the initial and equilibrium concentrations for this system can be written as follows:

	$[\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}]$	$[\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2^-]$	$[\text{H}_3\text{O}^+]$
Initial concentration (M)	0.0130	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.0130 - x	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that  $(0.0130 - x) \approx 0.0130$ , gives:

$$\frac{[\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}]} = \frac{(x)(x)}{(0.0130 - x)} \approx \frac{(x)(x)}{0.0130} = 3.0 \times 10^{-4}$$

Solving for  $x$  gives  $1.97 \times 10^{-3} M$ . Because this value is 15% of 0.0130, our assumption is incorrect. Therefore, use the quadratic formula. Using the above data gives the quadratic equation:

$$x^2 + 3.0 \times 10^{-4}x - 3.90 \times 10^{-6} = 0$$

Using the quadratic formula gives ( $a = 1$ ,  $b = 3.0 \times 10^{-4}$ , and  $c = -3.90 \times 10^{-6}$ )

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(3.0 \times 10^{-4}) \pm \sqrt{(3.0 \times 10^{-4})^2 - 4(1)(-3.90 \times 10^{-6})}}{2(1)}$$

$$= \frac{-(3.0 \times 10^{-4}) \pm (3.96 \times 10^{-3})}{2} = 1.83 \times 10^{-3} M \quad (\text{positive root})$$

Thus,  $[\text{H}^+] = 1.83 \times 10^{-3} M$

$$\text{pH} = -\log(1.83 \times 10^{-3}) = 2.737 = 2.74$$

76. The ion  $\text{HTe}^-$  is an amphiprotic species; it can act as either an acid or a base.

(a) What is  $K_a$  for the acid reaction of  $\text{HTe}^-$  with  $\text{H}_2\text{O}$ ?

(b) What is  $K_b$  for the reaction in which  $\text{HTe}^-$  functions as a base in water?

(c) Demonstrate whether or not the second ionization of  $\text{H}_2\text{Te}$  can be neglected in the calculation of  $[\text{HTe}^-]$  in a 0.10 M solution of  $\text{H}_2\text{Te}$ .

Solution

(a) as an acid,



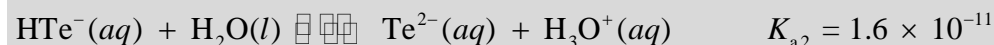
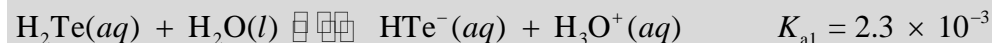
$$K_{a2} = \frac{[\text{Te}^{2-}][\text{H}_3\text{O}^+]}{[\text{HTe}^-]} = 1.6 \times 10^{-11};$$

(b) as a base,



$$K_b = \frac{[\text{H}_2\text{Te}][\text{OH}^-]}{[\text{HTe}^-]} = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-3}} = 4.3 \times 10^{-12};$$

(c) The reactions and ionization constants are:



As a general rule, if the first ionization constant is larger than the second by a factor of at least 20, then the second ionization can be neglected. Since  $K_{a1}$  is 230-times larger than  $K_{a2}$ , the assumption should hold true for  $\text{HTe}^-$ . To test the assumptions, find  $[\text{HTe}^-]$  from the first

reaction. The equilibrium expression for this reaction is  $K_{a1} = \frac{[\text{HTe}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{Te}]} = 2.3 \times 10^{-3}$ .

The initial and equilibrium concentrations for this system can be written as follows:

	$[\text{H}_2\text{Te}]$	$[\text{HTe}^-]$	$[\text{H}_3\text{O}^+]$
Initial concentration (M)	0.10	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	$0.10 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the

assumption that  $(0.10 - x) \approx 0.10$ , gives  $\frac{[\text{HTe}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{Te}]} = \frac{(x)(x)}{(0.10 - x)} \approx \frac{(x)(x)}{0.10} = 2.3 \times 10^{-3}$ .

Solving for  $x$  gives  $0.0152 M$ . Because this value is 15% of  $0.10 M$ , our assumption is incorrect.

Therefore, use the quadratic formula. Using the data gives the quadratic equation:

$$x^2 + 2.3 \times 10^{-3}x - 2.3 \times 10^{-4} = 0$$

Using the quadratic formula gives ( $a = 1$ ,  $b = 2.3 \times 10^{-3}$ , and  $c = -2.3 \times 10^{-4}$ )

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(2.3 \times 10^{-3}) \pm \sqrt{(2.3 \times 10^{-3})^2 - 4(1)(-2.3 \times 10^{-4})}}{2(1)}$$

$$= \frac{-(2.3 \times 10^{-3}) \pm (0.0304)}{2} = 0.0141 M \quad (\text{positive root})$$

Thus  $[\text{HTe}^-] = 0.014 M$ . For the second ionization,  $K_{a2} = \frac{[\text{Te}^{2-}][\text{H}_3\text{O}^+]}{[\text{HTe}^-]} = 1.6 \times 10^{-11}$ .

The initial and equilibrium concentrations for this system can be written as follows:

	$[\text{HTe}^-]$	$[\text{Te}^{2-}]$	$[\text{H}_3\text{O}^+]$
Initial concentration (M)	0.0141	0	0.0141
Change (M)	-x	+x	+x
Equilibrium (M)	$0.0141 - x$	x	$0.0141 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(0.0140 - x) \approx$  and  $(0.0141 + x) \approx 0.0141$ , gives:

$$\frac{[\text{Te}^{2-}][\text{H}_3\text{O}^+]}{[\text{HTe}^-]} = \frac{(x)(0.0141 + x)}{(0.0141 - x)} \approx \frac{(x)(0.0141)}{0.0141} = 1.6 \times 10^{-11}$$

Solving for  $x$  gives  $1.6 \times 10^{-11} M$ . Therefore, compared with  $0.014 M$ , this value is negligible ( $1.1 \times 10^{-7} \%$ ).

*Chemistry 2e*  
14: Acid-Base Equilibria  
14.6: Buffers

77. Explain why a buffer can be prepared from a mixture of  $\text{NH}_4\text{Cl}$  and  $\text{NaOH}$  but not from  $\text{NH}_3$  and  $\text{NaOH}$ .

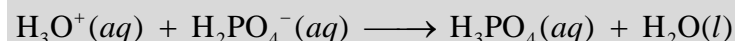
**Solution**

$\text{OH}^-$  is a base, and  $\text{NH}_4^+$  is a weak acid. They react with one another to form  $\text{NH}_3$ , thereby setting up the equilibrium  $\text{NH}_4^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{NH}_3(aq) + \text{H}_2\text{O}(l)$ . Because both the base ( $\text{NH}_3$ ) and the conjugate acid ( $\text{NH}_4^+$ ) are present, a buffer is formed. However, in the second case,  $\text{NH}_3$  and  $\text{OH}^-$  are both bases, so no buffer is possible.

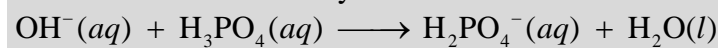
78. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid  $\text{H}_3\text{PO}_4$  and a salt of its conjugate base  $\text{NaH}_2\text{PO}_4$ .

**Solution**

Excess  $\text{H}_3\text{O}^+$  is removed primarily by the reaction:



Excess base is removed by the reaction:



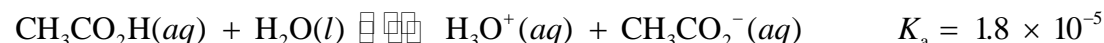
79. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base  $\text{NH}_3$  and a salt of its conjugate acid  $\text{NH}_4\text{Cl}$ .

**Solution**

A mixture of  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  is a buffer because it contains a weak base and its salt. If hydroxide ions are added, the ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration toward its original value:

$\text{NH}_4^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{NH}_3(aq) + \text{H}_2\text{O}(l)$ . If hydronium ions are added, the ammonia molecules in the buffer react with them to form ammonium ions, reducing the hydronium ion concentration toward its original value:  $\text{H}_3\text{O}^+(aq) + \text{NH}_3(aq) \rightleftharpoons \text{NH}_4^+(aq) + \text{H}_2\text{O}(l)$

80. What is  $[\text{H}_3\text{O}^+]$  in a solution of  $0.25 M \text{CH}_3\text{CO}_2\text{H}$  and  $0.030 M \text{NaCH}_3\text{CO}_2$ ?



**Solution**

The equilibrium expression is:

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[CH <sub>3</sub> CO <sub>2</sub> H]	[H <sub>3</sub> O <sup>+</sup> ]	[CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup> ]
Initial concentration (M)	0.25	0	0.030
Change (M)	-x	+x	+x
Equilibrium (M)	0.25 - x	x	0.030 + x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(0.25 - x) \approx 0.25$  and  $(0.030 - x) \approx 0.030$ , gives:

$$\frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(x)(0.030 - x)}{(0.25 - x)} \approx \frac{(x)(0.030)}{0.25} = 1.8 \times 10^{-5}$$

Solving for  $x$  gives  $1.50 \times 10^{-4} M$ . Because this value is less than 5% of both 0.25 and 0.030, our assumptions are correct. Therefore,  $[\text{H}_3\text{O}^+] = 1.5 \times 10^{-4} M$ .

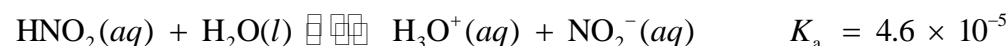
This problem can also be solved using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}; \text{p}K_a = -\log(K_a) = -\log(1.8 \times 10^{-5}) = 4.74; [\text{HA}] \approx [\text{HA}]_0 =$$

$[\text{CH}_3\text{CO}_2\text{H}]_0 = 0.25 M$ ;  $[\text{A}^-] \approx [\text{NaCH}_3\text{CO}_2] = 0.030 M$ . Using these data:

$$\text{pH} = 4.74 - \log \left( \frac{0.030 M}{0.25 M} \right) = 3.82; [\text{H}_3\text{O}^+] = 10^{-\text{pH}} M = 10^{-3.82} M = 1.5 \times 10^{-4} M$$

81. What is  $[\text{H}_3\text{O}^+]$  in a solution of 0.075 M HNO<sub>2</sub> and 0.030 M NaNO<sub>2</sub>?



Solution

The equilibrium expression is  $K_a = \frac{[\text{NO}_2^-][\text{H}_3\text{O}^+]}{[\text{HNO}_2]} = 4.6 \times 10^{-4}$ .

The initial and equilibrium concentrations for this system can be written as follows:

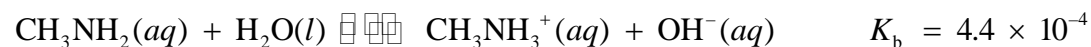
	[HNO <sub>2</sub> ]	[H <sub>3</sub> O <sup>+</sup> ]	[NO <sub>2</sub> <sup>-</sup> ]
Initial concentration (M)	0.075	0	0.030
Change (M)	-x	+x	+x
Equilibrium (M)	0.075 - x	x	0.030 + x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(0.075 - x) \approx 0.075$  and  $(0.030 - x) \approx 0.030$ , gives:

$$\frac{[\text{NO}_2^-][\text{H}_3\text{O}^+]}{[\text{HNO}_2]} = \frac{(x)(0.030 - x)}{(0.075 - x)} \approx \frac{(x)(0.030)}{0.075} = 4.6 \times 10^{-4}$$

Solving for  $x$  gives  $1.15 \times 10^{-3} M$ . Because this value is less than 5% of both 0.075 and 0.030, our assumptions are correct. Therefore,  $[\text{H}_3\text{O}^+] = 1.2 \times 10^{-3} M$ .

82. What is  $[\text{OH}^-]$  in a solution of 0.125 M CH<sub>3</sub>NH<sub>2</sub> and 0.130 M CH<sub>3</sub>NH<sub>3</sub>Cl?



Solution

The equilibrium expression is:

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = 4.4 \times 10^{-4}$$

The initial and equilibrium concentrations for this system can be written as follows:

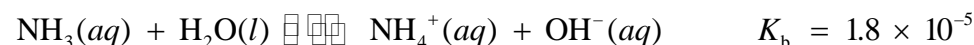
	$[\text{CH}_3\text{NH}_2]$	$[\text{CH}_3\text{NH}_3^+]$	$[\text{OH}^-]$
Initial concentration (M)	0.125	0.130	0
Change (M)	-x	+x	+x
Equilibrium (M)	$0.125 - x$	$0.130 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(0.125 - x) \approx 0.125$  and  $(0.130 - x) \approx 0.130$ , gives:

$$\frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(0.130 - x)(x)}{(0.125 - x)} \approx \frac{(0.130)(x)}{0.125} = 4.4 \times 10^{-4}$$

Solving for x gives  $4.23 \times 10^{-4} M$ . Because this value is less than 5% of both 0.125 and 0.130, our assumptions are correct. Therefore,  $[\text{OH}^-] = 4.2 \times 10^{-4} M$ .

83. What is  $[\text{OH}^-]$  in a solution of 1.25 M  $\text{NH}_3$  and 0.78 M  $\text{NH}_4\text{NO}_3$ ?



Solution

The equilibrium expression is  $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$ .

The initial and equilibrium concentrations for this system can be written as follows:

	$[\text{NH}_3]$	$[\text{NH}_4^+]$	$[\text{OH}^-]$
Initial concentration (M)	1.25	0.78	0
Change (M)	-x	+x	+x
Equilibrium (M)	$1.25 - x$	$0.78 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(1.25 - x) \approx 1.25$  and  $(0.78 + x) \approx 0.78$ , gives:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.78 - x)(x)}{(1.25 - x)} \approx \frac{(0.78)(x)}{1.25} = 1.8 \times 10^{-5}$$

Solving for x gives  $2.88 \times 10^{-5} M$ . Because this value is less than 5% of both 1.25 and 0.78, our assumptions are correct. Therefore,  $[\text{OH}^-] = 2.9 \times 10^{-5} M$ .

This problem can also be solved using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Let us rewrite the reaction in the reversed fashion:





In this case,  $A^-$  is  $\text{NH}_3$  and  $\text{AH}$  is  $\text{NH}_4^+$ ;  $[\text{NH}_3] \approx [\text{NH}_3]_0 = 1.25 \text{ M}$ ;  $[\text{NH}_4^+] \approx [\text{NH}_4\text{NO}_3] = 0.78 \text{ M}$ .

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

$$[\text{H}^+][\text{OH}^-] = K_w, \text{ so } [\text{H}^+] = \frac{K_w}{[\text{OH}^-]}, \text{ and } K_a = \frac{[\text{NH}_3]K_w}{([\text{NH}_4^+][\text{OH}^-])}$$

The Henderson-Hasselbalch equation becomes:

$$\text{pH} = \text{p}K_w - \text{p}K_b + \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4\text{NO}_3]}\right)$$

Since  $[\text{H}^+][\text{OH}^-] = K_w$ ,  $\text{pH} = \text{p}K_w - \text{pOH}$ , and

$$\text{pOH} = -\log([\text{OH}^-]) = \text{p}K_b - \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4\text{NO}_3]}\right) = 4.74 - 0.20 = 4.54$$

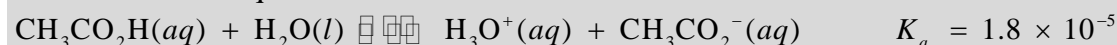
$$[\text{OH}^-] = 10^{-\text{pOH}} \text{ M} = 10^{-4.54} \text{ M} = 2.9 \times 10^{-5} \text{ M}$$

84. What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

- HCl
- $\text{KCH}_3\text{CO}_2$
- NaCl
- KOH
- $\text{CH}_3\text{CO}_2\text{H}$

**Solution**

The reaction and equilibrium constant are:



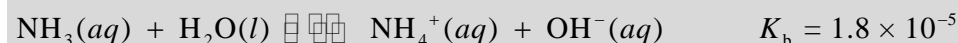
- The added HCl will increase the concentration of  $\text{H}_3\text{O}^+$  slightly, which will react with  $\text{CH}_3\text{CO}_2^-$  and produce  $\text{CH}_3\text{CO}_2\text{H}$  in the process. Thus,  $[\text{CH}_3\text{CO}_2^-]$  decreases and  $[\text{CH}_3\text{CO}_2\text{H}]$  increases.
- The added  $\text{KCH}_3\text{CO}_2$  will increase the concentration of  $[\text{CH}_3\text{CO}_2^-]$  which will react with  $\text{H}_3\text{O}^+$  and produce  $\text{CH}_3\text{CO}_2\text{H}$  in the process. Thus,  $[\text{H}_3\text{O}^+]$  decreases slightly and  $[\text{CH}_3\text{CO}_2\text{H}]$  increases.
- The added NaCl will have no effect on the concentration of the ions.
- The added KOH will produce  $\text{OH}^-$  ions, which will react with the  $\text{H}_3\text{O}^+$ , thus reducing  $[\text{H}_3\text{O}^+]$ . Some additional  $\text{CH}_3\text{CO}_2\text{H}$  will dissociate, producing  $[\text{CH}_3\text{CO}_2^-]$  ions in the process. Thus,  $[\text{CH}_3\text{CO}_2\text{H}]$  decreases slightly and  $[\text{CH}_3\text{CO}_2^-]$  increases.
- The added  $\text{CH}_3\text{CO}_2\text{H}$  will increase its concentration, causing more of it to dissociate and producing more  $[\text{CH}_3\text{CO}_2^-]$  and  $\text{H}_3\text{O}^+$  in the process. Thus,  $[\text{H}_3\text{O}^+]$  increases slightly and  $[\text{CH}_3\text{CO}_2^-]$  increases.

85. What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

- (a) KI
- (b) NH<sub>3</sub>
- (c) HI
- (d) NaOH
- (e) NH<sub>4</sub>Cl

**Solution**

The reaction and equilibrium constant are:

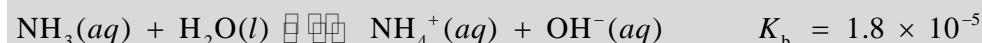


- (a) The added KI will have no effect on the concentrations of the ions.
- (b) The added NH<sub>3</sub> will increase its concentration, causing more of it to dissociate and producing more OH<sup>-</sup> and NH<sub>4</sub><sup>+</sup> in the process. Thus, [OH<sup>-</sup>] increases slightly and [NH<sub>4</sub><sup>+</sup>] increases.
- (c) The added HI will increase the concentrations of H<sub>3</sub>O<sup>+</sup>, which will then react with some OH<sup>-</sup> thus reducing [OH<sup>-</sup>] slightly. Some additional NH<sub>3</sub> will dissociate, producing NH<sub>4</sub><sup>+</sup> in the process. Thus [NH<sub>3</sub>] decreases and [NH<sub>4</sub><sup>+</sup>] increases.
- (d) The added NaOH will increase the concentration of OH<sup>-</sup> slightly, which will react with NH<sub>4</sub><sup>+</sup> and produce NH<sub>3</sub> in the process. Thus, [NH<sub>4</sub><sup>+</sup>] decreases and [NH<sub>3</sub>] increases.
- (e) The added NH<sub>4</sub>Cl will dissociate to yield [NH<sub>4</sub><sup>+</sup>], increasing its concentration. It will then react with some OH<sup>-</sup> ions, thus reducing [OH<sup>-</sup>] slightly. Some additional NH<sub>3</sub> will form in the process. Thus, [NH<sub>3</sub>] increases.

86. What will be the pH of a buffer solution prepared from 0.20 mol NH<sub>3</sub>, 0.40 mol NH<sub>4</sub>NO<sub>3</sub>, and just enough water to give 1.00 L of solution?

**Solution**

The reaction and equilibrium constant are:



The equilibrium expression is:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

The initial concentrations of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> are 0.20 M and 0.40 M, respectively. The equilibrium concentrations for this system can be written as follows:

	[NH <sub>3</sub> ]	[NH <sub>4</sub> <sup>+</sup> ]	[OH <sup>-</sup> ]
<b>Initial concentration (M)</b>	0.20	0.40	0
<b>Change (M)</b>	-x	+x	+x
<b>Equilibrium (M)</b>	0.20 - x	0.40 + x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that (0.20 - x) ≈ 0.20 and (0.40 + x) ≈ 0.40, gives:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.40 + x)(x)}{(0.20 - x)} \approx \frac{(0.40)(x)}{0.20} = 1.8 \times 10^{-5}$$

Solving for  $x$  gives  $9.00 \times 10^{-6} M$ . Because this value is less than 5% of both 0.20 and 0.40, our assumptions are correct. Therefore,  $[\text{OH}^-] = 9.00 \times 10^{-6} M$ . Thus:

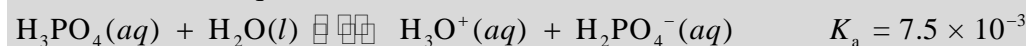
$$\text{pOH} = -\log(9.00 \times 10^{-6}) = 5.046$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 5.046 = 8.954 = 8.95$$

87. Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of  $\text{KH}_2\text{PO}_4$ , and enough water to make 0.500 L of solution.

**Solution**

The reaction and equilibrium constant are:



The equilibrium expression is  $K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3}$ .

The initial concentrations of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$  are 0.310 M and 0.500 M, respectively.

The equilibrium concentrations for this system can be written as follows:

	$[\text{H}_3\text{PO}_4]$	$[\text{H}_3\text{O}^+]$	$[\text{H}_2\text{PO}_4^-]$
<b>Initial concentration (M)</b>	0.310	0	0.500
<b>Change (M)</b>	-x	+x	+x
<b>Equilibrium (M)</b>	$0.310 - x$	x	$0.500 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(0.310 - x) \approx 0.310$  and  $(0.500 + x) \approx 0.500$ , gives:

$$\frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{(x)(0.500 + x)}{(0.310 - x)} \approx \frac{(x)(0.500)}{0.310} = 7.5 \times 10^{-3}$$

Solving for  $x$  gives  $4.65 \times 10^{-3} M$ . Because this value is less than 5% of both 0.310 and 0.500, our assumptions are correct. Therefore,  $[\text{H}_3\text{O}^+] = 4.65 \times 10^{-3} M$ . Thus:

$$\text{pH} = -\log(4.65 \times 10^{-3}) = 2.333 = 2.33$$

88. How much solid  $\text{NaCH}_3\text{CO}_2 \cdot 3\text{H}_2\text{O}$  must be added to 0.300 L of a 0.50-M acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

**Solution**

This problem is most conveniently solved using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log [\text{base}] / [\text{acid}]$$

where the base is acetate ion and the acid is acetic acid.

The  $\text{pK}_a$  for acetic acid is

$$\text{pK}_a = -\log K_a = -\log 1.8 \times 10^{-5} = 4.74$$

Substitution of this value and the provided pH into the Henderson-Hasselbalch equation and rearranging to isolate the conjugate acid/base ratio yields

$$[\text{C}_2\text{H}_3\text{O}_2^-] / [\text{HC}_2\text{H}_3\text{O}_2] = 10^{(5.00 - 4.74)} = 10^{0.26} = 1.82$$

The small  $K_a$  for acetic acid means very little will undergo acid ionization, and so its concentration will be  $\sim 0.50$  M. The molarity of acetate ion required is therefore

$$[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{HC}_2\text{H}_3\text{O}_2] \times 1.82 = 0.50 \times 1.82 = 0.91 \text{ M}$$

The mass of sodium acetate trihydrate required is then

$$0.91 \text{ mol/L} \times 136.1 \text{ g/mol} \times 0.300 \text{ L} = 37 \text{ g}$$

89. What mass of  $\text{NH}_4\text{Cl}$  must be added to 0.750 L of a 0.100- $M$  solution of  $\text{NH}_3$  to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

Solution

This problem is most conveniently solved using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log [\text{base}] / [\text{acid}]$$

where the base is ammonia and the acid is ammonium ion.

The  $\text{p}K_a$  for ammonium ion is

$$\text{p}K_a = \text{p}K_w - \text{p}K_b = 14.00 - (-\log K_b) = 14.00 - 4.74 = 9.26$$

Substitution of this value and the provided pH into the Henderson-Hasselbalch equation and rearranging to isolate the conjugate acid/base ratio yields

$$[\text{NH}_3] / [\text{NH}_4^+] = 10^{(9.26 - 9.26)} = 10^{0.00} = 1.0$$

The small  $K_b$  for ammonia means very little will undergo base ionization, and so its concentration will be  $\sim 0.100$  M. The molarity of ammonium ion required is therefore

$$[\text{NH}_4^+] = [\text{NH}_3] / 1.0 = 0.100 / 1.00 = 0.10 \text{ M}$$

The mass of ammonium chloride required is then

$$0.10 \text{ mol/L} \times 53.49 \text{ g/mol} \times 0.750 \text{ L} = 4.0 \text{ g}$$

90. A buffer solution is prepared from equal volumes of 0.200  $M$  acetic acid and 0.600  $M$  sodium acetate. Use  $1.80 \times 10^{-5}$  as  $K_a$  for acetic acid.

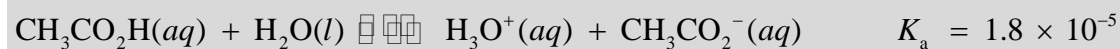
(a) What is the pH of the solution?

(b) Is the solution acidic or basic?

(c) What is the pH of a solution that results when 3.00 mL of 0.034  $M$  HCl is added to 0.200 L of the original buffer?

Solution

(a) The reaction and equilibrium constant are:



The equilibrium expression is:

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$

The molar mass of  $\text{NH}_4\text{Cl}$  is 53.4912 g/mol. The moles of  $\text{NH}_4\text{Cl}$  are:

$$\frac{5.36 \text{ g}}{53.4912 \text{ g mol}^{-1}} = 0.1002 \text{ mol}$$

Assume 0.500 L of each solution is present. The total volume is thus 1.000 L. The initial concentrations of the ions is obtained using  $M_1V_1 = M_2V_2$ , or:

$$[\text{CH}_3\text{CO}_2\text{H}] = M_1 \times \frac{V_1}{V_2} = (0.200) \times \frac{0.500 \text{ L}}{1.000 \text{ L}} = 0.100 \text{ M}$$

$$[\text{CH}_3\text{CO}_2^-] = M_1 \times \frac{V_1}{V_2} = (0.600) \times \frac{0.500 \text{ L}}{1.000 \text{ L}} = 0.300 \text{ M}$$

The initial and equilibrium concentrations of this system can be written as follows:

	$[\text{CH}_3\text{CO}_2\text{H}]$	$[\text{H}_3\text{O}^+]$	$[\text{CH}_3\text{CO}_2^-]$
Initial concentration (M)	0.100	0	0.300
Change (M)	-x	+x	+x
Equilibrium (M)	$0.100 - x$	x	$0.300 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(0.100 - x) \approx 0.100$  and  $(0.300 + x) \approx 0.300$ , gives:

$$\frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(x)(0.300 + x)}{(0.100 - x)} \approx \frac{(x)(0.300)}{0.100} = 1.80 \times 10^{-5}$$

Solving for  $x$  gives  $6.000 \times 10^{-6} \text{ M}$ . Because this value is less than 5% of both 0.100 and 0.300, our assumptions are correct. Therefore  $[\text{H}_3\text{O}^+] = 6.000 \times 10^{-6} \text{ M}$ :

$$\text{pH} = -\log(6.000 \times 10^{-6}) = 5.2218 = 5.222;$$

(b) The solution is acidic.

(c) Assume that the added  $\text{H}^+$  reacts completely with an equal amount of  $\text{CH}_3\text{CO}_2^-$ , forming an equal amount of  $\text{CH}_3\text{CO}_2\text{H}$  in the process. The moles of  $\text{H}^+$  added equal  $0.034 \text{ M} \times 0.00300 \text{ L} = 1.02 \times 10^{-4} \text{ mol}$ . For the acetic acid, the initial moles present equal  $0.2000 \text{ M} \times 0.500 \text{ L} = 0.1000 \text{ mol}$ , and for acetate ion,  $0.600 \text{ M} \times 0.500 \text{ L} = 0.3000 \text{ mol}$ . Thus:

$$\text{mol CH}_3\text{CO}_2\text{H} = 0.1000 + 1.02 \times 10^{-4} = 0.1001 \text{ mol}$$

$$\text{mol CH}_3\text{CO}_2^- = 0.3000 - 1.02 \times 10^{-4} = 0.2999 \text{ mol}$$

$$\text{Final volume} = 1.000 \text{ L} + 3.00 \times 10^{-3} \text{ L} = 1.0030 \text{ L}$$

The initial concentrations are therefore:

$$[\text{CH}_3\text{CO}_2\text{H}] = \frac{0.1001 \text{ mol}}{1.0030 \text{ L}} = 0.09980 \text{ M}$$

$$[\text{CH}_3\text{CO}_2^-] = \frac{0.2999 \text{ mol}}{1.0030 \text{ L}} = 0.2990 \text{ M}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[CH <sub>3</sub> CO <sub>2</sub> H]	[H <sub>3</sub> O <sup>+</sup> ]	[CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup> ]
Initial concentration (M)	0.09980	0	0.2990
Change (M)	-x	+x	+x
Equilibrium (M)	0.09980 - x	x	0.2990 + x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(0.09980 - x) \approx 0.09980$  and  $(0.2990 - x) \approx 0.2990$ , gives:

$$\frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(x)(0.2990 + x)}{(0.09980 - x)} \approx \frac{(x)(0.2990)}{0.09980} = 1.80 \times 10^{-5}$$

Solving for  $x$  gives  $6.008 \times 10^{-6} M$ . Because this value is less than 5% of both 0.09980 and 0.2990, our assumptions are correct. Therefore,  $[\text{H}_3\text{O}^+] = 6.008 \times 10^{-6} M$ .

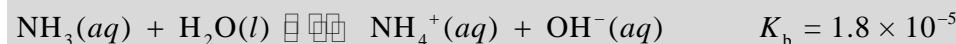
$$\text{pH} = -\log(6.008 \times 10^{-6}) = 5.2213 = 5.221$$

91. A 5.36-g sample of NH<sub>4</sub>Cl was added to 25.0 mL of 1.00 M NaOH and the resulting solution diluted to 0.100 L.

- What is the pH of this buffer solution?
- Is the solution acidic or basic?
- What is the pH of a solution that results when 3.00 mL of 0.034 M HCl is added to the solution?

Solution

(a) The reaction and equilibrium constant are:



The equilibrium expression is  $K_a = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$ .

The molar mass of NH<sub>4</sub>Cl is 53.4912 g/mol. The moles of NH<sub>4</sub>Cl are:

$$\frac{5.36 \text{ g}}{53.4912 \text{ g mol}^{-1}} = 0.1002 \text{ mol. The moles of OH}^- \text{ ion are given by } 1.00 M \times 0.0250 \text{ L} =$$

0.0250 mol. Assume that the hydroxide ions react completely with an equal number of moles of NH<sub>4</sub><sup>+</sup> ions to form an equal number of moles of NH<sub>3</sub>. Therefore, the initial numbers of moles

are: mol NH<sub>4</sub><sup>+</sup> = 0.1002 - 0.0250 = 0.0752 mol; mol NH<sub>3</sub> = 0.0250 mol. The initial concentrations are:

$$[\text{NH}_4^+] = \frac{0.0752 \text{ mol}}{0.100 \text{ L}} = 0.752 M$$

$$[\text{NH}_3] = \frac{0.0250 \text{ mol}}{0.100 \text{ L}} = 0.2500 M$$

The initial and equilibrium concentrations of this system can be written as follows:

	[NH <sub>3</sub> ]	[NH <sub>4</sub> <sup>+</sup> ]	[OH <sup>-</sup> ]
Initial concentration (M)	0.250	0.752	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.250 - x	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(0.250 - x) \approx 0.250$  and  $(0.752 - x) \approx 0.752$ , gives:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.752 + x)(x)}{(0.250 - x)} \approx \frac{(0.752)(x)}{0.250} = 1.8 \times 10^{-5}$$

Solving for  $x$  gives  $5.98 \times 10^{-6} M$ . Because this value is less than 5% of both 0.250 and 0.752, our assumptions are correct. Therefore,  $[\text{OH}^-] = 5.98 \times 10^{-6} M$ :

$$\text{pOH} = -\log(5.98 \times 10^{-6}) = 5.223$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 5.223 = 8.777 = 8.78;$$

(b) The solution is basic.

(c) Assume that the added  $\text{H}^+$  reacts completely with an equal amount of  $\text{NH}_3$ , forming an equal amount of  $\text{NH}_4^+$  in the process. The moles of  $\text{H}^+$  added equal  $0.034 M \times 0.00300 L = 1.02 \times 10^{-4} \text{ mol}$ ;  $\text{mol NH}_3 = 0.02500 - 1.02 \times 10^{-4} = 0.02490 \text{ mol}$ ;  $\text{mol NH}_4^+ = 0.0752 + 1.02 \times 10^{-4} = 0.0753 \text{ mol}$ . Final volume =  $0.100 L + 3.00 \times 10^{-3} L = 0.1030 L$ . The initial concentrations are therefore  $[\text{NH}_3] = \frac{0.02490 \text{ mol}}{0.1030 L} = 0.2417 M$  and  $[\text{NH}_4^+] = \frac{0.0753 \text{ mol}}{0.1030 L} = 0.731 M$ . The initial and equilibrium concentrations for this system can be written as follows:

	[NH <sub>3</sub> ]	[NH <sub>4</sub> <sup>+</sup> ]	[OH <sup>-</sup> ]
Initial concentration (M)	0.2417	0.731	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.2417 - x	0.731 + x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(0.2417 - x) \approx 0.2417$  and  $(0.731 - x) \approx 0.731$ , gives:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.731 + x)(x)}{(0.2417 - x)} \approx \frac{(0.731)(x)}{0.2417} = 1.8 \times 10^{-5}$$

Solving for  $x$  gives  $5.95 \times 10^{-6} M$ . Because this value is less than 5% of both 0.2417 and 0.731, our assumptions are correct. Therefore,  $[\text{OH}^-] = 5.95 \times 10^{-6} M$ :

$$\text{pOH} = -\log(5.95 \times 10^{-6}) = 5.226$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 5.226 = 8.774 = 8.77$$

92. Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

**Solution**

At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

93. Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

**Solution**

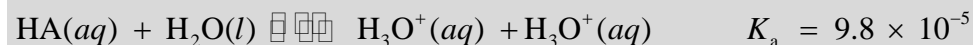
The color in an indicator depends on the ratio of nonionized to ionized forms. The predominant color in acid requires at least a 1:10 ratio of forms, whereas the predominant color in base requires a 10:1 ratio of forms. The transition from one condition to the other comes about by addition of acid or base requiring, in general, a change of two pH units between colors.

94. Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 M barbituric acid ( $K_a = 9.8 \times 10^{-5}$ ) with 0.100 M KOH.

- (a) no KOH added
- (b) 20 mL of KOH solution added
- (c) 39 mL of KOH solution added
- (d) 40 mL of KOH solution added
- (e) 41 mL of KOH solution added

**Solution**

(a) Let HA represent barbituric acid and  $A^-$  represent the conjugate base. The reaction and equilibrium constant are:



$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = 9.8 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HA]	[H <sub>3</sub> O <sup>+</sup> ]	[A <sup>-</sup> ]
Initial concentration (M)	0.100	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.100 - x	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that  $(0.100 - x) \approx 0.100$ , gives:

$$\frac{[H_3O^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.100 - x)} \approx \frac{(x)(x)}{0.100} = 9.8 \times 10^{-5}$$

Solving for  $x$  gives  $3.13 \times 10^{-3} M$ . Because this value is less than 5% of 0.100, our assumption is correct. Therefore,  $[H_3O^+] = 3.13 \times 10^{-3} M$ :

$$pH = -\log(3.13 \times 10^{-3}) = 2.504 = 2.50;$$

(b) The moles of  $OH^-$  added are given by:

$$\text{mol } OH^- = M \times V = (0.100 M) \times (0.020 L) = 0.00200 \text{ mol}$$



The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100 \text{ M}) \times (0.040 \text{ L}) = 0.00400 \text{ mol}$$

Assume that the added hydroxide ion reacts completely with an equal number of moles of HA, forming an equal number of moles of  $\text{A}^-$  in the process. Thus, the moles of the ions are given by:

$$\text{mol HA} = 0.00400 - 0.00200 = 0.00200 \text{ mol}$$

$$\text{mol A}^- = 0.00200 \text{ mol}$$

The total volume is:

$$40.0 \text{ mL} + 20.0 \text{ mL} = 60.0 \text{ mL} = 0.0600 \text{ L}$$

The initial concentrations of the ions are given by:

$$[\text{HA}] = \frac{0.00200 \text{ mol}}{0.0600 \text{ L}} = 0.0333 \text{ M}$$

$$[\text{A}^-] = \frac{0.00200 \text{ mol}}{0.0600 \text{ L}} = 0.0333 \text{ M}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HA]	$[\text{H}_3\text{O}^+]$	$[\text{A}^-]$
Initial concentration (M)	0.0333	0	0.0333
Change (M)	-x	+x	+x
Equilibrium (M)	$0.0333 - x$	x	$0.0333 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that  $(0.0333 - x) \approx 0.0333$  and  $(0.0333 + x) \approx 0.0333$ , gives:

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(0.0333 + x)}{(0.0333 - x)} \approx \frac{(x)(0.0333)}{0.0333} = 9.8 \times 10^{-5}$$

Solving for  $x$  gives  $9.8 \times 10^{-5} \text{ M}$ . Because this value is less than 5% of 0.0333, our assumptions

are correct. Therefore,  $[\text{H}_3\text{O}^+] = 9.8 \times 10^{-5} \text{ M}$ :

$$\text{pH} = -\log(9.8 \times 10^{-5}) = 4.009 = 4.01;$$

(c) The moles of  $\text{OH}^-$  added are given by:

$$\text{mol OH}^- = M \times V = (0.100 \text{ M}) \times (0.039 \text{ L}) = 0.00390 \text{ mol}$$

The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100 \text{ M}) \times (0.040 \text{ L}) = 0.00400 \text{ mol}$$

Assume that the added hydroxide ion reacts completely with an equal number of moles of HA, forming an equal number of moles of  $\text{A}^-$  in the process. Thus, the moles of the ions are given by:

$$\text{mol HA} = 0.00400 - 0.00390 = 0.00010 \text{ mol}$$

$$\text{mol A}^- = 0.00390 \text{ mol}$$

The total volume is:

$$40.0 \text{ mL} + 39.0 \text{ mL} = 79.0 \text{ mL} = 0.0790 \text{ L}$$

The initial concentrations of the ions are given by:

$$[\text{HA}] = \frac{0.00010 \text{ mol}}{0.0790 \text{ L}} = 0.00127 \text{ M}$$

$$[\text{A}^-] = \frac{0.00390 \text{ mol}}{0.0790 \text{ L}} = 0.0494 \text{ M}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HA]	[H <sub>3</sub> O <sup>+</sup> ]	[A <sup>-</sup> ]
Initial concentration (M)	0.00127	0	0.0494
Change (M)	-x	+x	+x
Equilibrium (M)	0.00127 - x	x	0.0494 + x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that  $(0.00127 - x) \approx 0.00127$  and  $(0.0494 + x) \approx 0.0494$ , gives:

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(0.0494 + x)}{(0.00127 - x)} \approx \frac{(x)(0.0494)}{0.00127} = 9.8 \times 10^{-5}$$

Solving for  $x$  gives  $2.52 \times 10^{-6} M$ . Because this value is less than 5% of 0.00127 and 0.0494, our assumptions are correct. Therefore,  $[\text{H}_3\text{O}^+] = 2.52 \times 10^{-6} M$ :

$$\text{pH} = -\log(2.52 \times 10^{-6}) = 5.599 = 5.60;$$

(d) The moles of OH<sup>-</sup> added are given by:

$$\text{mol OH}^- = M \times V = (0.100 M) \times (0.040 L) = 0.00400 \text{ mol}$$

The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100 M) \times (0.040 L) = 0.00400 \text{ mol}$$

This is the equivalence point, where the moles of base added equal the moles of acid present initially. At the equivalence point:

$$\text{mol A}^- = 0.00400 \text{ mol}$$

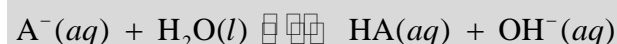
The total volume is:

$$40.0 \text{ mL} + 40.0 \text{ mL} = 80.0 \text{ mL} = 0.0800 L$$

The initial concentration of the conjugate base is:

$$[\text{A}^-] = \frac{0.00400 \text{ mol}}{0.0800 L} = 0.0500 M$$

The reaction and equilibrium constant are:



$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{9.8 \times 10^{-4}} = 1.02 \times 10^{-10}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[A <sup>-</sup> ]	[HA]	[OH <sup>-</sup> ]
Initial concentration (M)	0.0500	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	0.0500 - x	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that  $(0.0500 - x) \approx 0.0500$ , gives:

$$\frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{(x)(x)}{(0.0500 - x)} \approx \frac{(x)(x)}{0.0500} = 1.02 \times 10^{-10}$$

Solving for  $x$  gives  $2.26 \times 10^{-6} M$ . Because this value is less than 5% of 0.0500, our assumption is correct. Therefore,  $[\text{OH}^-] = 2.26 \times 10^{-6} M$ :

$$\text{pOH} = -\log(2.26 \times 10^{-6}) = 5.646$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 5.646 = 8.354 = 8.35;$$

(e) The moles of  $\text{OH}^-$  added are given by:

$$\text{mol OH}^- = M \times V = (0.100 \text{ M}) \times (0.041 \text{ L}) = 0.00410 \text{ mol}$$

The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100 \text{ M}) \times (0.040 \text{ L}) = 0.00400 \text{ mol}$$

This is past the equivalence point, where the moles of base added exceed the moles of acid present initially. The excess moles of hydroxide ion are given by:

$$\text{mol OH}^- = 0.00410 - 0.00400 = 0.00010 \text{ mol}$$

The total volume is:

$$40.0 \text{ mL} + 41.0 \text{ mL} = 81.0 \text{ mL} = 0.0810 \text{ L}$$

The concentration of  $\text{OH}^-$  is:

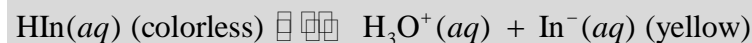
$$[\text{OH}^-] = \frac{0.00010 \text{ mol}}{0.0810 \text{ L}} = 0.0012 \text{ M}$$

$$\text{pOH} = -\log(0.0012) = 2.921$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 2.921 = 11.079 = 11.08$$

95. The indicator dinitrophenol is an acid with a  $K_a$  of  $1.1 \times 10^{-4}$ . In a  $1.0 \times 10^{-4}$ -M solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

Solution



$$\begin{aligned} [\text{H}_3\text{O}^+]_{\text{acid form}} &= \frac{K_a[\text{HIn}]}{[\text{In}^-]} = 1.1 \times 10^{-4} \frac{(9.0 \times 10^{-5})}{(1.0 \times 10^{-5})} \\ &= 9.9 \times 10^{-4} \text{ M} \quad \text{pH} = 3.00 \end{aligned}$$

$$[\text{H}_3\text{O}^+]_{\text{base form}} = 1.1 \times 10^{-4} \frac{(1.0 \times 10^{-5})}{(9.0 \times 10^{-5})} = 1.22 \times 10^{-5} \quad \text{pH} = 4.91$$

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