fied. The prediction based upon the empirical definition of a buffer was accurate. It appears that we can continue to have confidence in this concept.

# **CHAPTER 8 SUMMARY**

#### **MAKE A SUMMARY**

#### (Page 630)

(Answers may vary, but should include a page for each of the following six sections: The Nature of Acid–Base Equilibria; Weak Acids and Bases; Acid–Base Properties of Salt Solutions; Acid–Base Titration; Buffers; and The Science of Acid Deposition.)

# **CHAPTER 8 SELF-QUIZ**

#### (Page 631)

- 1. False. The stronger a Brønsted-Lowry acid is, the weaker its conjugate base.
- 2. False. Group I metal ions produce neutral solutions.
- 3. True
- 4. True
- 5. False. A solution of the bicarbonate ion is basic.
- 6. False. The pH of water would be less than 7.
- 7. True
- 8. False. Most dyes that act as acid-base indicators are weak acids.
- 9. True
- 10. (b)
- 11. (b)
- 12. (e)
- 13. (a)
- 14. (b)
- 15. (c)
- 16. (e)
- 17. (a) 18. (b)
- 19. (a)

### **CHAPTER 8 REVIEW**

#### (Page 632)

# **Understanding Concepts**

1. 
$$n_{\text{NaOH}} = \frac{8.50 \text{ g}}{40.00 \text{ g/mol}}$$
  
 $n_{\text{NaOH}} = 0.2125 \text{ mol}$  (extra digits carried)  
 $[\text{OH}^-] = \frac{0.2125 \text{ mol}}{0.500 \text{ L}}$   
 $[\text{OH}^-] = 0.425 \text{ mol/L}$   
 $p\text{OH} = -\log 0.425$   
 $p\text{OH} = -0.372$ 

The pOH of sodium hydroxide is -0.372.

2. (a) 
$$n_{HCl} = \frac{3.05 \times 10^4 \text{ g}}{36.46 \text{ g/mol}}$$
  
 $n_{HCl} = 836.5 \text{ mol}$  (extra digits carried)  
 $[H^+] = \frac{836.5 \text{ mol}}{806 \text{ L}}$   
 $[H^+] = 1.038 \text{ mol/L}$   
 $pH = -\log 1.038$   
 $pH = 0.016$   
 $pOH = 14 - 0.016$   
 $pOH = 13.984$ 

The pH and pOH of the hydrochloric acid are 0.016 and 13.984, respectively.

(b) Assumptions are that the temperature remains constant, and that water does not contribute a significant amount of  $H_{(aq)}^+$  or  $OH_{(aq)}^-$ .

$$3. \text{ H}_2\text{O} \rightleftharpoons \begin{matrix} \text{H}^+ & + & \text{OH}^- \\ -\log[\text{H}^+] & & \text{-log[OH}^-] \\ \text{PH} & + & \text{POH} \end{matrix} \downarrow 14$$

4. 
$$HF_{(aq)} \rightleftharpoons H_{(aq)}^{+} + F_{(aq)}^{-}$$

$$K_{a} = \frac{[H_{(aq)}^{+}][F_{(aq)}^{-}]}{[HF_{(aq)}]}$$

ICE Table for the Dissociation of Hydrofluoric Acid						
$HF_{(aq)} \  ightharpoons \ H^+_{(aq)} \ \ + F^{(aq)}$						
Initial concentration (mol/L)	2.0	0.0	0.0			
Change in concentration (mol/L)	-x	+ <i>x</i>	+ <i>x</i>			
Equilibrium concentration (mol/L) 2.0 – x x x						

$$K_{a} = \frac{[H_{(aq)}^{+}][F_{(aq)}^{-}]}{[HF_{(aq)}]}$$
$$K_{a} = 6.6 \times 10^{-4}$$

Predict whether a simplifying assumption is justified:

$$\frac{\mathrm{[HA]}_{\mathrm{initial}}}{K_{\mathrm{a}}} = \frac{2.0}{6.6 \times 10^{-4}}$$
$$\frac{\mathrm{[HA]}_{\mathrm{initial}}}{K_{\mathrm{a}}} = 3000$$

Since 3000 > 100, we may assume that 2.0 - x = 2.0.

The equilibrium expression becomes

$$\frac{x^2}{2.00} \doteq 6.6 \times 10^{-4}$$
$$x \doteq 0.036$$

The 5% rule justifies the assumption that 2.0 - x = 2.0.

$$[H_{(aq)}^+] = [F_{(aq)}^-] = 0.036 \text{ mol/L}$$

The concentrations of hydrogen and fluoride in a 2.0 mol/L hydrofluoric acid solution are 0.036 mol/L.

Copyright © 2003 Nelson Acid-Base Equilibrium 34:

5. 
$$[H^{+}] = \frac{K_{w}}{[OH^{-}]}$$

$$= \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-7}}$$

$$[H^{+}] = 4.0 \times 10^{-8} \text{ mol/L}$$

$$pH = -\log 4.0 \times 10^{-8}$$

$$pH = 7.40$$

The hydrogen ion concentration and pH of blood are  $4.0 \times 10^{-8}$  mol/L and 7.40, respectively.

$$\begin{aligned} 6. \quad & n_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} = \frac{60\ 000\ \text{g}}{60.06\ \text{g/mol}} \\ & n_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} = 999\ \text{mol} \\ & C_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} = \frac{999\ \text{mol}}{1250\ \text{L}} \\ & C_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} = 0.799\ \text{mol/L} \end{aligned}$$

ICE Table for the Dissociation of Acetic Acid						
$HC_2H_3O_{2(aq)} \rightleftharpoons H^+_{(aq)} + C_2H_3O^{2(aq)}$						
Initial concentration (mol/L)	0.799	0.0	0.0			
Change in concentration (mol/L)	-x	+ <i>x</i>	+ <i>x</i>			
Equilibrium concentration (mol/L)	0.799 – x	Х	х			

$$\frac{[H_{(aq)}^+][C_2H_3O_{2(aq)}^-]}{[HC_2H_3O_{2(aq)}]} = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.799 - x} = 1.8 \times 10^{-5}$$

Predicting whether  $0.799 - x = 0.799 - x \dots$ 

$$\frac{[\text{HA}]_{\text{initial}}}{K_{\text{a}}} = \frac{0.799 \text{ mol/L}}{1.8 \times 10^{-5}}$$
$$\frac{[\text{HA}]_{\text{initial}}}{K_{\text{a}}} = 44400$$

Since 44400 > 100, we assume that 0.799 - x = 0.799

$$\frac{x^2}{0.799} \doteq 1.8 \times 10^{-5}$$

$$x = 1.8 \times 10^{-5}$$
 (extra digits carried)

The 5% rule justifies the assumption.

$$[H_{(aq)}^{+}] = 3.795 \times 10^{-3} \text{ mol/L}$$

$$pH = -\log [H_{(aq)}^{+}]$$

$$= -\log [3.795 \times 10^{-3}]$$

$$pH = 2.421$$

$$pOH = 14 - 2.421$$

$$pOH = 11.579$$

The pH and pOH of the acetic acid solution are 2.421 and 11.579.

7. (a)

ICE Table for the Ionization of ASA					
$HC_{10}H_7CO_{4(aq)} \rightleftharpoons H_{(aq)}^+ + C_{10}H_7CO_{4(aq)}^-$					
Initial concentration (mol/L)	0.018	0.0	0.0		
Change in concentration (mol/L)	-x	+x	+x		
Equilibrium concentration (mol/L) $0.018 - x$ $x$ $x$					

$$\frac{[\mathrm{H}^{+}_{(\mathrm{aq})}][\mathrm{C}_{10}\mathrm{H}_{7}\mathrm{CO}_{4(\mathrm{aq})}^{-}]}{[\mathrm{HC}_{10}\mathrm{H}_{7}\mathrm{CO}_{4(\mathrm{aq})}]} = 3.27 \times 10^{-4}$$

$$\frac{x^{2}}{0.018 - x} = 3.27 \times 10^{-4}$$

Predicting whether  $0.018 - x = 0.018 \dots$ 

$$\frac{\mathrm{[HA]_{initial}}}{K_{\mathrm{a}}} = \frac{0.018 \; \mathrm{mol/L}}{3.27 \times 10^{-4}}$$
$$\frac{\mathrm{[HA]_{initial}}}{K_{\mathrm{a}}} = 55$$

Since 55 < 100, we cannot assume that 0.018 - x = 0.018.  $\frac{x^2}{0.018} = 3.27 \times 10^{-4}$ 

$$\frac{x^2}{0.018} \doteq 3.27 \times 10^{-4}$$
$$\frac{x^2}{0.018 - x} = 3.27 \times 10^{-4}$$

$$(0.018 - x)(3.27 \times 10^{-4}) = x^2$$

$$5.89 \times 10^{-6} - 3.27 \times 10^{-4} x = x^2$$

$$x^2 + 3.27 \times 10^{-4}x - 5.89 \times 10^{-6} = 0$$

$$x = \frac{-3.27 \times 10^{-4} \pm \sqrt{(3.27 \times 10^{-4})^2 - 4(1)(-5.89 \times 10^{-6})}}{2(1)}$$
$$= \frac{-3.27 \times 10^{-4} \pm 4.86 \times 10^{-3}}{2}$$

$$x = 2.27 \times 10^{-3} \,\mathrm{or} - 8.13 \times 10^{-4}$$

Since negative concentrations are meaningless,

$$x = 2.27 \times 10^{-3}$$

$$[H_{(aq)}^+] = 2.27 \times 10^{-3} \text{ mol/L}$$

$$pH = -\log[H_{(aq)}^+]$$

$$pH = -\log[2.27 \times 10^{-3}]$$

$$pH = 2.644$$

The pH of the ASA solution is 2.644.

(b) An increase in temperature shifts the autoionization equilibrium of water to the right, producing more  $H_{(aq)}^+$ . As a result, the pH of the solution would decrease.

8. (a) 
$$\begin{array}{c} 7.9 \times 10^{-3} \% \\ HCN_{(aq)} \rightleftharpoons H_{(aq)}^{+} + CN_{(aq)}^{-} \\ \\ \frac{[H_{(aq)}^{+}][CN_{(aq)}^{-}]}{[HCN_{(aq)}]} = 6.2 \times 10^{-10} \end{array}$$

(b) 
$$HCN_{(aq)} \rightleftharpoons H_{(aq)}^+ + CN_{(aq)}^-$$

$$\frac{[H_{(aq)}^+][CN_{(aq)}^-]}{[HCN_{(aq)}]} = 6.2 \times 10^{-10}$$

$$\frac{x^2}{0.10 - x} = 6.2 \times 10^{-10}$$

Predicting whether  $0.10 - x = 0.10 \dots$ 

$$\frac{\mathrm{[HA]}_{\mathrm{initial}}}{K_{\mathrm{a}}} = \frac{0.10 \; \mathrm{mol/L}}{6.2 \times 10^{-10}}$$
$$\frac{\mathrm{[HA]}_{\mathrm{initial}}}{K_{\mathrm{a}}} \doteq 10^{9}$$

Since  $10^9 > 100$ , we assume that 0.10 - x = 0.10.  $\frac{x^2}{(0.10)} = 6.2 \times 10^{-10}$ 

$$x = 7.9 \times 10^{-6}$$

The 5% rule justifies the assumption.

$$\begin{split} [H^{+}_{(aq)}] &= 7.9 \times 10^{-6} \text{ mol/L} \\ pH &= -\log[H^{+}_{(aq)}] \\ &= -\log[7.9 \times 10^{-6}] \\ pH &= 5.10 \end{split}$$

The pH of the hydrocyanic acid is 5.10. Calculating percent ionization ...

$$[H_{(aq)}^{+}] = \frac{p}{100} \times [HA_{(aq)}]$$

$$p = \frac{[H_{(aq)}^{+}]}{[HA_{(aq)}]} \times 100\%$$

$$= \frac{7.9 \times 10^{-6} \text{ mol/L}}{0.100 \text{ mol/L}} \times 100\%$$

$$= 7.9 \times 10^{-3} \%$$

The percent ionization of hydrocyanic acid is  $7.9 \times 10^{-3}$  %.

$$\begin{array}{l} 9. \; HC_6H_6O_{2(aq)}^{-} + \; H_2O_{(l)} \; \Longleftrightarrow \; H_2C_6H_6O_{2(aq)} + OH_{(aq)}^{-} \\ \\ pH = 8.65 \\ pOH = 5.35 \\ [OH_{(aq)}^{+}] = 10^{-5.35} \\ \\ = 4.47 \times 10^{-6} \; mol/L \; (extra \; digits \; carried) \\ [OH_{(aq)}^{+}] = [H_2C_6H_6O_{2(aq)}] \end{array}$$

ICE Table for the Ionization of Ascorbate					
$HC_6H_6O_{2(aq)^-} + \qquad H_2O_{(I)} \rightleftharpoons \qquad H_2C_6H_6O_{2(aq)} + \qquad OH_{(aq)^-}$					
Initial concentration (mol/L)	0.15	_	0.00	0.00	
Change in concentration (mol/L)	$-4.47 \times 10^{-6}$	_	4.47 × 10 <sup>-6</sup>	$4.47 \times 10^{-6}$	
Equilibrium concentration (mol/L) $0.15 - (4.47 \times 10^{-6})$ $ 4.47 \times 10^{-6}$ $4.47 \times 10^{-6}$					

$$\begin{split} \frac{[\mathrm{H}_2\mathrm{C}_6\mathrm{H}_6\mathrm{O}_{2(\mathrm{aq})}][\mathrm{OH}_{(\mathrm{aq})}^-]}{[\mathrm{H}\mathrm{C}_6\mathrm{H}_6\mathrm{O}_{2(\mathrm{aq})}^-]} &= K_\mathrm{b} \\ \frac{(4.47 \times 10^{-6})^2}{0.15 - 4.47 \times 10^{-6}} &= K_\mathrm{b} \end{split}$$

Assume that  $0.15 - 4.47 \times 10^{-6} = 0.15$ .

$$\frac{(4.47 \times 10^{-6})^2}{0.15} = 1.3 \times 10^{-10}$$

 $K_{\rm b}$  for the ascorbate ion is  $1.3 \times 10^{-10}$ .

10. (a)

acid	conjugate base	acid	conjugate base
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CH	(C <sub>6</sub> H <sub>5</sub> )C <sup>-</sup>	C <sub>4</sub> H <sub>4</sub> NH	C <sub>4</sub> H <sub>4</sub> N <sup>-</sup>
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	H <sub>2</sub> S	HS <sup>-</sup>
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CH	(C <sub>6</sub> H <sub>5</sub> )C <sup>-</sup>	OH-	O <sup>2-</sup>
C <sub>4</sub> H <sub>4</sub> NH	C <sub>4</sub> H <sub>4</sub> N <sup>-</sup>	H <sub>2</sub> S	HS <sup>-</sup>

- (b) (strongest acid)  $HC_2H_3O_2$ ;  $H_2S$ ;  $C_4H_4NH$ ;  $(C_6H_5)_3CH$  (weakest acid)
- 11. The final solution is basic because of the hydrolysis of the methanoate ion:

$$\mathrm{CH_3O_{(aq)}^-} + \mathrm{H_2O_{(l)}} \rightleftharpoons \mathrm{HCH_3O_{(aq)}} + \mathrm{OH_{(aq)}^-}$$

Ionic		Molecular			
neutral	acidic	basic	neutral	acidic	basic
CaCl <sub>2</sub>	NH₄CI	NaOH	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	HCI	NH <sub>3</sub>
NaNO <sub>3</sub>	AI(NO <sub>3</sub> ) <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	O <sub>2</sub>	H <sub>2</sub> S	N <sub>2</sub> H <sub>4</sub>

- 13. (a) yellow
  - (b) red
  - (c) yellow-green
  - (d) colourless
  - (e) yellow

$$\begin{aligned} 14. \ & \text{H}_{3}\text{PO}_{4(\text{aq})} + 2 \ \text{NaOH}_{(\text{aq})} \rightarrow \text{Na}_{2}\text{HPO}_{4(\text{aq})} + 2 \ \text{H}_{2}\text{O}_{(\text{I})} \\ 25.0 \ \text{mL} & 17.9 \ \text{mL} \\ C & 1.5 \ \text{mol/L} \\ \\ & n_{\text{NaOH}_{(\text{aq})}} = 17.9 \ \text{mL} \times \frac{1.50 \ \text{mol}}{1 \ \text{L}} \\ \\ & n_{\text{NaOH}_{(\text{aq})}} = 26.9 \ \text{mmol} \\ \\ & n_{\text{H}_{3}\text{PO}_{4(\text{aq})}} = 26.9 \ \text{mmol} \times \frac{1}{2} = 13.4 \ \text{mmol} \\ \\ & C_{\text{H}_{3}\text{PO}_{4(\text{aq})}} = \frac{13.4 \ \text{mmol}}{25.0 \ \text{mL}} \\ \\ & C_{\text{H}_{3}\text{PO}_{4(\text{aq})}} = 0.537 \ \text{mol/L} \end{aligned}$$

The concentration of the phosphoric acid solution is 0.537 mol/L.

15. (a) 
$$\text{HCl}_{(\text{aq})} + \text{NH}_{3(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})} + \text{NH}_4\text{Cl}_{(\text{aq})}$$

$$n_{\text{NH}_{3(\text{aq})}} = C_{\text{NH}_{3(\text{aq})}} \times V_{\text{NH}_{3(\text{aq})}}$$

 $= 0.10 \text{ mol/L} \times 10.0 \text{ mL}$ 

$$n_{\text{NH}_{3(\text{aq})}} = 1.0 \text{ mmol}$$

Final solution volume = 20.0 mL

Entities remaining in solution at the equivalence point:  $Cl_{(aq)}^-$ ,  $NH_{4(aq)}^+$ ,  $H_2O_{(1)}$ 

Since Cl<sub>(aq)</sub> does not hydrolyze, the pH of the solution is determined by NH<sub>4(aq)</sub>.

$$NH_{4(aq)}^+ \rightleftharpoons NH_{3(aq)} + H_{(aq)}^+$$

Since 1.0 mmol of  $NH_{3(aq)}$  was present initially, 1.0 mmol of  $NH_{4(aq)}^{+}$  is present at the equivalence point.

$$[NH_{4(aq)}^{\phantom{4}+}] = \frac{1.0 \ mmol}{20.0 \ mL}$$

$$[NH_{4(aq)}^{+}] = 0.050 \text{ mol/L}$$

$$NH_{4(aq)}^+ \rightleftharpoons NH_{3(aq)} + H_{(aq)}^+$$

$$\frac{[H_{(aq)}^+][NH_{3(aq)}]}{[NH_{4(aq)}^+]} = 5.8 \times 10^{-10}$$

ICE Table for the Hydrolysis of NH <sub>4(aq)</sub>						
$NH_{4(aq)^+} \rightleftharpoons H_{(aq)^+} + NH_{3(aq)}$						
Initial concentration (mol/L)	0.050	0.000	0.000			
Change in concentration (mol/L)	-x	+ <i>x</i>	+x			
Equilibrium concentration (mol/L) $0.050 - x$ $x$ $x$						

$$NH_{4(aq)}^+ \rightleftharpoons NH_{3(aq)} + H_{(aq)}^+$$

$$\frac{[H_{(aq)}^+][NH_{3(aq)}]}{[NH_{4(aq)}^+]} = 5.8 \times 10^{-10}$$

$$\frac{x^2}{0.050 - x} = 5.8 \times 10^{-10}$$

Applying the hundred rule ...

$$\frac{[\text{NH}_{4(\text{aq})}^+]_{\text{initial}}}{K_a} = \frac{0.050}{5.8 \times 10^{-10}} > 100$$

The equilibrium simplifies to

$$\frac{x^2}{0.050} = 5.8 \times 10^{-10}$$

$$x = 5.385 \times 10^{-6}$$
 (extra digits carried)

The 5% rule verifies the assumption.

$$[H_{(aq)}^+] \doteq 5.385 \times 10^{-6} \, \text{mol/L}$$
  
 $pH \doteq -\log [5.385 \times 10^{-6}]$   
 $pH = 5.27$ 

The pH of the solution at the equivalence point is 5.27.

(b) 
$$K_{b} = \frac{[\text{NH}_{4(\text{aq})}^{+}][\text{OH}_{(\text{aq})}^{-}]}{[\text{NH}_{3(\text{aq})}]}$$

$$K_{b} = 1.8 \times 10^{-5}$$

$$\frac{x^{2}}{0.10 - x} = 1.8 \times 10^{-5}$$

Predicting the validity of the assumption ...

$$\frac{0.10}{1.8 \times 10^{-5}} > 100$$

 $\therefore$  we many assume that 0.10 - x = 0.10

The equilibrium expression becomes

$$\frac{x^2}{0.10} \doteq 1.8 \times 10^{-5}$$
$$x \doteq 1.342 \times 10^{-3} \quad \text{(extra digits carried)}$$

The 5% rule verifies the simplification assumption.

$$\begin{aligned} [OH^-_{(aq)}] &= 1.342 \times 10^{-3} \text{ mol/L} \\ pOH &= -\log[1.342 \times 10^{-3}] \\ pOH &= 2.872 \\ pH &= 14 - pOH \\ &= 14.0 - 2.872 \\ pH &= 11.13 \end{aligned}$$

The initial pH of the ammonia solution is 11.13.

$$\begin{array}{llll} \text{(c)} & V_{\text{HCl}_{(aq)}} = 5.00 \text{ mL} \\ & C_{\text{HCl}_{(aq)}} = 0.100 \text{ mol/L} \\ & n_{\text{HCl}_{(aq)}} = V_{\text{HCl}_{(aq)}} \times C_{\text{HCl}_{(aq)}} \\ & = 5.00 \text{ mL} \times 0.100 \text{ mol/L} \\ & n_{\text{HCl}_{(aq)}} = 0.50 \text{ mmol} \\ & V_{\text{NH}_{3(aq)}} = 10.00 \text{ mL} \\ & C_{\text{NH}_{3(aq)}} = 0.100 \text{ mol/L} \\ & n_{\text{NH}_{3(aq)}} = V_{\text{NH}_{3(aq)}} \times C_{\text{NH}_{3(aq)}} \\ & n_{\text{NH}_{3(aq)}} = 10.00 \text{ mL} \times 0.100 \text{ mol/L} \\ & n_{\text{NH}_{3(aq)}} = 1.00 \text{ mmol} \\ & n_{\text{NH}_{3(aq)}} = 1.00 \text{ mmol} \\ & n_{\text{NH}_{3(aq)}} = 0.50 \text{ mmol} \\ & n_{\text{NH}_{3(aq)}} = 0.50 \text{ mmol} \\ & C_{\text{NH}_{3(aq)}} = \frac{0.50 \text{ mmol}}{15.00 \text{ mL}} \\ & C_{\text{NH}_{4(aq)}} = \frac{0.50 \text{ mmol}}{15.00 \text{ mL}} \\ & C_{\text{NH}_{4(aq)}} = \frac{0.50 \text{ mmol}}{15.00 \text{ mL}} \\ & C_{\text{NH}_{4(aq)}} = \frac{0.50 \text{ mmol}}{15.00 \text{ mL}} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH}_{4(aq)}} = 0.0333 \text{ mol/L} \qquad \text{(extra digits carried)} \\ & C_{\text{NH$$

Let x represent the changes in concentration that occur as the system reestablishes equilibrium.

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ICE Table for the Ionization of Ammonia						
$NH_{3(aq)}$ + $H_2O_{(I)} \rightleftharpoons OH_{(aq)}^-$ + $NH_{4(aq)}^+$						
Initial concentration (mol/L)	0.0333	_	0.00	0.0333		
Change in concentration (mol/L)	-x	_	+x	+x		
Equilibrium concentration (mol/L) $0.0333 - x$ - $x$ $0.0333 + x$						

$$\frac{[\text{NH}_{4(\text{aq})}^{+}][\text{OH}_{(\text{aq})}^{-}]}{[\text{NH}_{3(\text{aq})}]} = K_{\text{b}}$$
$$\frac{x(0.0333 + x)}{0.0333 - x} = 1.8 \times 10^{-5}$$

Applying the hundred rule ...

$$\frac{[\text{NH}_{3(\text{aq})}]_{\text{initial}}}{K_{\text{a}}} = \frac{0.0333}{1.8 \times 10^{-5}}$$
$$\frac{[\text{NH}_{3(\text{aq})}]_{\text{initial}}}{K_{\text{a}}} = 1850$$

Since 1850 > 100, we can assume that 0.0333 + x = 0.0333 and that 0.0333 - x = 0.0333

The equilibrium simplifies to

$$\frac{x(0.0333)}{0.0333} = 1.8 \times 10^{-5}$$
$$x = 1.8 \times 10^{-5}$$

The 5% rule validates the assumption.

$$[OH_{(aq)}^{-}] \doteq 1.8 \times 10^{-5} \text{ mol/L}$$

$$pOH \doteq -\log [1.8 \times 10^{-5}]$$

$$= 4.7445 \qquad \text{(extra digits carried)}$$

$$pH = 9.26$$

The pH after adding 5.0 mL of HCl is 9.26.

- (d) Entities at the equivalence point are:  $H_2O_{(l)}$ ,  $NH_{4(aq)}^+$ ,  $Cl_{(aq)}^-$
- (e) The equivalence point is reached after 10.0 mL of  $HCl_{(aq)}$  is added. The pH of this solution is 5.27. (See calculation in (a).)

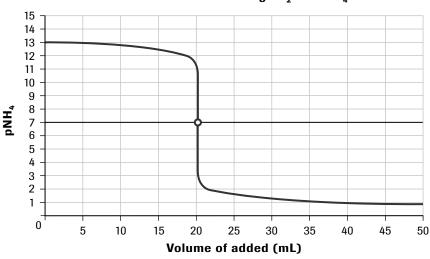
$$\begin{split} \text{(f)} & n_{\text{HCl}_{(\text{aq})}} = V_{\text{HCl}_{(\text{aq})}} \times C_{\text{HCl}_{(\text{aq})}} \\ &= 15.0 \text{ mL} \times 0.10 \text{ mol/L} \\ n_{\text{HCl}_{(\text{aq})}} = 1.5 \text{ mmol} \qquad \text{(extra digits carried)} \\ n_{\text{NH}_{3(\text{aq})}} = V_{\text{NH}_{3(\text{aq})}} \times C_{\text{NH}_{3(\text{aq})}} \\ n_{\text{NH}_{3(\text{aq})}} = 10.0 \text{ mL} \times 0.10 \text{ mol/L} \\ &= 1.0 \text{ mmol} \\ n_{\text{HCl}_{(\text{aq})}} \text{remaining} = 1.5 \text{ mmol} - 1.0 \text{ mmol} \\ C_{\text{HCl}_{(\text{aq})}} = \frac{n_{\text{HCl}_{(\text{aq})}}}{V_{\text{HCl}_{(\text{aq})}}} \\ &= \frac{0.5 \text{ mmol}}{25 \text{ mL}} \end{split}$$

$$C_{\text{HCl}_{(aq)}} = 0.020 \text{ mol/L}$$
  
 $[H^{+}_{(aq)}] = 0.020 \text{ mol/L}$   
 $pH = -\log 0.020$   
 $pH = 1.70$ 

After 15.0 mL of acid is added, the pH of the solution is 1.70.

- (g) A suitable indicator for this titration would be methyl red (pH range 4.4–6.2).
- 16. (a)  $NH_4^+$ 
  - (b) NH<sub>2</sub>
  - (c)  $2 \text{ NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$
  - (d)

#### Titration Curve for Titrating NH<sub>2</sub> with NH<sub>4</sub>



17. The pH would be between 5.0 and 5.4. An estimate of the hydrogen ion concentration is  $1 \times 10^{-5}$  mol/L.

#### **Applying Inquiry Skills**

- 19. (i) Test the solutions with a pH meter. The strongest bases have the largest pH values.
  - (ii) Test the solutions with universal indicator. Compare the indicator colour with a colour chart to determine the approximate pH.
- 20. (a) (i) neutral
  - (ii) basic
  - (iii) basic
  - (iv) <7
  - (v) < 7
  - (vi) basic
  - (vii) <7
  - (b) The predictions could be tested with a pH meter. (The meter should be carefully calibrated, and rinsed between solutions.)
- 21. (Sample answer—there are many possible correct solutions to this problem.) If the solutions are tested with a pH meter, and the pH values are ordered from smallest to largest, then the solutions are sulfuric acid, hydrochloric acid, acetic acid, ethanediol, ammonia, sodium hydroxide, and barium hydroxide, respectively.

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Diagnostic Tests on the Unlabelled Solutions				
Litmus	Conductivity	Acid/Base titration	Analysis	
red	low	one volume	CH <sub>3</sub> COOH <sub>(aq)</sub>	
blue	very high	two volumes	Ba(OH) <sub>2(aq)</sub>	
blue	low	one volume	NH <sub>3(aq)</sub>	
no change	none	not applicable	C <sub>2</sub> H <sub>4</sub> (OH) <sub>2(aq)</sub>	
red	higher	two volumes	H <sub>2</sub> SO <sub>4(aq)</sub>	
red	high	one volume	HCI <sub>(aq)</sub>	
blue	high	one volume	NaOH <sub>(aq)</sub>	

- 22. (a) There is no third pH endpoint and therefore, no third equivalence point in this titration.
  - (b) Removing the hydroxide ions by precipitation will cause the equilibrium to shift to the right, producing more hydroxide ions.
  - (c) Hydrochloric acid is not a primary standard.
  - (d) Both reactants and products form basic solutions and litmus cannot be used to distinguish among basic solutions.
  - (e) Cobalt chloride paper is used in a diagnostic test for the production of water in a strong acid-strong base reaction.
  - (f) The strength of an acid is determined by titration.

### **Making Connections**

23. (a) 
$$Mg(OH)_{2(s)} + 2 HCl \rightleftharpoons 2 H_2O_{(l)} + MgCl_{2(aq)}$$

(b) Alkalosis is based on the carbonic acid/bicarbonate equilibrium:

$$H_2CO_{3(aq)} \rightleftharpoons H_{(aq)}^+ + HCO_{3(aq)}^-$$

During alkalosis, an increase in blood levels of the bicarbonate ion removes hydrogen ions, thereby increasing blood pH. Symptoms of alkalosis include vomiting, headache, and nausea.

(c) Hydroxide-based antacids are very common.

#### **Extension**

24. 
$$H_2SO_{4(aq)} + Ba(OH)_{2(aq)} \rightleftharpoons 2 H_2O_{(l)} + BaSO_{4(s)}$$

Place an accurately measured volume of  $Ba(OH)_{2(aq)}$  into a beaker and immerse the leads from a conductivity meter in the solution. Measure and record the initial conductivity reading. Titrate with standardized  $H_2SO_{4(aq)}$  and record the conductivity readings. A sudden drop in the conductivity serves as the endpoint of the titration. This drop in conductivity corresponds to the removal of most of the ions through the production of water and insoluble barium sulfate. When the  $H_2SO_{4(aq)}$  is added in excess, the conductivity increases due to the ions present in the acid.

25. 
$$H_2SO_{4(aq)} \rightleftharpoons H_{(aq)}^+ + HSO_{4(aq)}^-$$

From the first ionization:

Since sulfuric acid is a strong acid  $[H_{(aq)}^+] = 1.0 \times 10^{-2} \text{ mol/L}$ 

From the second ionization:

$$HSO_{4(aq)}^- \rightleftharpoons H_{(aq)}^+ + SO_{4(aq)}^{2-}$$

$$K_{\rm a} = \frac{[{\rm H}_{\rm (aq)}^+][{\rm HSO}_{4({\rm aq})}^-]}{[{\rm HSO}_{4({\rm aq})}^-]}$$

$$K_a = 1.0 \times 10^{-2}$$

ICE Table for the Ionization of the Hydrogen Sulfate Ion						
$HSO^{4(aq)} \  ightharpoons \ H^+_{(aq)} \ + \ SO^{2-}_{4(aq)}$						
Initial concentration (mol/L)	0.010	0.00	0.00			
Change in concentration (mol/L)	-x	+x	+x			
Equilibrium concentration (mol/L)	0.010 - x	Х	х			

$$\begin{split} \text{HSO}_{4(\text{aq})}^{-} &\rightleftharpoons \text{H}_{(\text{aq})}^{+} + \text{SO}_{4(\text{aq})}^{2-} \\ K_{\text{a}} &= \frac{[\text{H}_{(\text{aq})}^{+}][\text{HSO}_{4(\text{aq})}^{-}]}{[\text{HSO}_{4(\text{aq})}^{-}]} = 1.0 \times 10^{-2} \\ \frac{x^{2}}{0.010 - x} &= 1.0 \times 10^{-2} \end{split}$$

Predict whether a simplifying assumption is justified ...

$$\frac{[\text{HA}]_{\text{initial}}}{K_{\text{a}}} = \frac{0.010}{1.0 \times 10^{-2}}$$
$$= 1$$

Therefore, we may not assume that 0.010 - x = 0.010.  $\frac{x^2}{0.010 - x} = 1.0 \times 10^{-2}$ 

$$\frac{x^2}{0.010 - x} = 1.0 \times 10^{-2}$$

$$x^{2} + 0.01x - 0.0001 = 0$$

$$x = \frac{-0.01 \pm \sqrt{(0.01)^{2} - 4(-0.0001)}}{2}$$

The only positive root is  $x = 6.18 \times 10^{-3}$  (extra digits carried)

Total 
$$[H^+_{(aq)}] = 6.18 \times 10^{-3} \text{ mol/L} + 1.0 \times 10^{-2} \text{ mol/L}$$
  
=  $1.618 \times 10^{-2} \text{ mol/L}$   
pH =  $1.79$ 

The pH of the sulfuric acid solution is 1.79.

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