$\begin{array}{ll} As_2O_{3(s)} & \text{insoluble - no solution produced. The water remains neutral.} \\ SiO_{2(s)} & \text{insoluble - no solution produced. The water remains neutral.} \\ P_2O_{3(s)} & \text{acidic} \\ SO_{3(g)} & \text{acidic} \\ Cl_2O_{(g)} & \text{acidic} \end{array}$ 

#### **Extension**

7. Rainwater containing dissolved NO<sub>2(g)</sub> is acidic because of the formation of nitric acid in this reaction:

$$4 \text{ NO}_{2(g)} + 2 \text{ H}_2\text{O}_{(l)} + \text{O}_{2(g)} \rightarrow 4 \text{ HNO}_{3(aq)}.$$

# 8.4 ACID-BASE TITRATION

#### **PRACTICE**

(Page 599)

# **Understanding Concepts**

- 1. (a) pH 7
  - (b) Since this is a titration of a strong acid with a strong base, the equivalence point occurs at pH 7. Any indicator with pH 7 within its range would be suitable, e.g., bromothymol blue, litmus, neutral red, phenol red.

2. 
$$n_{\rm HI} = V_{\rm HI} \times C_{\rm HI}$$

$$= 11 \, \rm mL \times 0.18 \, mol/L$$

$$= 1.98 \, \rm mmol \qquad (extra \, digits \, carried)$$

$$n_{\rm HI} = n_{\rm NaOH} \, \rm required$$

$$C_{\rm NaOH} = \frac{n_{\rm NaOH}}{V_{\rm NaOH}}$$

$$V_{\rm NaOH} = \frac{n_{\rm NaOH}}{C_{\rm NaOH}}$$

$$= \frac{1.98 \, \rm mmol}{0.23 \, mol/L}$$

$$V_{\rm NaOH} = 8.6 \, \rm mL$$

8.6 mL of 0.23 mol/L sodium hydroxide is required to reach the equivalence point.

#### **Applying Inquiry Skills**

- (a) The last drop is washed into the flask because the titrant volume level in the buret already includes the volume of the drop.
  - (b) The results of the titration depend only on the moles of acid or base present, not their concentration. Adding water changes concentration but not the moles present.

#### **PRACTICE**

(Page 607)

# **Understanding Concepts**

4. (a)

ICE Table for the Ionization of HCO <sub>2</sub> H <sub>(aq)</sub>					
$HCO_2H_{(aq)} \rightleftharpoons H_{(aq)^+} + CO_2H_{(aq)^-}$					
Initial concentration (mol/L)	0.20	0.00	0.00		
Change in concentration (mol/L)	-x	+ <i>x</i>	+x		
Equilibrium concentration (mol/L)	0.20 - x	Х	Х		

Copyright © 2003 Nelson Acid–Base Equilibrium 317

$$K_{\rm a} = \frac{[{\rm H}^{+}_{\rm (aq)}][{\rm CO}_2{\rm H}^{-}_{\rm (aq)}]}{[{\rm HCO}_2{\rm H}_{\rm (aq)}]}$$
$$\frac{x^2}{0.20-x} = 1.8\times 10^{-4}$$

Predicting whether  $0.20 - x = 0.20 \dots$ 

$$\frac{\text{[HA]}_{\text{initial}}}{K_{\text{a}}} = \frac{0.20 \text{ mol/L}}{1.8 \times 10^{-4}}$$
$$= 1100$$

Since 1100 > 100, we assume that 0.20 - x = 0.20.

$$\frac{x^2}{(0.20)} \doteq 1.8 \times 10^{-4}$$
$$x^2 \doteq 3.6 \times 10^{-5}$$
$$x \doteq 6.0 \times 10^{-3}$$

Validating the assumption ...

$$\frac{6.0 \times 10^{-3}}{0.20} \times 100\% = 3.0\%$$

Since 3.0% < 5.0%, the assumption is valid.

$$\begin{split} [H^+_{(aq)}] &= 6.0 \times 10^{-3} \text{ mol/L} \\ pH &= -log \ [H^+_{(aq)}] \\ &= -log \ [6.0 \times 10^{-3}] \\ pH &= 2.22 \end{split}$$

The pH of the 0.20 mol/L formic acid solution is 2.22.

$$\begin{array}{lll} \text{(b)} & V_{\text{HCO}_2\text{H}_{(\text{aq})}} = 25.00 \text{ mL} \\ & C_{\text{HCO}_2\text{H}_{(\text{aq})}} = 0.20 \text{ mol/L} \\ & n_{\text{HCO}_2\text{H}_{(\text{aq})}} = V_{\text{HCO}_2\text{H}_{(\text{aq})}} \times C_{\text{HCO}_2\text{H}_{(\text{aq})}} \\ & = 25.00 \text{ mL} \times 0.20 \text{ mol/L} \\ & n_{\text{HCO}_2\text{H}_{(\text{aq})}} = 5.0 \text{ mmol} \\ & V_{\text{NaOH}_{(\text{aq})}} = 10.00 \text{ mL} \\ & C_{\text{NaOH}_{(\text{aq})}} = 0.20 \text{ mol/L} \\ & n_{\text{NaOH}_{(\text{aq})}} = V_{\text{NaOH}_{(\text{aq})}} \times C_{\text{NaOH}_{(\text{aq})}} \\ & = 10.00 \text{ mL} \times 0.20 \text{ mol/L} \\ & n_{\text{NaOH}_{(\text{aq})}} = 2.0 \text{ mmol} \\ & n_{\text{HCO}_2\text{H}_{(\text{aq})}} = 2.0 \text{ mmol} \\ & n_{\text{HCO}_2\text{H}_{(\text{aq})}} = 5.0 \text{ mmol} - 2.0 \text{ mmol} \\ & n_{\text{HCO}_2\text{H}_{(\text{aq})}} = 3.0 \text{ mmol} \\ & \text{Total volume} = 25.00 \text{ mL} + 10.00 \text{ mL} \\ & = 35.00 \text{ mL} \\ & C_{\text{HCO}_2\text{H}_{(\text{aq})}} = \frac{3.0 \text{ mmol}}{35.00 \text{ mL}} \end{array}$$

$$\begin{split} C_{\mathrm{HCO_2H_{(aq)}}} &= 0.08571 \; \mathrm{mol/L} \qquad \qquad \text{(extra digits carried)} \\ C_{\mathrm{CO_2H_{(aq)}^-}} &= \frac{2.0 \; \mathrm{mmol}}{35.00 \; \mathrm{mL}} \\ C_{\mathrm{CO_2H_{(aq)}^-}} &= 0.05714 \; \mathrm{mol/L} \qquad \qquad \text{(extra digits carried)} \end{split}$$

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

ICE Table for the Ionization of $HCO_2H_{(aq)}$						
$HCO_2H_{(aq)} \rightleftharpoons H_{(aq)^+} + CO_2H_{(aq)^-}$						
Initial concentration (mol/L)	0.08571	0.00	0.05714			
Change in concentration (mol/L)	-x	+ <b>x</b>	+ <b>x</b>			
Equilibrium concentration (mol/L)	0.08571 – <i>x</i>	Х	0.05714 +x			

$$\frac{[H_{(aq)}^+][CO_2H_{(aq)}^-]}{[HCO_2H_{(aq)}]} = K_a$$

$$\frac{x(0.05714 + x)}{0.08571 - x} = 1.8 \times 10^{-4}$$

Checking whether an approximation is warranted:

$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}{K_{\text{a}}} = \frac{0.08571}{1.8 \times 10^{-4}}$$
$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}{K_{\text{a}}} = 480$$

Since 480 > 100, we can assume that

$$0.08571 - x \doteq 0.08571$$
 and that  $0.05714 + x \doteq 0.05714$ 

The equilibrium simplifies to

$$\frac{x(0.05714)}{0.08571} = 1.8 \times 10^{-4}$$
$$x = 2.70 \times 10^{-4}$$

Verifying the assumption with the 5% rule:

$$\frac{2.70 \times 10^{-4}}{0.20} \times 100\% = 0.14\%$$

Since 0.14% < 5%, the simplifying assumption is justified.

$$[H_{(aq)}^+] \doteq 2.70 \times 10^{-4} \text{ mol/L}$$
  
 $pH \doteq -\log[2.70 \times 10^{-4}]$   
 $pH = 3.569$ 

The pH after the addition of 10.00 mL of  $NaOH_{(aq)}$  is 3.57.

(c) At the equivalence point, 25.00 mL of 0.20 mol/L NaOH<sub>(aq)</sub> were added. Entities remaining in solution:  $Na_{(aq)}^+$ ,  $CO_2H_{(aq)}^-$ ,  $H_2O_{(l)}$  Since  $Na_{(aq)}^+$  does not hydrolyze, the pH of the solution is determined by the methanoate ion.

$$\begin{split} \mathrm{CO_2H_{(aq)}^-} + \mathrm{H_2O_{(l)}} & \rightleftharpoons \mathrm{OH_{(aq)}^-} + \mathrm{HCO_2H_{(aq)}} \\ & \frac{[\mathrm{HCO_2H_{(aq)}}][\mathrm{OH_{(aq)}^-}]}{[\mathrm{CO_2H_{(aq)}^-}]} = K_b \\ & K_a = 1.8 \times 10^{-4} \\ & K_b = \frac{K_w}{K_a} \\ & = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} \\ & K_b = 5.6 \times 10^{-11} \\ & \mathrm{Therefore,} \\ & \frac{[\mathrm{HCO_2H_{(aq)}}][\mathrm{OH_{(aq)}^-}]}{[\mathrm{CO_2H_{(aq)}^-}]} = 5.6 \times 10^{-11} \end{split}$$

At the equivalence point, the total volume = 50.00 mL.

Since 5.00 mmol of  $HCO_2H_{(aq)}$  was present initially, 5.00 mmol of  $CO_2H_{(aq)}^-$  is present at the equivalence point.

$$[CO_2H_{(aq)}^-] = \frac{5.00 \text{ mmol}}{50.00 \text{ mL}}$$
  
 $[CO_2H_{(aq)}^-] = 0.100 \text{ mol/L}$ 

ICE Table for the Hydrolysis of CO <sub>2</sub> H <sup>-</sup> <sub>(aq)</sub>					
$CO_2H_{(aq)}^- + H_2O_{(I)} \rightleftharpoons HCO_2H_{(aq)} + OH_{(aq)}^-$					
Initial concentration (mol/L)	0.100	_	0.000	0.000	
Change in concentration (mol/L)	-x	_	+ <i>x</i>	+χ	
Equilibrium concentration (mol/L)	0.100 - x	_	х	х	

$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{CO}_2\text{H}_{(\text{aq})}^-]} = 5.6 \times 10^{-11}$$
$$\frac{x^2}{0.100 - x} = 5.6 \times 10^{-11}$$

Checking whether an approximation is warranted:

$$\frac{[\text{CO}_2\text{H}_{(\text{aq})}^-]_{\text{initial}}}{K} = \frac{0.10}{5.6 \times 10^{-11}}$$

$$\frac{[\mathrm{CO_2H^-_{(aq)}]_{initial}}}{K} = 1.8 \times 10^9$$

Since  $1.8 \times 10^9 > 100$ , we can assume that

$$0.100 - x \doteq 0.100$$
 The equilibrium simplifies to 
$$\frac{x^2}{0.100} = 5.6 \times 10^{-11}$$

$$x = 2.37 \times 10^{-6}$$

Verifying the assumption with the 5% rule:

$$\frac{2.37 \times 10^{-6}}{0.100} \times 100\% = 2.4 \times 10^{-3}\%$$

Since  $2.4 \times 10^{-3}$ % < 5%, the simplifying assumption is justified.

$$[OH_{(aq)}^{-}] \doteq 2.37 \times 10^{-6} \text{ mol/L}$$

$$pOH \doteq -\log[2.37 \times 10^{-6}]$$

$$pOH = 5.625$$

$$pH = 14 - pOH$$

$$pH = 8.37$$

The pH at the equivalence point is 8.37.

$$\begin{split} 5. \qquad V_{\text{HOCN}_{(aq)}} &= 30.00 \text{ mL} \\ C_{\text{HOCN}_{(aq)}} &= 0.17 \text{ mol/L} \\ n_{\text{HOCN}_{(aq)}} &= V_{\text{HOCN}_{(aq)}} \times C_{\text{HOCN}_{(aq)}} \\ &= 30.00 \text{ mL} \times 0.17 \text{ mol/L} \\ n_{\text{HOCN}_{(aq)}} &= 5.1 \text{ mmol} \\ V_{\text{NaOH}_{(aq)}} &= 10.00 \text{ mL} \\ C_{\text{NaOH}_{(aq)}} &= 0.250 \text{ mol/L} \\ n_{\text{NaOH}_{(aq)}} &= V_{\text{NaOH}_{(aq)}} \times C_{\text{NaOH}_{(aq)}} \\ &= 10.00 \text{ mL} \times 0.250 \text{ mol/L} \\ n_{\text{NaOH}_{(aq)}} &= 2.50 \text{ mmol} \\ n_{\text{HCON}_{(aq)}} \text{ remaining} \dots \\ n_{\text{HOCN}_{(aq)}} &= 5.1 \text{ mmol} - 2.50 \text{ mmol} \\ n_{\text{HOCN}_{(aq)}} &= 2.6 \text{ mmol} \\ Total \text{ volume} &= 30.00 \text{ mL} + 10.00 \text{ mL} \\ &= 40.00 \text{ mL} \\ C_{\text{HOCN}_{(aq)}} &= \frac{2.6 \text{ mmol}}{40.00 \text{ mL}} \\ C_{\text{HOCN}_{(aq)}} &= 0.0625 \text{ mol/L} \\ C_{\text{OCN}_{(aq)}} &= \frac{2.5 \text{ mmol}}{40.00 \text{ mL}} \\ C_{\text{OCN}_{(aq)}} &= 0.0625 \text{ mol/L} \\ C_{\text{OCN}_{(aq)}} &= 0.0625 \text{ mol/L} \\ \end{split}$$

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

ICE Table for the Ionization of HOCN <sub>(aq)</sub>						
$HOCN_{(aq)} \rightleftharpoons H^+_{(aq)} + OCN^{(aq)}$						
Initial concentration (mol/L)	0.0625	0.00	0.0625			
Change in concentration (mol/L)	-x	+ <b>x</b>	+ <b>x</b>			
Equilibrium concentration (mol/L)	0.0625 – x	Х	0.0625 + x			

Copyright © 2003 Nelson Acid-Base Equilibrium 321

$$\frac{[H_{(aq)}^{+}][OCN_{(aq)}^{-}]}{[HOCN_{(aq)}]} = K_{a}$$
$$\frac{x(0.0625 + x)}{0.0625 - x} = 3.5 \times 10^{-4}$$

$$\frac{[\text{HOCN}_{(aq)}]_{\text{initial}}}{K_{\text{a}}} = \frac{0.0625}{3.5 \times 10^{-4}}$$

$$\frac{[\text{HOCN}_{(\text{aq})}]_{\text{initial}}}{K_{\text{a}}} = 180$$

Since 180 > 100, we can assume that

0.0625 + x = 0.0625 and that 0.0625 - x = 0.0625

The equilibrium simplifies to

$$\frac{x(0.0625)}{0.0625} = 1.8 \times 10^{-4}$$
$$x = 1.8 \times 10^{-4}$$

Verifying the assumption with the 5% rule:

$$\frac{1.8 \times 10^{-4}}{0.0625} \times 100\% = 0.29\%$$

Since 0.29% < 5%, the simplifying assumption is justified.

$$[H_{(aq)}^{+}] \doteq 1.8 \times 10^{-4} \,\text{mol/L}$$
  
 $pH \doteq -\log[1.8 \times 10^{-4}]$   
 $pH = 3.74$ 

The  $OCN_{(aq)}$  is such a weak base ( $K_b = 2.10 \times 10^{12}$ ) that any hydrolysis to produce  $OH_{(aq)}^-$  is insignificant. The pH of the resulting solution is 3.74.

## **PRACTICE**

(Page 608)

# **Understanding Concepts**

6. (a) 
$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^-$$

$$K_b = \frac{[HH_{4(aq)}^+][OH_{(aq)}^-]}{[NH_{3(aq)}]}$$

$$K_b = 1.8 \times 10^{-5}$$

ICE Table for the Ionization of Ammonia					
$NH_{3(aq)} + H_2O_{(I)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^-$					
Initial concentration (mol/L)	0.15	_	0.00	0.00	
Change in concentration (mol/L)	-x	-	+x	+χ	
Equilibrium concentration (mol/L)	0.15 – x	-	х	х	

$$K_{\rm b} = \frac{[{\rm NH_4}^+_{\rm (aq)}][{\rm OH}^-_{\rm (aq)}]}{[{\rm NH}_{3({\rm aq})}]}$$
 $K_{\rm b} = 1.8 \times 10^{-5}$ 

$$\frac{x^2}{0.15 - x} = 1.8 \times 10^{-5}$$

Predicting the validity of the assumption ...

$$\frac{0.15}{1.8 \times 10^{-5}} = 8300$$

Since 8300 > 100, we may assume that 0.15 - x = 0.15.

The equilibrium expression becomes

$$\frac{x^2}{0.15} \doteq 1.8 \times 10^{-5}$$
 which yields

which yield 
$$x^2 \doteq 2.7 \times 10^{-6}$$

$$x \doteq 1.643 \times 10^{-3}$$

(extra digits carried)

Justifying the simplification assumption ...

$$\frac{1.643 \times 10^{-3}}{0.15} \times 100\% = 1.1\%$$

Since 1.1% < 5%, the assumption is justified.

Therefore,

$$[OH_{(aq)}^{-}] = 1.643 \times 10^{-3} \text{ mol/L}$$
  
 $pOH = -log[1.643 \times 10^{-3}]$   
 $pOH = 2.7844$  (extra digits carried)  
 $pH = 14 - pOH$   
 $= 14.0 - 2.7844$   
 $pH = 11.216$ 

The pH before any  $HI_{(aq)}$  is added is 11.22.

(b) At the equivalence point, the entities remaining in solution are  $NH_{4(aq)}^+$ ,  $I_{(aq)}^-$ , and  $H_2O_{(l)}$ . Since  $I_{(aq)}^-$  does not hydrolyze, the pH of the solution is determined by the ammonium ion.

$$\begin{split} C_{\rm NH_{3(aq)}} &= 0.1500 \; {\rm mol/L} \\ n_{\rm NH_{3(aq)}} &= V_{\rm NH_{3(aq)}} \times C_{\rm NH_{3(aq)}} \\ &= 20.0 \; {\rm mL} \times 0.1500 \; {\rm mol/L} \\ n_{\rm NH_{3(aq)}} &= 3.00 \; {\rm mmoL} \; ({\rm amount \; of \; NH_{4(aq)}^{+} \; produced}) \end{split}$$

Final volume = 40.0 mL

$$[NH_{4(aq)}^{+}] = \frac{3.00 \text{ mmol}}{40.0 \text{ mL}}$$

$$[NH_{4(aq)}^{+}] = 0.075 \text{ mol/L}$$

$$K_{\rm a} = \frac{[{\rm H}^+_{\rm (aq)}][{\rm NH}_4^+_{\rm (aq)}]}{[{\rm NH}_{3({\rm aq})}]}$$

Copyright © 2003 Nelson Acid-Base Equilibrium 323

$$\frac{x^2}{0.075 - x} = 5.8 \times 10^{-10}$$

Predicting whether 0.075 - x = 0.075:

$$\frac{[\text{HA}]_{\text{initial}}}{K_{\text{a}}} = \frac{0.075 \text{ mol/L}}{5.8 \times 10^{-10}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_{\text{a}}} = 1.3 \times 10^9$$

Since  $1.3 \times 10^9 > 100$ , we assume that 0.075 - x = 0.075.

$$\frac{x^2}{(0.075)} \doteq 5.8 \times 10^{-10}$$

$$x \doteq 6.595 \times 10^{-6} \qquad \text{(extra digits carried)}$$

$$[H^+_{(aq)}] = 6.595 \times 10^{-6} \text{ mol/L}$$

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

$$= -\log[6.595 \times 10^{-6}]$$

$$pH = 5.181$$

The pH at the equivalence point is 5.18.

#### **PRACTICE**

(Page 611)

## **Understanding Concepts**

- 7. Since this is a titration of a weak base with a strong acid, the equivalence point will occur at pH less than 7. Alizarin yellow's pH range is 10.1–12.0, beyond the required equivalence point.
- 8. Indicators are weak acids in equilibrium with their conjugate base. At the endpoint some titrant is required to "neutralize" the indicator. A small volume of indicator solution is used to keep the titrant volume required to produce the colour change insignificant to the results of the titration.
- 9. Since this is a titration of a weak acid with a strong base, the equivalence point will occur at pH greater than 7. However, methyl red has a pH range of 4.8–6.0, well below the equivalence point. As a result, the endpoint of the titration occurs before the equivalence point is reached.

#### **PRACTICE**

(Page 613)

# **Understanding Concepts**

10. (a) 
$$PO_{4(aq)}^{3-} + H_{(aq)}^{+} \rightarrow HPO_{4(aq)}^{2-}$$
  
 $HPO_{4(aq)}^{2-} + H_{(aq)}^{+} \rightarrow H_{2}PO_{4(aq)}^{-}$   
 $H_{2}PO_{4(aq)}^{-} + H_{(aq)}^{+} \rightarrow H_{3}PO_{4(aq)}$ 

- (b) 25 mL and 50 mL
- (c) The hydrogen phosphate ion,  $HPO_{4(aq)}^{2-}$  is an extremely weak acid ( $K_a = 4.2 \times 10^{-13}$ ) and does not lose its proton quantitatively. Only quantitative reactions produce detectable endpoints in an acid-base titration.

# **SECTION 8.4 QUESTIONS**

(Page 613)

#### **Understanding Concepts**

- 1. (a) The endpoint is at pH 9 and the equivalence point is at 26 mL.
  - (b) Phenolphthalein
  - (c)  $HC_2H_3O_{2(aq)} + OH_{(aq)}^- \rightarrow C_2H_3O_{2(aq)}^- + H_2O_{(1)}$
- 2. (a) 7
  - (b) >7

- (c) 7
- (d) < 7
- 3. (a) <7
  - (b) >7
  - (c) = 7
- 4. A pH curve is used to determine the pH of the solution at the equivalence point of a titration, so that a suitable indicator that will change colour at that endpoint can be chosen.
- 5. (a) pink
  - (b) yellow
  - (c) blue
  - (d) red-orange
- 6. (a)

ICE Table for the Ionization of HC <sub>7</sub> H <sub>5</sub> O <sub>2(aq)</sub>						
$HC_7H_5O_{2(aq)} \rightleftharpoons H^+_{(aq)} + C_7H_5O^{2(aq)}$						
Initial concentration (mol/L)	0.100	0.000	0.000			
Change in concentration (mol/L)	-х	+ <b>x</b>	+ <b>x</b>			
Equilibrium concentration (mol/L)	0.100 - x	Х	х			

$$\begin{aligned} \text{HC}_7 \text{H}_5 \text{O}_{2(\text{aq})} &\rightleftharpoons \text{H}^+_{(\text{aq})} + \text{C}_7 \text{H}_5 \text{O}^-_{2(\text{aq})} \\ K_\text{a} &= \frac{[\text{H}^+_{(\text{aq})}][\text{C}_7 \text{H}_5 \text{O}^-_{2(\text{aq})}]}{[\text{HC}_7 \text{H}_5 \text{O}_{2(\text{aq})}]} \\ \frac{x^2}{0.100 - x} &= 6.3 \times 10^{-5} \end{aligned}$$

Predicting whether  $0.100 - x = 0.100 \dots$ 

$$\frac{[\text{HA}]_{\text{initial}}}{K_{\text{a}}} = \frac{0.100 \text{ mol/L}}{6.3 \times 10^{-5}}$$
$$\frac{[\text{HA}]_{\text{initial}}}{K_{\text{a}}} = 1580$$

Since 1580 > 100, we assume that 0.100 - x = 0.100.

$$\frac{x^2}{(0.100)} \doteq 6.3 \times 10^{-5}$$

$$x^2 \doteq 6.3 \times 10^{-6}$$

$$x = 2.51 \times 10^{-3}$$
 (extra digits carried)

The 5% rule justifies the assumption.

$$\begin{split} [H^+_{(aq)}] &= 2.51 \times 10^{-3} \text{ mol/L} \\ pH &= -log \ [H^+_{(aq)}] \\ &= -log \ [2.51 \times 10^{-3}] \\ pH &= 2.600 \end{split}$$

The pH of the solution is 2.600.

$$\begin{array}{ll} \text{(b)} & V_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = 25.00 \text{ mL} \\ & C_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = 0.100 \text{ mol/L} \\ & n_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = V_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} \times C_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} \\ & = 25.00 \text{ mL} \times 0.100 \text{ mol/L} \\ & n_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = 2.50 \text{ mmol} \end{array}$$

$$\begin{split} V_{\text{NaOH}_{(\text{aq})}} &= 10.00 \text{ mL} \\ C_{\text{NaOH}_{(\text{aq})}} &= 0.100 \text{ mol/L} \\ n_{\text{NaOH}_{(\text{aq})}} &= V_{\text{NaOH}_{(\text{aq})}} \times C_{\text{NaOH}_{(\text{aq})}} \\ &= 10.00 \text{ mL} \times 0.100 \text{ mol/L} \\ n_{\text{NaOH}_{(\text{aq})}} &= 1.00 \text{ mmol} \\ n_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} \text{ remaining} \dots \\ n_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} &= 2.50 \text{ mmol} - 1.00 \text{ mmol} \\ n_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} &= 1.50 \text{ mmol} \\ \text{Total volume} &= 25.00 \text{ mL} + 10.00 \text{ mL} \\ &= 35.00 \text{ mL} \\ C_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} &= \frac{1.50 \text{ mmol}}{35.00 \text{ mL}} \\ C_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} &= 0.04286 \text{ mol/L} \qquad \text{(extra digits carried)} \\ C_{\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}} &= \frac{1.00 \text{ mmol}}{35.00 \text{ mL}} \\ C_{\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}} &= 0.02857 \text{ mol/L} \qquad \text{(extra digits carried)} \end{split}$$

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

ICE Table for the Ionization of $HC_7H_5O_{2(aq)}$					
$HC_7H_5O_{2(aq)} \rightleftharpoons H_{(aq)}^+ + C_7H_5O_{2(aq)}^-$					
Initial concentration (mol/L)	0.04286	0.000	0.02857		
Change in concentration (mol/L)	-x	+ <b>x</b>	+ <b>x</b>		
Equilibrium concentration (mol/L)	0.04286 – x	х	0.02857 + x		

$$\frac{[H_{(aq)}^+][C_7H_5O_{2(aq)}^-]}{[HC_7H_5O_{2(aq)}]} = K_a$$

$$\frac{x(0.02857 + x)}{0.04286 - x} = 6.3 \times 10^{-5}$$

$$\frac{[HC_7H_5O_{2(aq)}]_{initial}}{K_a} = \frac{0.100}{6.3 \times 10^{-5}}$$
$$= 1600$$

Since 1600 > 100, we can assume that 0.04286 - x = 0.04286 and that 0.02857 + x = 0.02857. The equilibrium simplifies to

$$\frac{x(0.02857)}{0.04286} = 6.3 \times 10^{-5}$$
$$x = 9.45 \times 10^{-5}$$

The 5% rule validates the assumption:

$$[H_{(aq)}^{+}] \doteq 9.45 \times 10^{-5} \text{ mol/L}$$
  
 $pH \doteq -\log[9.45 \times 10^{-5}]$   
 $pH = 4.03$ 

(c) At the equivalence point, 25.00 mL of 0.100 mol/L NaOH $_{(aq)}$  were added. Entities remaining in solution: Na $_{(aq)}^+$ , C $_7$ H $_5$ O $_{2(aq)}^-$ , H $_2$ O $_{(l)}$ 

Since Na<sub>(aq)</sub> does not hydrolyze, the pH is determined by the benzoate ion.

$$C_7H_5O_{2(aq)}^- + H_2O_{(l)} \rightleftharpoons OH_{(aq)}^- + HC_7H_5O_{2(aq)}$$

$$\frac{[\mathrm{OH}_{(\mathrm{aq})}^{-}][\mathrm{HC}_{7}\mathrm{H}_{5}\mathrm{O}_{2(\mathrm{aq})}]}{[\mathrm{C}_{7}\mathrm{H}_{5}\mathrm{O}_{2(\mathrm{aq})}^{-}]}=K_{\mathrm{b}}$$

$$K_a = 6.3 \times 10^{-5}$$

$$K_{b} = \frac{K_{w}}{K_{a}}$$
$$= \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}}$$

$$K_{\rm h} = 1.587 \times 10^{-10}$$
 (extra digits carried)

Therefore,

$$\frac{[\mathrm{OH}_{(\mathrm{aq})}^{-}][\mathrm{HC}_{7}\mathrm{H}_{5}\mathrm{O}_{2(\mathrm{aq})}]}{[\mathrm{C}_{7}\mathrm{H}_{5}\mathrm{O}_{2(\mathrm{aq})}^{-}]} = 1.587 \times 10^{-10}$$

At the equivalence point, the total volume is 50 mL.

Since 2.50 mmol of  $HC_7H_5O_{2(aq)}$  was present initially, 2.50 mmol of  $C_7H_5O_{2(aq)}^-$  is present at the equivalence point.

$$[C_7H_5O_{2(aq)}^{-}] = \frac{2.50 \text{ mmol}}{50.00 \text{ mL}}$$

$$[C_7H_5O_{2(aq)}^{-}] = 0.0500 \text{ mol/L}$$

ICE Table for the Hydrolysis of C <sub>7</sub> H <sub>5</sub> O <sub>2(aq)</sub>					
$C_7H_5O_{2(aq)}^- + H_2O_{(I)} \rightleftharpoons OH_{(aq)}^- + HC_7H_5O_{2(aq)}^-$					
Initial concentration (mol/L)	0.0500	_	0.000	0.000	
Change in concentration (mol/L)	-x	_	+ <i>x</i>	+ <i>x</i>	
Equilibrium concentration (mol/L)	0.0500 - x	_	х	х	

$$\frac{[\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}^-]} = 1.587 \times 10^{-10}$$
$$\frac{x^2}{0.0500 - x} = 1.587 \times 10^{-10}$$

Checking whether an approximation is warranted:

$$\frac{[C_7 H_5 O_{2(aq)}^{-}]_{initial}}{K} = \frac{0.0500}{1.587 \times 10^{-10}}$$
$$= 3.2 \times 10^8$$

Since  $3.2 \times 10^8 > 100$ , we can assume that 0.0500 - x = 0.0500.

The equilibrium simplifies to

$$\frac{x^2}{0.0500} = 1.587 \times 10^{-10}$$

$$x = 2.82 \times 10^{-6}$$

(The 5% rule verifies the assumption.)

Copyright © 2003 Nelson Acid—Base Equilibrium 327

$$[OH_{(aq)}^{-}] \doteq 2.82 \times 10^{-6} \text{ mol/L}$$
  
 $pOH \doteq -\log[2.82 \times 10^{-6}]$   
 $pOH = 5.550$   
 $pH = 14 - pOH$   
 $pH = 8.450$ 

The pH at the equivalence point is 8.450.

7. An appropriate indicator for this titration is alizarin yellow.

8. (i) 
$$HCl_{(aq)} + NH_{3(aq)} \rightarrow H_2O_{(1)} + NH_4Cl_{(aq)}$$

At the equivalence point,  $n_{\text{acid}} = n_{\text{base}}$ 

$$\begin{split} & \therefore C_{\text{acid}} V_{\text{acid}} = C_{\text{base}} V_{\text{base}} \\ V_{\text{HCl}_{(\text{aq})} \text{required}} &= \frac{C_{\text{NH}_{3(\text{aq})}} \times V_{\text{NH}_{3(\text{aq})}}}{C_{\text{HCl}_{(\text{aq})}}} \\ &= \frac{0.100 \text{ mol/L} \times 20.0 \text{ mI}}{0.200 \text{ mol/L}} \end{split}$$

$$V_{\text{HCl}_{(aq)}\text{required}} = 10.0 \text{ mL NaOH}$$

Final solution volume = 30.0 mL

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

Since  $Cl_{(aq)}^-$  does not hydrolyze, pH is determined by the ammonium ion.

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

Since 2.00 mmol of  $NH_{3(aq)}$  was present initially, 2.00 mmol of  $NH_{4(aq)}^{+}$  is present at the equivalence point.

$$[NH_{4(aq)}^{+}] = \frac{2.00 \text{ mmol}}{30.0 \text{ mL}}$$
  
 $[NH_{4(aq)}^{+}] = 0.0667 \text{ mol/L}$ 

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

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

ICE Table for the Hydrolysis of NH <sub>4(aq)</sub>						
$NH_{4(aq)}^{+} \rightleftharpoons H_{(aq)}^{+} + NH_{3(aq)}$						
Initial concentration (mol/L)	0.0667	0.000	0.000			
Change in concentration (mol/L)	-x	+x	+x			
Equilibrium concentration (mol/L)	0.0667 – x	Х	х			

$$\frac{[H_{(aq)}^+][NH_{3(aq)}]}{[NH_{4(aq)}^+]} = 5.8 \times 10^{-10}$$
$$\frac{x^2}{0.0667 - x} = 5.8 \times 10^{-10}$$

Checking whether an approximation is warranted:

$$\frac{[\text{NH}_{4(\text{aq})}^{+}]_{\text{initial}}}{K_{\text{a}}} = \frac{0.0667}{5.8 \times 10^{-10}} > 100$$

The equilibrium simplifies to

$$\frac{x^2}{0.0667} = 5.8 \times 10^{-10}$$
$$x = 6.22 \times 10^{-6}$$

The 5% rule verifies the assumption.

$$[H_{(aq)}^{+}] \doteq 6.22 \times 10^{-6} \,\text{mol/L}$$
  
 $pH \doteq -\log[6.22 \times 10^{-6}]$   
 $pH = 5.206$ 

The pH at the equivalence point is 5.206.

$$\begin{split} \text{(ii)} \quad & \text{HC}_2\text{H}_3\text{O}_{2(\text{aq})} + \text{NaOH}_{(\text{aq})} \to \text{H}_2\text{O}_{(\text{l})} + \text{NaC}_2\text{H}_3\text{O}_{2(\text{aq})} \\ & V_{\text{NaOH required}} = \frac{C_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} \times V_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}}}{C_{\text{NaOH}}} \\ & = \frac{0.350 \text{ mol/L} \times 10.0 \text{ mL}}{0.150 \text{ mol/L}} \end{split}$$

 $V_{\text{NaOH required}} = 23.3 \text{ mL NaOH}$ 

Entities remaining in solution at the equivalence point: Na<sub>(aq)</sub><sup>+</sup>, C<sub>2</sub>H<sub>3</sub>O<sub>2(aq)</sub><sup>-</sup>, H<sub>2</sub>O<sub>(1)</sub>

Since Na<sub>(aq)</sub><sup>+</sup> does not hydrolyze, the pH of the solution is determined by the acetate ion.

$$\begin{split} \mathbf{C}_2\mathbf{H}_3\mathbf{O}_{2(\mathrm{aq})}^{-} + \mathbf{H}_2\mathbf{O}_{(1)} & \rightleftharpoons \mathbf{OH}_{(\mathrm{aq})}^{-} + \mathbf{H}\mathbf{C}_2\mathbf{H}_3\mathbf{O}_{2(\mathrm{aq})} \\ & \frac{[\mathbf{OH}_{(\mathrm{aq})}^{-}][\mathbf{H}\mathbf{C}_2\mathbf{H}_3\mathbf{O}_{2(\mathrm{aq})}]}{[\mathbf{C}_2\mathbf{H}_3\mathbf{O}_{2(\mathrm{aq})}^{-}]} = K_b \\ & K_b = 1.8 \times 10^{-5} \\ & K_b = \frac{K_w}{K_a} \\ & = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \\ & K_b = 5.555 \times 10^{-10} \qquad \text{(extra digits carried)} \\ & \text{Therefore,} \end{split}$$

$$\frac{[\mathrm{OH}_{(\mathrm{aq})}^{-}][\mathrm{HC}_{2}\mathrm{H}_{3}\mathrm{O}_{2(\mathrm{aq})}]}{[\mathrm{C}_{2}\mathrm{H}_{3}\mathrm{O}_{2(\mathrm{aq})}^{-}]} = 5.555 \times 10^{-10}$$

At the equivalence point, the total volume = 33.33 mL.

Since 3.50 mmol of  $HC_2H_3O_{2(aq)}$  was present initially, 3.50 mmol of  $C_2H_3O_{2(aq)}^-$  is present at the equivalence point.

$$[C_2H_3O_{2(aq)}^-] = \frac{3.50 \text{ mmol}}{33.33 \text{ mL}}$$
  
 $[C_2H_3O_{2(aq)}^-] = 0.105 \text{ mol/L}$ 

Copyright © 2003 Nelson Acid–Base Equilibrium 329

ICE Table for the Hydrolysis of C <sub>2</sub> H <sub>3</sub> O <sub>2(aq)</sub>					
$C_2H_3O_{2(\mathsf{aq)}^-} + H_2O_{(\mathsf{I)}} \rightleftharpoons OH_{(\mathsf{aq)}^-} + HC_2H_3O_{2(\mathsf{aq)}}$					
Initial concentration (mol/L)	0.105	_	0.000	0.000	
Change in concentration (mol/L)	-x	_	+x	+x	
Equilibrium concentration (mol/L)	0.105 – x	-	х	х	

$$\frac{[\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]} = 5.556 \times 10^{-10}$$
$$\frac{x^2}{0.105 - x} = 5.556 \times 10^{-10}$$

$$\frac{[C_2H_3O_{2(aq)}^{-}]_{initial}}{K} = \frac{0.105}{5.556 \times 10^{-10}} > 100$$

The equilibrium simplifies to

$$\frac{x^2}{0.105} = 5.556 \times 10^{-10}$$

$$x = 7.64 \times 10^{-6}$$

The 5% rule verifies the assumption.

$$[OH_{(aq)}^{-}] \doteq 7.64 \times 10^{-6} \text{ mol/L}$$
  
 $pOH \doteq -\log[7.64 \times 10^{-6}]$   
 $= 5.117$   
 $pH = 14 - pOH$   
 $= 14 - 5.117$ 

$$pH = 8.883$$

The pH at the equivalence point is 8.883.

$$\begin{split} \text{(iii) HBr}_{(\text{aq})} + \text{N}_2 \text{H}_{4(\text{aq})} &\rightarrow \text{H}_2 \text{O}_{(\text{l})} + \text{N}_2 \text{H}_5 \text{Br}_{(\text{aq})} \\ \text{at the equivalence point, } n_{\text{acid}} = n_{\text{base}} \\ V_{\text{HBr}_{(\text{aq})} \text{ required}} &= \frac{C_{\text{N}_2 \text{H}_{4(\text{aq})}} \times V_{\text{N}_2 \text{H}_{4(\text{aq})}}}{C_{\text{HBr}_{(\text{aq})}}} \\ &= \frac{0.150 \text{ mol/L} \times 15.0 \text{ mL}}{0.250 \text{ mol/L}} \\ V_{\text{HBr}_{(\text{aq})} \text{ required}} &= 9.00 \text{ mL HBr}_{(\text{aq})} \\ \text{Final solution volume} &= 24.0 \text{ mL} \end{split}$$

\_ -----

Entities remaining in solution at the equivalence point:  $Br_{(aq)}^-$ ,  $N_2H_{5(aq)}^+$ ,  $H_2O_{(1)}$ 

Since  $Br_{(aq)}^-$  does not hydrolyze, the pH of the solution is determined by  $N_2H_{5(aq)}^+.$ 

$$N_2H_{5(aq)}^{\phantom{5}+} \rightleftharpoons H_{(aq)}^+ + N_2H_{4(aq)}$$

Since 2.25 mmol of  $N_2H_{4(aq)}$  was present initially, 2.25 mmol of  $N_2H_{5(aq)}^+$  is present at the equivalence point.

$$[N_2H_{5(aq)}^+] = \frac{2.25 \text{ mmol}}{24.0 \text{ mL}}$$
  
 $[N_2H_{5(aq)}^+] = 0.0938 \text{ mol/L}$ 

$$\begin{split} \mathbf{N}_2 \mathbf{H}_{5(\mathrm{aq})}^+ &\rightleftharpoons \ \mathbf{H}_{(\mathrm{aq})}^+ + \mathbf{N}_2 \mathbf{H}_{4(\mathrm{aq})} \\ &\frac{[\mathbf{H}_{(\mathrm{aq})}^+][\mathbf{N}_2 \mathbf{H}_{4(\mathrm{aq})}]}{[\mathbf{N}_2 \mathbf{H}_{5(\mathrm{aq})}^+]} = \frac{K_\mathrm{w}}{K_\mathrm{b}} \\ &= \frac{1.0 \times 10^{-14}}{9.6 \times 10^{-7}} \end{split}$$

$$= 1.04 \times 10^{-8}$$
 (extra digits carried)

ICE Table for the Hydrolysis of N <sub>2</sub> H <sub>5(aq)</sub>					
$N_2H_{5(aq)}^+ + H_2O_{(I)} \rightleftharpoons OH_{(aq)}^- + N_2H_{4(aq)}$					
Initial concentration (mol/L)	0.0938	_	0.000	0.000	
Change in concentration (mol/L)	-x	_	+x	+x	
Equilibrium concentration (mol/L)	0.0938 - x	_	х	х	

$$\begin{split} \mathbf{N}_2 \mathbf{H}_{5(\mathrm{aq})}^+ &\rightleftharpoons \mathbf{N}_2 \mathbf{H}_{4(\mathrm{aq})} + \mathbf{H}_{(\mathrm{aq})}^+ \\ &\frac{[\mathbf{H}_{(\mathrm{aq})}^+][\mathbf{N}_2 \mathbf{H}_{4(\mathrm{aq})}]}{[\mathbf{N}_2 \mathbf{H}_{5(\mathrm{aq})}^+]} = 1.04 \times 10^{-8} \\ &\frac{x^2}{0.0938 - x} = 1.04 \times 10^{-8} \end{split}$$

$$\frac{[N_2 H_{5(aq)}^+]_{\text{initial}}}{K_a} = \frac{0.0938}{1.04 \times 10^{-8}} > 100$$

The equilibrium simplifies to 
$$\frac{x^2}{0.0938} = 1.04 \times 10^{-8}$$

$$x = 3.12 \times 10^{-5}$$

The 5% rule verifies the assumption.

$$[H_{(aq)}^+] \doteq 3.12 \times 10^{-5} \text{ mol/L}$$

$$pH \doteq -\log[3.12 \times 10^{-5}]$$
  
 $pH = 4.505$ 

The pH at the equivalence point is 4.505.

(b) Appropriate indicators: methyl orange, bromophenol blue.

9. 
$$V_{\rm HC_2H_3O_{2(aq)}} = 45.00 \; \rm mL$$
 
$$C_{\rm HC_2H_3O_{2(aq)}} = 0.10 \; \rm mol/L$$

Copyright © 2003 Nelson Acid-Base Equilibrium

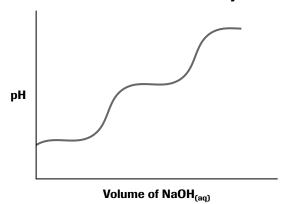
$$\begin{split} n_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} &= V_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} \times C_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} \\ &= 45.00 \text{ mL} \times 0.10 \text{ mol/L} \\ n_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} &= 4.5 \text{ mmol} \\ V_{\text{NaOH}_{(\text{aq})}} &= 25.00 \text{ mL} \\ C_{\text{NaOH}_{(\text{aq})}} &= 0.23 \text{ mol/L} \\ n_{\text{NaOH}_{(\text{aq})}} &= V_{\text{NaOH}_{(\text{aq})}} \times C_{\text{NaOH}_{(\text{aq})}} \\ &= 25.00 \text{ mL} \times 0.23 \text{ mol/L} \\ n_{\text{NaOH}_{(\text{aq})}} &= 5.75 \text{ mmol} \qquad \text{(extra digit carried)} \\ n_{\text{NaOH}_{(\text{aq})}} &= 5.75 \text{ mmol} - 4.5 \text{ mmol} \\ n_{\text{NaOH}_{(\text{aq})}} &= 1.25 \text{ mmol} \\ \text{Total volume} &= 25.00 \text{ mL} + 45.00 \text{ mL} \\ &= 70.00 \text{ mL} \\ C_{\text{NaOH}_{(\text{aq})}} &= \frac{1.25 \text{ mmol}}{70.00 \text{ mL}} \\ C_{\text{NaOH}_{(\text{aq})}} &= 0.0179 \text{ mol/L} \qquad \text{(extra digits carried)} \\ [\text{OH}_{(\text{aq})}^-] &= 0.0179 \text{ mol/L} \\ p\text{OH} &= -\log (0.0179) \\ p\text{OH} &= 1.748 \\ p\text{H} &= 12.25 \end{split}$$

The pH of the resulting solution is 12.25.

- 10. (a) The pH is between 5.6 and 6.0.
  - (b) The pH is approximately 6, which corresponds to a  $[H_{(aq)}^+]$  of  $1.0 \times 10^{-6}$  mol/L.

## **Applying Inquiry Skills**

## 11. Oxalic Acid Reacted with Sodium Hydroxide



- 12. A: between 4.4 and 4.8
  - B: between 6.0 and 6.6
  - C: between 2.8 and 3.2

- 13. The three solutions are tested with bromocresol green indicator. The pH 3.5 solution is the only solution that is yellow in bromocresol green indicator. The two remaining solutions are tested with cresol red indicator. The pH 7.8 solution is the only solution that is red in cresol red indicator. The remaining solution must be pH 5.8. This can be verified by testing the solution with litmus and bromophenol blue. It should be red in litmus and blue–violet in bromophenol blue.
- 14. From strongest to weakest: nitric and hydrochloric acid are identical, hydrofluoric acid, methanoic acid, acetic acid, and hydrocyanic acid.

# 8.5 BUFFERS

#### **PRACTICE**

(Page 620)

## **Understanding Concepts**

- 1. (a) A good buffer solution maintains a nearly constant pH when diluted or when a strong acid or base is added.
  - (b) A buffer contains equimolar amounts of a weak acid and its conjugate base.
- 2. (a) (i)  $NH_{4(aq)}^{+} \rightleftharpoons H_{(aq)}^{+} + NH_{3(aq)}$ (ii)  $HC_7H_5O_{2(aq)} \rightleftharpoons H_{(aq)}^{+} + C_7H_5O_{2(aq)}^{-}$ 
  - (b) The equilibrium will shift in the direction of the conjugate acid:

$$NH_{4(aq)}^{+} \rightarrow NH_{3(aq)}^{+} + H_{(aq)}^{+}$$
3. 
$$[CO_{2}H_{(aq)}^{-}] = 1.5 \text{ mol/L}$$

$$[HCO_{2}H_{(aq)}] = 1.5 \text{ mol/L}$$

$$HCO_{2}H_{(aq)} \rightleftharpoons H_{(aq)}^{+} + CO_{2}H_{(aq)}^{-}$$

$$\frac{[H_{(aq)}^{+}][CO_{2}H_{(aq)}^{-}]}{[HCO_{2}H_{(aq)}]} = 1.8 \times 10^{-4}$$

$$[H_{(aq)}^{+}] = K_a \frac{[HCO_2H_{(aq)}]}{[CO_2H_{(aq)}]}$$

$$= 1.8 \times 10^{-4} \times \frac{1.5 \text{ mol/L}}{1.5 \text{ mol/L}}$$

$$[H^{+}_{(aq)}] = 1.8 \times 10^{-4}$$

$$pH = -\log[1.8 \times 10^{-4}]$$

$$pH = 3.74$$

The addition of 
$$H_{(aq)}^+$$
 ...

$$[\mathrm{H_{(aq)}^+}]_{added} = 0.13 \; \mathrm{mol/L}$$

$$[HCO_2H_{(aq)}]_{final} = (1.5 + 0.13) \text{ mol/L}$$

$$[HCO_2H_{(aq)}]_{final} = 1.63 \text{ mol/L}$$

$$[CO_2H_{(aq)}^-]_{final} = (1.5 - 0.13) \text{ mol/L}$$

$$[\mathrm{CO_2H^-_{(aq)}}]_{final} = 1.37 \; \mathrm{mol/L}$$

$$[H_{(aq)}^+] = K_a \frac{[HCO_2H_{(aq)}]}{[CO_2H_{(aq)}^-]}$$

$$= 1.8 \times 10^{-4} \times \frac{1.63}{1.37}$$
$$[H_{(aq)}^+] = 2.1 \times 10^{-4}$$

$$pH = 3.67$$

Copyright © 2003 Nelson Acid—Base Equilibrium 333