

# CHAPTER 19 IONIC EQUILIBRIA IN AQUEOUS SYSTEMS

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- 19.1 The purpose of an acid-base buffer is to maintain a relatively constant pH in a solution.
- 19.2 The weak acid component neutralizes added base and the weak base component neutralizes added acid so that the pH of the buffer solution remains relatively constant. The components of a buffer do not neutralize one another when they are a conjugate acid-base pair.
- 19.3 The presence of an ion in common between two solutes will cause any equilibrium involving either of them to shift in accordance with Le Châtelier's principle. For example, addition of NaF to a solution of HF will cause the equilibrium
- $$\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$$
- to shift to the left, away from the excess of  $\text{F}^-$  the common ion.
- 19.4 a) **Buffer C** has equal, high concentrations of both HA and  $\text{A}^-$ . It has the highest buffering capacity.  
 b) **All** of the buffers have the same pH range. The practical buffer range of  $\text{pH} = \text{pK}_a \pm 1$ , and is independent of concentration.  
 c) **Buffer B** has the greatest amount of weak base and can therefore neutralize the greatest amount of added acid.
- 19.5 A buffer is a mixture of a weak acid and its conjugate base (or weak base and its conjugate acid). The pH of a buffer changes only slightly with added  $\text{H}_3\text{O}^+$  because the added  $\text{H}_3\text{O}^+$  reacts with the base of the buffer. The net result is that the concentration of  $\text{H}_3\text{O}^+$  does not change much from the original concentration, keeping the pH nearly constant.
- 19.6 A buffer with a high capacity has a great resistance to pH change. A high buffer capacity results when the weak acid and weak base are both present at high concentration. Addition of 0.01 mol of HCl to a high-capacity buffer will cause a smaller change in pH than with a low-capacity buffer, since the ratio  $[\text{HA}]/[\text{A}^-]$  will change less.
- 19.7 Only (c) has an affect on the buffer capacity. In theory, **any** conjugate pair (of any  $\text{pK}_a$ ) can be used to make a high capacity buffer. With proper choice of components, it can be at any pH. The buffer range changes along with the buffer capacity, but does not determine it. A high-capacity buffer will result when comparable quantities (i.e., buffer-component ratio < 10:1) of weak acid and weak base are dissolved so that their concentrations are relatively high.
- 19.8 The buffer component ratio refers to the ratio of concentrations of the acid and base that make up the buffer. When this ratio is equal to 1, the buffer resists changes in pH with added acid to the same extent that it resists changes in pH with added base. The buffer range extends equally in both the acidic and basic direction. When the ratio shifts with higher [base] than [acid], the buffer is more effective at neutralizing added acid than base so the range extends further in the acidic than basic direction. The opposite is true for a buffer where [acid] > [base]. Buffers with a ratio equal to 1 have the greatest buffer range. The more the buffer component ratio deviates from 1, the smaller the buffer range.
- 19.9  $\text{pK}_a$  (formic) = 3.74;  $\text{pK}_a$  (acetic) = 4.74. Formic acid would be the buffer choice, since its  $\text{pK}_a$  is closer to the desired pH of 3.5. If acetic acid were used, the buffer component ratio would be far from 1:1 and the buffer's effectiveness would be lower. The NaOH serves to partially neutralize the acid and produce its conjugate base.
- 19.10 The buffer components are propanoic acid and propanoate ion. The sodium ions are spectator ions and are ignored because they are not involved in the buffer. The reaction table that describes this buffer is:

| Concentration (M) | $\text{CH}_3\text{CH}_2\text{COOH}(aq)$ | $+$ | $\text{H}_2\text{O}(l)$ | $\rightleftharpoons$ | $\text{CH}_3\text{CH}_2\text{COO}^-(aq)$ | $+$ | $\text{H}_3\text{O}^+(aq)$ |
|-------------------|-----------------------------------------|-----|-------------------------|----------------------|------------------------------------------|-----|----------------------------|
| Initial           | 0.15                                    | —   |                         |                      | 0.35                                     |     | 0                          |
| Change            | $-x$                                    | —   |                         |                      | $+x$                                     |     | $+x$                       |
| Equilibrium       | $0.15 - x$                              | —   |                         |                      | $0.35 + x$                               |     | $x$                        |

Assume that  $x$  is negligible with respect to both 0.15 and 0.35 since both concentrations are much larger than  $K_a$ .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]} = \frac{[x][0.35 + x]}{[0.15 - x]} = \frac{[x][0.35]}{[0.15]} = 1.3 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{CH}_3\text{CH}_2\text{COOH}]}{[\text{CH}_3\text{CH}_2\text{COO}^-]} = (1.3 \times 10^{-5}) \left( \frac{0.15}{0.35} \right) = 5.57143 \times 10^{-6} = \mathbf{5.6 \times 10^{-6} \text{ M}}$$

Check assumption: percent error =  $(5.6 \times 10^{-6}/0.15)100\% = 0.0037\%$ . The assumption is valid.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.57143 \times 10^{-6}) = 5.2540 = \mathbf{5.25}$$

Another solution path to find pH is using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right) \quad \text{p}K_a = -\log(1.3 \times 10^{-5}) = 4.886$$

$$\text{pH} = 4.886 + \log \left( \frac{[\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]} \right) = 4.886 + \log \left( \frac{[0.35]}{[0.15]} \right)$$

$$\text{pH} = 5.25398 = \mathbf{5.25}$$

- 19.11 CA =  $\text{C}_6\text{H}_5\text{COOH}$  CB =  $\text{C}_6\text{H}_5\text{COO}^-$  Neglect  $\text{Na}^+$ . Assume  $+x$  and  $-x$  are negligible.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CB}]}{[\text{CA}]} = \frac{[x][0.28 + x]}{[0.33 - x]} = \frac{[x][0.28]}{[0.33]} = 6.3 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{CA}]}{[\text{CB}]} = (6.3 \times 10^{-5}) (0.33/0.28) = 7.425 \times 10^{-5} = \mathbf{7.4 \times 10^{-5} \text{ M}}$$

Check assumption: percent error =  $(7.425 \times 10^{-5}/0.28)100\% = 0.026\%$ . The assumption is valid.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.425 \times 10^{-5}) = 4.1293 = \mathbf{4.13}$$

- 19.12 The buffer components are phenol,  $\text{C}_6\text{H}_5\text{OH}$ , and phenolate ion,  $\text{C}_6\text{H}_5\text{O}^-$ . The sodium ions are ignored because they are not involved in the buffer. Calculate  $K_a$  from  $\text{p}K_a$  and set up the problem with a reaction table.

$$K_a = 10^{-\text{p}K_a} = 10^{-10.00} = 1.0 \times 10^{-10}$$

| Concentration (M) | $\text{C}_6\text{H}_5\text{OH}(aq)$ | $+$ | $\text{H}_2\text{O}(l)$ | $\rightleftharpoons$ | $\text{C}_6\text{H}_5\text{O}^-(aq)$ | $+$ | $\text{H}_3\text{O}^+(aq)$ |
|-------------------|-------------------------------------|-----|-------------------------|----------------------|--------------------------------------|-----|----------------------------|
| Initial           | 1.2                                 |     | —                       |                      | 1.3                                  |     | 0                          |
| Change            | $-x$                                |     | —                       |                      | $+x$                                 |     | $+x$                       |
| Equilibrium       | $1.2 - x$                           |     | —                       |                      | $1.3 + x$                            |     | $x$                        |

Assume that  $x$  is negligible with respect to both 1.0 and 1.2 because both concentrations are much larger than  $K_a$ .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} = \frac{[x][1.3 + x]}{[1.2 - x]} = \frac{[x][1.3]}{[1.2]} = 1.0 \times 10^{-10}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{C}_6\text{H}_5\text{OH}]}{[\text{C}_6\text{H}_5\text{O}^-]} = (1.0 \times 10^{-10}) \left( \frac{1.2}{1.3} \right) = 9.23077 \times 10^{-11} \text{ M}$$

Check assumption: percent error =  $(9.23077 \times 10^{-11}/1.2)100\% = 7.7 \times 10^{-9}\%$ . The assumption is valid.

$$\text{pH} = -\log (9.23077 \times 10^{-11}) = 10.03476 = \mathbf{10.03}$$

Verify the pH using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

$$\text{pH} = 10.00 + \log \left( \frac{[\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} \right) = 10.00 + \log \left( \frac{[1.3]}{[1.2]} \right)$$

$$\mathbf{\text{pH} = 10.03}$$

- 19.13  $K_a = 10^{-pK_a} = 10^{-9.24} = 5.7543993 \times 10^{-10}$  (unrounded)  
 $CA = H_3BO_3$      $CB = H_2BO_3^-$     Neglect  $Na^+$ . Assume  $+x$  and  $-x$  are negligible.

$$K_a = \frac{[H_3O^+][CB]}{[CA]} = \frac{[x][0.82 + x]}{[0.12 - x]} = \frac{[x][0.82]}{[0.12]} = 5.7543993 \times 10^{-10} \text{ (unrounded)}$$

$$[H_3O^+] = K_a \frac{[CA]}{[CB]} = (5.7543993 \times 10^{-10}) (0.12/0.82) = 8.4210722 \times 10^{-11} M \text{ (unrounded)}$$

Check assumption: percent error =  $(8.4210722 \times 10^{-11}/0.12)100\% = 7.0 \times 10^{-8}\%$ . The assumption is valid.

$$pH = -\log [H_3O^+] = -\log (8.4210722 \times 10^{-11}) = 10.07463261 = \mathbf{10.07}$$

Verify the pH using the Henderson-Hasselbalch equation.

- 19.14 The buffer components are phenol,  $NH_3$ , and ammonium ion,  $NH_4^+$ . The chloride ions are ignored because they are not involved in the buffer. Calculate  $K_b$  from  $pK_b$  and set up the problem with a reaction table.

$$K_b = 10^{-pK_b} = 10^{-4.75} = 1.7782794 \times 10^{-5} \text{ (unrounded)}$$

| Concentration (M) | $NH_3(aq)$ | + | $H_2O(l)$ | $\rightleftharpoons$ | $NH_4^+(aq)$ | + | $OH^-(aq)$ |
|-------------------|------------|---|-----------|----------------------|--------------|---|------------|
| Initial           | 0.25       |   | —         |                      | 0.15         |   | 0          |
| Change            | $-x$       |   | —         |                      | $+x$         |   | $+x$       |
| Equilibrium       | $0.25 - x$ |   | —         |                      | $0.15 + x$   |   | $x$        |

Assume that  $x$  is negligible with respect to both 0.25 and 0.15 because both concentrations are much larger than  $K_b$ .

$$K_b = 10^{-pK_b} = 10^{-4.75} = 1.7782794 \times 10^{-5} \text{ (unrounded)}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[0.15 + x][OH^-]}{[0.25 - x]} = \frac{[0.15][OH^-]}{[0.25]} = 1.7782794 \times 10^{-5} \text{ (unrounded)}$$

$$[OH^-] = K_b \frac{[NH_3]}{[NH_4^+]} = (1.7782794 \times 10^{-5}) \left( \frac{0.25}{0.15} \right) = 2.963799 \times 10^{-5} M \text{ (unrounded)}$$

Check assumption: percent error =  $(2.963799 \times 10^{-5}/0.25)100\% = 0.012\%$ . The assumption is valid.

$$pOH = -\log [OH^-] = -\log (2.963799 \times 10^{-5}) = 4.52815 \text{ (unrounded)}$$

$$14.00 = pH + pOH$$

$$pH = 14.00 - pOH = 14.00 - 4.52815 = 9.4718 = \mathbf{9.47}$$

Verify the pH using the Henderson-Hasselbalch equation. To do this, you must find the  $pK_a$  of the acid  $NH_4^+$ :

$$14 = pK_a + pK_b$$

$$pK_a = 14 - pK_b = 14 - 4.75 = 9.25$$

$$pH = pK_a + \log \left( \frac{[base]}{[acid]} \right)$$

$$pH = 9.25 + \log \left( \frac{[NH_3]}{[NH_4^+]} \right) = 9.25 + \log \left( \frac{[0.25]}{[0.15]} \right)$$

$$\mathbf{pH = 9.47}$$

- 19.15  $K_b = 10^{-pK_b} = 10^{-3.35} = 4.4668359 \times 10^{-4}$  (unrounded)  
 $CB = CH_3NH_2$      $CA = CH_3NH_3^+$     Neglect  $Cl^-$ . Assume  $+x$  and  $-x$  are negligible.

$$K_b = \frac{[CA][OH^-]}{[CB]} = \frac{[0.60 + x][OH^-]}{[0.50 - x]} = \frac{[0.60][OH^-]}{[0.50]} = 4.4668359 \times 10^{-4}$$

$$[OH^-] = K_b \frac{[CB]}{[CA]} = (4.4668359 \times 10^{-4}) (0.50/0.60) = 3.7223632 \times 10^{-4} M \text{ (unrounded)}$$

Check assumption: percent error =  $(3.7223632 \times 10^{-4}/0.50)100\% = 0.074\%$ . The assumption is valid.

$$pOH = -\log [OH^-] = -\log (3.7223632 \times 10^{-4}) = 3.429181246 \text{ (unrounded)}$$

$$pH = 14.00 - pOH = 14.00 - 3.429181246 = 10.57081875 = \mathbf{10.57}$$

- 19.16 Given the pH and  $K_a$  of an acid, the buffer-component ratio can be calculated from the Henderson-Hasselbalch equation.

$$pK_a = -\log K_a = -\log (1.3 \times 10^{-5}) = 4.8860566 \text{ (unrounded)}$$

$$pH = pK_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

$$5.44 = 4.8860566 + \log \left( \frac{[\text{Pr}^-]}{[\text{HPr}]} \right)$$

$$0.5539434 = \log \left( \frac{[\text{Pr}^-]}{[\text{HPr}]} \right) \quad \text{Raise each side to } 10^x.$$

$$\frac{[\text{Pr}^-]}{[\text{HPr}]} = 3.5805 = \mathbf{3.6}$$

- 19.17 Given the pH and  $K_a$  of an acid, the buffer-component ratio can be calculated from the Henderson-Hasselbalch equation.

$$pK_a = -\log K_a = -\log (7.1 \times 10^{-4}) = 3.148741651 \text{ (unrounded)}$$

$$pH = pK_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

$$2.95 = 3.14874165 + \log \left( \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \right)$$

$$-0.19874165 = \log \left( \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \right) \quad \text{Raise each side to } 10^x$$

$$\frac{[\text{NO}_2^-]}{[\text{HNO}_2]} = 0.632788 = \mathbf{0.63}$$

- 19.18 Determine the  $pK_a$  of the acid from the concentrations of the conjugate acid and base, and the pH of the solution. This requires the Henderson-Hasselbalch equation.

$$pH = pK_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

$$3.35 = pK_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right) = pK_a + \log \left( \frac{[0.1500]}{[0.2000]} \right)$$

$$3.35 = pK_a - 0.1249387$$

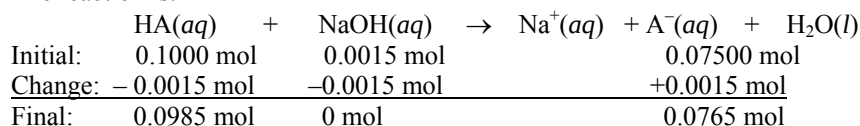
$$pK_a = 3.474939 = 3.47$$

Determine the moles of conjugate acid (HA) and conjugate base ( $\text{A}^-$ ) using  $(M)(V) = \text{moles}$

$$\text{Moles HA} = (0.5000 \text{ L}) (0.2000 \text{ mol HA/L}) = 0.1000 \text{ mol HA}$$

$$\text{Moles A}^- = (0.5000 \text{ L}) (0.1500 \text{ mol A}^-/\text{L}) = 0.07500 \text{ mol A}^-$$

The reaction is:



NaOH is the limiting reagent. The addition of 0.0015 mol NaOH produces an additional 0.0015 mol  $\text{A}^-$  and consumes 0.0015 mol of HA.

Then

$$[\text{A}^-] = \frac{0.0765 \text{ mol A}^-}{0.5000 \text{ L}} = 0.153 \text{ M A}^-$$

$$[\text{HA}] = \frac{0.0985 \text{ mol HA}}{0.5000 \text{ L}} = 0.197 \text{ M HA}$$

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

$$\text{pH} = 3.474938737 + \log\left(\frac{[0.153]}{[0.197]}\right) = 3.365163942 = \mathbf{3.37}$$

- 19.19 Determine the  $\text{p}K_a$  of the acid from the concentrations of the conjugate acid and base and the pH of the solution. This requires the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

$$8.88 = \text{p}K_a + \log\left(\frac{[\text{B}]}{[\text{BH}^+]}\right) = \text{p}K_a + \log\left(\frac{[0.40]}{[0.25]}\right)$$

$$8.88 = \text{p}K_a + 0.20411998$$

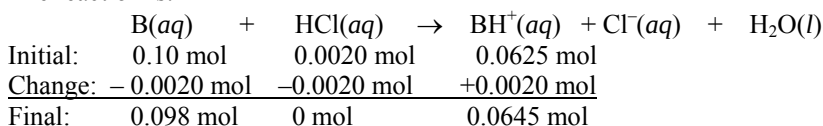
$$\text{p}K_a = 8.67588 = 8.68$$

Determine the moles of conjugate acid ( $\text{BH}^+$ ) and conjugate base (B) using  $(M)(V) = \text{moles}$ .

$$\text{Moles BH}^+ = (0.25 \text{ L}) (0.25 \text{ mol BH}^+/\text{L}) = 0.0625 \text{ mol BH}^+$$

$$\text{Moles B} = (0.25 \text{ L}) (0.40 \text{ mol B/L}) = 0.10 \text{ mol B}$$

The reaction is:



HCl is the limiting reagent. The addition of 0.0020 mol HCl produces an additional 0.0020 mol  $\text{BH}^+$  and consumes 0.0020 mol of B.

Then

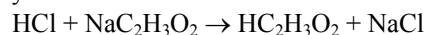
$$[\text{B}] = \frac{0.098 \text{ mol B}}{0.25 \text{ L}} = 0.392 \text{ M B}$$

$$[\text{BH}^+] = \frac{0.0645 \text{ mol BH}^+}{0.25 \text{ L}} = 0.258 \text{ M BH}^+$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{B}]}{[\text{BH}^+]}\right)$$

$$\text{pH} = 8.67588 + \log\left(\frac{[0.392]}{[0.258]}\right) = 8.857546361 = \mathbf{8.86}$$

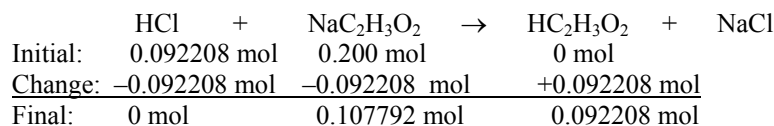
- 19.20 a) The hydrochloric acid will react with the sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2$ , to form acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ :



Calculate the number of moles of HCl and  $\text{NaC}_2\text{H}_3\text{O}_2$ . All of the HCl will be consumed to form  $\text{HC}_2\text{H}_3\text{O}_2$ , and the number of moles of  $\text{C}_2\text{H}_3\text{O}_2^-$  will decrease.

$$\text{Initial moles HCl} = \left(\frac{0.452 \text{ mol HCl}}{\text{L}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(204 \text{ mL}) = 0.092208 \text{ mol HCl (unrounded)}$$

$$\text{Initial moles NaC}_2\text{H}_3\text{O}_2 = \left(\frac{0.400 \text{ mol NaC}_2\text{H}_3\text{O}_2}{\text{L}}\right)(0.500 \text{ L}) = 0.200 \text{ mol NaC}_2\text{H}_3\text{O}_2$$



$$\text{Total volume} = 0.500 \text{ L} + (204 \text{ mL}) (10^{-3} \text{ L/1 mL}) = 0.704 \text{ L}$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{0.092208 \text{ mol}}{0.704 \text{ L}} = 0.1309773 \text{ M (unrounded)}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.107792 \text{ mol}}{0.704 \text{ L}} = 0.1531136 \text{ M (unrounded)}$$

$$\text{p}K_a = -\log K_a = -\log (1.8 \times 10^{-5}) = 4.744727495$$

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

$$\text{pH} = 4.744727495 + \log \left( \frac{[0.1531136]}{[0.1309773]} \right) = 4.812545 = \mathbf{4.81}$$

b) The addition of base would increase the pH, so the new pH is  $(4.81 + 0.15) = 4.96$ .

The new  $[\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2]$  ratio is calculated using the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

$$4.96 = 4.744727495 + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

$$0.215272505 = \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

$$\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.64162 \text{ (unrounded)}$$

From part (a), we know that  $[\text{HC}_2\text{H}_3\text{O}_2] + [\text{C}_2\text{H}_3\text{O}_2^-] = (0.1309773 \text{ M} + 0.1531136 \text{ M}) = 0.2840909 \text{ M}$ . Although the *ratio* of  $[\text{C}_2\text{H}_3\text{O}_2^-]$  to  $[\text{HC}_2\text{H}_3\text{O}_2]$  can change when acid or base is added, the *absolute amount* does not change unless acetic acid or an acetate salt is added.

Given that  $[\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2] = 1.64162$  and  $[\text{HC}_2\text{H}_3\text{O}_2] + [\text{C}_2\text{H}_3\text{O}_2^-] = 0.2840909 \text{ M}$ , solve for  $[\text{C}_2\text{H}_3\text{O}_2^-]$  and substitute into the second equation.

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 1.64162 [\text{HC}_2\text{H}_3\text{O}_2] \text{ and } [\text{HC}_2\text{H}_3\text{O}_2] + 1.64162 [\text{HC}_2\text{H}_3\text{O}_2] = 0.2840909 \text{ M}$$

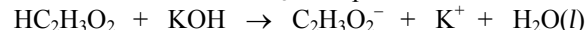
$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.1075441 \text{ M and } [\text{C}_2\text{H}_3\text{O}_2^-] = 0.176547 \text{ M}$$

$$\text{Moles of } \text{C}_2\text{H}_3\text{O}_2^- \text{ needed} = (0.176547 \text{ mol } \text{C}_2\text{H}_3\text{O}_2^-/\text{L}) (0.500 \text{ L}) = 0.0882735 \text{ mol (unrounded)}$$

$$\text{Moles of } \text{C}_2\text{H}_3\text{O}_2^- \text{ initially} = (0.1531136 \text{ mol } \text{C}_2\text{H}_3\text{O}_2^-/\text{L}) (0.500 \text{ L}) = 0.0765568 \text{ mol (unrounded)}$$

This would require the addition of  $(0.0882735 \text{ mol} - 0.0765568 \text{ mol}) = 0.0117167 \text{ mol } \text{C}_2\text{H}_3\text{O}_2^-$  (unrounded)

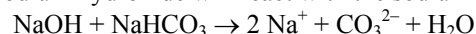
The KOH added reacts with  $\text{HC}_2\text{H}_3\text{O}_2$  to produce additional  $\text{C}_2\text{H}_3\text{O}_2^-$ :



To produce  $0.0117167 \text{ mol } \text{C}_2\text{H}_3\text{O}_2^-$  would require the addition of  $0.0117167 \text{ mol KOH}$ .

$$\text{Mass KOH} = (0.0117167 \text{ mol KOH}) \left( \frac{56.11 \text{ g KOH}}{1 \text{ mol KOH}} \right) = 0.657424 = \mathbf{0.66 \text{ g KOH}}$$

19.21 a) The sodium hydroxide will react with the sodium bicarbonate,  $\text{NaHCO}_3$ , to form carbonate ion,  $\text{CO}_3^{2-}$ :



Calculate the number of moles of NaOH and  $\text{NaHCO}_3$ . All of the NaOH will be consumed to form  $\text{CO}_3^{2-}$ , and the number of moles of  $\text{NaHCO}_3$  will decrease. The  $\text{HCO}_3^-$  is the important part of  $\text{NaHCO}_3$ .

$$\text{Initial moles NaOH} = \left( \frac{0.10 \text{ mol NaOH}}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (10.7 \text{ mL}) = 0.00107 \text{ mol NaOH (unrounded)}$$

$$\begin{aligned} \text{Initial moles } \text{HCO}_3^- &= \left( \frac{0.050 \text{ mol NaHCO}_3}{\text{L}} \right) \left( \frac{1 \text{ mol HCO}_3^-}{1 \text{ mol NaHCO}_3} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (50.0 \text{ mL}) \\ &= 0.0025 \text{ mol HCO}_3^- \end{aligned}$$

|          |              |   |                    |   |                   |   |                               |   |                  |
|----------|--------------|---|--------------------|---|-------------------|---|-------------------------------|---|------------------|
|          | NaOH         | + | NaHCO <sub>3</sub> | → | 2 Na <sup>+</sup> | + | CO <sub>3</sub> <sup>2-</sup> | + | H <sub>2</sub> O |
| Initial: | 0.00107 mol  |   | 0.0025 mol         |   |                   |   | 0 mol                         |   |                  |
| Change:  | -0.00107 mol |   | -0.00107 mol       |   |                   |   | +0.00107 mol                  |   |                  |
| Final:   | 0 mol        |   | 0.00143 mol        |   |                   |   | 0.000107 mol                  |   |                  |

$$\text{Total volume} = (50.0 \text{ mL} + 10.7 \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.0607 \text{ L}$$

$$[\text{HCO}_3^-] = \frac{0.00143 \text{ mol}}{0.0607 \text{ L}} = 0.023558484 \text{ M (unrounded)}$$

$$[\text{CO}_3^{2-}] = \frac{0.00107 \text{ mol}}{0.0607 \text{ L}} = 0.017627677 \text{ M (unrounded)}$$

$$\text{p}K_a = -\log K_a = -\log (4.7 \times 10^{-11}) = 10.32790214$$

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right)$$

$$\text{pH} = 10.32790214 + \log \left( \frac{[0.017627677]}{[0.023558484]} \right) = 10.2019 = \mathbf{10.20}$$

b) The addition of acid would decrease the pH, so the new pH is  $(10.20 - 0.07) = 10.13$   
The new  $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$  ratio is calculated using the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right)$$

$$10.13 = 10.32790214 + \log \left( \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right)$$

$$-0.19790214 = \log \left( \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right)$$

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 0.63401 \text{ (unrounded)}$$

From part (a), we know that  $[\text{HCO}_3^-] + [\text{CO}_3^{2-}] = (0.023558484 \text{ M} + 0.017627677 \text{ M}) = 0.041185254 \text{ M}$ .  
Although the *ratio* of  $[\text{CO}_3^{2-}]$  to  $[\text{HCO}_3^-]$  can change when acid or base is added, the *absolute amount* does not change unless acetic acid or an acetate salt is added.

Given that  $[\text{CO}_3^{2-}]/[\text{HCO}_3^-] = 0.63401$  and  $[\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 0.041185254 \text{ M}$ , solve for  $[\text{CO}_3^{2-}]$  and substitute into the second equation.

$$[\text{CO}_3^{2-}] = 0.63401 [\text{HCO}_3^-] \text{ and } [\text{HCO}_3^-] + 0.63401 [\text{HCO}_3^-] = 0.041185254 \text{ M}$$

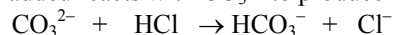
$$[\text{HCO}_3^-] = 0.025205019 \text{ M and } [\text{CO}_3^{2-}] = 0.015980234 \text{ M (unrounded)}$$

$$\begin{aligned} \text{Moles of HCO}_3^- \text{ needed} &= (0.025205019 \text{ mol HCO}_3^-/\text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (25.0 \text{ mL}) \\ &= 0.0006301255 \text{ mol (unrounded)} \end{aligned}$$

$$\begin{aligned} \text{Moles of HCO}_3^- \text{ initially} &= (0.023558484 \text{ mol HCO}_3^-/\text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (25.0 \text{ mL}) \\ &= 0.000588962 \text{ mol (unrounded)} \end{aligned}$$

$$\begin{aligned} \text{This would require the addition of} & (0.0006301255 \text{ mol} - 0.000588962 \text{ mol}) \\ &= 0.0000411635 \text{ mol HCO}_3^- \text{ (unrounded)} \end{aligned}$$

The HCl added reacts with  $\text{CO}_3^{2-}$  to produce additional  $\text{HCO}_3^-$ :



To produce 0.0000411635 mol  $\text{HCO}_3^-$  would require the addition of 0.0000411635 mol HCl.

$$\text{Mass HCl} = (0.0000411635 \text{ mol HCl}) \left( \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} \right) = 0.0015008 = \mathbf{0.0015 \text{ g HCl}}$$

- 19.22 Select conjugate pairs with  $K_a$  values close to the desired  $[\text{H}_3\text{O}^+]$ .
- a) For  $\text{pH} \approx 4.5$ ,  $[\text{H}_3\text{O}^+] = 10^{-4.5} = 3.2 \times 10^{-5} \text{ M}$ . Some good selections are the  $\text{HOOC}(\text{CH}_2)_4\text{COOH}/\text{HOOC}(\text{CH}_2)_4\text{COOH}^-$  conjugate pair with  $K_a$  equal to  $3.8 \times 10^{-5}$  or  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}/\text{C}_6\text{H}_5\text{CH}_2\text{COO}^-$  conjugate pair with  $K_a$  equal to  $4.9 \times 10^{-5}$ . From the base list, the  $\text{C}_6\text{H}_5\text{NH}_2/\text{C}_6\text{H}_5\text{NH}_3^+$  conjugate pair comes close with  $K_a = 1.0 \times 10^{-14}/4.0 \times 10^{-10} = 2.5 \times 10^{-5}$ .
- b) For  $\text{pH} \approx 7.0$ ,  $[\text{H}_3\text{O}^+] = 10^{-7.0} = 1.0 \times 10^{-7} \text{ M}$ . Two choices are the  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  conjugate pair with  $K_a$  of  $6.3 \times 10^{-8}$  and the  $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$  conjugate pair with  $K_a$  of  $1.1 \times 10^{-7}$ .
- 19.23 Select conjugate pairs that have  $K_a$  or  $K_b$  values close to the desired  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$ .
- a) For  $[\text{H}_3\text{O}^+] \approx 1 \times 10^{-9} \text{ M}$ , the  $\text{HOBr}/\text{OBr}^-$  conjugate pair comes close with  $K_a$  equal to  $2.3 \times 10^{-9}$ . From the base list,  $K_b = 1.0 \times 10^{-14}/1 \times 10^{-9} = 1 \times 10^{-5}$ , the  $\text{NH}_3/\text{NH}_4^+$  conjugate pair comes close with  $K_b = 1.76 \times 10^{-5}$ .
- b) For  $[\text{OH}^-] \approx 3 \times 10^{-5} \text{ M}$ , the  $\text{NH}_3/\text{NH}_4^+$  conjugate pair comes close; also, it is possible to choose  $K_a = 1.0 \times 10^{-14}/3 \times 10^{-5} = 3.3 \times 10^{-10}$ , the  $\text{C}_6\text{H}_5\text{OH}/\text{C}_6\text{H}_5\text{O}^-$  comes close with  $K_a = 1.0 \times 10^{-10}$ .
- 19.24 The value of the  $K_a$  from the appendix:  $K_a = 2.9 \times 10^{-8}$   
 $\text{p}K_a = -\log 2.9 \times 10^{-8} = 7.5376$  (unrounded)  
 Use the Henderson-Hasselbalch equation to determine the pH.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{ClO}^-]}{[\text{HClO}]} \right)$$

a)  $\text{pH} = 7.5376 + \log \left( \frac{[0.100]}{[0.100]} \right) = 7.5376 = \mathbf{7.54}$

b)  $\text{pH} = 7.5376 + \log \left( \frac{[0.150]}{[0.100]} \right) = 7.71369 = \mathbf{7.71}$

c)  $\text{pH} = 7.5376 + \log \left( \frac{[0.100]}{[0.150]} \right) = 7.3615 = \mathbf{7.36}$

d) The reaction is  $\text{NaOH} + \text{HClO} \rightarrow \text{Na}^+ + \text{ClO}^- + \text{H}_2\text{O}$

The original moles of  $\text{HClO}$  and  $\text{OCl}^-$  are both =  $(0.100 \text{ mol/L}) (L) = 0.100 \text{ mol}$

|          |               |   |               |               |               |   |                |   |                      |
|----------|---------------|---|---------------|---------------|---------------|---|----------------|---|----------------------|
|          | $\text{NaOH}$ | + | $\text{HClO}$ | $\rightarrow$ | $\text{Na}^+$ | + | $\text{ClO}^-$ | + | $\text{H}_2\text{O}$ |
| Initial: | 0.0050 mol    |   | 0.100 mol     |               |               |   | 0.100 mol      |   |                      |
| Change:  | -0.0050 mol   |   | -0.0050 mol   |               |               |   | +0.0050 mol    |   |                      |
| Final:   | 0 mol         |   | 0.095 mol     |               |               |   | 0.105 mol      |   |                      |

$$\text{pH} = 7.5376 + \log \left( \frac{[0.105]}{[0.095]} \right) = 7.5811 = \mathbf{7.58}$$

- 19.25 The value of the  $K_a$  from the appendix:  $K_a = 6.3 \times 10^{-8}$  (we are using  $K_{a2}$  since we are dealing with the equilibrium in which the second hydrogen ion is being lost).  
 Determine the  $\text{p}K_a$  using  $\text{p}K_a = -\log 6.3 \times 10^{-8} = 7.200659451$  (unrounded)  
 Use the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)$$

$$7.40 = 7.200659451 + \log \left( \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)$$

$$0.19934055 = \log \left( \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)$$

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 1.582486 = \mathbf{1.6}$$

- 19.26 You need to know the  $pK_a$  value for the indicator. (Its transition range is approximately  $pK_a \pm 1$ .) If the indicator is a diprotic acid, it will have two transition ranges.
- 19.27 To see a distinct color in a mixture of two colors, you need one color to be about 10 times the intensity of the other. For this to take place, the concentration ratio  $[HIn]/[In^-]$  needs to be greater than 10:1 or less than 1:10. This will occur when  $pH = pK_a - 1$  or  $pH = pK_a + 1$ , respectively, giving a transition range of about two units.
- 19.28 This is because the concentration of indicator is very small.
- 19.29 The equivalence point in a titration is the point at which the number of moles of  $OH^-$  equals the number of moles of  $H_3O^+$  (be sure to account for stoichiometric ratios, e.g., 1 mol of  $Ca(OH)_2$  produces 2 moles of  $OH^-$ ). The endpoint is the point at which the added indicator changes color. If an appropriate indicator is selected, the endpoint is close to the equivalence point, but not normally the same. Using an indicator that changes color at a pH after the equivalence point means the equivalence point is reached first. However, if an indicator is selected that changes color at a pH before the equivalence point, then the endpoint is reached first.
- 19.30 At the equivalence point, the slope of the titration curve is its maximum value.
- 19.31 a) The initial pH is lowest for flask solution of the strong acid, followed by the weak acid and then the weak base. In other words, **strong acid-strong base < weak acid-strong base < strong acid-weak base**.  
 b) At the equivalence point, the moles of  $H_3O^+$  equal the moles of  $OH^-$ , regardless of the type of titration. However, the strong acid-strong base equivalence point occurs at  $pH = 7.00$  because the resulting cation-anion combination does not react with water. An example is the reaction  $NaOH + HCl \rightarrow H_2O + NaCl$ . Neither  $Na^+$  nor  $Cl^-$  ions dissociate in water.  
 The weak acid-strong base equivalence point occurs at  $pH > 7$ , because the anion of the weak acid is weakly basic, whereas the cation of the strong base does not react with water. An example is the reaction  $HCOOH + NaOH \rightarrow HCOO^- + H_2O + Na^+$ . The conjugate base,  $HCOO^-$ , reacts with water according to this reaction:  
 $HCOO^- + H_2O \rightarrow HCOOH + OH^-$ .  
 The strong acid-weak base equivalence point occurs at  $pH < 7$ , because the anion of the strong acid does not react with water, whereas the cation of the weak base is weakly acidic. An example is the reaction  $HCl + NH_3 \rightarrow NH_4^+ + Cl^-$ . The conjugate acid,  $NH_4^+$ , dissociates slightly in water:  $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$ .  
 In rank order of pH of equivalence point, **strong acid-weak base < strong acid-strong base < weak acid-strong base**.
- 19.32 In the buffer region, comparable amounts of weak acid and its conjugate base are present. At the equivalence point, the predominant species is the conjugate base. In a strong acid-weak base titration, the weak base and its conjugate acid are the predominant species present.
- 19.33 At the very center of the buffer region of a weak acid-strong base titration, the concentration of the weak acid and its conjugate base are equal, which means that at this point the pH of the solution equals the  $pK_a$  of the weak acid.
- 19.34 a) The reactions are:  
 $OH^-(aq) + H_3PO_4(aq) \rightarrow H_2PO_4^-(aq) + H_2O(l) \quad K_{a1} = 7.2 \times 10^{-3}$   
 $OH^-(aq) + H_2PO_4^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(l) \quad K_{a2} = 6.3 \times 10^{-8}$   
 The correct order is **C, B, D, A**. Scene C shows the solution before the addition of any NaOH. Scene B is halfway to the first equivalence point; Scene D is halfway to the second equivalence point and Scene A is at end of the titration.  
 b) Scene B is the second scene in the correct order. This is halfway towards the first equivalence point when there are equal amounts of the acid and conjugate base, which constitutes a buffer.

$$pH = pK_a + \log \left( \frac{[H_2PO_4^-]}{[H_3PO_4]} \right)$$

Determine the  $pK_a$  using  $pK_a = -\log 7.2 \times 10^{-3} = 2.142668$

$$pH = 2.1426675 + \log \left( \frac{[3]}{[3]} \right) = 2.1426675 = \mathbf{2.14}$$

c) 10.00 mL of NaOH is required to reach the first half-equivalence point. Therefore, an additional 10.00 mL of NaOH is required to reach the first equivalence point, for a total of 20 mL for the first equivalence point. An additional 20.00 mL of NaOH will be required to reach the second equivalence point where only  $HPO_4^{2-}$  remains. A total of **40.00 mL** of NaOH is required to reach Scene A.

19.35 Indicators have a pH range that is approximated by  $pK_a \pm 1$ . The  $pK_a$  of cresol red is  $-\log (3.5 \times 10^{-9}) = 8.5$ , so the indicator changes color over an approximate range of **7.5 to 9.5**.

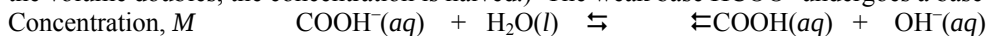
19.36 Indicators have a pH range that is approximated by  $pK_a \pm 1$ . The  $pK_a$  of ethyl red is  $-\log (3.8 \times 10^{-6}) = 5.42$ , so the indicator changes color over an approximate range of **4.4 to 6.4**.

19.37 Choose an indicator that changes color at a pH close to the pH of the equivalence point.

a) The equivalence point for a strong acid-strong base titration occurs at pH = 7.0. **Bromthymol blue** is an indicator that changes color around pH 7.

b) The equivalence point for a weak acid-strong base is above pH 7. Estimate the pH at equivalence point from equilibrium calculations.

At the equivalence point, all of the HCOOH and NaOH have been consumed; the solution is 0.050 M  $HCOO^-$ . (The volume doubles because equal volumes of base and acid are required to reach the equivalence point. When the volume doubles, the concentration is halved.) The weak base  $HCOO^-$  undergoes a base reaction:



Initial: 0.050 M — 0 0

Change: -x — +x +x

Equilibrium: 0.050 - x x x

The  $K_a$  for HCOOH is  $1.8 \times 10^{-4}$ , so  $K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-4} = 5.5556 \times 10^{-11}$  (unrounded)

$$K_b = \frac{[HCOOH][OH^-]}{[HCOO^-]} = \frac{[x][x]}{[0.050 - x]} = \frac{[x][x]}{[0.050]} = 5.5556 \times 10^{-11}$$

$$[OH^-] = x = 1.666673 \times 10^{-6} M$$

$$pOH = -\log (1.666673 \times 10^{-6}) = 5.7781496 \text{ (unrounded)}$$

$$pH = 14.00 - pOH = 14.00 - 5.7781496 = 8.2218504 = 8.22$$

Choose **thymol blue** or **phenolphthalein**.

19.38 a) Determine the  $K_a$  (of the conjugate acid) from the  $K_b$  reported in the Appendix for  $CH_3NH_2$ .

$$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (4.4 \times 10^{-4}) = 2.2727 \times 10^{-11} \text{ (unrounded)}$$

An acid-base titration of two components of equal concentration and at a 1:1 ratio gives a solution of the conjugates with half the concentration. In this case, the concentration of  $CH_3NH_3^+ = 0.050 M$ .

$$K_a = \frac{[H_3O^+][CH_3NH_2]}{[CH_3NH_3^+]} = \frac{x^2}{0.050 - x} = \frac{x^2}{0.050} = 2.2727 \times 10^{-11}$$

$$x = [H_3O^+] = 1.0659971 \times 10^{-6} M \text{ (unrounded)}$$

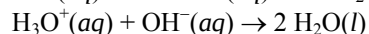
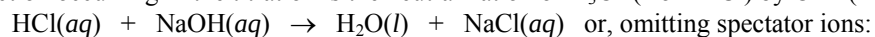
$$pH = -\log [H_3O^+] = -\log (1.0659971 \times 10^{-6}) = 5.97224 = 5.97$$

Either **methyl red** or **alizarin** is acceptable.

b) This is a strong acid-strong base titration; thus, the equivalence point is at pH = 7.00.

The best choice would be **bromthymol blue**; alizarin might be acceptable.

19.39 The reaction occurring in the titration is the neutralization of  $\text{H}_3\text{O}^+$  (from HCl) by  $\text{OH}^-$  (from NaOH):



For the titration of a strong acid with a strong base, the pH before the equivalence point depends on the excess concentration of acid and the pH after the equivalence point depends on the excess concentration of base. At the equivalence point, there is not an excess of either acid or base so the pH is 7.0. The equivalence point occurs when 40.00 mL of base has been added. Use (M)(V) to determine the number of moles.

The initial number of moles of HCl =  $(0.1000 \text{ mol HCl} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (40.00 \text{ mL}) = 4.000 \times 10^{-3} \text{ mol HCl}$

a) At 0 mL of base added, the concentration of hydronium ion equals the original concentration of HCl.

$$\text{pH} = -\log (0.1000 \text{ M}) = \mathbf{1.0000}$$

b) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (25.00 \text{ mL}) = 2.500 \times 10^{-3} \text{ mol NaOH}$$

|          |                                     |   |                                     |               |                         |   |                                     |
|----------|-------------------------------------|---|-------------------------------------|---------------|-------------------------|---|-------------------------------------|
|          | $\text{HCl}(aq)$                    | + | $\text{NaOH}(aq)$                   | $\rightarrow$ | $\text{H}_2\text{O}(l)$ | + | $\text{NaCl}(aq)$                   |
| Initial: | $4.000 \times 10^{-3} \text{ mol}$  |   | $2.500 \times 10^{-3} \text{ mol}$  |               | —                       |   | 0                                   |
| Change:  | $-2.500 \times 10^{-3} \text{ mol}$ |   | $-2.500 \times 10^{-3} \text{ mol}$ |               | —                       |   | $+2.500 \times 10^{-3} \text{ mol}$ |
| Final:   | $1.500 \times 10^{-3} \text{ mol}$  |   | 0                                   |               | —                       |   | $2.500 \times 10^{-3} \text{ mol}$  |

The volume of the solution at this point is  $[(40.00 + 25.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.06500 \text{ L}$

The molarity of the excess HCl is  $(1.500 \times 10^{-3} \text{ mol HCl}) / (0.06500 \text{ L}) = 0.02307 \text{ M}$  (unrounded)

$$\text{pH} = -\log (0.02307) = \mathbf{1.6368}$$

(Note that the NaCl product is a neutral salt that does not affect the pH.)

c) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (39.00 \text{ mL}) = 3.900 \times 10^{-3} \text{ mol NaOH}$$

|          |                                     |   |                                     |               |                         |   |                                     |
|----------|-------------------------------------|---|-------------------------------------|---------------|-------------------------|---|-------------------------------------|
|          | $\text{HCl}(aq)$                    | + | $\text{NaOH}(aq)$                   | $\rightarrow$ | $\text{H}_2\text{O}(l)$ | + | $\text{NaCl}(aq)$                   |
| Initial: | $4.000 \times 10^{-3} \text{ mol}$  |   | $4.900 \times 10^{-3} \text{ mol}$  |               | —                       |   | 0                                   |
| Change:  | $-3.900 \times 10^{-3} \text{ mol}$ |   | $-3.900 \times 10^{-3} \text{ mol}$ |               | —                       |   | $+3.900 \times 10^{-3} \text{ mol}$ |
| Final:   | $1.000 \times 10^{-4} \text{ mol}$  |   | 0                                   |               | —                       |   | $3.900 \times 10^{-3} \text{ mol}$  |

The volume of the solution at this point is  $[(40.00 + 39.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.07900 \text{ L}$

The molarity of the excess HCl is  $(1.00 \times 10^{-4} \text{ mol HCl}) / (0.07900 \text{ L}) = 0.0012658 \text{ M}$  (unrounded)

$$\text{pH} = -\log (0.0012658) = \mathbf{2.898}$$

d) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (39.90 \text{ mL}) = 3.990 \times 10^{-3} \text{ mol NaOH}$$

|          |                                     |   |                                     |               |                         |   |                                     |
|----------|-------------------------------------|---|-------------------------------------|---------------|-------------------------|---|-------------------------------------|
|          | $\text{HCl}(aq)$                    | + | $\text{NaOH}(aq)$                   | $\rightarrow$ | $\text{H}_2\text{O}(l)$ | + | $\text{NaCl}(aq)$                   |
| Initial: | $4.000 \times 10^{-3} \text{ mol}$  |   | $3.990 \times 10^{-3} \text{ mol}$  |               | —                       |   | 0                                   |
| Change:  | $-3.990 \times 10^{-3} \text{ mol}$ |   | $-3.990 \times 10^{-3} \text{ mol}$ |               | —                       |   | $+3.990 \times 10^{-3} \text{ mol}$ |
| Final:   | $1.000 \times 10^{-5} \text{ mol}$  |   | 0                                   |               | —                       |   | $3.990 \times 10^{-3} \text{ mol}$  |

The volume of the solution at this point is  $[(40.00 + 39.90) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.07990 \text{ L}$

The molarity of the excess HCl is  $(1.0 \times 10^{-5} \text{ mol HCl}) / (0.07990 \text{ L}) = 0.000125156 \text{ M}$  (unrounded)

$$\text{pH} = -\log (0.000125156) = \mathbf{3.903}$$

e) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (40.00 \text{ mL}) = 4.000 \times 10^{-3} \text{ mol NaOH}$$

|          |                                     |   |                                     |               |                         |   |                                     |
|----------|-------------------------------------|---|-------------------------------------|---------------|-------------------------|---|-------------------------------------|
|          | $\text{HCl}(aq)$                    | + | $\text{NaOH}(aq)$                   | $\rightarrow$ | $\text{H}_2\text{O}(l)$ | + | $\text{NaCl}(aq)$                   |
| Initial: | $4.000 \times 10^{-3} \text{ mol}$  |   | $4.000 \times 10^{-3} \text{ mol}$  |               | —                       |   | 0                                   |
| Change:  | $-4.000 \times 10^{-3} \text{ mol}$ |   | $-4.000 \times 10^{-3} \text{ mol}$ |               | —                       |   | $+4.000 \times 10^{-3} \text{ mol}$ |
| Final:   | 0                                   |   | 0                                   |               | —                       |   | $4.000 \times 10^{-3} \text{ mol}$  |

The NaOH will react with an equal amount of the acid and 0.0 mol HCl will remain. This is the equivalence point of a strong acid-strong base titration, thus, the pH is **7.00**. Only the neutral salt NaCl is in solution at the equivalence point.

f) The NaOH is now in excess. It will be necessary to calculate the excess base after reacting with the HCl. The excess strong base will give the pOH, which can be converted to the pH.

Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (40.10 \text{ mL}) = 4.010 \times 10^{-3} \text{ mol NaOH}$$

The HCl will react with an equal amount of the base, and  $1.0 \times 10^{-5} \text{ mol NaOH}$  will remain.

|          |                                     |   |                                     |               |                         |   |                                     |
|----------|-------------------------------------|---|-------------------------------------|---------------|-------------------------|---|-------------------------------------|
|          | $\text{HCl(aq)}$                    | + | $\text{NaOH(aq)}$                   | $\rightarrow$ | $\text{H}_2\text{O(l)}$ | + | $\text{NaCl(aq)}$                   |
| Initial: | $4.000 \times 10^{-3} \text{ mol}$  |   | $4.010 \times 10^{-3} \text{ mol}$  |               | —                       |   | 0                                   |
| Change:  | $-4.000 \times 10^{-3} \text{ mol}$ |   | $-4.000 \times 10^{-3} \text{ mol}$ |               | —                       |   | $+4.000 \times 10^{-3} \text{ mol}$ |
| Final:   | 0                                   |   | $1.000 \times 10^{-5} \text{ mol}$  |               |                         |   | $4.000 \times 10^{-3} \text{ mol}$  |

The volume of the solution at this point is  $[(40.00 + 40.10) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.08010 \text{ L}$

The molarity of the excess NaOH is  $(1.0 \times 10^{-5} \text{ mol NaOH}) / (0.08010 \text{ L}) = 0.00012484 \text{ M}$  (unrounded)

$$\text{pOH} = -\log(0.00012484) = 3.9036 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.9036 = 10.09637 = \mathbf{10.10}$$

g) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH/L}) (10^{-3} \text{ L/1 mL}) (50.00 \text{ mL}) = 5.000 \times 10^{-3} \text{ mol NaOH}$$

The HCl will react with an equal amount of the base, and  $1.000 \times 10^{-3} \text{ mol NaOH}$  will remain.

|          |                                     |   |                                     |               |                         |   |                                     |
|----------|-------------------------------------|---|-------------------------------------|---------------|-------------------------|---|-------------------------------------|
|          | $\text{HCl(aq)}$                    | + | $\text{NaOH(aq)}$                   | $\rightarrow$ | $\text{H}_2\text{O(l)}$ | + | $\text{NaCl(aq)}$                   |
| Initial: | $4.000 \times 10^{-3} \text{ mol}$  |   | $5.000 \times 10^{-3} \text{ mol}$  |               | —                       |   | 0                                   |
| Change:  | $-4.000 \times 10^{-3} \text{ mol}$ |   | $-4.000 \times 10^{-3} \text{ mol}$ |               | —                       |   | $+4.000 \times 10^{-3} \text{ mol}$ |
| Final:   | 0                                   |   | $1.000 \times 10^{-3} \text{ mol}$  |               |                         |   | $4.000 \times 10^{-3} \text{ mol}$  |

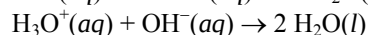
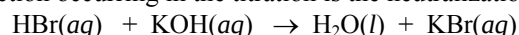
The volume of the solution at this point is  $[(40.00 + 50.00) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.09000 \text{ L}$

The molarity of the excess NaOH is  $(1.000 \times 10^{-3} \text{ mol NaOH}) / (0.09000 \text{ L}) = 0.011111 \text{ M}$  (unrounded)

$$\text{pOH} = -\log(0.011111) = 1.95424 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.95424 = 12.04576 = \mathbf{12.05}$$

19.40 The reaction occurring in the titration is the neutralization of  $\text{OH}^-$  (from KOH) by  $\text{H}_3\text{O}^+$  (from HBr):



For the titration of a strong base with a strong acid, the pH before the equivalence point depends on the excess concentration of base and the pH after the equivalence point depends on the excess concentration of acid. At the equivalence point, there is not an excess of either acid or base so pH is 7.0. The equivalence point occurs when 30.00 mL of acid has been added.

The initial number of moles of KOH =  $(0.1000 \text{ mol KOH/L}) (10^{-3} \text{ L/1 mL}) (30.00 \text{ mL})$   
 $= 3.000 \times 10^{-3} \text{ mol KOH}$

a) At 0 mL of acid added, the concentration of hydroxide ion equals the original concentration of KOH.

$$\text{pOH} = -\log(0.1000 \text{ M}) = 1.0000$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.0000 = \mathbf{13.00}$$

b) Determine the moles of HBr added:

$$\text{Moles of HBr} = (0.1000 \text{ mol HBr/L}) (10^{-3} \text{ L/1 mL}) (15.00 \text{ mL}) = 1.500 \times 10^{-3} \text{ mol HBr}$$

The HBr will react with an equal amount of the base, and  $1.500 \times 10^{-3} \text{ mol KOH}$  will remain.

The volume of the solution at this point is  $[(30.00 + 15.00) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.04500 \text{ L}$

The molarity of the excess KOH is  $(1.500 \times 10^{-3} \text{ mol KOH}) / (0.04500 \text{ L}) = 0.03333 \text{ M}$  (unrounded)

$$\text{pOH} = -\log(0.03333) = 1.4772$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.4772 = 12.5228 = \mathbf{12.52}$$

c) Determine the moles of HBr added:

$$\text{Moles of HBr} = (0.1000 \text{ mol HBr/L}) (10^{-3} \text{ L/1 mL}) (29.00 \text{ mL}) = 2.900 \times 10^{-3} \text{ mol HBr}$$

The HBr will react with an equal amount of the base, and  $1.00 \times 10^{-4} \text{ mol KOH}$  will remain.

The volume of the solution at this point is  $[(30.00 + 29.00) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.05900 \text{ L}$

The molarity of the excess KOH is  $(1.00 \times 10^{-4} \text{ mol KOH}) / (0.05900 \text{ L}) = 0.0016949 \text{ M}$  (unrounded)

$$\text{pOH} = -\log(0.0016949) = 2.7708559$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.7708559 = 11.2291441 = \mathbf{11.23}$$

d) Determine the moles of HBr added:

$$\text{Moles of HBr} = (0.1000 \text{ mol HBr/L}) (10^{-3} \text{ L/1 mL}) (29.90 \text{ mL}) = 2.990 \times 10^{-3} \text{ mol HBr}$$

The HBr will react with an equal amount of the base, and  $1.0 \times 10^{-5} \text{ mol KOH}$  will remain.

The volume of the solution at this point is  $[(30.00 + 29.90) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.05990 \text{ L}$

The molarity of the excess KOH is  $(1.0 \times 10^{-5} \text{ mol KOH}) / (0.05990 \text{ L}) = 0.000166944 \text{ M}$  (unrounded)

$$\text{pOH} = -\log(0.000166944) = 3.7774268$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.7774268 = 10.2225732 = \mathbf{10.2}$$

e) Determine the moles of HBr added:

$$\text{Moles of HBr} = (0.1000 \text{ mol HBr/L}) (10^{-3} \text{ L/mL}) (30.00 \text{ mL}) = 3.000 \times 10^{-3} \text{ mol HBr}$$

The HBr will react with an equal amount of the base and 0.0 mol KOH will remain. This is the equivalence point of a strong acid–strong base titration; thus, the pH is **7.00**.

f) The HBr is now in excess. It will be necessary to calculate the excess base after reacting with the HCl. The excess strong acid will give the pH.

Determine the moles of HBr added:

$$\text{Moles of HBr} = (0.1000 \text{ mol HBr/L}) (10^{-3} \text{ L/mL}) (30.10 \text{ mL}) = 3.010 \times 10^{-3} \text{ mol HBr}$$

The HBr will react with an equal amount of the base, and  $1.0 \times 10^{-5}$  mol HBr will remain.

The volume of the solution at this point is  $[(30.00 + 30.10) \text{ mL}] (10^{-3} \text{ L/mL}) = 0.06010 \text{ L}$

The molarity of the excess HBr is  $(1.0 \times 10^{-5} \text{ mol HBr}) / (0.06010 \text{ L}) = 0.000166389 \text{ M}$  (unrounded)

$$\text{pH} = -\log (0.000166389) = 3.778874 = \mathbf{3.8}$$

g) Determine the moles of HBr added:

$$\text{Moles of HBr} = (0.1000 \text{ mol HBr/L}) (10^{-3} \text{ L/mL}) (40.00 \text{ mL}) = 4.000 \times 10^{-3} \text{ mol HBr}$$

The HBr will react with an equal amount of the base, and  $1.000 \times 10^{-3}$  mol HBr will remain.

The volume of the solution at this point is  $[(30.00 + 40.00) \text{ mL}] (10^{-3} \text{ L/mL}) = 0.07000 \text{ L}$

The molarity of the excess HBr is  $(1.000 \times 10^{-3} \text{ mol HBr}) / (0.07000 \text{ L}) = 0.0142857 \text{ M}$  (unrounded)

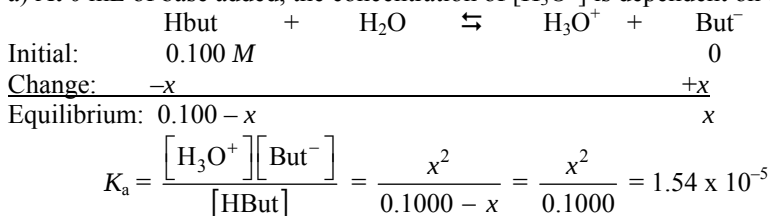
$$\text{pH} = -\log (0.0142857) = 1.845098 = \mathbf{1.85}$$

19.41 This is a titration between a weak acid and a strong base. The pH before addition of the base is dependent on the  $K_a$  of the acid (labeled HBut). Prior to reaching the equivalence point, the added base reacts with the acid to form butanoate ion (labeled But<sup>-</sup>). The equivalence point occurs when 20.00 mL of base is added to the acid because at this point, moles acid = moles base. Addition of base beyond the equivalence point is simply the addition of excess OH<sup>-</sup>.

The initial number of moles of HBut = (M)(V) =

$$(0.1000 \text{ mol HBut/L}) (10^{-3} \text{ L/mL}) (20.00 \text{ mL}) = 2.000 \times 10^{-3} \text{ mol HBut}$$

a) At 0 mL of base added, the concentration of [H<sub>3</sub>O<sup>+</sup>] is dependent on the dissociation of butanoic acid:



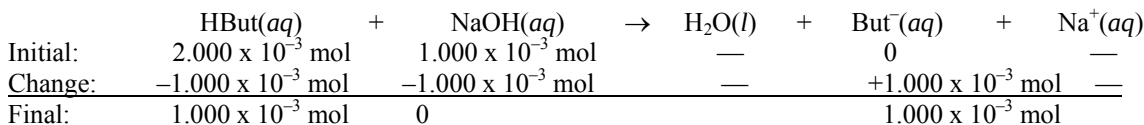
$$x = [\text{H}_3\text{O}^+] = 1.2409673 \times 10^{-3} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.2409673 \times 10^{-3}) = 2.9062 = \mathbf{2.91}$$

b) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH/L}) (10^{-3} \text{ L/mL}) (10.00 \text{ mL}) = 1.000 \times 10^{-3} \text{ mol NaOH}$$

The NaOH will react with an equal amount of the acid, and  $1.000 \times 10^{-3}$  mol HBut will remain. An equal number of moles of But<sup>-</sup> will form.

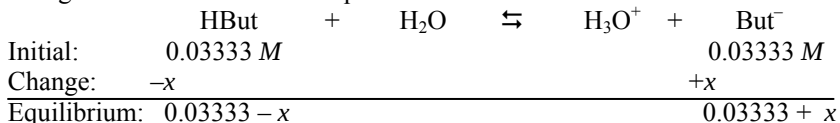


The volume of the solution at this point is  $[(20.00 + 10.00) \text{ mL}] (10^{-3} \text{ L/mL}) = 0.03000 \text{ L}$

The molarity of the excess HBut is  $(1.000 \times 10^{-3} \text{ mol HBut}) / (0.03000 \text{ L}) = 0.03333 \text{ M}$  (unrounded)

The molarity of the But<sup>-</sup> formed is  $(1.000 \times 10^{-3} \text{ mol But}^-) / (0.03000 \text{ L}) = 0.03333 \text{ M}$  (unrounded)

Using a reaction table for the equilibrium reaction of HBut:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x(0.0333 + x)}{0.0333 - x} = \frac{x(0.0333)}{0.0333} = 1.54 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 1.54 \times 10^{-5} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.54 \times 10^{-5}) = 4.812479 = \mathbf{4.81}$$

c) Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10<sup>-3</sup> L/1 mL) (15.00 mL) = 1.500 x 10<sup>-3</sup> mol NaOH

The NaOH will react with an equal amount of the acid, and 5.00 x 10<sup>-4</sup> mol HBut will remain, and 1.500 x 10<sup>-3</sup> moles of But<sup>-</sup> will form.

|          |                               |   |                               |   |                     |   |                               |   |                      |
|----------|-------------------------------|---|-------------------------------|---|---------------------|---|-------------------------------|---|----------------------|
|          | HBut(aq)                      | + | NaOH(aq)                      | → | H <sub>2</sub> O(l) | + | But <sup>-</sup> (aq)         | + | Na <sup>+</sup> (aq) |
| Initial: | 2.000 x 10 <sup>-3</sup> mol  |   | 1.500 x 10 <sup>-3</sup> mol  |   | —                   |   | 0                             |   | —                    |
| Change:  | -1.500 x 10 <sup>-3</sup> mol |   | -1.500 x 10 <sup>-3</sup> mol |   | —                   |   | +1.500 x 10 <sup>-3</sup> mol |   | —                    |
| Final:   | 5.000 x 10 <sup>-4</sup> mol  |   | 0                             |   |                     |   | 1.500 x 10 <sup>-3</sup> mol  |   |                      |

The volume of the solution at this point is [(20.00 + 15.00) mL] (10<sup>-3</sup> L/1 mL) = 0.03500 L

The molarity of the excess HBut is (5.00 x 10<sup>-4</sup> mol HBut)/(0.03500 L) = 0.0142857 M (unrounded)

The molarity of the But<sup>-</sup> formed is (1.500 x 10<sup>-3</sup> mol But<sup>-</sup>)/(0.03500 L) = 0.0428571 M (unrounded)

Using a reaction table for the equilibrium reaction of HBut:

|              |               |   |                  |   |                               |   |                  |
|--------------|---------------|---|------------------|---|-------------------------------|---|------------------|
|              | HBut          | + | H <sub>2</sub> O | ⇌ | H <sub>3</sub> O <sup>+</sup> | + | But <sup>-</sup> |
| Initial:     | 0.0142857 M   |   |                  |   |                               |   | 0.0428571 M      |
| Change:      | -x            |   |                  |   |                               |   | +x               |
| Equilibrium: | 0.0142857 - x |   |                  |   |                               |   | 0.0428571 + x    |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x(0.0428571 + x)}{0.0142857 - x} = \frac{x(0.0428571)}{0.0142857} = 1.54 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 5.1333 \times 10^{-6} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.1333 \times 10^{-6}) = 5.2896 = \mathbf{5.29}$$

d) Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10<sup>-3</sup> L/1 mL) (19.00 mL) = 1.900 x 10<sup>-3</sup> mol NaOH

The NaOH will react with an equal amount of the acid, and 1.00 x 10<sup>-4</sup> mol HBut will remain, and 1.900 x 10<sup>-3</sup> moles of But<sup>-</sup> will form.

|          |                               |   |                               |   |                     |   |                               |   |                      |
|----------|-------------------------------|---|-------------------------------|---|---------------------|---|-------------------------------|---|----------------------|
|          | HBut(aq)                      | + | NaOH(aq)                      | → | H <sub>2</sub> O(l) | + | But <sup>-</sup> (aq)         | + | Na <sup>+</sup> (aq) |
| Initial: | 2.000 x 10 <sup>-3</sup> mol  |   | 1.900 x 10 <sup>-3</sup> mol  |   | —                   |   | 0                             |   | —                    |
| Change:  | -1.900 x 10 <sup>-3</sup> mol |   | -1.900 x 10 <sup>-3</sup> mol |   | —                   |   | +1.900 x 10 <sup>-3</sup> mol |   | —                    |
| Final:   | 1.000 x 10 <sup>-4</sup> mol  |   | 0                             |   |                     |   | 1.900 x 10 <sup>-3</sup> mol  |   |                      |

The volume of the solution at this point is [(20.00 + 19.00) mL] (10<sup>-3</sup> L/1 mL) = 0.03900 L

The molarity of the excess HBut is (1.00 x 10<sup>-4</sup> mol HBut)/(0.03900 L) = 0.0025641 M (unrounded)

The molarity of the But<sup>-</sup> formed is (1.900 x 10<sup>-3</sup> mol But<sup>-</sup>)/(0.03900 L) = 0.0487179 M (unrounded)

Using a reaction table for the equilibrium reaction of HBut:

|              |               |   |                  |   |                               |   |                  |
|--------------|---------------|---|------------------|---|-------------------------------|---|------------------|
|              | HBut          | + | H <sub>2</sub> O | ⇌ | H <sub>3</sub> O <sup>+</sup> | + | But <sup>-</sup> |
| Initial:     | 0.0025641 M   |   |                  |   |                               |   | 0.0487179 M      |
| Change:      | -x            |   |                  |   |                               |   | +x               |
| Equilibrium: | 0.0025641 - x |   |                  |   |                               |   | 0.0487179 + x    |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x(0.0487179 + x)}{0.0025641 - x} = \frac{x(0.0487179)}{0.0025641} = 1.54 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 8.1052631 \times 10^{-7} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (8.1052631 \times 10^{-7}) = 6.09123 = \mathbf{6.09}$$

e) Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10<sup>-3</sup> L/1 mL) (19.95 mL) = 1.995 x 10<sup>-3</sup> mol NaOH

The NaOH will react with an equal amount of the acid, and 5 x 10<sup>-6</sup> mol HBut will remain, and 1.995 x 10<sup>-3</sup> moles of But<sup>-</sup> will form.

|          |                               |   |                               |   |                     |   |                               |   |                      |
|----------|-------------------------------|---|-------------------------------|---|---------------------|---|-------------------------------|---|----------------------|
|          | HBut(aq)                      | + | NaOH(aq)                      | → | H <sub>2</sub> O(l) | + | But <sup>-</sup> (aq)         | + | Na <sup>+</sup> (aq) |
| Initial: | 2.000 x 10 <sup>-3</sup> mol  |   | 1.995 x 10 <sup>-3</sup> mol  |   | —                   |   | 0                             |   | —                    |
| Change:  | -1.995 x 10 <sup>-3</sup> mol |   | -1.995 x 10 <sup>-3</sup> mol |   | —                   |   | +1.995 x 10 <sup>-3</sup> mol |   | —                    |
| Final:   | 5.000 x 10 <sup>-6</sup> mol  |   | 0                             |   |                     |   | 1.995 x 10 <sup>-3</sup> mol  |   |                      |

The volume of the solution at this point is [(20.00 + 19.95) mL] (10<sup>-3</sup> L/1 mL) = 0.03995 L

The molarity of the excess HBut is (5 x 10<sup>-6</sup> mol HBut)/(0.03995 L) = 0.000125156 M (unrounded)

The molarity of the But<sup>-</sup> formed is (1.995 x 10<sup>-3</sup> mol But<sup>-</sup>)/(0.03995 L) = 0.0499374 M (unrounded)

Using a reaction table for the equilibrium reaction of HBut:

|              |                 |   |                  |   |                               |   |                  |
|--------------|-----------------|---|------------------|---|-------------------------------|---|------------------|
|              | HBut            | + | H <sub>2</sub> O | ⇌ | H <sub>3</sub> O <sup>+</sup> | + | But <sup>-</sup> |
| Initial:     | 0.000125156 M   |   |                  |   |                               |   | 0.0499374 M      |
| Change:      | -x              |   |                  |   |                               |   | +x               |
| Equilibrium: | 0.000125156 - x |   |                  |   |                               |   | 0.0499374 + x    |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x(0.0499374 + x)}{0.000125156 - x} = \frac{x(0.0499374)}{0.000125156} = 1.54 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 3.859637 \times 10^{-8} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.859637 \times 10^{-8}) = 7.41345 = \mathbf{7.41}$$

f) Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10<sup>-3</sup> L/1 mL) (20.00 mL) = 2.000 x 10<sup>-3</sup> mol NaOH

The NaOH will react with an equal amount of the acid, and 0 mol HBut will remain, and

2.000 x 10<sup>-3</sup> moles of But<sup>-</sup> will form. This is the equivalence point.

|          |                               |   |                               |   |                     |   |                               |   |                      |
|----------|-------------------------------|---|-------------------------------|---|---------------------|---|-------------------------------|---|----------------------|
|          | HBut(aq)                      | + | NaOH(aq)                      | → | H <sub>2</sub> O(l) | + | But <sup>-</sup> (aq)         | + | Na <sup>+</sup> (aq) |
| Initial: | 2.000 x 10 <sup>-3</sup> mol  |   | 2.000 x 10 <sup>-3</sup> mol  |   | —                   |   | 0                             |   | —                    |
| Change:  | -2.000 x 10 <sup>-3</sup> mol |   | -2.000 x 10 <sup>-3</sup> mol |   | —                   |   | +2.000 x 10 <sup>-3</sup> mol |   | —                    |
| Final:   | 0                             |   | 0                             |   |                     |   | 2.000 x 10 <sup>-3</sup> mol  |   |                      |

The K<sub>b</sub> of But<sup>-</sup> is now important.

The volume of the solution at this point is [(20.00 + 20.00) mL] (10<sup>-3</sup> L/1 mL) = 0.04000 L

The molarity of the But<sup>-</sup> formed is (2.000 x 10<sup>-3</sup> mol But<sup>-</sup>)/(0.04000 L) = 0.05000 M (unrounded)

$$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.54 \times 10^{-5}) = 6.4935 \times 10^{-10} \text{ (unrounded)}$$

Using a reaction table for the equilibrium reaction of But<sup>-</sup>:

|              |                  |   |                  |   |      |   |                 |
|--------------|------------------|---|------------------|---|------|---|-----------------|
|              | But <sup>-</sup> | + | H <sub>2</sub> O | ⇌ | HBut | + | OH <sup>-</sup> |
| Initial:     | 0.05000 M        |   |                  |   | 0    |   | 0               |
| Change:      | -x               |   |                  |   | +x   |   | +x              |
| Equilibrium: | 0.05000 - x      |   |                  |   | x    |   | x               |

$$K_b = \frac{[\text{HBut}][\text{OH}^-]}{[\text{But}^-]} = \frac{[x][x]}{[0.05000 - x]} = \frac{[x][x]}{[0.05000]} = 6.4935 \times 10^{-10}$$

$$[\text{OH}^-] = x = 5.6980259 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log (5.6980259 \times 10^{-6}) = 5.244275575 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.244275575 = 8.755724425 = \mathbf{8.76}$$

g) After the equivalence point, the excess strong base is the primary factor influencing the pH.

Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10<sup>-3</sup> L/1 mL) (20.05 mL) = 2.005 x 10<sup>-3</sup> mol NaOH

The NaOH will react with an equal amount of the acid, 0 mol HBut will remain, and 5 x 10<sup>-6</sup> moles of NaOH will be in excess. There will be 2.000 x 10<sup>-3</sup> mol of But<sup>-</sup> produced, but this weak base will not affect the pH compared to the excess strong base, NaOH.

|          |                               |   |                               |   |                     |   |                               |   |                      |
|----------|-------------------------------|---|-------------------------------|---|---------------------|---|-------------------------------|---|----------------------|
|          | HBut(aq)                      | + | NaOH(aq)                      | → | H <sub>2</sub> O(l) | + | But <sup>-</sup> (aq)         | + | Na <sup>+</sup> (aq) |
| Initial: | 2.000 x 10 <sup>-3</sup> mol  |   | 2.005 x 10 <sup>-3</sup> mol  |   | —                   |   | 0                             |   | —                    |
| Change:  | -2.000 x 10 <sup>-3</sup> mol |   | -2.000 x 10 <sup>-3</sup> mol |   | —                   |   | +2.000 x 10 <sup>-3</sup> mol |   | —                    |
| Final:   | 0                             |   | 5.000 x 10 <sup>-6</sup> mol  |   |                     |   | 2.000 x 10 <sup>-3</sup> mol  |   |                      |

The volume of the solution at this point is [(20.00 + 20.05) mL] (10<sup>-3</sup> L/1 mL) = 0.04005 L

The molarity of the excess OH<sup>-</sup> is (5 x 10<sup>-6</sup> mol OH<sup>-</sup>)/(0.04005 L) = 1.2484 x 10<sup>-4</sup> M (unrounded)

$$\text{pOH} = -\log (1.2484 \times 10^{-4}) = 3.9036 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.9036 = 10.0964 = \mathbf{10.10}$$

h) Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10<sup>-3</sup> L/1 mL) (25.00 mL) = 2.500 x 10<sup>-3</sup> mol NaOH  
 The NaOH will react with an equal amount of the acid, 0 mol HBut will remain, and  
 5.00 x 10<sup>-4</sup> moles of NaOH will be in excess.

|          | HBut(aq)                      | + | NaOH(aq)                      | → | H <sub>2</sub> O(l) | + | But <sup>-</sup> (aq)         | + | Na <sup>+</sup> (aq) |
|----------|-------------------------------|---|-------------------------------|---|---------------------|---|-------------------------------|---|----------------------|
| Initial: | 2.000 x 10 <sup>-3</sup> mol  |   | 2.500 x 10 <sup>-3</sup> mol  |   | —                   |   | 0                             |   | —                    |
| Change:  | -2.000 x 10 <sup>-3</sup> mol |   | -2.000 x 10 <sup>-3</sup> mol |   | —                   |   | +2.000 x 10 <sup>-3</sup> mol |   | —                    |
| Final:   | 0                             |   | 5.000 x 10 <sup>-4</sup> mol  |   |                     |   | 2.000 x 10 <sup>-3</sup> mol  |   |                      |

The volume of the solution at this point is [(20.00 + 25.00) mL] (10<sup>-3</sup> L/1 mL) = 0.04500 L

The molarity of the excess OH<sup>-</sup> is (5.00 x 10<sup>-4</sup> mol OH<sup>-</sup>)/(0.04500 L) = 1.1111 x 10<sup>-2</sup> M (unrounded)

pOH = -log (1.1111 x 10<sup>-2</sup>) = 1.9542 (unrounded)

pH = 14.00 - pOH = 14.00 - 1.9542 = 12.0458 = **12.05**

19.42 This is a titration between a weak base and a strong acid. The pH before addition of the acid is dependent on the K<sub>b</sub> of the base ((CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N). Prior to reaching the equivalence point, the added acid reacts with base to form (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup> ion. The equivalence point occurs when 20.00 mL of acid is added to the base because at this point, moles acid = moles base. Addition of acid beyond the equivalence point is simply the addition of excess H<sub>3</sub>O<sup>+</sup>.

The initial number of moles of (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N = (0.1000 mol (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N/L) (10<sup>-3</sup> L/1 mL) (20.00 mL)  
 = 2.000 x 10<sup>-3</sup> mol (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N

a) Since no acid has been added, only the weak base (K<sub>b</sub>) is important.

$$K_b = \frac{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_3\text{N}]} = \frac{[x][x]}{[0.1000-x]} = \frac{[x][x]}{[0.1000]} = 5.2 \times 10^{-4}$$

[OH<sup>-</sup>] = x = 7.2111 x 10<sup>-3</sup> M

pOH = -log (7.2111 x 10<sup>-3</sup>) = 2.141998 (unrounded)

pH = 14.00 - pOH = 14.00 - 2.141998 = 11.8580 = **11.86**

b) Determine the moles of HCl added:

Moles of HCl = (0.1000 mol HCl/L) (10<sup>-3</sup> L/1 mL) (10.00 mL) = 1.000 x 10<sup>-3</sup> mol HCl

The HCl will react with an equal amount of the base, and 1.000 x 10<sup>-3</sup> mol (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N will remain; an equal number of moles of (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup> will form.

The volume of the solution at this point is [(20.00 + 10.00) mL] (10<sup>-3</sup> L/1 mL) = 0.03000 L

The molarity of the excess (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N is (1.000 x 10<sup>-3</sup> mol (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N)/(0.03000 L)  
 = 0.03333 M (unrounded)

The molarity of the (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup> formed is (1.000 x 10<sup>-3</sup> mol (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup>)/(0.03000 L)  
 = 0.03333 M (unrounded)

$$K_b = \frac{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_3\text{N}]} = \frac{[x][0.0333+x]}{[0.0333-x]} = \frac{[x][0.0333]}{[0.0333]} = 5.2 \times 10^{-4}$$

[OH<sup>-</sup>] = x = 5.2 x 10<sup>-4</sup> M

pOH = -log (5.2 x 10<sup>-4</sup>) = 3.283997 (unrounded)

pH = 14.00 - pOH = 14.00 - 3.283997 = 10.7160 = **10.72**

c) Determine the moles of HCl added:

Moles of HCl = (0.1000 mol HCl/L) (10<sup>-3</sup> L/1 mL) (15.00 mL) = 1.500 x 10<sup>-3</sup> mol HCl

The HCl will react with an equal amount of the base, and 5.00 x 10<sup>-4</sup> mol (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N will remain; and 1.500 x 10<sup>-3</sup> moles of (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup> will form.

The volume of the solution at this point is [(20.00 + 15.00) mL] (10<sup>-3</sup> L/1 mL) = 0.03500 L

The molarity of the excess (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N is (5.00 x 10<sup>-4</sup> mol (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N)/(0.03500 L)  
 = 0.0142857 M (unrounded)

The molarity of the (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup> formed is (1.500 x 10<sup>-3</sup> mol (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup>)/(0.03500 L)  
 = 0.0428571 M (unrounded)

$$K_b = \frac{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_3\text{N}]} = \frac{[x][0.0428571+x]}{[0.0142857-x]} = \frac{[x][0.0428571]}{[0.0142857]} = 5.2 \times 10^{-4}$$

$$[\text{OH}^-] = x = 1.7333 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log(1.7333 \times 10^{-4}) = 3.761126 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.761126 = 10.23887 = \mathbf{10.24}$$

d) Determine the moles of HCl added:

Moles of HCl =  $(0.1000 \text{ mol HCl/L}) (10^{-3} \text{ L/1 mL}) (19.00 \text{ mL}) = 1.900 \times 10^{-3} \text{ mol HCl}$   
 The HCl will react with an equal amount of the base, and  $1.00 \times 10^{-4} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{N}$  will remain; and  $1.900 \times 10^{-3} \text{ moles of } (\text{CH}_3\text{CH}_2)_3\text{NH}^+$  will form.

The volume of the solution at this point is  $[(20.00 + 19.00) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.03900 \text{ L}$

The molarity of the excess  $(\text{CH}_3\text{CH}_2)_3\text{N}$  is  $(1.00 \times 10^{-4} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{N}) / (0.03900 \text{ L})$   
 $= 0.002564102 \text{ M (unrounded)}$

The molarity of the  $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$  formed is  $(1.900 \times 10^{-3} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{NH}^+) / (0.03900 \text{ L})$   
 $= 0.0487179 \text{ M (unrounded)}$

$$K_b = \frac{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_3\text{N}]} = \frac{[x][0.0487179 + x]}{[0.002564102 - x]} = \frac{[x][0.0487179]}{[0.002564102]} = 5.2 \times 10^{-4}$$

$$[\text{OH}^-] = x = 2.73684 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(2.73684 \times 10^{-5}) = 4.56275 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.56275 = 9.43725 = \mathbf{9.44}$$

e) Determine the moles of HCl added:

Moles of HCl =  $(0.1000 \text{ mol HCl/L}) (10^{-3} \text{ L/1 mL}) (19.95 \text{ mL}) = 1.995 \times 10^{-3} \text{ mol HCl}$

The HCl will react with an equal amount of the base, and  $5 \times 10^{-6} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{N}$  will remain; and  $1.995 \times 10^{-3} \text{ moles of } (\text{CH}_3\text{CH}_2)_3\text{NH}^+$  will form.

The volume of the solution at this point is  $[(20.00 + 19.95) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.03995 \text{ L}$

The molarity of the excess  $(\text{CH}_3\text{CH}_2)_3\text{N}$  is  $(5 \times 10^{-6} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{N}) / (0.03995 \text{ L})$   
 $= 0.000125156 \text{ M (unrounded)}$

The molarity of the  $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$  formed is  $(1.995 \times 10^{-3} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{NH}^+) / (0.03995 \text{ L})$   
 $= 0.0499374 \text{ M (unrounded)}$

$$K_b = \frac{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_3\text{N}]} = \frac{[x][0.0499374 + x]}{[0.000125156 - x]} = \frac{[x][0.0499374]}{[0.000125156]} = 5.2 \times 10^{-4}$$

$$[\text{OH}^-] = x = 1.303254 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(1.303254 \times 10^{-6}) = 5.88497 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.88497 = 8.11503 = \mathbf{8.1}$$

f) Determine the moles of HCl added:

Moles of HCl =  $(0.1000 \text{ mol HCl/L}) (10^{-3} \text{ L/1 mL}) (20.00 \text{ mL}) = 2.000 \times 10^{-3} \text{ mol HCl}$

The HCl will react with an equal amount of the base, and 0 mol  $(\text{CH}_3\text{CH}_2)_3\text{N}$  will remain; and  $2.000 \times 10^{-3} \text{ moles of } (\text{CH}_3\text{CH}_2)_3\text{NH}^+$  will form. This is the equivalence point.

The volume of the solution at this point is  $[(20.00 + 20.00) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.04000 \text{ L}$

The molarity of the  $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$  formed is  $(2.000 \times 10^{-3} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{NH}^+) / (0.04000 \text{ L})$   
 $= 0.05000 \text{ M}$

$$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (5.2 \times 10^{-4}) = 1.923 \times 10^{-11} \text{ (unrounded)}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][(\text{CH}_3\text{CH}_2)_3\text{N}]}{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+]} = \frac{[x][x]}{[0.05000 - x]} = \frac{[x][x]}{[0.05000]} = 1.923 \times 10^{-11}$$

$$x = [\text{H}_3\text{O}^+] = 9.8056 \times 10^{-7} \text{ M (unrounded)}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(9.8056 \times 10^{-7}) = 6.0085 = \mathbf{6.01}$$

g) After the equivalence point, the excess strong acid is the primary factor influencing the pH.

Determine the moles of HCl added:

Moles of HCl =  $(0.1000 \text{ mol HCl/L}) (10^{-3} \text{ L/1 mL}) (20.05 \text{ mL}) = 2.005 \times 10^{-3} \text{ mol HCl}$

The HCl will react with an equal amount of the base, and 0 mol  $(\text{CH}_3\text{CH}_2)_3\text{N}$  will remain, and  $5 \times 10^{-6} \text{ moles of HCl}$  will be in excess.

The volume of the solution at this point is  $[(20.00 + 20.05) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.04005 \text{ L}$

The molarity of the excess  $\text{H}_3\text{O}^+$  is  $(5 \times 10^{-6} \text{ mol } \text{H}_3\text{O}^+) / (0.04005 \text{ L}) = 1.2484 \times 10^{-4} \text{ M (unrounded)}$

$$\text{pH} = -\log(1.2484 \times 10^{-4}) = 3.9036 = \mathbf{3.90}$$

h) Determine the moles of HCl added:

$$\text{Moles of HCl} = (0.1000 \text{ mol HCl/L}) (10^{-3} \text{ L/mL}) (25.00 \text{ mL}) = 2.500 \times 10^{-3} \text{ mol HCl}$$

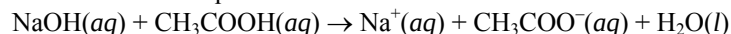
The HCl will react with an equal amount of the base, and 0 mol  $(\text{CH}_3\text{CH}_2)_3\text{N}$  will remain, and  $5.00 \times 10^{-4}$  mol of HCl will be in excess.

The volume of the solution at this point is  $[(20.00 + 25.00) \text{ mL}] (10^{-3} \text{ L/mL}) = 0.04500 \text{ L}$

The molarity of the excess  $\text{H}_3\text{O}^+$  is  $(5.00 \times 10^{-4} \text{ mol H}_3\text{O}^+)/ (0.04500 \text{ L}) = 1.1111 \times 10^{-2} \text{ M}$  (unrounded)

$$\text{pH} = -\log (1.1111 \times 10^{-2}) = 1.9542 = \mathbf{1.95}$$

19.43 a) The balanced chemical equation is:



The sodium ions on the product side are written as separate species because they have no effect on the pH of the solution. Calculate the volume of NaOH needed:

Volume =

$$\left( \frac{0.0520 \text{ mol CH}_3\text{COOH}}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (42.2 \text{ mL}) \left( \frac{1 \text{ mol NaOH}}{1 \text{ mol CH}_3\text{COOH}} \right) \left( \frac{\text{L}}{0.0372 \text{ mol NaOH}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 58.989247 = \mathbf{59.0 \text{ mL NaOH}}$$

Determine the moles of  $\text{CH}_3\text{COOH}$  present:

$$\text{Moles} = \left( \frac{0.0520 \text{ mol CH}_3\text{COOH}}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (42.2 \text{ mL})$$

$$= 0.0021944 \text{ mol CH}_3\text{COOH (unrounded)}$$

At the equivalence point, 0.0021944 mol NaOH will be added so the moles acid = moles base.

The NaOH will react with an equal amount of the acid, 0 mol  $\text{CH}_3\text{COOH}$  will remain, and 0.0021944 moles of  $\text{CH}_3\text{COO}^-$  will be formed.

|          | $\text{CH}_3\text{COOH(aq)}$ | + | $\text{NaOH(aq)}$ | $\rightarrow$ | $\text{H}_2\text{O(l)}$ | + | $\text{CH}_3\text{COO}^-(\text{aq})$ | + | $\text{Na}^+(\text{aq})$ |
|----------|------------------------------|---|-------------------|---------------|-------------------------|---|--------------------------------------|---|--------------------------|
| Initial: | 0.0021944 mol                |   | 0.0021944 mol     |               | —                       |   | 0                                    |   | —                        |
| Change:  | -0.0021944 mol               |   | -0.0021944 mol    |               | —                       |   | +0.0021944 mol                       |   | —                        |
| Final:   | 0                            |   | 0                 |               |                         |   | 0.0021944 mol                        |   |                          |

Determine the liters of solution present at the equivalence point:

$$\text{Volume} = [(42.0 + 58.989247) \text{ mL}] (10^{-3} \text{ L/mL}) = 0.100989 \text{ L (unrounded)}$$

Concentration of  $\text{CH}_3\text{COO}^-$  at equivalence point:

$$\text{Molarity} = (0.0021944 \text{ mol CH}_3\text{COO}^-) / (0.100989 \text{ L}) = 0.021729 \text{ M (unrounded)}$$

Calculate  $K_b$  for  $\text{CH}_3\text{COO}^-$ :

$$K_a \text{ CH}_3\text{COOH} = 1.8 \times 10^{-5}$$

$$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) = 5.556 \times 10^{-10} \text{ (unrounded)}$$

Using a reaction table for the equilibrium reaction of  $\text{CH}_3\text{COO}^-$ :

|              | $\text{CH}_3\text{COO}^-$ | + | $\text{H}_2\text{O}$ | $\rightleftharpoons$ | $\text{CH}_3\text{COOH}$ | + | $\text{OH}^-$ |
|--------------|---------------------------|---|----------------------|----------------------|--------------------------|---|---------------|
| Initial:     | 0.021729 M                |   |                      |                      | 0                        |   | 0             |
| Change:      | -x                        |   |                      |                      | +x                       |   | +x            |
| Equilibrium: | $0.021729 - x$            |   |                      |                      | x                        |   | x             |

Determine the hydroxide ion concentration from the  $K_b$ , and then determine the pH from the pOH.

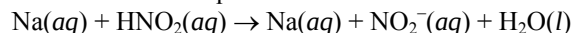
$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{[x][x]}{[0.021729 - x]} = \frac{[x][x]}{[0.021729]} = 5.556 \times 10^{-10}$$

$$[\text{OH}^-] = x = 3.4745693 \times 10^{-6} \text{ M (unrounded)}$$

$$\text{pOH} = -\log (3.4745693 \times 10^{-6}) = 5.459099012 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.459099012 = 8.54090 = \mathbf{8.54}$$

b) The balanced chemical equation is:



The sodium ions on the product side are written as separate species because they have no effect on the pH of the solution. Calculate the volume of NaOH needed:

$$\text{Volume} = \left( \frac{0.0390 \text{ mol HNO}_2}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (23.4 \text{ mL}) \left( \frac{1 \text{ mol NaOH}}{1 \text{ mol HNO}_2} \right) \left( \frac{\text{L}}{0.0372 \text{ mol NaOH}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 24.532 = \mathbf{24.5 \text{ mL NaOH}}$$

Determine the moles of  $\text{HNO}_2$  present:

$$\begin{aligned}\text{Moles} &= \left( \frac{0.0390 \text{ mol HNO}_2}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (23.4 \text{ mL}) \\ &= 0.0009126 \text{ mol HNO}_2\end{aligned}$$

At the equivalence point, 0.0009126 mol NaOH will be added so the moles acid = moles base.

The NaOH will react with an equal amount of the acid, 0 mol  $\text{HNO}_2$  will remain, and 0.0009126 moles of  $\text{NO}_2^-$  will be formed.

|          |                    |   |                   |               |                         |   |                     |   |                   |
|----------|--------------------|---|-------------------|---------------|-------------------------|---|---------------------|---|-------------------|
|          | $\text{HNO}_2(aq)$ | + | $\text{NaOH}(aq)$ | $\rightarrow$ | $\text{H}_2\text{O}(l)$ | + | $\text{NO}_2^-(aq)$ | + | $\text{Na}^+(aq)$ |
| Initial: | 0.0009126 mol      |   | 0.0009126 mol     |               | —                       |   | 0                   |   | —                 |
| Change:  | -0.0009126 mol     |   | -0.0009126 mol    |               | —                       |   | +0.0009126 mol      |   | —                 |
| Final:   | 0                  |   | 0                 |               |                         |   | 0.0009126 mol       |   |                   |

Determine the liters of solution present at the equivalence point:

$$\text{Volume} = [(23.4 + 24.532) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.047932 \text{ L (unrounded)}$$

Concentration of  $\text{NO}_2^-$  at equivalence point:

$$\text{Molarity} = (0.0009126 \text{ mol NO}_2^-) / (0.047932 \text{ L}) = 0.0190395 \text{ M (unrounded)}$$

Calculate  $K_b$  for  $\text{NO}_2^-$ :

$$K_a \text{ HNO}_2 = 7.1 \times 10^{-4}$$

$$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (7.1 \times 10^{-4}) = 1.40845 \times 10^{-11} \text{ (unrounded)}$$

Using a reaction table for the equilibrium reaction of  $\text{NO}_2^-$ :

|              |                 |   |                      |                      |                |   |               |
|--------------|-----------------|---|----------------------|----------------------|----------------|---|---------------|
|              | $\text{NO}_2^-$ | + | $\text{H}_2\text{O}$ | $\rightleftharpoons$ | $\text{HNO}_2$ | + | $\text{OH}^-$ |
| Initial:     | 0.0190395 M     |   |                      |                      | 0              |   | 0             |
| Change:      | -x              |   |                      |                      | +x             |   | +x            |
| Equilibrium: | 0.0190395 - x   |   |                      |                      | x              |   | x             |

Determine the hydroxide ion concentration from the  $K_b$ , and then determine the pH from the pOH.

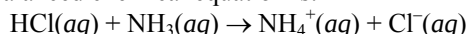
$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} = \frac{[x][x]}{[0.0190395 - x]} = \frac{[x][x]}{[0.0190395]} = 1.40845 \times 10^{-11}$$

$$[\text{OH}^-] = x = 5.178431 \times 10^{-7} \text{ M (unrounded)}$$

$$\text{pOH} = -\log(5.178431 \times 10^{-7}) = 6.285802 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 6.285802 = 7.714198 = \mathbf{7.71}$$

19.44 a) The balanced chemical equation is:



The chloride ions on the product side are written as separate species because they have no effect on the pH of the solution. Calculate the volume of HCl needed:

Volume =

$$\begin{aligned}&\left( \frac{0.234 \text{ mol NH}_3}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (55.5 \text{ mL}) \left( \frac{1 \text{ mol HCl}}{1 \text{ mol NH}_3} \right) \left( \frac{\text{L}}{0.135 \text{ mol HCl}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ &= \mathbf{96.2 \text{ mL HCl}}\end{aligned}$$

Determine the moles of  $\text{NH}_3$  present:

$$\begin{aligned}\text{Moles} &= \left( \frac{0.234 \text{ mol NH}_3}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (55.5 \text{ mL}) \\ &= 0.012987 \text{ mol NH}_3 \text{ (unrounded)}\end{aligned}$$

At the equivalence point, 0.012987 mol HCl will be added so the moles acid = moles base.

The HCl will react with an equal amount of the base, 0 mol  $\text{NH}_3$  will remain, and 0.012987 moles of  $\text{NH}_4^+$  will be formed.

|          |                  |   |                   |               |                     |   |                   |
|----------|------------------|---|-------------------|---------------|---------------------|---|-------------------|
|          | $\text{HCl}(aq)$ | + | $\text{NH}_3(aq)$ | $\rightarrow$ | $\text{NH}_4^+(aq)$ | + | $\text{Cl}^-(aq)$ |
| Initial: | 0.012987 mol     |   | 0.012987 mol      |               | 0                   |   | —                 |
| Change:  | -0.012987 mol    |   | -0.012987 mol     |               | +0.012987 mol       |   | —                 |
| Final:   | 0                |   | 0                 |               | 0.012987 mol        |   |                   |

Determine the liters of solution present at the equivalence point:

$$\text{Volume} = [(55.5 + 96.2) \text{ mL}] (10^{-3} \text{ L/1 mL}) = 0.1517 \text{ L}$$

Concentration of  $\text{NH}_4^+$  at equivalence point:

$$\text{Molarity} = (0.012987 \text{ mol } \text{NH}_4^+) / (0.1517 \text{ L}) = 0.0856098 \text{ M (unrounded)}$$

Calculate  $K_a$  for  $\text{NH}_4^+$ :  $K_b \text{ NH}_3 = 1.76 \times 10^{-5}$

$$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (1.76 \times 10^{-5}) = 5.6818 \times 10^{-10} \text{ (unrounded)}$$

Using a reaction table for the equilibrium reaction of  $\text{NH}_4^+$ :

|              |                 |   |                      |                      |               |   |                        |
|--------------|-----------------|---|----------------------|----------------------|---------------|---|------------------------|
|              | $\text{NH}_4^+$ | + | $\text{H}_2\text{O}$ | $\rightleftharpoons$ | $\text{NH}_3$ | + | $\text{H}_3\text{O}^+$ |
| Initial:     | 0.0856098 M     |   |                      |                      | 0             |   | 0                      |
| Change:      | -x              |   |                      |                      | +x            |   | +x                     |
| Equilibrium: | 0.0856098 - x   |   |                      |                      | x             |   | x                      |

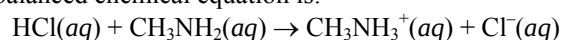
Determine the hydrogen ion concentration from the  $K_a$ , and then determine the pH.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{[x][x]}{[0.0856098 - x]} = \frac{[x][x]}{[0.0856098]} = 5.6818 \times 10^{-10}$$

$$x = [\text{H}_3\text{O}^+] = 6.974366 \times 10^{-6} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.974366 \times 10^{-6}) = 5.1565 = \mathbf{5.16}$$

b) The balanced chemical equation is:



The chloride ions on the product side are written as separate species because they have no effect on the pH of the solution. Calculate the volume of HCl needed:

Volume =

$$\left( \frac{1.11 \text{ mol } \text{CH}_3\text{NH}_2}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (17.8 \text{ mL}) \left( \frac{1 \text{ mol HCl}}{1 \text{ mol } \text{CH}_3\text{NH}_2} \right) \left( \frac{\text{L}}{0.135 \text{ mol HCl}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 146.3556 = \mathbf{146 \text{ mL HCl}}$$

Determine the moles of  $\text{CH}_3\text{NH}_2$  present:

$$\text{Moles} = \left( \frac{1.11 \text{ mol } \text{CH}_3\text{NH}_2}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (17.8 \text{ mL})$$

$$= 0.019758 \text{ mol } \text{CH}_3\text{NH}_2 \text{ (unrounded)}$$

At the equivalence point, 0.019758 mol HCl will be added so the moles acid = moles base.

The HCl will react with an equal amount of the base, 0 mol  $\text{CH}_3\text{NH}_2$  will remain, and 0.019758 moles of  $\text{CH}_3\text{NH}_3^+$  will be formed.

|          |                  |   |                                     |               |                                       |   |                          |
|----------|------------------|---|-------------------------------------|---------------|---------------------------------------|---|--------------------------|
|          | $\text{HCl(aq)}$ | + | $\text{CH}_3\text{NH}_2(\text{aq})$ | $\rightarrow$ | $\text{CH}_3\text{NH}_3^+(\text{aq})$ | + | $\text{Cl}^-(\text{aq})$ |
| Initial: | 0.019758 mol     |   | 0.019758 mol                        |               | 0                                     |   | -                        |
| Change:  | -0.019758 mol    |   | -0.019758 mol                       |               | +0.019758 mol                         |   | -                        |
| Final:   | 0                |   | 0                                   |               | 0.019758 mol                          |   |                          |

Determine the liters of solution present at the equivalence point:

$$\text{Volume} = [(17.8 + 146.3556) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.1641556 \text{ L (unrounded)}$$

Concentration of  $\text{CH}_3\text{NH}_3^+$  at equivalence point:

$$\text{Molarity} = (0.019758 \text{ mol } \text{CH}_3\text{NH}_3^+) / (0.161556 \text{ L}) = 0.122298 \text{ M (unrounded)}$$

Calculate  $K_a$  for  $\text{CH}_3\text{NH}_3^+$ :  $K_b \text{ CH}_3\text{NH}_2 = 4.4 \times 10^{-4}$

$$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (4.4 \times 10^{-4}) = 2.2727 \times 10^{-11} \text{ (unrounded)}$$

Using a reaction table for the equilibrium reaction of  $\text{CH}_3\text{NH}_3^+$ :

|              |                            |   |                      |                      |                          |   |                        |
|--------------|----------------------------|---|----------------------|----------------------|--------------------------|---|------------------------|
|              | $\text{CH}_3\text{NH}_3^+$ | + | $\text{H}_2\text{O}$ | $\rightleftharpoons$ | $\text{CH}_3\text{NH}_2$ | + | $\text{H}_3\text{O}^+$ |
| Initial:     | 0.122298 M                 |   |                      |                      | 0                        |   | 0                      |
| Change:      | -x                         |   |                      |                      | +x                       |   | +x                     |
| Equilibrium: | 0.122298 - x               |   |                      |                      | x                        |   | x                      |

Determine the hydrogen ion concentration from the  $K_a$ , and then determine the pH.

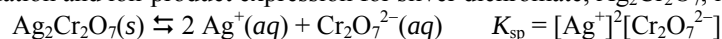
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]} = \frac{[x][x]}{[0.122298 - x]} = \frac{[x][x]}{[0.122298]} = 2.2727 \times 10^{-11}$$

$$x = [\text{H}_3\text{O}^+] = 1.66717 \times 10^{-6} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.66717 \times 10^{-6}) = 5.778019 = \mathbf{5.78}$$

- 19.45  $M_2X(s) \rightleftharpoons 2M^+(aq) + X^{2-}(aq)$   
 $K_{sp} = [M^+]^2[X^{2-}]$ , assuming  $M_2X$  is a strong electrolyte.  
 $S = \text{molar solubility} = 5 \times 10^{-5} M$   
 $[M^+] = 2S = 1 \times 10^{-4} M$   
 $[X^{2-}] = S = 5 \times 10^{-5} M$   
 The actual  $K_{sp}$  is lower than the calculated value because the assumption that  $M_2X$  is a strong electrolyte (i.e., exists as  $M^+ + X^{2-}$ ) is in error to some degree. There would be some (probably significant) amount of ion pairing to form  $MX^-(aq)$ ,  $M_2X(aq)$ , etc., which reduces the effective concentrations of the ions.
- 19.46 Fluoride ion in  $BaF_2$  is the conjugate base of the weak acid  $HF$ . The base hydrolysis reaction of fluoride ion  
 $F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$   
 therefore is influenced by the pH of the solution. As the pH increases,  $[OH^-]$  increases and the equilibrium shifts to the left to decrease  $[OH^-]$  and increase the  $[F^-]$ . As the pH decreases,  $[OH^-]$  decreases and the equilibrium shifts to the right to increase  $[OH^-]$  and decrease  $[F^-]$ . The changes in  $[F^-]$  influence the solubility of  $BaF_2$ . Chloride ion is the conjugate base of a strong acid so it does not react with water. Thus, its concentration is not influenced by pH, and solubility of  $BaCl_2$  does not change with pH.
- 19.47 Consider the reaction  $AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$ , where  $Q_{sp} = [A^+][B^-]$ . If  $Q_{sp} > K_{sp}$ , then there are more ions dissolved than expected at equilibrium, and the equilibrium shifts to the left and the compound  $AB$  precipitates. The excess ions precipitate as solid from the solution.
- 19.48 a)  $Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$   
 Ion-product expression:  $K_{sp} = [Ag^+]^2[CO_3^{2-}]$   
 b)  $BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$   
 Ion-product expression:  $K_{sp} = [Ba^{2+}][F^-]^2$   
 c)  $CuS(s) + H_2O(l) \rightleftharpoons Cu^{2+}(aq) + HS^-(aq) + OH^-(aq)$   
 Ion-product expression:  $K_{sp} = [Cu^{2+}][HS^-][OH^-]$
- 19.49 a)  $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$   
 Ion-product expression:  $K_{sp} = [Fe^{3+}][OH^-]^3$   
 b)  $Ba_3(PO_4)_2(s) \rightleftharpoons 3Ba^{2+}(aq) + 2PO_4^{3-}(aq)$   
 Ion-product expression:  $K_{sp} = [Ba^{2+}]^3[PO_4^{3-}]^2$   
 c)  $SnS(s) + H_2O(l) \rightleftharpoons Sn^{2+}(aq) + HS^-(aq) + OH^-(aq)$   
 Ion-product expression:  $K_{sp} = [Sn^{2+}][HS^-][OH^-]$
- 19.50 Write a reaction table, where  $S$  is the molar solubility of  $Ag_2CO_3$ :
- | Concentration (M) | $Ag_2CO_3(s)$ | $\rightleftharpoons$ | $2Ag^+(aq)$ | + | $CO_3^{2-}(aq)$ |
|-------------------|---------------|----------------------|-------------|---|-----------------|
| Initial           | —             |                      | 0           |   | 0               |
| Change            | —             |                      | +2S         |   | +S              |
| Equilibrium       | —             |                      | 2S          |   | S               |
- $S = [Ag_2CO_3] = 0.032 M$  so  $[Ag^+] = 2S = 0.064 M$  and  $[CO_3^{2-}] = S = 0.032 M$   
 $K_{sp} = [Ag^+]^2[CO_3^{2-}] = (0.064)^2(0.032) = 1.31072 \times 10^{-4} = \mathbf{1.3 \times 10^{-4}}$
- 19.51 Write a reaction table, where  $S$  is the molar solubility of  $ZnC_2O_4$ :
- | Concentration (M) | $ZnC_2O_4(s)$ | $\rightleftharpoons$ | $Zn^{2+}(aq)$ | + | $C_2O_4^{2-}(aq)$ |
|-------------------|---------------|----------------------|---------------|---|-------------------|
| Initial           | —             |                      | 0             |   | 0                 |
| Change            | —             |                      | +S            |   | +S                |
| Equilibrium       | —             |                      | S             |   | S                 |
- $S = [ZnC_2O_4] = 7.9 \times 10^{-3} M$  so  $[Zn^{2+}] = [C_2O_4^{2-}] = S = 7.9 \times 10^{-3} M$   
 $K_{sp} = [Zn^{2+}][C_2O_4^{2-}] = (7.9 \times 10^{-3})^2 = 6.241 \times 10^{-5} = \mathbf{6.2 \times 10^{-5}}$

- 19.52 The equation and ion-product expression for silver dichromate,  $\text{Ag}_2\text{Cr}_2\text{O}_7$ , is:



The solubility of  $\text{Ag}_2\text{Cr}_2\text{O}_7$ , converted from g / 100 mL to M is:

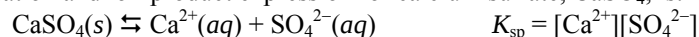
$$\text{Molar solubility} = S = \left( \frac{8.3 \times 10^{-3} \text{ g Ag}_2\text{Cr}_2\text{O}_7}{100 \text{ mL}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left( \frac{1 \text{ mol Ag}_2\text{Cr}_2\text{O}_7}{431.8 \text{ g Ag}_2\text{Cr}_2\text{O}_7} \right) = 0.00019221861 \text{ M (unrounded)}$$

Since 1 mole of  $\text{Ag}_2\text{Cr}_2\text{O}_7$  dissociates to form 2 moles of  $\text{Ag}^+$ , the concentration of  $\text{Ag}^+$  is

$2S = 2(0.00019221861 \text{ M}) = 0.00038443723 \text{ M (unrounded)}$ . The concentration of  $\text{Cr}_2\text{O}_7^{2-}$  is  $S = 0.00019221861 \text{ M}$  because 1 mole of  $\text{Ag}_2\text{Cr}_2\text{O}_7$  dissociates to form 1 mole of  $\text{Cr}_2\text{O}_7^{2-}$ .

$$K_{sp} = [\text{Ag}^+]^2[\text{Cr}_2\text{O}_7^{2-}] = (2S)^2(S) = (0.00038443723)^2(0.00019221861) = 2.8408 \times 10^{-11} = \mathbf{2.8 \times 10^{-11}}$$

- 19.53 The equation and ion-product expression for calcium sulfate,  $\text{CaSO}_4$ , is:



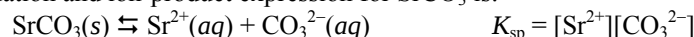
The solubility of  $\text{CaSO}_4$ , converted from g / 100 mL to M is:

$$\text{Molar solubility} = S = \left( \frac{0.209 \text{ g CaSO}_4}{100 \text{ mL}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left( \frac{1 \text{ mol CaSO}_4}{136.15 \text{ g CaSO}_4} \right) = 0.015350716 \text{ M (unrounded)}$$

Since 1 mole of  $\text{CaSO}_4$  dissociates to form 1 mole of  $\text{Ca}^{2+}$ , the concentration of  $\text{Ca}^{2+}$  is  $S = 0.015350716 \text{ M}$  (unrounded). The concentration of  $\text{SO}_4^{2-}$  is  $S = 0.015350716 \text{ M}$  because 1 mole of  $\text{CaSO}_4$  dissociates to form 1 mole of  $\text{SO}_4^{2-}$ .

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (S)(S) = (0.015350716)(0.015350716) = 2.35644 \times 10^{-4} = \mathbf{2.36 \times 10^{-4}}$$

- 19.54 The equation and ion-product expression for  $\text{SrCO}_3$  is:



a) The solubility,  $S$ , in pure water equals  $[\text{Sr}^{2+}]$  and  $[\text{CO}_3^{2-}]$

Write a reaction table, where  $S$  is the molar solubility of  $\text{SrCO}_3$ :

| Concentration (M) | $\text{SrCO}_3(s)$ | $\rightleftharpoons$ | $\text{Sr}^{2+}(aq)$ | + | $\text{CO}_3^{2-}(aq)$ |
|-------------------|--------------------|----------------------|----------------------|---|------------------------|
| Initial           | —                  |                      | 0                    |   | 0                      |
| Change            | —                  |                      | +S                   |   | +S                     |
| Equilibrium       | —                  |                      | S                    |   | S                      |

$$K_{sp} = 5.4 \times 10^{-10} = [\text{Sr}^{2+}][\text{CO}_3^{2-}] = [S][S] = S^2$$

$$S = 2.32379 \times 10^{-5} = \mathbf{2.3 \times 10^{-5} \text{ M}}$$

b) In  $0.13 \text{ M Sr(NO}_3)_2$ , the initial concentration of  $\text{Sr}^{2+}$  is  $0.13 \text{ M}$ .

Equilibrium  $[\text{Sr}^{2+}] = 0.13 + S$  and equilibrium  $[\text{CO}_3^{2-}] = S$  where  $S$  is the solubility of  $\text{SrCO}_3$ .

| Concentration (M) | $\text{SrCO}_3(s)$ | $\rightleftharpoons$ | $\text{Sr}^{2+}(aq)$ | + | $\text{CO}_3^{2-}(aq)$ |
|-------------------|--------------------|----------------------|----------------------|---|------------------------|
| Initial           | —                  |                      | 0.13                 |   | 0                      |
| Change            | —                  |                      | +S                   |   | +S                     |
| Equilibrium       | —                  |                      | 0.13 + S             |   | S                      |

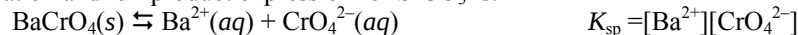
$$K_{sp} = 5.4 \times 10^{-10} = [\text{Sr}^{2+}][\text{CO}_3^{2-}] = (0.13 + S)S$$

This calculation may be simplified by assuming  $S$  is small and setting  $(0.13 + S) = (0.13)$ .

$$K_{sp} = 5.4 \times 10^{-10} = (0.13)S$$

$$S = 4.1538 \times 10^{-9} = \mathbf{4.2 \times 10^{-9} \text{ M}}$$

- 19.55 The equation and ion-product expression for  $\text{SrCO}_3$  is:



a) The solubility,  $S$ , in pure water equals  $[\text{Ba}^{2+}]$  and  $[\text{CrO}_4^{2-}]$

$$K_{sp} = 2.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{CrO}_4^{2-}] = S^2$$

$$S = 1.4491 \times 10^{-5} = \mathbf{1.4 \times 10^{-5} \text{ M}}$$

b) In  $0.13 \text{ M Na}_2\text{CrO}_4$ , the initial concentration of  $\text{CrO}_4^{2-}$  is  $1.5 \times 10^{-3} \text{ M}$ .

Equilibrium  $[\text{Ba}^{2+}] = S$  and equilibrium  $[\text{CrO}_4^{2-}] = 1.5 \times 10^{-3} + S$  where  $S$  is the solubility of  $\text{BaCrO}_4$ .

$$K_{sp} = 2.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{CrO}_4^{2-}] = S(1.5 \times 10^{-3} + S)$$

Assume  $S$  is small so  $(1.5 \times 10^{-3} + S) = (1.5 \times 10^{-3})$

$$K_{sp} = 2.1 \times 10^{-10} = S(1.5 \times 10^{-3})$$

$$S = 1.4 \times 10^{-7} \text{ M}$$

- 19.56 The equilibrium is:  $\text{Ca}(\text{IO}_3)_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2 \text{IO}_3^{-}(\text{aq})$ . From the Appendix,  $K_{\text{sp}}(\text{Ca}(\text{IO}_3)_2) = 7.1 \times 10^{-7}$ .  
a) Write a reaction table that reflects an initial concentration of  $\text{Ca}^{2+} = 0.060 \text{ M}$ . In this case,  $\text{Ca}^{2+}$  is the common ion.

| Concentration (M) | $\text{Ca}(\text{IO}_3)_2(\text{s})$ | $\rightleftharpoons$ | $\text{Ca}^{2+}(\text{aq})$ | + | $2 \text{IO}_3^{-}(\text{aq})$ |
|-------------------|--------------------------------------|----------------------|-----------------------------|---|--------------------------------|
| Initial           | —                                    |                      | 0.060                       |   | 0                              |
| Change            | —                                    |                      | +S                          |   | +2S                            |
| Equilibrium       | —                                    |                      | $0.060 + S$                 |   | 2S                             |

Assume that  $0.060 + S \approx 0.060$  because the amount of compound that dissolves will be negligible in comparison to  $0.060 \text{ M}$ .

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^{-}]^2 = (0.060)(2S)^2 = 7.1 \times 10^{-7}$$

$$S = 1.71998 \times 10^{-3} = 1.7 \times 10^{-3} \text{ M}$$

Check assumption:  $(1.71998 \times 10^{-3} \text{ M}) / (0.060 \text{ M}) \times 100\% = 2.9\% < 5\%$ , so the assumption is good.

S represents both the molar solubility of  $\text{Ca}^{2+}$  and  $\text{Ca}(\text{IO}_3)_2$ , so the molar solubility of  $\text{Ca}(\text{IO}_3)_2$  is  **$1.7 \times 10^{-3} \text{ M}$** .

b) In this case,

| Concentration (M) | $\text{Ca}(\text{IO}_3)_2(\text{s})$ | $\rightleftharpoons$ | $\text{Ca}^{2+}(\text{aq})$ | + | $2 \text{IO}_3^{-}(\text{aq})$ |
|-------------------|--------------------------------------|----------------------|-----------------------------|---|--------------------------------|
| Initial           | —                                    |                      | 0                           |   | 0.060                          |
| Change            | —                                    |                      | +S                          |   | +2S                            |
| Equilibrium       | —                                    |                      | S                           |   | $0.060 + 2S$                   |

The equilibrium concentration of  $\text{Ca}^{2+}$  is S, and the  $\text{IO}_3^{-}$  concentration is  $0.060 + 2S$ . The iodate ion is the common ion in this problem.

$$\text{Assume that } 0.060 + 2S \approx 0.060$$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^{-}]^2 = (S)(0.060)^2 = 7.1 \times 10^{-7}$$

$$S = 1.97222 \times 10^{-4} = 2.0 \times 10^{-4} \text{ M}$$

Check assumption:  $(1.97222 \times 10^{-4} \text{ M}) / (0.060 \text{ M}) \times 100\% = 0.3\% < 5\%$ , so the assumption is good.

S represents both the molar solubility of  $\text{Ca}^{2+}$  and  $\text{Ca}(\text{IO}_3)_2$ , so the molar solubility of  $\text{Ca}(\text{IO}_3)_2$  is  **$2.0 \times 10^{-4} \text{ M}$** .

- 19.57 The equilibrium is:  $\text{Ag}_2\text{SO}_4(\text{s}) \rightleftharpoons 2 \text{Ag}^{+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ . From the Appendix,  $K_{\text{sp}}(\text{Ag}_2\text{SO}_4) = 1.5 \times 10^{-5}$ .

a) Write a reaction table that reflects an initial concentration of  $\text{Ag}^{+} = 0.22 \text{ M}$ . In this case,  $\text{Ag}^{+}$  is the common ion.

| Concentration (M) | $\text{Ag}_2\text{SO}_4(\text{s})$ | $\rightleftharpoons$ | $2 \text{Ag}^{+}(\text{aq})$ | + | $\text{SO}_4^{2-}(\text{aq})$ |
|-------------------|------------------------------------|----------------------|------------------------------|---|-------------------------------|
| Initial           | —                                  |                      | 0.22                         |   | 0                             |
| Change            | —                                  |                      | +2S                          |   | +S                            |
| Equilibrium       | —                                  |                      | $0.22 + 2S$                  |   | S                             |

Assume that  $0.22 + 2S \approx 0.22$  because the amount of compound that dissolves will be negligible in comparison to  $0.22 \text{ M}$ .

$$K_{\text{sp}} = [\text{Ag}^{+}]^2[\text{SO}_4^{2-}] = (0.22)^2(S) = 1.5 \times 10^{-5}$$

$$S = 3.099175 \times 10^{-4} = 3.1 \times 10^{-4}$$

Check assumption:  $(3.099175 \times 10^{-4} \text{ M}) / (0.22 \text{ M}) \times 100\% = 1.4\% < 5\%$ , so the assumption is good.

S represents both the molar solubility of  $\text{SO}_4^{2-}$  and  $\text{Ag}_2\text{SO}_4(\text{s})$ , so the molar solubility of  $\text{Ag}_2\text{SO}_4(\text{s})$  is  **$3.1 \times 10^{-4} \text{ M}$** .

b) In this case,

| Concentration (M) | $\text{Ag}_2\text{SO}_4(\text{s})$ | $\rightleftharpoons$ | $2 \text{Ag}^{+}(\text{aq})$ | + | $\text{SO}_4^{2-}(\text{aq})$ |
|-------------------|------------------------------------|----------------------|------------------------------|---|-------------------------------|
| Initial           | —                                  |                      | 0                            |   | 0.22                          |
| Change            | —                                  |                      | +2S                          |   | +S                            |
| Equilibrium       | —                                  |                      | 2S                           |   | $0.22 + S$                    |

The equilibrium concentration of  $\text{Ag}^{+}$  is 2S, and the  $\text{SO}_4^{2-}$  concentration is  $0.22 + S$ . The sulfate ion is the common ion in this problem.

$$\text{Assume that } 0.22 + S \approx 0.22$$

$$K_{\text{sp}} = [\text{Ag}^{+}]^2[\text{SO}_4^{2-}] = (2S)^2(0.22) = 1.5 \times 10^{-5}$$

$$S = 4.1286 \times 10^{-3} = 4.1 \times 10^{-3}$$

Check assumption:  $(4.1286 \times 10^{-3} \text{ M}) / (0.22 \text{ M}) \times 100\% = 1.9\% < 5\%$ , so the assumption is good.

S represents the molar solubility of  $\text{Ag}_2\text{SO}_4$ , so the molar solubility of  $\text{Ag}_2\text{SO}_4$  is  **$4.1 \times 10^{-3} \text{ M}$** .

- 19.58 The larger the  $K_{sp}$ , the larger the molar solubility if the number of ions are equal.  
 a) **Mg(OH)<sub>2</sub>** with  $K_{sp} = 6.3 \times 10^{-10}$  has higher molar solubility than **Ni(OH)<sub>2</sub>** with  $K_{sp} = 6 \times 10^{-16}$ .  
 b) **PbS** with  $K_{sp} = 3 \times 10^{-25}$  has higher molar solubility than **CuS** with  $K_{sp} = 8 \times 10^{-34}$ .  
 c) **Ag<sub>2</sub>SO<sub>4</sub>** with  $K_{sp} = 1.5 \times 10^{-5}$  has higher molar solubility than **MgF<sub>2</sub>** with  $K_{sp} = 7.4 \times 10^{-9}$ .
- 19.59 The larger the  $K_{sp}$ , the larger the molar solubility if the number of ions are equal.  
 a) **SrSO<sub>4</sub>** with  $K_{sp} = 3.2 \times 10^{-7}$  has higher molar solubility than **BaCrO<sub>4</sub>** with  $K_{sp} = 2.1 \times 10^{-10}$ .  
 b) **CaCO<sub>3</sub>** with  $K_{sp} = 3.3 \times 10^{-9}$  has higher molar solubility than **CuCO<sub>3</sub>** with  $K_{sp} = 3 \times 10^{-12}$ .  
 c) **Ba(IO<sub>3</sub>)<sub>2</sub>** with  $K_{sp} = 1.5 \times 10^{-9}$  has higher molar solubility than **Ag<sub>2</sub>CrO<sub>4</sub>** with  $K_{sp} = 2.6 \times 10^{-12}$ .
- 19.60 a)  $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$   
 The chloride ion is the anion of a strong acid, so it does not react with  $\text{H}_3\text{O}^+$ . The solubility is not affected by pH.  
 b)  $\text{SrCO}_3(s) \rightleftharpoons \text{Sr}^{2+}(aq) + \text{CO}_3^{2-}(aq)$   
 The strontium ion is the cation of a strong base, so pH will not affect its solubility.  
 The carbonate ion is the conjugate base of a weak acid and will act as a base:  

$$\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$$

$$\text{and } \text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq)$$
  
 The  $\text{H}_2\text{CO}_3$  will decompose to  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$ . The gas will escape and further shift the equilibrium. Changes in pH will change the  $[\text{CO}_3^{2-}]$ , so the solubility of  $\text{SrCO}_3$  will increase with decreasing pH. **Solubility increases with addition of  $\text{H}_3\text{O}^+$  (decreasing pH).**
- 19.61 a)  $\text{CuBr}(s) \rightleftharpoons \text{Cu}^+(aq) + \text{Br}^-(aq)$   
 The bromide ion is the anion of a strong acid, so it does not react with  $\text{H}_3\text{O}^+$ . At high pH the copper ion may precipitate.  

$$\text{Cu}^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{CuOH}(s)$$
  
 b)  $\text{Ca}_3(\text{PO}_4)_2(s) \rightleftharpoons 3 \text{Ca}^{2+}(aq) + 2 \text{PO}_4^{3-}(aq)$   
 The calcium ion is the cation of a strong base so pH will not affect its solubility.  
 $\text{PO}_4^{3-}$  is the anion of a weak acid, so the following equilibria would be present.  

$$\text{PO}_4^{3-}(aq) + n \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_n\text{PO}_4^{(3-n)-}(aq) + n \text{OH}^-(aq) \quad (n = 1, 2, 3)$$
  
 Since these involve  $\text{OH}^-$ , the solubility will change with changing pH. **Solubility increases with addition of  $\text{H}_3\text{O}^+$  (decreasing pH).**
- 19.62 The ion-product expression for  $\text{Cu(OH)}_2$  is  $K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2$  and, from Appendix C,  $K_{sp}$  equals  $2.2 \times 10^{-20}$ .  
 To decide if a precipitate will form, calculate  $Q_{sp}$  with the given quantities and compare it to  $K_{sp}$ .  

$$[\text{Cu}^{2+}] = \left( \frac{1.0 \times 10^{-3} \text{ mol Cu(NO}_3)_2}{\text{L}} \right) \left( \frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol Cu(NO}_3)_2} \right) = 1.0 \times 10^{-3} \text{ M Cu}^{2+}$$

$$[\text{OH}^-] = \left( \frac{0.075 \text{ g KOH}}{1.0 \text{ L}} \right) \left( \frac{1 \text{ mol KOH}}{56.11 \text{ g KOH}} \right) \left( \frac{1 \text{ mol OH}^-}{1 \text{ mol KOH}} \right) = 1.33666 \times 10^{-3} \text{ M OH}^- \text{ (unrounded)}$$

$$Q_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2 = (1.0 \times 10^{-3})(1.33666 \times 10^{-3})^2 = 1.7866599 \times 10^{-9} \text{ (unrounded)}$$
 $Q_{sp}$  is greater than  $K_{sp}$  ( $1.8 \times 10^{-9} > 2.2 \times 10^{-20}$ ), so  **$\text{Cu(OH)}_2$  will precipitate.**
- 19.63 The ion-product expression for  $\text{PbCl}_2$  is  $K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$  and, from the Appendix,  $K_{sp}$  equals  $1.7 \times 10^{-5}$ .  
 To decide if a precipitate will form, calculate  $Q_{sp}$  with the given quantities and compare it to  $K_{sp}$ .  

$$[\text{Pb}^{2+}] = \left( \frac{0.12 \text{ mol Pb(NO}_3)_2}{\text{L}} \right) \left( \frac{1 \text{ mol Pb}^{2+}}{1 \text{ mol Pb(NO}_3)_2} \right) = 0.12 \text{ M Pb}^{2+}$$

$$[\text{Cl}^-] = \left( \frac{3.5 \text{ mg NaCl}}{0.250 \text{ L}} \right) \left( \frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left( \frac{1 \text{ mol NaCl}}{58.45 \text{ g NaCl}} \right) \left( \frac{1 \text{ mol Cl}^-}{1 \text{ mol NaCl}} \right) = 2.3952 \times 10^{-4} \text{ M Cl}^- \text{ (unrounded)}$$

$$Q_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = (0.12)(2.3952 \times 10^{-4})^2 = 6.8843796 \times 10^{-9} \text{ (unrounded)}$$
 $Q_{sp}$  is greater than  $K_{sp}$  ( $6.9 \times 10^{-9} < 1.7 \times 10^{-5}$ ), so  **$\text{PbCl}_2$  will not precipitate.**

$$19.64 \quad \text{Original moles of Ca}^{2+} = \left( \frac{9.7 \times 10^{-5} \text{ g Ca}^{2+}}{\text{mL}} \right) (104 \text{ mL}) \left( \frac{1 \text{ mol Ca}^{2+}}{40.08 \text{ g Ca}^{2+}} \right) = 2.5170 \times 10^{-4} \text{ mol Ca}^{2+}$$

$$\text{Moles of C}_2\text{O}_4^{2-} \text{ added} = \left( \frac{0.1550 \text{ mol Na}_2\text{C}_2\text{O}_4}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100.0 \text{ mL}) \left( \frac{1 \text{ mol C}_2\text{O}_4^{2-}}{1 \text{ mol Na}_2\text{C}_2\text{O}_4} \right) = 0.01550 \text{ mol C}_2\text{O}_4^{2-}$$

The  $\text{Ca}^{2+}$  is limiting leaving 0 M, and after the reactions there will be  $(0.01550 - 0.010088)$  mol of  $\text{C}_2\text{O}_4^{2-}$  remaining.

$$[\text{C}_2\text{O}_4^{2-}] = \left( \frac{(0.01550 - 0.00025170) \text{ mol C}_2\text{O}_4^{2-}}{(104 + 100.0) \text{ mL}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.0747466 \text{ M C}_2\text{O}_4^{2-} \text{ (unrounded)}$$

| Concentration (M) | $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{s})$ | $\rightleftharpoons$ | $\text{Ca}^{2+}(\text{aq})$ | + | $\text{C}_2\text{O}_4^{2-}(\text{aq})$ | + | $\text{H}_2\text{O}(\text{l})$ |
|-------------------|-------------------------------------------------------------|----------------------|-----------------------------|---|----------------------------------------|---|--------------------------------|
| Initial           | —                                                           |                      | 0                           |   | 0.0747466                              |   | —                              |
| Change            | —                                                           |                      | +S                          |   | +S                                     |   | —                              |
| Equilibrium       | —                                                           |                      | S                           |   | 0.0747466 + S                          |   | —                              |

Assume that  $0.0747466 + S \approx 0.0747466$  because the amount of compound that dissolves will be negligible in comparison to 0.0747466 M. The  $K_{\text{sp}}$  from the Appendix is:  $2.3 \times 10^{-9}$

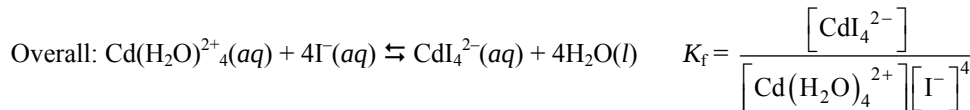
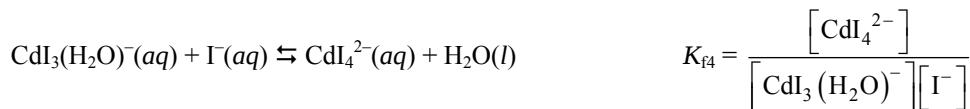
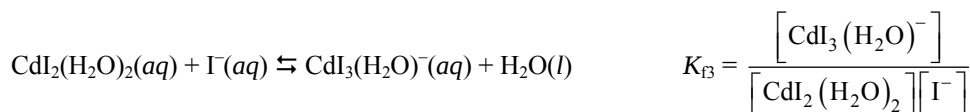
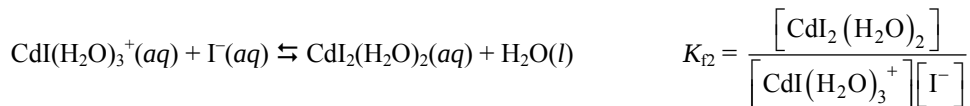
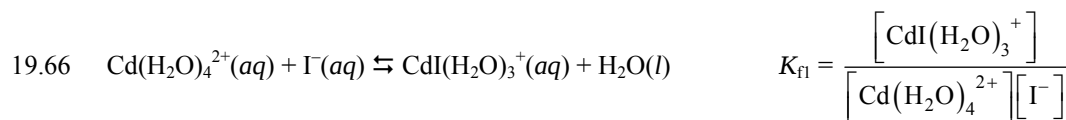
$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (S)(0.0747466) = 2.3 \times 10^{-9}$$

$$S = 3.07706 \times 10^{-8} = 3.1 \times 10^{-8}$$

Check assumption:  $(3.07706 \times 10^{-8} \text{ M}) / (0.0747466 \text{ M}) \times 100\% = 0.00004\% < 5\%$ , so the assumption is good.

S represents both the molar solubility of  $\text{Ca}^{2+}$  and  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{s})$ , so the concentration of  $\text{Ca}^{2+}$  is  **$3.1 \times 10^{-8} \text{ M}$** .

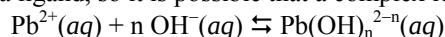
- 19.65 The metal ion can act as a Lewis acid and bond to one or more negatively charged ligands. If the total negative charge of the ligands exceeds the positive charge on the metal ion, the complex will be negative.



$$K_{\text{f}} = \frac{[\text{CdI}(\text{H}_2\text{O})_3^+]}{[\text{Cd}(\text{H}_2\text{O})_4^{2+}][\text{I}^-]} \times \frac{[\text{CdI}_2(\text{H}_2\text{O})_2]}{[\text{CdI}(\text{H}_2\text{O})_3^+][\text{I}^-]} \times \frac{[\text{CdI}_3(\text{H}_2\text{O})^-]}{[\text{CdI}_2(\text{H}_2\text{O})_2][\text{I}^-]} \times \frac{[\text{CdI}_4^{2-}]}{[\text{CdI}_3(\text{H}_2\text{O})^-][\text{I}^-]}$$

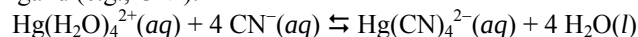
$$= K_{\text{f1}} \times K_{\text{f2}} \times K_{\text{f3}} \times K_{\text{f4}}$$

- 19.67 In the context of this equilibrium only, the increased solubility with added  $\text{OH}^-$  appears to be a violation of Le Châtelier's Principle. Adding  $\text{OH}^-$  should cause the equilibrium to shift towards the left, decreasing the solubility of  $\text{PbS}$ . Before accepting this conclusion, other possible equilibria must be considered. Lead is a metal ion and hydroxide ion is a ligand, so it is possible that a complex ion forms between the lead ion and hydroxide ion:



This decreases the concentration of  $\text{Pb}^{2+}$ , shifting the solubility equilibrium to the right to dissolve more  $\text{PbS}$ .

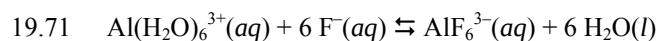
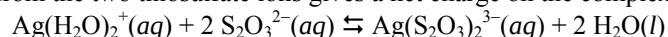
- 19.68 In many cases, a hydrated metal complex (e.g.,  $\text{Hg}(\text{H}_2\text{O})_4^{2+}$ ) will exchange ligands when placed in a solution of another ligand (e.g.,  $\text{CN}^-$ ):



Note that both sides of the equation have the same "overall" charge of  $-2$ . The mercury complex changes from  $+2$  to  $-2$  because water is a neutral *molecular* ligand, whereas cyanide is an *ionic* ligand.

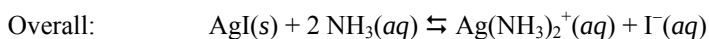
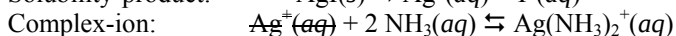
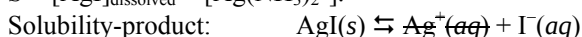


- 19.70 The two water ligands are replaced by two thiosulfate ion ligands. The  $+1$  charge from the silver ion plus  $-4$  charge from the two thiosulfate ions gives a net charge on the complex ion of  $-3$ .



- 19.72 Write the ion-product equilibrium reaction and the complex-ion equilibrium reaction. Sum the two reactions to yield an overall reaction; multiply the two constants to obtain  $K_{\text{overall}}$ . Write a reaction table where

$$S = [\text{AgI}]_{\text{dissolved}} = [\text{Ag}(\text{NH}_3)_2^+]$$



$$K_{\text{overall}} = K_{\text{sp}} \times K_{\text{f}} = (8.3 \times 10^{-17}) (1.7 \times 10^7) = 1.411 \times 10^{-9} \text{ (unrounded)}$$

Reaction table:

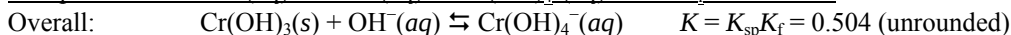
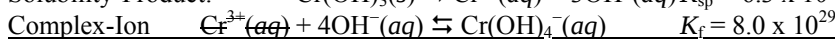
| Concentration (M) | $\text{AgI}(\text{s})$ | + | $2 \text{NH}_3(\text{aq})$ | $\rightleftharpoons$ | $\text{Ag}(\text{NH}_3)_2^+(\text{aq})$ | + | $\text{I}^-(\text{aq})$ |
|-------------------|------------------------|---|----------------------------|----------------------|-----------------------------------------|---|-------------------------|
| Initial           | —                      |   | 2.5                        |                      | 0                                       |   | 0                       |
| Change            | —                      |   | $-2S$                      |                      | $+S$                                    |   | $+S$                    |
| Equilibrium       | —                      |   | $2.5 - 2S$                 |                      | $S$                                     |   | $S$                     |

Assume that  $2.5 - 2S \approx 2.5$  because  $K_{\text{overall}}$  is so small.

$$K_{\text{overall}} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{I}^-]}{[\text{NH}_3]^2} = \frac{[S][S]}{[2.5 - S]^2} = \frac{[S][S]}{[2.5]^2} = 1.411 \times 10^{-9}$$

$$S = 9.3908 \times 10^{-5} = \mathbf{9.4 \times 10^{-5} M}$$

- 19.73 Solubility-Product: 
$$\text{Cr}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + 3 \text{OH}^-(\text{aq}) \quad K_{\text{sp}} = 6.3 \times 10^{-31}$$



At pH 13.0, the pOH is 1.0 and  $[\text{OH}^-] = 10^{-1.0} = 0.1 \text{ M}$ .

$$K_{\text{overall}} = \frac{[\text{Cr}(\text{OH})_4^-]}{[\text{OH}^-]} = \frac{[S]}{[0.1]} = 0.504$$

$$S = [\text{Cr}(\text{OH})_4^-] = 0.0504 = \mathbf{0.05 M}$$

- 19.74  $pK_a = -\log K_a = -\log 6.3 \times 10^{-8} = 7.200659$  (unrounded). The  $K_a$  comes from Appendix C; it is  $K_{a2}$  for phosphoric acid.

$$pH = pK_a + \log \left( \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \right)$$

$$7.00 = 7.200659 + \log \left( \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \right)$$

$$-0.200659 = \log \left( \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \right)$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.63000 \text{ (unrounded)}$$

Since they are equimolar,  $\frac{V_{HPO_4^{2-}}}{V_{H_2PO_4^-}} = 0.63000$

and  $V_{HPO_4^{2-}} + V_{H_2PO_4^-} = 100. \text{ mL}$

so  $(0.63000)V_{H_2PO_4^-} + V_{H_2PO_4^-} = 100. \text{ mL}$

$V_{H_2PO_4^-} = \mathbf{61 \text{ mL}}$  and  $V_{HPO_4^{2-}} = \mathbf{39 \text{ mL}}$

- 19.75 This is because  $K_a$  depends on temperature (like all other equilibrium constants). In this case, since the pH drops as the temperature increases,  $K_a$  must increase with temperature, indicating that the dissociation reaction is endothermic.

- 19.76  $H_2SO_4$  is a strong acid and will be completely ionized:  $H_2SO_4(aq) + 2 H_2O(l) \rightarrow SO_4^{2-}(aq) + 2 H_3O^+(aq)$   
Calculate the moles of  $H_3O^+(aq)$  from the  $H_2SO_4$  in the  $8.0 \times 10^3 \text{ lb}$  of water and then the amount of sodium acetate trihydrate ( $NaC_2H_3O_2 \cdot 3 H_2O$ ) that will be required to neutralize that amount of  $H_3O^+(aq)$ .

$$(8.0 \times 10^3 \text{ lb water}) \left( \frac{1 \text{ kg}}{2.205 \text{ lb}} \right) \left( \frac{1000 \text{ g}}{1 \text{ kg}} \right) = 3.628118 \times 10^6 \text{ g } H_2O$$

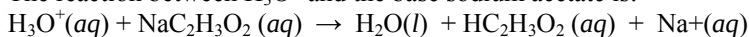
$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

$$10 \text{ ppm} = \frac{\text{mass of } H_2SO_4}{3.628118 \times 10^6 \text{ g}} \times 10^6$$

$$\text{Mass of } H_2SO_4 = 36.28118 \text{ g}$$

$$\text{Moles of } H_3O^+ = (36.28118 \text{ g } H_2SO_4) \left( \frac{1 \text{ mol } H_2SO_4}{98.09 \text{ g } H_2SO_4} \right) \left( \frac{2 \text{ mol } H_3O^+}{1 \text{ mol } H_2SO_4} \right) = 0.7398 \text{ mol } H_3O^+$$

The reaction between  $H_3O^+$  and the base sodium acetate is:



lb of  $NaC_2H_3O_2 \cdot 3 H_2O$  required to neutralize the  $H_2SO_4$  =

$$(0.7398 \text{ mol } H_3O^+) \left( \frac{1 \text{ mol } NaC_2H_3O_2 \cdot 3H_2O}{1 \text{ mol } H_3O^+} \right) \left( \frac{136.08 \text{ g } NaC_2H_3O_2 \cdot 3H_2O}{1 \text{ mol } NaC_2H_3O_2 \cdot 3H_2O} \right) \left( \frac{1 \text{ kg}}{1000 \text{ g } NaC_2H_3O_2 \cdot 3H_2O} \right) \left( \frac{2.205 \text{ lb}}{1 \text{ kg}} \right) \\ = 0.22198 \text{ lb } NaC_2H_3O_2 \cdot 3 H_2O$$

Now consider the acetic acid. Calculate the amount of acetic acid in  $8.0 \times 10^3 \text{ lb}$  or  $3.628118 \times 10^6 \text{ g } H_2O$ .

$$\text{Mol of acetic acid} = (3.628118 \times 10^6 \text{ g } H_2O) \left( \frac{0.015\%}{100\%} \right) \left( \frac{1 \text{ mol } HC_2H_3O_2}{60.05 \text{ g } HC_2H_3O_2} \right) = 9.0627 \text{ mol}$$

Find the amount of  $\text{C}_2\text{H}_3\text{O}_2^-$  necessary to maintain a pH of 5.

$$\text{pH} = \text{pK}_a + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

$$5.0 = 4.7447 + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[9.0627 \text{ mol}]} \right)$$

$$0.2552725 = \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[9.0627 \text{ mol}]} \right)$$

$$1.8 = \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[9.0627 \text{ mol}]}$$

16.31286 mol of  $\text{C}_2\text{H}_3\text{O}_2^-$  ( $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$ ) will be required to maintain the pH

lb of  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$  required =

$$(16.31286 \text{ mol } \text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}) \left( \frac{136.08 \text{ g } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}}{1 \text{ mol } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}} \right) \left( \frac{1 \text{ kg}}{1000 \text{ g}} \right) \left( \frac{2.205 \text{ lb}}{1 \text{ kg}} \right) = 4.89478 \text{ lb}$$

Total amount of  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$  required =  $0.22198 \text{ lb} + 4.89478 \text{ lb} = 5.11676 = \mathbf{5.1 \text{ lb}}$

- 19.77 The minimum urate ion concentration necessary to cause a deposit of sodium urate is determined by the  $K_{\text{sp}}$  for the salt. Convert solubility in g/100. mL to molar solubility and calculate  $K_{\text{sp}}$ . Substituting  $[\text{Na}^+]$  and  $K_{\text{sp}}$  into the ion-product expression allows one to find  $[\text{Ur}^-]$ .

Molar solubility of NaUr:

$$[\text{NaUr}] = \left( \frac{0.085 \text{ g NaUr}}{100. \text{ mL}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left( \frac{1 \text{ mol NaUr}}{190.10 \text{ mol NaUr}} \right) = 4.47133 \times 10^{-3} \text{ M NaUr (unrounded)}$$

$$4.47133 \times 10^{-3} \text{ M NaUr} = [\text{Na}^+] = [\text{Ur}^-]$$

$$K_{\text{sp}} = [\text{Na}^+][\text{Ur}^-] = (4.47133 \times 10^{-3})(4.47133 \times 10^{-3}) = 1.999279 \times 10^{-5} \text{ M (unrounded)}$$

When  $[\text{Na}^+] = 0.15 \text{ M}$ :

$$K_{\text{sp}} = 1.999279 \times 10^{-5} \text{ M} = [0.15][\text{Ur}^-]$$

$$[\text{Ur}^-] = 1.33285 \times 10^{-4} \text{ (unrounded)}$$

The minimum urate ion concentration that will cause precipitation of sodium urate is  $\mathbf{1.3 \times 10^{-4} \text{ M}}$ .

- 19.78  $\text{CdS}(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Cd}^{2+}(aq) + \text{HS}^-(aq) + \text{OH}^-(aq)$   $K_{\text{sp}} = 1.0 \times 10^{-24}$  (Appendix)

(The sulfide ion  $\text{S}^{2-}$  reacts in water to form  $\text{HS}^-$  and  $\text{OH}^-$ )

$$K_{\text{sp}} = 1.0 \times 10^{-24} = [\text{Cd}^{2+}][\text{HS}^-][\text{OH}^-] = \text{S}^3$$

$$\text{S} = \mathbf{1.0 \times 10^{-8} \text{ M}}$$

- 19.79 a) The solubility equilibrium for KCl is:  $\text{KCl}(s) \rightleftharpoons \text{K}^+(aq) + \text{Cl}^-(aq)$

$$K_{\text{sp}} = [\text{K}^+][\text{Cl}^-] = (3.7)(3.7) = 13.69 = \mathbf{14}$$

b) Determine the total concentration of chloride ion in each beaker after the HCl has been added. This requires the moles originally present and the moles added.

Original moles from the KCl:

$$\text{Moles } \text{K}^+ = \text{Moles } \text{Cl}^- = \left( \frac{3.7 \text{ mol KCl}}{1 \text{ L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100. \text{ mL}) \left( \frac{1 \text{ mol } \text{Cl}^- \text{ ion}}{1 \text{ mol KCl}} \right) = 0.37 \text{ mol } \text{Cl}^-$$

Original moles from the 6.0 M HCl:

$$\text{Moles } \text{Cl}^- = \left( \frac{6.0 \text{ mol HCl}}{1 \text{ L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100. \text{ mL}) \left( \frac{1 \text{ mol } \text{Cl}^-}{1 \text{ mol HCl}} \right) = 0.60 \text{ mol } \text{Cl}^-$$

This results in  $(0.37 + 0.60) \text{ mol} = 0.97 \text{ mol } \text{Cl}^-$

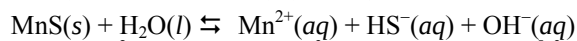
Original moles from the 12 M HCl:

$$\text{Moles } \text{Cl}^- = \left( \frac{12 \text{ mol HCl}}{1 \text{ L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100. \text{ mL}) \left( \frac{1 \text{ mol } \text{Cl}^-}{1 \text{ mol HCl}} \right) = 1.2 \text{ mol } \text{Cl}^-$$

This results in  $(0.37 + 1.2) \text{ mol} = 1.57 \text{ mol Cl}^-$  (unrounded)  
 Volume of mixed solutions =  $(100. \text{ mL} + 100. \text{ mL}) (10^{-3} \text{ L/1 mL}) = 0.200 \text{ L}$   
 After the mixing:  
 $[\text{K}^+] = (0.37 \text{ mol K}^+)/ (0.200 \text{ L}) = 1.85 \text{ M K}^+$  (unrounded)  
 From  $6.0 \text{ M HCl}$ :  
 $[\text{Cl}^-] = (0.97 \text{ mol Cl}^-)/ (0.200 \text{ L}) = 4.85 \text{ M Cl}^-$  (unrounded)  
 From  $12 \text{ M HCl}$ :  
 $[\text{Cl}^-] = (1.57 \text{ mol Cl}^-)/ (0.200 \text{ L}) = 7.85 \text{ M Cl}^-$  (unrounded)  
 Determine a  $Q_{\text{sp}}$  value to see if  $K_{\text{sp}}$  is exceeded. If  $Q < K_{\text{sp}}$ , nothing will precipitate.  
 From  $6.0 \text{ M HCl}$   
 $Q_{\text{sp}} = [\text{K}^+][\text{Cl}^-] = (1.85)(4.85) = 8.9725 = 9.0 < 14$ , so no KCl will precipitate.  
 From  $12 \text{ M HCl}$   
 $Q_{\text{sp}} = [\text{K}^+][\text{Cl}^-] = (1.85)(7.85) = 14.5225 = 15 > 14$ , so KCl will precipitate.  
 The mass of KCl that will precipitate when  $12 \text{ M HCl}$  is added:  
 Equal amounts of K and Cl will precipitate. Let  $x$  be the molarity change.  
 $K_{\text{sp}} = [\text{K}^+][\text{Cl}^-] = (1.85 - x)(7.85 - x) = 13.69$   
 $x = 0.088697657 = 0.09$  This is the change in the molarity of each of the ions.  
 Mass KCl =  $\left( \frac{0.088697657 \text{ mol K}^+}{\text{L}} \right) (0.200 \text{ L}) \left( \frac{1 \text{ mol KCl}}{1 \text{ mol K}^+} \right) \left( \frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} \right) = 1.32248 = \mathbf{1 \text{ g KCl}}$

19.80 Determine the solubility of MnS:

$$S = \left( \frac{4.7 \times 10^{-4} \text{ g MnS}}{100 \text{ mL}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left( \frac{1 \text{ mol MnS}}{87.01 \text{ g MnS}} \right) = 5.4016779 \times 10^{-5} \text{ M (unrounded)}$$



$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{HS}^-][\text{OH}^-] = S^3 = (5.4016779 \times 10^{-5})^3 = 1.5761 \times 10^{-13} = \mathbf{1.6 \times 10^{-13}}$$

19.81 a) Use the Henderson-Hasselbalch equation.  $K_{\text{a}1} = 4.5 \times 10^{-7}$  (From Appendix C)  
 $\text{pK}_{\text{a}} = -\log K_{\text{a}} = -\log(4.5 \times 10^{-7}) = 6.34679$  (unrounded)

$$\text{pH} = \text{pK}_{\text{a}} + \log \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$7.40 = 6.34679 + \log \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$1.05321 = \log \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 11.3034235 \text{ (unrounded)}$$

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = 0.0884688 = \mathbf{0.088}$$

b) Use the Henderson-Hasselbalch equation.

$$\text{pH} = \text{pK}_{\text{a}} + \log \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$7.20 = 6.34679 + \log \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$0.85321 = \log \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 7.131978 \text{ (unrounded)}$$

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = 0.14021 = \mathbf{0.14}$$

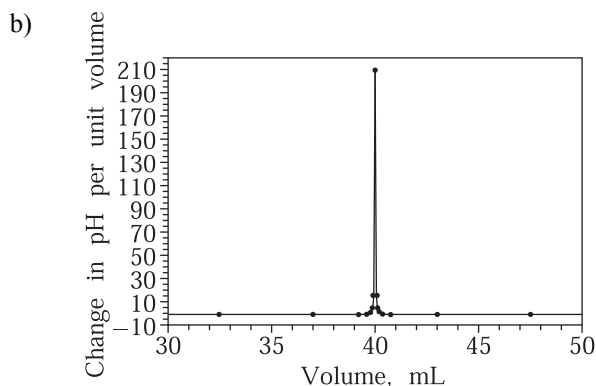
- 19.82 The equilibrium is:  $\text{Ca}_5(\text{PO}_4)_3\text{OH(s)} \rightleftharpoons 5 \text{Ca}^{2+}(\text{aq}) + 3 \text{PO}_4^{3-}(\text{aq}) + \text{OH}^-(\text{aq})$   
 $K_{\text{sp}} = 6.8 \times 10^{-37} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{OH}^-] = (5\text{S})^5(3\text{S})^3(\text{S}) = 84375 \text{ S}^9$   
 $\text{S} = 2.7166443 \times 10^{-5} = 2.7 \times 10^{-5} \text{ M}$   
Solubility =  $(2.7166443 \times 10^{-5} \text{ mol/L}) (502.32 \text{ g/mol}) = 0.013646248 = \mathbf{0.014 \text{ g/L Ca}_5(\text{PO}_4)_3\text{OH}}$

The equilibrium is:  $\text{Ca}_5(\text{PO}_4)_3\text{F(s)} \rightleftharpoons 5 \text{Ca}^{2+}(\text{aq}) + 3 \text{PO}_4^{3-}(\text{aq}) + \text{F}^-(\text{aq})$   
 $K_{\text{sp}} = 1.0 \times 10^{-60} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{F}^-] = (5\text{S})^5(3\text{S})^3(\text{S}) = 84375 \text{ S}^9$   
 $\text{S} = 6.1090861 \times 10^{-8} = 6.1 \times 10^{-8} \text{ M}$   
Solubility =  $(6.1090861 \times 10^{-8} \text{ mol/L}) (504.31 \text{ g/mol})$   
 $= 3.0808732 \times 10^{-5} = \mathbf{3.1 \times 10^{-5} \text{ g/L Ca}_5(\text{PO}_4)_3\text{F}}$

- 19.83 An indicator changes color when the buffer component ratio of the two forms of the indicator changes from a value greater than 1 to a value less than 1. The pH at which the ratio equals 1 is equal to  $\text{p}K_{\text{a}}$ . The midpoint in the pH range of the indicator is a good estimate of the  $\text{p}K_{\text{a}}$  of the indicator.  
 $\text{p}K_{\text{a}} = (3.4 + 4.8) / 2 = 4.1 \quad K_{\text{a}} = 10^{-4.1} = 7.943 \times 10^{-5} = \mathbf{8 \times 10^{-5}}$

- 19.84 a) A spreadsheet will help you to quickly calculate  $\Delta\text{pH} / \Delta V$  and average volume for each data point. At the equivalence point, the pH changes drastically when only a small amount of base is added, therefore,  $\Delta\text{pH} / \Delta V$  is at a maximum at the equivalence point.

| V(mL) | pH    | $\frac{\Delta\text{pH}}{\Delta V}$ | $V_{\text{average}}(\text{mL})$ |
|-------|-------|------------------------------------|---------------------------------|
| 0.00  | 1.00  |                                    |                                 |
| 10.00 | 1.22  | 0.022                              | 5.00                            |
| 20.00 | 1.48  | 0.026                              | 15.00                           |
| 30.00 | 1.85  | 0.037                              | 25.00                           |
| 35.00 | 2.18  | 0.066                              | 32.50                           |
| 39.00 | 2.89  | 0.18                               | 37.00                           |
| 39.50 | 3.20  | 0.62                               | 39.25                           |
| 39.75 | 3.50  | 1.2                                | 39.63                           |
| 39.90 | 3.90  | 2.67                               | 39.83                           |
| 39.95 | 4.20  | 6                                  | 39.93                           |
| 39.99 | 4.90  | 18                                 | 39.97                           |
| 40.00 | 7.00  | 200                                | 40.00                           |
| 40.01 | 9.40  | 200                                | 40.01                           |
| 40.05 | 9.80  | 10                                 | 40.03                           |
| 40.10 | 10.40 | 10                                 | 40.08                           |
| 40.25 | 10.50 | 0.67                               | 40.18                           |
| 40.50 | 10.79 | 1.2                                | 40.38                           |
| 41.00 | 11.09 | 0.60                               | 40.75                           |
| 45.00 | 11.76 | 0.17                               | 43.00                           |
| 50.00 | 12.05 | 0.058                              | 47.50                           |
| 60.00 | 12.30 | 0.025                              | 55.00                           |
| 70.00 | 12.43 | 0.013                              | 65.00                           |
| 80.00 | 12.52 | 0.009                              | 75.00                           |



Maximum slope (equivalence point) is at  $V = 40.00 \text{ mL}$

- 19.85 a) The equilibrium is:  $\text{MCl}_2(\text{s}) \rightleftharpoons \text{M}^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq})$ . The ion-product expression is  $K_{\text{sp}} = [\text{M}^{2+}][\text{Cl}^{-}]^2$ . Based on the picture, the ion concentrations are:

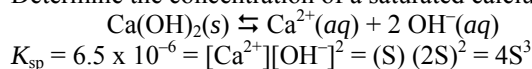
$$[\text{M}^{2+}] = \frac{(3 \text{ spheres}) \left( \frac{1.0 \times 10^{-6} \text{ mol}}{1 \text{ sphere}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)}{250.0 \text{ mL}} = 1.2 \times 10^{-5} \text{ M}$$

$$[\text{Cl}^{-}] = \frac{(10 \text{ spheres}) \left( \frac{1.0 \times 10^{-6} \text{ mol}}{1 \text{ sphere}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)}{250.0 \text{ mL}} = 4.0 \times 10^{-5} \text{ M}$$

$$K_{\text{sp}} = [\text{M}^{2+}][\text{Cl}^{-}]^2 = [1.2 \times 10^{-5}][4.0 \times 10^{-5}]^2 = \mathbf{1.9 \times 10^{-14}}$$

b)  $\text{M}^{2+}$  is a common ion for  $\text{M}(\text{NO}_3)_2$  and  $\text{MCl}_2$ . If  $\text{M}(\text{NO}_3)_2$  is added to the solution,  $[\text{M}^{2+}]$  is increased and, according to Le Châtelier's principle, the solubility equilibrium will shift to the left, precipitating more  $\text{MCl}_2$ . The number of  $\text{Cl}^{-}$  particles decreases, the mass of  $\text{MCl}_2$  increases, and the  $K_{\text{sp}}$  value remains the same.

- 19.86 Check to see if the concentration of  $\text{Ca}(\text{OH})_2$  exceeds the  $K_{\text{sp}}$ .  
 $M \text{ Ca}(\text{OH})_2 = (6.5 \times 10^{-9} \text{ mol Ca}(\text{OH})_2) / (10.0 \text{ L}) = 6.5 \times 10^{-10} \text{ M Ca}(\text{OH})_2$   
 Determine the concentration of a saturated calcium hydroxide solution from the  $K_{\text{sp}}$ .



$$K_{\text{sp}} = 6.5 \times 10^{-6} = [\text{Ca}^{2+}][\text{OH}^{-}]^2 = (\text{S})(2\text{S})^2 = 4\text{S}^3$$

$$\text{S} = \sqrt[3]{\frac{6.5 \times 10^{-6}}{4}} = 0.01175667 = 0.012 \text{ M}$$

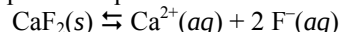
Thus, the solution is less than saturated so the  $K_{\text{sp}}$  does not affect the concentration of  $\text{Ca}(\text{OH})_2$ .

$$M \text{ OH}^{-} \text{ from } \text{Ca}(\text{OH})_2 = (6.5 \times 10^{-10} \text{ M Ca}(\text{OH})_2) (2 \text{ mol OH}^{-} / 1 \text{ mol Ca}(\text{OH})_2) = 1.3 \times 10^{-9} \text{ M OH}^{-}$$

Pure water has  $1 \times 10^{-7} \text{ M OH}^{-}$ , thus the contribution from the  $\text{Ca}(\text{OH})_2$  is not significant.

pH of pure water = **7.0**

- 19.87 The ion-product equilibrium reaction is:



$\text{F}^{-}$  is a weak base with the following equilibrium reaction:



(I) Pure water: There is no common ion effect and the pH is neutral.

(II) 0.01M HF: Because of the common ion effect, less  $\text{CaF}_2$  would dissolve in this solution than in pure water.

(III) 0.01M NaOH: additional  $\text{OH}^{-}$  ions shift the base equilibrium reaction to the left, producing more  $\text{F}^{-}$ . The additional  $\text{F}^{-}$  shifts the ion-product equilibrium to the left so less  $\text{CaF}_2$  would dissolve.

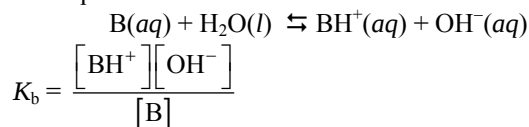
(IV) 0.01M HCl:  $\text{H}^{+}$  ions remove  $\text{OH}^{-}$  ions from solution so the base equilibrium reaction shifts to the right, consuming  $\text{F}^{-}$ . This shifts the ion-product equilibrium to the right so that more  $\text{CaF}_2$  dissolves in this solution than in pure water.

(V) 0.01M Ca(OH)<sub>2</sub>: Because of the common ion effect, less CaF<sub>2</sub> would dissolve in this solution than in pure water. The presence of OH<sup>-</sup> ions also removes H<sup>+</sup> ions and decreases the ability to form HF, thus, decreasing the solubility of CaF<sub>2</sub>.

a) **0.01M HCl**

b) **0.01M Ca(OH)<sub>2</sub>**

19.88 The equation that describes the behavior of a weak base in water is:

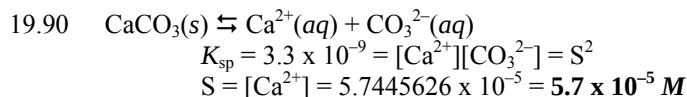
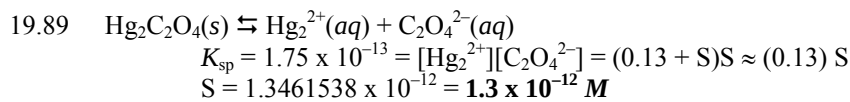


$$-\log K_b = -\log \frac{[BH^+][OH^-]}{[B]}$$

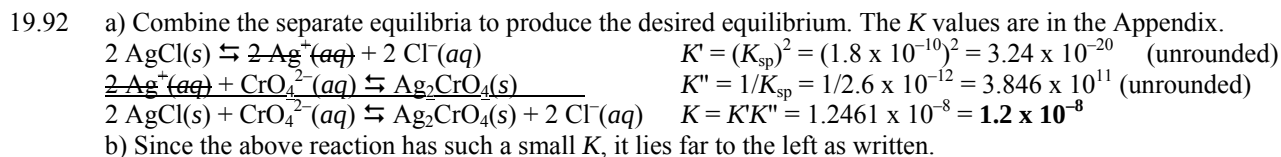
$$-\log K_b = -\log \frac{[BH^+]}{[B]} - \log [OH^-]$$

$$pK_b = -\log \frac{[BH^+]}{[B]} + pOH$$

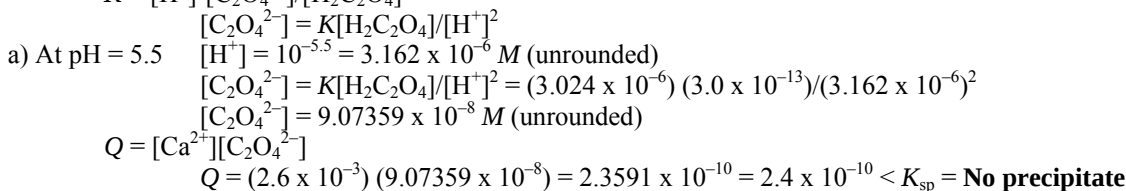
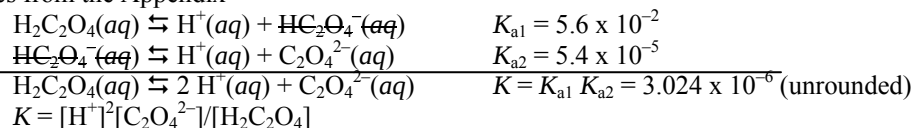
$$pOH = pK_b + \log \frac{[BH^+]}{[B]}$$



19.91 Refer to Figure 19.5. Litmus paper indicates the pH is below 7. The result from thymol blue, which turns yellow at a pH above 2.5, indicates that the pH is above 2.5. Bromphenol blue is the best indicator as it is green in a fairly narrow range of 3.5 < pH < 4. Methyl red turns red below a pH of 4.3. Therefore, a reasonable estimate for the rainwater pH is **3.5 to 4**.



19.93  $K$  values from the Appendix



- b) At pH = 7.0  $[H^+] = 10^{-7.0} = 1 \times 10^{-7} M$   
 $[C_2O_4^{2-}] = K[H_2C_2O_4]/[H^+]^2 = (3.024 \times 10^{-6})(3.0 \times 10^{-13})/(1 \times 10^{-7})^2$   
 $[C_2O_4^{2-}] = 9.072 \times 10^{-5} M$  (unrounded)  
 $Q = (2.6 \times 10^{-3})(9.072 \times 10^{-5}) = 2.35872 \times 10^{-7} = 2.4 \times 10^{-7} > K_{sp} = \text{Precipitate forms}$
- c) The higher pH would favor precipitation.

19.94 a)  $K_a = 6.8 \times 10^{-4} = \frac{[H_3O^+][F^-]}{[HF]} = \frac{x^2}{0.2500 - x} \approx \frac{x^2}{0.2500}$

$$x = [H_3O^+] = 0.0130384 M \text{ (unrounded)}$$

$$pH = -\log [H_3O^+] = -\log (0.0130384 M) = 1.8847757 = \mathbf{1.88}$$

b) Volume =  $(35.00 \text{ mL}) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{0.2500 \text{ mol HF}}{1 \text{ L}} \right) \left( \frac{1 \text{ mol NaOH}}{1 \text{ mol HF}} \right) \left( \frac{1 \text{ L}}{0.1532 \text{ mol NaOH}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$   
 $= 57.11488 = \mathbf{57.11 \text{ mL NaOH}}$

c) Moles HF (original) =  $(35.00 \text{ mL}) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{0.2500 \text{ mol HF}}{1 \text{ L}} \right) = 8.750 \times 10^{-3} \text{ mol HF}$

$$\text{Moles NaOH added} = ((57.11488 - 0.50) \text{ mL}) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{0.1532 \text{ mol NaOH}}{1 \text{ L}} \right) = 8.673 \times 10^{-3} \text{ mol NaOH}$$

Moles  $F^-$  formed = moles NaOH

$$\text{Moles HF remaining} = (8.750 \times 10^{-3} - 8.673 \times 10^{-3}) \text{ mol} = 7.7 \times 10^{-5} \text{ mol HF}$$

$$\text{Volume of solution} = (35.00 + 57.11488 - 0.50) (10^{-3} \text{ L}/1 \text{ mL}) = 0.09161 \text{ L}$$

$$[HF] = (7.7 \times 10^{-5} \text{ mol HF})/(0.09161 \text{ L}) = 0.0008405 M \text{ HF}$$

$$[F^-] = (8.673 \times 10^{-3} \text{ mol F}^-)/(0.09161 \text{ L}) = 0.09467 M F^-$$

$$pK_a = -\log K_a = -\log 6.8 \times 10^{-4} = 3.1675 \text{ (unrounded)}$$

$$pH = pK_a + \log [F^-]/[HF]$$

$$= 3.1675 + \log (0.09467)/(8.405 \times 10^{-4})$$

$$= 5.21917 = \mathbf{5.22}$$

- d) At this point there are  $8.750 \times 10^{-3} \text{ mol}$  of  $F^-$  in  $(35.00 + 57.11488) \text{ mL}$  of solution.

The molarity of  $F^-$  is

$$M F^- = \left( \frac{8.750 \times 10^{-3} \text{ mol } F^-}{(35.00 + 57.11488) \text{ mL}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.09499 M F^- \text{ (unrounded)}$$

$$K_b = K_w/K_a = (1.0 \times 10^{-14})/(6.8 \times 10^{-4}) = 1.470588 \times 10^{-11} \text{ (unrounded)}$$

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{x^2}{0.09499 - x} \approx \frac{x^2}{0.09499} = 1.470588 \times 10^{-11}$$

$$x = [OH^-] = 1.1819 \times 10^{-6} M \text{ (unrounded)}$$

$$[H_3O^+] = K_w/[OH^-] = (1.0 \times 10^{-14})/(1.1819 \times 10^{-6}) = 8.4609527 \times 10^{-9} M \text{ (unrounded)}$$

$$pH = -\log [H_3O^+] = -\log (8.4609527 \times 10^{-9} M) = 8.07258 = \mathbf{8.07}$$

e) Moles NaOH excess =  $(0.50 \text{ mL}) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{0.1532 \text{ mol NaOH}}{1 \text{ L}} \right) = 7.66 \times 10^{-5} \text{ mol NaOH (unrounded)}$

$$\text{Volume of solution} = (35.00 + 57.11488 + 0.50) (10^{-3} \text{ L}/1 \text{ mL}) = 0.09261 \text{ L}$$

$$[OH^-] = (7.66 \times 10^{-5} \text{ mol F}^-)/(0.09261 \text{ L}) = 8.271 \times 10^{-4} M \text{ OH}^- \text{ (unrounded)}$$

The excess  $OH^-$  will predominate and essentially control the pH.

$$[H_3O^+] = K_w/[OH^-] = (1.0 \times 10^{-14})/(8.271 \times 10^{-4}) = 1.2090436 \times 10^{-11} M \text{ (unrounded)}$$

$$pH = -\log [H_3O^+] = -\log (1.2090436 \times 10^{-11} M) = 10.917558 = \mathbf{10.92}$$

- 19.95 a) The formula is  $\text{Hg}_2\text{Cl}_2$  which simplifies to the empirical formula **HgCl**.  
 b) The equilibrium is:  $\text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{Hg}_2^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq})$   $K_{\text{sp}} = 1.5 \times 10^{-18}$   
 $K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^{-}]^2 = (\text{S})(2\text{S})^2 = 4\text{S}^3 = 1.5 \times 10^{-18}$   
 $\text{S} = 7.2112478 \times 10^{-7} = \mathbf{7.2 \times 10^{-7} M}$   
 c)  $[\text{Hg}_2^{2+}] = K_{\text{sp}}/[\text{Cl}^{-}]^2 =$

$$\frac{1.5 \times 10^{-18}}{\left[ \left( \frac{0.20 \text{ lb NaCl}}{\text{gal}} \right) \left( \frac{1 \text{ kg}}{2.205 \text{ lb}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \right) \left( \frac{1 \text{ mol Cl}^{-}}{1 \text{ mol NaCl}} \right) \left( \frac{1 \text{ gal}}{4 \text{ qt}} \right) \left( \frac{1.057 \text{ qt}}{1 \text{ L}} \right) \right]^2}$$

$$= 8.9174129 \times 10^{-18} = \mathbf{8.9 \times 10^{-18} M \text{ Hg}_2^{2+}}$$

- d) Use the value of S for a saturated solution (see part (b)).

$$\text{Mass} = \left( \frac{7.2112478 \times 10^{-7} \text{ mol Hg}_2\text{Cl}_2}{\text{L}} \right) \left( \frac{1 \text{ L}}{10^{-3} \text{ m}^3} \right) \left( \frac{10^3 \text{ m}}{1 \text{ km}} \right)^3 (4900 \text{ km}^3) \left( \frac{472.1 \text{ g Hg}_2\text{Cl}_2}{1 \text{ mol Hg}_2\text{Cl}_2} \right)$$

$$= 1.6681707 \times 10^{12} = \mathbf{1.7 \times 10^{12} g \text{ Hg}_2\text{Cl}_2}$$

- e) Use the value determined in part (c).

$$\text{Mass} = \left( \frac{8.9174129 \times 10^{-18} \text{ mol Hg}_2^{2+}}{\text{L}} \right) \left( \frac{1 \text{ mol Hg}_2\text{Cl}_2}{1 \text{ mol Hg}_2^{2+}} \right) \left( \frac{1 \text{ L}}{10^{-3} \text{ m}^3} \right) \left( \frac{10^3 \text{ m}}{1 \text{ km}} \right)^3 (4900 \text{ km}^3) \left( \frac{472.1 \text{ g Hg}_2\text{Cl}_2}{1 \text{ mol Hg}_2\text{Cl}_2} \right)$$

$$= 20.62856 = \mathbf{21 g \text{ Hg}_2\text{Cl}_2}$$

- 19.96 To find the volume of rain, first convert the inches to yards and find the volume in  $\text{yd}^3$ . Then convert units to  $\text{cm}^3$  and on to L.

$$(10.0 \text{ acres}) \left( \frac{4.840 \times 10^3 \text{ yd}^2}{1 \text{ acre}} \right) \left( \frac{36 \text{ in}}{1 \text{ yd}} \right)^2 (1.00 \text{ in}) \left( \frac{2.54 \text{ cm}}{1 \text{ in}} \right)^3 \left( \frac{1 \text{ mL}}{1 \text{ cm}^3} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 1.0279015 \times 10^6 \text{ L (unrounded)}$$

- a) At  $\text{pH} = 4.20$ ,  $[\text{H}_3\text{O}^{+}] = 10^{-4.20} = 6.3095734 \times 10^{-5} M$  (unrounded)

$$\text{Mol H}_3\text{O}^{+} = (6.3095734 \times 10^{-5} M) (1.0279015 \times 10^6 \text{ L}) = 64.8562 = \mathbf{65 \text{ mol}}$$

$$\text{b) Volume} = (10.0 \text{ acres}) \left( \frac{4.840 \times 10^3 \text{ yd}^2}{1 \text{ acre}} \right) \left( \frac{36 \text{ in}}{1 \text{ yd}} \right)^2 (10.0 \text{ ft}) \left( \frac{12 \text{ in}}{1 \text{ ft}} \right) \left( \frac{2.54 \text{ cm}}{1 \text{ in}} \right)^3 \left( \frac{1 \text{ mL}}{1 \text{ cm}^3} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right)$$

$$= 1.23348 \times 10^8 \text{ L (unrounded)}$$

$$\text{Total volume of lake after rain} = 1.23348 \times 10^8 \text{ L} + 1.0279015 \times 10^6 \text{ L} = 1.243759 \times 10^8 \text{ L (unrounded)}$$

$$[\text{H}_3\text{O}^{+}] = 64.8562 \text{ mol H}_3\text{O}^{+} / 1.243759 \times 10^8 \text{ L} = 5.214531 \times 10^{-7} M$$

$$\text{pH} = -\log(5.214531 \times 10^{-7}) = 6.2827847 = \mathbf{6.28}$$

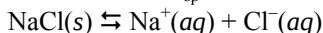
- c) Each mol of  $\text{H}_3\text{O}^{+}$  requires one mole of  $\text{HCO}_3^{-}$  for neutralization.

$$\text{Mass} = (64.8562 \text{ mol H}_3\text{O}^{+}) \left( \frac{1 \text{ mol HCO}_3^{-}}{1 \text{ mol H}_3\text{O}^{+}} \right) \left( \frac{61.02 \text{ g HCO}_3^{-}}{1 \text{ mol HCO}_3^{-}} \right) = 3.97575 \times 10^3 = \mathbf{4.0 \times 10^3 g \text{ HCO}_3^{-}}$$

- 19.97 The molarity of a saturated NaCl solution must be found.

$$M \text{ NaCl} = \left( \frac{317 \text{ g NaCl}}{\text{L}} \right) \left( \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \right) = 5.42436687 M \text{ NaCl (unrounded)}$$

Determine the  $K_{\text{sp}}$  from the molarity just calculated.



$$K_{\text{sp}} = [\text{Na}^{+}][\text{Cl}^{-}] = \text{S}^2 = (5.42436687)^2 = 29.42375594 = 29.4$$

$$\text{Moles of Cl}^{-} \text{ initially} = \left( \frac{5.42436687 \text{ mol NaCl}}{\text{L}} \right) (0.100 \text{ L}) \left( \frac{1 \text{ mol Cl}^{-}}{1 \text{ mol NaCl}} \right) = 0.54236687 \text{ mol Cl}^{-} \text{ (unrounded)}$$

This is the same as the moles of  $\text{Na}^{+}$  in the solution.

$$\text{Moles of Cl}^{-} \text{ added} = \left( \frac{7.85 \text{ mol HCl}}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (25.5 \text{ mL}) \left( \frac{1 \text{ mol Cl}^{-}}{1 \text{ mol HCl}} \right) = 0.200175 \text{ mol Cl}^{-} \text{ (unrounded)}$$

0.100 L of saturated solution contains 0.542 mol each  $\text{Na}^+$  and  $\text{Cl}^-$ , to which you are adding 0.2 mol of additional  $\text{Cl}^-$  from  $\text{HCl}$ .

Volume of mixed solutions =  $0.100 \text{ L} + (25.5 \text{ mL}) (10^{-3} \text{ L/1 mL}) = 0.1255 \text{ L}$  (unrounded)

Molarity of  $\text{Cl}^-$  in mixture =  $[(0.54236687 + 0.200175) \text{ mol Cl}^-] / (0.1255 \text{ L}) = 5.916668 \text{ M Cl}^-$  (unrounded)

Molarity of  $\text{Na}^+$  in mixture =  $(0.54236687 \text{ mol Na}^+) / (0.1255 \text{ L}) = 4.321648 \text{ M Na}^+$  (unrounded)

Determine a  $Q$  value and compare this value to the  $K_{\text{sp}}$  to determine if precipitation will occur.

$$Q_{\text{sp}} = [\text{Na}^+][\text{Cl}^-] = (4.321648)(5.916668) = 25.569756 = 25.6$$

Since  $Q_{\text{sp}} < K_{\text{sp}}$ , no  $\text{NaCl}$  will precipitate.

19.98 In both cases the equilibrium is:  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = S^2$$

At  $10^\circ\text{C}$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = S^2 = 4.4 \times 10^{-9}$$

$$S = 6.6332495 \times 10^{-5} = \mathbf{6.6 \times 10^{-5} \text{ M CaCO}_3}$$

At  $30^\circ\text{C}$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = S^2 = 3.1 \times 10^{-9}$$

$$S = 5.5677643 \times 10^{-5} = \mathbf{5.6 \times 10^{-5} \text{ M CaCO}_3}$$

19.99 a) For the solution to be a buffer, both  $\text{HA}$  and  $\text{A}^-$  must be present in the solution. This situation occurs in **A** and **D**.

b) Box A

The amounts of  $\text{HA}$  and  $\text{A}^-$  are equal.

$$\text{pH} = \text{p}K_{\text{a}} + \log \left( \frac{[\text{A}^-]}{[\text{HA}]}} \right) \quad \left( \frac{[\text{A}^-]}{[\text{HA}]} \right) = 1 \text{ when the amounts of HA and A}^- \text{ are equal}$$

$$\text{pH} = \text{p}K_{\text{a}} + \log 1$$

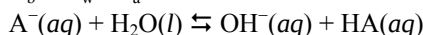
$$\text{pH} = \text{p}K_{\text{a}} = -\log (4.5 \times 10^{-5}) = 4.346787 = \mathbf{4.35}$$

Box B

Only  $\text{A}^-$  is present at a concentration of  $0.10 \text{ M}$ .

The  $K_{\text{b}}$  for  $\text{A}^-$  is needed.

$$K_{\text{b}} = K_{\text{w}} / K_{\text{a}} = 1.0 \times 10^{-14} / 4.5 \times 10^{-5} = 2.222 \times 10^{-10} \text{ (unrounded)}$$



|          |        |   |   |
|----------|--------|---|---|
| Initial: | 0.10 M | 0 | 0 |
|----------|--------|---|---|

|         |    |    |    |
|---------|----|----|----|
| Change: | -x | -x | -x |
|---------|----|----|----|

|              |          |   |   |
|--------------|----------|---|---|
| Equilibrium: | 0.10 - x | x | x |
|--------------|----------|---|---|

$$K_{\text{b}} = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = 2.222 \times 10^{-10}$$

$$K_{\text{b}} = \frac{[x][x]}{[0.10 - x]} = 2.222 \times 10^{-10} \quad \text{Assume that } x \text{ is small compared to } 0.10.$$

$$K_{\text{b}} = 2.222 \times 10^{-10} = \frac{(x)(x)}{(0.10)}$$

$$x = 4.7138095 \times 10^{-6} \text{ M OH}^- \text{ (unrounded)}$$

Check assumption:  $(4.7138095 \times 10^{-6} / 0.10) \times 100\% = 0.005\%$  error, so the assumption is valid.

$$[\text{H}_3\text{O}^+] = K_{\text{w}} / [\text{OH}^-] = (1.0 \times 10^{-14}) / (4.7138095 \times 10^{-6}) = 2.1214264 \times 10^{-9} \text{ M H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.1214264 \times 10^{-9}) = 8.67337 = \mathbf{8.67}$$

Box C

This is a  $0.10 \text{ M HA}$  solution. The hydrogen ion, and hence the pH, can be determined from the  $K_{\text{a}}$ .

|             |                        |   |                                |                      |                                   |   |                         |
|-------------|------------------------|---|--------------------------------|----------------------|-----------------------------------|---|-------------------------|
|             | $\text{HA}(\text{aq})$ | + | $\text{H}_2\text{O}(\text{l})$ | $\rightleftharpoons$ | $\text{H}_3\text{O}^+(\text{aq})$ | + | $\text{A}^-(\text{aq})$ |
| Initial     | 0.10                   |   | —                              |                      | 0                                 |   | 0                       |
| Change      | -x                     |   |                                |                      | +x                                |   | +x                      |
| Equilibrium | 0.10 - x               |   |                                |                      | x                                 |   | x                       |

(The  $\text{H}_3\text{O}^+$  contribution from water has been neglected.)

$$K_a = 4.5 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$K_a = 4.5 \times 10^{-5} = \frac{(x)(x)}{(0.10 - x)} \quad \text{Assume that } x \text{ is small compared to } 0.10.$$

$$K_a = 4.5 \times 10^{-5} = \frac{(x)(x)}{(0.10)}$$

$$[\text{H}_3\text{O}^+] = x = 2.12132 \times 10^{-3} \text{ (unrounded)}$$

Check assumption:  $(2.12132 \times 10^{-3} / 0.10) \times 100\% = 2\%$  error, so the assumption is valid.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.12132 \times 10^{-3}) = 2.67339 = \mathbf{2.67}$$

Box D

This is a buffer with a ratio of  $[\text{A}^-] / [\text{HA}] = 5/3$ .

Use the Henderson-Hasselbalch equation for this buffer.

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

$$\text{pH} = -\log (4.5 \times 10^{-5}) + \log \left[ \frac{5}{3} \right] = 4.568636 = \mathbf{4.57}$$

c) The initial stage in the titration would only have HA present. The amount of HA will decrease, and the amount of  $\text{A}^-$  will increase until only  $\text{A}^-$  remains. The sequence will be: **C, A, D, and B**.

d) At the equivalence point, all the HA will have reacted with the added base. This occurs in scene **B**.

19.100 a) The dissolution of MX will produce equal amounts of  $\text{M}^{2+}$  and  $\text{X}^{2-}$ . The only way unequal amounts of these ions could be present would be either if one of the ions were already present or if one of the ions were removed from the solution. Distilled water will neither add nor remove ions, thus the  $\text{M}^{2+}$  and  $\text{X}^{2-}$  must be equal; this is in box **B**.

b) Using box B; there are  $4(2.5 \times 10^{-6} M) = 1.0 \times 10^{-5} M$  for each ion.

$$K_{sp} = [\text{M}^{2+}][\text{X}^{2-}] = (1.0 \times 10^{-5})(1.0 \times 10^{-5}) = \mathbf{1.0 \times 10^{-10}}$$

c) The addition of  $\text{Na}_2\text{X}$  would increase the  $\text{X}^{2-}$ . There will be more  $\text{X}^{2-}$  than  $\text{M}^{2+}$ . This occurs in box **C**.

d) Lowering the pH will protonate some  $\text{X}^{2-}$ . This will decrease the  $\text{X}^{2-}$  concentration, thus,  $\text{X}^{2-} < \text{M}^{2+}$ . This occurs in box **A**.