CHAPTER 19 IONIC EQUILIBRIA IN AQUEOUS SYSTEMS

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

$$HF(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + F^-(aq)$$

to shift to the left, away from the excess of F^- the common ion.

19.4 a) **Buffer C** has equal, high concentrations of both HA and A^-. It has the highest buffering capacity.
b) **All** of the buffers have the same pH range. The practical buffer range of pH = pKa ± 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 H_3O^+ because the added H_3O^+ reacts with the base of the buffer. The net result is that the concentration of H_3O^+ 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 $[HA]/[A^-]$ will change less.

19.7 Only (c) has an affect on the buffer capacity. In theory, **any** conjugate pair (of any 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 pK_a (formic) = 3.74; pK_a (acetic) = 4.74. Formic acid would be the buffer choice, since its 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*)	$CH_3CH_2COOH(aq)$	+ $H_2O(l)$	$\leftrightarrows$	$CH_3CH_2COO^-(aq)$	+ $H_3O^+(aq)$
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.

$$K_a = \frac{\left[H_3O^+\right]\left[CH_3CH_2COO^-\right]}{\left[CH_3CH_2COOH\right]} = \frac{[x][0.35 + x]}{[0.15 - x]} = \frac{[x][0.35]}{[0.15]} = 1.3 \text{ x } 10^{-5}$$

$$[H_3O^+] = K_a \frac{\left[CH_3CH_2COOH\right]}{\left[CH_3CH_2COO^-\right]} = \left(1.3 \text{ x } 10^{-5}\right)\left(\frac{0.15}{0.35}\right) = 5.57143 \text{ x } 10^{-6} = \mathbf{5.6 \text{ x } 10^{-6}}\ \boldsymbol{M}$$

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

$$\text{pH} = -\log [H_3O^+] = -\log (5.57143 \text{ x } 10^{-6}) = 5.2540 = \mathbf{5.25}$$

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

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

$$\text{pH} = 4.886 + \log\left(\frac{[CH_3CH_2COO^-]}{[CH_3CH_2COOH]}\right) = 4.886 + \log\left(\frac{[0.35]}{[0.15]}\right)$$

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

19.11 CA = C_6H_5COOH CB = $C_6H_5COO^-$ Neglect Na^+. Assume + x and – x are negligible.

$$K_a = \frac{\left[H_3O^+\right]\left[CB\right]}{\left[CA\right]} = \frac{[x][0.28+x]}{[0.33-x]} = \frac{[x][0.28]}{[0.33]} = 6.3 \text{ x } 10^{-5}$$

$$[H_3O^+] = K_a \frac{\left[CA\right]}{\left[CA\right]} = (6.3 \text{ x } 10^{-5})\ (0.33/0.28) = 7.425 \text{ x } 10^{-5} = \mathbf{7.4 \text{ x } 10^{-5}}\ \boldsymbol{M}$$

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

$$\text{pH} = -\log [H_3O^+] = -\log (7.425 \text{ x } 10^{-5}) = 4.1293 = \mathbf{4.13}$$

19.12 The buffer components are phenol, C_6H_5OH, and phenolate ion, $C_6H_5O^-$. The sodium ions are ignored because they are not involved in the buffer. Calculate K_a from pK_a and set up the problem with a reaction table.

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

Concentration (M)	$C_6H_5OH(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$C_6H_5O^-(aq)$	+	$H_3O^+(aq)$
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.

$$K_a = \frac{\left[H_3O^+\right]\left[C_6H_5O^-\right]}{\left[C_6H_5OH\right]} = \frac{[x][1.3 + x]}{[1.2 - x]} = \frac{[x][1.3]}{[1.2]} = 1.0 \text{ x } 10^{-10}$$

$$[H_3O^+] = K_a \frac{\left[C_6H_5OH\right]}{\left[C_6H_5O^-\right]} = \left(1.0 \text{ x } 10^{-10}\right)\left(\frac{1.2}{1.3}\right) = 9.23077 \text{ x } 10^{-11}\ M$$

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

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

Verify the pH using the Henderson-Hasselbalch equation:

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

$$\text{pH} = 10.00 + \log\left(\frac{[C_6H_5O^-]}{[C_6H_5OH]}\right) = 10.00 + \log\left(\frac{[1.3]}{[1.2]}\right)$$

pH = 10.03

19.13 $K_a = 10^{-pK_a} = 10^{-9.24} = 5.7543993 \text{ x } 10^{-10}$ (unrounded)

$CA = H_3BO_3$ $CB = H_2BO_3^-$ Neglect Na^+. Assume $+x$ and $-x$ are negligible.

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

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

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

$pH = -\log [H_3O^+] = -\log (8.4210722 \text{ x } 10^{-11}) = 10.07463261 =$ **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.

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

Concentration (M)	$NH_3(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$NH_4+(aq)$	+	$OH^-(aq)$
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.

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

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

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

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

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

$14.00 = pH + pOH$

$pH = 14.00 - pOH = 14.00 - 4.52815 = 9.4718 =$ **9.47**

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

$14 = pK_a + pK_b$

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

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

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

pH = 9.47

19.15 $K_b = 10^{-pK_b} = 10^{-3.35} = 4.4668359 \text{ x } 10^{-4}$ (unrounded)

$CB = CH_3NH_2$ $CA = CH_3NH_3^+$ Neglect Cl^-. Assume $+x$ and $-x$ are negligible.

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

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

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

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

$pH = 14.00 - pOH = 14.00 - 3.429181246 = 10.57081875 =$ **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.

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

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

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

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

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

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

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

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

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

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

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

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.

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

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

$$3.35 = pK_a - 0.1249387$$

$$pK_a = 3.474939 = 3.47$$

Determine the moles of conjugate acid (HA) and conjugate base (A^-) using (M)(V) = moles

Moles HA = (0.5000 L) (0.2000 mol HA/L) = 0.1000 mol HA

Moles A^- = (0.5000 L) (0.1500 mol A^-/L) = 0.07500 mol A^-

The reaction is:

	$\text{HA}(aq)$	+	$\text{NaOH}(aq)$	$\rightarrow$	$\text{Na}^+(aq)$	+ $\text{A}^-(aq)$	+	$\text{H}_2\text{O}(l)$
Initial:	0.1000 mol		0.0015 mol			0.07500 mol		
Change:	– 0.0015 mol		–0.0015 mol			+0.0015 mol		
Final:	0.0985 mol		0 mol			0.0765 mol		

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

Then

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

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

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

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

19.19 Determine the 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.

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

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

$$8.88 = \text{p}K_\text{a} + 0.20411998$$

$$\text{p}K_\text{a} = 8.67588 = 8.68$$

Determine the moles of conjugate acid (BH^+) and conjugate base (B) using (M)(V) = moles.

Moles BH^+ = (0.25 L) (0.25 mol BH^+/L) = 0.0625 mol BH^+

Moles B = (0.25 L) (0.40 mol B/L) = 0.10 mol B

The reaction is:

	$B(aq)$	+	$HCl(aq)$	→	$BH^+(aq)$	$+\ Cl^-(aq)$	+	$H_2O(l)$
Initial:	0.10 mol		0.0020 mol		0.0625 mol			
Change:	– 0.0020 mol		–0.0020 mol		+0.0020 mol			
Final:	0.098 mol		0 mol		0.0645 mol			

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

Then

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

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

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

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

19.20 a) The hydrochloric acid will react with the sodium acetate, $NaC_2H_3O_2$, to form acetic acid, $HC_2H_3O_2$:

$$HCl + NaC_2H_3O_2 \rightarrow HC_2H_3O_2 + NaCl$$

Calculate the number of moles of HCl and $NaC_2H_3O_2$. All of the HCl will be consumed to form $HC_2H_3O_2$, and the number of moles of $C_2H_3O_2^-$ will decrease.

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

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

	HCl	+	$NaC_2H_3O_2$	→	$HC_2H_3O_2$	+	$NaCl$
Initial:	0.092208 mol		0.200 mol		0 mol		
Change:	–0.092208 mol		–0.092208 mol		+0.092208 mol		
Final:	0 mol		0.107792 mol		0.092208 mol		

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

$$[HC_2H_3O_2] = \frac{0.092208 \text{ mol}}{0.704 \text{ L}} = 0.1309773\ M \text{ (unrounded)}$$

$$[C_2H_3O_2^-] = \frac{0.107792 \text{ mol}}{0.704 \text{ L}} = 0.1531136\ M \text{ (unrounded)}$$

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

$$\text{pH} = pK_a + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

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

b) The addition of base would increase the pH, so the new pH is (4.81 + 0.15) = 4.96.
The new $[C_2H_3O_2^-]/[HC_2H_3O_2]$ ratio is calculated using the Henderson-Hasselbalch equation.

$$\text{pH} = pK_a + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

$$4.96 = 4.744727495 + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

$$0.215272505 = \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

$$\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.64162 \text{ (unrounded)}$$

From part (a), we know that $[HC_2H_3O_2] + [C_2H_3O_2^-] = (0.1309773\ M + 0.1531136\ M) = 0.2840909\ M$. Although the *ratio* of $[C_2H_3O_2^-]$ to $[HC_2H_3O_2]$ 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 $[C_2H_3O_2^-]/[HC_2H_3O_2] = 1.64162$ and $[HC_2H_3O_2] + [C_2H_3O_2^-] = 0.2840909\ M$, solve for $[C_2H_3O_2^-]$ and substitute into the second equation.

$[C_2H_3O_2^-] = 1.64162\ [HC_2H_3O_2]$ and $[HC_2H_3O_2] + 1.64162\ [HC_2H_3O_2] = 0.2840909\ M$

$[HC_2H_3O_2] = 0.1075441\ M$ and $[C_2H_3O_2^-] = 0.176547\ M$

Moles of $C_2H_3O_2^-$ needed = (0.176547 mol $C_2H_3O_2^-$/L) (0.500 L) = 0.0882735 mol (unrounded)

Moles of $C_2H_3O_2^-$ initially = (0.1531136 mol $C_2H_3O_2^-$/L) (0.500 L) = 0.0765568 mol (unrounded)

This would require the addition of (0.0882735 mol – 0.0765568 mol) = 0.0117167 mol $C_2H_3O_2^-$ (unrounded)

The KOH added reacts with $HC_2H_3O_2$ to produce additional $C_2H_3O_2^-$:

$$HC_2H_3O_2 + KOH \rightarrow C_2H_3O_2^- + K^+ + H_2O(l)$$

To produce 0.0117167 mol $C_2H_3O_2^-$ would require the addition of 0.0117167 mol KOH.

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

19.21 a) The sodium hydroxide will react with the sodium bicarbonate, $NaHCO_3$, to form carbonate ion, CO_3^{2-}:

$$NaOH + NaHCO_3 \rightarrow 2\ Na^+ + CO_3^{2-} + H_2O$$

Calculate the number of moles of NaOH and $NaHCO_3$. All of the NaOH will be consumed to form CO_3^{2-}, and the number of moles of $NaHCO_3$ will decrease. The HCO_3^- is the important part of $NaHCO_3$.

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

$$\text{Initial moles } HCO_3^- = \left(\frac{0.050 \text{ mol } NaHCO_3}{\text{L}}\right)\left(\frac{1 \text{ mol } HCO_3^-}{1 \text{ mol } NaHCO_3}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(50.0 \text{ mL})$$

$$= 0.0025 \text{ mol } HCO_3^-$$

	$NaOH$ +	$NaHCO_3 \rightarrow$	$2\ Na^+$ +	CO_3^{2-} +	H_2O
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	

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

$$[HCO_3^-] = \frac{0.00143\text{ mol}}{0.0607\text{ L}} = 0.023558484\ M\text{ (unrounded)}$$

$$[CO_3^{2-}] = \frac{0.00107\text{ mol}}{0.0607\text{ L}} = 0.017627677\ M\text{ (unrounded)}$$

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

$$pH = pK_a + \log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right)$$

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

b) The addition of acid would decrease the pH, so the new pH is (10.20 – 0.07) = 10.13

The new $[CO_3^{2-}]/[HCO_3^-]$ ratio is calculated using the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right)$$

$$10.13 = 10.32790214 + \log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right)$$

$$-0.19790214 = \log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right)$$

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = 0.63401\text{ (unrounded)}$$

From part (a), we know that $[HCO_3^-] + [CO_3^{2-}] = (0.023558484\ M + 0.017627677\ M) = 0.041185254\ M$. Although the *ratio* of $[CO_3^{2-}]$ to $[HCO_3^-]$ 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 $[CO_3^{2-}]/[HCO_3^-] = 0.63401$ and $[HCO_3^-] + [CO_3^{2-}] = 0.041185254\ M$, solve for $[CO_3^{2-}]$ and substitute into the second equation.

$[CO_3^{2-}] = 0.63401\ [HCO_3^-]$ and $[HCO_3^-] + 0.63401\ [HCO_3^-] = 0.041185254\ M$

$[HCO_3^-] = 0.025205019\ M$ and $[CO_3^{2-}] = 0.015980234\ M$ (unrounded)

Moles of HCO_3^- needed = (0.025205019 mol HCO_3^-/L) (10^{-3}L/1 mL) (25.0 mL)

= 0.0006301255 mol (unrounded)

Moles of HCO_3^- initially = (0.023558484 mol HCO_3^-/L) (10^{-3}L/1 mL) (25.0 mL)

= 0.000588962 mol (unrounded)

This would require the addition of (0.0006301255 mol – 0.000588962 mol)

= 0.0000411635 mol HCO_3^- (unrounded)

The HCl added reacts with CO_3^{2-} to produce additional HCO_3^-:

$$CO_3^{2-} + HCl \rightarrow HCO_3^- + Cl^-$$

To produce 0.0000411635 mol HCO_3^- would require the addition of 0.0000411635 mol HCl.

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

19.22 Select conjugate pairs with K_a values close to the desired $[H_3O^+]$.

a) For pH ≈ 4.5, $[H_3O^+] = 10^{-4.5} = 3.2 \text{ x } 10^{-5}\ M$. Some good selections are the $HOOC(CH_2)_4COOH$/ $HOOC(CH_2)_4COOH^-$ conjugate pair with K_a equal to $3.8 \text{ x } 10^{-5}$ or $C_6H_5CH_2COOH/C_6H_5CH_2COO^-$ conjugate pair with K_a equal to $4.9 \text{ x } 10^{-5}$. From the base list, the $C_6H_5NH_2/C_6H_5NH_3^+$ conjugate pair comes close with $K_a = 1.0 \text{ x } 10^{-14}/4.0 \text{ x } 10^{-10} = 2.5 \text{ x } 10^{-5}$.

b) For pH ≈ 7.0, $[H_3O^+] = 10^{-7.0} = 1.0 \text{ x } 10^{-7}\ M$. Two choices are the $H_2PO_4^-/HPO_4^{2-}$ conjugate pair with K_a of $6.3 \text{ x } 10^{-8}$ and the $H_2AsO_4^-/HAsO_4^{2-}$ conjugate pair with K_a of $1.1 \text{ x } 10^{-7}$.

19.23 Select conjugate pairs that have K_a or K_b values close to the desired $[H_3O^+]$ or $[OH^-]$.

a) For $[H_3O^+] \approx 1 \text{ x } 10^{-9}\ M$, the $HOBr/OBr^-$ conjugate pair comes close with K_a equal to $2.3 \text{ x } 10^{-9}$. From the base list, $K_b = 1.0 \text{ x } 10^{-14}/1 \text{ x } 10^{-9} = 1 \text{ x } 10^{-5}$, the NH_3/NH_4^+ conjugate pair comes close with $K_b = 1.76 \text{ x } 10^{-5}$.

b) For $[OH^-] \approx 3 \text{ x } 10^{-5}\ M$, the NH_3/NH_4^+ conjugate pair comes close; also, it is possible to choose $K_a = 1.0 \text{ x } 10^{-14}/3 \text{ x } 10^{-5} = 3.3 \text{ x } 10^{-10}$, the $C_6H_5OH/C_6H_5O^-$ comes close with $K_a = 1.0 \text{ x } 10^{-10}$.

19.24 The value of the K_a from the appendix: $K_a = 2.9 \text{ x } 10^{-8}$

$pK_a = -\log 2.9 \text{ x } 10^{-8} = 7.5376$ (unrounded)

Use the Henderson-Hasselbalch equation to determine the pH.

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

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 $NaOH + HClO \rightarrow Na^+ + ClO^- + H_2O$

The original moles of HClO and OCl^- are both = (0.100 mol/L) (L) = 0.100 mol

	NaOH	+	HClO	→	Na^+	+	ClO^-	+	H_2O
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: $K_a = 6.3 \text{ x } 10^{-8}$ (we are using K_{a2} since we are dealing with the equilibrium in which the second hydrogen ion is being lost).

Determine the pK_a using $pK_a = -\log 6.3 \text{ x } 10^{-8} = 7.200659451$ (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 ± 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:

$$OH^-(aq) + H_3PO_4(aq) \rightarrow H_2PO_4^-(aq) + H_2O(l) \qquad K_{a1} = 7.2 \times 10^{-3}$$

$$OH^-(aq) + H_2PO_4^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(l) \qquad K_{a2} = 6.3 \times 10^{-8}$$

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.

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

Determine the pK_a using pK_a = –log 7.2 x 10^{-3} = 2.142668

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

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 ± 1. The pK_a of cresol red is –log (3.5 x 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 ± 1. The pK_a of ethyl red is –log (3.8 x 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:

Concentration, *M*	$COOH^-(aq)$	+	$H_2O(l)$	⇆	⇇$COOH(aq)$	+	$OH^-(aq)$
Initial:	0.050 M		—		0		0
Change:	$-x$				$+x$		$+x$
Equilibrium:	$0.050 - x$				x		x

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

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

$[OH^-]$ = x = 1.666673 x 10^{-6} *M*
pOH = –log (1.666673 x 10^{-6}) = 5.7781496 (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 x 10^{-14})/(4.4 x 10^{-4}) = 2.2727 x 10^{-11} (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.*

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]} = \frac{x^2}{0.050 - x} = \frac{x^2}{0.050} = 2.2727 \text{ x } 10^{-11}$$

$x = [H_3O^+]$ = 1.0659971 x 10^{-6} *M* (unrounded)
pH = –log $[H_3O^+]$ = –log (1.0659971 x 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 H_3O^+ (from HCl) by OH^- (from NaOH):

$HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$ or, omitting spectator ions:

$H_3O^+(aq) + OH^-(aq) \rightarrow 2\ H_2O(l)$

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 mol HCl / L) (10^{-3} L / 1 mL) (40.00 mL) = 4.000×10^{-3} mol HCl

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

pH = –log (0.1000 *M*) = **1.0000**

b) Determine the moles of NaOH added:

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

	$HCl(aq)$	+	$NaOH(aq)$	→	$H_2O(l)$	+	$NaCl(aq)$
Initial:	4.000×10^{-3} mol		2.500×10^{-3} mol		—		0
Change:	-2.500×10^{-3} mol		-2.500×10^{-3} mol		—		$+2.500 \times 10^{-3}$ mol
Final:	1.500×10^{-3} mol		0				2.500×10^{-3} mol

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

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

pH = –log (0.02307) = **1.6368**

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

c) Determine the moles of NaOH added:

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

	$HCl(aq)$	+	$NaOH(aq)$	→	$H_2O(l)$	+	$NaCl(aq)$
Initial:	4.000×10^{-3} mol		4.900×10^{-3} mol		—		0
Change:	-3.900×10^{-3} mol		-3.900×10^{-3} mol		—		$+3.900 \times 10^{-3}$ mol
Final:	1.000×10^{-4} mol		0				3.900×10^{-3} mol

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

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

pH = –log (0.0012658) = **2.898**

d) Determine the moles of NaOH added:

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

	$HCl(aq)$	+	$NaOH(aq)$	→	$H_2O(l)$	+	$NaCl(aq)$
Initial:	4.000×10^{-3} mol		3.990×10^{-3} mol		—		0
Change:	-3.990×10^{-3} mol		-3.990×10^{-3} mol		—		$+3.990 \times 10^{-3}$ mol
Final:	1.000×10^{-5} mol		0				3.990×10^{-3} mol

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

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

pH = –log (0.000125156) = **3.903**

e) Determine the moles of NaOH added:

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

	$HCl(aq)$	+	$NaOH(aq)$	→	$H_2O(l)$	+	$NaCl(aq)$
Initial:	4.000×10^{-3} mol		4.000×10^{-3} mol		—		0
Change:	-4.000×10^{-3} mol		-4.000×10^{-3} mol		—		$+4.000 \times 10^{-3}$ mol
Final:	0		0				4.000×10^{-3} 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:

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

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

	$HCl(aq)$ +	$NaOH(aq)$ →	$H_2O(l)$ +	$NaCl(aq)$
Initial:	4.000×10^{-3} mol	4.010×10^{-3} mol	—	0
Change:	-4.000×10^{-3} mol	-4.000×10^{-3} mol	—	$+4.000 \times 10^{-3}$ mol
Final:	0	1.000×10^{-5} mol		4.000×10^{-3} mol

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

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

pOH = –log (0.00012484) = 3.9036 (unrounded)

pH = 14.00 – pOH = 14.00 – 3.9036 = 10.09637 = **10.10**

g) Determine the moles of NaOH added:

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

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

	$HCl(aq)$ +	$NaOH(aq)$ →	$H_2O(l)$ +	$NaCl(aq)$
Initial:	4.000×10^{-3} mol	5.000×10^{-3} mol	—	0
Change:	-4.000×10^{-3} mol	-4.000×10^{-3} mol	—	$+4.000 \times 10^{-3}$ mol
Final:	0	1.000×10^{-3} mol		4.000×10^{-3} mol

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

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

pOH = –log (0.011111) = 1.95424 (unrounded)

pH = 14.00 – pOH = 14.00 – 1.95424 = 12.04576 = **12.05**

19.40 The reaction occurring in the titration is the neutralization of OH^- (from KOH) by H_3O^+ (from HBr):

$HBr(aq) + KOH(aq) \rightarrow H_2O(l) + KBr(aq)$

$H_3O^+(aq) + OH^-(aq) \rightarrow 2\ H_2O(l)$

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 mol KOH/L) (10^{-3} L/1 mL) (30.00 mL)
= 3.000×10^{-3} mol KOH

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

pOH = –log (0.1000 *M*) = 1.0000

pH = 14.00 – pOH = 14.00 – 1.0000 = **13.00**

b) Determine the moles of HBr added:

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

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

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

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

pOH = –log (0.03333) = 1.4772

pH = 14.00 – pOH = 14.00 – 1.4772 = 12.5228 = **12.52**

c) Determine the moles of HBr added:

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

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

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

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

pOH = –log (0.0016949) = 2.7708559

pH = 14.00 – pOH = 14.00 – 2.7708559 = 11.2291441 = **11.23**

d) Determine the moles of HBr added:

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

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

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

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

pOH = –log (0.000166944) = 3.7774268

pH = 14.00 – pOH = 14.00 – 3.7774268 = 10.2225732 = **10.2**

e) Determine the moles of HBr added:

Moles of HBr = (0.1000 mol HBr/L) (10^{-3} L/1 mL) (30.00 mL) = 3.000 x 10^{-3} 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 titrations; 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:

Moles of HBr = (0.1000 mol HBr/L) (10^{-3} L/1 mL) (30.10 mL) = 3.010 x 10^{-3} mol HBr

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

The volume of the solution at this point is [(30.00 + 30.10) mL] (10^{-3} L/1 mL) = 0.06010 L

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

pH = –log (0.000166389) = 3.778874 = **3.8**

g) Determine the moles of HBr added:

Moles of HBr = (0.1000 mol HBr/L) (10^{-3} L/1 mL) (40.00 mL) = 4.000 x 10^{-3} mol HBr

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

The volume of the solution at this point is [(30.00 + 40.00) mL] (10^{-3} L/1 mL) = 0.07000 L

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

pH = –log (0.0142857) = 1.845098 = **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^-). 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^-.

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

(0.1000 mol HBut/L) (10^{-3} L/1 mL) (20.00 mL) = 2.000 x 10^{-3} mol HBut

a) At 0 mL of base added, the concentration of [H_3O^+] is dependent on the dissociation of butanoic acid:

	Hbut	+	H_2O	⇆	H_3O^+	+	But^-
Initial:	0.100 *M*						0
Change:	$-x$						$+x$
Equilibrium:	$0.100 - x$						x

$$K_a = \frac{\left[H_3O^+\right]\left[But^-\right]}{\left[HBut\right]} = \frac{x^2}{0.1000 - x} = \frac{x^2}{0.1000} = 1.54 \text{ x } 10^{-5}$$

x = [H_3O^+] = 1.2409673 x 10^{-3} *M* (unrounded)

pH = –log [H_3O^+] = –log (1.2409673 x 10^{-3}) = 2.9062 = **2.91**

b) Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10^{-3} L/1 mL) (10.00 mL) = 1.000 x 10^{-3} mol NaOH

The NaOH will react with an equal amount of the acid, and 1.000 x 10^{-3} mol HBut will remain. An equal number of moles of But^- will form.

	HBut(*aq*)	+	NaOH(*aq*)	→	$H_2O(l)$	+	$But^-(aq)$	+	$Na^+(aq)$
Initial:	2.000 x 10^{-3} mol		1.000 x 10^{-3} mol		—		0		—
Change:	–1.000 x 10^{-3} mol		–1.000 x 10^{-3} mol		—		+1.000 x 10^{-3} mol		—
Final:	1.000 x 10^{-3} mol		0				1.000 x 10^{-3} mol		

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

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

The molarity of the But^- formed is (1.000 x 10^{-3} mol But^-)/(0.03000 L) = 0.03333 *M* (unrounded)

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H_2O	⇆	H_3O^+	+	But^-
Initial:	0.03333 *M*						0.03333 *M*
Change:	$-x$						$+x$
Equilibrium:	$0.03333 - x$						$0.03333 + x$

$$K_a = \frac{\left[H_3O^+\right]\left[But^-\right]}{\left[HBut\right]} = \frac{x\left(0.0333 + x\right)}{0.03333 - x} = \frac{x\left(0.03333\right)}{0.03333} = 1.54 \text{ x } 10^{-5}$$

$x = [H_3O^+] = 1.54 \text{ x } 10^{-5}$ *M* (unrounded)

pH = $-\log [H_3O^+] = -\log (1.54 \text{ x } 10^{-5}) = 4.812479 =$ **4.81**

c) Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10^{-3} L/1 mL) (15.00 mL) = 1.500 x 10^{-3} mol NaOH

The NaOH will react with an equal amount of the acid, and 5.00 x 10^{-4} mol HBut will remain, and 1.500 x 10^{-3} moles of But^- will form.

	HBut(*aq*)	+	NaOH(*aq*)	→	H_2O(*l*)	+	But^-(*aq*)	+	Na^+(*aq*)
Initial:	2.000 x 10^{-3} mol		1.500 x 10^{-3} mol		—		0		—
Change:	–1.500 x 10^{-3} mol		–1.500 x 10^{-3} mol		—		+1.500 x 10^{-3} mol		—
Final:	5.000 x 10^{-4} mol		0				1.500 x 10^{-3} mol		

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

The molarity of the excess HBut is (5.00 x 10^{-4} mol HBut)/(0.03500 L) = 0.0142857 *M* (unrounded)

The molarity of the But^- formed is (1.500 x 10^{-3} mol But^-) (0.03500 L) = 0.0428571 *M* (unrounded)

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H_2O	⇆	H_3O^+	+	But^-
Initial:	0.0142857 *M*						0.0428571 *M*
Change:	–*x*						+*x*
Equilibrium:	0.0142857 – *x*						0.0428571 + *x*

$$K_a = \frac{\left[H_3O^+\right]\left[But^-\right]}{\left[HBut\right]} = \frac{x\left(0.0428571 + x\right)}{0.0142857 - x} = \frac{x\left(0.0428571\right)}{0.0142857} = 1.54 \text{ x } 10^{-5}$$

$x = [H_3O^+] = 5.1333 \text{ x } 10^{-6}$ *M* (unrounded)

pH = $-\log [H_3O^+] = -\log (5.1333 \text{ x } 10^{-6}) = 5.2896 =$ **5.29**

d) Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10^{-3} L/1 mL) (19.00 mL) = 1.900 x 10^{-3} mol NaOH

The NaOH will react with an equal amount of the acid, and 1.00 x 10^{-4} mol HBut will remain, and 1.900 x 10^{-3} moles of But^- will form.

	HBut(*aq*)	+	NaOH(*aq*)	→	H_2O(*l*)	+	But^-(*aq*)	+	Na^+(*aq*)
Initial:	2.000 x 10^{-3} mol		1.900 x 10^{-3} mol		—		0		—
Change:	–1.900 x 10^{-3} mol		–1.900 x 10^{-3} mol		—		+1.900 x 10^{-3} mol		—
Final:	1.000 x 10^{-4} mol		0				1.900 x 10^{-3} mol		

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

The molarity of the excess HBut is (1.00 x 10^{-4} mol HBut)/(0.03900 L) = 0.0025641 *M* (unrounded)

The molarity of the But^- formed is (1.900 x 10^{-3} mol But^-)/(0.03900 L) = 0.0487179 *M* (unrounded)

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H_2O	⇆	H_3O^+	+	But^-
Initial:	0.0025641 *M*						0.0487179 *M*
Change:	–*x*						+*x*
Equilibrium:	0.0025641 – *x*						0.0487179 + *x*

$$K_a = \frac{\left[H_3O^+\right]\left[But^-\right]}{\left[HBut\right]} = \frac{x\left(0.0487179 + x\right)}{0.0025641 - x} = \frac{x\left(0.0487179\right)}{0.0025641} = 1.54 \text{ x } 10^{-5}$$

$x = [H_3O^+] = 8.1052631 \text{ x } 10^{-7}$ *M* (unrounded)

pH = $-\log [H_3O^+] = -\log (8.1052631 \text{ x } 10^{-7}) = 6.09123 =$ **6.09**

e) Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10^{-3} L/1 mL) (19.95 mL) = 1.995 x 10^{-3} mol NaOH

The NaOH will react with an equal amount of the acid, and 5 x 10^{-6} mol HBut will remain, and 1.995 x 10^{-3} moles of But^- will form.

	$HBut(aq)$	+	$NaOH(aq)$	→	$H_2O(l)$	+	$But^-(aq)$	+	$Na^+(aq)$
Initial:	2.000×10^{-3} mol		1.995×10^{-3} mol		—		0		—
Change:	-1.995×10^{-3} mol		-1.995×10^{-3} mol		—		$+1.995 \times 10^{-3}$ mol		—
Final:	5.000×10^{-6} mol		0				1.995×10^{-3} mol		

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

The molarity of the excess HBut is (5×10^{-6} mol HBut)/(0.03995 L) = 0.000125156 M (unrounded)

The molarity of the But^- formed is (1.995×10^{-3} mol But^-)/(0.03995 L) = 0.0499374 M (unrounded)

Using a reaction table for the equilibrium reaction of HBut:

	$HBut$	+	H_2O	⇆	H_3O^+	+	But^-
Initial:	0.000125156 M						0.0499374 M
Change:	$-x$						$+x$
Equilibrium:	$0.000125156 - x$						$0.0499374 + x$

$$K_a = \frac{[H_3O^+][But^-]}{[HBut]} = \frac{x(0.0499374 + x)}{0.000125156 - x} = \frac{x(0.0499374)}{0.000125156} = 1.54 \times 10^{-5}$$

$x = [H_3O^+] = 3.859637 \times 10^{-8}$ M (unrounded)

pH = $-\log [H_3O^+] = -\log (3.859637 \times 10^{-8}) = 7.41345 =$ **7.41**

f) Determine the moles of NaOH added:

Moles of NaOH = (0.1000 mol NaOH/L) (10^{-3} L/1 mL) (20.00 mL) = 2.000×10^{-3} mol NaOH

The NaOH will react with an equal amount of the acid, and 0 mol HBut will remain, and 2.000×10^{-3} moles of But^- will form. This is the equivalence point.

	$HBut(aq)$	+	$NaOH(aq)$	→	$H_2O(l)$	+	$But^-(aq)$	+	$Na^+(aq)$
Initial:	2.000×10^{-3} mol		2.000×10^{-3} mol		—		0		—
Change:	-2.000×10^{-3} mol		-2.000×10^{-3} mol		—		$+2.000 \times 10^{-3}$ mol		—
Final:	0		0				2.000×10^{-3} mol		

The K_b of But^- is now important.

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

The molarity of the But^- formed is (2.000×10^{-3} mol But^-)/(0.04000 L) = 0.05000 M (unrounded)

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

Using a reaction table for the equilibrium reaction of But^-:

	But^-	+	H_2O	⇆	$HBut$	+	OH^-
Initial:	0.05000 M				0		0
Change:	$-x$				$+x$		$+x$
Equilibrium:	$0.05000 - x$				x		x

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

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

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

pH = 14.00 – pOH = 14.00 – 5.244275575 = 8.755724425 = **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^{-3} L/1 mL) (20.05 mL) = 2.005×10^{-3} mol NaOH

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

	$HBut(aq)$	+	$NaOH(aq)$	→	$H_2O(l)$	+	$But^-(aq)$	+	$Na^+(aq)$
Initial:	2.000×10^{-3} mol		2.005×10^{-3} mol		—		0		—
Change:	-2.000×10^{-3} mol		-2.000×10^{-3} mol		—		$+2.000 \times 10^{-3}$ mol		—
Final:	0		5.000×10^{-6} mol				2.000×10^{-3} mol		

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

The molarity of the excess OH^- is (5×10^{-6} mol OH^-)/(0.04005 L) = 1.2484×10^{-4} M (unrounded)

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

pH = 14.00 – pOH = 14.00 – 3.9036 = 10.0964 = **10.10**

h) Determine the moles of NaOH added:

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

The NaOH will react with an equal amount of the acid, 0 mol HBut will remain, and 5.00 x 10^{-4} moles of NaOH will be in excess.

	HBut(*aq*)	+	NaOH(*aq*)	→	H_2O(*l*)	+	But^-(*aq*)	+	Na^+(*aq*)
Initial:	2.000 x 10^{-3} mol		2.500 x 10^{-3} mol		—		0		—
Change:	–2.000 x 10^{-3} mol		–2.000 x 10^{-3} mol		—		+2.000 x 10^{-3} mol		—
Final:	0		5.000 x 10^{-4} mol				2.000 x 10^{-3} mol		

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

The molarity of the excess OH^- is (5.00 x 10^{-4} mol OH^-)/(0.04500 L) = 1.1111 x 10^{-2} *M* (unrounded)

pOH = –log (1.1111 x 10^{-2}) = 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_b of the base (($(CH_3CH_2)_3N$)). Prior to reaching the equivalence point, the added acid reacts with base to form $(CH_3CH_2)_3NH^+$ 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_3O^+.

The initial number of moles of $(CH_3CH_2)_3N$ = (0.1000 mol $(CH_3CH_2)_3N$)/L) (10^{-3} L/1 mL) (20.00 mL)
= 2.000 x 10^{-3} mol $(CH_3CH_2)_3N$

a) Since no acid has been added, only the weak base (K_b) is important.

$$K_b = \frac{\left[(CH_3CH_2)_3NH^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_3N\right]} = \frac{[x][x]}{[0.1000-x]} = \frac{[x][x]}{[0.1000]} = 5.2 \text{ x } 10^{-4}$$

$[OH^-] = x = 7.2111 \text{ x } 10^{-3}$ *M*

pOH = –log (7.2111 x 10^{-3}) = 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^{-3} L/1 mL) (10.00 mL) = 1.000 x 10^{-3} mol HCl

The HCl will react with an equal amount of the base, and 1.000 x 10^{-3} mol $(CH_3CH_2)_3N$ will remain; an equal number of moles of $(CH_3CH_2)_3NH^+$ will form.

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

The molarity of the excess $(CH_3CH_2)_3N$ is (1.000 x 10^{-3} mol $(CH_3CH_2)_3N$)/(0.03000 L)
= 0.03333 *M* (unrounded)

The molarity of the $(CH_3CH_2)_3NH^+$ formed is (1.000 x 10^{-3} mol $(CH_3CH_2)_3NH^+$)/(0.03000 L)
= 0.03333 *M* (unrounded)

$$K_b = \frac{\left[(CH_3CH_2)_3NH^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_3N\right]} = \frac{[x][0.0333+x]}{[0.03333-x]} = \frac{[x][0.0333]}{[0.03333]} = 5.2 \text{ x } 10^{-4}$$

$[OH^-] = x = 5.2 \text{ x } 10^{-4}$ *M*

pOH = –log (5.2 x 10^{-4}) = 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^{-3} L/1 mL) (15.00 mL) = 1.500 x 10^{-3} mol HCl

The HCl will react with an equal amount of the base, and 5.00 x 10^{-4} mol $(CH_3CH_2)_3N$ will remain; and 1.500 x 10^{-3} moles of $(CH_3CH_2)_3NH^+$ will form.

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

The molarity of the excess $(CH_3CH_2)_3N$ is (5.00 x 10^{-4} mol $(CH_3CH_2)_3N$)/(0.03500 L)
= 0.0142857 *M* (unrounded)

The molarity of the $(CH_3CH_2)_3NH^+$ formed is (1.500 x 10^{-3} mol $(CH_3CH_2)_3NH^+$)/(0.03500 L)
= 0.0428571 *M* (unrounded)

$$K_b = \frac{\left[(CH_3CH_2)_3NH^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_3N\right]} = \frac{[x][0.0428571+x]}{[0.0142857-x]} = \frac{[x][0.0428571]}{[0.0142857]} = 5.2 \text{ x } 10^{-4}$$

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

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

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

d) Determine the moles of HCl added:

Moles of HCl = (0.1000 mol HCl/L) (10^{-3} L/1 mL) (19.00 mL) = 1.900×10^{-3} mol HCl

The HCl will react with an equal amount of the base, and 1.00×10^{-4} mol $(CH_3CH_2)_3N$ will remain; and 1.900×10^{-3} moles of $(CH_3CH_2)_3NH^+$ will form.

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

The molarity of the excess $(CH_3CH_2)_3N$ is (1.00×10^{-4} mol $(CH_3CH_2)_3N$)/(0.03900 L)

= 0.002564102 *M* (unrounded)

The molarity of the $(CH_3CH_2)_3NH^+$ formed is (1.900×10^{-3} mol $(CH_3CH_2)_3NH^+$)/(0.03900 L)

= 0.0487179 *M* (unrounded)

$$K_b = \frac{\left[(CH_3CH_2)_3NH^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_3N\right]} = \frac{[x][0.0487179 + x]}{[0.002564102 - x]} = \frac{[x][0.0487179]}{[0.002564102]} = 5.2 \times 10^{-4}$$

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

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

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

e) Determine the moles of HCl added:

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

The HCl will react with an equal amount of the base, and 5×10^{-6} mol $(CH_3CH_2)_3N$ will remain; and 1.995×10^{-3} moles of $(CH_3CH_2)_3NH^+$ will form.

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

The molarity of the excess $(CH_3CH_2)_3N$ is (5×10^{-6} mol $(CH_3CH_2)_3N$)/(0.03995 L)

= 0.000125156 *M* (unrounded)

The molarity of the $(CH_3CH_2)_3NH^+$ formed is (1.995×10^{-3} mol $(CH_3CH_2)_3NH^+$)/(0.03995 L)

= 0.0499374 *M* (unrounded)

$$K_b = \frac{\left[(CH_3CH_2)_3NH^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_3N\right]} = \frac{[x][0.0499374 + x]}{[0.000125156 - x]} = \frac{[x][0.0499374]}{[0.000125156]} = 5.2 \times 10^{-4}$$

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

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

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

f) Determine the moles of HCl added:

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

The HCl will react with an equal amount of the base, and 0 mol $(CH_3CH_2)_3N$ will remain; and 2.000×10^{-3} moles of $(CH_3CH_2)_3NH^+$ will form. This is the equivalence point.

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

The molarity of the $(CH_3CH_2)_3NH^+$ formed is (2.000×10^{-3} mol $(CH_3CH_2)_3NH^+$)/(0.04000 L)

= 0.05000 *M*

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

$$K_a = \frac{\left[H_3O^+\right]\left[(CH_3CH_2)_3N\right]}{\left[(CH_3CH_2)_3NH^+\right]} = \frac{[x][x]}{[0.05000 - x]} = \frac{[x][x]}{[0.05000]} = 1.923 \times 10^{-11}$$

$x = [H_3O^+] = 9.8056 \times 10^{-7}\ M$ (unrounded)

$pH = -\log[H_3O^+] = -\log(9.8056 \times 10^{-7}) = 6.0085 = \mathbf{6.01}$

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 mol HCl/L) (10^{-3} L/1 mL) (20.05 mL) = 2.005×10^{-3} mol HCl

The HCl will react with an equal amount of the base, and 0 mol $(CH_3CH_2)_3N$ will remain, and 5×10^{-6} moles of HCl will be in excess.

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

The molarity of the excess H_3O^+ is (5×10^{-6} mol H_3O^+)/(0.04005 L) = 1.2484×10^{-4} *M* (unrounded)

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

h) Determine the moles of HCl added:

Moles of HCl = (0.1000 mol HCl/L) (10^{-3} L/1 mL) (25.00 mL) = 2.500 x 10^{-3} mol HCl

The HCl will react with an equal amount of the base, and 0 mol $(CH_3CH_2)_3N$ will remain, and 5.00 x 10^{-4} mol of HCl will be in excess.

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

The molarity of the excess H_3O^+ is (5.00 x 10^{-4} mol H_3O^+)/(0.04500 L) = 1.1111 x 10^{-2} *M* (unrounded)

pH = –log (1.1111 x 10^{-2}) = 1.9542 = **1.95**

19.43 a) The balanced chemical equation is:

$$NaOH(aq) + CH_3COOH(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq) + H_2O(l)$$

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 =

$$\left(\frac{0.0520 \text{ mol } CH_3COOH}{L}\right)\left(\frac{10^{-3}\text{ L}}{1 \text{ mL}}\right)(42.2 \text{ mL})\left(\frac{1 \text{ mol NaOH}}{1 \text{ mol } CH_3COOH}\right)\left(\frac{L}{0.0372 \text{ mol NaOH}}\right)\left(\frac{1 \text{ mL}}{10^{-3}\text{ L}}\right)$$

= 58.989247 = **59.0 mL NaOH**

Determine the moles of CH_3COOH present:

$$\text{Moles} = \left(\frac{0.0520 \text{ mol } CH_3COOH}{L}\right)\left(\frac{10^{-3}\text{ L}}{1 \text{ mL}}\right)(42.2 \text{ mL})$$

= 0.0021944 mol CH_3COOH (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 CH_3COOH will remain, and 0.0021944 moles of CH_3COO^- will be formed.

	$CH_3COOH(aq)$	+	$NaOH(aq)$	→	$H_2O(l)$	+	$CH_3COO^-(aq)$	+	$Na^+(aq)$
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:

Volume = [(42.0 + 58.989247) mL] (10^{-3} L/1 mL) = 0.100989 L (unrounded)

Concentration of CH_3COO^- at equivalence point:

Molarity = (0.0021944 mol CH_3COO^-)/(0.100989 L) = 0.021729 *M* (unrounded)

Calculate K_b for CH_3COO^-: K_a CH_3COOH = 1.8 x 10^{-5}

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

Using a reaction table for the equilibrium reaction of CH_3COO^-:

	CH_3COO^-	+	H_2O	⇆	CH_3COOH	+	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.

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{[x][x]}{[0.021729 - x]} = \frac{[x][x]}{[0.021729]} = 5.556 \times 10^{-10}$$

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

pOH = –log (3.4745693 x 10^{-6}) = 5.459099012 (unrounded)

pH = 14.00 – pOH = 14.00 – 5.459099012 = 8.54090 = **8.54**

b) The balanced chemical equation is:

$$Na(aq) + HNO_2(aq) \rightarrow Na(aq) + NO_2^-(aq) + H_2O(l)$$

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:

$$\text{Volume} = \left(\frac{0.0390 \text{ mol } HNO_2}{L}\right)\left(\frac{10^{-3}\text{ L}}{1 \text{ mL}}\right)(23.4 \text{ mL})\left(\frac{1 \text{ mol NaOH}}{1 \text{ mol } HNO_2}\right)\left(\frac{L}{0.0372 \text{ mol NaOH}}\right)\left(\frac{1 \text{ mL}}{10^{-3}\text{ L}}\right)$$

= 24.532 = **24.5 mL NaOH**

Determine the moles of HNO_2 present:

$$\text{Moles} = \left(\frac{0.0390\text{ mol }HNO_2}{\text{L}}\right)\left(\frac{10^{-3}\text{ L}}{1\text{ mL}}\right)(23.4\text{ mL})$$

$= 0.0009126$ mol HNO_2

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 HNO_2 will remain, and 0.0009126 moles of NO_2^- will be formed.

	$HNO_2(aq)$	+	$NaOH(aq)$	→	$H_2O(l)$	+	$NO_2^-(aq)$	+	$Na^+(aq)$
Initial:	0.0009126 mol		0.0009126 mol		—		0		—
Change:	–0.0009126 mol		–0.0009126 mol		—		+0.0009126 mol		—
Final:	0		0				0.0009126mol		

Determine the liters of solution present at the equivalence point:

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

Concentration of NO_2^- at equivalence point:

Molarity = (0.0009126 mol NO_2^-)/(0.047932 L) = 0.0190395 M (unrounded)

Calculate K_b for NO_2^-: K_a $HNO_2 = 7.1 \times 10^{-4}$

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

Using a reaction table for the equilibrium reaction of NO_2^-:

	NO_2^-	+	H_2O	⇆	HNO_2	+	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.

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} = \frac{[x][x]}{[0.0190395\ - x]} = \frac{[x][x]}{[0.0190395]} = 1.40845 \times 10^{-11}$$

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

pOH = –log (5.178431×10^{-7}) = 6.285802 (unrounded)

pH = 14.00 – pOH = 14.00 – 6.285802 = 7.714198 = **7.71**

19.44 a) The balanced chemical equation is:

$HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

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 =

$$\left(\frac{0.234\text{ mol }NH_3}{\text{L}}\right)\left(\frac{10^{-3}\text{ L}}{1\text{ mL}}\right)(55.5\text{ mL})\left(\frac{1\text{ mol HCl}}{1\text{ mol }NH_3}\right)\left(\frac{\text{L}}{0.135\text{ mol HCl}}\right)\left(\frac{1\text{ mL}}{10^{-3}\text{ L}}\right)$$

= **96.2 mL HCl**

Determine the moles of NH_3 present:

$$\text{Moles} = \left(\frac{0.234\text{ mol }NH_3}{\text{L}}\right)\left(\frac{10^{-3}\text{ L}}{1\text{ mL}}\right)(55.5\text{ mL})$$

$= 0.012987$ mol NH_3 (unrounded)

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 NH_3 will remain, and 0.012987 moles of NH_4^+ will be formed.

	$HCl(aq)$	+	$NH_3(aq)$	→	$NH_4^+(aq)$	+	$Cl^-(aq)$
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:

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

Concentration of NH_4^+ at equivalence point:

Molarity = (0.012987 mol NH_4^+)/(0.1517 L) = 0.0856098 M (unrounded)

Calculate K_a for NH_4^+: K_b NH_3 = 1.76×10^{-5}

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

Using a reaction table for the equilibrium reaction of NH_4^+:

	NH_4^+	+	H_2O	⇆	NH_3	+	H_3O^+
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.

$$K_a = \frac{\left[H_3O^+\right]\left[NH_3\right]}{\left[NH_4^+\right]} = \frac{[x][x]}{[0.0856098\ - x]} = \frac{[x][x]}{[0.0856098]} = 5.6818 \times 10^{-10}$$

$x = [H_3O^+] = 6.974366 \times 10^{-6}$ M (unrounded)

pH = $-\log [H_3O^+] = -\log (6.974366 \times 10^{-6}) = 5.1565 =$ **5.16**

b) The balanced chemical equation is:

$HCl(aq) + CH_3NH_2(aq) \rightarrow CH_3NH_3^+(aq) + Cl^-(aq)$

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 =

$$\left(\frac{1.11\text{ mol }CH_3NH_2}{L}\right)\left(\frac{10^{-3}\text{ L}}{1\text{ mL}}\right)(17.8\text{ mL})\left(\frac{1\text{ mol HCl}}{1\text{ mol }CH_3NH_2}\right)\left(\frac{L}{0.135\text{ mol HCl}}\right)\left(\frac{1\text{ mL}}{10^{-3}\text{ L}}\right)$$

= 146.3556 = **146 mL HCl**

Determine the moles of CH_3NH_2 present:

$$\text{Moles} = \left(\frac{1.11\text{ mol }CH_3NH_2}{L}\right)\left(\frac{10^{-3}\text{ L}}{1\text{ mL}}\right)(17.8\text{ mL})$$

= 0.019758 mol CH_3NH_2 (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 CH_3NH_2 will remain, and 0.019758 moles of $CH_3NH_3^+$ will be formed.

	$HCl(aq)$	+	$CH_3NH_2(aq)$	→	$CH_3NH_3^+(aq)$	+	$Cl^-(aq)$
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:

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

Concentration of $CH_3NH_3^+$ at equivalence point:

Molarity = (0.019758 mol $CH_3NH_3^+$)/(0.161556 L) = 0.122298 M (unrounded)

Calculate K_a for $CH_3NH_3^+$: K_b CH_3NH_2 = 4.4×10^{-4}

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

Using a reaction table for the equilibrium reaction of $CH_3NH_3^+$:

	$CH_3NH_3^+$	+	H_2O	⇆	CH_3NH_2	+	H_3O^+
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.

$$K_a = \frac{\left[H_3O^+\right]\left[CH_3NH_2\right]}{\left[CH_3NH_3^+\right]} = \frac{[x][x]}{[0.122298\ - x]} = \frac{[x][x]}{[0.122298]} = 2.2727 \times 10^{-11}$$

$x = [H_3O^+] = 1.66717 \times 10^{-6}$ M (unrounded)

pH = $-\log [H_3O^+] = -\log (1.66717 \times 10^{-6}) = 5.778019 =$ **5.78**

19.45 $M_2X(s) \leftrightarrows 2M^+(aq) + X^{2-}(aq)$

$K_{sp} = [M^+]^2[X^{2-}]$, assuming M_2X is a strong electrolyte.

S = molar solubility = 5×10^{-5} *M*

$[M^+] = 2\text{ S} = 1 \times 10^{-4}$ *M*

$[X^{2-}] = \text{S} = 5 \times 10^{-5}$ *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

$F^-(aq) + H_2O(l) \leftrightarrows HF(aq) + OH^-(aq)$

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 $AB(s) \leftrightarrows A^+(aq) + B^-(aq)$, 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) $Ag_2CO_3(s) \leftrightarrows 2\,Ag^+(aq) + CO_3^{2-}(aq)$

Ion-product expression: $\boldsymbol{K_{sp} = [Ag^+]^2[CO_3^{2-}]}$

b) $BaF_2(s) \leftrightarrows Ba^{2+}(aq) + 2\,F^-(aq)$

Ion-product expression: $\boldsymbol{K_{sp} = [Ba^{2+}][F^-]^2}$

c) $CuS(s) + H_2O(l) \leftrightarrows Cu^{2+}(aq) + HS^-(aq) + OH^-(aq)$

Ion-product expression: $\boldsymbol{K_{sp} = [Cu^{2+}][HS^-][OH^-]}$

19.49 a) $Fe(OH)_3(s) \leftrightarrows Fe^{3+}(aq) + 3\,OH^-(aq)$

Ion-product expression: $\boldsymbol{K_{sp} = [Fe^{3+}]\,[OH^-]^3}$

b) $Ba_3(PO_4)_2(s) \leftrightarrows 3\,Ba^{2+}(aq) + 2\,PO_4^{3-}(aq)$

Ion-product expression: $\boldsymbol{K_{sp} = [Ba^{2+}]^3\,[PO_4^{3-}]^2}$

c) $SnS(s) + H_2O(l) \leftrightarrows Sn^{2+}(aq) + HS^-(aq) + OH^-(aq)$

Ion-product expression: $\boldsymbol{K_{sp} = [Sn^{2+}][HS^-][OH^-]}$

19.50 Write a reaction table, where S is the molar solubility of Ag_2CO_3:

Concentration (*M*)	$Ag_2CO_3(s)$	$\leftrightarrows$	$2\,Ag^+(aq)$	+	$CO_3^{2-}(aq)$
Initial	—		0		0
Change	—		+2 S		+S
Equilibrium	—		2 S		S

$S = [Ag_2CO_3] = 0.032$ *M* so $[Ag^+] = 2\text{ S} = 0.064$ *M* and $[CO_3^{2-}] = \text{S} = 0.032$ *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*)	$ZnC_2O_4(s)$	$\leftrightarrows$	$Zn^{2+}(aq)$	+	$C_2O_4^{2-}(aq)$
Initial	—		0		0
Change	—		+S		+S
Equilibrium	—		S		S

$S = [ZnC_2O_4] = 7.9 \times 10^{-3}$ *M* so $[Zn^{2+}] = [C_2O_4^{2-}] = \text{S} = 7.9 \times 10^{-3}$ *M*

$K_{sp} = [Zn^{2+}][C_2O_4^{2-}] = (7.9 \times 10^{-3})\,(7.9 \times 10^{-3}) = 6.241 \times 10^{-5} = \mathbf{6.2 \times 10^{-4}}$

19.52 The equation and ion-product expression for silver dichromate, $Ag_2Cr_2O_7$, is:

$Ag_2Cr_2O_7(s) \rightleftarrows 2\ Ag^+(aq) + Cr_2O_7^{2-}(aq) \qquad K_{sp} = [Ag^+]^2[Cr_2O_7^{2-}]$

The solubility of $Ag_2Cr_2O_7$, converted from g / 100 mL to M is:

$$\text{Molar solubility} = S = \left(\frac{8.3 \text{ x } 10^{-3}\text{ g } Ag_2Cr_2O_7}{100\text{ mL}}\right)\left(\frac{1\text{ mL}}{10^{-3}\text{ L}}\right)\left(\frac{1\text{ mol } Ag_2Cr_2O_7}{431.8\text{ g } Ag_2Cr_2O_7}\right) = 0.00019221861\ M\text{ (unrounded)}$$

Since 1 mole of $Ag_2Cr_2O_7$ dissociates to form 2 moles of Ag^+, the concentration of Ag^+ is $2\ S = 2(0.00019221861\ M) = 0.00038443723\ M$ (unrounded). The concentration of $Cr_2O_7^{2-}$ is $S = 0.00019221861\ M$ because 1 mole of $Ag_2Cr_2O_7$ dissociates to form 1 mole of $Cr_2O_7^{2-}$.

$K_{sp} = [Ag^+]^2[Cr_2O_7^{2-}] = (2\ S)^2(S) = (0.00038443723)^2(0.00019221861) = 2.8408 \text{ x } 10^{-11} = \mathbf{2.8 \text{ x } 10^{-11}}$.

19.53 The equation and ion-product expression for calcium sulfate, $CaSO_4$, is:

$CaSO_4(s) \rightleftarrows Ca^{2+}(aq) + SO_4^{2-}(aq) \qquad K_{sp} = [Ca^{2+}][SO_4^{2-}]$

The solubility of $CaSO_4$, converted from g / 100 mL to M is:

$$\text{Molar solubility} = S = \left(\frac{0.209\text{ g } CaSO_4}{100\text{ mL}}\right)\left(\frac{1\text{ mL}}{10^{-3}\text{ L}}\right)\left(\frac{1\text{ mol } CaSO_4}{136.15\text{ g } CaSO_4}\right) = 0.015350716\ M\text{ (unrounded)}$$

Since 1 mole of $CaSO_4$ dissociates to form 1 mole of Ca^{2+}, the concentration of Ca^{2+} is $S = 0.015350716\ M$ (unrounded). The concentration of SO_4^{2-} is $S = 0.015350716\ M$ because 1 mole of $CaSO_4$ dissociates to form 1 mole of SO_4^{2-}.

$K_{sp} = [Ca^{2+}][SO_4^{2-}] = (S)\ (S) = (0.015350716)\ (\ 0.015350716) = 2.35644 \text{ x } 10^{-4} = \mathbf{2.36 \text{ x } 10^{-4}}$

19.54 The equation and ion-product expression for $SrCO_3$ is:

$SrCO_3(s) \rightleftarrows Sr^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp} = [Sr^{2+}][CO_3^{2-}]$

a) The solubility, S, in pure water equals $[Sr^{2+}]$ and $[CO_3^{2-}]$

Write a reaction table, where S is the molar solubility of $SrCO_3$:

Concentration (M)	$SrCO_3(s)$	$\rightleftarrows$	$Sr^{2+}(aq)$	+	$CO_3^{2-}(aq)$
Initial	—		0		0
Change	—		+S		+S
Equilibrium	—		S		S

$K_{sp} = 5.4 \text{ x } 10^{-10} = [Sr^{2+}][CO_3^{2-}] = [S][S] = S^2$

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

b) In 0.13 M $Sr(NO_3)_2$, the initial concentration of Sr^{2+} is 0.13 M.

Equilibrium $[Sr^{2+}] = 0.13 + S$ and equilibrium $[CO_3^{2-}] = S$ where S is the solubility of $SrCO_3$.

Concentration (M)	$SrCO_3(s)$	$\rightleftarrows$	$Sr^{2+}(aq)$	+	$CO_3^{2-}(aq)$
Initial	—		0.13		0
Change	—		+S		+S
Equilibrium	—		0.13 + S		S

$K_{sp} = 5.4 \text{ x } 10^{-10} = [Sr^{2+}][CO_3^{2-}] = (0.13 + S)S$

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

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

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

19.55 The equation and ion-product expression for $SrCO_3$ is:

$BaCrO_4(s) \rightleftarrows Ba^{2+}(aq) + CrO_4^{2-}(aq) \qquad K_{sp} =[Ba^{2+}][CrO_4^{2-}]$

a) The solubility, S, in pure water equals $[Ba^{2+}]$ and $[CrO_4^{2-}]$

$K_{sp} = 2.1 \text{ x } 10^{-10} = [Ba^{2+}][CrO_4^{2-}] = S^2$

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

b) In 0.13 M Na_2CrO_4, the initial concentration of CrO_4^{2-} is $1.5 \text{ x } 10^{-3}\ M$.

Equilibrium $[Ba^{2+}] = S$ and equilibrium $[CrO_4^{2-}] = 1.5 \text{ x } 10^{-3} + S$ where S is the solubility of $BaCrO_4$.

$K_{sp} = 2.1 \text{ x } 10^{-10} = [Ba^{2+}][CrO_4^{2-}] = S(1.5 \text{ x } 10^{-3} + S)$

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

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

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

19.56 The equilibrium is: $Ca(IO_3)_2(s) \leftrightarrows Ca^{2+}(aq) + 2\ IO_3^-(aq)$. From the Appendix, $K_{sp}(Ca(IO_3)_2) = 7.1 \times 10^{-7}$.
a) Write a reaction table that reflects an initial concentration of $Ca^{2+} = 0.060\ M$. In this case, Ca^{2+} is the common ion.

Concentration (M)	$Ca(IO_3)_2(s)$	$\leftrightarrows$	$Ca^{2+}(aq)$	+	$2\ IO_3^-(aq)$
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 M.

$K_{sp} = [Ca^{2+}][IO_3^-]^2 = (0.060)\ (2S)^2 = 7.1 \times 10^{-7}$

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

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

S represents both the molar solubility of Ca^{2+} and $Ca(IO_3)_2$, so the molar solubility of $Ca(IO_3)_2$ is **$1.7 \times 10^{-3}\ M$**.

b) In this case,

Concentration (M)	$Ca(IO_3)_2(s)$	$\leftrightarrows$	$Ca^{2+}(aq)$	+	$2\ IO_3^-(aq)$
Initial	—		0		0.060
Change	—		+S		+2S
Equilibrium	—		S		0.060 + 2S

The equilibrium concentration of Ca^{2+} is S, and the IO_3^- concentration is 0.060 + 2S. The iodate ion is the common ion in this problem.

Assume that $0.060 + 2S \approx 0.060$

$K_{sp} = [Ca^{2+}][IO_3^-]^2 = (S)\ (0.060)^2 = 7.1 \times 10^{-7}$

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

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

S represents both the molar solubility of Ca^{2+} and $Ca(IO_3)_2$, so the molar solubility of $Ca(IO_3)_2$ is **$2.0 \times 10^{-4}\ M$**.

19.57 The equilibrium is: $Ag_2SO_4(s) \leftrightarrows 2\ Ag^+(aq) + SO_4^{2-}(aq)$. From the Appendix, $K_{sp}(Ag_2SO_4) = 1.5 \times 10^{-5}$.
a) Write a reaction table that reflects an initial concentration of $Ag^+ = 0.22\ M$. In this case, Ag^+ is the common ion.

Concentration (M)	$Ag_2SO_4(s)$	$\leftrightarrows$	$2\ Ag^+(aq)$	+	$SO_4^{2-}(aq)$
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 M.

$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (0.22)^2(S) = 1.5 \times 10^{-5}$

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

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

S represents both the molar solubility of SO_4^{2-} and $Ag_2SO_4(s)$, so the molar solubility of $Ag_2SO_4(s)$ is **$3.1 \times 10^{-4}\ M$**.

b) In this case,

Concentration (M)	$Ag_2SO_4(s)$	$\leftrightarrows$	$2\ Ag^+(aq)$	+	$SO_4^{2-}(aq)$
Initial	—		0		0.22
Change	—		+2S		+S
Equilibrium	—		2S		0.22 + S

The equilibrium concentration of Ag^+ is 2S, and the SO_4^{2-} concentration is 0.22 + S. The sulfate ion is the common ion in this problem.

Assume that $0.22 + S \approx 0.22$.

$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2S)^2(0.22) = 1.5 \times 10^{-5}$

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

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

S represents the molar solubility of Ag_2SO_4, so the molar solubility of Ag_2SO_4 is **$4.1 \times 10^{-3}\ M$**.

19.58 The larger the K_{sp}, the larger the molar solubility if the number of ions are equal.
a) **$Mg(OH)_2$** with $K_{sp} = 6.3 \text{ x } 10^{-10}$ has higher molar solubility than $Ni(OH)_2$ with $K_{sp} = 6 \text{ x } 10^{-16}$.
b) **PbS** with $K_{sp} = 3 \text{ x } 10^{-25}$ has higher molar solubility than CuS with $K_{sp} = 8 \text{ x } 10^{-34}$.
c) **Ag_2SO_4** with $K_{sp} = 1.5 \text{ x } 10^{-5}$ has higher molar solubility than MgF_2 with $K_{sp} = 7.4 \text{ x } 10^{-9}$.

19.59 The larger the K_{sp}, the larger the molar solubility if the number of ions are equal.
a) **$SrSO_4$** with $K_{sp} = 3.2 \text{ x } 10^{-7}$ has higher molar solubility than $BaCrO_4$ with $K_{sp} = 2.1 \text{ x } 10^{-10}$.
b) **$CaCO_3$** with $K_{sp} = 3.3 \text{ x } 10^{-9}$ has higher molar solubility than $CuCO_3$ with $K_{sp} = 3 \text{ x } 10^{-12}$.
c) **$Ba(IO_3)_2$** with $K_{sp} = 1.5 \text{ x } 10^{-9}$ has higher molar solubility than Ag_2CrO_4 with $K_{sp} = 2.6 \text{ x } 10^{-12}$.

19.60 a) $AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq)$
The chloride ion is the anion of a strong acid, so it does not react with H_3O^+. The solubility is not affected by pH.
b) $SrCO_3(s) \leftrightarrows Sr^{2+}(aq) + CO_3^{2-}(aq)$
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:

$CO_3^{2-}(aq) + H_2O(l) \leftrightarrows HCO_3^-(aq) + OH^-(aq)$
and $HCO_3^-(aq) + H_2O(l) \leftrightarrows H_2CO_3(aq) + OH^-(aq)$

The H_2CO_3 will decompose to $CO_2(g)$ and $H_2O(l)$. The gas will escape and further shift the equilibrium. Changes in pH will change the $[CO_3^{2-}]$, so the solubility of $SrCO_3$ will increase with decreasing pH. **Solubility increases with addition of H_3O^+ (decreasing pH)**.

19.61 a) $CuBr(s) \leftrightarrows Cu^+(aq) + Br^-(aq)$
The bromide ion is the anion of a strong acid, so it does not react with H_3O^+. At high pH the copper ion may precipitate.
$Cu^+(aq) + OH^-(aq) \leftrightarrows CuOH(s)$
b) $Ca_3(PO_4)_2(s) \leftrightarrows 3\ Ca^{2+}(aq) + 2\ PO_4^{3-}(aq)$
The calcium ion is the cation of a strong base so pH will not affect its solubility.
PO_4^{3-} is the anion of a weak acid, so the following equilibria would be present.
$PO_4^{3-}(aq) + n\ H_2O(l) \leftrightarrows H_nPO_4^{(3-n)-}(aq) + n\ OH^-(aq)$ (n = 1,2,3)
Since these involve OH^-, the solubility will change with changing pH. **Solubility increases with addition of H_3O^+ (decreasing pH)**.

19.62 The ion-product expression for $Cu(OH)_2$ is $K_{sp} = [Cu^{2+}][OH^-]^2$ and, from Appendix C, K_{sp} equals $2.2 \text{ x } 10^{-20}$.
To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp}.

$$[Cu^{2+}] = \left(\frac{1.0 \text{ x } 10^{-3} \text{ mol } Cu(NO_3)_2}{L}\right)\left(\frac{1 \text{ mol } Cu^{2+}}{1 \text{ mol } Cu(NO_3)_2}\right) = 1.0 \text{ x } 10^{-3}\ M\ Cu^{2+}$$

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

$Q_{sp} = [Cu^{2+}][OH^-]^2 = (1.0 \text{ x } 10^{-3})(1.33666 \text{ x } 10^{-3})^2 = 1.7866599 \text{ x } 10^{-9}$ (unrounded)
Q_{sp} is greater than K_{sp} ($1.8 \text{ x } 10^{-9} > 2.2 \text{ x } 10^{-20}$), so **$Cu(OH)_2$ will precipitate**.

19.63 The ion-product expression for $PbCl_2$ is $K_{sp} = [Pb^{2+}][Cl^-]^2$ and, from the Appendix, K_{sp} equals $1.7 \text{ x } 10^{-5}$.
To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp}.

$$[Pb^{2+}] = \left(\frac{0.12 \text{ mol } Pb(NO_3)_2}{L}\right)\left(\frac{1 \text{ mol } Pb^{2+}}{1 \text{ mol } Pb(NO_3)_2}\right) = 0.12\ M\ Pb^{2+}$$

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

$Q_{sp} = [Pb^{2+}][Cl^-]^2 = (0.12)(2.3952 \text{ x } 10^{-4})^2 = 6.8843796 \text{ x } 10^{-9}$ (unrounded)
Q_{sp} is greater than K_{sp} ($6.9 \text{ x } 10^{-9} < 1.7 \text{ x } 10^{-5}$), so **$PbCl_2$ will not precipitate**.

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

Moles of $C_2O_4^{2-}$ added = $\left(\frac{0.1550 \text{ mol } Na_2C_2O_4}{\text{L}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(100.0 \text{ mL})\left(\frac{1 \text{mol} C_2O_4{}^{2-}}{1 \text{mol} Na_2C_2O_4}\right)$ = 0.01550 mol $C_2O_4^{2-}$

The Ca^{2+} is limiting leaving 0 *M*, and after the reactions there will be (0.01550 – 0.010088) mol of $C_2O_4^{2-}$ remaining.

$[C_2O_4^{2-}]$ = $\left(\frac{(0.01550 - 0.00025170) \text{mol } C_2O_4{}^{2-}}{(104 + 100.0) \text{mL}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$ = 0.0747466 *M* $C_2O_4^{2-}$ (unrounded)

Concentration (*M*)	$CaC_2O_4 \bullet H_2O(s)$	$\leftrightarrows$	$Ca^{2+}(aq)$	+	$C_2O_4^{2-}(aq)$	+	$H_2O(l)$
Initial	—		0		0.0747466		—
Change	—		+S		+S		—
Equilibrium	—		S		0.0747466 + S		—

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

$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$ = (S) (0.0747466) = 2.3 x 10^{-9}

S = 3.07706 x 10^{-8} = 3.1 x 10^{-8}

Check assumption: (3.07706 x 10^{-8} *M*)/(0.0747466 *M*) x 100% = 0.00004% < 5%, so the assumption is good.
S represents both the molar solubility of Ca^{2+} and $CaC_2O_4 \bullet H_2O(s)$, so the concentration of Ca^{2+} is **3.1 x 10^{-8} *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.

19.66 $Cd(H_2O)_4^{2+}(aq) + I^-(aq) \leftrightarrows CdI(H_2O)_3^+(aq) + H_2O(l)$ $\quad K_{f1} = \frac{[CdI(H_2O)_3{}^+]}{[Cd(H_2O)_4{}^{2+}][I^-]}$

$CdI(H_2O)_3^+(aq) + I^-(aq) \leftrightarrows CdI_2(H_2O)_2(aq) + H_2O(l)$ $\quad K_{f2} = \frac{[CdI_2(H_2O)_2]}{[CdI(H_2O)_3{}^+][I^-]}$

$CdI_2(H_2O)_2(aq) + I^-(aq) \leftrightarrows CdI_3(H_2O)^-(aq) + H_2O(l)$ $\quad K_{f3} = \frac{[CdI_3(H_2O)^-]}{[CdI_2(H_2O)_2][I^-]}$

$CdI_3(H_2O)^-(aq) + I^-(aq) \leftrightarrows CdI_4^{2-}(aq) + H_2O(l)$ $\quad K_{f4} = \frac{[CdI_4{}^{2-}]}{[CdI_3(H_2O)^-][I^-]}$

Overall: $Cd(H_2O)^{2+}{}_4(aq) + 4I^-(aq) \leftrightarrows CdI_4^{2-}(aq) + 4H_2O(l)$ $\quad K_f = \frac{[CdI_4{}^{2-}]}{[Cd(H_2O)_4{}^{2+}][I^-]^4}$

$$K_f = \frac{[CdI(H_2O)_3{}^+]}{[Cd(H_2O)_4{}^{2+}][I^-]} \text{ x } \frac{[CdI_2(H_2O)_2]}{[CdI(H_2O)_3{}^+][I^-]} \text{ x } \frac{[CdI_3(H_2O)^-]}{[CdI_2(H_2O)_2][I^-]} \text{ x } \frac{[CdI_4{}^{2-}]}{[CdI_3(H_2O)^-][I^-]}$$

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

19.67 In the context of this equilibrium only, the increased solubility with added OH^- appears to be a violation of Le Châtelier's Principle. Adding OH^- should cause the equilibrium to shift towards the left, decreasing the solubility of 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:

$$Pb^{2+}(aq) + n\ OH^-(aq) \leftrightarrows Pb(OH)_n^{2-n}(aq)$$

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

19.68 In many cases, a hydrated metal complex (e.g., $Hg(H_2O)_4^{2+}$) will exchange ligands when placed in a solution of another ligand (e.g., CN^-):

$$Hg(H_2O)_4^{2+}(aq) + 4\ CN^-(aq) \leftrightarrows Hg(CN)_4^{2-}(aq) + 4\ H_2O(l)$$

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.

19.69 $Zn(H_2O)_4^{2+}(aq) + 4\ CN^-\ (aq) \leftrightarrows Zn(CN)_4^{2-}{}_{(aq)} + 4\ H_2O(l)$

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.

$$Ag(H_2O)_2^+(aq) + 2\ S_2O_3^{2-}(aq) \leftrightarrows Ag(S_2O_3)_2^{3-}(aq) + 2\ H_2O(l)$$

19.71 $Al(H_2O)_6^{3+}(aq) + 6\ F^-(aq) \leftrightarrows AlF_6^{3-}(aq) + 6\ H_2O(l)$

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 $K_{overall}$. Write a reaction table where $S = [AgI]_{dissolved} = [Ag(NH_3)_2^+]$.

Solubility-product: $AgI(s) \leftrightarrows \cancel{Ag^+(aq)} + I^-(aq)$

Complex-ion: $\cancel{Ag^+(aq)} + 2\ NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq)$

Overall: $AgI(s) + 2\ NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq) + I^-(aq)$

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

Reaction table:

Concentration (M)	$AgI(s)$	+	$2\ NH_3(aq)$	$\leftrightarrows$	$Ag(NH_3)_2^+(aq)$	+ $I^-(aq)$
Initial	—		2.5		0	0
Change	—		–2S		+S	+S
Equilibrium	—		2.5 – 2S		S	S

Assume that 2.5 – 2S ≈ 2.5 because $K_{overall}$ is so small.

$$K_{overall} = \frac{\left[Ag(NH_3)_2^+\right]\left[I^-\right]}{\left[NH_3\right]^2} = \frac{[S][S]}{[2.5 - S]^2} = \frac{[S][S]}{[2.5]^2} = 1.411 \times 10^{-9}$$

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

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

Complex-Ion $\cancel{Cr^{3+}(aq)} + 4OH^-(aq) \leftrightarrows Cr(OH)_4^-(aq)$ $K_f = 8.0 \times 10^{29}$

Overall: $Cr(OH)_3(s) + OH^-(aq) \leftrightarrows Cr(OH)_4^-(aq)$ $K = K_{sp}K_f = 0.504$ (unrounded)

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

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

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

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

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

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

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

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

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

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

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

$V_{\mathrm{H_2PO_4}^{-}} =$ **61 mL** and $V_{\mathrm{HPO_4}^{2-}} =$ **39 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 8.0×10^3 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 $H_3O^+(aq)$.

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

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

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

Mass of $H_2SO_4 = 36.28118$ g

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

The reaction between H_3O^+ and the base sodium acetate is:
$H_3O^+(aq) + NaC_2H_3O_2\ (aq) \rightarrow H_2O(l) + HC_2H_3O_2\ (aq) + \text{Na+}(aq)$
lb of $NaC_2H_3O_2 \cdot 3\ H_2O$ required to neutralize the H_2SO_4 =

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

$$= 0.22198 \text{ lb } \mathrm{NaC_2H_3O_2 \cdot 3\ H_2O}$$

Now consider the acetic acid. Calculate the amount of acetic acid in 8.0×10^3 lb or 3.628118×10^6 g H_2O.

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

Find the amount of $C_2H_3O_2^-$ necessary to maintain a pH of 5.

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

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

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

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

16.31286 mol of $C_2H_3O_2^-$ ($NaC_2H_3O_2 \bullet 3\ H_2O$) will be required to maintain the pH
lb of $NaC_2H_3O_2 \bullet 3\ H_2O$ required =

$$\left(16.31286\text{ mol CH}_3\text{COONa}\bullet3\text{H}_2\text{O}\right)\left(\frac{136.08\text{ g NaC}_2\text{H}_3\text{O}_2\bullet3\text{H}_2\text{O}}{1\text{ mol NaC}_2\text{H}_3\text{O}_2\bullet3\text{H}_2\text{O}}\right)\left(\frac{1\text{ kg}}{1000\text{ g}}\right)\left(\frac{2.205\text{ lb}}{1\text{ kg}}\right) = 4.89478\text{ lb}$$

Total amount of $NaC_2H_3O_2 \bullet 3\ H_2O$ required = 0.22198 lb + 4.89478 lb = 5.11676 = **5.1 lb**

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

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

$4.47133 \times 10^{-3}\ M$ NaUr = $[Na^+] = [Ur^-]$
$K_{sp} = [Na^+][Ur^-] = (4.47133 \times 10^{-3})(4.47133 \times 10^{-3}) = 1.999279 \times 10^{-5}\ M$ (unrounded)
When $[Na^+] = 0.15\ M$:
$K_{sp} = 1.999279 \times 10^{-5}\ M = [0.15][Ur^-]$
$[Ur^-] = 1.33285 \times 10^{-4}$ (unrounded)
The minimum urate ion concentration that will cause precipitation of sodium urate is $\mathbf{1.3 \times 10^{-4}}$ ***M***.

19.78 $CdS(s) + H_2O(l) \rightleftarrows Cd^{2+}(aq) + HS^-(aq) + OH^-(aq)$ $K_{sp} = 1.0 \times 10^{-24}$ (Appendix)
(The sulfide ion S^{2-} reacts in water to form HS^- and OH^-)
$K_{sp} = 1.0 \times 10^{-24} = [Cd^{2+}][HS^-][OH^-] = S^3$
S = $\mathbf{1.0 \times 10^{-8}}$ ***M***

19.79 a) The solubility equilibrium for KCl is: $KCl(s) \rightleftarrows K^+(aq) + Cl^-(aq)$
$K_{sp} = [K^+][Cl^-] = (3.7)(3.7) = 13.69 =$ **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:

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

Original moles from the 6.0 *M* HCl:

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

This results in (0.37 + 0.60) mol = 0.97 mol Cl^-

Original moles from the 12 *M* HCl:

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

This results in (0.37 + 1.2) mol = 1.57 mol Cl^- (unrounded)

Volume of mixed solutions = (100. mL + 100. mL) (10^{-3} L/1 mL) = 0.200 L

After the mixing:

$[K^+] = (0.37 \text{ mol } K^+)/(0.200 \text{ L}) = 1.85\ M\ K^+$ (unrounded)

From 6.0 *M* HCl:

$[Cl^-] = (0.97 \text{ mol } Cl^-)/(0.200 \text{ L}) = 4.85\ M\ Cl^-$ (unrounded)

From 12 *M* HCl:

$[Cl^-] = (1.57 \text{ mol } Cl^-)/(0.200 \text{ L}) = 7.85\ M\ Cl^-$ (unrounded)

Determine a Q_{sp} value to see if K_{sp} is exceeded. If $Q < K_{sp}$, nothing will precipitate.

From 6.0 *M* HCl

$Q_{sp} = [K^+][Cl^-] = (1.85)(4.85) = 8.9725 = 9.0 < 14$, so no KCl will precipitate.

From 12 *M* HCl

$Q_{sp} = [K^+][Cl^-] = (1.85)(7.85) = 14.5225 = 15 > 14$, so KCl will precipitate.

The mass of KCl that will precipitate when 12 *M* HCl is added:

Equal amounts of K and Cl will precipitate. Let x be the molarity change.

$K_{sp} = [K^+][Cl^-] = (1.85 - x)(7.85 - x) = 13.69$

x = 0.088697657 = 0.09 This is the change in the molarity of each of the ions.

$$\text{Mass KCl} = \left(\frac{0.088697657 \text{ mol } K^+}{\text{L}}\right)(0.200 \text{ L})\left(\frac{1 \text{ mol KCl}}{1 \text{ mol } K^+}\right)\left(\frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}}\right) = 1.32248 = \mathbf{1\ g\ KCl}$$

19.80 Determine the solubility of MnS:

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

$MnS(s) + H_2O(l) \leftrightarrows Mn^{2+}(aq) + HS^-(aq) + OH^-(aq)$

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

19.81 a) Use the Henderson-Hasselbalch equation. $K_{a1} = 4.5 \times 10^{-7}$ (From Appendix C)

$pK_a = -\log K_a = -\log(4.5 \times 10^{-7}) = 6.34679$ (unrounded)

$$pH = pK_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$7.40 = 6.34679 + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$1.05321 = \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 11.3034235 \text{ (unrounded)}$$

$$\frac{[H_2CO_3]}{[HCO_3^-]} = 0.0884688 = \mathbf{0.088}$$

b) Use the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$7.20 = 6.34679 + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$0.85321 = \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$\frac{[\mathrm{HCO_3^-}]}{[\mathrm{H_2CO_3}]} = 7.131978 \text{ (unrounded)}$$

$$\frac{[\mathrm{H_2CO_3}]}{[\mathrm{HCO_3^-}]} = 0.14021 = \mathbf{0.14}$$

19.82 The equilibrium is: $\mathrm{Ca_5(PO_4)_3OH}(s) \leftrightarrows 5\ \mathrm{Ca^{2+}}(aq) + 3\ \mathrm{PO_4^{3-}}(aq) + \mathrm{OH^-}(aq)$

$K_{sp} = 6.8 \times 10^{-37} = [\mathrm{Ca^{2+}}]^5[\mathrm{PO_4^{3-}}][\mathrm{OH^-}] = (5S)^5(3S)^3(S) = 84375\ S^9$

$S = 2.7166443 \times 10^{-5} = 2.7 \times 10^{-5}\ M$

Solubility = $(2.7166443 \times 10^{-5}$ mol/L) (502.32 g/mol) = 0.013646248 = **0.014 g/L $\mathbf{Ca_5(PO_4)_3OH}$**

The equilibrium is: $\mathrm{Ca_5(PO_4)_3F}(s) \leftrightarrows 5\ \mathrm{Ca^{2+}}(aq) + 3\ \mathrm{PO_4^{3-}}(aq) + \mathrm{F^-}(aq)$

$K_{sp} = 1.0 \times 10^{-60} = [\mathrm{Ca^{2+}}]^5[\mathrm{PO_4^{3-}}][\mathrm{F^-}] = (5S)^5(3S)^3(S) = 84375\ S^9$

$S = 6.1090861 \times 10^{-8} = 6.1 \times 10^{-8}\ M$

Solubility = $(6.1090861 \times 10^{-8}$ mol/L) (504.31 g/mol)

$= 3.0808732 \times 10^{-5} = \mathbf{3.1 \times 10^{-5}}$ **g/L $\mathbf{Ca_5(PO_4)_3F}$**

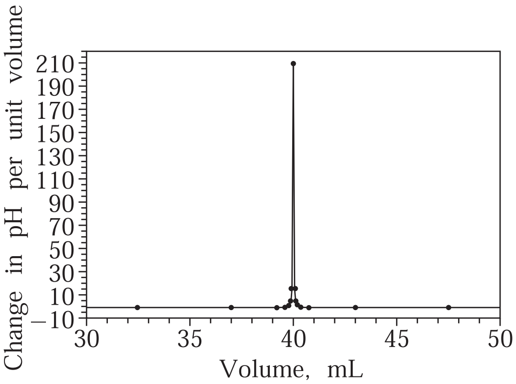
19.83 An indicator changes color when the buffer component ratio of the two forms of the indicator changes from a value greater than 1 to a value less than 1. The pH at which the ratio equals 1 is equal to pK_a. The midpoint in the pH range of the indicator is a good estimate of the pK_a of the indicator.

pK_a = (3.4 + 4.8) / 2 = 4.1 $\qquad K_a = 10^{-4.1} = 7.943 \times 10^{-5} = \mathbf{8 \times 10^{-5}}$

19.84 a) A spreadsheet will help you to quickly calculate ΔpH / ΔV 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, ΔpH / ΔV is at a maximum at the equivalence point.

V(mL)	pH	$\frac{\Delta \mathrm{pH}}{\Delta V}$	V_{average}(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

b)



Maximum slope (equivalence point) is at V = 40.00 mL

19.85 a) The equilibrium is: $MCl_2(s) \leftrightarrows M^{2+}(aq) + 2\ Cl^-(aq)$. The ion-product expression is $K_{sp} = [M^{2+}][Cl^-]^2$. Based on the picture, the ion concentrations are:

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

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

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

b) M^{2+} is a common ion for $M(NO_3)_2$ and MCl_2. If $M(NO_3)_2$ is added to the solution, $[M^{2+}]$ is increased and, according to Le Chatalier's principle, the solubility equilibrium will shift to the left, precipitating more MCl_2. The number of Cl^- particles decreases, the mass of MCl_2 increases, and the K_{sp} value remains the same.

19.86 Check to see if the concentration of $Ca(OH)_2$ exceeds the K_{sp}.

$M\ Ca(OH)_2 = (6.5 \times 10^{-9}\text{ mol } Ca(OH)_2)/(10.0\text{ L}) = 6.5 \times 10^{-10}\ M\ Ca(OH)_2$

Determine the concentration of a saturated calcium hydroxide solution from the K_{sp}.

$Ca(OH)_2(s) \leftrightarrows Ca^{2+}(aq) + 2\ OH^-(aq)$

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

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

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

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

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

pH of pure water = **7.0**

19.87 The ion-product equilibrium reaction is:

$CaF_2(s) \leftrightarrows Ca^{2+}(aq) + 2\ F^-(aq)$

F^- is a weak base with the following equilibrium reaction:

$F^-(aq) + H_2O(l) \leftrightarrows HF(aq) + OH^-(aq)$

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

(II) 0.01*M* HF: Because of the common ion effect, less CaF_2 would dissolve in this solution than in pure water.

(III) 0.01*M* NaOH: additional OH^- ions shift the base equilibrium reaction to the left, producing more F^-. The additional F^- shifts the ion-product equilibrium to the left so less CaF_2 would dissolve.

(IV) 0.01*M* HCl: H^+ ions remove OH^- ions from solution so the base equilibrium reaction shifts to the right, consuming F^-. This shifts the ion-product equilibrium to the right so that more CaF_2 dissolves in this solution than in pure water.

(V) 0.01*M* $Ca(OH)_2$: Because of the common ion effect, less CaF_2 would dissolve in this solution than in pure water. The presence of OH^- ions also removes H^+ ions and decreases the ability to form HF, thus, decreasing the solubility of CaF_2.
a) **0.01*M* HCl**
b) **0.01*M* $Ca(OH)_2$**

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

$$B(aq) + H_2O(l) \leftrightarrows BH^+(aq) + OH^-(aq)$$

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

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

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

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

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

19.89 $Hg_2C_2O_4(s) \leftrightarrows Hg_2^{2+}(aq) + C_2O_4^{2-}(aq)$
$K_{sp} = 1.75 \times 10^{-13} = [Hg_2^{2+}][C_2O_4^{2-}] = (0.13 + S)S \approx (0.13)\ S$
$S = 1.3461538 \times 10^{-12} =$ **1.3×10^{-12} *M***

19.90 $CaCO_3(s) \leftrightarrows Ca^{2+}(aq) + CO_3^{2-}(aq)$
$K_{sp} = 3.3 \times 10^{-9} = [Ca^{2+}][CO_3^{2-}] = S^2$
$S = [Ca^{2+}] = 5.7445626 \times 10^{-5} =$ **5.7×10^{-5} *M***

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**.

19.92 a) Combine the separate equilibria to produce the desired equilibrium. The *K* values are in the Appendix.
$2\ AgCl(s) \leftrightarrows$ ~~$2\ Ag^+(aq)$~~ $+ 2\ Cl^-(aq)$ $K' = (K_{sp})^2 = (1.8 \times 10^{-10})^2 = 3.24 \times 10^{-20}$ (unrounded)
~~$2\ Ag^+(aq)$~~ $+ CrO_4^{2-}(aq) \leftrightarrows Ag_2CrO_4(s)$ $K'' = 1/K_{sp} = 1/2.6 \times 10^{-12} = 3.846 \times 10^{11}$ (unrounded)
$2\ AgCl(s) + CrO_4^{2-}(aq) \leftrightarrows Ag_2CrO_4(s) + 2\ Cl^-(aq)$ $K = K'K'' = 1.2461 \times 10^{-8} =$ **1.2×10^{-8}**
b) Since the above reaction has such a small *K*, it lies far to the left as written.

19.93 *K* values from the Appendix
$H_2C_2O_4(aq) \leftrightarrows H^+(aq) +$ ~~$HC_2O_4^-(aq)$~~ $K_{a1} = 5.6 \times 10^{-2}$
~~$HC_2O_4^-(aq)$~~ $\leftrightarrows H^+(aq) + C_2O_4^{2-}(aq)$ $K_{a2} = 5.4 \times 10^{-5}$
$H_2C_2O_4(aq) \leftrightarrows 2\ H^+(aq) + C_2O_4^{2-}(aq)$ $K = K_{a1}\ K_{a2} = 3.024 \times 10^{-6}$ (unrounded)
$K = [H^+]^2[C_2O_4^{2-}]/[H_2C_2O_4]$
$[C_2O_4^{2-}] = K[H_2C_2O_4]/[H^+]^2$
a) At pH = 5.5 $[H^+] = 10^{-5.5} = 3.162 \times 10^{-6}$ *M* (unrounded)
$[C_2O_4^{2-}] = K[H_2C_2O_4]/[H^+]^2 = (3.024 \times 10^{-6})\ (3.0 \times 10^{-13})/(3.162 \times 10^{-6})^2$
$[C_2O_4^{2-}] = 9.07359 \times 10^{-8}$ *M* (unrounded)
$Q = [Ca^{2+}][C_2O_4^{2-}]$
$Q = (2.6 \times 10^{-3})\ (9.07359 \times 10^{-8}) = 2.3591 \times 10^{-10} = 2.4 \times 10^{-10} < K_{sp} =$ **No precipitate**

b) At pH = 7.0 $[H^+] = 10^{-7.0} = 1 \text{ x } 10^{-7}\ M$

$[C_2O_4^{2-}] = K[H_2C_2O_4]/[H^+]^2 = (3.024 \text{ x } 10^{-6})\ (3.0 \text{ x } 10^{-13})/(1 \text{ x } 10^{-7})^2$

$[C_2O_4^{2-}] = 9.072 \text{ x } 10^{-5}\ M$ (unrounded)

$Q = (2.6 \text{ x } 10^{-3})\ (9.072 \text{ x } 10^{-5}) = 2.35872 \text{ x } 10^{-7} = 2.4 \text{ x } 10^{-7} > K_{sp}$ = **Precipitate forms**

c) The higher pH would favor precipitation.

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

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

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

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

= 57.11488 = **57.11 mL NaOH**

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

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

Moles F^- formed = moles NaOH

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

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

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

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

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

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

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

$= 5.21917 =$ **5.22**

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

The molarity of F^- is

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

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

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

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

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

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

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

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

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

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

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

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

19.95 a) The formula is Hg_2Cl_2 which simplifies to the empirical formula **HgCl**.

b) The equilibrium is: $Hg_2Cl_2(s) \rightleftarrows Hg_2^{2+}(aq) + 2\ Cl^-(aq)$ $\quad K_{sp} = 1.5 \times 10^{-18}$

$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (S)\,(2S)^2 = 4S^3 = 1.5 \times 10^{-18}$

$S = 7.2112478 \times 10^{-7} = \mathbf{7.2 \times 10^{-7}}\ \boldsymbol{M}$

c) $[Hg_2^{2+}] = K_{sp}/[Cl^-]^2 =$

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

$= 8.9174129 \times 10^{-18} = \mathbf{8.9 \times 10^{-18}}\ \boldsymbol{M}\ \mathbf{Hg_2^{2+}}$

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

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

$= 1.6681707 \times 10^{12} = \mathbf{1.7 \times 10^{12}\ g\ Hg_2Cl_2}$

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

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

$= 20.62856 = \mathbf{21\ g\ Hg_2Cl_2}$

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

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

a) At pH = 4.20, $[H_3O^+] = 10^{-4.20} = 6.3095734 \times 10^{-5}\ M$ (unrounded)

Mol $H_3O^+ = (6.3095734 \times 10^{-5}\ M)\ (1.0279015 \times 10^6\text{ L}) = 64.8562 =$ **65 mol**

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

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

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

$[H_3O^+] = 64.8562\text{ mol }H_3O^+/1.243759 \times 10^8\text{ L} = 5.214531 \times 10^{-7}\ M$

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

c) Each mol of H_3O^+ requires one mole of HCO_3^- for neutralization.

$$\text{Mass} = (64.8562\text{ mol H}_3\text{O}^+)\left(\frac{1\text{ mol HCO}_3{}^-}{1\text{ mol H}_3\text{O}^+}\right)\left(\frac{61.02\text{ g HCO}_3{}^-}{1\text{ mol HCO}_3{}^-}\right) = 3.97575 \times 10^3 = \mathbf{4.0 \times 10^3\ g\ HCO_3^-}$$

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_{sp} from the molarity just calculated.

$NaCl(s) \rightleftarrows Na^+(aq) + Cl^-(aq)$

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

$$\text{Moles of Cl}^-\text{ initially} = \left(\frac{5.4236687\text{ mol NaCl}}{\text{L}}\right)\left(0.100\text{ L}\right)\left(\frac{1\text{ mol Cl}^-}{1\text{ mol NaCl}}\right) = 0.54236687\text{ mol Cl}^-\text{ (unrounded)}$$

This is the same as the moles of Na^+ in the solution.

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

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

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

Molarity of Cl^- in mixture = [(0.54236687 + 0.200175) mol Cl^-]/(0.1255 L) = 5.916668 *M* Cl^- (unrounded)

Molarity of Na^+ in mixture = (0.54236687 mol Na^+)/(0.1255 L) = 4.321648 *M* Na^+ (unrounded)

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

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

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

19.98 In both cases the equilibrium is: $CaCO_3(s) \leftrightarrows Ca^{2+}(aq) + CO_3^{2-}(aq)$

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = S^2$$

At 10°C

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = S^2 = 4.4 \text{ x } 10^{-9}$$

$$S = 6.6332495 \text{ x } 10^{-5} = \mathbf{6.6 \text{ x } 10^{-5}\ \mathit{M}\ CaCO_3}$$

At 30°C

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = S^2 = 3.1 \text{ x } 10^{-9}$$

$$S = 5.5677643 \text{ x } 10^{-5} = \mathbf{5.6 \text{ x } 10^{-5}\ \mathit{M}\ CaCO_3}$$

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

b) Box A

The amounts of HA and A^- are equal.

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

$$pH = pK_a + \log 1$$

$$pH = pK_a = -\log(4.5 \text{ x } 10^{-5}) = 4.346787 = \mathbf{4.35}$$

Box B

Only A^- is present at a concentration of 0.10 *M*.

The K_b for A^- is needed.

$$K_b = K_w / K_a = 1.0 \text{ x } 10^{-14} / 4.5 \text{ x } 10^{-5} = 2.222 \text{ x } 10^{-10} \text{ (unrounded)}$$

	$A^-(aq) + H_2O(l) \leftrightarrows$	$OH^-(aq)$	$+ HA(aq)$
Initial:	0.10 *M*	0	0
Change:	$-x$	$-x$	$-x$
Equilibrium:	$0.10 - x$	x	x

$$K_b = \frac{[HA][OH^-]}{[A^-]} = 2.222 \text{ x } 10^{-10}$$

$$K_b = \frac{[x][x]}{[0.10 - x]} = 2.222 \text{ x } 10^{-10} \qquad \text{Assume that } x \text{ is small compared to 0.10.}$$

$$K_b = 2.222 \text{ x } 10^{-10} = \frac{(x)(x)}{(0.10)}$$

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

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

$[H_3O]^+ = K_w / [OH^-] = (1.0 \text{ x } 10^{-14})/(4.7138095 \text{ x } 10^{-6}) = 2.1214264 \text{ x } 10^{-9}\ M\ H_3O^+$

$pH = -\log[H_3O^+] = -\log(2.1214264 \text{ x } 10^{-9}) = 8.67337 = \mathbf{8.67}$

Box C

This is a 0.10 *M* HA solution. The hydrogen ion, and hence the pH, can be determined from the K_a.

Concentration	$HA(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$H_3O^+(aq)$	$+ A^-(aq)$
Initial	0.10		—		0	0
Change	$-x$				$+x$	$+x$
Equilibrium	$0.10 - x$				x	x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 4.5 \text{ x } 10^{-5} = \frac{\left[H_3O^+\right]\left[A^-\right]}{\left[HA\right]}$$

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

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

$[H_3O^+] = x = 2.12132 \text{ x } 10^{-3}$ (unrounded)

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

pH = $-\log [H_3O^+] = -\log (2.12132 \text{ x } 10^{-3}) = 2.67339 =$ **2.67**

Box D

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

Use the Henderson-Hasselbalch equation for this buffer.

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

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

c) The initial stage in the titration would only have HA present. The amount of HA will decrease, and the amount of A^- will increase until only 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 M^{2+} and X^{2-}. The only way unequal amounts of 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 M^{2+} and X^{2-} must be equal; this is in box **B**.

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

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

c) The addition of Na_2X would increase the X^{2-}. There will be more X^{2-} than M^{2+}. This occurs in box **C**.

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