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
$$HF(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + F^-(aq)$$
to shift to the left, away from the excess of F^-, the common ion.

19.4   a) **Buffer 3** 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 2** has the greatest amount of weak base and can therefore neutralize the greatest amount of added acid.

19.5   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.

19.6   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.

19.7   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.

19.8 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.

19.9   a) The buffer component ratio and pH **increase** with added base. The OH^- reacts with HA to decrease its concentration and increase [NaA]. The ratio [NaA] / [HA] thus increases. The pH of the buffer will be more basic because the concentration of base, A^-, has increased and the concentration of acid, HA, decreased.
b) Buffer component ratio and pH **decrease** with added acid. The H_3O^+ reacts with A^- to decrease its concentration and increase [HA]. The ratio [NaA] / [HA] thus decreases. The pH of the buffer will be more acidic because the concentration of base, A^-, has decreased and the concentration of acid, HA, increased.

c) Buffer component ratio and pH **increase** with the added sodium salt. The additional NaA increases the concentration of both NaA and HA, but the relative increase in [NaA] is greater. Thus, the ratio increases and the solution becomes more basic. Whenever base is added to a buffer, the pH always increases, but only slightly if the amount of base is not too large.

d) Buffer component ratio and pH **decrease**. The concentration of HA increases more than the concentration of NaA, so the ratio is less and the solution is more acidic.

19.10 a) pH would **increase** by a small amount.
b) pH would **decrease** by a small amount.
c) pH would **increase** by a very small amount.
d) pH would **increase** by a large amount.

19.11 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)	$CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons$		$CH_3CH_2COO^-(aq) +$	$H_3O^+(aq)$
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.

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

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

Check assumption: percent error = $(5.6 \text{ x } 10^{-6} / 0.15)100\% = 0.0037\%$. The assumption is valid.
    pH = –log $[H_3O^+]$ = –log $(5.57143 \text{ x } 10^{-6})$ = 5.2540 = **5.25**.
Another solution path to find pH is using the Henderson–Hasselbalch equation:

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

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

$$pH = 5.25398 = 5.25$$

19.12 CA = C_6H_5COOH \qquad CB = $C_6H_5COO^-$ Neglect Na^+. Assume $+ x$ and $- x$ are negligible.

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

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

Check assumption: percent error = $(7.425 \text{ x } 10^{-5} / 0.28)100\% = 0.026\%$. The assumption is valid.
    pH = –log $[H_3O^+]$ = –log $(7.425 \text{ x } 10^{-5})$ = 4.1293 = **4.13**

19.13 The buffer components are nitrous acid, HNO_2, and nitrite ion, NO_2^-. The potassium ions are ignored because they are not involved in the buffer. Set up the problem with a reaction table.

Concentration (M)	$HNO_2(aq) +$	$H_2O(l) \rightleftharpoons$	$NO_2^-(aq) +$	$H_3O^+(aq)$
Initial	0.55	—	0.75	0
Change	$-x$	—	$+x$	$+x$
Equilibrium	$0.55 - x$	—	$0.75 + x$	x

Assume that x is negligible with respect to both 0.55 and 0.75 since both concentrations are much larger than K_a.

$$K_a = \frac{\left[H_3O^+\right]\left[NO_2^-\right]}{\left[HNO_2\right]} = \frac{[x][0.75 + x]}{[0.55 - x]} = \frac{[x][0.75]}{[0.55]} = 7.1 \text{ x } 10^{-4}$$

$$[H_3O^+] = K_a \frac{\left[HNO_2\right]}{\left[NO_2^-\right]} = \left(7.1 \text{ x } 10^{-4}\right)\frac{[0.55]}{[0.75]} = 5.2066667\text{x } 10^{-4} = \textbf{5.2 x } 10^{-4} \textbf{ M}$$

Check assumption: percent error = $(5.2066667 \text{ x } 10^{-4} / 0.55)100\% = 0.095\%$. The assumption is valid.
pH = $-[H_3O^+]$ = $-\log (5.2066667 \text{ x } 10^{-4}) = 3.28344 = \textbf{3.28}$
Verify the pH using the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \qquad\qquad pK_a = -\log(7.1 \text{ x } 10^{-4}) = 3.149$$

$$pH = 3.149 + \log\left(\frac{[NO_2^-]}{[HNO_2]}\right) = 3.149 + \log\left(\frac{[0.75]}{[0.55]}\right)$$

$$pH = 3.2837 = 3.28$$

19.14   The acid component is HF and the base component is F^-. Neglect K^+. Assume $+ x$ and $- x$ are negligible.

$$K_a = \frac{\left[H_3O^+\right]\left[F^-\right]}{\left[HF\right]} = \frac{[x][0.25 + x]}{[0.20 - x]} = \frac{[x][0.25]}{[0.20]} = 6.8 \text{ x } 10^{-4}$$

$$[H_3O^+] = K_a \frac{\left[HF\right]}{\left[F^-\right]} = (6.8 \text{ x } 10^{-4})\,(0.20 / 0.25) = 5.44 \text{ x } 10^{-4} = \textbf{5.4 x } 10^{-4} \textbf{ M}$$

Check assumption: percent error = $(5.44 \text{ x } 10^{-4} / 0.20)100\% = 0.27\%$. The assumption is valid.
$$pH = -\log [H_3O^+] = -\log (5.44 \text{ x } 10^{-4}) = 3.2644 = \textbf{3.26}$$
Verify the pH using the Henderson-Hasselbalch equation.

19.15   The buffer components are formic acid, HCOOH, and formate ion, HCOO⁻. The sodium ions are ignored because they are not involved in the buffer. Calculate K_a from pK_a and write a reaction table for the dissociation of formic acid.

$K_a = 10^{-pK_a} = 10^{-3.74} = 1.8197 \text{ x } 10^{-4}$ (unrounded)

Concentration (*M*)	HCOOH(*aq*) + H₂O(*l*)	⇌	HCOO⁻(*aq*) + H₃O⁺(*aq*)	
Initial	0.45	—	0.63	0
Change	− x	—	+ x	+ x
Equilibrium	0.45 − x	—	0.63 + x	x

Assume that x is negligible because both concentrations are much larger than K_a.

$$K_a = \frac{\left[H_3O^+\right]\left[HCOO^-\right]}{\left[HCOOH\right]} = \frac{[x][0.63 + x]}{[0.45 - x]} = \frac{[x][0.63]}{[0.45]} = 1.8197 \text{ x } 10^{-4} \text{ (unrounded)}$$

$$[H_3O^+] = K_a \frac{\left[HCOOH\right]}{\left[HCOO^-\right]} = \left(1.8197 \text{ x } 10^{-4}\right)\frac{[0.45]}{[0.63]} = 1.29979 \text{ x } 10^{-4} = 1.3 \text{ x } 10^{-4} \text{ M}$$

Check assumption: percent error = $(1.29979 \text{ x } 10^{-4} / 0.45)100\% = 0.029\%$. The assumption is valid.
pH = $-[H_3O^+]$ = $-\log (1.29979 \text{ x } 10^{-4}) = 3.886127 = \textbf{3.89}$
Verify the pH using the Henderson-Hasselbalch equation.

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

$$pH = 3.74 + \log\left(\frac{[HCOO^-]}{[HCOOH]}\right) = 3.74 + \log\left(\frac{[0.63]}{[0.45]}\right)$$

$$pH = 3.8861 = 3.89$$

19.16 $K_a = 10^{-pK} = 10^{-8.64} = 2.2908676 \times 10^{-9}$ (unrounded)

The acid component is HBr and the base component is BrO^-. Neglect K^+. Assume $+ x$ and $-x$ are negligible.

$$K_a = \frac{\left[H_3O^+\right]\left[BrO^-\right]}{\left[HBrO\right]} = \frac{[x][0.68 + x]}{[0.95 - x]} = \frac{[x][0.68]}{[0.95]} = 2.2908676 \times 10^{-9} \text{ (unrounded)}$$

$$[H_3O^+] = K_a \frac{\left[HBrO\right]}{\left[BrO^-\right]} = (2.2908676 \times 10^{-9})(0.95 / 0.68) = 3.2004768 \times 10^{-9} = 3.2 \times 10^{-9} \ M$$

Check assumption: percent error = $(3.2004768 \times 10^{-9} / 0.68)100\% = 0.00000047\%$. The assumption is valid.

$$pH = -\log [H_3O^+] = -\log (3.2004768 \times 10^{-9}) = 8.4947853 = \mathbf{8.49}$$

Verify the pH using the Henderson-Hasselbalch equation.

19.17   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.

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

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.

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

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

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

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

Verify the pH using the Henderson-Hasselbalch equation:

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

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

$\mathbf{pH = 10.03}$

19.18 $K_a = 10^{-pKa} = 10^{-9.24} = 5.7543993 \times 10^{-10}$ (unrounded)

The acid component is H_3BO_3 and the base component is $H_2BO_3^-$. Neglect Na^+. Assume $+ x$ and $- x$ are negligible.

$$K_a = \frac{\left[H_3O^+\right]\left[H_2BO_3^-\right]}{\left[H_3BO_3\right]} = \frac{[x][0.82 + x]}{[0.12 - x]} = \frac{[x][0.82]}{[0.12]} = 5.7543993 \times 10^{-10} \text{ (unrounded)}$$

$$[H_3O^+] = K_a \frac{\left[H_3BO_3\right]}{\left[H_2BO_3^-\right]} = (5.7543993 \times 10^{-10})(0.12 / 0.82) = 8.4210722 \times 10^{-11} \ M \text{ (unrounded)}$$

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

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

Verify the pH using the Henderson-Hasselbalch equation.

19.19 The buffer components are phenol, NH_3, and ammonium ion, NH_4^+. The chloride ions are ignored because they are not involved in the buffer. Calculate K_b from pK_b and set up the problem with a reaction table.
$K_b = 10^{-pK_b} = 10^{-4.75} = 1.7782794 \times 10^{-5}$ (unrounded)

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

Assume that x is negligible with respect to both 0.25 and 0.15 because both concentrations are much larger than K_b.
$K_b = 10^{-pK_b} = 10^{-4.75} = 1.7782794 \times 10^{-5}$ (unrounded)

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

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

Check assumption: percent error = $(2.963799 \times 10^{-5} / 0.25)100\% = 0.012\%$. The assumption is valid.
   $pOH = -\log [OH^-] = -\log (2.963799 \times 10^{-5}) = 4.52815$ (unrounded)
$14.00 = pH + pOH$
$pH = 14.00 - pOH = 14.00 - 4.52815 = 9.4718 = \mathbf{9.47}$
Verify the pH using the Henderson-Hasselbalch equation. To do this, you must find the pK_a of the acid NH_4^+:
$14 = pK_a + pK_b$
$pK_a = 14 - pK_b = 14 - 4.75 = 9.25$

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

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

$$\mathbf{pH = 9.47}$$

19.20 $K_b = 10^{-pK_b} = 10^{-3.35} = 4.4668359 \times 10^{-4}$ (unrounded)
The base component is CH_3NH_2 and the acid component is $CH_3NH_3^+$. Neglect Cl^-. Assume $+ x$ and $- x$ are negligible.

$$K_b = \frac{\left[CH_3NH_3^+\right]\left[OH^-\right]}{\left[CH_3NH_2\right]} = \frac{\left[0.60 + x\right]\left[OH^-\right]}{\left[0.50 - x\right]} = \frac{\left[0.60\right]\left[OH^-\right]}{\left[0.50\right]} = 4.4668359 \times 10^{-4}$$

$$[OH^-] = K_b \frac{\left[CH_3NH_2\right]}{\left[CH_3NH_3^+\right]} = (4.4668359 \times 10^{-4}) (0.50 / 0.60) = 3.7223632 \times 10^{-4} \, M \text{ (unrounded)}$$

Check assumption: percent error = $(3.7223632 \times 10^{-4} / 0.50)100\% = 0.074\%$. The assumption is valid.
   $pOH = -\log [OH^-] = -\log (3.7223632 \times 10^{-4}) = 3.429181246$ (unrounded)
$pH = 14.00 - pOH = 14.00 - 3.429181246 = 10.57081875 = \mathbf{10.57}$
Verify the pH using the Henderson-Hasselbalch equation.

19.21 a) The buffer components are HCO_3^- from the salt $KHCO_3$ and CO_3^{2-} from the salt K_2CO_3. Choose the K_a value that corresponds to the equilibrium with these two components. K_{a1} refers to carbonic acid, H_2CO_3 losing one proton to produce HCO_3^-. This is not the correct K_a because H_2CO_3 is not involved in the buffer. $\mathbf{K_{a2}}$ is the correct K_a to choose because it is the equilibrium constant for the loss of the second proton to produce CO_3^{2-} from HCO_3^-.
b) Set up the reaction table and use K_{a2} to calculate pH.

Concentration (M)	$HCO_3^-_{(aq)}$ +	$H_2O(l)$ $\rightleftarrows$	$CO_3^{2-}(aq)$ +	$H_3O^+(aq)$
Initial	0.22	—	0.37	0
Change	$-x$	—	$+x$	$+x$
Equilibrium	$0.22 - x$	—	$0.37 + x$	x

Assume that x is negligible with respect to both 0.22 and 0.37 because both concentrations are much larger than K_a.

$$K_a = \frac{\left[H_3O^+\right]\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]} = \frac{[x][0.37 + x]}{[0.22 - x]} = \frac{[x][0.37]}{[0.22]} = 4.7 \times 10^{-11}$$

$$[H_3O^+] = K_a \frac{\left[HCO_3^-\right]}{\left[CO_3^{2-}\right]} = \left(4.7 \times 10^{-11}\right)\left(\frac{0.22}{0.37}\right) = 2.79459 \times 10^{-11} \ M \ \text{(unrounded)}$$

Check assumption: percent error = $(2.79459 \times 10^{-11} / 0.22)100\% = 1.3 \times 10^{-8}\%$. The assumption is valid.
pH = $-[H_3O^+]$ = $-\log (2.79459 \times 10^{-11}) = 10.5537 = $ **10.55**.
Verify the pH using the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \qquad\qquad pK_a = -\log(4.7 \times 10^{-11}) = 10.328$$

$$pH = 10.328 + \log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right) = 10.328 + \log\left(\frac{[0.37]}{[0.22]}\right)$$

$$\mathbf{pH = 10.55}$$

19.22   a) The conjugate acid-base pair are related by K_{a2} (6.3 x 10^{-8}).
b) Assume that x is negligible with respect to both 0.50 and 0.40 because both concentrations are much larger than K_a. The acid component is $H_2PO_4^-$ and the base component is HPO_4^{2-}. Neglect Na$^+$. Assume + x and – x are negligible.

$$K_a = \frac{\left[H_3O^+\right]\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = \frac{[x][0.40 + x]}{[0.50 - x]} = \frac{[x][0.40]}{[0.50]} = 6.3 \times 10^{-8}$$

$$[H_3O^+] = K_a \frac{\left[H_2PO_4^-\right]}{\left[HPO_4^{2-}\right]} = (6.3 \times 10^{-8})\,(0.50 / 0.40) = 7.875 \times 10^{-8} \ M \ \text{(unrounded)}$$

Check assumption: percent error = $(7.875 \times 10^{-8} / 0.50)100\% = 1.6 \times 10^{-5}\%$. The assumption is valid.
$$pH = -\log [H_3O^+] = -\log (7.875 \times 10^{-8}) = 7.103749438 = \mathbf{7.10}$$
Verify the pH using the Henderson-Hasselbalch equation.

19.23   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)

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

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

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

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

19.24   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)

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

$$2.95 = 3.14874165 + \log\left(\frac{[NO_2^-]}{[HNO_2]}\right)$$

$$-0.19874165 = \log\left(\frac{[NO_2^-]}{[HNO_2]}\right) \qquad \text{Raise each side to } 10^x.$$

$$\frac{[NO_2^-]}{[HNO_2]} = 0.632788 = \mathbf{0.63}$$

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

$pK_a = -\log K_a = -\log (2.3 \times 10^{-9}) = 8.63827$

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

$$7.95 = 8.63827 + \log\left(\frac{[BrO^-]}{[HBrO]}\right)$$

$$-0.68827 = \log\left(\frac{[BrO^-]}{[HBrO]}\right) \qquad \text{Raise each side to } 10^x.$$

$$\frac{[BrO^-]}{[HBrO]} = 0.204989 = \mathbf{0.20}$$

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

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

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

$$4.39 = 4.74473 + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$-0.35473 = \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) \qquad \text{Raise each side to } 10^x.$$

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = 0.441845 = \mathbf{0.44}$$

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

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

$$3.35 = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log\left(\frac{[0.1500]}{[0.2000]}\right)$$
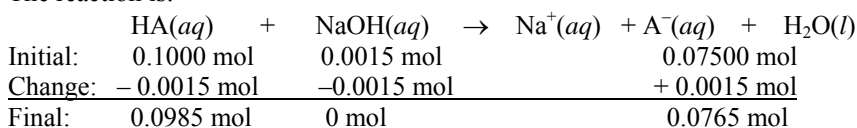
$$3.35 = pK_a - 0.1249387$$
$$pK_a = 3.474939 = 3.47$$

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:

	HA(aq)	+	NaOH(aq)	→	Na⁺(aq)	+ A⁻(aq)	+	H₂O(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:

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

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

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

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

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

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

$$8.88 = pK_a + \log\left(\frac{[B]}{[BH^+]}\right) = pK_a + \log\left(\frac{[0.40]}{[0.25]}\right)$$
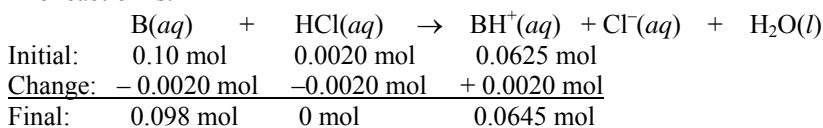
$$8.88 = pK_a + 0.20411998$$

$$pK_a = 8.67588 = 8.68$$

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)	+	H₂O(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:

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

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

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

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

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

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

$$8.77 = pK_a + \log\left(\frac{[Y^-]}{[HY]}\right) = pK_a + \log\left(\frac{[0.220]}{[0.110]}\right)$$
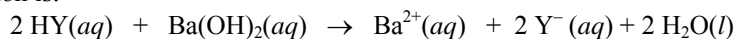
$8.77 = pK_a + 0.301029996$
$pK_a = 8.46897 = 8.47$

Determine the moles of conjugate acid (HY) and conjugate base (Y^-) using (M)(V) = moles.

Moles HY = (0.350 L) (0.110 mol HY / L) = 0.0385 mol HY
Moles Y^- = (0.350 L) (0.220 mol Y^- / L) = 0.077 mol Y^-)

The reaction is:

	2 HY(aq)	+	Ba(OH)$_2$(aq)	→	Ba^{2+}(aq)	+ 2 Y$^-$ (aq) + 2 H$_2$O(l)
Initial:	0.0385 mol		0.0015 mol			0.077 mol
Change:	− 0.0030 mol		−0.0015 mol			+ 0.0030 mol
Final:	0.0355 mol		0 mol			0.0800 mol

Ba(OH)$_2$ is the limiting reagent. The addition of 0.0015 mol Ba(OH)$_2$ will produce 2 x 0.0015 mol Y^- and consume 2 x 0.0015 mol of HY.

Then:

$$[Y^-] = \frac{0.0800 \text{ mol } Y^-}{0.350 \text{ L}} = 0.228571 \; M \; Y^-$$

$$[HY] = \frac{0.0355 \text{ mol } HY}{0.350 \text{ L}} = 0.101429 \; M \; HY$$

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

$$pH = 8.46897 + \log\left(\frac{[0.228571]}{[0.101429]}\right) = 8.82183 = \textbf{8.82}$$

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

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

$$9.50 = pK_a + \log\left(\frac{[B]}{[BH^+]}\right) = pK_a + \log\left(\frac{[1.05]}{[0.750]}\right)$$

$9.50 = pK_a + 0.146128036$
$pK_a = 9.353872 = 9.35$

Determine the moles of conjugate acid (BH$^+$) and conjugate base (B).

Moles BH$^+$ = (0.500 L) (0.750 mol BH$^+$ / L) = 0.375 mol BH$^+$ (unrounded)
Moles B = (0.500 L) (1.05 mol B / L) = 0.525 mol B

The reaction is:

	B(aq)	+	HCl(aq) →	BH$^+$(aq) + Cl$^-$ (aq) + H$_2$O(l)
Initial:	0.525 mol		0.0050 mol	0.375 mol
Change:	− 0.0050 mol		−0.0050 mol	+ 0.0050 mol
Final:	0.520 mol		0 mol	0.380 mol

HCl is the limiting reagent. The addition of 0.0050 mol HCl will produce 0.0050 mol BH$^+$ and consume 0.0050 mol of B.
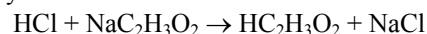
Then

$$[B] = \frac{0.520 \text{ mol B}}{0.500 \text{ L}} = 1.04 \text{ } M \text{ B}$$

$$[BH^+] = \frac{0.380 \text{ mol BH}^+}{0.500 \text{ L}} = 0.760 \text{ } M \text{ BH}^+$$

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

$$pH = 9.353872 + \log\left(\frac{[1.04]}{[0.760]}\right) = 9.490092 = \mathbf{9.49}$$

19.31 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.

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

$$\text{Initial moles } NaC_2H_3O_2 = \left(\frac{0.400 \text{ mol } NaC_2H_3O_2}{L}\right)(0.500 \text{ L}) = 0.200 \text{ mol } NaC_2H_3O_2$$

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

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

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

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

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

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

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.

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

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

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

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

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 $C_2H_3O_2^-$:

$HC_2H_3O_2\ +\ KOH\ \rightarrow C_2H_3O_2^-\ +\ K^+\ + H_2O(l)$
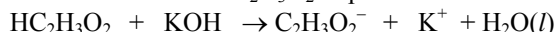
To produce $0.0117167\ mol\ C_2H_3O_2^-$ would require the addition of $0.0117167\ mol\ KOH$.

Mass KOH = $\left(0.0117167\ mol\ KOH\right)\left(\dfrac{56.11\ g\ KOH}{1\ mol\ KOH}\right) = 0.657424 =$ **0.66 g KOH**

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

$NaOH + NaHCO_3 \rightarrow 2\ Na^+ + CO_3^{2-} + H_2O$
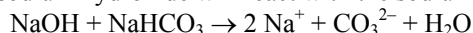
Calculate the number of moles of NaOH and $NaHCO_3$. All of the NaOH will be consumed to form CO_3^{2-}, and the number of moles of $NaHCO_3$ will decrease. The HCO_3^- is the important part of $NaHCO_3$.

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

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

$= 0.0025\ mol\ HCO_3^-$

	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		0.00107 mol	

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

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

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

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

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

$pH = 10.32790214 + \log\left(\dfrac{[0.017627677]}{[0.023558484]}\right) = 10.2019 =$ **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^-:

$$CO_3^{2-} + HCl \rightarrow HCO_3^- + Cl^-$$
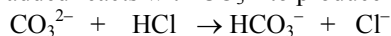
To produce 0.0000411635 mol HCO_3^- would require the addition of 0.0000411635 mol HCl.

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

19.33   Select conjugate pairs with K_a values close to the desired $[H_3O^+]$.
a) For pH ≈ 4.5, $[H_3O^+] = 10^{-4.5} = 3.2$ 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 x 10^{-5} or $C_6H_5CH_2COOH/C_6H_5CH_2COO^-$ conjugate pair
with K_a equal to 4.9 x 10^{-5}. From the base list, the $C_6H_5NH_2$ / $C_6H_5NH_3^+$ conjugate pair comes close with $K_a = 1.0$
x 10^{-14} / 4.0 x 10^{-10} = 2.5 x 10^{-5}.
b) For pH ≈ 7.0, $[H_3O^+] = 10^{-7.0} = 1.0$ x 10^{-7} M. Two choices are the $H_2PO_4^-$ / HPO_4^{2-} conjugate pair with K_a of
6.3 x 10^{-8} and the $H_2AsO_4^-$ / $HAsO_4^{2-}$ conjugate pair with K_a of 1.1 x 10^{-7}.

19.34   Select conjugate pairs that have K_a or K_b values close to the desired $[H_3O^+]$ or $[OH^-]$.
a) For $[H_3O^+]$ ≈ 1 x 10^{-9} M, the HOBr / OBr^- conjugate pair comes close with K_a equal to 2.3 x 10^{-9}. From the
base list, $K_b = 1.0$ x 10^{-14} / 1 x 10^{-9} = 1 x 10^{-5}, the NH_3 / NH_4^+ conjugate pair comes close with $K_b = 1.76$ x 10^{-5}.
b) For $[OH^-]$ ≈ 3 x 10^{-5} M, the NH_3 / NH_4^+ conjugate pair comes close; also, it is possible to choose
$K_a = 1.0$ x 10^{-14} / 3 x 10^{-5} = 3.3 x 10^{-10} , the C_6H_5OH / $C_6H_5O^-$ comes close with $K_a = 1.0$ x 10^{-10}.

19.35   Select conjugate pairs with pK_a values close to the desired pH. Convert pH to $[H_3O^+]$ for easy comparison to K_a
values. Determine an appropriate base by $[OH^-] = K_w$ / $[H_3O^+]$.
a) For pH ≈ 3.5 ($[H_3O^+] = 10^{-pH} = 10^{-3.5} = 3.2$ x 10^{-4}), the best selection is the $HOCH_2CH(OH)COOH/$
$HOCH_2CH(OH)COOH^-$ conjugate pair with a $K_a = 2.9$ x 10^{-4}. The $CH_3COOC_6H_4COOH$ / $CH_3COOC_6H_4COO^-$
pair, with $K_a = 3.6$ x 10^{-4}, is also a good choice. The $[OH^-] = 1.0$ x 10^{-14} / 3.2 x 10^{-4} = 3.1 x 10^{-11}, results in no
reasonable K_b values from the appendix.

b) For pH ≈ 5.5 ($[H_3O^+] = 10^{-pH} = 3 \times 10^{-6}$), no K_{a1} gives an acceptable pair; the K_{a2} values for adipic acid, malonic acid, and succinic acid are reasonable. The $[OH^-] = 1.0 \times 10^{-14} / 3 \times 10^{-6} = 3 \times 10^{-9}$, the K_b selection is $C_5H_5N / C_5H_5NH^+$.

19.36 Select conjugate pairs that have K_a or K_b values close to the desired $[H_3O^+]$ or $[OH^-]$.
a) For $[OH^-] \approx 1 \times 10^{-6}$ M, no K_b values work. The K_a values are $[H_3O^+] = K_w / [OH^-] = 1.0 \times 10^{-14} / 1 \times 10^{-6}$ $= 1 \times 10^{-8}$, giving the following acceptable pairs $H_2PO_4^- / HPO_4^{2-}$ or $HC_6H_5O_7^{2-} / C_6H_5O_7^{3-}$ or $HOCl / OCl^-$.
b) For $[H_3O^+] \approx 4 \times 10^{-4}$ M, the HF / F⁻ conjugate pair comes close with K_a equal to 6.8×10^{-4}. From the base list, $K_b = 1.0 \times 10^{-14} / 4 \times 10^{-4} = 2.5 \times 10^{-11}$, there are no reasonable choices.

19.37 The value of the K_a from the appendix: $K_a = 2.9 \times 10^{-8}$
$pK_a = -\log 2.9 \times 10^{-8} = 7.5376$ (unrounded)
Use the Henderson-Hasselbalch equation to determine the pH.

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

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

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

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

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⁻	+	H₂O
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		

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

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

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

$$7.40 = 7.200659451 + \log\left(\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}\right)$$

$$0.19934055 = \log\left(\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}\right)$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 1.582486 = \textbf{1.6}$$

19.39 You need to know the pK_a value for the indicator. (Its transition range is approximately $pK_a \pm 1$.) If the indicator is a diprotic acid, it will have two transition ranges, one for each of the two H_3O^+ ions lost.

19.40   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.

19.41   This is because the concentration of indicator is very small.

19.42   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.

19.43   a)   The reactions are:

OH⁻(*aq*)   + H_3PO_4(*aq*) → $H_2PO_4^-$(*aq*) + H_2O(*l*) K_{a1} = 7.2 x 10⁻³
OH⁻(*aq*)   + $H_2PO_4^-$ (*aq*) → HPO_4^{2-}(*aq*) + H_2O(*l*) K_{a2} = 6.3 x 10⁻⁸

The correct order is **C, B, D, A.** Scene C shows the solution before the addition of any NaOH. Scene B is half-way to the first equivalence point; Scene D is halfway to the second equivalence point and Scene A is at end of the titration.
b) Scene B is the second scene in the correct order. This is halfway towards the first equivalence point when there are equal amounts of the acid and conjugate base, which constitutes a buffer.

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

Determine the pK_a using pK_a = −log 7.2 x 10⁻³ = 2.142668

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

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.

19.44   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 → 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 → HCOO⁻ + H_2O + Na^+. The conjugate base, HCOO⁻, reacts with water according to this reaction: HCOO⁻ + H_2O → 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 → NH_4^+ + Cl⁻. The conjugate acid, NH_4^+, dissociates slightly in water: NH_4^+ + H_2O → NH_3 + H_3O^+.
In rank order of pH of equivalence point, strong acid -*weak base* < *strong acid*-strong base < *weak acid* -strong base.

19.45   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.

19.46   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.

19.47   The titration curve for a diprotic acid has two "breaks" i.e., two regions where the pH increases sharply. For a monoprotic acid, only one break occurs.

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

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

19.50   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)	+ H₂O(l) ⇌	⇌COOH(aq)	+ OH⁻(aq)
Initial:	0.050 M	—	0	0
Change:	$-x$		+x	+x
Equilibrium:	0.050 – x		x	x
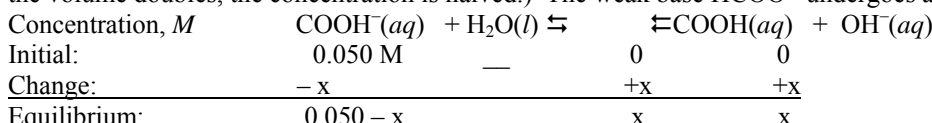
The K_a for HCOOH is 1.8×10^{-4}, so $K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-4} = 5.5556 \times 10^{-11}$ (unrounded)

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

$[\text{OH}^-] = x = 1.666673 \times 10^{-6}\ M$
$pOH = -\log (1.666673 \times 10^{-6}) = 5.7781496$ (unrounded)
$pH = 14.00 - pOH = 14.00 - 5.7781496 = 8.2218504 = 8.22$
Choose **thymol blue** or **phenolphthalein**.

19.51   a) Determine the K_a (of the conjugate acid) from the K_b for CH₃NH₂.
$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (4.4 \times 10^{-4}) = 2.2727 \times 10^{-11}$ (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 CH₃NH₃⁺ = 0.050 M.

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

$x = [\text{H}_3\text{O}^+] = 1.0659971 \times 10^{-6}\ M$ (unrounded)
$pH = -\log [\text{H}_3\text{O}^+] = -\log (1.0659971 \times 10^{-6}) = 5.97224 = 5.97$
Either **methyl red** or **alizarin** is acceptable.
b) This is a strong acid-strong base titration; thus, the equivalence point is at pH = 7.00.
The best choice would be **bromthymol blue**; alizarin might be acceptable.

19.52   a) The equivalence point for a weak base–strong acid is below pH 7. Estimate the pH at equivalence point from equilibrium calculations.
At the equivalence point, the solution is 0.25 M (CH₃)₂NH₂⁺. (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.)
$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (5.9 \times 10^{-4}) = 1.6949152 \times 10^{-11}$ (unrounded)

Concentration, M	(CH₃)₂NH₂⁺ (aq)	+ H₂O(l) ⇌	(CH₃)₂NH (aq)	+ H₃O⁺(aq)
Initial:	0.25 M	—	0	0
Change:	$-x$		+x	+x
Equilibrium:	0.25 – x		x	x

$$K_a = \frac{\left[H_3O^+\right]\left[(CH_3)_2\,NH\right]}{\left[(CH_3)_2\,NH_2{}^+\right]} = \frac{x^2}{0.25 - x} = \frac{x^2}{0.25} = 1.6949152 \times 10^{-11}$$

$x = [H_3O^+] = 2.0584674 \times 10^{-6}\ M$ (unrounded)

$pH = -\log\,[H_3O^+] = -\log\,(2.0584674 \times 10^{-6}) = 5.686456 = 5.69$
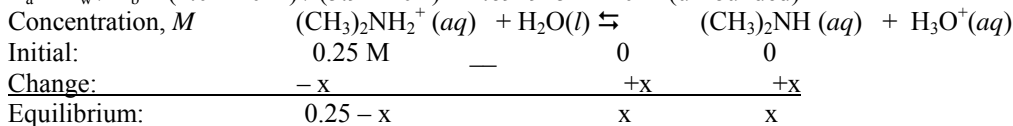
Methyl red is an indicator that changes color around pH 5.7.

b) This is a strong acid–strong base titration; thus, the equivalence point is at pH = 7.00. **Bromthymol blue** is an indicator that changes color around pH 7.

19.53   a) Determine the K_b (of the conjugate base) from the K_a for C_6H_5COOH.

$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (6.3 \times 10^{-5}) = 1.5873 \times 10^{-10}$ (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 $C_6H_5COO^- = 0.125\ M$ (unrounded).

$$K_b = \frac{\left[C_6H_5COOH\right]\left[OH^-\right]}{\left[C_6H_5COO^-\right]} = \frac{[x][x]}{[0.125 - x]} = \frac{[x][x]}{[0.125]} = 1.5873 \times 10^{-10}$$

$[OH^-] = x = 4.4543518 \times 10^{-6}\ M$

$pOH = -\log\,(4.4543518 \times 10^{-6}) = 5.351215485$ (unrounded)

$pH = 14.00 - pOH = 14.00 - 5.351215485 = 8.64878 = 8.65$

The choices are **phenolphthalein or thymol blue.**

b) The titration will produce a 0.25 M NH_3 solution at the equivalence point. Use the K_b for NH_3 from the Appendix.

$$K_b = \frac{\left[NH_4{}^+\right]\left[OH^-\right]}{\left[NH_3\right]} = \frac{[x][x]}{[0.25 - x]} = \frac{[x][x]}{[0.25]} = 1.76 \times 10^{-5}$$

$[OH^-] = x = 2.0976176 \times 10^{-3}\ M$

$pOH = -\log\,(2.0976176 \times 10^{-3}) = 2.67827$ (unrounded)

$pH = 14.00 - pOH = 14.00 - 2.67827 = 11.32173 = 11.32$

The best choice would be **alizarin yellow R**; alizarin might be acceptable.

19.54   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:

   $H_3O^+(aq) + OH^-(aq) \rightarrow 2\,H_2O(l)$
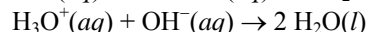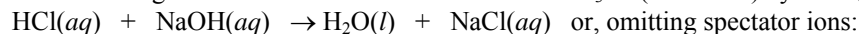
For the titration of a strong acid with a strong base, the pH before the equivalence point depends on the excess concentration of acid and the pH after the equivalence point depends on the excess concentration of base. At the equivalence point, there is not an excess of either acid or base so the pH 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 x 10^{-3} mol HCl

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

   $pH = -\log\,(0.1000\ M) = \textbf{1.0000}$

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 x 10^{-3} mol NaOH

	HCl(aq)	+	NaOH(aq)	$\rightarrow$	H₂O(l)	+	NaCl(aq)
Initial:	4.000 x 10^{-3} mol		2.500 x 10^{-3} mol		–		0
Change:	– 2.500 x 10^{-3} mol		–2.500 x 10^{-3} mol		–		+ 2.500 x 10^{-3} mol
Final:	1.500 x 10^{-3} mol		0				2.500 x 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 x 10^{-3} mol HCl) / (0.06500 L) = 0.02307 M (unrounded)

   $pH = -\log\,(0.02307) = \textbf{1.6368}$

(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 x 10^{-3} mol NaOH

	HCl(aq)	+	NaOH(aq)	→	H$_2$O(l)	+	NaCl(aq)
Initial:	4.000 x 10^{-3} mol		4.900 x 10^{-3} mol		–		0
Change:	– 3.900 x 10^{-3} mol		–3.900 x 10^{-3} mol		–		+ 3.900 x 10^{-3} mol
Final:	1.000 x 10^{-4} mol		0				3.900 x 10^{-3} mol
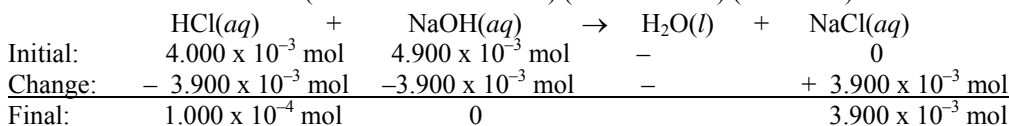
The volume of the solution at this point is [(40.00 + 39.00) mL] (10^{-3} L / 1 mL) = 0.07900 L
The molarity of the excess HCl is (1.00 x 10^{-4} mol HCl) / (0.07900 L) = 0.0012658 M (unrounded)

      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 x 10^{-3} mol NaOH

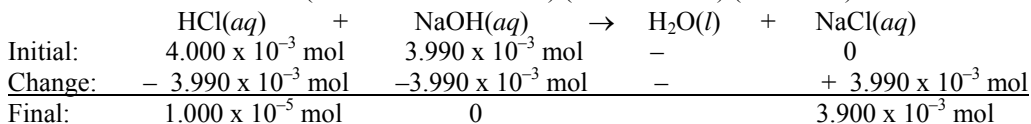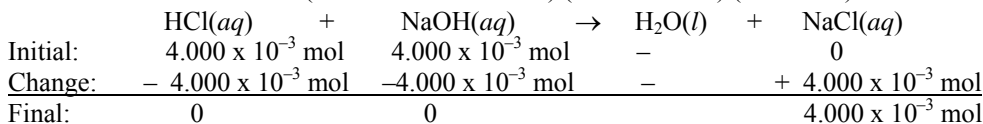|	HCl(aq)	+	NaOH(aq)	→	H$_2$O(l)	+	NaCl(aq)
Initial:	4.000 x 10^{-3} mol		3.990 x 10^{-3} mol		–		0
Change:	– 3.990 x 10^{-3} mol		–3.990 x 10^{-3} mol		–		+ 3.990 x 10^{-3} mol
Final:	1.000 x 10^{-5} mol		0				3.900 x 10^{-3} mol

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 x 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 x 10^{-3} mol NaOH.

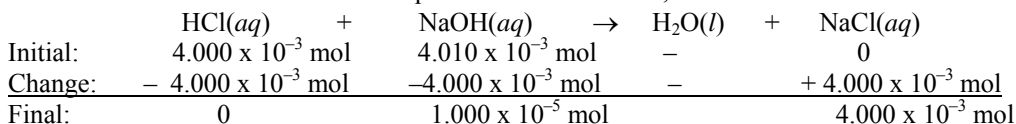|	HCl(aq)	+	NaOH(aq)	→	H$_2$O(l)	+	NaCl(aq)
Initial:	4.000 x 10^{-3} mol		4.000 x 10^{-3} mol		–		0
Change:	– 4.000 x 10^{-3} mol		–4.000 x 10^{-3} mol		–		+ 4.000 x 10^{-3} mol
Final:	0		0				4.000 x 10^{-3} mol

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 x 10^{-3} mol NaOH

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

	HCl(aq)	+	NaOH(aq)	→	H$_2$O(l)	+	NaCl(aq)
Initial:	4.000 x 10^{-3} mol		4.010 x 10^{-3} mol		–		0
Change:	– 4.000 x 10^{-3} mol		–4.000 x 10^{-3} mol		–		+ 4.000 x 10^{-3} mol
Final:	0		1.000 x 10^{-5} mol				4.000 x 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
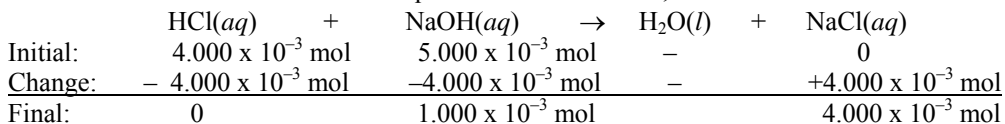The molarity of the excess NaOH is (1.0 x 10^{-5} mol NaOH) / (0.08010 L) = 0.00012484 M (unrounded)

      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 x 10^{-3} mol NaOH

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

|	HCl(aq)	+	NaOH(aq)	→	H$_2$O(l)	+	NaCl(aq)
Initial:	4.000 x 10^{-3} mol		5.000 x 10^{-3} mol		–		0
Change:	– 4.000 x 10^{-3} mol		–4.000 x 10^{-3} mol		–		+4.000 x 10^{-3} mol
Final:	0		1.000 x 10^{-3} mol				4.000 x 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 x 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**

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

$$HBr(aq) \ + \ KOH(aq) \ \rightarrow \ H_2O(l) \ + \ KBr(aq)$$
$$H_3O^+(aq) + OH^-(aq) \rightarrow 2 \ H_2O(l)$$
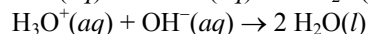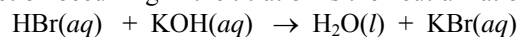
For the titration of a strong base with a strong acid, the pH before the equivalence point depends on the excess concentration of base and the pH after the equivalence point depends on the excess concentration of acid. At the equivalence point, there is not an excess of either acid or base so pH is 7.0. 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 x 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 x 10^{-3} mol HBr
        The HBr will react with an equal amount of the base, and 1.500 x 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 x 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 x 10^{-3} mol HBr
        The HBr will react with an equal amount of the base, and 1.00 x 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 x 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 x 10^{-3} mol HBr
        The HBr will react with an equal amount of the base, and 1.0 x 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 x 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**

19.56 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) =
$$(0.1000 \text{ mol HBut / L}) (10^{-3} \text{ L / 1 mL}) (20.00 \text{ mL}) = 2.000 \times 10^{-3} \text{ mol} \quad \text{HBut}$$

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

	HBut	+	H₂O	⇌	H₃O⁺	+	But⁻
Initial:	0.100 M						0
Change:	−x						+x
Equilibrium:	0.100 − x						x
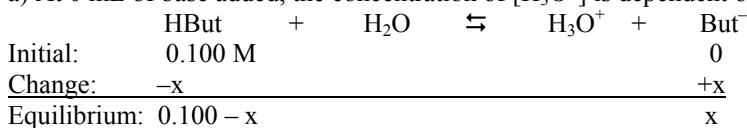
$$K_a = \frac{[H_3O^+][But^-]}{[HBut]} = \frac{x^2}{0.1000 - x} = \frac{x^2}{0.1000} = 1.54 \times 10^{-5}$$

$$x = [H_3O^+] = 1.2409673 \times 10^{-3} \ M \ (\text{unrounded})$$
$$pH = -\log[H_3O^+] = -\log(1.2409673 \times 10^{-3}) = 2.9062 = \mathbf{2.91}$$

b) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH / L}) (10^{-3} \text{ L / 1 mL}) (10.00 \text{ mL}) = 1.000 \times 10^{-3}$ mol NaOH
The NaOH will react with an equal amount of the acid, and 1.000×10^{-3} mol HBut will remain. An equal number of moles of But⁻ will form.
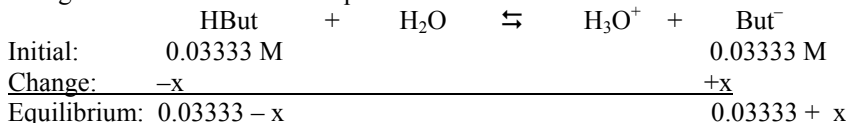
	HBut(aq)	+	NaOH(aq)	→	H₂O(l)	+	But⁻(aq)	+	Na⁺(aq)
Initial:	2.000 × 10⁻³ mol		1.000 × 10⁻³ mol		–		0		–
Change:	− 1.000 × 10⁻³ mol		−1.000 × 10⁻³ mol		–		+1.000 × 10⁻³ mol		–
Final:	1.000 × 10⁻³ mol		0				1.000 × 10⁻³ mol		
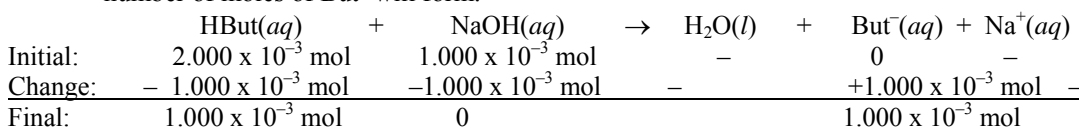
The volume of the solution at this point is $[(20.00 + 10.00) \text{ mL}] (10^{-3} \text{ L / 1 mL}) = 0.03000$ L
The molarity of the excess HBut is $(1.000 \times 10^{-3} \text{ mol HBut}) / (0.03000 \text{ L}) = 0.03333 \ M$ (unrounded)
The molarity of the But⁻ formed is $(1.000 \times 10^{-3} \text{ mol But}^-) / (0.03000 \text{ L}) = 0.03333 \ M$ (unrounded)
Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H₂O	⇌	H₃O⁺	+	But⁻
Initial:	0.03333 M						0.03333 M
Change:	−x						+x
Equilibrium:	0.03333 − x						0.03333 + x

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

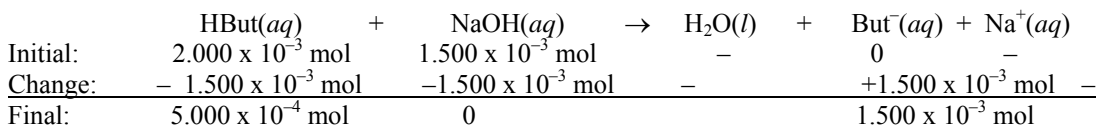$$x = [H_3O^+] = 1.54 \times 10^{-5} \ M \ (\text{unrounded})$$
$$pH = -\log[H_3O^+] = -\log(1.54 \times 10^{-5}) = 4.812479 = \mathbf{4.81}$$

c) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH / L}) (10^{-3} \text{ L / 1 mL}) (15.00 \text{ mL}) = 1.500 \times 10^{-3}$ mol NaOH
The NaOH will react with an equal amount of the acid, and 5.00×10^{-4} mol HBut will remain, and 1.500×10^{-3} moles of But⁻ will form.

	HBut(aq)	+	NaOH(aq)	→	H₂O(l)	+	But⁻(aq)	+	Na⁺(aq)
Initial:	2.000 × 10⁻³ mol		1.500 × 10⁻³ mol		–		0		–
Change:	− 1.500 × 10⁻³ mol		−1.500 × 10⁻³ mol		–		+1.500 × 10⁻³ mol		–
Final:	5.000 × 10⁻⁴ mol		0				1.500 × 10⁻³ mol		

The volume of the solution at this point is $[(20.00 + 15.00) \text{ mL}] (10^{-3} \text{ L / 1 mL}) = 0.03500$ L
The molarity of the excess HBut is $(5.00 \times 10^{-4} \text{ mol HBut}) / (0.03500 \text{ L}) = 0.0142857 \ M$ (unrounded)
The molarity of the But⁻ formed is $(1.500 \times 10^{-3} \text{ mol But}^-) / (0.03500 \text{ L}) = 0.0428571 \ M$ (unrounded)
Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H₂O	⇌	H₃O⁺	+	But⁻
Initial:	0.0142857 M						0.0428571 M
Change:	−x						+x
Equilibrium:	0.0142857 − x						0.0428571 + x

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

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

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

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.

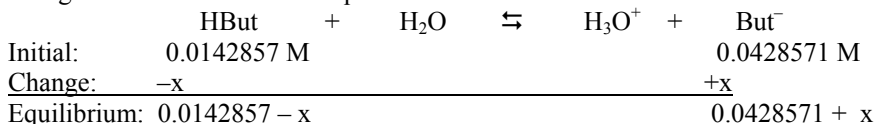|	HBut(aq)	+	NaOH(aq)	→	H₂O(l)	+	But⁻(aq) + Na⁺(aq)
Initial:	2.000 x 10^{-3} mol		1.900 x 10^{-3} mol		–		0 –
Change:	– 1.900 x 10^{-3} mol		–1.900 x 10^{-3} mol		–		+1.900 x 10^{-3} mol –
Final:	1.000 x 10^{-4} mol		0				1.900 x 10^{-3} mol

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	+	H₂O	⇋	H₃O⁺	+	But⁻
Initial:	0.0025641 M						0.0487179 M
Change:	–x						+x
Equilibrium:	0.0025641 – x						0.0487179 + x

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

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

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

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)	→	H₂O(l)	+	But⁻(aq) + Na⁺(aq)
Initial:	2.000 x 10^{-3} mol		1.995 x 10^{-3} mol		–		0 –
Change:	– 1.995 x 10^{-3} mol		–1.995 x 10^{-3} mol		–		+1.995 x 10^{-3} mol –
Final:	5.000 x 10^{-6} mol		0				1.995 x 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 x 10^{-6} mol HBut) / (0.03995 L) = 0.000125156 M (unrounded)

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

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H₂O	⇋	H₃O⁺	+	But⁻
Initial:	0.000125156 M						0.0499374 M
Change:	–x						+x
Equilibrium:	0.000125156 – x						0.0499374 + x

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

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

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

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 x 10^{-3} mol NaOH

The NaOH will react with an equal amount of the acid, and 0 mol HBut will remain, and 2.000 x 10^{-3} moles of But⁻ will form. This is the equivalence point.
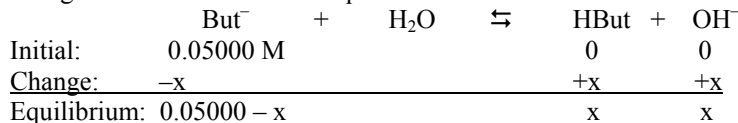
	HBut(*aq*)	+	NaOH(*aq*)	→	$H_2O(l)$	+	But⁻(*aq*) + Na⁺(*aq*)

$$\text{HBut}(aq) \quad + \quad \text{NaOH}(aq) \quad \rightarrow \quad H_2O(l) \quad + \quad \text{But}^-(aq) + \text{Na}^+(aq)$$

Initial: 2.000×10^{-3} mol 2.000×10^{-3} mol   –   0   –

Change: $- 2.000 \times 10^{-3}$ mol -2.000×10^{-3} mol   – $+2.000 \times 10^{-3}$ mol   –

Final: 0   0 2.000×10^{-3} mol
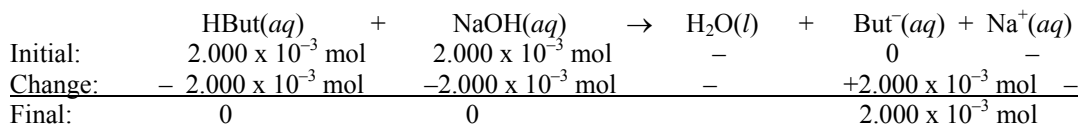
The K_b of But⁻ is now important.

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

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

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

Using a reaction table for the equilibrium reaction of But–:

$$\text{But}^- \quad + \quad H_2O \quad \leftrightarrows \quad \text{HBut} \quad + \quad OH^-$$

Initial: 0.05000 M   0   0

Change: –x   +x   +x

Equilibrium: 0.05000 – x   x   x

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

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

$pOH = -\log(5.6980259 \times 10^{-6}) = 5.244275575$ (unrounded)
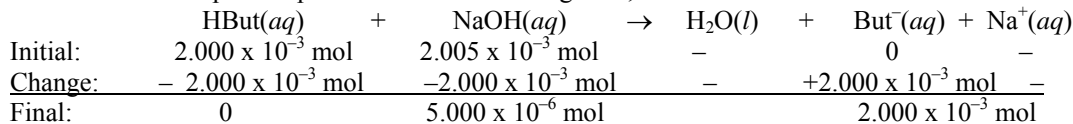
$pH = 14.00 - pOH = 14.00 - 5.244275575 = 8.755724425 = \mathbf{8.76}$

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

     Determine the moles of NaOH added:

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

     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.

$$\text{HBut}(aq) \quad + \quad \text{NaOH}(aq) \quad \rightarrow \quad H_2O(l) \quad + \quad \text{But}^-(aq) + \text{Na}^+(aq)$$

Initial: 2.000×10^{-3} mol 2.005×10^{-3} mol   –   0   –

Change: $- 2.000 \times 10^{-3}$ 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 $[(20.00 + 20.05)\ \text{mL}]\ (10^{-3}\ \text{L} / 1\ \text{mL}) = 0.04005\ \text{L}$

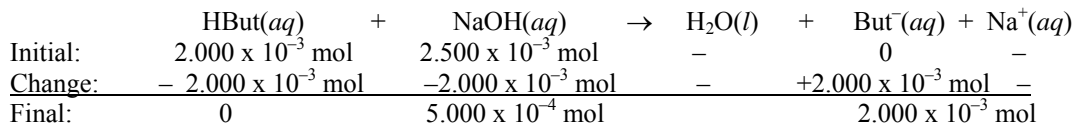The molarity of the excess OH⁻ is $(5 \times 10^{-6}\ \text{mol OH}^-) / (0.04005\ \text{L}) = 1.2484 \times 10^{-4}\ M$ (unrounded)

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

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

h) Determine the moles of NaOH added:

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

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

$$\text{HBut}(aq) \quad + \quad \text{NaOH}(aq) \quad \rightarrow \quad H_2O(l) \quad + \quad \text{But}^-(aq) + \text{Na}^+(aq)$$

Initial: 2.000×10^{-3} mol 2.500×10^{-3} mol   –   0   –

Change: $- 2.000 \times 10^{-3}$ mol -2.000×10^{-3} mol   – $+2.000 \times 10^{-3}$ mol   –

Final: 0 5.000×10^{-4} mol 2.000×10^{-3} mol

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

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

             $pOH = -\log(1.1111 \times 10^{-2}) = 1.9542$ (unrounded)

             $pH = 14.00 - pOH = 14.00 - 1.9542 = 12.0458 = \mathbf{12.05}$

19.57   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 $(CH_3CH_2)_3N = (0.1000\ \text{mol } (CH_3CH_2)_3N) / \text{L})\ (10^{-3}\ \text{L} / 1\ \text{mL})\ (20.00\ \text{mL})$

         $= 2.000 \times 10^{-3}\ \text{mol } (CH_3CH_2)_3N$

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

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

$[OH^-] = x = 7.2111 \times 10^{-3} \, M$

$pOH = -\log(7.2111 \times 10^{-3}) = 2.141998$ (unrounded)

$pH = 14.00 - pOH = 14.00 - 2.141998 = 11.8580 = \textbf{11.86}$

b) Determine the moles of HCl added:

Moles of HCl = $(0.1000 \text{ mol HCl} / L)(10^{-3} \, L / 1 \text{ mL})(10.00 \text{ mL}) = 1.000 \times 10^{-3}$ mol HCl

The HCl will react with an equal amount of the base, and 1.000×10^{-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 $[(20.00 + 10.00) \text{ mL}](10^{-3} \, L / 1 \text{ mL}) = 0.03000 \, L$

The molarity of the excess $(CH_3CH_2)_3N$ is $(1.000 \times 10^{-3} \text{ mol } (CH_3CH_2)_3N) / (0.03000 \, L)$

$= 0.03333 \, M$ (unrounded)

The molarity of the $(CH_3CH_2)_3NH^+$ formed is $(1.000 \times 10^{-3} \text{ mol } (CH_3CH_2)_3NH^+) / (0.03000 \, L)$

$= 0.03333 \, M$ (unrounded)

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

$[OH^-] = x = 5.2 \times 10^{-4} \, M$

$pOH = -\log(5.2 \times 10^{-4}) = 3.283997$ (unrounded)

$pH = 14.00 - pOH = 14.00 - 3.283997 = 10.7160 = \textbf{10.72}$

c) Determine the moles of HCl added:

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

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

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

The molarity of the excess $(CH_3CH_2)_3N$ is $(5.00 \times 10^{-4} \text{ mol } (CH_3CH_2)_3N) / (0.03500 \, L)$

$= 0.0142857 \, M$ (unrounded)

The molarity of the $(CH_3CH_2)_3NH^+$ formed is $(1.500 \times 10^{-3} \text{ mol } (CH_3CH_2)_3NH^+) / (0.03500 \, L)$

$= 0.0428571 \, M$ (unrounded)

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

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

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

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

d) Determine the moles of HCl added:

Moles of HCl = $(0.1000 \text{ mol HCl} / L)(10^{-3} \, L / 1 \text{ mL})(19.00 \text{ mL}) = 1.900 \times 10^{-3}$ 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 $[(20.00 + 19.00) \text{ mL}](10^{-3} \, L / 1 \text{ mL}) = 0.03900 \, L$

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

$= 0.002564102 \, M$ (unrounded)

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

$= 0.0487179 \, M$ (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)

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

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 x 10^{-3} mol HCl

The HCl will react with an equal amount of the base, and 5 x 10^{-6} mol $(CH_3CH_2)_3N$ will remain; and 1.995 x 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 x 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 x 10^{-3} mol $(CH_3CH_2)_3NH^+$) / (0.03995 L)
= 0.0499374 M (unrounded)

$$K_b = \frac{\left[(CH_3CH_2)_3\,NH^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_3\,N\right]} = \frac{[x][0.0499374 + x]}{[0.000125156 - x]} = \frac{[x][0.0499374]}{[0.000125156]} = 5.2 \times 10^{-4}$$

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

pOH = –log (1.303254 x 10^{-6}) = 5.88497 (unrounded)

pH = 14.00 – pOH = 14.00 – 5.88497 = 8.11503 = **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 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 2.000 x 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 x 10^{-3} mol $(CH_3CH_2)_3NH^+$) / (0.04000 L)
= 0.05000 M

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

$$K_a = \frac{\left[H_3O^+\right]\left[(CH_3CH_2)_3\,N\right]}{\left[(CH_3CH_2)_3\,NH^+\right]} = \frac{[x][x]}{[0.05000 - x]} = \frac{[x][x]}{[0.05000]} = 1.923 \times 10^{-11}$$

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

pH = –log $[H_3O^+]$ = –log (9.8056 x 10^{-7}) = 6.0085 = **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 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 x 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 x 10^{-6} mol H_3O^+) / (0.04005 L) = 1.2484 x 10^{-4} M (unrounded)

pH = –log (1.2484 x 10^{-4}) = 3.9036 = **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**

19.58   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 =

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

= 58.989247 = **59.0 mL NaOH**

Determine the moles of CH_3COOH present:

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

$$= 0.0021944 \text{ mol } CH_3COOH \text{ (unrounded)}$$

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

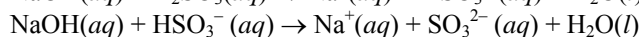Determine the hydroxide ion concentration from the K_b, and then determine the pH from the pOH.

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

$[OH^-]$ = 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 equations are:

$NaOH(aq) + H_2SO_3(aq) \rightarrow Na^+(aq) + HSO_3^-(aq) + H_2O(l)$

$NaOH(aq) + HSO_3^-(aq) \rightarrow Na^+(aq) + SO_3^{2-}(aq) + H_2O(l)$

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:

Volume =

$$\left(\frac{0.0850 \text{ mol } H_2SO_3}{L}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(28.9 \text{ mL})\left(\frac{1 \text{ mol NaOH}}{1 \text{ mol } H_2SO_3}\right)\left(\frac{L}{0.0372 \text{ mol NaOH}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

= 66.034943 = **66.0 mL NaOH**

It will require an equal volume to reach the second equivalence point for a total of 2 x 66.034943 = **132.1 mL**.

Determine the moles of HSO_3^- produced:

$$Moles = \left(\frac{0.0850 \text{ mol } H_2SO_3}{L}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(28.9 \text{ mL})\left(\frac{1 \text{ mol } HSO_3^{2-}}{1 \text{ mol } H_2SO_3}\right)$$

= 0.0024565 mol HSO_3^-

An equal number of moles of SO_3^{2-} will be present at the second equivalence point.

Determine the liters of solution present at the first equivalence point:

Volume = [(28.9 + 66.034943) mL] (10^{-3} L / 1 mL) = 0.094934943 L

Determine the liters of solution present at the second equivalence point:

Volume = [(28.9 + 66.034943 + 66.034943) mL] (10^{-3} L / 1 mL) = 0.160969886 L

Concentration of HSO_3^- at equivalence point:

Molarity = (0.0024565 moles HSO_3^-) / (0.094934943 L) = 0.0258756 M

Concentration of SO_3^{2-} at equivalence point:

Molarity = (0.0024565 moles SO_3^{2-}) / (0.160969886 L) = 0.0152606 M

Calculate K_b for HSO_3^-: $\qquad$ K_a $H_2SO_3 = 1.4 \times 10^{-2}$

$\qquad$ $K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.4 \times 10^{-2}) = 7.142857 \times 10^{-13}$

Calculate K_b for SO_3^{2-}: $\qquad$ K_a $HSO_3^- = 6.5 \times 10^{-8}$

$\qquad$ $K_b = K_w / K_a = (1.0 \times 10^{-14}) / (6.5 \times 10^{-8}) = 1.53846 \times 10^{-7}$

For the first equivalence point:

Using a reaction table for the equilibrium reaction of HSO_3^-:

	HSO_3^-	$+$	H_2O	$\leftrightarrows$	H_2SO_3	$+$	OH^-
Initial:	0.0258756 M				0		0
Change:	$-x$				$+x$		$+x$
Equilibrium:	$0.0258756 - x$				x		x

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

$$K_b = \frac{\left[H_2SO_3 \right]\left[OH^- \right]}{\left[HSO_3^- \right]} = \frac{[x][x]}{[0.0258756 - x]} = \frac{[x][x]}{[0.0258756]} = 7.142857 \times 10^{-13}$$

$[OH^-] = x = 1.359506 \times 10^{-7}\ M$ (unrounded)

pOH $= -\log (1.359506 \times 10^{-7}) = 6.8666188$ (unrounded)

pH $= 14.00 - $ pOH $= 14.00 - 6.8666188 = 7.13338 = $ **7.13**

For the second equivalence point:

Using a reaction table for the equilibrium reaction of SO_3^{2-}:

	SO_3^{2-}	$+$	H_2O	$\leftrightarrows$	HSO_3^-	$+$	OH^-
Initial:	0.0152606 M				0		0
Change:	$-x$				$+x$		$+x$
Equilibrium:	$0.0152606 - x$				x		x

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

$$K_b = \frac{\left[HSO_3^- \right]\left[OH^- \right]}{\left[SO_3^{2-} \right]} = \frac{[x][x]}{[0.0152606 - x]} = \frac{[x][x]}{[0.0152606]} = 1.53846 \times 10^{-7}$$

$[OH^-] = x = 4.84539 \times 10^{-5}\ M$ (unrounded)

pOH $= -\log (4.84539 \times 10^{-5}) = 4.31467$ (unrounded)

pH $= 14.00 - $ pOH $= 14.00 - 4.31467 = 9.68533 = $ **9.69**

19.59 The balanced chemical equation is:
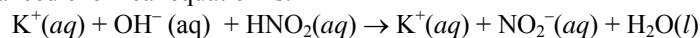
$\qquad$ $K^+(aq) + OH^- (aq) + HNO_2(aq) \rightarrow K^+(aq) + NO_2^-(aq) + H_2O(l)$

The potassium 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:

$\qquad$ Volume =

$$\left(\frac{0.0390\ \text{mol } HNO_2}{L} \right)\left(\frac{10^{-3}\ L}{1\ mL} \right)(23.4\ mL)\left(\frac{1\ \text{mol } KOH}{1\ \text{mol } HNO_2} \right)\left(\frac{L}{0.0588\ \text{mol } KOH} \right)\left(\frac{1\ mL}{10^{-3}\ L} \right)$$

$\qquad$ $= 15.5204 = $ **15.5 mL KOH**

Determine the moles of HNO_2 present:

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

$\qquad$ $= 0.0009126\ \text{mol } HNO_2$

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

The KOH 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)	+	KOH(aq)	→	H$_2$O(l)	+	NO$_2^-$(aq)	+	K$^+$(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 + 15.5204) mL] (10^{-3} L / 1 mL) = 0.0389204 L (unrounded)

Concentration of NO$_2^-$ at equivalence point:

Molarity = (0.0009126 mol NO$_2^-$) / (0.0389204 L) = 0.023447858 M

Calculate K_b for NO$_2^-$: K_a HNO$_2$ = 7.1 x 10^{-4}

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

Using a reaction table for the equilibrium reaction of NO$_2^-$:

	NO$_2^-$	+	H$_2$O	⇌	HNO$_2$	+	OH$^-$
Initial:	0.023447858 M				0		0
Change:	−x				+x		+x
Equilibrium:	0.023447858 – x				x		x

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

$$K_b = \frac{\left[\text{HNO}_2\right]\left[\text{OH}^-\right]}{\left[\text{NO}_2^-\right]} = \frac{[x][x]}{[0.023447858 - x]} = \frac{[x][x]}{[0.023447858]} = 1.40845 \times 10^{-11}$$

[OH$^-$] = x = 5.7467 x 10^{-7} M (unrounded)

pOH = –log (5.7467 x 10^{-7}) = 6.240577 (unrounded)

pH = 14.00 – pOH = 14.00 – 6.240577 = 7.759422 = **7.76**

b) The balanced chemical equations are:

KOH(aq) + H$_2$CO$_3$(aq) → K$^+$(aq) + HCO$_3^-$ (aq) + H$_2$O(l)

KOH(aq) + HCO$_3^-$(aq) → K$^+$(aq) + CO$_3^{2-}$ (aq) + H$_2$O(l)

The potassium 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 KOH needed:

Volume =

$$\left(\frac{0.130 \text{ mol H}_2\text{CO}_3}{\text{L}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(17.3 \text{ mL})\left(\frac{1 \text{ mol KOH}}{1 \text{ mol H}_2\text{CO}_3}\right)\left(\frac{\text{L}}{0.0588 \text{ mol KOH}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

= 38.248299 = **38.2 mL KOH**

It will require an equal volume to reach the second equivalence point (**76.4 mL**).

Determine the moles of HCO$_3^-$ produced:

$$\text{Moles} = \left(\frac{0.130 \text{ mol H}_2\text{CO}_3}{\text{L}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(17.3 \text{ mL})\left(\frac{1 \text{ mol HCO}_3^-}{1 \text{ mol H}_2\text{CO}_3}\right)$$

= 0.002249 mol HCO$_3^-$ (unrounded)

An equal number of moles of CO$_3^{2-}$ will be present at the second equivalence point.

Determine the liters of solution present at the first equivalence point:

Volume = [(17.3 + 38.248299) mL] (10^{-3} L / 1 mL) = 0.055548 L (unrounded)

Determine the liters of solution present at the second equivalence point:

Volume = [(17.3 + 38.248299 + 38.248299) mL] (10^{-3} L / 1 mL) = 0.0937966 L (unrounded)

Concentration of HCO$_3^-$ at equivalence point:

Molarity = (0.002249 mol HCO$_3^-$) / (0.055548 L) = 0.0404875 M (unrounded)

Concentration of CO$_3^{2-}$ at equivalence point:

Molarity = (0.002249 mol CO$_3^{2-}$) / (0.0937966 L) = 0.023977 M (unrounded)

Calculate K_b for HCO$_3^-$: K_a H$_2$CO$_3$ = 4.5 x 10^{-7}

$K_b = K_w / K_a$ = (1.0 x 10^{-14}) / (4.5 x 10^{-7}) = 2.222 x 10^{-8} (unrounded)

Calculate K_b for CO$_3^{2-}$: K_a HCO$_3^-$ = 4.7 x 10^{-11}

$K_b = K_w / K_a$ = (1.0 x 10^{-14}) / (4.7 x 10^{-11}) = 2.1276595 x 10^{-4} (unrounded)

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

For the first equivalence point:

$$K_b = \frac{\left[H_2CO_3\right]\left[OH^-\right]}{\left[HCO_3^-\right]} = \frac{[x][x]}{[0.0404875 - x]} = \frac{[x][x]}{[0.0404875]} = 2.222 \times 10^{-8}$$

$[OH^-] = x = 2.999387 \times 10^{-5} \, M$
$pOH = -\log (2.999387 \times 10^{-5}) = 4.522967492$ (unrounded)
$pH = 14.00 - pOH = 14.00 - 4.522967492 = 9.4770 = \mathbf{9.48}$
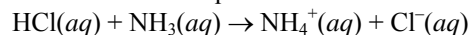
For the second equivalence point:

$$K_b = \frac{\left[HCO_3^-\right]\left[OH^-\right]}{\left[CO_3^{2-}\right]} = \frac{[x][x]}{[0.023977 - x]} = \frac{[x][x]}{[0.023977]} = 2.1276595 \times 10^{-4}$$

$[OH^-] = x = 2.2586476 \times 10^{-3} \, M$
$pOH = -\log (2.2586476 \times 10^{-3}) = 2.646151515$ (unrounded)
$pH = 14.00 - pOH = 14.00 - 2.646151515 = 11.3538 = \mathbf{11.35}$

19.60   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 =

$$\left(\frac{0.234 \text{ mol } NH_3}{L}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(65.5 \text{ mL})\left(\frac{1 \text{ mol HCl}}{1 \text{ mol } NH_3}\right)\left(\frac{L}{0.125 \text{ mol HCl}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

$= 122.616 = \mathbf{123 \text{ mL HCl}}$

Determine the moles of NH_3 present:

$$\text{Moles} = \left(\frac{0.234 \text{ mol } NH_3}{L}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(65.5 \text{ mL})$$

$= 0.015327 \text{ mol } NH_3$ (unrounded)

At the equivalence point, 0.05327 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 0.015327 moles of NH_4^+ will be formed.

	$HCl(aq)$	+	$NH_3(aq)$	$\rightarrow$	$NH_4^+(aq)$ +	$Cl^-(aq)$
Initial:	0.015327 mol		0.015327 mol		0	–
Change:	– 0.015327 mol		–0.015327 mol		+0.015327 mol	–
Final:	0		0		0.015327 mol	

Determine the liters of solution present at the equivalence point:
Volume = $[(65.5 + 122.616) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.188116 \text{ L}$
Concentration of NH_4^+ at equivalence point:
Molarity = $(0.015327 \text{ mol } NH_4^+) / (0.188116 \text{ L}) = 0.081476 \, M$
Calculate K_a for NH_4^+: $K_b \, NH_3 = 1.76 \times 10^{-5}$
$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (1.76 \times 10^{-5}) = 5.6818 \times 10^{-10}$ (unrounded)
Using a reaction table for the equilibrium reaction of NH_4^+:

	NH_4^+	+	H_2O	$\leftrightarrows$	NH_3 +	H_3O^+
Initial:	0.081476 M				0	0
Change:	–x				+x	+x
Equilibrium:	0.081476 – x				x	x

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

$$K_a = \frac{\left[H_3O^+\right]\left[NH_3\right]}{\left[NH_4^+\right]} = \frac{[x][x]}{[0.081476 - x]} = \frac{[x][x]}{[0.081476]} = 5.6818 \times 10^{-10}$$

$x = [H_3O^+] = 6.803911 \times 10^{-6} \, M$ (unrounded)
$pH = -\log [H_3O^+] = -\log (6.803911 \times 10^{-6}) = 5.1672 = \mathbf{5.17}$

b) The balanced chemical equation is:
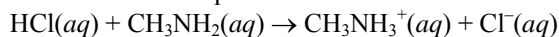
$$HCl(aq) + CH_3NH_2(aq) \rightarrow CH_3NH_3^+(aq) + Cl^-(aq)$$

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 =

$$\left(\frac{1.11 \text{ mol CH}_3\text{NH}_2}{L}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(21.8 \text{ mL})\left(\frac{1 \text{ mol HCl}}{1 \text{ mol CH}_3\text{NH}_2}\right)\left(\frac{L}{0.125 \text{ mol HCl}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

$$= 193.584 = \textbf{194 mL HCl}$$

Determine the moles of CH_3NH_2 present:

$$\text{Moles} = \left(\frac{1.11 \text{ mol CH}_3\text{NH}_2}{L}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(21.8 \text{ mL})$$

$$= 0.024198 \text{ mol CH}_3\text{NH}_2 \text{ (unrounded)}$$

At the equivalence point, 0.024198 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 0.024198 moles of $CH_3NH_3^+$ will be formed.

	HCl(aq)	+	CH₃NH₂(aq)	→	CH₃NH₃⁺(aq)	+	Cl⁻(aq)
Initial:	0.024198 mol		0.024198 mol		0		–
Change:	− 0.024198 mol		−0.024198 mol		+0.024198 mol		–
Final:	0		0		0.024198 mol		

Determine the liters of solution present at the equivalence point:

Volume = [(21.8 + 193.584) mL] $(10^{-3}$ L / 1 mL) = 0.215384 L (unrounded)

Concentration of $CH_3NH_3^+$ at equivalence point:

Molarity = (0.024198 mol $CH_3NH_3^+$) / (0.215384 L) = 0.1123482 M

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

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

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

	CH₃NH₃⁺	+	H₂O	⇌	CH₃NH₂	+	H₃O⁺
Initial:	0.1123482 M				0		0
Change:	−x				+x		+x
Equilibrium:	0.1123482 − x				x		x

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

$$K_a = \frac{\left[H_3O^+\right]\left[CH_3NH_2\right]}{\left[CH_3NH_3^+\right]} = \frac{[x][x]}{[0.1123482 - x]} = \frac{[x][x]}{[0.1123482]} = 2.2727 \times 10^{-11}$$

$$x = [H_3O^+] = 1.5979 \times 10^{-6} \ M \text{ (unrounded)}$$

$$pH = -\log [H_3O^+] = -\log (1.5979 \times 10^{-6}) = 5.7964 = \textbf{5.80}$$

19.61   a) The balanced chemical equation is:
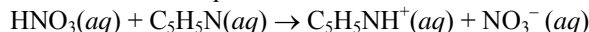
$$HNO_3(aq) + C_5H_5N(aq) \rightarrow C_5H_5NH^+(aq) + NO_3^-(aq)$$

The nitrate 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 HNO_3 needed:

Volume =

$$\left(\frac{0.0750 \text{ mol C}_5\text{H}_5\text{N}}{L}\right)(2.65 \text{ L})\left(\frac{1 \text{ mol HNO}_3}{1 \text{ mol C}_5\text{H}_5\text{N}}\right)\left(\frac{L}{0.447 \text{ mol HNO}_3}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

$$= 444.63087 = \textbf{445 mL HNO}_3$$

Determine the moles of $C_5H_5NH^+$ produced:

$$\text{Moles} = \left(\frac{0.0750 \text{ mol C}_5\text{H}_5\text{N}}{L}\right)(2.65 \text{ L})\left(\frac{1 \text{ mol C}_5\text{H}_5\text{NH}^+}{1 \text{ mol C}_5\text{H}_5\text{N}}\right)$$

$$= 0.19875 \text{ mol C}_5\text{H}_5\text{NH}^+ \text{ (unrounded)}$$

Determine the liters of solution present at the equivalence point:

Volume = 2.65 L + (444.63087mL) $(10^{-3}$ L / 1 mL) = 3.09463 L

Concentration of $C_5H_5NH^+$ at equivalence point:

Molarity = (0.19875 mol $C_5H_5NH^+$) / (3.09463 L) = 0.064224 M (unrounded)

Calculate K_a for $C_5H_5NH^+$: K_b C_5H_5N = 1.7 x 10^{-9}

$K_a = K_w / K_b$ = (1.0 x 10^{-14}) / (1.7 x 10^{-9}) = 5.88235 x 10^{-6} (unrounded)

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

$$K_a = \frac{\left[H_3O^+\right]\left[C_5H_5N\right]}{\left[C_5H_5NH^+\right]} = \frac{[x][x]}{[0.064224 - x]} = \frac{[x][x]}{[0.064224]} = 5.88235 \times 10^{-6}$$

x = $[H_3O^+]$ = 6.1464 x 10^{-4} M (unrounded)

pH = $-\log [H_3O^+]$ = $-\log$ (6.1464 x 10^{-4}) = 3.211379 = **3.21**

b) The balanced chemical equations are:
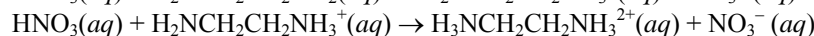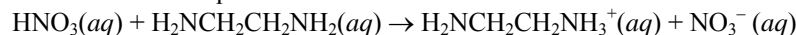
$HNO_3(aq) + H_2NCH_2CH_2NH_2(aq) \rightarrow H_2NCH_2CH_2NH_3^+(aq) + NO_3^-(aq)$

$HNO_3(aq) + H_2NCH_2CH_2NH_3^+(aq) \rightarrow H_3NCH_2CH_2NH_3^{2+}(aq) + NO_3^-(aq)$

The nitrate 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 HNO_3 needed:

Volume =

$$\left(\frac{0.250 \text{ mol } H_2NCH_2CH_3NH_2}{L}\right)(0.188 \text{ L})\left(\frac{1 \text{ mol } HNO_3}{1 \text{ mol } H_2NCH_2CH_3NH_2}\right)\left(\frac{L}{0.447 \text{ mol } HNO_3}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

= 105.1454 = **105 mL HCl**

It will require an equal volume to reach the second equivalence point. (**210. mL**)

Determine the moles of $H_2NCH_2CH_2NH_3^+$ produced:

$$\text{Moles} = \left(\frac{0.250 \text{ mol } H_2NCH_2CH_3NH_2}{L}\right)(0.188 \text{ L})\left(\frac{1 \text{ mol } H_2NCH_2CH_3NH_3^+}{1 \text{ mol } H_2NCH_2CH_3NH_2}\right)$$

= 0.0470 mol $H_2NCH_2CH_2NH_3^+$

An equal number of moles of $H_3NCH_2CH_2NH_3^{2+}$ will be present at the second equivalence point.

Determine the liters of solution present at the first equivalence point:

Volume = 0.188 L + (105.1454 mL) (10^{-3} L / 1 mL) = 0.293145 L (unrounded)

Determine the liters of solution present at the second equivalence point:

Volume = 0.188 L + 2(105.1454 mL) (10^{-3} L / 1 mL) = 0.39829 L (unrounded)

Concentration of $H_2NCH_2CH_2NH_3^+$ at equivalence point:

Molarity = (0.0470 mol $H_2NCH_2CH_2NH_3^+$) / (0.293145 L) = 0.16033 M (unrounded)

Concentration of $H_3NCH_2CH_2NH_3^{2+}$ at equivalence point:

Molarity = (0.0470 mol $H_3NCH_2CH_2NH_3^{2+}$) / (0.39829 L) = 0.11800 M (unrounded)

Calculate K_a for $H_2NCH_2CH_2NH_3^+$: K_b $H_2NCH_2CH_2NH_2$ = 8.5 x 10^{-5}

$K_a = K_w / K_b$ = (1.0 x 10^{-14}) / (8.5 x 10^{-5}) = 1.17647 x 10^{-10} (unrounded)

Calculate K_a for $H_3NCH_2CH_2NH_3^{2+}$: K_b $H_2NCH_2CH_2NH_3^+$ = 7.1 x 10^{-8}

$K_a = K_w / K_b$ = (1.0 x 10^{-14}) / (7.1 x 10^{-8}) = 1.40845 x 10^{-7} (unrounded)

Determine the hydrogen ion concentration from the K_a, and then determine the pH for the first equivalence point.

$$K_a = \frac{\left[H_3O^+\right]\left[H_2NCH_2CH_3NH_2\right]}{\left[H_2NCH_2CH_3NH_3^+\right]} = \frac{[x][x]}{[0.16033 - x]} = \frac{[x][x]}{[0.16033]} = 1.17647 \times 10^{-10}$$

x = $[H_3O^+]$ = 4.3430799 x 10^{-6} M (unrounded)

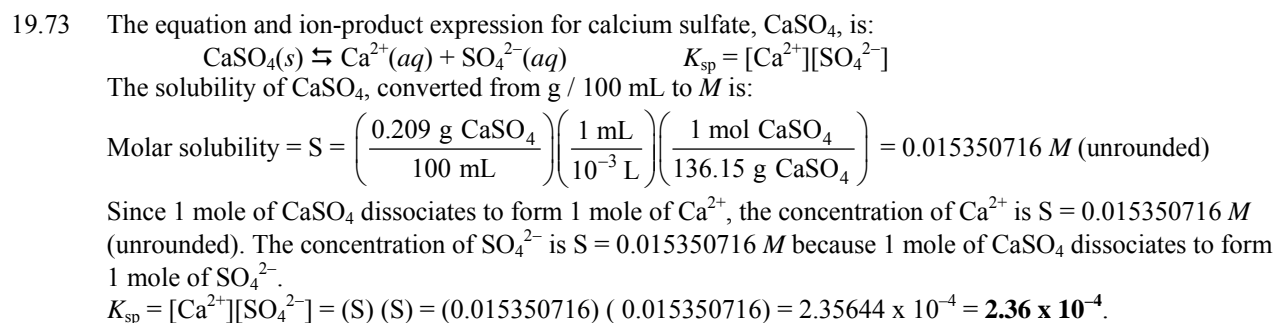pH = $-\log [H_3O^+]$ = $-\log$ (4.3430799 x 10^{-6}) = 5.36220 = **5.36**
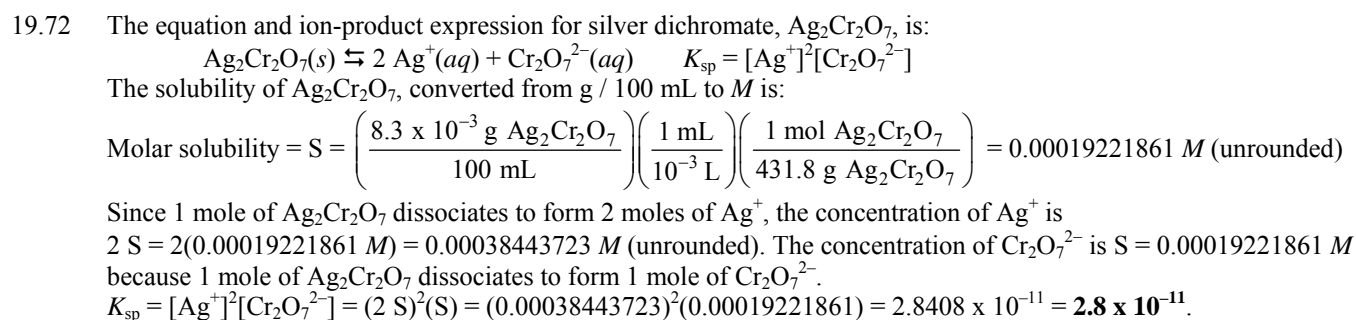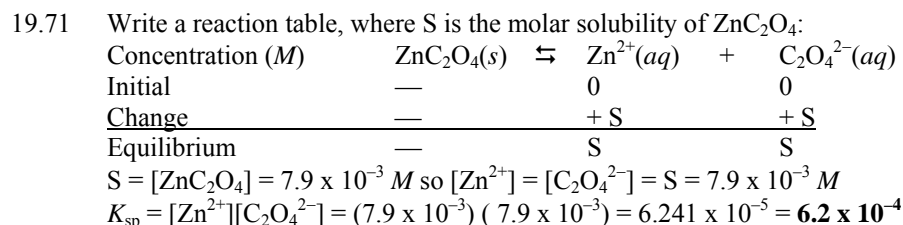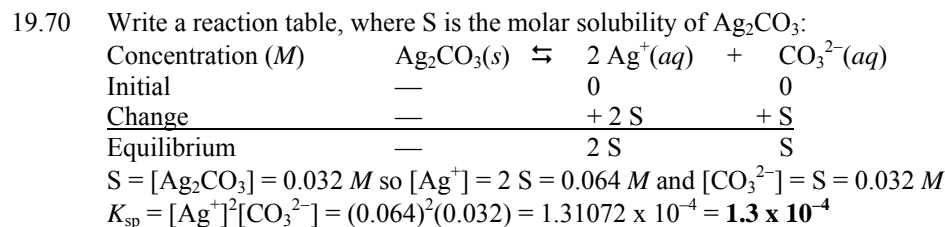
Determine the hydrogen ion concentration from the K_a, and then determine the pH for the second equivalence point.

$$K_a = \frac{\left[H_3O^+\right]\left[H_2NCH_2CH_3NH_3^+\right]}{\left[H_3NCH_2CH_3NH_3^{2+}\right]} = \frac{[x][x]}{[0.11800 - x]} = \frac{[x][x]}{[0.11800]} = 1.40845 \times 10^{-7}$$

x = $[H_3O^+]$ = 1.2891745 x 10^{-4} M (unrounded)

pH = $-\log [H_3O^+]$ = $-\log$ (1.2891745 x 10^{-4}) = 3.889688 = **3.89**

19.62 $M_2X(s) \leftrightarrows 2M^+(aq) + X^{2-}(aq)$
$K_{sp} = [M^+]^2[X^{2-}]$, assuming M_2X is a strong electrolyte.
S = molar solubility = 5 x 10^{-5} M
$[M^+] = 2 S = 1$ x 10^{-4} M
$[X^{2-}] = S = 5$ x 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.

19.63 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.

19.64 To use K_{sp} for comparing solubilities, the K_{sp} expressions must be of the same mathematical form. Stated differently, AgCl and AgBr are both 1:1 electrolytes, while Ag_2CrO_4 is a 2:1 electrolyte.

19.65 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.

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

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

19.68 a) $CaCrO_4(s) \leftrightarrows Ca^{2+}(aq) + CrO_4^{2-}(aq)$
Ion-product expression: $\boldsymbol{K_{sp} = [Ca^{2+}][CrO_4^{2-}]}$
b) $AgCN(s) \leftrightarrows Ag^+(aq) + CN^-(aq)$
Ion-product expression: $\boldsymbol{K_{sp} = [Ag^+][CN^-]}$
c) $NiS(s) + H_2O(l) \leftrightarrows Ni^{2+}(aq) + HS^-(aq) + OH^-(aq)$
Ion-product expression: $\boldsymbol{K_{sp} = [Ni^{2+}][HS^-][OH^-]}$

19.69 a) $PbI_2(s) \leftrightarrows Pb^{2+}(aq) + 2 I^- (aq)$
Ion-product expression: $\boldsymbol{K_{sp} = [Pb^{2+}][I^-]^2}$
b) $SrSO_4(s) \leftrightarrows Sr^{2+}(aq) + SO_4^{2-} (aq)$
Ion-product expression: $\boldsymbol{K_{sp} = [Sr^{2+}][SO_4^{2-}]}$
c) $CdS(s) + H_2O(l) \leftrightarrows Cd^{2+}(aq) + HS^-(aq) + OH^-(aq)$
Ion-product expression: $\boldsymbol{K_{sp} = [Cd^{2+}][HS^-][OH^-]}$

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

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

S = $[Ag_2CO_3]$ = 0.032 M so $[Ag^+]$ = 2 S = 0.064 M and $[CO_3^{2-}]$ = S = 0.032 M
$K_{sp} = [Ag^+]^2[CO_3^{2-}] = (0.064)^2(0.032) = 1.31072 \times 10^{-4} =$ **1.3 x 10^{-4}**

19.71   Write a reaction table, where S is the molar solubility of ZnC_2O_4:

Concentration (M)	$ZnC_2O_4(s)$	$\rightleftharpoons$	$Zn^{2+}(aq)$	$+$	$C_2O_4^{2-}(aq)$
Initial	—		0		0
Change	—		$+S$		$+S$
Equilibrium	—		S		S

S = $[ZnC_2O_4]$ = 7.9 x 10^{-3} M so $[Zn^{2+}]$ = $[C_2O_4^{2-}]$ = S = 7.9 x 10^{-3} M
$K_{sp} = [Zn^{2+}][C_2O_4^{2-}] = (7.9 \times 10^{-3})\,(7.9 \times 10^{-3}) = 6.241 \times 10^{-5} =$ **6.2 x 10^{-4}**

19.72   The equation and ion-product expression for silver dichromate, $Ag_2Cr_2O_7$, is:
$$Ag_2Cr_2O_7(s) \rightleftharpoons 2\,Ag^+(aq) + Cr_2O_7^{2-}(aq) \qquad K_{sp} = [Ag^+]^2[Cr_2O_7^{2-}]$$
The solubility of $Ag_2Cr_2O_7$, converted from g / 100 mL to M is:

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

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

19.73   The equation and ion-product expression for calcium sulfate, $CaSO_4$, is:
$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq) \qquad K_{sp} = [Ca^{2+}][SO_4^{2-}]$$
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-}.
$K_{sp} = [Ca^{2+}][SO_4^{2-}] = (S)\,(S) = (0.015350716)\,(0.015350716) = 2.35644 \times 10^{-4} =$ **2.36 x 10^{-4}**.

19.74   The equation and ion-product expression for $SrCO_3$ is:
$$SrCO_3(s) \rightleftharpoons Sr^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp} = [Sr^{2+}][CO_3^{2-}]$$
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)	$SrCO_3(s)$	$\rightleftharpoons$	$Sr^{2+}(aq)$	$+$	$CO_3^{2-}(aq)$
Initial	—		0		0
Change	—		$+S$		$+S$
Equilibrium	—		S		S

$K_{sp} = 5.4 \times 10^{-10} = [Sr^{2+}][CO_3^{2-}] = [S][S] = S^2$
S = 2.32379 x 10^{-5} = **2.3 x 10^{-5} 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)	$SrCO_3(s)$	$\rightleftharpoons$	$Sr^{2+}(aq)$	$+$	$CO_3^{2-}(aq)$
Initial	—		0.13		0
Change	—		$+S$		$+S$
Equilibrium	—		$0.13 + S$		S

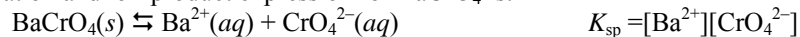$K_{sp} = 5.4 \times 10^{-10} = [Sr^{2+}][CO_3^{2-}] = (0.13 + S)S$

This calculation may be simplified by assuming S is small and setting $0.13 + S = 0.13$.
$$K_{sp} = 5.4 \times 10^{-10} = (0.13)S$$
$$S = 4.1538 \times 10^{-9} = \mathbf{4.2 \times 10^{-9} \ M}$$

19.75 The equation and ion-product expression for $BaCrO_4$ is:
$$BaCrO_4(s) \leftrightarrows Ba^{2+}(aq) + CrO_4^{2-}(aq) \qquad\qquad K_{sp} = [Ba^{2+}][CrO_4^{2-}]$$
a) The solubility, S, in pure water equals $[Ba^{2+}]$ and $[CrO_4^{2-}]$
$$K_{sp} = 2.1 \times 10^{-10} = [Ba^{2+}][CrO_4^{2-}] = S^2$$
$$S = 1.4491 \times 10^{-5} = \mathbf{1.4 \times 10^{-5} \ M}$$
b) In $1.5 \times 10^{-3} \ M \ Na_2CrO_4$, the initial concentration of CrO_4^{2-} is $1.5 \times 10^{-3} \ M$.
Equilibrium $[Ba^{2+}] = S$ and equilibrium $[CrO_4^{2-}] = 1.5 \times 10^{-3} + S$ where S is the solubility of $BaCrO_4$.
$$K_{sp} = 2.1 \times 10^{-10} = [Ba^{2+}][CrO_4^{2-}] = S(1.5 \times 10^{-3} + S)$$
Assume S is small so $1.5 \times 10^{-3} + S = 1.5 \times 10^{-3}$
$$K_{sp} = 2.1 \times 10^{-10} = S(1.5 \times 10^{-3})$$
$$S = \mathbf{1.4 \times 10^{-7} \ M}$$

19.76 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	+ 2 S
Equilibrium	—	0.060 + S	2 S

Assume that $0.060 + S \approx 0.060$ because the amount of compound that dissolves will be negligible in comparison to $0.060 \ M$.
$$K_{sp} = [Ca^{2+}][IO_3^-]^2 = (0.060) (2 \ S)^2 = 7.1 \times 10^{-7}$$
$$S = 1.71998 \times 10^{-3} = 1.7 \times 10^{-3} \ M$$
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 $\mathbf{1.7 \times 10^{-3} \ M}$.
b) Write a reaction table that reflects an initial concentration of $IO_3^- = 0.060 \ M$. IO_3^- is the common ion.

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

The equilibrium concentration of Ca^{2+} is S, and the IO_3^- concentration is $0.060 + 2 \ S$.
Assume that $0.060 + 2 \ S \approx 0.060$
$$K_{sp} = [Ca^{2+}][IO_3^-]^2 = (S) (0.060)^2 = 7.1 \times 10^{-7}$$
$$S = 1.97222 \times 10^{-4} = 2.0 \times 10^{-4} \ M$$
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 $\mathbf{2.0 \times 10^{-4} \ M}$.

19.77 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	—	+2 S	+ S
Equilibrium	—	0.22 +2 S	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 $\mathbf{3.1 \times 10^{-4} \ M}$.

b) Write a reaction table that reflects an initial concentration of $SO_4^{2-} = 0.22\ M$. In this case, SO_4^{2-} is the common ion.

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

The equilibrium concentration of Ag^+ is 2 S, and the SO_4^{2-} concentration is 0.22 + S.

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 **$4.1 \times 10^{-3}\ M$**.

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

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

19.80   The larger the K_{sp}, the more water-soluble the compound if the number of ions are equal.
a) **$CaSO_4$** with $K_{sp} = 2.4 \times 10^{-5}$ is more water-soluble than $BaSO_4$ with $K_{sp} = 1.1 \times 10^{-10}$.
b) **$Mg_3(PO_4)_2$** with $K_{sp} = 5.2 \times 10^{-24}$ is more water soluble than $Ca_3(PO_4)_2$ with $K_{sp} = 1.2 \times 10^{-29}$.
c) **$PbSO_4$** with $K_{sp} = 1.6 \times 10^{-8}$ is more water soluble than AgCl with $K_{sp} = 1.8 \times 10^{-10}$.

19.81   The larger the K_{sp}, the more water-soluble the compound if the number of ions are equal.
a) **$Ca(IO_3)_2$** with $K_{sp} = 7.1 \times 10^{-7}$ is more water-soluble than $Mn(OH)_2$ with $K_{sp} = 1.6 \times 10^{-13}$.
b) **$SrCO_3$** with $K_{sp} = 5.4 \times 10^{-10}$ is more water soluble than CdS with $K_{sp} = 1.0 \times 10^{-24}$.
c) **CuI** with $K_{sp} = 1 \times 10^{-12}$ is more water soluble than AgCN with $K_{sp} = 2.2 \times 10^{-16}$.

19.82   a) $AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$
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) $SrCO_3(s) \rightleftarrows Sr^{2+}(aq) + CO_3^{2-}(aq)$
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:
    $CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq)$
    and $HCO_3^-(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq) + OH^-(aq)$
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)**. A decrease in pH will decrease $[OH^-]$, causing the base equilibrium to shift to the right which decreases $[CO_3^{2-}]$, causing the solubility equilibrium to shift to the right, dissolving more solid.

19.83   a) $CuBr(s) \rightleftarrows Cu^+(aq) + Br^-(aq)$
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.
$Cu^+(aq) + OH^-(aq) \rightleftarrows CuOH(s)$
b) $Ca_3(PO_4)_2(s) \rightleftarrows 3\ Ca^{2+}(aq) + 2\ PO_4^{3-}(aq)$
The calcium ion is the cation of a strong base so pH will not affect its solubility.
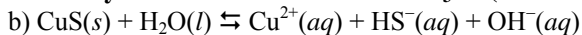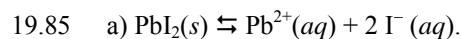PO_4^{3-} is the anion of a weak acid, so the following equilibria would be present.
$PO_4^{3-}(aq) + n\ H_2O(l) \rightleftarrows H_nPO_4^{(3-n)-}(aq) + n\ OH^-(aq)$ (n = 1,2,3)

Since these involve OH⁻, the solubility will change with changing pH. **Solubility increases with addition of** $\mathbf{H_3O^+}$ **(decreasing pH)**. A decrease in pH will decrease [OH⁻], causing the base equilibrium to shift to the right which decreases [PO₄³⁻], causing the solubility equilibrium to shift to the right, dissolving more solid.
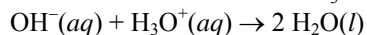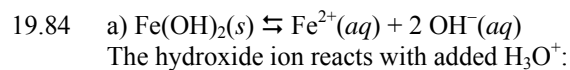
19.84   a) $Fe(OH)_2(s) \leftrightarrows Fe^{2+}(aq) + 2\ OH^-(aq)$
The hydroxide ion reacts with added H_3O^+:
$$OH^-(aq) + H_3O^+(aq) \rightarrow 2\ H_2O(l)$$
The added H_3O^+ consumes the OH⁻, driving the equilibrium toward the right to dissolve more $Fe(OH)_2$.
Solubility increases with addition of $\mathbf{H_3O^+}$ (decreasing pH).
b) $CuS(s) + H_2O(l) \leftrightarrows Cu^{2+}(aq) + HS^-(aq) + OH^-(aq)$
Both HS⁻ and OH⁻ are anions of weak acids, so both ions react with added H_3O^+. **Solubility increases with addition of $\mathbf{H_3O^+}$ (decreasing pH)**.

19.85   a) $PbI_2(s) \leftrightarrows Pb^{2+}(aq) + 2\ I^-(aq)$.
The iodide ion is the anion of a strong acid, so it does not react with H_3O^+. Thus, the solubility does not increase in acid solution. At high pH the lead ion may precipitate.
b) $Hg_2(CN)_2(s) \leftrightarrows Hg_2^{2+}(aq) + 2\ CN^-(aq)$
At high pH the mercury(I) ion may precipitate.
CN⁻ is the anion of a weak acid, so the equilibrium would be
$CN^-(aq) + H_2O(l) \leftrightarrows HCN(aq) + OH^-(aq)$
Since this involves OH⁻, it would shift with changing pH. **Solubility increases with addition of $\mathbf{H_3O^+}$ (decreasing pH)**.
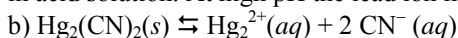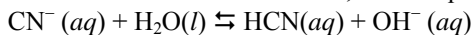
19.86   The equilibrium is: $Cu(OH)_2(s) \leftrightarrows Cu^{2+}(aq) + 2\ OH^-(aq)$. The ion-product expression is $K_{sp} = [Cu^{2+}][OH^-]^2$ and, from the Appendix, K_{sp} equals 2.2×10^{-20}.
To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp}.

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

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

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

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

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

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

$Q_{sp} = [Pb^{2+}][Cl^-]^2 = (0.12)(2.3952 \times 10^{-4})^2 = 6.8843796 \times 10^{-9}\ (unrounded)$
Q_{sp} is smaller than K_{sp} ($6.9 \times 10^{-9} < 1.7 \times 10^{-5}$), so **PbCl₂ will not precipitate**.

19.88   The equilibrium is: $Ba(IO_3)_2(s) \leftrightarrows Ba^{2+}(aq) + 2\ IO_3^-(aq)$. The ion-product expression for is $K_{sp} = [Ba^{2+}][IO_3^-]^2$ and, from the Appendix, K_{sp} equals 1.5×10^{-9}.
To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp}.

$$[Ba^{2+}] = \left(\frac{7.5\ mg\ BaCl_2}{500.\ mL}\right)\left(\frac{10^{-3}\ g}{1\ mg}\right)\left(\frac{1\ mL}{10^{-3}\ L}\right)\left(\frac{1\ mol\ BaCl_2}{208.2\ g\ BaCl_2}\right)\left(\frac{1\ mol\ Ba^{2+}}{1\ mol\ BaCl_2}\right)$$
$$= 7.204611 \times 10^{-5}\ M\ Ba^{2+}\ (unrounded)$$

$$[\text{IO}_3^-] = \left(\frac{0.023 \text{ mol NaIO}_3}{L}\right)\left(\frac{1 \text{ mol IO}_3^-}{1 \text{ mol NaIO}_3}\right) = 0.023 \ M \ \text{IO}_3^-$$

$Q_{sp} = [\text{Ba}^{2+}][\text{IO}_3^-]^2 = (7.204611 \times 10^{-5})(0.023)^2 = 3.81124 \times 10^{-8}$ (unrounded)
Since $Q_{sp} > K_{sp}$ ($3.8 \times 10^{-8} > 1.5 \times 10^{-9}$), **Ba(IO₃)₂ will precipitate**.

19.89   The ion-product expression for Ag_2CrO_4 is $K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$ and, from the Appendix, K_{sp} equals 2.6×10^{-12}.
To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp}.

$$[\text{Ag}^+] = \left(\frac{2.7 \times 10^{-5} \text{ g AgNO}_3}{15.0 \text{ mL}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1 \text{ mol AgNO}_3}{169.9 \text{ g AgNO}_3}\right)\left(\frac{1 \text{ mol Ag}^+}{1 \text{ mol AgNO}_3}\right) = 1.0594467 \times 10^{-5} \ M \ \text{Ag}^+ \text{ (unrounded)}$$

$$[\text{CrO}_4^{2-}] = \left(\frac{4.0 \times 10^{-4} \text{ mol K}_2\text{CrO}_4}{L}\right)\left(\frac{1 \text{ mol CrO}_4^{2-}}{1 \text{ mol K}_2\text{CrO}_4}\right) = 4.0 \times 10^{-4} \ M \ \text{IO}_3^-$$

$Q_{sp} = [\text{Ba}^{2+}][\text{IO}_3^-]^2 = (1.0594467 \times 10^{-5})^2(4.0 \times 10^{-4}) = 4.4897 \times 10^{-14}$ (unrounded)
Since $Q_{sp} < K_{sp}$ ($4.5 \times 10^{-14} < 2.6 \times 10^{-12}$), **Ag₂CrO₄ will not precipitate**.

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

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

The Ca^{2+} is limiting leaving $0 \ M$, and after the reactions there will be $(0.01550 - 0.00025170)$ mol of $\text{C}_2\text{O}_4^{2-}$ left.

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

Concentration (M)	CaC₂O₄•H₂O(s)	⇌	Ca²⁺(aq)	+	C₂O₄²⁻(aq)	+	H₂O(l)
Initial	—		0		0.0747466		—
Change	—		+ S		+ S		—
Equilibrium	—		S		0.0747466 + S		—

Assume that $0.0747466 + S \approx 0.0747466$ because the amount of compound that dissolves will be negligible in comparison to $0.0747466 \ M$. The K_{sp} from the Appendix is: 2.3×10^{-9}
$\quad K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (S)(0.0747466) = 2.3 \times 10^{-9}$.
$\quad S = 3.07706 \times 10^{-8} = 3.1 \times 10^{-8}$
Check assumption: $(3.07706 \times 10^{-8} M) / (0.0747466 M) \times 100\% = 0.00004\% < 5\%$, so the assumption is good.
S represents both the molar solubility of Ca^{2+} and CaC₂O₄•H₂O(s), so the concentration of Ca^{2+} is **3.1 x 10⁻⁸ M**.

19.91   a) **Fe(OH)₃** will precipitate first because its K_{sp} (1.6×10^{-39}) is smaller than the K_{sp} for Cd(OH)₂ at 7.2×10^{-15}.
The precipitation reactions are:
$\quad\quad \text{Fe}^{3+}(aq) + 3 \text{ OH}^- (aq) \rightarrow \text{Fe(OH)}_3(s) \quad\quad\quad\quad K_{sp} = [\text{Fe}^{3+}][\text{ OH}^-]^3$
$\quad\quad \text{Cd}^{2+}(aq) + 2 \text{ OH}^- (aq) \rightarrow \text{Cd(OH)}_2(s) \quad\quad\quad\quad K_{sp} = [\text{Cd}^{2+}][\text{ OH}^-]^2$
The concentrations of Fe^{3+} and Cd^{2+} in the mixed solution are found from $M_{conc}V_{conc} = M_{dil}V_{dil}$
$[\text{Fe}^{3+}] = [(0.50 \ M)(50.0 \text{ mL})] / [(50.0 + 125) \text{ mL}] = 0.142857 \ M \ \text{Fe}^{3+}$ (unrounded)
$[\text{Cd}^{2+}] = [(0.25 \ M)(125 \text{ mL})] / [(50.0 + 125) \text{ mL}] = 0.178571 \ M \ \text{Cd}^{2+}$ (unrounded)
The hydroxide ion concentration required to precipitate the metal ions comes from the metal ion concentrations and the K_{sp}.
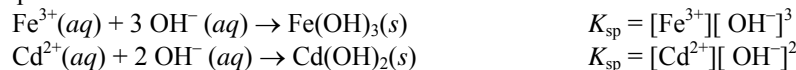
$$[\text{OH}^-]_{\text{Fe}} = \sqrt[3]{\frac{K_{sp}}{[\text{Fe}^{3+}]}} = \sqrt[3]{\frac{1.6 \times 10^{-39}}{[0.142857]}} = 2.237 \times 10^{-13} = 2.2 \times 10^{-13} \ M$$

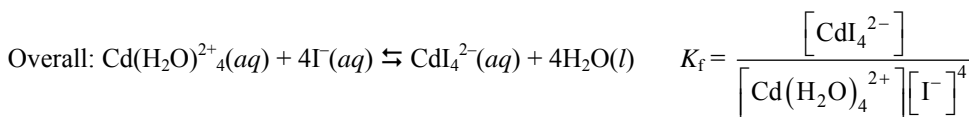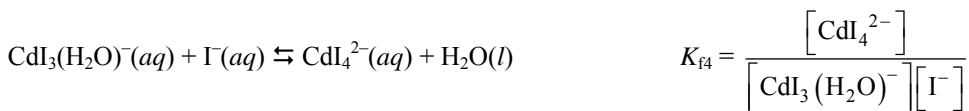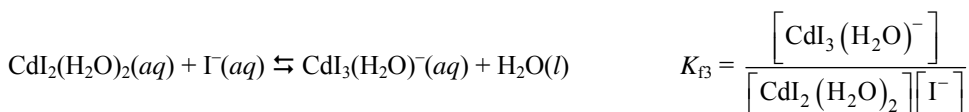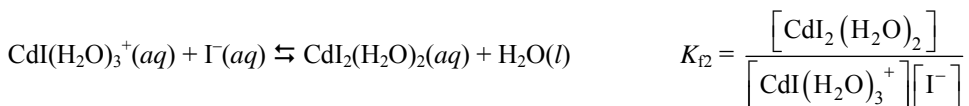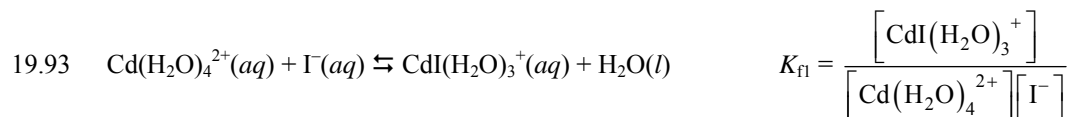$$[\text{OH}^-]_{\text{Cd}} = \sqrt{\frac{K_{sp}}{[\text{Cd}^{2+}]}} = \sqrt{\frac{7.2 \times 10^{-15}}{[0.178571]}} = 2.0079864 \times 10^{-7} = 2.0 \times 10^{-7} \ M$$

A lower hydroxide ion concentration is required to precipitate the Fe^{3+}.

b) The two ions are separated by adding just enough NaOH to precipitate the iron(III) hydroxide, but precipitating no more than 0.01% of the cadmium. The Fe^{3+} is found in the solid precipitate while the Cd^{2+} remains in the solution.

c) A hydroxide concentration between the values calculated in part (a) will work. The best separation would be when $Q_{sp} = K_{sp}$ for $Cd(OH)_2$. This occurs when $[OH^-] = $ **2.0 x 10^{-7} M**.

19.92   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.

19.93 $Cd(H_2O)_4{}^{2+}(aq) + I^-(aq) \leftrightarrows CdI(H_2O)_3{}^+(aq) + H_2O(l)$

$$K_{f1} = \frac{\left[CdI(H_2O)_3{}^+\right]}{\left[Cd(H_2O)_4{}^{2+}\right]\left[I^-\right]}$$

$CdI(H_2O)_3{}^+(aq) + I^-(aq) \leftrightarrows CdI_2(H_2O)_2(aq) + H_2O(l)$

$$K_{f2} = \frac{\left[CdI_2(H_2O)_2\right]}{\left[CdI(H_2O)_3{}^+\right]\left[I^-\right]}$$

$CdI_2(H_2O)_2(aq) + I^-(aq) \leftrightarrows CdI_3(H_2O)^-(aq) + H_2O(l)$

$$K_{f3} = \frac{\left[CdI_3(H_2O)^-\right]}{\left[CdI_2(H_2O)_2\right]\left[I^-\right]}$$

$CdI_3(H_2O)^-(aq) + I^-(aq) \leftrightarrows CdI_4{}^{2-}(aq) + H_2O(l)$

$$K_{f4} = \frac{\left[CdI_4{}^{2-}\right]}{\left[CdI_3(H_2O)^-\right]\left[I^-\right]}$$

Overall: $Cd(H_2O)^{2+}{}_4(aq) + 4I^-(aq) \leftrightarrows CdI_4{}^{2-}(aq) + 4H_2O(l)$

$$K_f = \frac{\left[CdI_4{}^{2-}\right]}{\left[Cd(H_2O)_4{}^{2+}\right]\left[I^-\right]^4}$$

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

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

19.94   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:

$$Pb^{2+}(aq) + n\ OH^-(aq) \leftrightarrows Pb(OH)_n{}^{2-n}(aq)$$
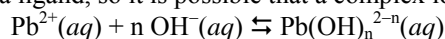
This decreases the concentration of Pb^{2+}, shifting the solubility equilibrium to the right to dissolve more PbS.

19.95   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^-),

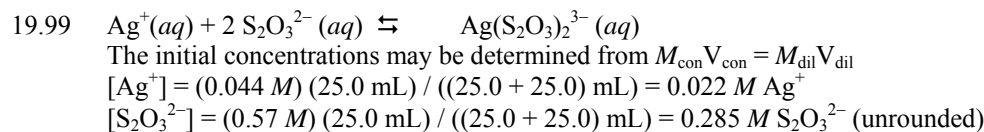$$Hg(H_2O)_4{}^{2+}(aq) + 4\ CN^-(aq) \leftrightarrows Hg(CN)_4{}^{2-}(aq) + 4\ H_2O(l)$$
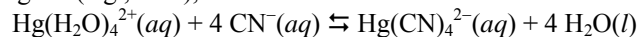
Note that both sides of the equation have the same "overall" charge of -2. The mercury complex changes from $+2$ to -2 because water is a neutral *molecular* ligand, whereas cyanide is an *ionic* ligand.

19.96 $Zn(H_2O)_4{}^{2+}(aq) + 4\ CN^-\ (aq) \leftrightarrows Zn(CN)_4{}^{2-}{}_{(aq)} + 4\ H_2O(l)$

19.97   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.

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

19.98 $Al(H_2O)_6{}^{3+}(aq) + 6\ F^-(aq) \leftrightarrows AlF_6{}^{3-}(aq) + 6\ H_2O(l)$
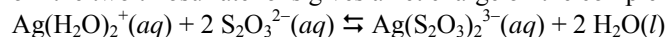
19.99 $Ag^+(aq) + 2 S_2O_3^{2-} (aq) \leftrightarrows Ag(S_2O_3)_2^{3-} (aq)$
The initial concentrations may be determined from $M_{con}V_{con} = M_{dil}V_{dil}$
$[Ag^+] = (0.044 \, M) (25.0 \, mL) / ((25.0 + 25.0) \, mL) = 0.022 \, M \, Ag^+$
$[S_2O_3^{2-}] = (0.57 \, M) (25.0 \, mL) / ((25.0 + 25.0) \, mL) = 0.285 \, M \, S_2O_3^{2-}$ (unrounded)
The reaction gives:

Concentration (M)	$Ag^+(aq)$	+	$2 S_2O_3^{2-} (aq)$	$\rightarrow$	$Ag(S_2O_3)_2^{3-} (aq)$	
Initial	0.022		0.285		0	
Change	−0.022		−2 (0.022)		+ 0.022	1:2:1 mole ratio
Equilibrium	0		0.241		0.022	

To reach equilibrium:

Concentration (M)	$Ag^+(aq)$	+	$2 S_2O_3^{2-} (aq)$	$\leftrightarrows$	$Ag(S_2O_3)_2^{3-} (aq)$
Initial	0		0.241		0.022
Change	+ x		+ 2 x		− x
Equilibrium	+ x		0.241 + 2 x		0.022 − x

K_f is large, so $[Ag(S_2O_3)_2^{3-}] \approx 0.022 \, M$ and $[S_2O_3^{2-}]_{equil} \approx 0.241 \, M$ (unrounded)

$$K_f = \frac{\left[Ag(S_2O_3)_2^{3-}\right]}{\left[Ag^+\right]\left[S_2O_3^{2-}\right]^2} = \frac{[0.022]}{[x][0.241]^2} = 4.7 \times 10^{13}$$

$x = [Ag^+] = 8.0591778 \times 10^{-15} = \mathbf{8.1 \times 10^{-15} \, M}$

19.100 The reaction between SCN^- and Fe^{3+} produces the red complex $FeSCN^{2+}$. One can assume from the much larger concentration of SCN^- and large K_f that all of the Fe^{3+} ions react to form the complex. Calculate the initial concentrations of SCN^- and Fe^{3+} and write a reaction table in which x is the concentration of $FeSCN^{2+}$ formed.

$$[Fe^{3+}]_{initial} = \frac{(0.0015 \, M \, Fe(NO_3)_3)(0.50 \, L)}{((0.50+0.50) \, L)} \left(\frac{1 \, mol \, Fe^{3+}}{1 \, mol \, Fe(NO_3)_3}\right) = 0.00075 \, M \, Fe^{3+}$$

$$[SCN^-]_{initial} = \frac{(0.20 \, M \, KSCN)(0.50 \, L)}{((0.50+0.50) \, L)} \left(\frac{1 \, mol \, SCN^-}{1 \, mol \, KSCN}\right) = 0.10 \, M \, SCN^-$$

Set up a reaction table:

Concentration (M)	$Fe^{3+}(aq)$	+	$SCN^-(aq)$	$\leftrightarrows$	$FeSCN^{2+}$
Initial	7.5×10^{-4}		0.10		0
Change	− x		− x		+ x
Equilibrium	7.5×10^{-4} − x		0.10 − x		x

It is reasonable to assume that x is much less than 0.10, so $0.10 - x \approx 0.10$. However, it is not reasonable to assume that $0.00075 - x \approx 0.00075$, because x may be significant in relation to such a small number. The equilibrium expression and the constant, from the problem, are:

$$K_f = \frac{\left[FeSCN^{2+}\right]}{\left[Fe^{3+}\right]\left[SCN^-\right]} = \frac{[x]}{\left[7.5 \times 10^{-4} - x\right][0.10 - x]} = \frac{[x]}{\left[7.5 \times 10^{-4} - x\right][0.10]} = 8.9 \times 10^2$$

$x = (7.5 \times 10^{-4} - x) (0.10) (8.9 \times 10^2) = (7.5 \times 10^{-4} - x) (89)$
$x = 6.675 \times 10^{-2} - 89 \, x$ (unrounded)
$x = 7.416667 \times 10^{-4}$
From the reaction table, $[Fe^{3+}]_{eq} = 7.5 \times 10^{-4} - x$. Therefore, $[Fe^{3+}]_{eq} = 7.5 \times 10^{-4} - 7.416667 \times 10^{-4}$
$\qquad = 8.33333 \times 10^{-6} = \mathbf{1 \times 10^{-5} \, M}$.

19.101 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
$S = [Cr(OH)_3]_{dissolved} = [Cr(OH)_4^-]$.

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 $[OH^-] = 10^{-1.0} = 0.1\ M$.
Reaction table:

Concentration (M)	$Cr(OH)_3(s)$ +	$OH^-(aq) \leftrightarrows$	$Cr(OH)_4^-(aq)$
Initial	——	0.1	0
Change	——	– S	+ S
Equilibrium	——	0.1 – S	S

Assume that $0.1 - S \approx 0.1$.

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

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

19.102 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: $AgI(s) \leftrightarrows Ag^+(aq) + I^-(aq)$ $K_{sp} = 8.3 \times 10^{-17}$
Complex-ion: $Ag^+(aq) + 2\ NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq)$ $K_f = 1.7 \times 10^7$
Overall: $AgI(s) + 2\ NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq) + I^-(aq)$
$K_{overall} = K_{sp} \times K_f = (8.3 \times 10^{-17})(1.7 \times 10^7) = 1.411 \times 10^{-9}$ (unrounded)
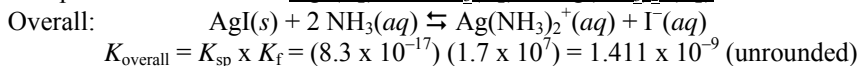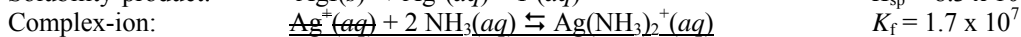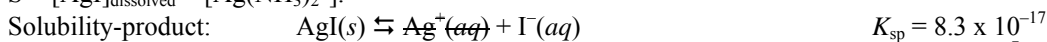
Reaction table:

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

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

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

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

19.103 The complex formation equilibrium is:
$$Zn^{2+}(aq) + 4\ CN^-(aq) \leftrightarrows Zn(CN)_4^{2-}(aq) \qquad K_f = 4.2 \times 10^{19}$$
First, calculate the initial moles of Zn^{2+} and CN^-, then set up reaction table assuming that the reaction first goes to completion, and then calculate back to find the reactant concentrations.

$$\text{Moles } Zn^{2+} = (0.84\ g\ ZnCl_2)\left(\frac{1\ mol\ ZnCl_2}{136.31\ g\ ZnCl_2}\right)\left(\frac{1\ mol\ Zn^{2+}}{1\ mol\ ZnCl_2}\right) = 0.0061624\ mol\ Zn^{2+}\text{ (unrounded)}$$

$$\text{Moles } CN^- = \left(\frac{0.150\ mol\ NaCN}{L}\right)\left(\frac{10^{-3}\ L}{1\ mL}\right)(245\ mL)\left(\frac{1\ mol\ CN^-}{1\ mol\ NaCN}\right) = 0.03675\ mol\ CN^-\text{ (unrounded)}$$

The Zn^{2+} is limiting because there are significantly fewer moles of this ion, thus, $[Zn^{2+}] = 0$, and the moles of CN^- remaining are: $[0.03675 - 4(0.0061624)]$.

$$[CN^-] = \frac{\left[0.03675 - 4(0.0061624)\right]mol\ CN^-}{(245\ mL)}\left(\frac{1\ mL}{10^{-3}\ L}\right) = 0.0493894\ M\ CN^-$$

The Zn^{2+} will produce an equal number of moles of the complex with the concentration:

$$[Zn(CN)_4^{2-}] = \left(\frac{0.0061624\ mol\ Zn^{2+}}{245\ mL}\right)\left(\frac{1\ mL}{10^{-3}\ L}\right)\left(\frac{1\ mol\ Zn(CN)_4^{2-}}{1\ mol\ Zn^{2+}}\right) = 0.025153\ M\ Zn(CN)_4^{2-}$$

Concentration (M)	$Zn^{2+}(aq)$ +	$4\ CN^-(aq)$	$\leftrightarrows$	$Zn(CN)_4^{2-}(aq)$
Initial	0	0.0493894		0.025153
Change	+ x	+ 4 x		– x
Equilibrium	x	0.0493894 + 4 x		0.025153 – x

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Assume the –x and the +4x do not significantly change the associated concentrations.

$$K_f = \frac{\left[Zn(CN)_4^{2-}\right]}{\left[Zn^{2+}\right]\left[CN^-\right]^4} = \frac{[0.025153 - x]}{[x][0.0493894 + 4x]^4} = \frac{[0.025153]}{[x][0493894]^4} = 4.2 \times 10^{19}$$

x = 1.006481 x 10^{-16} = 1.0 x 10^{-16}
$[Zn^{2+}]$ = **1.0 x 10^{-16} M Zn^{2+}**
$[Zn(CN)_4^{2-}]$ = 0.025153 – x = 0.025153 = **0.025 M $Zn(CN)_4^{2-}$**
$[CN^-]$ = 0.0493894 + 4 x = 0.0493894 = **0.049 M CN^-**

19.104   The complex formation equilibrium is:
$$Co^{2+}(aq) + 4\ OH^-(aq) \leftrightarrows Co(OH)_4^{2-}(aq)\ K_f = 5 \times 10^9$$
First, calculate the initial moles of Co^{2+} and OH^-, then set up reaction table assuming that the reaction first goes to completion and then calculate back to find reactant concentrations.

$$\text{Moles } Co^{2+} = \left(2.4 \text{ g } Co(NO_3)_2\right)\left(\frac{1 \text{ mol } Co(NO_3)_2}{182.95 \text{ g } Co(NO_3)_2}\right)\left(\frac{1 \text{ mol } Co^{2+}}{1 \text{ mol } Co(NO_3)_2}\right) = 0.013118 \text{ mol } Co^{2+} \text{ (unrounded)}$$

$$\text{Moles } OH^- = \left(\frac{0.22 \text{ mol KOH}}{L}\right)(0.350 \text{ L})\left(\frac{1 \text{ mol } OH^-}{1 \text{ mol KOH}}\right) = 0.077 \text{ mol } OH^-$$

The Co^{2+} is limiting, thus, $[Co^{2+}]$ = 0, and the moles of OH^- remaining are: [0.077 - 4(0.013118)]

$$[OH^-] = \frac{\left[0.077 - 4(0.013118)\right]mol\,OH^-}{(0.350 \text{ L})} = 0.07008 \ M\ OH^- \text{ (unrounded)}$$

The Co^{2+} will produce an equal number of moles of the complex with the concentration:

$$[Co(OH)_4^{2-}] = \left(\frac{0.013118 \text{ mol } Co^{2+}}{0.350 \text{ L}}\right)\left(\frac{1 \text{ mol } Co(OH)_4^{2-}}{1 \text{ mol } Co^{2+}}\right) = 0.03748 \ M\ Co(OH)_4^{2-} \text{ (unrounded)}$$

Concentration (M)	$Co^{2+}(aq)$	+	$4\ OH^-(aq)$	$\leftrightarrows$	$Co(OH)_4^{2-}(aq)$
Initial	0		0.07008		0.03748
Change	+ x		+ 4 x		– x
Equilibrium	x		0.07008 + 4 x		0.03748 – x

Assume the –x and the + 4x do not significantly change the associated concentrations.

$$K_f = \frac{\left[Co(OH)_4^{2-}\right]}{\left[Co^{2+}\right]\left[OH^-\right]^4} = \frac{[0.03748 - x]}{[x][0.07008 + 4x]^4} = \frac{[0.03748]}{[x][0.07008]^4} = 5 \times 10^9$$

x = 3.1078 x 10^{-7} = 3.1 x 10^{-7}
$[Co^{2+}]$ = **3.1 x 10^{-7} M Co^{2+}**
$[Co(OH)_4^{2-}]$ = 0.03748 – x = 0.037479689 = **0.037 M $Co(OH)_4^{2-}$**
$[OH^-]$ = 0.07008 + 4 x = 0.070078756 = **0.070 M OH^-**

19.105   Calculate the pH of the benzoic acid/benzoate buffer, using the Henderson-Hasselbalch equation. The K_a for benzoic acid is 6.3 x 10^{-5} (from the Appendix). The pK_a is -log (6.3 x 10^{-5}) = 4.201. The reaction of benzoic acid with sodium hydroxide is:
$$C_6H_5COOH(aq) + NaOH(aq) \rightarrow Na^+(aq) + C_6H_5COO^-(aq) + H_2O(l)$$
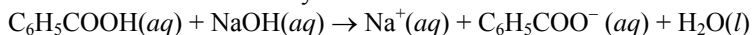
$$\text{Moles of } C_6H_5COOH = \left(\frac{0.200 \text{ mol } C_6H_5COOH}{L}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(475 \text{ mL}) = 0.0950 \text{ mol } C_6H_5COOH$$

$$\text{Moles NaOH} = \left(\frac{2.00 \text{ mol NaOH}}{L}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(25 \text{ mL}) = 0.050 \text{ mol NaOH}$$

NaOH is the limiting reagent:

The reaction table gives:

$$C_6H_5COOH(aq) + NaOH(aq) \rightarrow Na^+(aq) + C_6H_5COO^-(aq) + H_2O(l)$$

Initial	0.0950 mol	0.050 mol	—	0	—
Reacting	− 0.050 mol	− 0.050 mol		+ 0.050 mol
Final	0.045 mol	0 mol		0.050 mol

The concentrations after the reactions are:

$$[C_6H_5COOH] = \left(\frac{0.045 \text{ mol } C_6H_5COOH}{(475 + 25)\text{mL}} \right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.090 \ M \ C_6H_5COOH$$

$$[C_6H_5COO^-] = \left(\frac{0.050 \text{ mol } C_6H_5COO^-}{(475 + 25)\text{mL}} \right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.10 \ M \ C_6H_5COO^-$$

Calculating the pH from the Henderson-Hasselbalch equation:

$$pH = pKa + \log\left(\frac{[C_6H_5CO^-]}{[C_6H_5COOH]} \right) = 4.201 + \log\left(\frac{[0.10]}{[0.090]} \right) = 4.24676 = 4.2$$

Calculations on formic acid (HCOOH) also use the Henderson-Hasselbalch equation. The K_a for formic acid is 1.8×10^{-4} and the $pK_a = -\log(1.8 \times 10^{-4}) = 3.7447$.

The formate to formic acid ratio may now be determined:

$$pH = pKa + \log\left(\frac{[HCOO^-]}{[HCOOH]} \right)$$

$$4.24676 = 3.7447 + \log\left(\frac{[HCOO^-]}{[HCOOH]} \right)$$

$$0.50206 = \log\left(\frac{[HCOO^-]}{[HCOOH]} \right)$$

$$\left(\frac{[HCOO^-]}{[HCOOH]} \right) = 3.177313$$

$$[HCOO^-] = 3.177313 \ [HCOOH]$$

Since the conjugate acid and the conjugate base are in the same volume, the mole ratio and the molarity ratios are identical.

Moles $HCOO^- = 3.177313$ mol HCOOH

The total volume of the solution is $(500. \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.500 \text{ L}$

Let V_a = volume of acid solution added, and V_b = volume of base added. Thus:

$V_a + V_b = 0.500 \text{ L}$

The reaction between the formic acid and the sodium hydroxide is:

$$HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$$
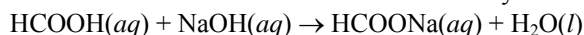
The moles of NaOH added equals the moles of HCOOH reacted and the moles of HCOONa formed.

Moles NaOH = (2.00 mol NaOH / L) (V_b) = 2.00 V_b mol

Total moles HCOOH = (0.200 mol HCOOH / L) (V_a) = 0.200 V_a mol

The stoichiometric ratios in this reaction are all 1:1.

Moles HCOOH remaining after the reaction = (0.200 V_a − 2.00 V_b) mol

Moles $HCOO^-$ = moles HCOONa = moles NaOH = 2.00 V_b

Using these moles and the mole ratio determined for the buffer gives:

Moles $HCOO^- = 3.177313$ mol HCOOH

2.00 V_b mol = 3.177313 (0.200 V_a − 2.00 V_b) mol

2.00 V_b = 0.6354626 V_a − 6.354626 V_b

8.354626 V_b = 0.6354626 V_a

The volume relationship given above gives $V_a = (0.500 - V_b)$ L.

$8.354626\, V_b = 0.6354626\, (0.500 - V_b)$

$8.354626\, V_b = 0.3177313 - 0.6354626\, V_b$

$8.9900886\, V_b = 0.3177313$

$V_b = 0.0353424 = \textbf{0.035 L NaOH}$

$V_a = 0.500 - 0.0353424 = 0.4646576 = \textbf{0.465 L HCOOH}$

Limitations due to the significant figures lead to a solution with only an approximately correct pH.

19.106 $pK_a = -\log K_a = -\log 6.3 \times 10^{-8} = 7.200659$ (unrounded). The K_a comes from Appendix C; it is K_{a2} for phosphoric acid.

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

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

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

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

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

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

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

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

19.107 A formate buffer contains formate ($HCOO^-$) as the base and formic acid (HCOOH) as the acid. From the Appendix, the K_a for formic acid is 1.8×10^{-4} and the $pK_a = -\log(1.8 \times 10^{-4}) = 3.7447$ (unrounded).

a) The Henderson-Hasselbalch equation gives the component ratio, $[HCOO^-] / [HCOOH]$:

$$pH = pKa + \log\left(\frac{[HCOO^-]}{[HCOOH]}\right)$$

$$3.74 = 3.7447 + \log\left(\frac{[HCOO^-]}{[HCOOH]}\right)$$

$$-0.0047 = \log\left(\frac{[HCOO^-]}{[HCOOH]}\right)$$

$$\left(\frac{[HCOO^-]}{[HCOOH]}\right) = 0.989236 = \textbf{0.99}$$

b) To prepare solutions, set up equations for concentrations of formate and formic acid with x equal to the volume, in L, of 1.0 *M* HCOOH added. The equations are based on the neutralization reaction between HCOOH and NaOH that produces $HCOO^-$.

$$HCOOH(aq) + NaOH(aq) \rightarrow HCOO^-(aq) + Na^+(aq) + H_2O(l)$$
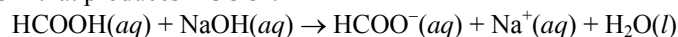
$$[HCOO^-] = (1.0\,M\ NaOH)\left(\frac{(0.700 - x)L\ NaOH}{0.700\ L\ solution}\right)\left(\frac{1\ mol\ HCOO^-}{1\ mol\ NaOH}\right)$$

$$[HCOOH] = (1.0\ M\ HCOOH)\left(\frac{x\ L\ HCOOH}{0.700\ L\ solution}\right) - (1.0\ M\ NaOH)\left(\frac{(0.700 - x)L\ NaOH}{0.700\ L\ solution}\right)\left(\frac{1\ mol\ HCOO^-}{1\ mol\ NaOH}\right)$$

The component ratio equals 0.99 (from part a). Simplify the above equations and plug into ratio:

$$\frac{\left[\text{HCOO}^-\right]}{\left[\text{HCOOH}\right]} = \frac{\left[\left(^{0.700-x}\big/_{0.700}\right)\text{M HCOO}^-\right]}{\left[\left(x-^{(0.700-x)}\big/_{0.700}\right)\text{M HCOOH}\right]} = \frac{0.700-x}{2x-0.700} = 0.989236$$

Solving for x:

x = 0.46751 = 0.468 L

Mixing **0.468 L of 1.0 M HCOOH** and 0.700 − 0.468 = **0.232 L of 1.0 M NaOH** gives a buffer of pH 3.74.

c) The final concentration of HCOOH from the equation in part b:

$$[\text{HCOOH}] = \left(1.0 \text{ M HCOOH}\right)\left(\frac{0.468 \text{ L HCOOH}}{0.700 \text{ L solution}}\right) - \left(1.0 \text{ M NaOH}\right)\left(\frac{0.232 \text{ L NaOH}}{0.700 \text{ L solution}}\right)\left(\frac{1 \text{ mole HCOO}^-}{1 \text{ mole NaOH}}\right)$$

$$= 0.33714 = \textbf{0.34 } \textit{M}\textbf{ HCOOH}$$

19.108   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.

19.109 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 $H_3O^+(aq)$.

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

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

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

Mass of H_2SO_4 = 36.28118 g

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

The reaction between H_3O^+ and the base sodium acetate is:
$H_3O^+(aq) + NaC_2H_3O_2\ (aq) \rightarrow H_2O(l) + HC_2H_3O_2\ (aq) + Na+(aq)$
lb of $NaC_2H_3O_2 \cdot 3\ H_2O$ required to neutralize the H_2SO_4 =
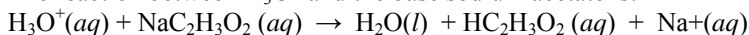
$$\left(0.7398 \text{ mol } H_3O^+\right)\left(\frac{1 \text{ mol } NaC_2H_3O_2 \cdot 3H_2O}{1 \text{ mol } H_3O^+}\right)\left(\frac{136.08 \text{ g } NaC_2H_3O_2 \cdot 3H_2O}{1 \text{ mol } NaC_2H_3O_2 \cdot 3H_2O}\right)\left(\frac{1 \text{ kg}}{1000 \text{ g } NaC_2H_3O_2 \cdot 3H_2O}\right)\left(\frac{2.205 \text{ lb}}{1 \text{ kg}}\right)$$

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

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

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

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

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

$$5.0 = 4.7447 + \log\left(\frac{[C_2H_3O_2^-]}{[9.0627 \text{ mol}]}\right)$$

$$0.2552725 = \log\left(\frac{[C_2H_3O_2^-]}{[9.0627 \text{ mol}]}\right)$$

$$1.8 = \frac{[C_2H_3O_2^-]}{[9.0627 \text{ mol}]}$$

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

lb of $NaC_2H_3O_2 \cdot 3\ H_2O$ required =

$$\left(16.31286 \text{ mol } CH_3COONa \cdot 3H_2O\right)\left(\frac{136.08 \text{ g } NaC_2H_3O_2 \cdot 3H_2O}{1 \text{ mol } NaC_2H_3O_2 \cdot 3H_2O}\right)\left(\frac{1 \text{ kg}}{1000 \text{ g}}\right)\left(\frac{2.205 \text{ lb}}{1 \text{ kg}}\right) = 4.89478 \text{ lb}$$

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

19.110 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:

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

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

19.111 $CdS(s) + H_2O(l) \leftrightarrows Cd^{2+}(aq) + HS^-(aq) + OH^-(aq)$ $K_{sp} = 1.0 \text{ x } 10^{-24}$
(The sulfide ion S^{2-} reacts in water to form HS^- and OH^-)
$K_{sp} = 1.0 \text{ x } 10^{-24} = [Cd^{2+}][HS^-][OH^-] = S^3$
$S = $ **1.0 x 10^{-8} M**

19.112 a. $K = [CO_2(aq)] / [CO_2(g)] = 3.1 \text{ x } 10^{-2}$
        $[CO_2(aq)] = K[CO_2(aq)] = (3.1 \text{ x } 10^{-2})(3 \text{ x } 10^{-4})$
        $= 9.3 \text{ x } 10^{-6} \text{ } M = $ **9 x 10^{-6} M CO_2**
b. $K = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = (x)(2x)^2 / (9.3 \text{ x } 10^{-6} - x) = 1 \text{ x } 10^{-12}$
                Neglect –x
        $x = 1.325 \text{ x } 10^{-6} = $ **1 x 10^{-6} M Ca^{2+}**
c. $K = [CO_2(aq)] / [CO_2(g)] = 3.1 \text{ x } 10^{-2}$
        $[CO_2(aq)] = K[CO_2(aq)] = (3.1 \text{ x } 10^{-2})(2 \text{ x } 3 \text{ x } 10^{-4})$
        $= 1.86 \text{ x } 10^{-5} \text{ } M$
        $K = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = (x)(2x)^2 / (1.86 \text{ x } 10^{-5} - x) = 1 \text{ x } 10^{-12}$
                Neglect –x
        $x = 1.669 \text{ x } 10^{-6} = $ **2 x 10^{-6} M Ca^{2+}**

19.113 The buffer is made by starting with phosphoric acid and neutralizing some of the acid by adding sodium hydroxide:
$$H_3PO_4(aq) + OH^-(aq) \rightarrow H_2PO_4^-(aq) + H_2O(l)$$
Present initially is $(0.50 \text{ L})(1.0 \text{ } M \text{ } H_3PO_4) = 0.50 \text{ mol } H_3PO_4$. Adding 0.80 mol NaOH converts all the phosphoric acid to dihydrogen phosphate ions (0.50 mol) and 0.30 mol NaOH are left. The remaining OH^- will react with the dihydrogen phosphate:
$$H_2PO_4^-(aq) + OH^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(l)$$
The 0.50 mol $H_2PO_4^-$ reacts with the 0.30 mol OH^- to produce 0.30 mol HPO_4^{2-}. 0.20 mol $H_2PO_4^-$ will remain.
The pH is determined from the equilibrium involving the conjugate pair $HPO_4^{2-}/H_2PO_4^-$.
$$H_2PO_4^-(aq) + H_2O(l) \leftrightarrows HPO_4^{2-}(aq) + H_3O^+(aq) \qquad K_a = 6.3 \text{ x } 10^{-8}$$
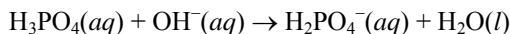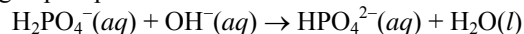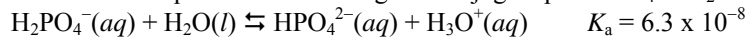
$$pH = pK_a + \log [HPO_4^{2-}] / [H_2PO_4^-]$$

$$pH = -\log (6.3 \times 10^{-8}) + \log \left(\frac{0.30 \text{ mol } HPO_4^{2-} \Big/ 0.50 \text{ L}}{0.20 \text{ mol } H_2PO_4^- \Big/ 0.50 \text{ L}} \right) = 7.37675 = \mathbf{7.38}$$

19.114 a) The solubility equilibrium for KCl is: $KCl(s) \leftrightarrows K^+(aq) + Cl^-(aq)$
The solubility of KCl is 3.7 M.
$K_{sp} = [K^+][Cl^-] = (3.7) (3.7) = 13.69 = \mathbf{14}$
b) Determine the total concentration of chloride ion in each beaker after the HCl has been added. This requires the moles originally present and the moles added.

Original moles from the KCl:

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

Original moles from the 6.0 M HCl in the first beaker:

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

This results in $(0.37 + 0.60)$ mol $= 0.97$ mol Cl^-.
Original moles from the 12 M HCl in the second beaker:

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

This results in $(0.37 + 1.2)$ mol $= 1.57$ mol Cl^- (unrounded)
Volume of mixed solutions $= (100. \text{ mL} + 100. \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.200 \text{ L}$
After the mixing:
$[K^+] = (0.37 \text{ mol } K^+) / (0.200 \text{ L}) = 1.85 \ M \ K^+$ (unrounded)
From 6.0 M HCl in the first beaker:
$[Cl^-] = (0.97 \text{ mol } Cl^-) / (0.200 \text{ L}) = 4.85 \ M \ Cl^-$ (unrounded)
From 12 M HCl in the second beaker:
$[Cl^-] = (1.57 \text{ mol } Cl^-) / (0.200 \text{ L}) = 7.85 \ M \ Cl^-$ (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 in the first beaker:
$Q_{sp} = [K^+][Cl^-] = (1.85) (4.85) = 8.9725 = 9.0 < 14$, so no KCl will precipitate.
From 12 M HCl in the second beaker:
$Q_{sp} = [K^+][Cl^-] = (1.85) (7.85) = 14.5225 = 15 > 14$, 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.

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

19.115 $[NH_3] + [NH_4^+] = 0.15$. If $[NH_3] = 0.01 \ M$, then $[NH_4^+] = 0.14 \ M$.
$K_b = 1.76 \times 10^{-5}$ (from the Appendix)
$K_a = K_w / K_b = 1.0 \times 10^{-14} / 1.76 \times 10^{-5} = 5.6818 \times 10^{-10}$ (unrounded)
$pH = pK_a + \log [NH_3] / [NH_4^+]$
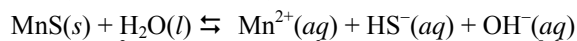$pH = -\log K_a + \log [NH_3] / [NH_4^+]$
$pH = -\log 5.6818 \times 10^{-10} + \log [0.01] / [0.14]$
          $= 8.099386 = \mathbf{8.10}$

19.116 Determine the solubility of MnS:

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

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

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

19.117 a) Use the Henderson-Hasselbalch equation. $K_{a1} = 4.5 \times 10^{-7}$

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

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

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

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

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

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

19.118 The buffer components will be TRIS, $(HOCH_2)_3CNH_2$, and its conjugate acid TRISH$^+$, $(HOCH_2)_3CNH_3^+$. The conjugate acid is formed from the reaction between TRIS and HCl. Since HCl is the limiting reactant in this problem, the concentration of conjugate acid will equal the starting concentration of HCl, 0.095 M. The concentration of TRIS is the initial concentration minus the amount reacted.

$$\text{Mole TRIS} = \left(43.0 \text{ g TRIS}\right)\left(\frac{1 \text{ mol TRIS}}{121.14 \text{ g TRIS}}\right) = 0.354961 \text{ mol (unrounded)}$$

$$\text{Mole HCl added} = \left(\frac{0.095 \text{ mol HCl}}{L}\right)(1.00 \text{ L}) = 0.095 \text{ mol HCl} = \text{mol TRISH}^+$$

	$(HOCH_2)_3CNH_2$ (aq) + HCl(aq) $\leftrightarrows$	$(HOCH_2)_3CNH_3^+$ (aq) + Cl$^-(aq)$	
Initial	0.354961 mol	0.095 mol	0	0
Reacting	−0.095 mol	− 0.095 mol	+ 0.095 mol	
Final	0.259961 mol	0 mol	0.095 mol	

Since there is 1.00 L of solution, the moles of TRIS and TRISH$^+$ equals their molarities.

$$pOH = pK_b + \log \frac{[acid]}{[base]} = 5.91 + \log \frac{[0.095]}{[0.259961]} = 5.472815 \text{ (unrounded)}$$

Therefore, pH of the buffer is 14.00 - 5.472815 = 8.527185 = **8.53**

19.119

mol HCl/mol ethylenediamine
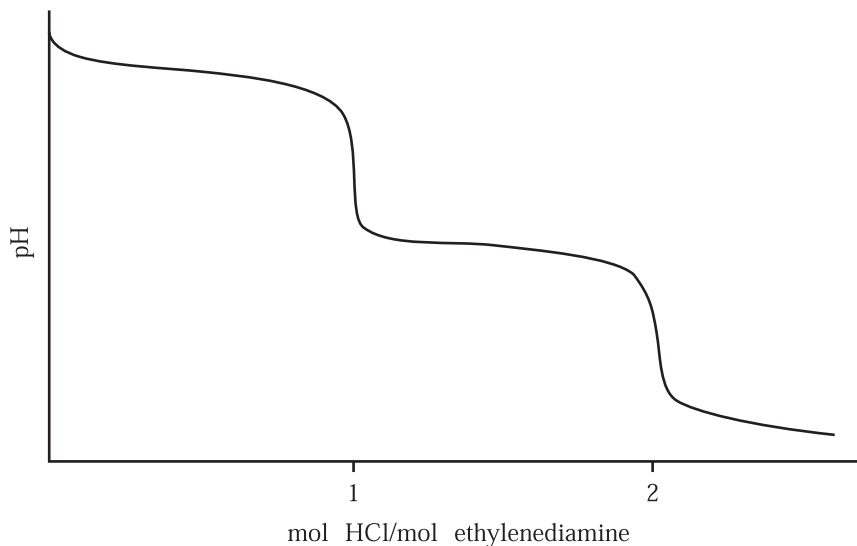
19.120 Zinc sulfide, ZnS, is much less soluble than manganese sulfide, MnS. Convert $ZnCl_2$ and $MnCl_2$ to ZnS and MnS by saturating the solution with H_2S; $[H_2S]_{sat'd} = 0.10\ M$. Adjust the pH so that the greatest amount of ZnS will precipitate and not exceed the solubility of MnS as determined by $K_{sp}(MnS)$.

$K_{sp}(MnS) = [Mn^{2+}][HS^-][OH^-] = 3 \times 10^{-11}$

$\quad\quad [Mn^{2+}] = [MnCl_2] = 0.020\ M$

$[HS^-]$ is calculated using the K_{a1} expression:

Concentration: $H_2S(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HS^-(aq)$
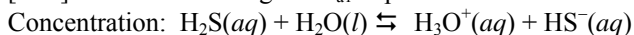
Initial	0.10 mol	0	0
Reacting	$-$ x	$+$ x	$+$ x
Final	0.10 $-$ x	x	x

$$K_{a1} = \frac{\left[H_3O^+\right]\left[HS^-\right]}{[H_2S]} = \frac{\left[H_3O^+\right]\left[HS^-\right]}{[0.10-x]} = 9 \times 10^{-8} \quad \text{Assume } 0.10 - x = 0.10$$

$[H_3O^+][HS^-] = 9 \times 10^{-9}$

$[HS^-] = 9 \times 10^{-9} / [H_3O^+]$

Substituting $[Mn^{2+}]$ and $[HS^-]$ into the $K_{sp}(MnS)$ above gives:

$K_{sp}(MnS) = [Mn^{2+}][HS^-][OH^-] = 3 \times 10^{-11}$

$K_{sp}(MnS) = [Mn^{2+}] (9 \times 10^{-9} / [H_3O^+])[OH^-] = 3 \times 10^{-11}$

Substituting $K_w / [H_3O^+]$ for $[OH^-]$:

$$K_{sp}(MnS) = \left[Mn^{2+}\right]\left(\frac{9 \times 10^{-9}}{\left[H_3O^+\right]}\right)\left(\frac{K_w}{\left[H_3O^+\right]}\right) = 3 \times 10^{-11}$$

$$3 \times 10^{-11} \times [H_3O^+]^2 = \left[Mn^{2+}\right]\left(9 \times 10^{-9}\right)(K_w)$$

$$[H_3O^+] = \sqrt{\frac{\left[Mn^{2+}\right]\left[9 \times 10^{-9}\right]K_w}{3 \times 10^{-11}}} = \sqrt{\frac{(0.020)\left(9 \times 10^{-9}\right)\left(1.0 \times 10^{-14}\right)}{3 \times 10^{-11}}} = 2.4494897 \times 10^{-7} \text{ (unrounded)}$$

pH $= -\log [H_3O^+] = -\log (2.4494897 \times 10^{-7}) = 6.610924 = $ **6.6**

Maintain the pH below 6.6 to separate the ions as their sulfides.

19.121   a) Since K_a (−COOH) > K_b (−NH$_2$), the proton will be transferred from the −COOH to the −NH$_2$, producing
−COO⁻ and −NH$_3^+$

b) pK_a = −log K_a = −log 4.47 x 10^{-3} = 2.34969 (unrounded)

$pH = pK_a + \log [B] / [BH^+]$

5.5 = 2.35 + log [($^+$NH$_3$CH$_2$COO⁻] / [$^+$NH$_3$CH$_2$COOH]

$$\dfrac{\left[{}^+\text{NH}_3\text{CH}_2\text{COO}^-\right]}{\left[{}^+\text{NH}_3\text{CH}_2\text{COOH}\right]} = 1 \text{ x } 10^3$$

c)

pH = 1   pH = 7   pH = 13
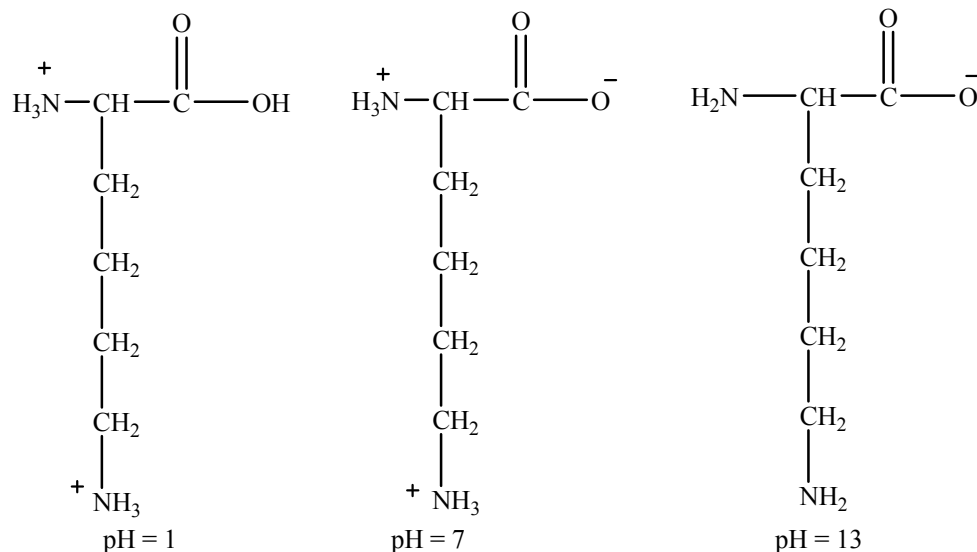
d) at pH 1: D, at pH 7: A, at pH 13: B

19.122   a)The equilibrium is: MCl$_2$(s) ⇌ M^{2+}(aq) + 2 Cl⁻(aq). The ion-product expression is $K_{sp} = [M^{2+}][Cl^-]^2$
Based on the picture, the ion concentration are:

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

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

$K_{sp} = [M^{2+}][Cl^-]^2 = [1.2 \text{ x } 10^{-5}][\ 4.0 \text{ x } 10^{-5}]^2 = $ **1.9 x 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.

19.123   The equilibrium is: Ca$_5$(PO$_4$)$_3$OH(s) ⇌ 5 Ca^{2+}(aq) + 3 PO$_4^{3-}$(aq) + OH⁻(aq)

K_{sp} = 6.8 x 10^{-37} = [Ca^{2+}]^5[PO$_4^{3-}$]^3[OH⁻] = (5S)^5(3S)^3(S) = 84375 S^9

S = 2.7166443 x 10^{-5} = 2.7 x 10^{-5} M

Solubility = (2.7166443 x 10^{-5} mol/L) (502.32 g/mol) = 0.013646248 = **0.014 g/L Ca$_5$(PO$_4$)$_3$OH**

The equilibrium is: Ca$_5$(PO$_4$)$_3$F(s) ⇌ 5 Ca^{2+}(aq) + 3 PO$_4^{3-}$(aq) + F⁻(aq)

K_{sp} = 1.0 x 10^{-60} = [Ca^{2+}]^5[PO$_4^{3-}$]^3[F⁻] = (5S)^5(3S)^3(S) = 84375 S^9

S = 6.1090861 x 10^{-8} = 6.1 x 10^{-8} M

Solubility = (6.1090861 x 10^{-8} mol/L) (504.31 g/mol)
= 3.0808732 x 10^{-5} = **3.1 x 10^{-5} g/L Ca$_5$(PO$_4$)$_3$F**

19.124 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.

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

19.125
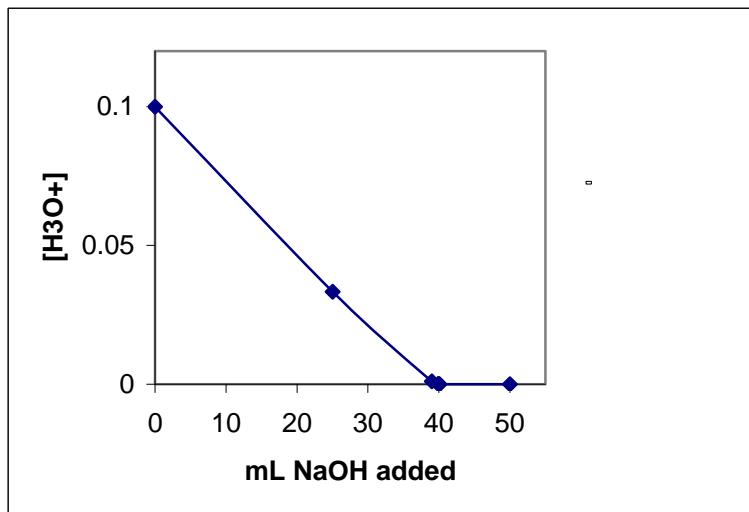
Due to the large range of $[H_3O^+]$, this plot is difficult to prepare and does not easily show the end point. A logarithmic scale (pH versus mL OH^- added) shows this more clearly.

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

Example calculation: For the first 2 lines of data: $\Delta pH = 1.22 - 1.00 = 0.22$; $\Delta V = 10.00 - 0.00 = 10.00$

$$\frac{\Delta pH}{\Delta V} = \frac{0.22}{10.00} = 0.022 \qquad\qquad V_{average}(mL) = (0.00 + 10.00)/2 = 5.00$$

| V(mL)	pH	$\dfrac{\Delta pH}{\Delta V}$	$V_{average}(mL)$
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)
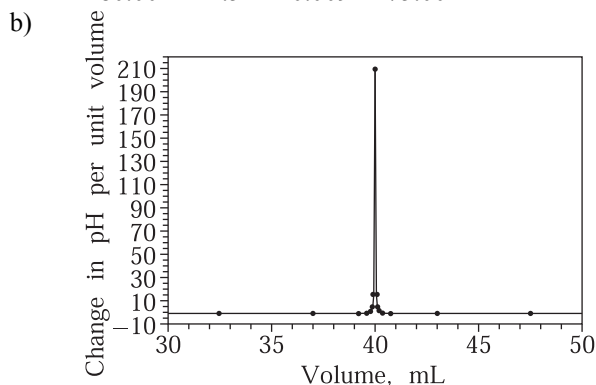
Maximum slope (equivalence point) is at V = 40.00 mL

19.127 Check to see if the concentration of $Ca(OH)_2$ exceeds the K_{sp}.
$M\ Ca(OH)_2 = (6.5\ x\ 10^{-9}\ mol\ Ca(OH)_2) / (10.0\ L) = 6.5\ x\ 10^{-10}\ M\ Ca(OH)_2$
Determine the concentration of a saturated calcium hydroxide solution from the K_{sp}.
$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ OH^-(aq)$$
$$K_{sp} = 6.5\ x\ 10^{-6} = [Ca^{2+}][OH^-]^2 = (S)\ (2S)^2 = 4S^3$$
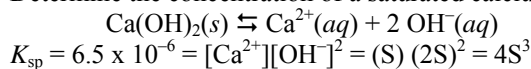
$$S = \sqrt[3]{\frac{6.5\ x\ 10^{-6}}{4}} = 0.01175667 = 0.012\ M$$

Thus, the solution is less than saturated so the K_{sp} does not affect the concentration of $Ca(OH)_2$.
$M\ OH^-$ from $Ca(OH)_2 = (6.5\ x\ 10^{-10}\ M\ Ca(OH)_2)\ (2\ mol\ OH^- / 1\ mol\ Ca(OH)_2) = 1.3\ x\ 10^{-9}\ M\ OH^-$
Pure water has $1\ x\ 10^{-7}\ M\ OH^-$, thus the contribution from the $Ca(OH)_2$ is not significant.
pH of pure water = **7.0**.

19.128 The equation that describes the behavior of a weak base in water is:
$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$
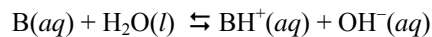
$$K_b = \frac{\left[BH^+\right]\left[OH^-\right]}{[B]}$$

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

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

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

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

19-49

19.129 Use HLac to indicate lactic acid and Lac$^-$ to indicate the lactate ion. The Henderson-Hasselbalch equation gives the pH of the buffer. Determine the final concentrations of the buffer components from $M_{conc}V_{conc} = M_{dil}V_{dil}$. Determine the p$K_a$ of the acid from the K_a.

$$pK_a = -\log K_a = -\log 1.38 \times 10^{-4} = 3.86012 \text{ (unrounded)}$$

Determine the molarity of the diluted buffer component as $M_{dil} = M_{conc}V_{conc} / V_{dil}$.

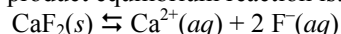[HLac] = [(0.85 M) (225 mL)] / [(225 + 435) mL] = 0.28977 M HLac (unrounded)

[Lac$^-$] = [(0.68 M) (435 mL)] / [(225 + 435) mL] = 0.44818 M Lac$^-$ (unrounded)

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

$$pH = 3.86012 + \log\left(\frac{[0.44818]}{[0.28977]}\right) = 4.049519 = \textbf{4.05}$$

19.130 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) 0.01M HF: Because of the common ion effect, less CaF$_2$ would dissolve in this solution than in pure water.

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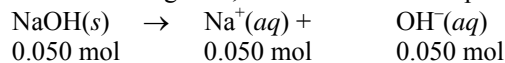
(IV) 0.01M HCl: H$^+$ ions remove OH$^-$ ions from solution so the base equilibrium reaction shifts to the right, consuming F$^-$. This shifts the ion-product equilibrium to the right so that more CaF$_2$ dissolves in this solution than in pure water.

(V) 0.01M Ca(OH)$_2$: Because of the common ion effect, less CaF$_2$ would dissolve in this solution than in pure water. 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.
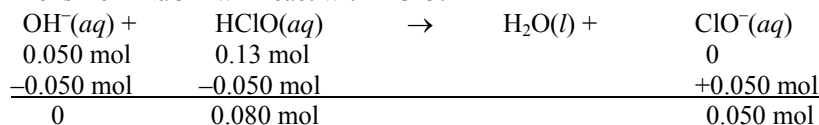
a) **0.01M HCl**

b) **0.01M Ca(OH)$_2$**

19.131 a) The NaOH is a strong base, so it dissociates completely.

NaOH(s)	$\rightarrow$	Na$^+$(aq) +	OH$^-$(aq)
0.050 mol		0.050 mol	0.050 mol

The OH$^-$ ions from NaOH will react with HClO.

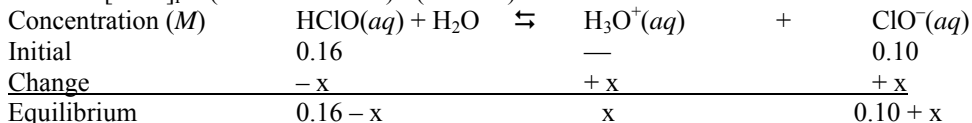| OH$^-$(aq) +	HClO(aq)	$\rightarrow$	H$_2$O(l) +	ClO$^-$(aq)
0.050 mol	0.13 mol			0
$-$0.050 mol	$-$0.050 mol			+0.050 mol
0	0.080 mol			0.050 mol

The initial amount of HClO is 0.13 mol – 0.050 mol = 0.08 mol

The initial amount of ClO$^-$ is 0.050 mol ClO$^-$.

The volume of the solution is (500. mL) (10^{-3} L / 1 mL) = 0.500 L

[HClO]$_i$ = (0.080 mol HClO) / (0.500 L) = 0.16 M HClO

[ClO$^-$]$_I$ = (0.050 mol ClO$^-$) / (0.500 L) = 0.10 M OCl$^-$

Concentration (M)	HClO(aq) + H$_2$O	$\leftrightarrows$	H$_3$O$^+$(aq)	+	ClO$^-$(aq)
Initial	0.16		—		0.10
Change	$-$ x		+ x		+ x
Equilibrium	0.16 – x		x		0.10 + x

x is small, so [HClO] $\approx$ **0.16 M HClO** and [ClO$^-$] $\approx$ **0.10 M ClO$^-$**

$$K_a = \frac{\left[H_3O^+\right]\left[ClO^-\right]}{\left[HClO\right]}$$

$$[H_3O^+] = \frac{K_a\left[HClO\right]}{\left[ClO^-\right]}$$

$$[H_3O^+] = \frac{\left(3.0 \times 10^{-8}\right)(0.16)}{(0.10)} = \mathbf{4.8 \times 10^{-8}} \textbf{ M H}_3\textbf{O}^+$$

$[OH^-] = K_w / [H_3O^+] = (1.0 \times 10^{-14}) / (4.8 \times 10^{-8}) = 2.08333 \times 10^{-7} = \mathbf{2.1 \times 10^{-7}} \textbf{ M OH}^-$

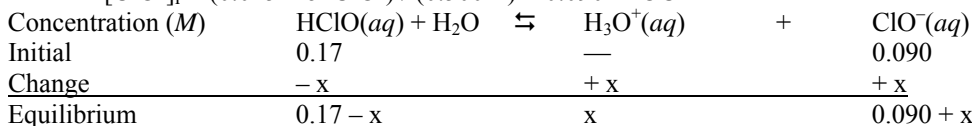$[Na^+] = (0.050 \text{ mol}) / (0.500 \text{ L}) = \mathbf{0.10} \textbf{ M Na}^+$

b) $pH = -\log [H_3O^+] = -\log (4.8 \times 10^{-8} M) = 7.31875876 = \mathbf{7.32}$

c) If 0.0050 mol HCl is added then the ClO$^-$ will react with the H$^+$ to form HClO.

H$^+$ (aq) +	ClO$^-$(aq)	→	HClO(aq)
0.0050 mol	0.050 mol		0.080 mol
–0.0050 mol	–0.0050 mol		+0.0050 mol
0	0.045 mol		0.085 mol
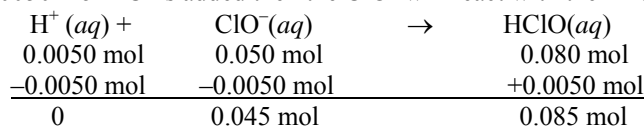
$[HClO]_i = (0.085 \text{ mol HClO}) / (0.500 \text{ L}) = 0.17 \text{ M HClO}$

$[ClO^-]_l = (0.045 \text{ mol ClO}^-) / (0.500 \text{ L}) = 0.090 \text{ M OCl}^-$

Concentration (M)	HClO(aq) + H$_2$O	⇆	H$_3$O$^+$(aq)	+	ClO$^-$(aq)
Initial	0.17		—		0.090
Change	– x		+ x		+ x
Equilibrium	0.17 – x		x		0.090 + x

x is small, so [HClO] ≈ 0.17 M and [ClO$^-$] ≈ 0.090 M

$$[H_3O^+] = \frac{K_a \left[HClO\right]}{\left[ClO^-\right]}$$

$$[H_3O^+] = \frac{\left(3.0 \times 10^{-8}\right)(0.17)}{(0.090)} = 5.6667 \times 10^{-8} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$pH = -\log [H_3O^+] = -\log (5.6667 \times 10^{-8} M) = 7.246669779 = \mathbf{7.25}$

19.132   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

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

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

At 30°C

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

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

19.133 $Hg_2C_2O_4(s) \leftrightarrows Hg_2^{2+}(aq) + C_2O_4^{2-}(aq)$

$K_{sp} = 1.75 \times 10^{-13} = [Hg_2^{2+}][C_2O_4^{2-}] = (0.13 + S)S \approx (0.13) S$

$S = 1.3461538 \times 10^{-12} = \mathbf{1.3 \times 10^{-12}} \textbf{ M}$

19.134 $CaCO_3(s) \leftrightarrows Ca^{2+}(aq) + CO_3^{2-}(aq)$

$K_{sp} = 3.3 \times 10^{-9} = [Ca^{2+}][CO_3^{2-}] = S^2$

$S = [Ca^{2+}] = 5.7445626 \times 10^{-5} = \mathbf{5.7 \times 10^{-5}} \textbf{ M}$

19.135 $[H^+] = 10^{-9.5} = 3.1622776 \times 10^{-10} \text{ M H}^+ \text{ (unrounded)}$

$pOH = 14.0 - pH = 14.0 - 9.5 = 4.5$

$[OH^-] = 10^{-4.5} = 3.1622776 \times 10^{-5} \text{ M OH}^- \text{ (unrounded)}$

$$[HCO_3^-] = \left(\frac{65.0 \text{ mg HCO}_3^-}{L}\right)\left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right)\left(\frac{1 \text{ mol HCO}_3^-}{61.02 \text{ g HCO}_3^-}\right) = 1.0652245 \times 10^{-3} \text{ M HCO}_3^- \text{ (unrounded)}$$
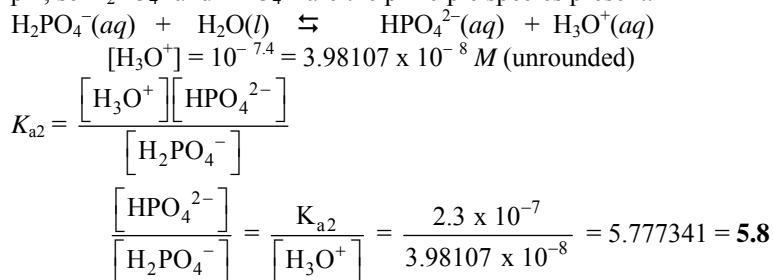
$$[CO_3^{2-}] = \left(\frac{26.0 \text{ mg CO}_3^{2-}}{L}\right)\left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right)\left(\frac{1 \text{ mol CO}_3^{2-}}{60.01 \text{ g CO}_3^{2-}}\right) = 4.3326112 \times 10^{-4} \text{ M CO}_3^{2-} \text{ (unrounded)}$$

Alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$

Alkalinity = $(1.0652245 \times 10^{-3}) + 2(4.3326112 \times 10^{-4}) + (3.1622776 \times 10^{-5}) - (3.1622776 \times 10^{-10})$

Alkalinity = $1.9633692 \times 10^{-3} = \mathbf{1.96 \times 10^{-3}} \textbf{ M}$
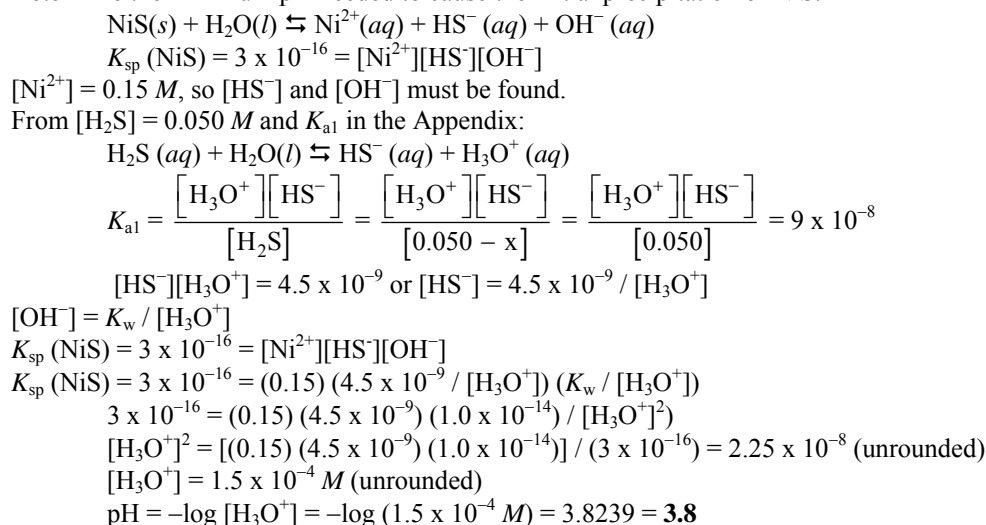
19.136   To determine which species are present from a buffer system of a polyprotic acid, check the pK_a values for the one that is closest to the pH of the buffer. The two components involved in the equilibrium associated with this K_a are the principle species in the buffer. For carbonic acid, pK_{a1} [$-\log(8 \times 10^{-7}) = 6.1$]is closest to the pH of 7.4, so H_2CO_3 and HCO_3^- are the species present. For phosphoric acid, pK_{a2} [$-\log(2.3 \times 10^{-7}) = 6.6$]is closest to the pH, so $H_2PO_4^-$ and HPO_4^{2-} are the principle species present.

$$H_2PO_4^-(aq) + H_2O(l) \leftrightarrows HPO_4^{2-}(aq) + H_3O^+(aq)$$

$$[H_3O^+] = 10^{-7.4} = 3.98107 \times 10^{-8} \ M \ \text{(unrounded)}$$

$$K_{a2} = \frac{\left[H_3O^+\right]\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]}$$

$$\frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = \frac{K_{a2}}{\left[H_3O^+\right]} = \frac{2.3 \times 10^{-7}}{3.98107 \times 10^{-8}} = 5.777341 = \mathbf{5.8}$$
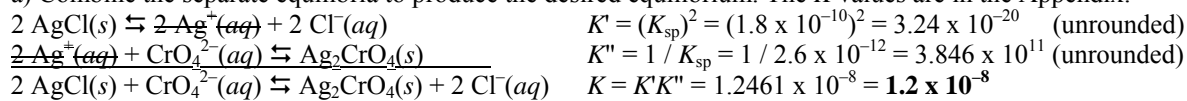
19.137   The pH 3 buffer holds the pH close to 3 and the litmus changes color accordingly. The 0.001 M HCl is initially at pH 3, but it is diluted when added to the litmus. Due to the dilution the pH rises above 3, and will not cause the litmus to change color.

19.138   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**.

19.139   Determine the minimum pH needed to cause the initial precipitation of NiS.

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

$$K_{sp} \ (NiS) = 3 \times 10^{-16} = [Ni^{2+}][HS^-][OH^-]$$

$[Ni^{2+}] = 0.15 \ M$, so $[HS^-]$ and $[OH^-]$ must be found.
From $[H_2S] = 0.050 \ M$ and K_{a1} in the Appendix:

$$H_2S \ (aq) + H_2O(l) \leftrightarrows HS^- \ (aq) + H_3O^+ \ (aq)$$

$$K_{a1} = \frac{\left[H_3O^+\right]\left[HS^-\right]}{\left[H_2S\right]} = \frac{\left[H_3O^+\right]\left[HS^-\right]}{\left[0.050 - x\right]} = \frac{\left[H_3O^+\right]\left[HS^-\right]}{\left[0.050\right]} = 9 \times 10^{-8}$$

$$[HS^-][H_3O^+] = 4.5 \times 10^{-9} \ \text{or} \ [HS^-] = 4.5 \times 10^{-9} / [H_3O^+]$$

$[OH^-] = K_w / [H_3O^+]$
$K_{sp} \ (NiS) = 3 \times 10^{-16} = [Ni^{2+}][HS^-][OH^-]$
$K_{sp} \ (NiS) = 3 \times 10^{-16} = (0.15) \ (4.5 \times 10^{-9} / [H_3O^+]) \ (K_w / [H_3O^+])$

$$3 \times 10^{-16} = (0.15) \ (4.5 \times 10^{-9}) \ (1.0 \times 10^{-14}) / [H_3O^+]^2)$$

$$[H_3O^+]^2 = [(0.15) \ (4.5 \times 10^{-9}) \ (1.0 \times 10^{-14})] / (3 \times 10^{-16}) = 2.25 \times 10^{-8} \ \text{(unrounded)}$$

$$[H_3O^+] = 1.5 \times 10^{-4} \ M \ \text{(unrounded)}$$

$$pH = -\log [H_3O^+] = -\log (1.5 \times 10^{-4} \ M) = 3.8239 = \mathbf{3.8}$$

19.140   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$_2$CrO$_4$(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$_2$CrO$_4$(s) + 2 Cl$^-$(aq) $K = K'K'' = 1.2461 \times 10^{-8} = \mathbf{1.2 \times 10^{-8}}$

b) Since the above reaction has such a small K, it lies far to the left as written.
c) The mixing of equal amounts of equal molar solutions would precipitate all the AgCl, thus the silver ion concentration comes entirely from the K_{sp} of AgCl.

$$K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-] = S^2$$

$$S = [Ag^+] = 1.34164 \times 10^{-5} \ M = \mathbf{1.3 \times 10^{-5} \ M \ Ag^+}$$

Use the K_{sp} for silver chromate.

$K_{sp} = 2.6 \times 10^{-12} = [Ag^+]^2[CrO_4^{2-}]$

$[CrO_4^{2-}] = (2.6 \times 10^{-12}) / (1.34164 \times 10^{-5})^2 = 0.01444 = 0.014\ M$

If the chromate ion concentration exceeds 0.014 M, Ag_2CrO_4 will precipitate.

19.141 a) To find the concentration of HCl after neutralizing the quinidine, calculate the concentration of quinidine and the amount of HCl required to neutralize it, remembering that the mole ratio for the neutralization is 2 mol HCl / 1 mol quinidine.

$$\text{Moles quinidine} = \left(33.85 \text{ mg quinidine}\right)\left(\frac{10^{-3}\ g}{1\ mg}\right)\left(\frac{1 \text{ mol quinidine}}{324.41 \text{ g quinidine}}\right)$$

$$= 1.0434326 \times 10^{-4} \text{ mol quinidine (unrounded)}$$

$$\text{Moles HCl excess} = \left(6.55 \text{ mL}\right)\left(\frac{10^{-3}\ L}{1\ mL}\right)\left(\frac{0.150 \text{ mol HCl}}{L}\right)$$

$$- \left(1.0434326 \times 10^{-4} \text{ mol quinidine}\right)\left(\frac{2 \text{ mol HCl}}{1 \text{ mol quinidine}}\right) = 7.7381348 \times 10^{-4} \text{ mol HCl}$$

(unrounded)

$$\text{Volume needed} = \left(7.7381348 \times 10^{-4} \text{ mol HCl}\right)\left(\frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}}\right)\left(\frac{1\ L}{0.0133 \text{ mol NaOH}}\right)\left(\frac{1\ mL}{10^{-3}\ L}\right)$$

$$= 58.18146 = \textbf{58.2 mL NaOH solution}$$

b) Use the moles of quinidine and the concentration of the NaOH to determine the milliliters.

$$\text{Volume} = \left(1.043436 \times 10^{-4} \text{ mol quinidine}\right)\left(\frac{1 \text{ mol NaOH}}{1 \text{ mol quinidine}}\right)\left(\frac{1\ L}{0.0133 \text{ mol NaOH}}\right)\left(\frac{1\ mL}{10^{-3}\ L}\right)$$

$$= 7.84538 = \textbf{7.84 mL NaOH solution}$$

c) When quinidine (QNN) is first acidified, it has the general form QNH^+NH^+. At the first equivalence point, one of the acidified nitrogen atoms has completely reacted, leaving a singly protonated form, $QNNH^+$. This form of quinidine can react with water as either an acid or a base, so both must be considered. If the concentration of quinidine at the first equivalence point is greater than K_{b1}, then the $[OH^-]$ at the first equivalence point can be estimated as:

$$[OH^-] = \sqrt{K_{b1}K_{b2}} = \sqrt{\left(4.0 \times 10^{-6}\right)\left(1.0 \times 10^{-10}\right)} = 2.0 \times 10^{-8}\ M$$
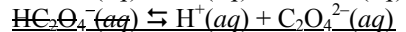
$[H_3O^+] = K_w / [OH^-] = (1.0 \times 10^{-14}) / (2.0 \times 10^{-8}) = 5.0 \times 10^{-7}\ M$

$pH = -\log [H_3O^+] = -\log (5.0 \times 10^{-7}\ M) = 6.3010 = \textbf{6.30}$

19.142 K values from the Appendix:

$H_2C_2O_4(aq) \leftrightarrows H^+(aq) + \text{HC}_2\text{O}_4^-\text{(aq)}$ $K_{a1} = 5.6 \times 10^{-2}$

$\text{HC}_2\text{O}_4^-\text{(aq)} \leftrightarrows H^+(aq) + C_2O_4^{2-}(aq)$ $K_{a2} = 5.4 \times 10^{-5}$
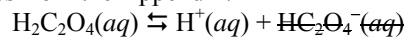
$H_2C_2O_4(aq) \leftrightarrows 2 H^+(aq) + C_2O_4^{2-}(aq)$ $K = K_{a1} K_{a2} = 3.024 \times 10^{-6}$ (unrounded)

$K = [H^+]^2[C_2O_4^{2-}] / [H_2C_2O_4]$

     $[C_2O_4^{2-}] = K[H_2C_2O_4] / [H^+]^2$

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)

$Q = [Ca^{2+}][C_2O_4^{2-}]$

     $Q = (2.6 \times 10^{-3}) (9.07359 \times 10^{-8}) = 2.3591 \times 10^{-10} = 2.4 \times 10^{-10} < K_{sp} = \textbf{No precipitate}$

b. At pH = 7.0: $[H^+] = 10^{-7.0} = 1 \times 10^{-7}\ M$

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

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

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

c. The higher pH would favor precipitation.

19.143 The Henderson-Hasselbalch equation demonstrates that the pH changes when the ratio of acid to base in the buffer changes (pK_a is constant at a given temperature):
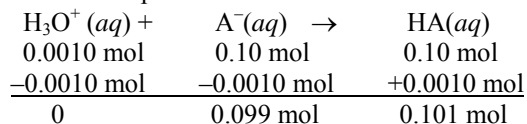
$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

The pH of the A^- / HA buffer cannot be calculated because the identity of "A" and, thus, the value of pK_a are unknown. However, the change in pH can be described:

$$\Delta pH = \log\left(\frac{[A^-]}{[HA]}\right)_{final} - \log\left(\frac{[A^-]}{[HA]}\right)_{initial}$$

Since both [HA] and $[A^-] = 0.10$ M, $\log\left(\frac{[A^-]}{[HA]}\right)_{initial} = 0$ because $[HA] = [A^-]$, and $\log(1) = 0$

So the change in pH is equal to the concentration ratio of base to acid after the addition of H_3O^+.
Consider the buffer prior to addition to the medium.

H_3O^+ (aq) +	A^-(aq) $\rightarrow$	HA(aq)
0.0010 mol	0.10 mol	0.10 mol
−0.0010 mol	−0.0010 mol	+0.0010 mol
0	0.099 mol	0.101 mol

When 0.0010 mol H_3O^+ is added to 1 L of the undiluted buffer, the $[A^-]$ / [HA] ratio changes from 0.10 / 0.10 to (0.099) / (0.101). The change in pH is:

$$\Delta pH = \log(0.099 / 0.101) = -0.008686 \text{ (unrounded)}$$

If the undiluted buffer changes 0.009 pH units with addition of 0.0010 mol H_3O^+, how much can the buffer be diluted and still not change by 0.05 pH units ($\Delta pH < 0.05$)?
Let x = fraction by which the buffer can be diluted. Assume 0.0010 mol H_3O^+ is added to 1 L.

$$\log\frac{[base]}{[acid]} = \log\left(\frac{(0.10x - 0.0010)}{(0.10x + 0.0010)}\right) = -0.05$$

$$\left(\frac{(0.10x - 0.0010)}{(0.10x + 0.0010)}\right) = 10^{-0.05} = 0.89125 \text{ (unrounded)}$$

$$0.10x - 0.0010 = 0.89125 (0.10x + 0.0010)$$
$$x = 0.173908 = 0.17$$

The buffer concentration can be decreased by a factor of 0.17, or **170 mL** of buffer can be diluted to 1 L of medium. At least this amount should be used to adequately buffer the pH change.

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

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

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

$= 57.11488 = $ **57.11 mL NaOH**

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

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

Moles F^- formed = moles NaOH
Moles HF remaining $= (8.750 \times 10^{-3} - 8.673 \times 10^{-3})$ mol $= 7.7 \times 10^{-5}$ mol HF
Volume of solution $= (35.00 + 57.11488 - 0.50) (10^{-3}$ L / 1 mL$) = 0.09161$ L

[HF] = (7.7 x 10^{-5} mol HF) / (0.09161 L) = 0.0008405 M HF
[F$^-$] = (8.673 x 10^{-3} mol F$^-$) / (0.09161 L) = 0.09467 M F$^-$

$pK_a = -\log K_a = -\log 6.8$ x 10^{-4} = 3.1675 (unrounded)
pH = pK_a + log [F$^-$] / [HF]
= 3.1675 + log (0.09467) / (8.405 x 10^{-4})
= 5.21917 = **5.22**

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

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

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

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

x = [OH$^-$] = 1.1819 x 10^{-6} M (unrounded)
[H$_3$O$^+$] = K_w / [OH$^-$] = (1.0 x 10^{-14}) / (1.1819 x 10^{-6}) = 8.4609527 x 10^{-9} M (unrounded)
pH = $-\log$ [H$_3$O$^+$] = $-\log$ (8.4609527 x 10^{-9} M) = 8.07258 = **8.07**

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

Volume of solution = (35.00 + 57.11488 + 0.50) (10^{-3} L / 1 mL) = 0.09261 L
[OH$^-$] = (7.66 x 10^{-5} mol F$^-$) / (0.09261 L) = 8.271 x 10^{-4} M OH$^-$ (unrounded)
The excess OH$^-$ will predominate and essentially control the pH.
[H$_3$O$^+$] = K_w / [OH$^-$] = (1.0 x 10^{-14}) / (8.271 x 10^{-4}) = 1.2090436 x 10^{-11} M (unrounded)
pH = $-\log$ [H$_3$O$^+$] = $-\log$ (1.2090436 x 10^{-11} M) = 10.917558 = **10.92**

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

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

= 8.9174129 x 10^{-18} = **8.9 x 10^{-18} M Hg$_2^{2+}$**
d) Use the value of S for a saturated solution (see part (b)).

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

= 1.6681707 x 10^{12} = **1.7 x 10^{12} g Hg$_2$Cl$_2$**
e) Use the value determined in part (c).

$$\text{Mass} = \left(\frac{8.9174129 \times 10^{-18} \text{ mol Hg}_2^{2+}}{\text{L}}\right)\left(\frac{1 \text{ mol Hg}_2\text{Cl}_2}{1 \text{ mol Hg}_2^{2+}}\right)\left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3}\right)\left(\frac{10^3 \text{ m}}{1 \text{ km}}\right)^3 (4900 \text{ km}^3)\left(\frac{472.1 \text{ g Hg}_2\text{Cl}_2}{1 \text{ mol Hg}_2\text{Cl}_2}\right)$$
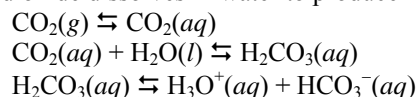
= 20.62856 = **21 g Hg$_2$Cl$_2$**

19.146   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.

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

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

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

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

= 1.23348 x 10^8 L (unrounded)

Total volume of lake after rain = 1.23348 x 10^8 L + 1.0279015 x 10^6 L = 1.243759 x 10^8 L (unrounded)

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

pH = –log(5.214531 x 10^{-7}) = 6.2827847 = **6.28**

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

$$\text{Mass} = (64.8562 \text{ mol } H_3O^+)\left(\frac{1 \text{ mol } HCO_3^-}{1 \text{ mol } H_3O^+}\right)\left(\frac{61.02 \text{ g } HCO_3^-}{1 \text{ mol } HCO_3^-}\right) = 3.97575 \times 10^3 = \textbf{4.0 x 10}^{\textbf{3}} \textbf{ g } \textbf{HCO}_3^-$$

19.147 a) **CaF_2** with K_{sp} = 3.2 x 10^{-11} will precipitate before BaF_2 with K_{sp} = 1.5 x 10^{-6}.

b) Add KF until $[F^-]$ is such that the CaF_2 precipitates but just lower than the concentration required to precipitate BaF_2.

c) Determine the barium concentration after mixing from $M_{con}V_{con} = M_{dil}V_{dil}$.

$[Ba^{2+}]$ = [(0.090 M) (25.0 mL)] / [(25.0 + 35.0) mL] = 0.0375 M (unrounded)

Use the barium ion concentration and the K_{sp} to find the fluoride ion concentration.

$[F^-]^2 = K_{sp}$ / $[Ba^{2+}]$ = (1.5 x 10^{-6}) / (0.0375) = 4.0 x 10^{-5}

$[F^-]$ = 6.324555 x 10^{-3} = **6.3 x 10^{-3}** M or less

19.148 Carbon dioxide dissolves in water to produce H_3O^+ ions:

$CO_2(g) \leftrightarrows CO_2(aq)$

$CO_2(aq) + H_2O(l) \leftrightarrows H_2CO_3(aq)$

$H_2CO_3(aq) \leftrightarrows H_3O^+(aq) + HCO_3^-(aq)$

The molar concentration of CO_2, $[CO_2]$, depends on how much $CO_2(g)$ from the atmosphere can dissolve in pure water. At 25°C and 1 atm CO_2, 88 mL of CO_2 can dissolve in 100 mL of H_2O. The number of moles of CO_2 in 88 mL of CO_2 is:

$$\text{Moles } CO_2 = PV / RT = \frac{(1 \text{ atm})(88 \text{ mL})}{\left(0.0821 \dfrac{L \cdot atm}{mol \cdot K}\right)((273 + 25)K)}\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)\left(\frac{0.033\%}{100\%}\right)$$

= 1.186963 x 10^{-6} mol CO_2 (unrounded)

Since air is not pure CO_2, account for the volume fraction of air (0.033 L / 100 L) when determining the moles.

$[CO_2]$ = (1.186963 x 10^{-6} mol CO_2) / [(100 mL) (10^{-3} L / 1 mL)] = 1.186963 x 10^{-5} M CO_2 (unrounded)

$$K_{a1} = \frac{\left[H_3O^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3\right]} = \frac{\left[H_3O^+\right]\left[HCO_3^-\right]}{\left[CO_2\right]} = 4.5 \times 10^{-7}$$

Let x = $[H_3O^+]$ = $[HCO_3^-]$

$$\frac{[x][x]}{\left[1.186963 \times 10^{-5} - x\right]} = 4.5 \times 10^{-7}$$

x^2 + 4.5 x 10^{-7} x – 5.341336 x 10^{-12} = 0

x = 2.0970596 x 10^{-6} M = $[H_3O^+]$ (unrounded)

pH = –log(2.0970596 x 10^{-6}) = 5.678389 = **5.68**

19.149 a) For H_2CO_3,

pK_a = –log K_a

pK_{a1} = –log 4.5 x 10^{-7} = 6.3468 (unrounded)

pK_{a2} = –log 4.7 x 10^{-11} = 10.3279 (unrounded)

pK_{a1} = 6.35 and pK_{a2} = 10.33. Since pK_{a1} > pH < pK_{a2}, the base in the first dissociation (HCO_3^-) and the acid in the second dissociation (also HCO_3^-) will predominate.

b) $pH = pK_a + \log [\text{base}] / [\text{acid}]$

$\quad\quad 8.5 = 6.35 + \log [HCO_3^-] / [H_2CO_3]$

$\quad\quad [HCO_3^-] / [H_2CO_3] = 1.4125 \times 10^2 = 1 \times 10^2\ M$ (unrounded) (8.5 limits the significant figures)

$\quad\quad pH = pK_a + \log [\text{base}] / [\text{acid}]$

$\quad\quad 8.5 = 10.33 + \log [CO_3^{2-}] / [HCO_3^-]$

$\quad\quad [CO_3^{2-}] / [HCO_3^-] = 1.4791 \times 10^- = 1 \times 10^{-2}\ M$ (unrounded)

c) In deep water, animals can exist but plants, which depend on light for photosynthesis, cannot. Photosynthesis converts carbon dioxide to oxygen; animals convert oxygen to carbon dioxide. Near the surface, plants remove carbon dioxide (which, in water, can be represented as the weak acid H_2CO_3) and thus the pH is higher than in deep water, where higher concentrations of carbon dioxide (H_2CO_3) accumulate. Also, at greater depths, the pressure is higher and so is the concentration of CO_2 (Henry's Law).

19.150 Initial concentrations of Pb^{2+} and $Ca(EDTA)^{2-}$ before reaction based on mixing 100. mL of 0.10 M $Na_2Ca(EDTA)$ with 1.5 L blood:

$$[Pb^{2+}] = \left(\frac{120\ \mu g\ Pb^{2+}}{100\ mL}\right)\left(\frac{1\ mL}{10^{-3}\ L}\right)\left(\frac{1.5\ L\ blood}{1.6\ L\ mixture}\right)\left(\frac{10^{-6}\ g}{1\ \mu g}\right)\left(\frac{1\ mol\ Pb^{2+}}{207.2\ g\ Pb^{2+}}\right) = 5.4295366 \times 10^{-6}\ M\ Pb^{2+}\ \text{(unrounded)}$$

$M_{con}V_{con} = M_{dil}V_{dil}$

$\quad\quad [Ca(EDTA)^{2-}] = M_{con}V_{con} / V_{dil} = [(0.10\ M)\ (100\ mL)\ (10^{-3}\ L\ /\ 1\ mL)] / (1.6\ L)$

$\quad\quad\quad\quad = 6.25 \times 10^{-3}\ M$ (unrounded)

Set up a reaction table assuming the reaction goes to completion:

Concentration (M)	$[Ca(EDTA)]^{2-}(aq) +$	$Pb^{2+}(aq)$	$\rightleftarrows$	$[Pb(EDTA)]^{2-}(aq) +$	$Ca^{2+}(aq)$
Initial	6.25×10^{-3}	5.4295366×10^{-6}		0	0
React	$-5.4295366 \times 10^{-6}$	$-5.4295366 \times 10^{-6}$		$+5.4295366 \times 10^{-6}$	$+5.4295366 \times 10^{-6}$
	6.24457×10^{-3}	0		5.4295366×10^{-6}	5.4295366×10^{-6}

Now set up a reaction table for the equilibrium process:

Concentration (M)	$[Ca(EDTA)]^{2-}(aq) +$	$Pb^{2+}(aq)$	$\rightleftarrows$	$[Pb(EDTA)]^{2-}(aq) +$	$Ca^{2+}(aq)$
Initial	6.24457×10^{-3}	0		5.4295366×10^{-6}	5.4295366×10^{-6}
Change	$+x$	$+x$		$-x$	$-x$
Equilibrium	$6.24457 \times 10^{-3} + x$	x		$5.4295366 \times 10^{-6} - x$	$5.4295366 \times 10^{-6} - x$

$$K_c = 2.5 \times 10^7 = \frac{\left[Pb(EDTA)^{2-}\right]\left[Ca^{2+}\right]}{\left[Ca(EDTA)^{2-}\right]\left[Pb^{2+}\right]} = \frac{\left[5.4295366 \times 10^{-6}\right]\left[5.4295366 \times 10^{-6}\right]}{\left[6.24457 \times 10^{-3}\right][x]}$$

$x = [Pb^{2+}] = 1.8883521 \times 10^{-16}\ M$ (unrounded)

Convert concentration from M to μg in 100 mL:

$$\left(\frac{1.8883521 \times 10^{-16}\ mol\ Pb^{2+}}{L}\right)\left(\frac{10^{-3}\ L}{1\ mL}\right)(100\ mL)\left(\frac{207.2\ g\ Pb^{2+}}{1\ mol\ Pb^{2+}}\right)\left(\frac{1\ \mu g}{10^{-6}\ g}\right) = 3.9126655 \times 10^{-9}\ \mu g\ Pb^{2+}\ \text{(unrounded)}$$

The final concentration is **$3.9 \times 10^{-9}\ \mu g / 100\ mL$**.

19.151 Assume that pK_a is in the center of the range, and calculate the K_a from the average pK_a.

$\quad\quad$ Average pK_a (center of range) $= (7.9 + 6.5) / 2 = 7.2$

$\quad\quad K_a\ 10^{-7.2} = 6.3095734 \times 10^{-8} = \mathbf{6 \times 10^{-8}}$

There is only one digit after the decimal point in the pK_a values; thus, there is only one significant figure.

19.152 The molarity of a saturated NaCl solution must be found.

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

Determine the K_{sp} from the molarity just calculated.

$NaCl(s) \rightleftarrows Na^+(aq) + Cl^-(aq)$.
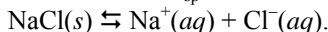
$K_{sp} = [Na^+][Cl^-] = S^2 = (5.42436687)^2 = 29.42375594 = 29.4$

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

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

Moles of Cl⁻ added = $\left(\dfrac{8.65 \text{ mol HCl}}{\text{L}}\right)\left(\dfrac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(28.5 \text{ mL})\left(\dfrac{1 \text{ mol Cl}^-}{1 \text{ mol HCl}}\right)$ = 0.246525 mol Cl⁻ (unrounded)

0.100 L of saturated solution contains 0.542 mol each Na⁺ and Cl⁻, to which you are adding 0.246525 mol of additional Cl⁻ from HCl.
Volume of mixed solutions = 0.100 L + (28.5 mL) (10⁻³ L / 1 mL) = 0.1285 L (unrounded)
Molarity of Cl⁻ in mixture = [(0.54236687 + 0.246525) mol Cl⁻] / (0.1285 L) = 6.13924 *M* Cl⁻ (unrounded)
Molarity of Na⁺ in mixture = (0.54236687 mol Na⁺) / (0.1285 L) = 4.220754 *M* Na⁺ (unrounded)
Determine a *Q* value and compare this value to the K_{sp} to determine if precipitation will occur.
$\qquad Q_{sp}$ = [Na⁺][Cl⁻] = (4.220754) (6.13924) = 25.91222 = 25.9
Since $Q_{sp} < K_{sp}$, no NaCl will precipitate.

19.153   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.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \qquad\qquad \left(\frac{[A^-]}{[HA]}\right) = 1 \text{ when the amounts of HA and A}^- \text{ are equal}$$
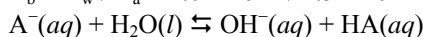
$pH = pK_a + \log 1$
$pH = pK_a = -\log (4.5 \times 10^{-5}) = 4.346787 = \mathbf{4.35}$
           Box B:
           Only A⁻ is present at a concentration of 0.10 *M*.
           The K_b for A⁻ is needed.
$\qquad\qquad K_b = K_w / K_a = 1.0 \times 10^{-14} / 4.5 \times 10^{-5} = 2.222 \times 10^{-10}$ (unrounded)
$\qquad\qquad$ A⁻(*aq*) + H₂O(*l*) ⇆ OH⁻(*aq*) + HA(*aq*)

Initial:	0.10 M	0	0
Change:	−x	−x	−x
Equilibrium:	0.10 − x	x	x

$$K_b = \frac{[HA]\left[OH^-\right]}{\left[A^-\right]} = 2.222 \times 10^{-10}$$

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

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

x = 4.7138095 × 10⁻⁶ *M* OH⁻ (unrounded)
Check assumption: (4.7138095 × 10⁻⁶ / 0.10) × 100% = 0.005% error, so the assumption is valid.
[H₃O]⁺ = K_w / [OH⁻] = (1.0 × 10⁻¹⁴) / (4.7138095 × 10⁻⁶)
$\qquad$ = 2.1214264 × 10⁻⁹ *M* H₃O⁺ (unrounded)
pH = −log [H₃O⁺] = −log (2.1214264 × 10⁻⁹) = 8.67337 = **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*)	+	H₂O(*l*) ⇆	H₃O⁺(*aq*) + A⁻(*aq*)	
Initial	0.10		—	0	0
Change	− x			+ x	+ x
Equilibrium	0.10 − x			x	x

$\qquad\qquad$ (The H₃O⁺ contribution from water has been neglected.)

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

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

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

$[H_3O^+] = x = 2.12132 \times 10^{-3}$ (unrounded)
Check assumption: $(2.12132 \times 10^{-3} / 0.10) \times 100\% = 2\%$ error, so the assumption is valid.
$pH = -\log [H_3O^+] = -\log (2.12132 \times 10^{-3}) = 2.67339 = \textbf{2.67}$

Box D:

This is a buffer with a ratio of $[A^-] / [HA] = 5 / 3$.
Use the Henderson-Hasselbalch equation for this buffer.

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

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

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**.

19.154 a) The dissolution of MX will produce equal amounts of M^{2+} and X^{2-}. The only way unequal amounts of these ions could be present would be either if one of the ions were already present or if one of the ions were removed from the solution. Distilled water will neither add nor remove ions, thus the M^{2+} and X^{2-} must be equal; this is in box **B**.
b) Using box B; there are $4(2.5 \times 10^{-6}M) = 1.0 \times 10^{-5}$ M for each ion.
$\qquad K_{sp} = [M^{2+}][X^{2-}] = (1.0 \times 10^{-5})(1.0 \times 10^{-5}) = \textbf{1.0 x 10}^{\textbf{-10}}$
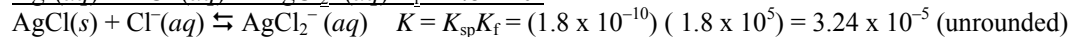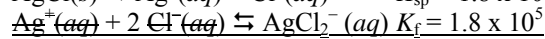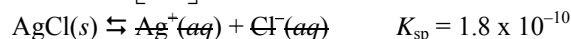c) The addition of Na_aX would increase the X^{2-}. There will be more X^{2-} than M^{2+}. This occurs in box **C**.
d) Lowering the pH will protonate some X^{2-}. This will decrease the X^{2-} concentration, thus, $X^{2-} < M^{2+}$. This occurs in box **A**.

19.155 a) Ag^+ ions come from the dissolution of AgCl(s).
$\qquad K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{\left[Cl^-\right]}$$

$AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.8 \times 10^{-10}$
$Ag^+(aq) + 2\,Cl^-(aq) \leftrightarrows AgCl_2^-(aq)\ K_f = 1.8 \times 10^5$
$AgCl(s) + Cl^-(aq) \leftrightarrows AgCl_2^-(aq) \qquad K = K_{sp}K_f = (1.8 \times 10^{-10})(1.8 \times 10^5) = 3.24 \times 10^{-5}$ (unrounded)

$$K = 3.24 \times 10^{-5} = \frac{\left[AgCl_2^-\right]}{\left[Cl^-\right]}$$

$[AgCl_2^-] = (3.24 \times 10^{-5})[Cl^-] = (3.2 \times 10^{-5})[Cl^-]$
b) $[Ag^+] = [AgCl_2^-]$

$$\frac{1.8 \times 10^{-10}}{\left[Cl^-\right]} = (3.24 \times 10^{-5})[Cl^-]$$

$$[Cl^-]^2 = \frac{1.8 \times 10^{-10}}{3.24 \times 10^{-5}}$$

$[Cl^-] = 2.3570226 \times 10^{-3} = \textbf{2.4} \times \textbf{10}^{-3} \textbf{ \textit{M} Cl}^-$

c) Both equilibria shift to the right as Cl^- ion concentration increases. At low Cl^- ion concentration, Ag^+ ions are present in solution. As Cl^- ion concentration increases, more $AgCl(s)$ is formed. At even higher Cl^- ion concentrations, $AgCl_2^-$ ions are present in solution.
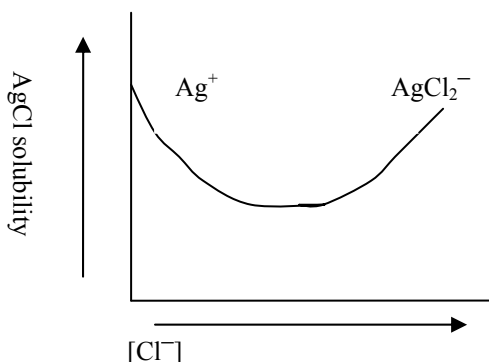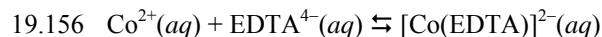

d) The solubility of $AgCl(s) = [Ag^+] + [AgCl_2^-]$

You can use either equation from part a) to calculate $[Ag^+]$ and $[AgCl_2^-]$.

$[Ag^+] = [AgCl_2^-] = (3.24 \times 10^{-5})(2.3570226 \times 10^{-3}) = 7.6367532 \times 10^{-8} = 7.6 \times 10^{-8} M$

The solubility of $AgCl(s) = (7.6367532 \times 10^{-8} + 7.6367532 \times 10^{-8}) M = 1.52735 \times 10^{-7} = \textbf{1.5} \times \textbf{10}^{-7} \textbf{\textit{M}}$

19.156 $Co^{2+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Co(EDTA)]^{2-}(aq)$
$K_f = 10^{16.31} = 2.0417379 \times 10^{16}$ (unrounded)

$$K_f = \frac{\left[Co(EDTA)^{2-}\right]}{\left[Co^{2+}\right]\left[EDTA^{4-}\right]}$$

Moles Co^{2+} (original) $= \left(\dfrac{0.048 \text{ mol } Co^{2+}}{L}\right)\left(\dfrac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(50.0 \text{ mL}) = 0.0024 \text{ mol } Co^{2+}$

a) Moles EDTA added $= \left(\dfrac{0.050 \text{ mol } EDTA^{4-}}{L}\right)\left(\dfrac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(25.0 \text{ mL}) = 0.00125 \text{ mol EDTA (unrounded)}$

The moles of EDTA added equals the moles of $[Co(EDTA)]^{2-}$ formed.
The EDTA is limiting so no EDTA is left after the reaction and the remaining Co^{2+}:

$Co^{2+} = (0.0024 - 0.00125) = 0.00115 \text{ mol } Co^{2+}$

Total volume $= (50.0 + 25.0)$ mL $(10^{-3} \text{ L} / 1 \text{ mL}) = 0.0750$ L

$[Co^{2+}] = (0.00115 \text{ mol } Co^{2+}) / (0.0750 \text{ L}) = 0.015333 M Co^{2+}$ (unrounded)

$[Co(EDTA)^{2-}] = (0.00125 \text{ mol } [Co(EDTA)]^{2-}) / (0.0750 \text{ L}) = 0.016667 M$ (unrounded)

To reach equilibrium the concentrations of the species involved are:

$[EDTA^{4-}] = x$
$[Co^{2+}] = 0.015333 + x$
$[Co(EDTA)^{2-}] = 0.016667 - x$

$$K_f = \frac{\left[Co(EDTA)^{2-}\right]}{\left[Co^{2+}\right]\left[EDTA^{4-}\right]} = \frac{[0.016667 - x]}{[0.01533 + x][x]} = \frac{[0.016667]}{[0.01533][x]} = 2.0417379 \times 10^{16}$$

$x = 5.3249468 \times 10^{-17}$ (unrounded)
$[EDTA] = \textbf{5.3} \times \textbf{10}^{-17} \textbf{\textit{M}}$
$[Co^{2+}] = \textbf{0.015 \textit{M}}$

b) Moles EDTA added $= \left(\dfrac{0.050 \text{ mol EDTA}^{4-}}{L} \right) \left(\dfrac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (75.0 \text{ mL}) = 0.00375 \text{ mol EDTA (unrounded)}$

The Co^{2+} is limiting so no Co^{2+} is left. The original moles Co^{2+} equals the moles of complex formed.
Moles EDTA remaining = (0.00375 – 0.0024) mol = 0.00135 mol EDTA (unrounded)
Total volume = (50.0 + 75.0) mL $(10^{-3}$ L / 1 mL) = 0.1250 L
[EDTA] = (0.00135 mol EDTA) / (0.1250 L) = 0.0108 M EDTA (unrounded)
$[Co(EDTA)^{2-}]$ = (0.0024 mol $[Co(EDTA)]^{2-}$) / (0.1250 L) = 0.0192 M (unrounded)
To reach equilibrium the concentrations of the species involved are:

$[EDTA^{4-}] = 0.0108 + x$
$[Co^{2+}] = x$
$[Co(EDTA)^{2-}] = 0.0192 – x$

$$K_f = \dfrac{\left[Co(EDTA)^{2-} \right]}{\left[Co^{2+} \right]\left[EDTA^{4-} \right]} = \dfrac{[0.0192 - x]}{[\, x\,][0.0108 + x]} = \dfrac{[0.0192]}{[\, x\,][0.0108]} = 2.0417379 \times 10^{16}$$

$x = 8.7071792 \times 10^{-17}$ (unrounded)
$[EDTA^{4-}] = 00108 + x = \mathbf{0.0108 \ M}$
$[Co^{2+}] = \mathbf{8.7 \times 10^{-17} \ M}$