CHAPTER 19 IONIC EQUILIBRIA IN AQUEOUS SYSTEMS

- 19.1 The purpose of an acid-base buffer is to maintain a relatively constant pH in a solution.
- 19.2 The weak acid component neutralizes added base and the weak base component neutralizes added acid so that the pH of the buffer solution remains relatively constant. The components of a buffer do not neutralize one another when they are a conjugate acid/base pair.
- 19.3 The presence of an ion in common between two solutes will cause any equilibrium involving either of them to shift in accordance with Le Châtelier's principle. For example, addition of NaF to a solution of HF will cause the equilibrium

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

- 19.4 A buffer is a mixture of a weak acid and its conjugate base (or weak base and its conjugate acid). The pH of a buffer changes only slightly with added H_3O^+ because the added H_3O^+ reacts with the base of the buffer. The net result is that the concentration of H_3O^+ does not change much from the original concentration, keeping the pH nearly constant.
- 19.5 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. If acetic acid were used, the buffer component ratio would be far from 1:1 and the buffer's effectiveness would be lower (see 18.7). The NaOH serves to partially neutralize the acid and produce its conjugate base.
- 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 H₃O⁺ 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 ignored because they are not involved in the buffer. The reaction table that describes this buffer is:

Concentration (M)	$HC_3H_6O_2(a)$	$(q) + H_2O(l) \leftrightarrows O(l)$	$C_{3}H_{5}O_{2}(aq) + 1$	$H_3O^+(aq)$
Initial	0.15		0.25	0
Change	- X	_	+ x	+ x
Equilibrium	0.15 - x		0.25 + x	х
		1 .1 0 1 5	1005 1 1	

Assume that x is negligible with respect to both 0.15 and 0.25 since both concentrations are much larger than K_a .

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[C_{3}H_{5}O_{2}^{-}\right]}{\left[HC_{3}H_{5}O_{2}\right]} = \frac{\left[x\right]\left[0.25 + x\right]}{\left[0.15 - x\right]} = \frac{\left[x\right]\left[0.25\right]}{\left[0.15\right]} = 1.3 \times 10^{-5}$$
$$\left[H_{3}O^{+}\right] = K_{a} \frac{\left[HC_{2}H_{5}O_{2}^{-}\right]}{\left[C_{2}H_{5}O_{2}^{-}\right]} = (1.3 \times 10^{-5}) (0.15 / 0.25) = 7.8 \times 10^{-6} M$$

Check assumption: percent error = $(7.8 \times 10^{-6} / 0.15)100\% = 0.0052\%$. The assumption is valid. pH = $-\log [H_3O^+] = -\log (7.8 \times 10^{-6}) = 5.107905 = 5.11$.

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

19.12
$$CA = C_6H_5COOH$$
 $CB = C_6H_5COO^-$ Neglect Na⁺. Assume + x and - x are negligible.
 $K_a = \frac{[H_3O^+][CB]}{[CA]} = \frac{[x][0.28 + x]}{[0.33 - x]} = \frac{[x][0.28]}{[0.33]} = 6.3 \times 10^{-5}$
 $[H_3O^+] = K_a \frac{[CA]}{[CA]} = (6.3 \times 10^{-5}) (0.33 / 0.28) = 7.425 \times 10^{-5} = 7.4 \times 10^{-5} M$

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

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)	$HNO_2(aq) +$	$H_2O(l)$	$NO_2^{-}(aq) +$	$H_3O^+(aq)$
Initial	0.50		0.65	0
Change	- X		+ x	+ x
Equilibrium	0.50 - x		0.65 + x	х
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Assume that x is negligible with respect to both 0.50 and 0.65 because both concentrations are much larger than K_{a} .

$$K_{a} = \frac{\left[H_{3}O^{+} \right] \left[NO_{2}^{-} \right]}{\left[HNO_{2} \right]} = \frac{\left[x \right] \left[0.65 + x \right]}{\left[0.50 - x \right]} = \frac{\left[x \right] \left[0.65 \right]}{\left[0.50 \right]} = 7.1 \text{ x } 10^{-4}$$
$$[H_{3}O^{+}] = K_{a} \frac{\left[HNO_{2} \right]}{\left[NO_{2}^{-} \right]} = (7.1 \text{ x } 10^{-4}) (0.50 / 0.65) = 5.4615384 \text{ x } 10^{-4} = 5.5 \text{ x } 10^{-4} M$$

Check assumption: percent error = $(5.4615384 \times 10^{-4} / 0.50)100\% = 0.11\%$. The assumption is valid. pH = $-\log (5.4615384 \times 10^{-4}) = 3.262685 = 3.26$

Verify the pH using the Henderson-Hasselbalch equation.

19.14 CA = HF CB = F⁻ Neglect K^+ . Assume + x and - x are negligible.

$$K_{a} = \frac{\left[H_{3}O^{+} \right] \left[CB \right]}{\left[CA \right]} = \frac{\left[x \right] \left[0.25 + x \right]}{\left[0.20 - x \right]} = \frac{\left[x \right] \left[0.25 \right]}{\left[0.20 \right]} = 6.8 \text{ x } 10^{-4}$$
$$\left[H_{3}O^{+} \right] = K_{a} \frac{\left[CA \right]}{\left[CA \right]} = (6.8 \text{ x } 10^{-4}) (0.20 / 0.25) = 5.44 \text{ x } 10^{-4} = 5.4 \text{ x } 10^{-4} M$$

Check assumption: percent error = $(5.44 \times 10^{-4} / 0.20)100\% = 0.27\%$. The assumption is valid. pH = -log [H₃O⁺] = -log (5.44 x 10⁻⁴) = 3.2644 = **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.

 $K_{\rm a} = 10^{-\rm pK_{\rm a}} = 10^{-3.74} = 1.8197 \text{ x } 10^{-4} \text{ (unrounded)}$ $HCOOH(aq) + H_2O(l)$ Concentration (*M*) ⇆ $HCOO^{-}(aq) + H_{3}O^{+}(aq)$ Initial 0.55 0.63 0 Change - X + x +xEquilibrium 0.55 - x ____ 0.63 + xх Assume that x is negligible because both concentrations are much larger than K_{a} . $\begin{bmatrix} H & O^+ \end{bmatrix} \begin{bmatrix} H & O & - \end{bmatrix} = \begin{bmatrix} -1 & (-1) & (-1) & (-1) \end{bmatrix} = \begin{bmatrix} -1 & (-1) & (-1) & (-1) \end{bmatrix}$

$$K_{a} = \frac{[11_{3}O^{+}][11CO_{2}]}{[11CO_{2}]} = \frac{[x][0.63 + x]}{[0.55 - x]} = \frac{[x][0.63]}{[0.55]} = 1.8197 \times 10^{-4} \text{ (unrounded)}$$
$$[H_{3}O^{+}] = K_{a} \frac{[HNO_{2}]}{[NO_{2}^{-}]} = (1.8197 \times 10^{-4}) (0.55 / 0.63) = 1.5886269 \times 10^{-4} = 1.6 \times 10^{-4} M$$

Check assumption: percent error = $(1.5886269 \times 10^{-4} / 0.55)100\% = 0.029\%$. The assumption is valid. pH = -log $(1.5886269 \times 10^{-4}) = 3.798978 = 3.80$ Verify the pH using the Henderson-Hasselbalch equation.

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

 $CA = HBrO \qquad CB = BrO \qquad \text{Neglect } K^+. \text{ Assume } + \text{ x and } - \text{ x are negligible.}$
 $K_a = \frac{[H_3O^+][CB]}{[CA]} = \frac{[x][0.68 + x]}{[0.95 - x]} = \frac{[x][0.68]}{[0.95]} = 2.2908676 \text{ x } 10^{-9} \text{ (unrounded)}$
 $[H_3O^+] = K_a \frac{[CA]}{[CA]} = (2.2908676 \text{ x } 10^{-9}) (0.95 / 0.68) = 3.2004768 \text{ x } 10^{-9} = 3.2 \text{ x } 10^{-9} M$
Check assumption: percent error = $(3.2004768 \text{ x } 10^{-9} / 0.68)100\% = 0.0000047\%$. The assumption is valid.
 $pH = -\log [H_3O^+] = -\log (3.2004768 \text{ x } 10^{-9}) = 8.4947853 = 8.49$

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

Concentration (M)	$C_6H_5OH(aq) +$	$H_2O(l)$	$C_6H_5O^-(aq) +$	$H_3O^+(aq)$
Initial	1.2	_	1.0	0
Change	- X	_	+ x	+x
Equilibrium	1.2 - x	—	1.0 + x	х

Assume that x is negligible with respect to both 1.0 and 1.2 because both concentrations are much larger than K_{a} .

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[C_{6}H_{5}O^{-}\right]}{\left[C_{6}H_{5}OH\right]} = \frac{\left[x\right]\left[1.0 + x\right]}{\left[1.2 - x\right]} = \frac{\left[x\right]\left[1.0\right]}{\left[1.2\right]} = 1.0 \times 10^{-10}$$
$$[H_{3}O^{+}] = K_{a} \frac{\left[C_{6}H_{5}OH\right]}{\left[C_{6}H_{5}O^{-}\right]} = (1.0 \times 10^{-10}) (1.2 / 1.0) = 1.2 \times 10^{-10} M$$

Check assumption: percent error = $(1.2 \times 10^{-10} / 1.0)100\% = 1.2 \times 10^{-8}\%$. The assumption is valid. $pH = -log (1.2 \times 10^{-10}) = 9.9208 = 9.92.$

Verify the pH using the Henderson-Hasselbalch equation.

19.18
$$K_{a} = 10^{-pK} = 10^{-9.24} = 5.7543993 \text{ x } 10^{-10} \text{ (unrounded)}$$

 $CA = H_{3}BO_{3}$ $CB = H_{2}BO_{3}^{-}$ Neglect Na⁺. Assume + x and - x are negligible.
 $K_{a} = \frac{\left[H_{3}O^{+}\right]\left[CB\right]}{\left[CA\right]} = \frac{\left[x\right]\left[0.82 + x\right]}{\left[0.12 - x\right]} = \frac{\left[x\right]\left[0.82\right]}{\left[0.12\right]} = 5.7543993 \text{ x } 10^{-10} \text{ (unrounded)}$
 $\left[H_{3}O^{+}\right] = K_{a} \frac{\left[CA\right]}{\left[CA\right]} = (5.7543993 \text{ x } 10^{-10}) (0.12 / 0.82) = 8.4210722 \text{ x } 10^{-11} M \text{ (unrounded)}$
Check assumption: percent error = $(8.4210722 \text{ x } 10^{-11} / 0.12)100\% = 7.0 \text{ x } 10^{-8}\%$. The assumption

eck assumption: percent error = $(8.4210722 \times 10^{-11} / 0.12)100\% = 7.0 \times 10^{-8}\%$. The assumption is valid. $pH = -log [H_3O^+] = -log (8.4210722 \times 10^{-11}) = 10.07463261 = 10.07$

Verify the pH using the Henderson-Hasselbalch equation.

19.19 Determine the K_b from the p K_b using the relationship $K_b = 10^{-pK_b}$. Use the K_b of ammonia to determine the hydroxide ion concentration of the solution. The pOH may be calculated from the hydroxide ion concentration. The pH comes from the relationship pH + pOH = 14.00 $K_b = 10^{-pK} = 10^{-4.75} = 1.7782794 \times 10^{-5}$ (unrounded)

$$K_{b} = \frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]} = \frac{\left[0.10 + \mathrm{x}\right]\left[\mathrm{OH}^{-}\right]}{\left[0.20 - \mathrm{x}\right]} = \frac{\left[0.10\right]\left[\mathrm{OH}^{-}\right]}{\left[0.20\right]} = 1.7782794 \text{ x } 10^{-5} \text{ (unrounded)}$$

$$\left[\mathrm{OH}^{-}\right] = K_{b} \frac{\left[\mathrm{NH}_{3}\right]}{\left[\mathrm{NH}_{4}^{+}\right]} = (1.7782794 \text{ x } 10^{-5}) (0.20 / 0.10) = 3.5565588 \text{ x } 10^{-5} M \text{ (unrounded)}$$

Check assumption: percent error = $(3.5565588 \times 10^{-5} / 0.10)100\% = 0.036\%$. The assumption is valid. $pOH = -log [OH^{-}] = -log (3.5565588 \times 10^{-5}) = 4.448970$ (unrounded)

pH = 14.00 - pOH = 14.00 - 4.448970 = 9.551030 = 9.55 Verify the pH using the Henderson-Hasselbalch equation.

19.20

 $K_{\rm b} = 10^{-{\rm p}K} = 10^{-3.35} = 4.4668359 \text{ x } 10^{-4} \text{ (unrounded)}$ CB = CH₃NH₂ CA = CH₃NH₃⁺ Neglect Cl⁻. Assume + x and - x are negligible.

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

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

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

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

pH = 14.00 - pOH = 14.00 - 3.429181246 = 10.57081875 = 10.57 Verify the pH using the Henderson-Hasselbalch equation.

19.21 a) The buffer components are HCO₃⁻ from the salt KHCO₃ and CO₃²⁻ from the salt K₂CO₃. Choose the K_a value that corresponds to the equilibrium with these two components. K_{a1} refers to carbonic acid, H₂CO₃ losing one proton to produce HCO₃⁻. This is not the correct K_a because H₂CO₃ is not involved in the buffer. K_{a2} is the correct K_a to choose because it is the equilibrium constant for the loss of the second proton to produce CO₃²⁻ from HCO₃⁻. b) Set up the reaction table and use K_{a2} to calculate pH.

Concentration (<i>M</i>)	$HCO_{3}(aq) + 0.25$	$H_2O(l) \leftrightarrows$	$CO_3^{2-}(aq) + 0.32$	$H_3O^+(aq)$
Change	- X		+ x	0 + x
Equilibrium	0.25 - x	—	0.32 + x	Х

Assume that x is negligible with respect to both 0.25 and 0.32 because both concentrations are much larger than K_{a} .

$$K_{a} = \frac{\left[H_{3}O^{+} \right] \left[CO_{3}^{2^{-}} \right]}{\left[HCO_{3}^{-} \right]} = \frac{\left[x \right] \left[0.32 + x \right]}{\left[0.25 - x \right]} = \frac{\left[x \right] \left[0.35 \right]}{\left[0.25 \right]} = 4.7 \text{ x } 10^{-11}$$
$$[H_{3}O^{+}] = K_{a} \frac{\left[CO_{3}^{2^{-}} \right]}{\left[HCO_{3}^{-} \right]} = (4.7 \text{ x } 10^{-11}) (0.25 / 0.35) = 3.3571428 \text{ x } 10^{-11} M \text{ (unrounded)}$$

Check assumption: percent error = $(3.3571428 \times 10^{-11} / 0.25)100\% = 1.3 \times 10^{-8}\%$. The assumption is valid. pH = -log $(3.3571428 \times 10^{-11}) = 10.47103 = 10.47$.

Verify the pH using the Henderson-Hasselbalch equation.

19.22 a) The conjugate acid-base pair are related by K_{a2} (6.3 x 10⁻⁸). Assume that x is negligible with respect to both 0.50 and 0.40 because both concentrations are much larger than K_{a} . $CA = H_2PO_4^{-1}$ $CB = HPO_4^{-2}$ Neglect Na⁺. Assume + x and - x are negligible. $\begin{bmatrix} H_2O^+ \end{bmatrix} \begin{bmatrix} CB \end{bmatrix} = \begin{bmatrix} x \end{bmatrix} \begin{bmatrix} 0.40 + x \end{bmatrix} = \begin{bmatrix} x \end{bmatrix} \begin{bmatrix} x \end{bmatrix} \begin{bmatrix} 0.40 \end{bmatrix}$

$$K_{a} = \frac{\left[\frac{H_{3}O}{[CA]}\right]\left[CB\right]}{[CA]} = \frac{\left[x\right]\left[0.40 + x\right]}{[0.50 - x]} = \frac{\left[x\right]\left[0.40\right]}{[0.50]} = 6.3 \times 10^{-8}$$
$$[H_{3}O^{+}] = K_{a} \frac{[CA]}{[CA]} = (6.3 \times 10^{-8}) (0.50 / 0.40) = 7.875 \times 10^{-8} M \text{ (unrounded)}$$

Check assumption: percent error = $(7.875 \times 10^{-8} / 0.40)100\% = 2.0 \times 10^{-5}\%$. The assumption is valid. pH = $-\log [H_3O^+] = -\log (7.875 \times 10^{-8}) = 7.103749438 = 7.10$

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) $pH = pK_a + \log([base] / [acid])$ $5.11 = 4.8860566 + \log ([Pr^-] / [HPr])$ $\log ([Pr^-] / [HPr]) = 0.2239434$ (unrounded) $[Pr^-] / [HPr] = 1.6747246 = 1.7$
- 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) $pH = pK_a + \log([base] / [acid])$ $2.95 = 3.148741651 + \log ([NO_2^-] / [HNO_2])$ $\log ([NO_2^-] / [HNO_2]) = -0.198741651$ (unrounded) $[NO_2^-] / [HNO_2] = 0.632788 = 0.63$

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

 $pK_a = -\log K_a = -\log (2.3 \times 10^{-9}) = 8.638272164$ (unrounded) $pH = pK_a + \log ([base] / [acid])$ $7.88 = 8.638272164 + \log ([BrO^-] / [HBrO])$ $\log ([BrO^-] / [HBrO]) = -0.758272164$ (unrounded) $[BrO^-] / [HBrO] = 0.174472842 = 0.17$

- 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) $pH = pK_a + \log ([base] / [acid])$ $4.39 = 4.744727495 + \log ([CH_3COO^-] / [CH_3COOH])$ $\log ([CH_3COO^-] / [CH_3COOH]) = -0.354727494$ (unrounded)
 - $[CH_3COO^-] / [CH_3COOH] = 0.441847604 = 0.44$
- 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.

 $pH = pK_a + \log [A^-] / [HA]$ 3.35 = pK_a + log (0.1500) / (0.2000) pK_a = 3.474938737 = 3.47

Determine the moles of conjugate acid (HA) and conjugate base (A⁻).

- Moles HA = (0.5000 L) (0.2000 mol HA / L) = 0.1000 mol HA
- Moles $A^{-} = (0.5000 \text{ L}) (0.1500 \text{ mol } A^{-} / \text{ L}) = 0.07500 \text{ mol } A^{-}$

The reaction is:

 $HA(aq) + NaOH(aq) \rightarrow Na^{+}(aq) + A^{-}(aq) + H_2O(l)$

The addition of 0.0015 mol NaOH will produce 0.0015 mol A⁻ and consume 0.0015 mol of HA.

This results in

(0.1000 mol HA) - (0.0015 mol HA) = 0.0985 mol HA $(0.07500 \text{ mol A}^{-}) + (0.0015 \text{ mol A}^{-}) = 0.0765 \text{ mol A}^{-}$

Then

 $[A^{-}] = (0.0765 \text{ mol } A^{-}) / (0.5000 \text{ L}) = 0.153 M \text{ A}^{-}$ [HA] = (0.0985 mol HA) / (0.5000 L) = 0.197 M HA $pH = pK_{a} + \log [A^{-}] / [HA]$ $= 3.474938737 + \log (0.153) / (0.197)$ = 3.365163942 = 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.

 $pH = pK_a + \log [B] / [BH^+]$ 8.88 = pK_a + log (0.40) / (0.25) pK_a = 8.67588 = 8.68

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

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

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

The reaction is:

 $B(aq) + HCl(aq) → BH^{+}(aq) + Cl^{-}(aq) + H_2O(l)$ The addition of 0.0020 mol HCl will produce 0.0020 mol BH⁺ and consume 0.0020 mol of B. This results in (0.10 mol B) - (0.0020 mol B) = 0.098 mol B (unrounded) (If the significant figures rules are followed, the moles of B do not change.) (0.0625 mol BH⁺) + (0.0020 mol BH⁺) = 0.0645 mol BH⁺ (unrounded) Then

$$\begin{split} & [B] = (0.098 \text{ mol } B) / (0.25 \text{ L}) = 0.392 \text{ M B (unrounded)} \\ & [BH^+] = (0.0645 \text{ mol } BH^+) / (0.25 \text{ L}) = 0.258 \text{ M } BH^+ \text{ (unrounded)} \\ & pH = pK_a + \log [B] / [BH^+] \\ & = 8.67588 + \log (0.392) / (0.258) \\ & = 8.857546361 = \textbf{8.86} \end{split}$$

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.

 $pH = pK_a + \log [Y] / [HY]$ $8.77 = pK_a + \log(0.220) / (0.110)$ $pK_a = 8.468970 = 8.47$ Determine the moles of conjugate acid (HY) and conjugate base (Y). Moles HY = (0.750 L) (0.110 mol HY / L) = 0.0825 mol HYMoles $Y^{-} = (0.750 \text{ L}) (0.220 \text{ mol } Y^{-} / \text{ L}) = 0.165 \text{ mol } Y^{-}$ The reaction is: $2 \operatorname{HY}(aq) + \operatorname{Ba}(OH)_2(aq) \rightarrow \operatorname{Ba}^{2+}(aq) + 2 \operatorname{Y}^{-}(aq) + 2 \operatorname{H}_2O(l)$ The addition of 0.0010 mol Ba(OH)₂ will produce 2 x 0.0010 mol Y⁻ and consume 2 x 0.0010 mol of HY. This results in (0.0825 mol HY) - (0.0020 mol HY) = 0.0805 mol HY $(0.165 \text{ mol } Y^{-}) + (0.0020 \text{ mol } Y^{-}) = 0.167 \text{ mol } Y^{-} \text{ (unrounded)}$ Then $[HY] = (0.0805 \text{ mol } \text{A}^{-}) / (0.750 \text{ L}) = 0.107333 M HY (unrounded)$ $[Y^{-}] = (0.167 \text{ mol } Y^{-}) / (0.750 \text{ L}) = 0.222667 M Y^{-}$ (unrounded) $pH = pK_a + \log [Y] / [HY]$ $= 8.468970 + \log(0.222667) / (0.107333)$ = 8.78589259 = **8.79**

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.

 $pH = pK_a + \log [B] / [BH^+]$ $9.50 = pK_a + \log(1.05) / (0.750)$ $pK_a = 9.353871964 = 9.35$ Determine the moles of conjugate acid (BH⁺) and conjugate base (B). Moles $BH^+ = (0.500 \text{ L}) (0.750 \text{ mol } BH^+ / \text{ L}) = 0.375 \text{ mol } BH^+ (unrounded)$ Moles B = (0.500 L) (1.05 mol B / L) = 0.525 mol BThe reaction is: $B(aq) + HCl(aq) \rightarrow BH^{+}(aq) + Cl^{-}(aq) + H_2O(l)$ The addition of 0.0050 mol HCl will produce 0.0050 mol BH⁺ and consume 0.0050 mol of B. This results in (0.525 mol B) - (0.0050 mol B) = 0.520 mol B $(0.375 \text{ mol BH}^+) + (0.0050 \text{ mol BH}^+) = 0.380 \text{ mol BH}^+$ Then [B] = (0.520 mol B) / (0.500 L) = 1.04 M B $[BH^+] = (0.380 \text{ mol } BH^+) / (0.500 \text{ L}) = 0.760 M BH^+ (unrounded)$ $pH = pK_a + \log [B] / [BH^+]$ $= 9.353871964 + \log(1.04) / (0.760)$ = 9.490091711 = **9.49**

 a) The hydrochloric acid will react with the sodium acetate, NaC₂H₃O₂, to form acetic acid, HC₂H₃O₂: HCl + NaC₂H₃O₂ → HC₂H₃O₂ + NaCl
 Calculate the number of moles of HCl and NaC₂H₃O₂. All of the HCl will be consumed to form HC₂H₃O₂, and the number of moles of C₂H₃O₂⁻ will decrease. Initial moles HCl = $\left(\frac{0.442 \text{ mol HCl}}{L}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (184 \text{ mL}) = 0.081328 \text{ mol HCl (unrounded)}$ Initial moles NaC₂H₃O₂ = $\left(\frac{0.400 \text{ mol NaC}_2\text{H}_3\text{O}_2}{L}\right) (0.500 \text{ L}) = 0.200 \text{ mol NaC}_2\text{H}_3\text{O}_2$

Moles $HC_2H_3O_2$ formed = 0.081328 mol $HC_2H_3O_2$

Moles $C_2H_3O_2^-$ remaining = 0.200 mol - 0.081328 mol = 0.118672 mol $C_2H_3O_2^-$ (unrounded) Total volume = $0.500 \text{ L} + (184 \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.684 \text{ L}$ $[HC_2H_3O_2] = (0.081328 \text{ mol}) / (0.684 \text{ L}) = 0.118900584 M \text{ (unrounded)}$ $[C_2H_3O_2^-] = (0.118672 \text{ mol}) / (0.684 \text{ L}) = 0.173497076 M \text{ (unrounded)}$ $pK_a = -\log(1.8 \times 10^{-5}) = 4.744727495$

$$pH = pK_{2} + log ([C_{2}H_{2}O_{2}^{-}] / [HC_{2}H_{2}O_{2}]$$

 $pH = pK_a + \log ([C_2H_3O_2^-] / [HC_2H_3O_2])$ = 4.744727495 + log (0.173497076 / 0.118900584) = 4.9088 = **4.91**

b) The addition of base would increase the pH, so the new pH is (4.91 + 0.15) = 5.06.

The new $[C_2H_3O_2]/[HC_2H_3O_2]$ ratio is calculated using the Henderson-Hasselbalch equation.

 $pH = pK_a + log ([C_2H_3O_2^-] / [HC_2H_3O_2])$ $5.06 = 4.744727495 + \log \left(\left[C_2 H_3 O_2^{-1} \right] / \left[H C_2 H_3 O_2 \right] \right)$ $\log ([C_2H_3O_2^-] / [HC_2H_3O_2]) = 0.315272505$ (unrounded) $[C_2H_3O_2^-] / [HC_2H_3O_2] = 2.06676519$ (unrounded)

From part (a), we know that $[HC_2H_3O_2] + [C_2H_3O_2] = (0.118900584 M + 0.173497076 M) = 0.29239766 M.$ 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 $[C_2H_3O_2] / [HC_2H_3O_2] = 2.06676519$ and $[HC_2H_3O_2] + [C_2H_3O_2] = 0.29239766 M$, solve for $[C_2H_3O_2]$ and substitute into the second equation.

 $[C_2H_3O_2^-] = 2.06676519 [HC_2H_3O_2]$ and $[HC_2H_3O_2] + 2.06676519 [HC_2H_3O_2] = 0.29239766 M$ $[HC_2H_3O_2] = 0.095343999 M \text{ and } [C_2H_3O_2^-] = 0.19705366 M.$

Moles of $C_2H_3O_2^-$ needed = (0.19705366 mol $C_2H_3O_2^-/L$) (0.500 L) = 0.09852683 mol (unrounded) Moles of $C_2H_3O_2^-$ initially = $(0.173497076 \text{ mol } C_2H_3O_2^- / L) (0.500 \text{ L}) = 0.086748538 \text{ mol (unrounded)}$

This would require the addition of (0.09852683 mol - 0.086748538 mol) = 0.011778292 mol KOH (unrounded)

Mass KOH = (0.011778292 mol KOH) (56.11 g KOH / mol KOH) = 0.660879964 = 0.66 g KOH

a) The sodium hydroxide will react with the sodium bicarbonate, NaHCO₃, to form carbonate ion, CO_3^{2-} : 19.32 $NaOH + NaHCO_3 \rightarrow 2 Na^+ + CO_3^{2-} + H_2O$

Calculate the number of moles of NaOH and NaHCO₃. All of the NaOH will be consumed to form CO₃²⁻, and the number of moles of NaHCO₃ will decrease. The HCO₃ is the important part of NaHCO₃.

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

Initial moles HCO₃⁻ = $\left(\frac{0.050 \text{ mol NaHCO}_3}{L}\right) \left(\frac{1 \text{ mol HCO}_3^{-1}}{1 \text{ mol NaHCO}_3}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (50.0 \text{ mL})$
= 0.0025 mol HCO₃⁻
Moles CO₃²⁻ formed = 0.00107 mol CO₃²⁻
Moles HCO₃⁻ remaining = 0.0025 mol - 0.00107 mol = 0.00143 mol HCO₃⁻ (unrounded)
Total volume = (50.0 mL + 10.7 mL) (10^{-3} L / 1 mL) = 0.0607 L
[HCO₃⁻] = (0.00143 mol) / (0.0607 L) = 0.023558484 M (unrounded)
[CO₃²⁻] = (0.00107 mol) / (0.0607 L) = 0.017627677 M (unrounded)
pK_a = -log (4.7 x 10⁻¹¹) = 10.32790214

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

$$= 10.32790214 + \log(0.017627677 / 0.023558484) = 10.2019 = 10.20$$

b) The addition of acid would decrease the pH, so the new pH is (10.20 - 0.07) = 10.13The new $[CO_3^{2-}] / [HCO_3^{-}]$ ratio is calculated using the Henderson-Hasselbalch equation.

 $pH = pK_a + \log ([CO_3^{2^-}] / [HCO_3^{-}])$ $10.13 = 10.32790214 + \log ([CO_3^{2^-}] / [HCO_3^{-}])$ $\log ([CO_3^{2^-}] / [HCO_3^{-}]) = -0.19790214 \text{ (unrounded)}$ $[CO_3^{2^-}] / [HCO_3^{-}] = 0.63401 \text{ (unrounded)}$ $m \text{ part (a) we know that [HCO_3^{-}] + [CO_2^{2^-}] = (0.023558484 M + 0.017627677 M) = 0.041185$

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.

 $\begin{bmatrix} CO_{3}^{2-}] = 0.63401 \ [HCO_{3}^{-}] \text{ and } \ [HCO_{3}^{-}] + 0.63401 \ [HCO_{3}^{-}] = 0.041185254 M \\ \ [HCO_{3}^{-}] = 0.025205019 M \text{ and } \ [CO_{3}^{2-}] = 0.015980234 M (unrounded) \\ \text{Moles of } CO_{3}^{2-} \text{ needed} = (0.015980234 \text{ mol } CO_{3}^{2-} / \text{L}) (10^{-3}\text{L} / 1 \text{ mL}) (25.0 \text{ mL}) \\ = 0.000399505 \text{ mol } (unrounded) \\ \text{Moles of } CO_{3}^{2-} \text{ initially} = (0.017627677 \text{ mol } CO_{3}^{2-} / \text{L}) (10^{-3}\text{L} / 1 \text{ mL}) (25.0 \text{ mL}) \\ = 0.000440691 \text{ mol } (unrounded) \\ \text{This would require the addition of } (0.000440691 \text{ mol } - 0.000399505 \text{ mol}) \\ = 0.000041186 \text{ mol } \text{HCl} (unrounded) \\ \text{Mass } \text{HCl} = (0.000041186 \text{ mol } \text{HCl}) (36.46 \text{ g } \text{HCl} / \text{ mol } \text{HCl}) = 0.001501675 = 0.0015 \text{ g } \text{HCl} \\ \end{bmatrix}$

19.33 Select conjugate pairs with K_a values close to the desired [H₃O⁺].
a) For pH ≈ 4.0, the best selection is the HCOOH / HCOO⁻ conjugate pair with K_a equal to 1.8 x 10⁻⁴. From the base list, the C₆H₅NH₂ / C₆H₅NH₃⁺ 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, two choices are the H₂PO₄⁻ / HPO₄²⁻ conjugate pair with K_a of 1.7 x 10⁻⁷ and the H₂AsO₄⁻ / HAsO₄²⁻ 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 $[H_3O^+] \approx 1 \times 10^{-9} M$, the HOBr / OBr⁻ conjugate pair comes close with K_a equal to 2.3 x 10⁻⁹. From the base list, $K_b = 1.0 \times 10^{-14} / 1 \times 10^{-9} = 1 \times 10^{-5}$, the NH₃ / NH₄⁺ conjugate pair comes close with $K_b = 1.76 \times 10^{-5}$. b) For $[OH^-] \approx 3 \times 10^{-5} M$, the NH₃ / NH₄⁺ conjugate pair comes close; also, it is possible to choose $K_a = 1.0 \times 10^{-14} / 3 \times 10^{-5} = 3.3 \times 10^{-10}$ the C₆H₅OH / C₆H₅O⁻ comes close with $K_a = 1.0 \times 10^{-10}$
- 19.35 Select conjugate pairs with pK_a values close to the desired pH. Convert pH to [H₃O⁺] for easy comparison to K_a values. Determine an appropriate base by [OH⁻] = K_w / [H₃O⁺].
 a) For pH ≈ 2.5 ([H₃O⁺] = 10^{-pH} = 3 x 10⁻³), the best selection is the H₃AsO₄ / H₂AsO₄⁻ conjugate pair with a K_a = 6 x 10⁻³. The H₃PO₄ / H₂PO₄⁻ pair, with K_a = 7.2 x 10⁻³, is also a good choice. The [OH⁻] = 1.0 x 10⁻¹⁴ / 3 x 10⁻³ = 3 x 10⁻¹², results in no reasonable K_b values from the appendix.
 b) For pH ≈ 5.5 ([H₃O⁺] = 10^{-pH} = 3 x 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 x 10⁻¹⁴ / 3 x 10⁻⁶ = 3 x 10⁻⁹, the K_b selection is C₅H₅N / C₅H₅NH⁺.
- 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 x 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. $pH = pK_a + \log [CIO^-] / [HCIO]$ a) $pH = 7.5376 + \log (0.100) / (0.100) = 7.5376 = 7.54$

b) pH = $7.5376 + \log (0.150) / (0.100) = 7.71369 = 7.71$ c) pH = $7.5376 + \log (0.100) / (0.150) = 7.3615 = 7.36$ d) The reaction is NaOH + HClO \rightarrow Na⁺ + ClO⁻ + H₂O The original moles of HClO and OCl⁻ are both = (0.100 mol / L) (L) = 0.100 mol The reaction gives: 0.100 mol HClO - (0.00500 mol NaOH) (1 mol HClO / 1 mol NaOH) = 0.095 mol HClO 0.100 mol ClO⁻ + (0.00500 mol NaOH) (1 mol ClO⁻ / 1 mol NaOH) = 0.105 mol HClO pH = $7.5376 + \log (0.105) / (0.095) = 7.5811 = 7.58$

19.38 The value of the K_a from the appendix: $K_a = 6.3 \times 10^{-8}$ Determine the pK_a using $pK_a = -\log 6.3 \times 10^{-8} = 7.200659451$ (unrounded) Use the Henderson-Hasselbalch equation: $pH = pK_a + \log [HPO_4^{2^-}] / [H_2PO_4^{-}]$ $7.40 = 7.200659451 + \log [HPO_4^{2^-}] / [H_2PO_4^{-}]$ $7.40 - 7.200659451 = \log [HPO_4^{2^-}] / [H_2PO_4^{-}] = 0.199340$ (unrounded) $[HPO_4^{2^-}] / [H_2PO_4^{-}] = 1.582486 = 1.6$

- 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.
- 19.40 To see a distinct color in a mixture of two, 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 base equals the number of moles of acid (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 At the equivalence point, the slope of the titration curve is its maximum value.

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 acid equal the moles of base, 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 → H₂O + 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

The weak acid - strong base equivalence point occurs at pH > 7, because the anion of the weak acid is weakly basic, whereas the cation of the strong base does not react with water. An example is the reaction HCOOH + NaOH \rightarrow HCOO⁻ + H₂O + Na⁺. The conjugate base, HCOO⁻, reacts with water according to this reaction: HCOO⁻ + H₂O \rightarrow HCOOH + OH⁻.

The strong acid - weak base equivalence point occurs at pH < 7, because the anion of the strong acid does not react with water, whereas the cation of the weak base is weakly acidic. An example is the reaction HCl + NH₃ \rightarrow NH₄⁺ + Cl⁻. The conjugate acid, NH₄⁺, dissociates slightly in water: NH₄⁺ + H₂O \rightarrow NH₃ + H₃O⁺. 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 $-\log (5.0 \times 10^{-9}) = 8.3$, so the indicator changes color over an approximate range of **7.3 to 9.3**.
- 19.49 Indicators have a pH range that is approximated by $pK_a \pm 1$. The pK_a of cresol red is $-\log (7.9 \times 10^{-11}) = 10.10$, so the indicator changes color over an approximate range of **9.1 11.1**.
- 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, the solution is $0.050 M \text{ HCOO}^-$. (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 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)

$$K_{b} = \frac{[\text{HCOOH}][\text{OH}^{-}]}{[\text{HCOO}^{-}]} = \frac{[x][x]}{[0.050 - x]} = \frac{[x][x]}{[0.050]} = 5.5556 \text{ x } 10^{-1}$$

[OH⁻] = x = 1.6666673 x 10⁻⁶ M
pOH = -log (1.666673 x 10⁻⁶) = 5.7781496 (unrounded)
pH = 14.00 - pOH = 14.00 - 5.7781496 = 8.2218504 = 8.22
Choose **thymol blue** or **phenolphthalein**.

19.51 a) Determine the K_a (of the conjugate acid) from the K_b reported in the Appendix 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
$$CH_3NH_3^+ = 0.050 M$$
.

$$K_{a} = \frac{\left[\text{H}_{3}\text{O}^{+} \right] \left[\text{CH}_{3}\text{NH}_{2} \right]}{\left[\text{CH}_{3}\text{NH}_{3}^{+} \right]} = \frac{x^{2}}{0.050 - x} = \frac{x^{2}}{0.050} = 2.2727 \text{ x } 10^{-11}$$

$$x = [\text{H}_{3}\text{O}^{+}] = 1.0659971 \text{ x } 10^{-6} M \text{ (unrounded)}$$

$$p\text{H} = -\log [\text{H}_{3}\text{O}^{+}] = -\log (1.0659971 \text{ x } 10^{-6}) = 5.97224 = 5.97$$
Either **methyl red** or **alizarin** is acceptable.

b) This is a strong acid-strong base titration; thus, the equivalence point is at pH = 7.00. The best choice would be bromthymol blue; alizarin might be acceptable.

19.52 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 $0.25 M (CH_3)_2 NH_2^+$. (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)

$$K_{a} = \frac{\left[H_{3}O^{+} \right] \left[(CH_{3})_{2} NH \right]}{\left[(CH_{3})_{2} NH_{2}^{+} \right]} = \frac{x^{2}}{0.25 - x} = \frac{x^{2}}{0.25} = 1.6949152 \text{ x } 10^{-11}$$

$$x = [H_{3}O^{+}] = 2.0584674 \text{ x } 10^{-6} M \text{ (unrounded)}$$

$$pH = -\log [H_{3}O^{+}] = -\log (2.0584674 \text{ x } 10^{-6}) = 5.686456 = 5.69$$

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 reported in the Appendix for C₆H₅COOH. $K_b = K_w / K_a = (1.0 \times 10^{-14}) / (6.3 \times 10^{-5}) = 1.5873 \times 10^{-10}$ (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 CH₃NH₃⁺ = 0.125 *M* (unrounded).

$$K_{b} = \frac{\left[C_{6}H_{5}COOH\right]OH^{-}\right]}{\left[C_{6}H_{5}COO^{-}\right]} = \frac{\left[x\right]\left[x\right]}{\left[0.125 - x\right]} = \frac{\left[x\right]\left[x\right]}{\left[0.125\right]} = 1.5873 \times 10^{-10}$$

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

 $pOH = -log (4.4543518 \times 10^{-6}) = 5.351215485$ (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 $0.25 M \text{ NH}_3$ solution at the equivalence point. Use the K_b for NH₃ from the Appendix.

$$K_{\rm b} = \frac{\left[\mathrm{NH_4}^+\right]\left[\mathrm{OH}^-\right]}{\left[\mathrm{NH_3}\right]} = \frac{\left[\mathrm{x}\right]\left[\mathrm{x}\right]}{\left[0.25 - \mathrm{x}\right]} = \frac{\left[\mathrm{x}\right]\left[\mathrm{x}\right]}{\left[0.25\right]} = 1.76 \text{ x } 10^{-5}$$

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

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

 $\mathrm{H}_{3}\mathrm{O}^{+}(aq) + \mathrm{OH}^{-}(aq) \rightarrow 2 \mathrm{H}_{2}\mathrm{O}(l)$

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 50.00 mL of base has been added.

The initial number of moles of HCl = $(0.1000 \text{ mol HCl} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (50.00 \text{ mL}) = 5.000 \text{ x} 10^{-3} \text{ mol HCl}$ a) At 0 mL of base added, the concentration of hydronium ion equals the original concentration of HCl.

pH = -log (0.1000 M) = 1.0000

b) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{L} / 1 \text{ mL}) (25.00 \text{ mL}) = 2.500 \text{ x} 10^{-3} \text{ mol NaOH}$ The NaOH will react with an equal amount of the acid, and $2.500 \text{ x} 10^{-3} \text{ mol HCl will remain}$. The volume of the solution at this point is $[(50.00 + 25.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.07500 \text{ L}$ The molarity of the excess HCl is $(2.500 \text{ x} 10^{-3} \text{ mol HCl}) / (0.07500 \text{ L}) = 0.03333 M (unrounded)$ pH = -log (0.03333) = 1.4772

c) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (49.00 \text{ mL}) = 4.900 \text{ x} 10^{-3} \text{ mol NaOH}$ The NaOH will react with an equal amount of the acid, and $1.00 \text{ x} 10^{-4} \text{ mol HCl will remain}$. The volume of the solution at this point is $[(50.00 + 49.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.09900 \text{ L}$ The molarity of the excess HCl is $(1.00 \text{ x} 10^{-4} \text{ mol HCl}) / (0.09900 \text{ L}) = 0.00101 M (unrounded)$ $\text{pH} = -\log (0.00101) = 2.996$

d) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (49.90 \text{ mL}) = 4.990 \text{ x} 10^{-3} \text{ mol NaOH}$ The NaOH will react with an equal amount of the acid, and $1.0 \text{ x} 10^{-5} \text{ mol HCl will remain}$. The volume of the solution at this point is $[(50.00 + 49.90) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.09990 \text{ L}$ The molarity of the excess HCl is $(1.0 \text{ x} 10^{-5} \text{ mol HCl}) / (0.09990 \text{ L}) = 0.0001001 M (unrounded)$ $\text{pH} = -\log (0.0001001) = 4.0000$ e) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (50.00 \text{ mL}) = 5.000 \text{ x} 10^{-3} \text{ mol NaOH}$ 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 titrations, thus, the pH is 7.00.

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 = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (50.10 \text{ mL}) = 5.010 \text{ x} 10^{-3} \text{ mol NaOH}$ The HCl will react with an equal amount of the base, and 1.0×10^{-5} mol NaOH will remain. The volume of the solution at this point is $[(50.00 + 50.10) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.1010 \text{ L}$

The molarity of the excess NaOH is $(1.0 \times 10^{-5} \text{ mol NaOH}) / (0.1010 \text{ L}) = 0.00009901 M (unrounded)$

pOH = -log (0.00009901) = 4.0043 (unrounded)

pH = 14.00 - pOH = 14.00 - 4.0043 = 9.9957 = 10.00

g) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (60.00 \text{ mL}) = 6.000 \text{ x} 10^{-3} \text{ mol NaOH}$ The HCl will react with an equal amount of the base, and 1.000×10^{-3} mol NaOH will remain. The volume of the solution at this point is $[(50.00 + 60.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.1100 \text{ L}$

The molarity of the excess NaOH is $(1.000 \times 10^{-3} \text{ mol NaOH}) / (0.1100 \text{ L}) = 0.0090909 M (unrounded)$ pOH = -log (0.0090909) = 2.041393 (unrounded)

pH = 14.00 - pOH = 14.00 - 2.041393 = 11.958607 = **11.96**

19.55 The reaction occurring in the titration is the neutralization of OH^- (from KOH) by H_3O^+ (from HBr): $H_3O^+(aq) + OH^-(aq) \rightarrow 2 H_2O(l)$

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 = $(0.1000 \text{ mol KOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (30.00 \text{ mL})$ $= 3.000 \text{ x} 10^{-3} \text{ mol KOH}$

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 = $(0.1000 \text{ mol HBr} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (15.00 \text{ mL}) = 1.500 \text{ x} 10^{-3} \text{ mol HBr}$ The HBr will react with an equal amount of the base, and 1.500×10^{-3} mol KOH will remain. The volume of the solution at this point is $[(30.00 + 15.00) \text{ mL}](10^{-3} \text{ L} / 1 \text{ mL}) = 0.04500 \text{ L}$ The molarity of the excess KOH is $(1.500 \times 10^{-3} \text{ mol KOH}) / (0.04500 \text{ L}) = 0.03333 M$ (unrounded) pOH = -log(0.03333) = 1.4772

c) Determine the moles of HBr added:

Moles of HBr = $(0.1000 \text{ mol HBr} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (29.00 \text{ mL}) = 2.900 \text{ x} 10^{-3} \text{ mol HBr}$ The HBr will react with an equal amount of the base, and 1.00×10^{-4} mol KOH will remain. The volume of the solution at this point is $[(30.00 + 29.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.05900 \text{ L}$ The molarity of the excess KOH is $(1.00 \times 10^{-4} \text{ mol KOH}) / (0.05900 \text{ L}) = 0.0016949 M (unrounded)$

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 = $(0.1000 \text{ mol HBr} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (29.90 \text{ mL}) = 2.990 \text{ x} 10^{-3} \text{ mol HBr}$ The HBr will react with an equal amount of the base, and 1.0×10^{-5} mol KOH will remain. The volume of the solution at this point is $[(30.00 + 29.90) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.05990 \text{ L}$ The molarity of the excess KOH is $(1.0 \times 10^{-5} \text{ mol KOH}) / (0.05990 \text{ L}) = 0.000166944 M (unrounded)$ 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 = $(0.1000 \text{ mol HBr} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (30.00 \text{ mL}) = 3.000 \text{ x} 10^{-3} \text{ mol HBr}$ The HBr will react with an equal amount of the base and 0.0 mol KOH will remain. This is the equivalence point of a strong acid-strong base 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 = $(0.1000 \text{ mol HBr} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (30.10 \text{ mL}) = 3.010 \text{ x} 10^{-3} \text{ mol HBr}$ The HBr will react with an equal amount of the base, and $1.0 \text{ x} 10^{-5} \text{ mol HBr}$ will remain. The volume of the solution at this point is $[(30.00 + 30.10) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.06010 \text{ L}$ The molarity of the excess HBr is $(1.0 \text{ x} 10^{-5} \text{ mol HBr}) / (0.06010 \text{ L}) = 0.000166389 M (unrounded)$ pH = -log (0.000166389) = 3.778874 = 3.8

g) Determine the moles of HBr added:

Moles of HBr = $(0.1000 \text{ mol HBr} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (40.00 \text{ mL}) = 4.000 \text{ x} 10^{-3} \text{ mol HBr}$ The HBr will react with an equal amount of the base, and $1.000 \text{ x} 10^{-3} \text{ mol HBr}$ will remain. The volume of the solution at this point is $[(30.00 + 40.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.07000 \text{ L}$ The molarity of the excess HBr is $(1.000 \text{ x} 10^{-3} \text{ mol HBr}) / (0.07000 \text{ L}) = 0.0142857 M (unrounded)$ 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 = $(0.1000 \text{ mol HBut / L}) (10^{-3} \text{ L / 1 mL}) (20.00 \text{ mL}) = 2.000 \text{ x } 10^{-3} \text{ mol HBut}$

a) At 0 mL of base added, the concentration of $[H_3O^+]$ is dependent on the dissociation of butanoic acid: HBut + H₂O \leftrightarrows H₃O⁺ + But⁻

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[But^{-}\right]}{\left[HBut\right]} = \frac{x^{2}}{0.1000 - x} = \frac{x^{2}}{0.1000} = 1.54 \times 10^{-5}$$
$$x = \left[H_{3}O^{+}\right] = 1.2409673 \times 10^{-3} M \text{ (unrounded)}$$
$$pH = -\log\left[H_{3}O^{+}\right] = -\log\left(1.2409673 \times 10^{-3}\right) = 2.9062 = 2.91$$

b) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (10.00 \text{ mL}) = 1.000 \text{ x} 10^{-3} \text{ mol NaOH}$ The NaOH will react with an equal amount of the acid, and $1.000 \text{ x} 10^{-3} \text{ mol HBut will remain}$. An equal number of moles of But⁻ will form.

The volume of the solution at this point is $[(20.00 + 10.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.03000 \text{ L}$ The molarity of the excess HBut is $(1.000 \times 10^{-3} \text{ mol HBut}) / (0.03000 \text{ L}) = 0.03333 M (unrounded)$ The molarity of the But formed is $(1.000 \times 10^{-3} \text{ mol But}) / (0.03000 \text{ L}) = 0.03333 M (unrounded)$

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[But^{-}\right]}{\left[HBut\right]} = \frac{x\left(0.0333 + x\right)}{0.03333 - x} = \frac{x\left(0.03333\right)}{0.03333} = 1.54 \times 10^{-5}$$

$$x = [H_{3}O^{+}] = 1.54 \times 10^{-5} M \text{ (unrounded)}$$

$$pH = -\log [H_{3}O^{+}] = -\log (1.54 \times 10^{-5}) = 4.812479 = 4.81$$

c) Determine the moles of NaOH added:

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

The volume of the solution at this point is $[(20.00 + 15.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.03500 \text{ L}$ 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 $(1.500 \times 10^{-3} \text{ mol But}) / (0.03500 \text{ L}) = 0.0428571 M (unrounded)$ $K_{\rm a} = \frac{\left[{\rm H}_{3}{\rm O}^{+}\right]\left[{\rm But}^{-}\right]}{\left[{\rm HBut}\right]} = \frac{x\left(0.0428571 + x\right)}{0.0142857 - x} = \frac{x\left(0.0428571\right)}{0.0142857} = 1.54 \text{ x } 10^{-5}$ $x = [H_3O^+] = 5.1333 \times 10^{-6} M$ (unrounded) $pH = -log [H_3O^+] = -log (5.1333 \times 10^{-6}) = 5.2896 = 5.29$

d) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (19.00 \text{ mL}) = 1.900 \text{ x} 10^{-3} \text{ mol NaOH}$ The NaOH will react with an equal amount of the acid, and 1.00×10^{-4} mol HBut will remain. and 1.900 x 10⁻³ moles of But⁻ will form.

The volume of the solution at this point is $[(20.00 + 19.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.03900 \text{ L}$ The molarity of the excess HBut is $(1.00 \times 10^{-4} \text{ mol HBut}) / (0.03900 \text{ L}) = 0.0025641 M (unrounded)$ The molarity of the But formed is $(1.900 \times 10^{-3} \text{ mol But}) / (0.03900 \text{ L}) = 0.0487179 M (unrounded)$

$$K_{a} = \frac{\left\lfloor H_{3}O^{+} \right\rfloor \left\lfloor But^{-} \right\rfloor}{\left[HBut\right]} = \frac{x\left(0.0487179 + x\right)}{0.0025641 - x} = \frac{x\left(0.0487179\right)}{0.0025641} = 1.54 \times 10^{-5}$$
$$x = \left[H_{2}O^{+}\right] = 8 \ 1052631 \times 10^{-7} \ M \ (unrounded)$$

e) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (19.95 \text{ mL}) = 1.995 \text{ x} 10^{-3} \text{ mol NaOH}$ The NaOH will react with an equal amount of the acid, and 5 x 10^{-6} mol HBut will remain, and 1.995×10^{-3} moles of But⁻ will form.

The volume of the solution at this point is $[(20.00 + 19.95) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.03995 \text{ L}$ The molarity of the excess HBut is $(5 \times 10^{-6} \text{ mol HBut}) / (0.03995 \text{ L}) = 0.000125156 M (unrounded)$ The molarity of the But⁻ formed is $(1.995 \times 10^{-3} \text{ mol But}) / (0.03995 \text{ L}) = 0.0499374 M (unrounded)$

$$K_{a} = \frac{\left\lfloor H_{3}O^{+} \right\rfloor \left\lfloor But^{-} \right\rfloor}{\left[HBut\right]} = \frac{x\left(0.0499374 + x\right)}{0.000125156 - x} = \frac{x\left(0.0499374\right)}{0.000125156} = 1.54 \times 10^{-5}$$
$$x = [H_{3}O^{+}] = 3.859637 \times 10^{-8} M \text{ (unrounded)}$$
$$pH = -\log [H_{3}O^{+}] = -\log (3.859637 \times 10^{-8}) = 7.41345 = 7.4$$
f) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (20.00 \text{ mL}) = 2.000 \text{ x} 10^{-3} \text{ mol NaOH}$ 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. The $K_{\rm b}$ 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) $K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.54 \times 10^{-5}) = 6.4935 \times 10^{-10}$ (unrounded)

$$K_{\rm b} = \frac{\left[\mathrm{HBut}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{But}^{-}\right]} = \frac{\left[\mathrm{x}\right]\left[\mathrm{x}\right]}{\left[0.05000 - \mathrm{x}\right]} = \frac{\left[\mathrm{x}\right]\left[\mathrm{x}\right]}{\left[0.05000\right]} = 6.4935 \text{ x } 10^{-10}$$

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

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

pH = 14.00 - pOH = 14.00 - 5.244275575 = 8.755724425 = 8.76

g) After the equivalence point, the excess strong base is the primary factor influencing the pH. Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (20.05 \text{ mL}) = 2.005 \text{ x} 10^{-3} \text{ mol NaOH}$ The NaOH will react with an equal amount of the acid. 0 mol HBut will remain, and 5 x 10^{-6} moles of NaOH will be in excess.

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 = 10.10

h) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (25.00 \text{ mL}) = 2.500 \text{ x} 10^{-3} \text{ mol NaOH}$ 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. 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 = 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 $K_{\rm b}$ of the base ((CH₃CH₂)₃N)). Prior to reaching the equivalence point, the added acid reacts with base to form $(CH_3CH_3)_3NH^+$ 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 $(CH_3CH_2)_3N = (0.1000 \text{ mol} (CH_3CH_2)_3N) / L) (10^{-3} L / 1 \text{ mL}) (20.00 \text{ mL})$ $= 2.000 \text{ x} 10^{-3} \text{ mol} (CH_3CH_2)_3 \text{ N}$

a) Since no acid has been added, only the weak base (K_b) is important. $K_b = \frac{[(CH_3CH_2)_3 NH^+][OH^-]}{[(CH_3CH_2)_3 N]} = \frac{[x][x]}{[0.1000 - x]} = \frac{[x][x]}{[0.1000]} = 5.2 \times 10^{-4}$

 $[OH^{-}] = x = 7.2111 \times 10^{-3} M$ $pOH = -log (7.2111 \times 10^{-3}) = 2.141998 (unrounded)$ pH = 14.00 - pOH = 14.00 - 2.141998 = 11.8580 = 11.86 b) Determine the moles of HCl added: Moles of HCl = $(0.1000 \text{ mol HCl} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (10.00 \text{ mL}) = 1.000 \text{ x} 10^{-3} \text{ mol HCl}$ The HCl will react with an equal amount of the base, and 1.000 x 10⁻³ mol (CH₃CH₂)₃N will remain; an equal number of moles of $(CH_3CH_2)_3NH^+$ will form. The volume of the solution at this point is $[(20.00 + 10.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.03000 \text{ L}$ The molarity of the excess $(CH_3CH_2)_3N$ is $(1.000 \times 10^{-3} \text{ mol} (CH_3CH_2)_3N) / (0.03000 \text{ L})$ = 0.03333 M (unrounded) The molarity of the $(CH_3CH_2)_3NH^+$ formed is $(1.000 \times 10^{-3} \text{ mol} (CH_3CH_2)_3NH^+) / (0.03000 \text{ L})$ $K_{\rm b} = \frac{\left[({\rm CH}_{3}{\rm CH}_{2})_{3}{\rm NH}^{+}\right][{\rm OH}^{-}]}{\left[({\rm CH}_{3}{\rm CH}_{2})_{3}{\rm N}\right]} = \frac{\left[x\right][0.0333 + x]}{\left[0.03333 - x\right]} = \frac{\left[x\right][0.0333]}{\left[0.03333\right]} = 5.2 \times 10^{-4}$ $[OH^{-}] = x = 5.2 \times 10^{-4} M$ $pOH = -log (5.2 \times 10^{-4}) = 3.283997$ (unrounded) pH = 14.00 - pOH = 14.00 - 3.283997 = 10.7160 = **10.72** c) Determine the moles of HCl added: Moles of HCl = $(0.1000 \text{ mol HCl} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (15.00 \text{ mL}) = 1.500 \text{ x} 10^{-3} \text{ mol HCl}$ The HCl will react with an equal amount of the base, and 5.00 x 10⁻⁴ mol (CH₃CH₂)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 $[(20.00 + 15.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.03500 \text{ L}$

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

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

 $K_{\rm b} = \frac{\left[({\rm CH}_{3}{\rm CH}_{2})_{3}{\rm NH}^{+}\right]\left[{\rm OH}^{-}\right]}{\left[({\rm CH}_{3}{\rm CH}_{2})_{3}{\rm N}\right]} = \frac{\left[x\right]\left[0.0428571 + x\right]}{\left[0.01428571 + x\right]} = \frac{\left[x\right]\left[0.0428571\right]}{\left[0.0142857\right]} = 5.2 \times 10^{-4}$ $[OH^{-}] = x = 1.7333 \times 10^{-4} M$ $pOH = -log (1.7333 \times 10^{-4}) = 3.761126$ (unrounded) pH = 14.00 - pOH = 14.00 - 3.761126 = 10.23887 = 10.24

d) Determine the moles of HCl added:

Moles of HCl = $(0.1000 \text{ mol HCl} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (19.00 \text{ mL}) = 1.900 \text{ x} 10^{-3} \text{ mol HCl}$ The HCl will react with an equal amount of the base, and $1.00 \text{ x} 10^{-4} \text{ mol} (CH_3CH_2)_3 \text{N}$ will remain; and $1.900 \text{ x} 10^{-3}$ moles of $(CH_3CH_2)_3 \text{NH}^+$ will form.

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

The molarity of the excess $(CH_3CH_2)_3N$ is $(1.00 \times 10^{-4} \text{ mol} (CH_3CH_2)_3N) / (0.03900 \text{ L})$ = 0.002564102 *M* (unrounded)

The molarity of the $(CH_3CH_2)_3NH^+$ formed is $(1.900 \times 10^{-3} \text{ mol} (CH_3CH_2)_3NH^+) / (0.03900 \text{ L}) = 0.0487179 M (unrounded)$

$$K_{\rm b} = \frac{\left[\left(\rm{CH}_{3}\rm{CH}_{2}\right)_{3}\rm{NH}^{+}\right]\left[\rm{OH}^{-}\right]}{\left[\left(\rm{CH}_{3}\rm{CH}_{2}\right)_{3}\rm{N}\right]} = \frac{\left[x\right]\left[0.0487179 + x\right]}{\left[0.002564102 - x\right]} = \frac{\left[x\right]\left[0.0487179\right]}{\left[0.002564102\right]} = 5.2 \times 10^{-4}$$

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

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

e) Determine the moles of HCl added:

Moles of HCl = $(0.1000 \text{ mol HCl} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (19.95 \text{ mL}) = 1.995 \text{ x} 10^{-3} \text{ mol HCl}$ The HCl will react with an equal amount of the base, and 5 x 10⁻⁶ mol (CH₃CH₂)₃N will remain; and 1.900 x 10⁻³ moles of (CH₃CH₂)₃NH⁺ will form.

The volume of the solution at this point is $[(20.00 + 19.95) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.03995 \text{ L}$ The molarity of the excess $(CH_3CH_2)_3N$ is $(5 \times 10^{-6} \text{ mol} (CH_3CH_2)_3N) / (0.03995 \text{ L})$

= 0.000125156 M (unrounded)

The molarity of the $(CH_3CH_2)_3NH^+$ formed is $(1.995 \times 10^{-3} \text{ mol} (CH_3CH_2)_3NH^+) / (0.03995 \text{ L}) = 0.0499374 M (unrounded)$

$$K_{\rm b} = \frac{\left\lfloor \left({\rm CH}_{3} {\rm CH}_{2} \right)_{3} {\rm NH}^{+} \right\rfloor \left\lfloor {\rm OH}^{-} \right\rfloor}{\left[\left({\rm CH}_{3} {\rm CH}_{2} \right)_{3} {\rm N} \right]_{4}} = \frac{\left[{\rm x} \right] \left[0.0499374 + {\rm x} \right]}{\left[0.000125156 - {\rm x} \right]} = \frac{\left[{\rm x} \right] \left[0.0499374 \right]}{\left[0.000125156 \right]} = 5.2 {\rm x} 10^{-4}$$

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

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

pH = 14.00 - pOH = 14.00 - 5.88497 = 8.11503 = 8.1

f) Determine the moles of HCl added:

Moles of HCl = $(0.1000 \text{ mol HCl} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (20.00 \text{ mL}) = 2.000 \text{ x} 10^{-3} \text{ mol HCl}$ 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 $[(20.00 + 20.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.04000 \text{ L}$ The molarity of the $(CH_3CH_2)_3NH^+$ formed is $(2.000 \text{ x} 10^{-3} \text{ mol} (CH_3CH_2)_3NH^+) / (0.04000 \text{ L}) = 0.05000 M$

$$K_{a} = K_{w} / K_{b} = (1.0 \text{ x } 10^{-14}) / (5.2 \text{ x } 10^{-4}) = 1.923 \text{ x } 10^{-11} \text{ (unrounded)}$$

$$K_{a} = \frac{\left[\text{H}_{3}\text{O}^{+}\right]\left[\left(\text{CH}_{3}\text{CH}_{2}\right)_{3}\text{N}\right]}{\left[\left(\text{CH}_{3}\text{CH}_{2}\right)_{3}\text{NH}^{+}\right]} = \frac{\left[\text{x}\right]\left[\text{x}\right]}{\left[0.05000 - \text{x}\right]} = \frac{\left[\text{x}\right]\left[\text{x}\right]}{\left[0.05000\right]} = 1.923 \text{ x } 10^{-11}$$

$$x = [\text{H}_{3}\text{O}^{+}] = 9.8056 \text{ x } 10^{-7} M \text{ (unrounded)}$$

$$p\text{H} = -\log [\text{H}_{3}\text{O}^{+}] = -\log (9.8056 \text{ x } 10^{-7}) = 6.0085 = 6.01$$

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 = $(0.1000 \text{ mol HCl} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (20.05 \text{ mL}) = 2.005 \text{ x} 10^{-3} \text{ mol HCl}$ The HCl will react with an equal amount of the base, and 0 mol (CH₃CH₂)₃N will remain, and 5 x 10⁻⁶ moles of HCl will be in excess.

The volume of the solution at this point is $[(20.00 + 20.05) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.04005 \text{ L}$ The molarity of the excess H_3O^+ is $(5 \times 10^{-6} \text{ mol H}_3\text{O}^+) / (0.04005 \text{ L}) = 1.2484 \times 10^{-4} M$ (unrounded) $\text{pH} = -\log (1.2484 \times 10^{-4}) = 3.9036 = 3.9$ h) Determine the moles of HCl added:

Moles of HCl = $(0.1000 \text{ mol HCl} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (25.00 \text{ mL}) = 2.500 \text{ x} 10^{-3} \text{ mol HCl}$ The HCl will react with an equal amount of the base, and 0 mol (CH₃CH₂)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 $[(20.00 + 25.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.04500 \text{ L}$ The molarity of the excess H_3O^+ is $(5.00 \text{ x} 10^{-4} \text{ mol } \text{H}_3\text{O}^+) / (0.04500 \text{ L}) = 1.1111 \text{ x} 10^{-2} M$ (unrounded) pH = -log $(1.1111 \text{ x} 10^{-2}) = 1.9542 = 1.95$

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 =

$$\left(\frac{0.0520 \text{ mol } \text{CH}_3\text{COOH}}{\text{L}}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (42.2 \text{ mL}) \left(\frac{1 \text{ mol } \text{NaOH}}{1 \text{ mol } \text{CH}_3\text{COOH}}\right) \left(\frac{\text{L}}{0.0372 \text{ mol } \text{NaOH}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$
$$= 58.989247 = 59.0 \text{ mL } \text{NaOH}$$

Determine the moles of CH_3COO^- produced:

$$Moles = \left(\frac{0.0520 \text{ mol } CH_3COOH}{L}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (42.2 \text{ mL}) \left(\frac{1 \text{ mol } CH_3COO^-}{1 \text{ mol } CH_3COOH}\right)$$

 $= 0.0021944 \text{ mol CH}_3\text{COO}^-$ (unrounded)

Determine the liters of solution present at the equivalence point:

Volume = $[(42.0 + 58.989247) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.100989 \text{ L} (unrounded)$ Concentration of CH₃COO⁻ at equivalence point:

Molarity = $(0.0021944 \text{ mol CH}_3\text{COO}^-) / (0.100989 \text{ L}) = 0.021729 M (unrounded)$ Calculate K_b for CH₃COO $^-$: K_a CH₃COOH = 1.8×10^{-5}

 $K_{\rm b} = K_{\rm w} / K_{\rm a} = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) = 5.556 \times 10^{-10}$ (unrounded)

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

$$K_{\rm b} = \frac{\left[\text{CH}_{3}\text{COOH} \right] \left[\text{OH} \right]}{\left[\text{CH}_{3}\text{COO}^{-} \right]} = \frac{\left[\mathbf{x} \right] \left[\mathbf{x} \right]}{\left[0.021729 - \mathbf{x} \right]} = \frac{\left[\mathbf{x} \right] \left[\mathbf{x} \right]}{\left[0.021729 \right]} = 5.556 \text{ x } 10^{-10}$$

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

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

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

b) The balanced chemical equations are:

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

$$\operatorname{NaOH}(aq) + \operatorname{HSO}_{3}(aq) \rightarrow \operatorname{Na}^{+}(aq) + \operatorname{SO}_{3}^{2}(aq) + \operatorname{H}_{2}O(l)$$

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 =

$$\left(\frac{0.0890 \text{ mol } \text{H}_2\text{SO}_3}{\text{L}}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (18.9 \text{ mL}) \left(\frac{1 \text{ mol } \text{NaOH}}{1 \text{ mol } \text{H}_2\text{SO}_3}\right) \left(\frac{\text{L}}{0.0372 \text{ mol } \text{NaOH}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

It will require an equal volume to reach the second equivalence point (90.4 mL). Determine the moles of HSO_3^- produced:

Moles =
$$\left(\frac{0.0890 \text{ mol } \text{H}_2\text{SO}_3}{\text{L}}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (18.9 \text{ mL}) \left(\frac{1 \text{ mol } \text{HSO}_3^{2^-}}{1 \text{ mol } \text{H}_2\text{SO}_3}\right)$$

 $= 0.0016821 \text{ mol HSO}_3^-$ (unrounded)

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 = $[(18.9 + 45.21774) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.06411774 \text{ L} (unrounded)$

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

Volume = $[(18.9 + 45.21774 + 45.21774) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.109335 \text{ L} (unrounded)$ Concentration of HSO₃⁻ at equivalence point:

Molarity = $(0.0016821 \text{ moles HSO}_3) / (0.06411774 \text{ L}) = 0.0262345 M (unrounded)$ Concentration of SO₃²⁻ at equivalence point:

Molarity = $(0.0016821 \text{ moles SO}_3^{-2}) / (0.109335 \text{ L}) = 0.0153848 M (unrounded)$ Calculate K_b for HSO₃: $K_a H_2 SO_3 = 1.4 \times 10^{-2}$

 $K_{a} \prod_{2} SO_{3} - 1.4 \times 10^{-7}$ $K_{b} = K_{w} / K_{a} = (1.0 \times 10^{-14}) / (1.4 \times 10^{-2}) = 7.142857 \times 10^{-13} \text{ (unrounded)}$ Calculate K_{b} for SO₃²⁻: K_{a} HSO₃⁻ = 6.5 x 10⁻⁸ $K_{b} = K_{w} / K_{a} = (1.0 \times 10^{-14}) / (6.5 \times 10^{-8}) = 1.53846 \times 10^{-7} \text{ (unrounded)}$

 $K_b = K_w / K_a = (1.0 \times 10^{-5}) / (6.5 \times 10^{-5}) = 1.53846 \times 10^{-5}$ (unrounded) Determine the hydroxide ion concentration from the K_b , and then determine the pH from the pOH. For the first equivalence point:

$$K_{\rm b} = \frac{\left[\mathrm{H}_{2}\mathrm{SO}_{3}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{HSO}_{3}^{-}\right]} = \frac{\left[\mathrm{x}\right]\left[\mathrm{x}\right]}{\left[0.0262345 - \mathrm{x}\right]} = \frac{\left[\mathrm{x}\right]\left[\mathrm{x}\right]}{\left[0.0262345\right]} = 7.142857 \,\mathrm{x} \, 10^{-13}$$

 $[OH^{-}] = x = 1.368902 \times 10^{-7} M$ (unrounded) pOH = -log (1.368902 x 10⁻⁷) = 6.863627626 (unrounded) pH = 14.00 - pOH = 14.00 - 6.863627626 = 7.13637 = **7.14**

For the second equivalence point:

$$K_{\rm b} = \frac{\left[\mathrm{HSO}_{3}^{-}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{SO}_{3}^{2^{-}}\right]} = \frac{\left[\mathrm{x}\right]\left[\mathrm{x}\right]}{\left[0.0153848 - \mathrm{x}\right]} = \frac{\left[\mathrm{x}\right]\left[\mathrm{x}\right]}{\left[0.0153848\right]} = 1.53846 \mathrm{x} \ 10^{-7}$$

$$[OH^{-}] = x = 4.8650693 \times 10^{-5} M$$

 $pOH = -log (4.8650693 \times 10^{-5}) = 4.312910968$ (unrounded)

19.59 a) The balanced chemical equation is:

 $\operatorname{KOH}(aq) + \operatorname{HNO}_2(aq) \to \operatorname{K}^+(aq) + \operatorname{NO}_2^-(aq) + \operatorname{H}_2O(l)$

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 KOH needed:

Volume =

$$\left(\frac{0.0390 \text{ mol HNO}_2}{\text{L}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(23.4 \text{ mL})\left(\frac{1 \text{ mol KOH}}{1 \text{ mol HNO}_2}\right)\left(\frac{\text{L}}{0.0588 \text{ mol KOH}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

= 15.5204 = **15.5 mL KOH**

Determine the moles of NO_2^- produced:

$$Moles = \left(\frac{0.0390 \text{ mol } HNO_2}{L}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (23.4 \text{ mL}) \left(\frac{1 \text{ mol } NO_2^{-1}}{1 \text{ mol } HNO_2}\right)$$

 $= 0.0009126 \text{ mol NO}_2^-$ (unrounded)

Determine the liters of solution present at the equivalence point:

Volume = $[(23.4 + 15.5204) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.0389204 \text{ L} (unrounded)$ Concentration of NO₂⁻ at equivalence point:

Molarity = $(0.0009126 \text{ mol NO}_2) / (0.0389204 \text{ L}) = 0.023447857 M (unrounded)$ Calculate K_b for NO₂: K_a HNO₂ = 7.1 x 10⁻⁴

 $K_{\rm b} = K_{\rm w} / K_{\rm a} = (1.0 \text{ x } 10^{-14}) / (7.1 \text{ x } 10^{-4}) = 1.40845 \text{ x } 10^{-11} \text{ (unrounded)}$

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

$$K_{b} = \frac{[\text{HNO}_{2}][\text{OH}^{-}]}{[\text{NO}_{2}^{-}]} = \frac{[\text{x}][\text{x}]}{[0.023447857 - \text{x}]} = \frac{[\text{x}][\text{x}]}{[0.023447857]} = 1.40845 \text{ x } 10^{-11}$$

[OH] = x = 5.7467498 x 10⁻⁷ M (unrounded)

 $pOH = -log (5.7467498 \times 10^{-7}) = 6.240577705$ (unrounded)

pH = 14.00 - pOH = 14.00 - 6.240577705 = 7.75942 = 7.76

b) The balanced chemical equations are:

 $\text{KOH}(aq) + \text{H}_2\text{CO}_3(aq) \rightarrow \text{K}^+(aq) + \text{HCO}_3(aq) + \text{H}_2\text{O}(l)$

$$\mathrm{KOH}(aq) + \mathrm{HCO}_{3}(aq) \to \mathrm{K}^{+}(aq) + \mathrm{CO}_{3}(aq) + \mathrm{H}_{2}\mathrm{O}(l)$$

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 =

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

= 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 HCO₃⁻ produced:

$$Moles = \left(\frac{0.130 \text{ mol } H_2CO_3}{L}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (17.3 \text{ mL}) \left(\frac{1 \text{ mol } HCO_3^{-1}}{1 \text{ mol } H_2CO_3}\right)$$

 $= 0.002249 \text{ mol HCO}_3^-$ (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 = $[(17.3 + 38.248299) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.055548 \text{ L} (unrounded)$ Determine the liters of solution present at the second equivalence point:

Volume = $[(17.3 + 38.248299 + 38.248299) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.0937966 \text{ L} (unrounded)$ Concentration of HCO₃⁻ at equivalence point:

Molarity = $(0.002249 \text{ mol HCO}_3) / (0.055548 \text{ L}) = 0.0404875 M$ (unrounded) Concentration of CO_3^{2-} at equivalence point:

Molarity = $(0.002249 \text{ mol } \text{CO}_3^{-2}) / (0.0937966 \text{ L}) = 0.023977 M \text{ (unrounded)}$ Calculate K_b for HCO₃⁻:

e K_b for HCO₃⁻: K_a H₂CO₃ = 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) $e K_b \text{ for } CO_3^{2-}$: $K_a \text{ HCO}_3^- = 4.7 \text{ x } 10^{-11}$ $K_b = K_w / K_a = (1.0 \text{ x } 10^{-14}) / (4.7 \text{ x } 10^{-11}) = 2.1276595 \text{ x } 10^{-4} \text{ (unrounded)}$ Calculate $K_{\rm b}$ for ${\rm CO_3}^2$:

Determine the hydroxide ion concentration from the $K_{\rm b}$, and then determine the pH from the pOH. For the first equivalence point:

$$K_{b} = \frac{\left[H_{2}CO_{3}\right]\left[OH^{-}\right]}{\left[HCO_{3}^{-}\right]} = \frac{\left[x\right]\left[x\right]}{\left[0.0404875 - x\right]} = \frac{\left[x\right]\left[x\right]}{\left[0.0404875\right]} = 2.222 \times 10^{-8}$$

[OH⁻] = x = 2.999387 x 10⁻⁵ *M*
pOH = -log (2.999387 x 10⁻⁵) = 4.522967492 (unrounded)
pH = 14.00 - pOH = 14.00 - 4.522967492 = 9.4770 = **9.48**

For the second equivalence point:

$$K_{\rm b} = \frac{\left[\text{HCO}_3^{-1} \right] \left[\text{OH}^{-1} \right]}{\left[\text{CO}_3^{2^{-1}} \right]} = \frac{\left[x \right] \left[x \right]}{\left[0.023977 - x \right]} = \frac{\left[x \right] \left[x \right]}{\left[0.023977 \right]} = 2.1276595 \text{ x } 10^{-4}$$

[OH⁻] = x = 2.2586476 x 10⁻³ M
pOH = -log (2.2586476 x 10⁻³) = 2.646151515 (unrounded)

pH = 14.00 - pOH = 14.00 - 2.646151515 = 11.3538 = 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 =

$$\left(\frac{0.234 \text{ mol } \text{NH}_3}{\text{L}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(55.5 \text{ mL})\left(\frac{1 \text{ mol } \text{HCl}}{1 \text{ mol } \text{NH}_3}\right)\left(\frac{\text{L}}{0.135 \text{ mol } \text{HCl}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

= 96.2 mL HCl

Determine the moles of NH_4^+ produced:

$$Moles = \left(\frac{0.234 \text{ mol } \text{NH}_3}{\text{L}}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (55.5 \text{ mL}) \left(\frac{1 \text{ mol } \text{NH}_4^+}{1 \text{ mol } \text{NH}_3}\right)$$

 $= 0.012987 \text{ mol NH}_4^+ \text{(unrounded)}$

Determine the liters of solution present at the equivalence point:

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

Concentration of NH_4^+ at equivalence point:

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

Calculate K_a for NH₄⁺: K_b NH₃ = 1.76 x 10⁻⁵ $K_a = K_w / K_b = (1.0 \text{ x } 10^{-14}) / (1.76 \text{ x } 10^{-5}) = 5.6818 \text{ x } 10^{-10} \text{ (unrounded)}$ Determine the hydrogen ion concentration from the K_a , and then determine the pH.

$$K_{a} = \frac{\left\lfloor H_{3}O^{+} \right\rfloor \left\lfloor NH_{3} \right\rfloor}{\left\lfloor NH_{4}^{+} \right\rfloor} = \frac{\left[x\right] \left[x\right]}{\left[0.0856098 - x\right]} = \frac{\left[x\right] \left[x\right]}{\left[0.0856098\right]} = 5.6818 \times 10^{-10}$$

$$x = \left[H_{3}O^{+}\right] = 6.974366 \times 10^{-6} M \text{ (unrounded)}$$

$$x = \left[H_{3}O^{+}\right] = \log \left[H_{3}$$

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

b) The balanced chemical equation is:

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

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

Volume =

$$\left(\frac{1.11 \text{ mol } CH_3 NH_2}{L}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (17.8 \text{ mL}) \left(\frac{1 \text{ mol } HCl}{1 \text{ mol } CH_3 NH_2}\right) \left(\frac{L}{0.135 \text{ mol } HCl}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

= 146.3556 = **146 mL HCl**

Determine the moles of $CH_3NH_3^+$ produced:

$$Moles = \left(\frac{1.11 \text{ mol } CH_3 NH_2}{L}\right) \left(\frac{10^{-3} L}{1 \text{ mL}}\right) (17.8 \text{ mL}) \left(\frac{1 \text{ mol } CH_3 NH_3^+}{1 \text{ mol } CH_3 NH_2}\right)$$

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

Determine the liters of solution present at the equivalence point:

Volume = $[(17.8 + 146.3556) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.1641556 \text{ L} (unrounded)$ Concentration of CH₃NH₃⁺ at equivalence point:

Molarity = $(0.019758 \text{ mol CH}_3\text{NH}_3^+) / (0.161556 \text{ L}) = 0.122298 M \text{ (unrounded)}$ $K_{\rm h}$ CH₃NH₂ = 4.4 x 10⁻⁴ Calculate K_a for CH₃NH₃⁺:

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

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

$$K_{a} = \frac{\begin{bmatrix} H_{3}O^{+} \end{bmatrix} \begin{bmatrix} CH_{3}NH_{2} \end{bmatrix}}{\begin{bmatrix} CH_{3}NH_{3}^{+} \end{bmatrix}} = \frac{\begin{bmatrix} x \end{bmatrix} \begin{bmatrix} x \end{bmatrix}}{\begin{bmatrix} 0.122298 - x \end{bmatrix}} = \frac{\begin{bmatrix} x \end{bmatrix} \begin{bmatrix} x \end{bmatrix}}{\begin{bmatrix} 0.122298 \end{bmatrix}} = 2.2727 \times 10^{-11}$$

x = $\begin{bmatrix} H_{3}O^{+} \end{bmatrix} = 1.66717 \times 10^{-6} M \text{ (unrounded)}$
pH = -log $\begin{bmatrix} H_{3}O^{+} \end{bmatrix} = -\log (1.66717 \times 10^{-6}) = 5.778019 = 5.78$

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 =

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

= 444.63087 = **445 mL HNO**₃

Determine the moles of C₅H₅NH⁺ produced:

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

 $= 0.19875 \text{ mol } C_5H_5NH^+ \text{ (unrounded)}$

Determine the liters of solution present at the equivalence point:

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

Concentration of $C_5H_5NH^+$ at equivalence point:

Molarity = $(0.19875 \text{ mol } C_5H_5NH^+) / (3.09463 \text{ L}) = 0.064224 M (unrounded)$ Calculate K_a for $C_5H_5NH^+$: $K_b C_5H_5N = 1.7 \times 10^{-9}$

 $K_{\rm a} = K_{\rm w} / K_{\rm b} = (1.0 \text{ x } 10^{-14}) / (1.7 \text{ x } 10^{-9}) = 5.88235 \text{ x } 10^{-6} \text{ (unrounded)}$ Determine the hydrogen ion concentration from the $K_{\rm a}$, and then determine the pH.

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[C_{5}H_{5}N\right]}{\left[C_{5}H_{5}NH^{+}\right]} = \frac{\left[x\right]\left[x\right]}{\left[0.064224 - x\right]} = \frac{\left[x\right]\left[x\right]}{\left[0.064224\right]} = 5.88235 \times 10^{-6}$$

$$x = \left[H_{3}O^{+}\right] = 6.1464 \times 10^{-4} M \text{ (unrounded)}$$

$$pH = -\log\left[H_{3}O^{+}\right] = -\log\left(6.1464 \times 10^{-4}\right) = 3.211379 = 3.21$$

b) The balanced chemical equations are:

 $HNO_{3}(aq) + H_{2}NCH_{2}CH_{2}NH_{2}(aq) \rightarrow H_{2}NCH_{2}CH_{2}NH_{3}^{+}(aq) + NO_{3}^{-}(aq)$ $HNO_{3}(aq) + H_{2}NCH_{2}CH_{2}NH_{3}^{+}(aq) \rightarrow H_{3}NCH_{2}CH_{2}NH_{3}^{2+}(aq) + NO_{3}^{-}(aq)$

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 =

$$\left(\frac{0.250 \text{ mol } \text{H}_2\text{NCH}_2\text{CH}_3\text{NH}_2}{\text{L}}\right) (0.188 \text{ L}) \left(\frac{1 \text{ mol } \text{HNO}_3}{1 \text{ mol } \text{H}_2\text{NCH}_2\text{CH}_3\text{NH}_2}\right) \left(\frac{1 \text{ mL}}{0.447 \text{ mol } \text{HNO}_3}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

= 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:

$$Moles = \left(\frac{0.250 \text{ mol } \text{H}_2\text{NCH}_2\text{CH}_3\text{NH}_2}{\text{L}}\right) (0.188 \text{ L}) \left(\frac{1 \text{ mol } \text{H}_2\text{NCH}_2\text{CH}_3\text{NH}_3^+}{1 \text{ mol } \text{H}_2\text{NCH}_2\text{CH}_3\text{NH}_2}\right)$$

 $= 0.0470 \text{ mol } H_2 \text{NCH}_2 \text{CH}_2 \text{NH}_3^+$

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 = $0.188 \text{ L} + (105.1454 \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.293145 \text{ L}$ (unrounded) Determine the liters of solution present at the second equivalence point:

Volume = $0.188 \text{ L} + 2(105.1454 \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.39829 \text{ L}$ (unrounded) Concentration of H₂NCH₂CH₂NH₃⁺ at equivalence point:

Molarity = $(0.0470 \text{ mol H}_2\text{NCH}_2\text{CH}_2\text{NH}_3^+) / (0.293145 \text{ L}) = 0.16033 M \text{ (unrounded)}$ Concentration of H₃NCH₂CH₂NH₃²⁺ at equivalence point:

Molarity = $(0.0470 \text{ mol } \text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3^{2+}) / (0.39829 \text{ L}) = 0.11800 M \text{ (unrounded)}$ Calculate K_a for $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_3^{+}$: $K_b \text{ H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 = 8.5 \text{ x } 10^{-5}$ $K_a = K_w / K_b = (1.0 \text{ x } 10^{-14}) / (8.5 \text{ x } 10^{-5}) = 1.17647 \text{ x } 10^{-10} \text{ (unrounded)}$ Calculate K_a for $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3^{2+}$: $K_b \text{ H}_2\text{NCH}_2\text{CH}_2\text{NH}_3^{+} = 7.1 \text{ x } 10^{-8}$

lculate
$$K_a$$
 for H₃NCH₂CH₂NH₃²⁺: K_b H₂NCH₂CH₂NH₃⁺ = 7.1 x 10
 $K_a = K_w / K_b = (1.0 \text{ x } 10^{-14}) / (7.1 \text{ x } 10^{-8}) = 1.40845 \text{ x } 10^{-7} \text{ (unrounded)}$

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

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[H_{2}NCH_{2}CH_{3}NH_{2}\right]}{\left[H_{2}NCH_{2}CH_{3}NH_{3}^{+}\right]} = \frac{\left[x\right]\left[x\right]}{\left[0.16033 - x\right]} = \frac{\left[x\right]\left[x\right]}{\left[0.16033\right]} = 1.17647 \times 10^{-10}$$

$$x = \left[H_{3}O^{+}\right] = 4.3430799 \times 10^{-6} M \text{ (unrounded)}$$

$$pH = -\log \left[H_{3}O^{+}\right] = -\log \left(4.3430799 \times 10^{-6}\right) = 5.36220 = 5.36$$

Determine the hydrogen ion concentration from the K_{a} , and then determine the pH for the second equivalence point.

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[H_{2}NCH_{2}CH_{3}NH_{3}^{+}\right]}{\left[H_{3}NCH_{2}CH_{3}NH_{3}^{2+}\right]} = \frac{\left[x\right]\left[x\right]}{\left[0.11800 - x\right]} = \frac{\left[x\right]\left[x\right]}{\left[0.11800\right]} = 1.40845 \times 10^{-7}$$

$$x = \left[H_{3}O^{+}\right] = 1.2891745 \times 10^{-4} M \text{ (unrounded)}$$

$$pH = -\log\left[H_{3}O^{+}\right] = -\log\left(1.2891745 \times 10^{-4}\right) = 3.889688 = 3.89$$

19.62 $K_{sp} = [M^+]^2 [X^{2-}]$, assuming M₂X is a strong electrolyte.

S = molar solubility

 $[M^+] = 2 S = 1 \times 10^{-4} M$ $[X^{2-}] = S = 5 \times 10^{-5} M$

The actual K_{sp} is lower than the calculated value because the assumption that M_2X is a strong electrolyte (i.e., exists as $M^+ + X^{2-}$) is in error to some degree. There would be some (probably significant) amount of ion pairing to form $MX^-(aq)$, $M_2X(aq)$, etc., which reduces the effective concentrations of the ions.

19.63 Fluoride ion is the conjugate base of a weak acid. The base hydrolysis reaction of fluoride ion: $F^{-}(aq) + H_2O(l) \iff HF(aq) + OH^{-}(aq)$

is influenced by the pH of the solution. As the pH increases, the equilibrium shifts to the left to increase the $[F^-]$. As the pH decreases, the equilibrium shifts to the right to decrease $[F^-]$. The changes in $[F^-]$ influence the solubility of CaF₂.

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 $CaCl_2$ 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 Ag₂CrO₄ 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) $\operatorname{Ag_2CO_3(s)} \rightleftharpoons 2 \operatorname{Ag^+}(aq) + \operatorname{CO_3^{2-}}(aq)$ Ion-product expression: $K_{sp} = [\operatorname{Ag^+}]^2[\operatorname{CO_3^{2-}}]$ b) $\operatorname{BaF_2(s)} \leftrightarrows \operatorname{Ba^{2+}}(aq) + 2 \operatorname{F^-}(aq)$ Ion-product expression: $K_{sp} = [\operatorname{Ba^{2+}}][\operatorname{F^-}]^2$ c) $\operatorname{CuS}(s) + \operatorname{H_2O}(l) \leftrightarrows \operatorname{Cu^{2+}}(aq) + \operatorname{HS^-}(aq) + \operatorname{OH^-}(aq)$ Ion-product expression: $K_{sp} = [\operatorname{Cu^{2+}}][\operatorname{HS^-}][\operatorname{OH^-}]$

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

Ion-product expression: $K_{sp} = [\operatorname{Fe}^{3^+}] [\operatorname{OH}^-]^3$
b) $\operatorname{Ba}_3(\operatorname{PO}_4)_2(s) \leftrightarrows 3 \operatorname{Ba}^{2^+}(aq) + 2 \operatorname{PO}_4^{3^-}(aq)$
Ion-product expression: $K_{sp} = [\operatorname{Ba}^{2^+}]^3 [\operatorname{PO}_4^{3^-}]^2$
c) $\operatorname{SnS}(s) + \operatorname{H}_2\operatorname{O}(l) \leftrightarrows \operatorname{Sn}^{2^+}(aq) + \operatorname{HS}^-(aq) + \operatorname{OH}^-(aq)$
Ion-product expression: $K_{sp} = [\operatorname{Sn}^{2^+}][\operatorname{HS}^-][\operatorname{OH}^-]$

19.68 a) $\operatorname{CaCrO}_4(s) \leftrightarrows \operatorname{Ca}^{2^+}(aq) + \operatorname{CrO}_4^{2^-}(aq)$ Ion-product expression: $K_{sp} = [\operatorname{Ca}^{2^+}][\operatorname{CrO}_4^{2^-}]$ b) $\operatorname{AgCN}(s) \leftrightarrows \operatorname{Ag}^+(aq) + \operatorname{CN}^-(aq)$ Ion-product expression: $K_{sp} = [\operatorname{Ag}^+][\operatorname{CN}^-]$ c) $\operatorname{NiS}(s) + \operatorname{H}_2\operatorname{O}(l) \leftrightarrows \operatorname{Ni}^{2^+}(aq) + \operatorname{HS}^-(aq) + \operatorname{OH}^-(aq)$ Ion-product expression: $K_{sp} = [\operatorname{Ni}^{2^+}][\operatorname{HS}^-][\operatorname{OH}^-]$ 19.69 a) $\operatorname{PbI}_2(s) \leftrightarrows \operatorname{Pb}^{2^+}(aq) + 2 \operatorname{I}^-(aq)$ Ion-product expression: $K_{sp} = [\operatorname{Pb}^{2^+}][\operatorname{I}^-]^2$ b) $\operatorname{SrSO}_4(s) \leftrightarrows \operatorname{Sr}^{2^+}(aq) + \operatorname{SO}_4^{2^-}(aq)$ Ion-product expression: $K_{sp} = [\operatorname{Sr}^{2^+}][\operatorname{SO}_4^{2^-}]$ c) $\operatorname{CdS}(s) + \operatorname{H}_2\operatorname{O}(l) \leftrightarrows \operatorname{Cd}^{2^+}(aq) + \operatorname{HS}^-(aq) + \operatorname{OH}^-(aq)$

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

- 19.70 Write a reaction table, where S is the molar solubility of Ag₂CO₃: $CO_{3}^{2-}(aq)$ Concentration (*M*) $Ag_2CO_3(s) \Leftrightarrow 2Ag^+(aq) +$ Initial 0 0 + 2 S Change +S2 S S Equilibrium $S = [Ag_2CO_3] = 0.032 M \text{ so } [Ag^+] = 2 S = 0.064 M \text{ and } [CO_3^{2-}] = S = 0.032 M$ $K_{\rm sp} = [{\rm Ag}^+]^2 [{\rm CO}_3^{2-}] = (0.064)^2 (0.032) = 1.31072 \text{ x } 10^{-4} = 1.3 \text{ x } 10^{-4}$
- 19.71 Write a reaction table, where S is the molar solubility of ZnC₂O₄: Concentration (M) $ZnC_2O_4(s) \Leftrightarrow Zn^{2+}(aq) +$ $C_2 O_4^{2-}(aq)$ Initial 0 0 + S Change +SS S Equilibrium $S = [ZnC_2O_4] = 0.032 M \text{ so } [Zn^{2+}] = [C_2O_4^{2-}] = S = 7.9 \text{ x } 10^{-3} M$ $K_{\rm sp} = [Zn^{2+}][C_2O_4^{2-}] = (7.9 \text{ x} 10^{-3})(7.9 \text{ x} 10^{-3}) = 6.241 \text{ x} 10^{-5} = 6.2 \text{ x} 10^{-4}$

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

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

Since 1 mole of Ag₂Cr₂O₇ 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 Cr₂O₇²⁻ is S = 0.00019221861 *M* because 1 mole of Ag₂Cr₂O₇ dissociates to form 1 mole of Cr₂O₇²⁻. $K_{sp} = [Ag^+]^2[Cr_2O_7^{-2}] = (2 S)^2(S) = (0.00038443723)^2(0.00019221861) = 2.8408 \times 10^{-11} = 2.8 \times 10^{-11}$.

19.73 The equation and ion-product expression for calcium sulfate, CaSO₄, is: CaSO₄(s) \Rightarrow Ca²⁺(aq) + SO₄²⁻(aq) $K_{sp} = [Ca^{2+}][SO_4^{2-}]$ The solubility of CaSO₄, converted from g / 100 mL to M is:

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 CaSO₄ dissociates to form 1 mole of Ca²⁺, the concentration of Ca²⁺ is S = 0.015350716 *M* (unrounded). The concentration of SO₄²⁻ is S = 0.015350716 *M* because 1 mole of CaSO₄ dissociates to form 1 mole of SO₄²⁻.

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

19.74 The equation and ion-product expression for SrCO₃ is: SrCO₃(s) \leftrightarrows Sr²⁺(aq) + CO₃²⁻(aq) $K_{sp} = [Sr^{2+}][CO_3^{2-}]$ a) The solubility, S, in pure water equals [Sr²⁺] and [CO₃²⁻] $K_{sp} = 5.4 \times 10^{-10} = [Sr^{2+}][CO_3^{2-}] = S^2$ S = 2.32379 x 10⁻⁵ = **2.3 x 10⁻⁵ M** b) In 0.13 *M* Sr(NO₃)₂, the initial concentration of Sr²⁺ is 0.13 *M*. Equilibrium [Sr²⁺] = 0.13 + S and equilibrium [CO₃²⁻] = S where S is the solubility of SrCO₃. $K_{sp} = 5.4 \times 10^{-10} = [Sr^{2+}][CO_3^{2-}] = (0.13 + S)S$ This calculation may be simplified by assuming S is small and setting (0.13 + S) = (0.13). S = 4.1538 x 10⁻⁹ = **4.2 x 10⁻⁹ M**

19.75 The equation and ion-product expression for SrCO₃ is: BaCrO₄(s) \leftrightarrows Ba²⁺(aq) + CrO₄²⁻(aq) $K_{sp} = [Ba^{2+}][CrO_4^{2-}]$ a) The solubility, S, in pure water equals $[Ba^{2+}]$ and $[CrO_4^{2-}]$ $K_{sp} = 2.1 \times 10^{-10} = [Ba^{2+}][CrO_4^{2-}] = S^2$ $S = 1.4491 \times 10^{-5} = 1.4 \times 10^{-5} M$ b) In 0.13 *M* Na₂CrO₄, the initial concentration of CrO₄²⁻ is 1.5 x 10⁻³ *M*. Equilibrium $[Ba^{2+}] = 1.5 \times 10^{-3} + S$ and equilibrium $[CrO_4^{2-}] = S$ where S is the solubility of BaCrO₄. $K_{sp} = 2.1 \times 10^{-10} = [Ba^{2+}][CrO_4^{2-}] = S(1.5 \times 10^{-3} + S)$ $S = 1.4 \times 10^{-7} M$

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)	$Ca(IO_3)_2(s) \leftrightarrows$	$Ca^{2+}(aq) +$	$2 \operatorname{IO}_3(aq)$
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*.

 $K_{\rm sp} = [{\rm Ca}^{2+}][{\rm IO}_3^{-}]^2 = (0.060) (2 \text{ S})^2 = 7.1 \text{ x } 10^{-7} \text{ S} = 1.71998 \text{ x } 10^{-3} = 1.7 \text{ x } 10^{-3} M$

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 Ca²⁺ and Ca(IO₃)₂, so the molar solubility of Ca(IO₃)₂ is **1.7 x 10⁻³ M**. b) In this case,

Concentration (M)	$Ca(IO_3)_2(s) \leftrightarrows$	$Ca^{2+}(aq) +$	$2 \operatorname{IO}_3(aq)$
Initial		0	0.060
Change	_	+ S	+ 2 S
Equilibrium	_	S	0.060 + 2 S
	2		

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

Assume that $0.060 + 2 \text{ S} \approx 0.060$ $K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^{-}]^2 = (\text{S}) (0.060)^2 = 7.1 \text{ x } 10^{-7}$ $\text{S} = 1.97222 \text{ x } 10^{-4} = 1.9 \text{ x } 10^{-4} M$

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 Ca²⁺ and Ca(IO₃)₂, so the molar solubility of Ca(IO₃)₂ is **2.0 x 10⁻⁴ M**.

The equilibrium is: $Ag_2SO_4(s) \rightleftharpoons 2 Ag^+(aq) + SO_4^{2-}(aq)$ From the Appendix, $K_{sp}(Ag_2SO_4) = 1.5 \times 10^{-5}$. 19.77 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)	$Ag_2SO_4(s)$	与	$2 \operatorname{Ag}^{+}(aq)$	+	$SO_4^{2-}(aq)$
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.

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

S = 3.099175 x 10⁻⁴ = 3.1 x 10⁻⁴

Check assumption: $(3.099175 \times 10^{-4} M) / (0.22 M) \times 100\% = 1.4\% < 5\%$, so the assumption is good. S represents both the molar solubility of SO_4^{2-} and $Ag_2SO_4(s)$, so the molar solubility of $Ag_2SO_4(s)$ is 3.1 x 10⁻⁴ M. b) In this case.

ib cubc,			
Concentration (M)	$Ag_2SO_4(s) \leftrightarrows$	$2 \text{ Ag}^{+}(aq) +$	$SO_4^{2-}(aq)$
Initial	—	0	0.22
Change	_	+2 S	+S
Equilibrium	_	2 S	0.22 + S
·····		a a 2-	

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

Assume that $0.22 + S \approx 0.22$. $K_{\rm sp} = [Ag^+]^2 [SO_4^{2^-}] = (2S)^2 (0.22) = 1.5 \text{ x } 10^{-5}$.

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

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 x 10⁻³ M.

- The larger the K_{sp} , the larger the molar solubility if the number of ions are equal. 19.78 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) **Ag₂SO₄** with $K_{sp} = 1.5 \times 10^{-5}$ has higher molar solubility than MgF₂ 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) SrSO₄ with $K_{sp} = 3.2 \times 10^{-7}$ has higher molar solubility than BaCrO₄ with $K_{sp} = 2.1 \times 10^{-10}$. b) **CaCO₃** with $K_{sp} = 3.3 \times 10^{-9}$ has higher molar solubility than CuCO₃ with $K_{sp} = 3 \times 10^{-12}$. c) **Ba(IO₃)**₂ with $K_{sp} = 1.5 \times 10^{-9}$ has higher molar solubility than Ag₂CrO₄ 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 BaSO₄ 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 Ca₃(PO₄)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 $K_{sp} = 1.8 \times 10^{-10}$.
- The larger the K_{sp} , the more water-soluble the compound if the number of ions are equal. 19.81 a) **Ca(IO₃)**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) **SrCO₃** 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) \leftrightarrows Ag⁺(aq) + Cl⁻(aq)

The chloride ion is the anion of a strong acid, so it does not react with H_3O^+ . Silver ion will not become more soluble at low pH; however, it will become less soluble at high pH, because Ag₂O precipitates at high pH. b) SrCO₃(s) \leftrightarrows Sr²⁺(aq) + CO₃²⁻(aq)

The strontium ion is the cation of a strong base, so pH will not affect its solubility.

The carbonate ion will act as a base:

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

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

The H₂CO₃ will decompose to CO₂(g) and H₂O(l). The gas will escape and further shift the equilibrium. Changes in pH will change the $[CO_3^{2-}]$, so the solubility of SrCO₃ will increase with decreasing pH. **Solubility increases** with addition of H₃O⁺ (decreasing pH).

19.83 a) $\operatorname{CuBr}(s) \leftrightarrows \operatorname{Cu}^+(aq) + \operatorname{Br}^-(aq)$

The bromide ion is the anion of a strong acid, so it does not react with H_3O^+ . At high pH the copper ion may precipitate.

 $Cu^+(aq) + OH^-(aq) \leftrightarrows CuOH(s)$

b) $Ca_3(PO_4)_2(s) \leftrightarrows 3 Ca^{2+}(aq) + 2 PO_4^{3-}(aq)$

The calcium ion is the cation of a strong base so pH will not affect its solubility.

 PO_4^{3-} is the anion of a weak acid, so the following equilibria would be present.

 $PO_4^{3-}(aq) + n H_2O(l) \leftrightarrows H_nPO_4^{(3-n)-}(aq) + n OH^{-}(aq) (n = 1,2,3)$

Since these involve OH^- , the solubility will change with changing pH. Solubility increases with addition of H_3O^+ (decreasing pH).

19.84 a) $\operatorname{Fe}(\operatorname{OH})_2(s) \leftrightarrows \operatorname{Fe}^{2+}(aq) + 2 \operatorname{OH}^-(aq)$

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 H_3O^+ (decreasing pH).

b) $\operatorname{CuS}(s) + \operatorname{H}_2\operatorname{O}(l) \leftrightarrows \operatorname{Cu}^{2+}(aq) + \operatorname{HS}^-(aq) + \operatorname{OH}^-(aq)$

Both HS⁻ and OH⁻ are anions of weak acids, so both ions react with added H_3O^+ . Solubility increases with addition of H_3O^+ (decreasing pH).

- a) PbI₂(s) ≒ Pb²⁺(aq) + 2 Γ(aq). The iodide ion is the anion of a strong acid, so it does not react with H₃O⁺. Thus, the solubility does not increase in acid solution. At high pH the lead ion may precipitate.
 b) Hg₂(CN)₂(s) ≒ Hg₂²⁺(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) + H₂O(I) ≒ HCN(aq) + OH⁻(aq) Since this involves OH⁻, it would shift with changing pH.
- 19.86 The ion-product expression for Cu(OH)₂ is $K_{sp} = [Cu^{2+}][OH^{-}]^2$ and, from the Appendix, K_{sp} equals 2.2 x 10⁻²⁰. To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp} .

$$[\operatorname{Cu}^{2+}] = \left(\frac{1.0 \text{ x } 10^{-3} \text{ mol } \operatorname{Cu}(\operatorname{NO}_3)_2}{\mathrm{L}}\right) \left(\frac{1 \text{ mol } \operatorname{Cu}^{2+}}{1 \text{ mol } \operatorname{Cu}(\operatorname{NO}_3)_2}\right) = 1.0 \text{ x } 10^{-3} M \operatorname{Cu}^{2+}$$
$$[\operatorname{OH}^-] = \left(\frac{0.075 \text{ g } \text{ KOH}}{1.0 \text{ L}}\right) \left(\frac{1 \text{ mol } \text{KOH}}{56.11 \text{ g } \text{ KOH}}\right) \left(\frac{1 \text{ mol } \text{OH}^-}{1 \text{ mol } \text{KOH}}\right) = 1.33666 \text{ x } 10^{-3} M \operatorname{OH}^- \text{ (unrounded)}$$
$$Q_{\rm sp} = (1.0 \text{ x } 10^{-3}) (1.33666 \text{ x } 10^{-3})^2 = 1.7866599 \text{ x } 10^{-9} \text{ (unrounded)}$$
$$Q_{\rm sp} \text{ is greater than } K_{\rm sp} (1.8 \text{ x } 10^{-9} > 2.2 \text{ x } 10^{-20}), \text{ so } \operatorname{Cu}(\operatorname{OH})_2 \text{ will precipitate.}$$

The ion-product expression for PbCl₂ is $K_{sp} = [Pb^{2+}][Cl^{-}]^2$ and, from the Appendix, K_{sp} equals 1.7 x 10⁻⁵. To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp} . 19.87

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

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

$$Q_{sp} = (0.12) (2.3952 \text{ x } 10^{-4})^2 = 6.8843796 \text{ x } 10^{-9} \text{ (unrounded)}$$

$$Q_{sp} \text{ is greater than } K_{sp} (6.9 \text{ x } 10^{-9} < 1.7 \text{ x } 10^{-5}), \text{ so } PbCl \text{ will not precipitate.}$$

The ion-product expression for Ba(IO₃)₂ is $K_{sp} = [Ba^{2+}][IO_3^-]^2$ and, from the Appendix, K_{sp} equals 1.5 x 10⁻⁹. To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp} . 19.88

$$[\operatorname{Ba}^{2+}] = \left(\frac{6.5 \text{ mg BaCl}_2}{500 \text{ mL}}\right) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right) \left(\frac{1 \text{ mol BaCl}_2}{208.2 \text{ g BaCl}_2}\right) \left(\frac{1 \text{ mol Ba}^{2+}}{1 \text{ mol BaCl}_2}\right)$$
$$= 6.2439961 \text{ x } 10^{-5} \text{ M Ba}^{2+} \text{ (unrounded)}$$
$$[\operatorname{IO}_3^-] = \left(\frac{0.033 \text{ mol NaIO}_3}{\text{L}}\right) \left(\frac{1 \text{ mol IO}_3^-}{1 \text{ mol NaIO}_3}\right) = 0.033 \text{ M IO}_3^-$$
$$Q_{\rm sp} = [\operatorname{Ba}^{2+}][\operatorname{IO}_3^-]^2 = (6.2439961 \text{ x } 10^{-5}) (0.033)^2 = 6.7997 \text{ x } 10^{-8} \text{ (unrounded)}$$
Since $Q_{\rm sp} > K_{\rm sp} (6.8 \text{ x } 10^{-8} > 1.5 \text{ x } 10^{-9}), \operatorname{Ba}(\operatorname{IO}_3)_2 \text{ will precipitate.}$

The ion-product expression for Ag₂CrO₄ is $K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$ and, from the Appendix, K_{sp} equals 2.6 x 10⁻¹². To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp} . 19.89

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

$$[CrO_{4}^{2-}] = \left(\frac{4.0 \times 10^{-4} \text{ mol } \text{K}_{2}\text{CrO}_{4}}{\text{L}}\right) \left(\frac{1 \text{ mol } \text{CrO}_{4}^{2-}}{1 \text{ mol } \text{K}_{2}\text{CrO}_{4}}\right) = 4.0 \times 10^{-4} M \text{ IO}_{3}^{-1}$$

$$Q_{\text{sp}} = [Ba^{2+}][IO_{3}^{-}]^{2} = (1.0594467 \times 10^{-5})^{2}(4.0 \times 10^{-4}) = 4.4897 \times 10^{-14} \text{ (unrounded)}$$
Since $Q_{\text{sp}} < K_{\text{sp}} (4.5 \times 10^{-14} < 2.6 \times 10^{-12}), \text{ Ag}_{2}\text{CrO}_{4} \text{ will not precipitate.}$

19.90 Original moles of
$$Ca^{2+} = (9.7 \text{ x } 10^{-5} \text{ g } Ca^{2+} / \text{mL}) (104 \text{ mL}) = 0.010088 \text{ mol } Ca^{2+} (\text{unrounded})$$

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

The Ca²⁺ is limiting leaving 0 M, and after the reactions there will be (0.01550 - 0.010088) mol of C₂O₄² remaining.

$$[C_{2}O_{4}^{2-}] = \left(\frac{(0.01550 - 0.010088) \operatorname{mol} C_{2}O_{4}^{2-}}{(104 + 100.0) \operatorname{mL}}\right) \left(\frac{1 \operatorname{mL}}{10^{-3} \operatorname{L}}\right) = 0.0265294 M \operatorname{C}_{2}O_{4}^{2-} \text{ (unrounded)}$$

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

$CaC_2O_4 \cdot H_2O(s)$	ţ	$Ca^{2+}(aq)$	+	$C_2O_4^{2-}(aq) +$	-	$H_2O(l)$
—		0		0.0265294		
_		+S		+ S		
_		S		0.0265294 + S		—
	$CaC_2O_4 \bullet H_2O(s)$	$CaC_2O_4 \bullet H_2O(s) \leftrightarrows$	$\begin{array}{ccc} \operatorname{CaC}_2\operatorname{O}_4 \cdot \operatorname{H}_2\operatorname{O}(s) & \leftrightarrows & \operatorname{Ca}^{2+}(aq) \\ - & & 0 \\ - & & + S \\ - & & S \end{array}$	$\begin{array}{ccc} \operatorname{CaC}_2 \mathcal{O}_4 \bullet \mathcal{H}_2 \mathcal{O}(s) & \leftrightarrows & \operatorname{Ca}^{2^+}(aq) & + \\ - & & 0 \\ - & & + S \\ - & & S \end{array}$	$\begin{array}{cccc} CaC_2O_4 \bullet H_2O(s) & \leftrightarrows & Ca^{2+}(aq) & + & C_2O_4^{-2-}(aq) & + \\ & & & 0 & & 0.0265294 \\ & & +S & + S & \\ & & S & & 0.0265294 + S \end{array}$	$\begin{array}{cccc} CaC_2O_4 \bullet H_2O(s) &\leftrightarrows & Ca^{2+}(aq) &+ & C_2O_4^{2-}(aq) &+ \\ & & & 0 & & 0.0265294 \\ & & +S & & +S \\ & & S & & 0.0265294 + S \end{array}$

Assume that $0.0265294 + S \approx 0.0265294$ because the amount of compound that dissolves will be negligible in comparison to 0.0265294 M. The K_{sp} from the Appendix is: 2.3 x 10^{-9} $K_{sp} = [Ca^{2+}][C_2O_4^{-2-}] = (S) (0.0265294) = 2.3 x <math>10^{-9}$. $S = 8.6696269 x 10^{-8} = 8.7 x 10^{-8}$

Check assumption: $(8.6696269 \times 10^{-8} M) / (0.0265294 M) \times 100\% = 0.0003\% < 5\%$, so the assumption is good. S represents both the molar solubility of Ca²⁺ and CaC₂O₄•H₂O(*s*), so the concentration of Ca²⁺ is **8.7 x 10⁻⁸ M**.

19.91 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.

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$$19.92 \quad Cd(H_{2}O)_{4}^{2^{+}}(aq) + \Gamma(aq) \leftrightarrows CdI(H_{2}O)_{3}^{+}(aq) + H_{2}O(l) \qquad K_{f1} = \frac{\left[CdI(H_{2}O)_{3}^{+}\right]}{\left[Cd(H_{2}O)_{2}^{2^{+}}\right]\left[\Gamma^{-}\right]} \\ CdI(H_{2}O)_{3}^{+}(aq) + \Gamma(aq) \leftrightarrows CdI_{2}(H_{2}O)_{2}(aq) + H_{2}O(l) \qquad K_{f2} = \frac{\left[CdI_{2}(H_{2}O)_{2}\right]}{\left[CdI(H_{2}O)_{3}^{+}\right]\left[\Gamma^{-}\right]} \\ CdI_{2}(H_{2}O)_{2}(aq) + \Gamma(aq) \leftrightarrows CdI_{3}(H_{2}O)^{-}(aq) + H_{2}O(l) \qquad K_{f3} = \frac{\left[CdI_{3}(H_{2}O)^{-}\right]}{\left[CdI_{2}(H_{2}O)_{2}\right]\left[\Gamma^{-}\right]} \\ CdI_{3}(H_{2}O)^{-}(aq) + \Gamma(aq) \leftrightarrows CdI_{4}^{2^{-}}(aq) + H_{2}O(l) \qquad K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[CdI_{3}(H_{2}O)^{-}\right]\left[\Gamma^{-}\right]} \\ Overall: Cd(H_{2}O)^{2^{+}}_{4}(aq) + 4\Gamma(aq) \leftrightarrows CdI_{4}^{2^{-}}(aq) + 4H_{2}O(l) \qquad K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[CdI(H_{2}O)_{4}^{2^{+}}\right]\left[\Gamma^{-}\right]} \\ K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[CdI_{4}(H_{2}O)_{4}^{2^{+}}\right]\left[\Gamma^{-}\right]} \\ K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[Cd(H_{2}O)_{4}^{2^{+}}\right]\left[\Gamma^{-}\right]} \\ K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[CdI(H_{2}O)_{4}^{2^{+}}\right]\left[\Gamma^{-}\right]} \\ K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[CdI_{4}(H_{2}O)_{4}^{2^{+}}\right]\left[\Gamma^{-}\right]} \\ K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[CdI_{4}(H_{2}O)_{4}^{2^{+}}\right]\left[\Gamma^{-}\right]} \\ K_{f4} = \frac{\left[CdI_{4}(H_{2}O)_{4}^{2^{+}}\right]\left[\Gamma^{-}\right]}{\left[CdI_{4}(H_{2}O)_{4}^{2^{+}}\right]\left[\Gamma^{-}\right]} \\ K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[CdI_{4}(H_{2}O)_{4}^{2^{+}}\right]\left[\Gamma^{-}\right]} \\ K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[CdI_{4}^{2^{-}}\right]} \\ K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[CdI_{4}^{2^{-}}\right]} \\ K_{f4} = \frac{\left[CdI_{4}^{2^{-}}\right]}{\left[CdI_{4}^{2^{$$

19.93 In the context of this equilibrium only, the increased solubility with added OH⁻ appears to be a violation of Le Châtelier's Principle. 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:

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

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

19.94 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^{-}),

 $\operatorname{Hg}(\operatorname{H}_2\operatorname{O})_4^{2^+}(aq) + 4 \operatorname{CN}^-(aq) \leftrightarrows \operatorname{Hg}(\operatorname{CN})_4^{2^-}(aq) + 4 \operatorname{H}_2\operatorname{O}(l)$

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.

19.95
$$\operatorname{Zn}(\operatorname{H}_2\operatorname{O})_4^{2^+}(aq) + 4 \operatorname{CN}^-(aq) \leftrightarrows \operatorname{Zn}(\operatorname{CN})_4^{2^-}(aq) + 4 \operatorname{H}_2\operatorname{O}(l)$$

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

19.97
$$Al(H_2O)_6^{3+}(aq) + 6 F(aq) \leftrightarrows AlF_6^{3-}(aq) + 6 H_2O(l)$$

19.98 The reaction between SCN⁻ and Fe³⁺ produces the red complex FeSCN²⁺. One can assume from the much larger concentration of SCN⁻ and large K_f that all of the Fe³⁺ ions react to form the complex. Calculate the initial concentrations of SCN⁻ and Fe³⁺ and write a reaction table in which x is the concentration of FeSCN²⁺ formed.

$$[Fe^{3+}]_{initial} = \frac{\left(0.0015 \text{ M Fe}(\text{NO}_3)_3\right)\left(0.50 \text{ L}\right)}{\left(\left(0.50+0.50\right)\text{ L}\right)} \left(\frac{1 \text{ mol Fe}^{3+}}{1 \text{ mol Fe}(\text{NO}_3)_3}\right) = 0.00075 \text{ M Fe}^{3+}$$

$$[SCN^-]_{initial} = \frac{\left(0.20 \text{ M KSCN}\right)\left(0.50 \text{ L}\right)}{\left(\left(0.50+0.50\right)\text{ L}\right)} \left(\frac{1 \text{ mol SCN}^-}{1 \text{ mol KSCN}}\right) = 0.10 \text{ M SCN}^-$$
Set up a reaction table:
Concentration (M) Fe^{3+}(aq) + SCN^-(aq) \leftrightarrows FeSCN^{2+}
Initial 7.5 x 10⁻⁴ 0.10 0
Change - x - x + x
Equilibrium 7.5 x 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:

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

x = (7.5 x 10⁻⁴ - x) (0.10) (8.9 x 10²) = (7.5 x 10⁻⁴ - x) (89)
x = 6.675 x 10⁻² - 89 x (unrounded)
x = 7.416667 x 10⁻⁴
From the reaction table, [Fe³⁺]_{eq} = 7.5 x 10⁻⁴ - x. Therefore, [Fe³⁺]_{eq} = 7.5 x 10⁻⁴ - 7.416667 x 10⁻⁴
= 8.33333 x 10⁻⁶ = 1 x 10⁻⁵ M.

19.99
$$\operatorname{Ag}^{+}(aq) + 2 \operatorname{S}_{2}\operatorname{O}_{3}^{2-}(aq) \leftrightarrows \operatorname{Ag}(\operatorname{S}_{2}\operatorname{O}_{3})_{2}^{3-}(aq)$$

The initial concentrations may be determined from $M_{\rm con}V_{\rm con} = M_{\rm dil}V_{\rm dil}$ $[Ag^{+}] = (0.44 M) (25.0 mL) / ((25.0 + 25.0) mL) = 0.022 M Ag^{+}$ $[S_2O_3^{2-}] = (0.57 M) (25.0 mL) / ((25.0 + 25.0) mL) = 0.285 M S_2O_3^{2-}$ (unrounded) The reaction gives: $\begin{array}{rcl} 2 \ S_2 O_3^{2^-}(aq) & \to & \mathrm{Ag}(S_2 O_3)_2^{3^-}(aq) \\ 0.285 & & 0 \end{array}$ Concentration (*M*) $Ag^+(aq) +$ Initial 0.022 Change 0.022 - 2 (0.022) +0.0220 Equilibrium 0.241 0.022 To reach equilibrium: $\begin{array}{rcl} 2 \ S_2 O_3^{2-}(aq) & \leftrightarrows & Ag(S_2 O_3)_2^{3-}(aq) \\ 0.241 & & 0.022 \end{array}$ $Ag^+(aq) +$ Concentration (M)0 Initial + 2 x Change + x+x+ x0.241 + 2 x0.022 + xEquilibrium $K_{\rm f}$ is large, so $[{\rm Ag}({\rm S}_{2}{\rm O}_{3})_{2}^{3^{-}}] \approx 0.022 M$ and $[{\rm S}_{2}{\rm O}_{3}^{2^{-}}]_{\rm equil} \approx 0.241 M$ (unrounded) $K_{\rm f} = \frac{\left[{\rm Ag} ({\rm S}_2 {\rm O}_3)_2^{3-} \right]}{\left[{\rm Ag}^+ \right] \left[{\rm S}_2 {\rm O}_3^{2-} \right]^2} = \frac{\left[0.022 \right]}{\left[{\rm x} \right] \left[0.241 \right]^2} = 4.7 \, {\rm x} \, 10^{13}$

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

19.100 The complex formation equilibrium is

$$Zn^{2+}(aq) + 4 CN^{-}(aq) \rightleftharpoons Zn(CN)_{4}^{2-}(aq) \qquad K_{f} = 4.2 \times 10^{19}$$

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.

$$Moles Zn^{2+} = (0.82 \text{ g } ZnCl_2) \left(\frac{1 \text{ mol } ZnCl_2}{136.31 \text{ g } ZnCl_2}\right) \left(\frac{1 \text{ mol } Zn^{2+}}{1 \text{ mol } ZnCl_2}\right) = 0.006015699 \text{ mol } Zn^{2+} \text{ (unrounded)}$$
$$Moles CN^- = \left(\frac{0.150 \text{ mol } NaCN}{L}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (255 \text{ mL}) \left(\frac{1 \text{ mol } CN^-}{1 \text{ mol } NaCN}\right) = 0.03825 \text{ mol } CN^- \text{ (unrounded)}$$

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: [0.03825 - 4(0.00615699)]

$$[CN^{-}] = \frac{\left[0.03825 - 4(0.00615699)\right] \text{mol CN}^{-}}{(255 \text{ mL})} \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right) = 0.053419764 \text{ M CN}^{-} \text{ (unrounded)}$$

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

$$[Zn(CN)_{4}^{2-}] = \left(\frac{0.006105699 \text{ mol } Zn^{2+}}{255 \text{ mL}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right) \left(\frac{1 \text{ mol } Zn(CN)_{4}^{2-}}{1 \text{ mol } Zn^{2+}}\right) = 0.023943917 M Zn(CN)_{4}^{2-}$$

Concentration (M) $Zn^{2+}(aq) + 4 CN^{-}(aq) \leftrightarrows Zn(CN)_{4}^{2-}(aq)$
Initial $0 \qquad 0.053419764 \qquad 0.023943917$
Change $+x \qquad +4x \qquad -x$
Equilibrium $x \qquad 0.053419764 + 4x \qquad 0.023943917 - x$

Assume the -x and the +4x do not significantly change the associated concentrations. Г 2 7

$$K_{\rm f} = \frac{\left[Zn \left(CN \right)_{4}^{2^{-}} \right]}{\left[Zn^{2^{+}} \right] \left[CN^{-} \right]^{4}} = \frac{\left[0.023943917 - x \right]}{\left[x \right] \left[0.053419764 + 4x \right]^{4}} = \frac{\left[0.023943917 \right]}{\left[x \right] \left[0.053419764 \right]^{4}} = 4.2 \times 10^{19}$$

$$x = 7.000645 \times 10^{-17} = 7.0 \times 10^{-17}$$

$$[Zn^{2^{+}}] = 7.0 \times 10^{-17} M Zn^{2^{+}}$$

$$[Zn(CN)_{4}^{2^{-}}] = 0.023943917 - x = 0.023943917 = 0.024 M Zn(CN)_{4}^{2^{-}}$$

$$[CN^{-}] = 0.053419764 + 4 \times 0.053419764 = 0.053 M CN^{-}$$

19.101 The complex formation equilibrium is

 $\operatorname{Co}^{2^+}(aq) + 4 \operatorname{OH}^-(aq) \leftrightarrows \operatorname{Co}(\operatorname{OH})_4^{2^-}(aq) K_f = 5 \ge 10^9$ 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.

$$Moles Co^{2+} = \left(2.4 \text{ g } Co(NO_3)_2\right) \left(\frac{1 \text{ mol } Co(NO_3)_2}{182.95 \text{ g } Co(NO_3)_2}\right) \left(\frac{1 \text{ mol } Co^{2+}}{1 \text{ mol } Co(NO_3)_2}\right) = 0.013118 \text{ mol } Co^{2+} \text{ (unrounded)}$$
$$Moles OH^- = \left(\frac{0.22 \text{ mol } KOH}{L}\right) (0.350 \text{ L}) \left(\frac{1 \text{ mol } OH^-}{1 \text{ mol } KOH}\right) = 0.077 \text{ mol } OH^-$$
$$The Co^{2+} is discription after the co^{2+} = 0 \text{ mol } the males a following the second second$$

The Co^{2+} is limiting, thus, $[Co^{2+}] = 0$, and the moles of OH⁻ remaining are: [0.077 - 4(0.013118)] $[OH^{-}] = \frac{\left[0.077 - 4(0.013118)\right] \text{mol} OH^{-}}{(0.350 \text{ L})} = 0.07008 M \text{ OH}^{-} \text{ (unrounded)}$

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

$$[Co(OH)_{4}^{2^{-}}] = \left(\frac{0.013118 \text{ mol } Co^{2^{+}}}{0.350 \text{ L}}\right) \left(\frac{1 \text{ mol } Co(OH)_{4}^{2^{-}}}{1 \text{ mol } Co^{2^{+}}}\right) = 0.03748 M \text{ Co}(OH)_{4}^{2^{-}} (\text{unrounded})$$
Concentration (M) Co²⁺(aq) + 4 OH⁻(aq) \leftrightarrows Co(OH)₄²⁻(aq)
Initial 0 0 0.07008 0.03748
Change +x +4x -x
Equilibrium x 0.07008 +4 x 0.03748 - x
Assume the x and the + 4x do not significantly change the associated concentrations

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

$$K_{\rm f} = \frac{\left[\operatorname{Co}(\operatorname{OH})_{4}^{2^{-}}\right]}{\left[\operatorname{Co}^{2^{+}}\right]\left[\operatorname{OH}^{-}\right]^{4}} = \frac{\left[0.03748 - \mathrm{x}\right]}{\left[\mathrm{x}\right]\left[0.07008 + 4\mathrm{x}\right]^{4}} = \frac{\left[0.03748\right]}{\left[\mathrm{x}\right]\left[0.07008\right]^{4}} = 5 \times 10^{9}$$

x = 3.1078 x 10⁻⁷ = 3.1 x 10⁻⁷
[Co²⁺] = **3.1 x 10⁻⁷ M Co²⁺**
[Co(OH)₄²⁻] = 0.03748 - x = 0.037479689 = **0.037 M Co(OH)₄²⁻**
[OH⁻] = 0.07008 + 4 x = 0.070078756 = **0.070 M OH**⁻

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: $AgI(s) \leftrightarrows Ag^{+}(aq) + I^{-}(aq)$ Complex-ion: $Ag^+(aq) + 2 NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq)$ Overall: $AgI(s) + 2 NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq) + I^-(aq)$ $K_{\text{overall}} = K_{\text{sp}} \times K_{\text{f}} = (8.3 \times 10^{-17}) (1.7 \times 10^7) = 1.411 \times 10^{-9} \text{ (unrounded)}$ Reaction table: Concentration (M)AgI(s)+ $2 \operatorname{NH}_3(aq) \leftrightarrows$ $\operatorname{Ag}(\operatorname{NH}_3)_2^+(aq) + I^-(aq)$ Initial 2.5 0 0 + S Change - 2 S +SEquilibrium 2.5 - 2 S Assume that $2.5 - 2S \approx 2.5$ because K_{overall} is so small. $\begin{bmatrix} & (\mathbf{x}_{\mathbf{T}\mathbf{T}}) + \end{bmatrix} \begin{bmatrix} \mathbf{z}_{\mathbf{T}} \end{bmatrix}$

$$K_{\text{overall}} = \frac{\left\lfloor \text{Ag}(\text{NH}_{3})_{2} \right\rfloor \left\lfloor 1 \right\rfloor}{\left[\text{NH}_{3} \right]^{2}} = \frac{\left[\text{S} \right] \left[\text{S} \right]}{\left[2.5 - \text{S} \right]^{2}} = \frac{\left[\text{S} \right] \left[\text{S} \right]}{\left[2.5 \right]^{2}} = 1.411 \text{ x } 10^{-9}$$

S = 9.3908 x 10⁻⁵ = **9.4 x 10⁻⁵** M

19.103 Solubility-Product: $\operatorname{Cr}(\operatorname{OH})_3(s) \leftrightarrows \operatorname{Cr}^{3+}(aq) + 3\operatorname{OH}^{-}(aq) K_{sp} = 6.3 \times 10^{-31}$ Complex-Ion $\operatorname{Cr}^{3+}(aq) + 4\operatorname{OH}^{-}(aq) \leftrightarrows \operatorname{Cr}(\operatorname{OH})_4(aq) K_{f} = 8.0 \times 10^{29}$ Overall: $Cr(OH)_3(s) + OH^2(aq) \leftrightarrows Cr(OH)_4(aq)$ At pH 13.0, the pOH is 1.0 and $[OH^2] = 10^{-1.0} = 0.1 M$. $K = K_{sp}K_f = 0.504$ (unrounded) $\begin{bmatrix} a & (arr) & - \end{bmatrix}$

$$K_{\text{overall}} = \frac{\left\lfloor \text{Cr}(\text{OH})_{4}^{-} \right\rfloor}{\left\lfloor \text{OH}^{-} \right\rfloor} = \frac{\left[\text{S}\right]}{\left[0.1\right]} = 0.504$$
$$\text{S} = \left[\text{Cr}(\text{OH})_{4}^{-}\right] = 0.0504 = 0.05 M$$

19.104 a) Fe(OH)₃ will precipitate first because its K_{sp} (1.6 x 10⁻³⁹) is smaller than the K_{sp} for Cd(OH)₂ at 7.2 x 10⁻¹⁵. The precipitation reactions are:

 $\operatorname{Fe}^{3+}(aq) + 3 \operatorname{OH}^{-}(aq) \rightarrow \operatorname{Fe}(\operatorname{OH})_{3}(s)$

 $Cd^{2+}(aq) + 2 OH(aq) \rightarrow Cd(OH)_{2}(s)$ The concrutations of Fe³⁺ and Cd²⁺ in the mixed solution are found from $M_{conc}V_{conc} = M_{dil}V_{dil}$ $[Fe^{3+}] = [(0.50 M) (50.0 mL)] / [(50.0 + 125) mL] = 0.142857 M Fe^{3+} (unrounded)$ $[Cd^{2+}] = [(0.25 M) (125 mL)] / [(50.0 + 125) mL] = 0.178571 M Cd^{2+} (unrounded)$ The hydroxide ion concentration required to precipitate the metal ions comes from the metal ion concentrations and the $K_{\rm sp}$.

$$[OH^{-}]_{Fe} = \sqrt[3]{\frac{K_{sp}}{\left[Fe^{3^{+}}\right]}} = \sqrt[3]{\frac{1.6 \times 10^{-39}}{\left[0.142857\right]}} = 2.237 \times 10^{-13} = 2.2 \times 10^{-13} M$$
$$[OH^{-}]_{Cd} = \sqrt{\frac{K_{sp}}{\left[Cd^{2^{+}}\right]}} = \sqrt{\frac{7.2 \times 10^{-15}}{\left[0.178571\right]}} = 2.0079864 \times 10^{-7} = 2.0 \times 10^{-7} M$$

A lower hydroxide ion concentration is required to precipitate the Fe³⁺.

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 $[OH^{-}] = 2.0 \times 10^{-7} M$.

19.105 a) The concentration may be found from K_{a1} for H₂S:

$$K_{a1} = \frac{\left\lfloor H_3 O^+ \right\rfloor \left\lfloor HS^- \right\rfloor}{\left[H_2 S\right]} = 9 \times 10^{-8} = \frac{\left[0.3\right] \left\lfloor HS^- \right\rfloor}{\left[0.1\right]}$$
$$[HS^-] = 3 \times 10^{-8} M$$

b) Potassium will not precipitate because its sulfide is soluble. If $[H_3O^+] = 0.3 M$ then $[OH^-] = K_w / [H_3O^+] = 1.0 \times 10^{-14} / 0.3 = 3.333 \times 10^{-14} M$ (unrounded) For silver sulfide $Q_{sp} = [Ag^+]^2 [HS^-][OH^-] = [0.01]^2 [3 \times 10^{-8}] [3.333 \times 10^{-14}] = 9.999 \times 10^{-26} = 1 \times 10^{-25}$ For the divalent metal ions: $Q_{sp} = [M^{2+}][HS^-][OH^-] = [0.01][3 \times 10^{-8}] [3.333 \times 10^{-14}] = 9.999 \times 10^{-24} = 1 \times 10^{-23}$ The K_{sp} values may be found in the Appendix: $Ag_2S = 8 \times 10^{-48}$; PbS = 3 $\times 10^{-25}$; MnS = 3 $\times 10^{-11}$; HgS = 2 $\times 10^{-50}$; $CuS = 8 \times 10^{-34}$; NiS = 3 $\times 10^{-16}$; FeS = 8 $\times 10^{-16}$

If $Q_{sp} > K_{sp}$ the metal would precipitate. The metal ions that will precipitate are: **Pb**²⁺, **Hg**²⁺, **Cu**²⁺, **and Ag**⁺.

19.106 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 p K_a is -log (6.3 x 10⁻⁵) = 4.201 (unrounded). The reaction of benzoic acid with sodium hydroxide is:

$$C_{6}H_{5}COOH(aq) + NaOH(aq) \rightarrow Na^{+}(aq) + C_{6}H_{5}COO^{-}(aq) + H_{2}O(l)$$

$$Moles of C_{6}H_{5}COOH = \left(\frac{0.200 \text{ mol } C_{6}H_{5}COOH}{L}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (475 \text{ mL}) = 0.0950 \text{ mol } C_{6}H_{5}COOH$$

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

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:

$$\begin{bmatrix} C_6H_5COOH \end{bmatrix} = \left(\frac{0.045 \text{ mol } C_6H_5COOH}{(475+25) \text{ mL}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right) = 0.090 \text{ } M \text{ } C_6H_5COOH \\ \begin{bmatrix} C_6H_5COO^- \end{bmatrix} = \left(\frac{0.050 \text{ mol } C_6H_5COO^-}{(475+25) \text{ mL}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right) = 0.10 \text{ } M \text{ } C_6H_5COO^- \\ \end{bmatrix}$$

Calculating the pH from the Henderson-Hasselbalch equation:

 $pH = pK_a + \log [C_6H_5COO^-] / [C_6H_5COOH] = 4.201 + \log (0.10) / (0.090) = 4.24676 = 4.2$

Calculations on formic acid (HCOOH) also use the Henderson-Hasselbalch equation. The K_a for formic acid is (see the Appendix) 1.8 x 10⁻⁴ and the $pK_a = -\log (1.8 \times 10^{-4}) = 3.7447$ (unrounded). The formate to formic acid ratio may now be determined:

pH = pK_a + log [HCOO⁻] / [HCOOH] = 4.24676 = 3.7447 + log [HCOO⁻] / [HCOOH] log [HCOO⁻] / [HCOOH] = 4.24676 - 3.7447 = 0.50206 [HCOO⁻] / [HCOOH] = 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. 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:

 $V_a + V_b = 0.500 L$

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 = $(2.00 \text{ mol NaOH} / \text{L}) (\text{V}_{\text{h}}) = 2.00 \text{ V}_{\text{h}} \text{ mol}$ Total moles HCOOH = $(0.200 \text{ mol HCOOH} / \text{L}) (\text{V}_a) = 0.200 \text{ V}_a \text{ mol}$ 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 $2.00 V_{\rm b} \text{ mol} = 3.177313 (0.200 V_{\rm a} - 2.00 V_{\rm b}) \text{ mol}$ $2.00 V_{b} = 0.6354626 V_{a} - 6.354626 V_{b}$ $8.354626 V_{\rm b} = 0.6354626 V_{\rm a}$ The volume relationship given above gives $V_a = (0.500 - V_b) L$ $8.354626 V_b = 0.6354626 (0.500 - V_b)$ $8.354626 V_{b} = 0.3177313 - 0.6354626 V_{b}$ $8.6723573 V_{\rm b} = 0.3177313$ $V_b = 0.036637247 = 0.037 L NaOH$ $V_a = 0.500 - 0.036637247 = 0.463362752 = 0.463 L HCOOH$ Limitations due to the significant figures lead to a solution with only an approximately correct pH.

19.107 $pK_a = -\log 6.3 \ge 10^{-8} = 7.200659$ (unrounded). The K_a comes from the Appendix; it is K_{a2} for phosphoric acid. $pH = pK_a + \log [base] / [acid]$ $7.00 = 7.200659 + \log [HPO_4^{2-}] / [H_2PO_4^{-}]$ $[HPO_4^{2-}] / [H_2PO_4^{-}] = 0.63000$ (unrounded) Since they are equimolar, $V_{HPO_4^{2-}} / V_{H_2PO_4} = 0.63000$ and $V_{HPO_4^{2-}} + V_{H_2PO_4} = 100$. mL so $V_{H_2PO_4^{-}} + (0.63000)V_{H_2PO_4^{-}} = 100$. mL $V_{HPO_4^{2-}} = 39 \text{ mL}$ and $V_{H_2PO_4^{-}} = 61 \text{ mL}$

19.108 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 x 10⁻⁴ and the p K_a = -log (1.8 x 10⁻⁴) = 3.7447 (unrounded). a) The Henderson-Hasselbalch equation gives the component ratio, [HCOO⁻] / [HCOOH]:

pH = pK_a + log [HCOO⁻] / [HCOOH] = 3.74 = 3.7447 + log [HCOO⁻] / [HCOOH] log [HCOO⁻] / [HCOOH] = 3.74 - 3.7447 = -0.0047 [HCOO⁻] / [HCOOH] = 0.989236 = **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⁻.

$$HCOOH(aq) + NaOH(aq) \rightarrow HCOO^{-}(aq) + Na^{+}(aq) + H_{2}O(l)$$

$$[HCOO^{-}] = (1.0 \text{ M NaOH}) \left(\frac{(0.600 - \text{x}) \text{ L NaOH}}{0.600 \text{ L solution}} \right) \left(\frac{1 \text{ mol } \text{HCOO}^{-}}{1 \text{ mol } \text{NaOH}} \right)$$

$$[HCOOH] = (1.0 \text{ M } \text{HCOOH}) \left(\frac{\text{x } \text{ L } \text{HCOOH}}{0.600 \text{ L solution}} \right) - (1.0 \text{ M } \text{NaOH}) \left(\frac{(0.600 - \text{x}) \text{ L } \text{NaOH}}{0.600 \text{ L solution}} \right) \left(\frac{1 \text{ mol } \text{HCOO}^{-}}{1 \text{ mol } \text{NaOH}} \right)$$

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

$$\frac{\left[\text{HCOO}^{-}\right]}{\left[\text{HCOOH}\right]} = \frac{\left[\left(\frac{0.600 - x}{0.600}\right)\text{M HCOO}^{-}\right]}{\left[\left(x - (0.600 - x)/0.600\right)\text{M HCOOH}\right]} = \frac{0.600 - x}{2x - 0.600} = 0.989236$$

Solving for x:

x = 0.40072 = 0.401 L

Mixing 0.401 L of 1.0 *M* HCOOH and 0.600 - 0.401 = 0.199 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:

 $[\text{HCOOH}] = (1.0 \text{ M HCOOH}) \left(\frac{0.401 \text{ L HCOOH}}{0.600 \text{ L solution}}\right) - (1.0 \text{ M NaOH}) \left(\frac{0.199 \text{ L NaOH}}{0.600 \text{ L solution}}\right) \left(\frac{1 \text{ mole HCOO}^-}{1 \text{ mole NaOH}}\right)$ = 0.336667 = 0.34 M HCOOH

- 19.109 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.
- 19.110 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:

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

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

19.111 $CdS(s) + H_2O(l) \Rightarrow Cd^{2+}(aq) + HS^{-}(aq) + OH^{-}(aq)$ $K_{sp} = 1.0 \times 10^{-24} \text{ (Appendix)}$ $K_{sp} = 1.0 \times 10^{-24} = [Cd^{2+}][HS^{-}][OH^{-}] = S^3$ $S = 1.0 \times 10^{-8} M$

19.112 a.
$$K = [CO_2(aq)] / [CO_2(g)] = 3.1 \times 10^{-2}$$

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

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 $(0.50 \text{ L}) (1.0 \text{ M H}_3\text{PO}_4) = 0.50 \text{ mol H}_3\text{PO}_4$. 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-} / $H_2PO_4^-$.

$$H_{2}PO_{4}^{-}(aq) + H_{2}O(l) \leftrightarrows HPO_{4}^{2-}(aq) + H_{3}O^{+}(aq) \qquad K_{a} = 6.3 \text{ x } 10$$

pH = pK_a + log [HPO₄²⁻] / [H₂PO₄⁻]
pH = -log (6.3 x 10⁻⁸) + log $\begin{pmatrix} 0.30 \text{ mol } \text{HPO}_{4}^{2-} \\ 0.50 \text{ L} \\ 0.20 \text{ mol } \text{H}_{2}PO_{4}^{-} \\ 0.50 \text{ L} \end{pmatrix}$ = 7.37675 = 7.38

19.114 a) The solubility equilibrium for KCl is: KCl(s) \leftrightarrows K⁺(aq) + Cl⁻(aq) $K_{sp} = [K^+][Cl^-] = (3.7) (3.7) = 13.69 = 14$

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

Original moles from the KCl:

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

Original moles from the 6.0 *M* HCl:

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

This results in (0.37 + 0.60) mol = 0.97 mol Cl⁻ Original moles from the 12 *M* HCl:

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

This results in (0.37 + 1.2) mol = 1.57 mol Cl⁻ (unrounded) Volume of mixed solutions = $(100. \text{ mL} + 100. \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.200 \text{ L}$ After the mixing: $[K^+] = (0.37 \text{ mol } K^+) / (0.200 \text{ L}) = 1.85 M \text{ K}^+ \text{ (unrounded)}$ From 6.0 *M* HCl: $[Cl^{-}] = (0.97 \text{ mol } Cl^{-}) / (0.200 \text{ L}) = 4.85 M \text{ Cl}^{-}$ (unrounded) From 12 *M* HCl: $[Cl^{-}] = (1.57 \text{ mol } Cl^{-}) / (0.200 \text{ L}) = 7.85 M \text{ Cl}^{-} (unrounded)$ Determine a Q_{sp} value to see if K_{sp} is exceeded. If $Q < K_{sp}$, nothing will precipitate. From 6.0 M HCl $Q_{sp} = [K^+][Cl^-] = (1.85) (4.85) = 8.9725 = 9.0 < 14$, so no KCl will precipitate. From 12 M HCl $Q_{sp} = [K^+][Cl^-] = (1.85) (7.85) = 14.5225 = 15 > 14$, so KCl will precipitate. The mass of KCl that will precipitate when 12 M HCl is added: Equal amounts of K and Cl will precipitate. Let x be the molarity change. $K_{\rm sp} = [K^+][Cl^-] = (1.85 - x) (7.85 - x) = 13.69$ x = 0.088697657 = 0.09This is the change in the molarity of each of the ions. Mass KCl = $\left(\frac{0.088697657 \text{ mol } \text{K}^+}{\text{L}}\right)(0.200 \text{ L})\left(\frac{1 \text{ mol } \text{KCl}}{1 \text{ mol } \text{K}^+}\right)\left(\frac{74.55 \text{ g } \text{KCl}}{1 \text{ mol } \text{KCl}}\right) = 1.32248 = 1 \text{ g } \text{KCl}$ 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 = 8.10

19.116 Determine the solubility of MnS:

$$S = \left(\frac{4.7 \text{ x } 10^{-4} \text{ g MnS}}{100 \text{ mL}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right) \left(\frac{1 \text{ mol MnS}}{87.01 \text{ g MnS}}\right) = 5.4016779 \text{ x } 10^{-5} M \text{ (unrounded)}$$
$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{HS}^{-}][\text{OH}^{-}] = \text{S}^{3} = (5.4016779 \text{ x } 10^{-5})^{3} = 1.5761 \text{ x } 10^{-13} = 1.6 \text{ x } 10^{-13}$$

19.117 a) Use the equilibrium expression (or Henderson-Hasselbalch equation) and convert the pH of 7.40 to $[H_3O^+]$. $[H_3O^+] = 10^{-7.40} = 3.98107 \times 10^{-8} M$ (unrounded)

$$K_{a1} = 4.5 \times 10^{-7} \text{ (from the Appendix)}$$

$$K_{a1} = \frac{\left[H_{3}O^{+}\right]\left[HCO_{3}^{-}\right]}{\left[H_{2}CO_{3}\right]} = 4.5 \times 10^{-7}$$

$$\frac{\left[H_{2}CO_{3}\right]}{\left[HCO_{3}^{-}\right]} = \frac{\left[H_{3}O^{+}\right]}{K_{a}} = \frac{3.98107 \times 10^{-8}}{4.5 \times 10^{-7}} = 0.88468 = 0.88$$
b) $[H_{3}O^{+}] = 10^{-7.20} = 6.30957 \times 10^{-8} M \text{ (unrounded)}$

$$K_{a1} = \frac{\left[H_{3}O^{+}\right]\left[HCO_{3}^{-}\right]}{\left[H_{2}CO_{3}\right]} = 4.5 \times 10^{-7}$$

$$\frac{\left[H_{2}CO_{3}\right]}{\left[HCO_{3}^{-}\right]} = \frac{\left[H_{3}O^{+}\right]}{K_{a}} = \frac{6.30957 \times 10^{-8}}{4.5 \times 10^{-7}} = 0.14021 = 0.14$$

19.118 a)
$$K_c = 4 \ge 10^{-5} = \frac{\left[\text{Fe}(\text{OH})_4^{-} \right]}{\left[\text{OH}^{-} \right]} = \frac{\left[\text{Fe}(\text{OH})_4^{-} \right]}{\left[0.010 \right]}$$

 $[Fe(OH)_4] = solubility = 4 \times 10^{-7} M$ b) The very small $[Fe(OH)_4]^-$ means that $Fe(OH)_3$ will not dissolve to any significant extent in base, allowing $Fe(OH)_3$ to be separated from Al(OH)₃.

19.119 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.

Mole TRIS = $(43.0 \text{ g TRIS})\left(\frac{1 \text{ mol TRIS}}{121.14 \text{ g TRIS}}\right) = 0.354961 \text{ mol (unrounded)}$ Mole HCl added = $\left(\frac{0.095 \text{ mol HCl}}{L}\right)(1.00 \text{ L}) = 0.095 \text{ mol HCl} = \text{mol TRISH}^+$ Mole TRIS remaining = (0.354961 - 0.095) mol = 0.259961 mol TRISSince there is 1.00 L of solution, the moles of TRIS (**0.260** *M*) and TRISH⁺ equals their molarities. pOH = $pK_b + \log \frac{[\text{acid}]}{[\text{base}]} = 5.91 + \log \frac{[0.095]}{[0.259961]} = 5.472815 \text{ (unrounded)}$ Therefore, pH of the buffer is 14.00 - 5.472815 = 8.527185 = 8.53



19.121 Zinc sulfide, ZnS, is much less soluble than manganese sulfide, MnS. Convert ZnCl₂ and MnCl₂ to ZnS and MnS by saturating the solution with H₂S; $[H_2S]_{sat'd} = 0.10 M$. 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) = $[Mn^{2+}][HS^{-}][OH^{-}] = 3 \times 10^{-11}$

$$[Mn^{2+}] = [Mn^{-1}][HS][OH] = 3 \times 10^{-10}$$

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

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

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

Assume x is negligible and $\left[H_3O^+\right] = \left[HS^-\right]$

Therefore, $[HS^{-}] = 9 \ge 10^{-9} / [H_{3}O^{+}]$ Substituting $[Mn^{2+}]$ and $[HS^{-}]$ into the $K_{sp}(MnS)$ above gives: $K_{sp}(MnS) = [Mn^{2+}] (9 \ge 10^{-9} / [H_{3}O^{+}])[OH^{-}] = 3 \ge 10^{-11}$ Substituting $K_w / [H_{3}O^{+}]$ for $[OH^{-}]$: $K_{sp}(MnS) = [Mn^{2+}] (9 \ge 10^{-9} / [H_{3}O^{+}]) (K_w / [H_{3}O^{+}]) = 3 \ge 10^{-11}$ $[H_{3}O^{+}]^2 = [Mn^{2+}][HS^{-}](K_w) / K_{sp}$ $[H_{3}O^{+}] = \sqrt{\frac{[Mn^{2+}][HS^{-}]K_w}{K_{sp}}} = \sqrt{\frac{(0.020)(9 \ge 10^{-9})(1.0 \ge 10^{-14})}{3 \ge 10^{-11}}} = 2.4494897 \ge 10^{-7} \text{ (unrounded)}$ $pH = -\log [H_{3}O^{+}] = -\log (2.4494897 \ge 10^{-7}) = 6.610924 = 6.6$

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

19.122 a) Since K_a (-COOH) > K_b (-NH₂), the proton will be transferred from the -COOH to the -NH₂, producing -COO⁻ and -NH₃⁺.

b) $pK_a = -\log K_a = -\log 4.47 \ge 10^{-3} = 2.34969$ (unrounded) $pH = pK_a + \log [B] / [BH^+]$ $5.5 = 2.35 + \log [(^+NH_3CH_2COO^-] / [^+NH_3CH_2COOH]$ $\frac{\left[{}^+NH_3CH_2COO^- \right]}{\left[{}^+NH_3CH_2COOH \right]} = 1 \ge 10^3$



- 19.123 The equilibrium is: $Ca_5(PO_4)_3OH(s) \Rightarrow 5 Ca^{2+}(aq) + 3 PO_4^{3-}(aq) + OH^{-}(aq)$ $K_{sp} = 6.8 \times 10^{-37} = [Ca^{2+}]^5[PO_4^{-3-}][OH^{-}] = (5S)^5(3S)^3(S) = 84375 S^9$ $S = 2.7166443 \times 10^{-5} = 2.7 \times 10^{-5} M$ Solubility = (2.7166443 x 10⁻⁵ mol/L) (502.32 g/mol) = 0.013646248 = **0.014 g/L Ca_5(PO_4)_3OH** The equilibrium is: $Ca_5(PO_4)_3OH(s) \Rightarrow 5 Ca^{2+}(aq) + 3 PO_4^{-3-}(aq) + F^{-}(aq)$ $K_{sp} = 1.0 \times 10^{-60} = [Ca^{2+}]^5[PO_4^{-3-}][F^{-}] = (5S)^5(3S)^3(S) = 84375 S^9$ $S = 6.1090861 \times 10^{-8} = 6.1 \times 10^{-8} M$ Solubility = (6.1090861 x 10⁻⁸ mol/L) (504.31 g/mol) $= 3.0808732 \times 10^{-5} = 3.1 \times 10^{-5} g/L Ca_5(PO_4)_3F$
- 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. $pK_a = (3.4 + 4.8) / 2 = 4.1$ $K_a = 10^{-4.1} = 7.943 \text{ x } 10^{-5} = 8 \text{ x } 10^{-5}$
- 19.125 The pH value is in the range for **phenolphthalein**.



mL NaOH added 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.

19.127 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.



19.128 Check to see if the concentration of Ca(OH)₂ exceeds the K_{sp} . $M \operatorname{Ca}(OH)_2 = (6.5 \times 10^{-9} \text{ mol Ca}(OH)_2) / (10.0 \text{ L}) = 6.5 \times 10^{-10} M \operatorname{Ca}(OH)_2$ Determine the concentration of a saturated calcium hydroxide solution from the K_{sp} . $\operatorname{Ca}(OH)_2(s) \leftrightarrows \operatorname{Ca}^{2+}(aq) + 2 \operatorname{OH}^-(aq)$ $K_{sp} = 6.5 \times 10^{-6} = [\operatorname{Ca}^{2+}][\operatorname{OH}^-]^2 = (S) (2S)^2 = 4S^3$ $S = \sqrt[3]{\frac{6.5 \times 10^{-6}}{4}} = 0.01175667 = 0.012 M$ Thus, the solution is less than saturated so the K_{sp} does not affect the concentration of Calcium for the formula of Calcium for the formula of Calcium form in the saturated for the formula of the formula of Calcium formula of C

Thus, the solution is less than saturated so the K_{sp} does not affect the concentration of Ca(OH)₂. $M \text{ OH}^-$ from Ca(OH)₂ = (6.5 x 10⁻¹⁰ $M \text{ Ca(OH)}_2$) (2 mol OH⁻ / 1 mol Ca(OH)₂) = 1.3 x 10⁻⁹ $M \text{ OH}^-$ Pure water has 1 x 10⁻⁷ $M \text{ OH}^-$, thus the contribution from the Ca(OH)₂ is not significant. 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 $M_{\text{conc}}V_{\text{conc}} = M_{\text{dil}}V_{\text{dil}}$. Determine the p K_a of the acid from the K_a .

Determine the pK_a of the acid from the K_a . $pK_a = -\log K_a = -\log 1.38 \times 10^{-4} = 3.86012$ (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) $[Lac^-] = [(0.68 M) (435 mL)] / [(225 + 435) mL] = 0.44818 M Lac^- (unrounded)$ Entering the values into the Henderson-Hasselbalch equation:

pH = pK_a + log [Lac⁻] / [HLac] pH = 3.86012 + log [0.44818] / [0.28977] pH = 4.049519 = **4.05**

19.130 (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 CaF₂ would dissolve in this solution than in pure water. (III) 0.01M NaOH: OH⁻ ions remove H⁺ ions from solution. H⁺ ions combine with F⁻ ions to form HF. The formation of HF would cause more CaF₂ to dissolve. With fewer H⁺ ions than in water this solution would dissolve less CaF₂.

(IV) 0.01M HCl: H⁺ ions combine with F⁻ ions to form HF. The formation of HF would cause more CaF₂ to dissolve in this solution than in pure water.

(V) 0.01M Ca(OH)₂: Because of the common ion effect, less CaF₂ would dissolve in this solution than in pure water. The presence of OH⁻ ions also removes H⁺ ions and decreases the ability to form HF, thus decreasing the solubility of CaF₂.

a) 0.01*M* 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 $H_2O(l) +$ $ClO^{-}(aq)$ 0.050 mol 0.050 mol 0.013 mol The initial amount of HClO is 0.13 mol - 0.050 mol = 0.08 molThe initial amount of ClO⁻ is 0.050 mol ClO⁻. The volume of the solution is (500. mL) $(10^{-3} \text{ L} / 1 \text{ mL}) = 0.500 \text{ L}$ $[HClO]_i = (0.080 \text{ mol } HClO) / (0.500 \text{ L}) = 0.16 M HClO$ $[ClO^{-}]_{I} = (0.050 \text{ mol } ClO^{-}) / (0.500 \text{ L}) = 0.10 M \text{ OCl}^{-}$ Concentration (M) $HClO(aq) + H_2O$ $ClO^{-}(aq)$ $H_3O^+(aq)$ Initial 0.16 0.10 Change - X +x+ x Equilibrium 0.016 - x 0.10 + xx x is small, so [HClO] \approx 0.16 *M* HClO and [ClO⁻] \approx 0.10 *M* ClO⁻ $K_{a} = \frac{\left[H_{3}O^{+}\right]\left[CIO^{-}\right]}{\left[HCIO\right]}$ $[\mathrm{H}_{3}\mathrm{O}^{+}] = \frac{\mathrm{K}_{a}[\mathrm{HClO}]}{\left[\mathrm{ClO}^{-}\right]}$ $[\mathrm{H}_{3}\mathrm{O}^{+}] = \frac{\left(3.0 \text{ x } 10^{-8}\right)(0.16)}{(0.10)} = 4.8 \text{ x } 10^{-8} M \mathrm{H}_{3}\mathrm{O}^{+}$ $[OH^{-}] = K_w / [H_3O^{+}] = (1.0 \text{ x } 10^{-14}) / (4.8 \text{ x } 10^{-8}) = 2.08333 \text{ x } 10^{-7} = 2.1 \text{ x } 10^{-7} M \text{ OH}^{-1}$ $[Na^+] = (0.050 \text{ mol}) / (0.500 \text{ L}) = 0.10 M \text{ Na}^+$ b) pH = $-\log [H_3O^+] = -\log (4.8 \times 10^{-8} M) = 7.31875876 = 7.32$

c) If 0.0050 mol HCl is added then the ClO⁻ will react with the H⁺ to form HClO.
The amount of HClO is 0.080 mol + 0.0050 = 0.085 mol HClO
The amount of ClO⁻ is 0.050 mol - 0.0050 mol = 0.045 mol ClO⁻
[HClO]_i = (0.085 mol HClO) / (0.500 L) = 0.17 *M* HClO
[ClO⁻]_i = (0.045 mol ClO⁻) / (0.500 L) = 0.090 *M* OCl⁻
Concentration (*M*) HClO(*aq*) + H₂O
$$\leftrightarrows$$
 H₃O⁺(*aq*) + ClO⁻(*aq*)
Initial 0.17 - - 0.090
Change -x +x +x +x
Equilibrium 0.17 - x x 0.090 *M*
[H₃O⁺] = $\frac{K_a [HClO]}{[ClO-]}$
[H₃O⁺] = $\frac{K_a [HClO]}{[ClO-]}$ = 5.6667 x 10⁻⁸ *M* H₃O⁺ (unrounded)
pH = -log [H₃O⁺] = -log (5.6667 x 10⁻⁸ *M*) = 7.246669779 = 7.25

 $+ OH^{-}(aq)$

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

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

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

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

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

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

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

- 19.133 Hg₂C₂O₄(s) \leftrightarrows Hg₂²⁺(aq) + C₂O₄²⁻(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 x 10⁻¹² = **1.3 x 10⁻¹² M**
- 19.134 $\operatorname{CaCO}_{3}(s) \leftrightarrows \operatorname{Ca}^{2^{+}}(aq) + \operatorname{CO}_{3}^{2^{-}}(aq)$ $K_{sp} = 3.3 \times 10^{-9} = [\operatorname{Ca}^{2^{+}}][\operatorname{CO}_{3}^{2^{-}}] = \mathrm{S}^{2}$ $\mathrm{S} = [\operatorname{Ca}^{2^{+}}] = 5.7445626 \times 10^{-5} = 5.7 \times 10^{-5} M$
- 19.135 The absence of any precipitates eliminates all ions except: Na^+ , K^+ , and NH_4^+ . When the litmus paper turns blue the presence of NH_4^+ is indicated. The violet flame test indicates the presence of K^+ .

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} is closest to the pH of 7.4, so H₂CO₃ and HCO₃⁻ are the species present. For phosphoric acid, pK_{a2} is closest to the pH, so H₂PO₄⁻ and HPO₄²⁻ are the principle species present.

$$K_{a2} = \frac{\left[H_{3}O^{+}\right] = 10^{-7.4} = 3.98107 \text{ x } 10^{-8} M \text{ (unrounded)}}{\left[H_{3}O^{+}\right] \left[HPO_{4}^{2^{-}}\right]}$$
$$\frac{\left[H_{2}PO_{4}^{-}\right]}{\left[H_{2}PO_{4}^{-}\right]} = \frac{K_{a2}}{\left[H_{3}O^{+}\right]} = \frac{2.3 \text{ x } 10^{-7}}{3.98107 \text{ x } 10^{-8}} = 5.777341 = 5.8$$

- 19.137 Treat the white precipitate with hot water, and then separate the solid and solution. Add K_2CrO_4 to the solution; formation of a yellow precipitate confirms the presence of Pb²⁺. Treat the solid from the first step with NH₃, and then separate the solid and solution. If the solid is gray or gray-black, this confirms the presence of Hg_2^{2+} . Treat the solution with HCl; formation of a white precipitate confirms the presence of Ag⁺.
- 19.138 Refer to Figure 19.5. Litrus 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. $NiS(s) + H_2O(l) \leftrightarrows Ni^{2+}(aq) + HS^{-}(aq) + OH^{-}(aq)$ $K_{sp} (NiS) = 3 \times 10^{-16} = [Ni^{2+}][HS^{-}][OH^{-}]$ $[Ni^{2+}] = 0.15 M, \text{ so } [HS^{-}] \text{ and } [OH^{-}] \text{ must be found.}$ From $[H_2S] = 0.050 M$ and K_{a1} in the Appendix: $K_{a1} = \frac{\left[H_3O^+\right]\left[HS^-\right]}{\left[H_2S\right]} = \frac{\left[H_3O^+\right]\left[HS^-\right]}{\left[0.050 - x\right]} = \frac{\left[H_3O^+\right]\left[HS^-\right]}{\left[0.050\right]} = 9 \times 10^{-8}$ $[HS^{-}][H_{3}O^{+}] = 4.5 \times 10^{-9} \text{ or } [HS^{-}] = 4.5 \times 10^{-9} / [H_{3}O^{+}]$

 $\begin{bmatrix} OH^{-} \end{bmatrix} = K_{w} / \begin{bmatrix} H_{3}O^{+} \end{bmatrix}$ $K = 10^{-16} = (0.15) (4.5 \times 10^{-9} / [H_{3}O^{+}]) (K_{w} / [H_{3}O^{+}])$ $3 \times 10^{-16} = (0.15) (4.5 \times 10^{-9}) (1.0 \times 10^{-14}) / [H_{3}O^{+}]^{2}$ $\begin{bmatrix} H_{3}O^{+} \end{bmatrix}^{2} = \begin{bmatrix} (0.15) (4.5 \times 10^{-9}) (1.0 \times 10^{-14}) / (3 \times 10^{-16}) = 2.25 \times 10^{-8} \text{ (unrounded)}$ $[H_3O^+] = 1.5 \times 10^{-4} M$ (unrounded) $pH = -log [H_3O^+] = -log (1.5 \times 10^{-4} M) = 3.8239 = 3.8$

19.140 a) Combine the separate equilibria to produce the desired equilibrium. The K values are in the Appendix. 2 AgCl(s) \Rightarrow 2 Ag⁺(aq) + 2 Cl⁻(aq) 2 Ag⁺(aq) + CrO₄²⁻(aq) \Rightarrow Ag₂CrO₄(s) 2 AgCl(s) + CrO₄²⁻(aq) \Rightarrow Ag₂CrO₄(s) 2 AgCl(s) + CrO₄²⁻(aq) \Rightarrow Ag₂CrO₄(s) 2 AgCl(s) + CrO₄²⁻(aq) \Rightarrow Ag₂CrO₄(s) + 2 Cl⁻(aq) 3 AgCl(s) + CrO₄²⁻(aq) \Rightarrow Ag₂CrO₄(s) + 2 Cl⁻(aq) 3 AgCl(s) + CrO₄²⁻(aq) \Rightarrow Ag₂CrO₄(s) + 2 Cl⁻(aq) 3 AgCl⁻(s) + 2 Cl⁻ $2 \operatorname{Ag}^{+}(aq) + \operatorname{CrO}_{4}^{2^{-}}(aq) \leftrightarrows \operatorname{Ag}_{2}\operatorname{CrO}_{4}(s)$ $2 \operatorname{AgCl}(s) + \operatorname{CrO}_{4}^{2^{-}}(aq) \leftrightarrows \operatorname{Ag}_{2}\operatorname{CrO}_{4}(s) + 2 \operatorname{Cl}^{-}(aq)$ 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. $K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-] = S^2$ $S = [Ag^+] = 1.34164 \times 10^{-5} M = 1.3 \times 10^{-5} M Ag^+$ 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, Ag₂CrO₄ 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.

Moles quinidine =
$$(33.85 \text{ mg quinidine}) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right) \left(\frac{1 \text{ mol quinidine}}{324.41 \text{ g quinidine}}\right)$$

= 1.0434326 x 10⁻⁴ mol quinidine (unrounded)
Moles HCl excess = $(6.55 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) \left(\frac{0.150 \text{ mol HCl}}{\text{L}}\right)$
- $(1.0434326 \text{ x } 10^{-4} \text{ mol quinidine}) \left(\frac{2 \text{ mol HCl}}{1 \text{ mol quinidine}}\right) = 7.7381348 \text{ x } 10^{-4} \text{ mol HCl}$ (unrounded)

$$Volume needed = \left(7.7381348 \text{ x } 10^{-4} \text{ mol HCl}\right) \left(\frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}}\right) \left(\frac{1 \text{ L}}{0.0133 \text{ mol NaOH}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

b) Use the moles of quinidine and the concentration of the NaOH to determine the milliliters.

$$Volume = (1.043436 \text{ x } 10^{-4} \text{ mol quinidine}) \left(\frac{1 \text{ mol NaOH}}{1 \text{ mol quinidine}}\right) \left(\frac{1 \text{ L}}{0.0133 \text{ mol NaOH}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

= 7.84538 = 7.4 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:

$$[OH^{-}] = \sqrt{K_{b1}K_{b2}} = \sqrt{(4.0 \times 10^{-6})(1.0 \times 10^{-10})} = 2.0 \times 10^{-8} M$$

$$[H_{3}O^{+}] = K_{w} / [OH^{-}] = (1.0 \times 10^{-14}) / (2.0 \times 10^{-8}) = 5.0 \times 10^{-7} M$$

$$pH = -\log [H_{3}O^{+}] = -\log (5.0 \times 10^{-7} M) = 6.3010 = 6.30$$

19.142 *K* values from the Appendix

 $\begin{aligned} H_{2}C_{2}O_{4}(aq) &\leftrightarrows H^{+}(aq) + HC_{2}O_{4}(aq) &K_{a1} = 5.6 \times 10^{-2} \\ HC_{2}O_{4}(aq) &\leftrightarrows H^{+}(aq) + C_{2}O_{4}^{-2}(aq) &K_{a2} = 5.4 \times 10^{-5} \\ H_{2}C_{2}O_{4}(aq) &\leftrightarrows 2 H^{+}(aq) + C_{2}O_{4}^{-2}(aq) &K_{a2} = 5.4 \times 10^{-5} \\ H_{2}C_{2}O_{4}(aq) &\leftrightarrows 2 H^{+}(aq) + C_{2}O_{4}^{-2}(aq) &K = K_{a1} K_{a2} = 3.024 \times 10^{-6} \text{ (unrounded)} \\ &K = [H^{+}]^{2}[C_{2}O_{4}^{-2}] - K[H_{2}C_{2}O_{4}] / [H^{+}]^{2} \\ a. At pH = 5.5 & [H^{+}] = 10^{-5.5} = 3.162 \times 10^{-6} M \text{ (unrounded)} \\ & [C_{2}O_{4}^{-2}] = K[H_{2}C_{2}O_{4}] / [H^{+}]^{2} = (3.024 \times 10^{-6}) (3.0 \times 10^{-13}) / (3.162 \times 10^{-6})^{2} \\ & [C_{2}O_{4}^{-2}] = 9.07359 \times 10^{-8} M \text{ (unrounded)} \\ Q = [Ca^{2+}][C_{2}O_{4}^{2-}] \\ & Q = (2.6 \times 10^{-3}) (9.07359 \times 10^{-8}) = 2.3591 \times 10^{-10} = 2.4 \times 10^{-10} < K_{sp} = \text{ No precipitate} \\ b. At pH = 7.0 & [H^{+}] = 10^{-7.0} = 1 \times 10^{-7} M \\ & [C_{2}O_{4}^{-2}] = K[H_{2}C_{2}O_{4}] / [H^{+}]^{2} = (3.024 \times 10^{-6}) (3.0 \times 10^{-13}) / (1 \times 10^{-7})^{2} \\ & [C_{2}O_{4}^{-2}] = 9.072 \times 10^{-5} M \text{ (unrounded)} \\ Q = (2.6 \times 10^{-3}) (9.072 \times 10^{-5}) = 2.35872 \times 10^{-7} = 2.4 \times 10^{-7} > K_{sp} = \text{ Precipitate forms} \end{aligned}$

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):

 $pH = pK_a + \log ([base] / [acid])$

r

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:

 $\Delta pH = \log ([base] / [acid])_{final} - \log ([base] / [acid])_{initial}$

In the given case $\log ([base] / [acid])_{initial} = 0$ because [base] = [acid], so the change in pH is equal to the concentration ratio of base to acid after the addition of H₃O⁺.

Consider the buffer prior to addition to the medium. When $0.0010 \text{ mol H}_3\text{O}^+$ is added to 1 L of the undiluted buffer, the $[A^-]/[HA]$ ratio changes from 0.10 / 0.10 to (0.10 - 0.0010) / (0.10 + 0.0010). The change in pH is:

 $\Delta pH = \log (0.099 / 0.101) = -0.008686$ (unrounded)

If the undiluted buffer changes 0.009 pH units with addition of 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.

$$\log \frac{[\text{base}]}{[\text{acid}]} = \log \left(\frac{(0.10\text{x} - 0.0010)}{(0.10\text{x} + 0.0010)} \right) = -0.05$$
$$\left(\frac{(0.10\text{x} - 0.0010)}{(0.10\text{x} + 0.0010)} \right) = 10^{-0.05} = 0.89125 \text{ (unrounded)}$$
$$0.10\text{x} - 0.0010 = 0.89125 \text{ (0.10x} + 0.0010)$$
$$\text{x} = 0.173908 = 0.17$$

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)
$$K_a = 6.8 \ge 10^4 = \frac{\left[H_3O^+\right]\left[F^-\right]}{\left[HF\right]} = \frac{1}{0.2500 - 1} = \frac{1}{0.2500} =$$

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

The molarity of F⁻ is $M F^{-} = \left(\frac{8.750 \times 10^{-3} \text{ mol } F^{-}}{(35.00 + 57.11488) \text{ mL}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right) = 0.09499 M F^{-} \text{ (unrounded)}$ $K_{b} = K_{w} / K_{a} = (1.0 \times 10^{-14}) / (6.8 \times 10^{-4}) = 1.470588 \times 10^{-11} \text{ (unrounded)}$ $K_{b} = \frac{[\text{HF}][\text{OH}^{-}]}{[\text{F}^{-}]} = \frac{x^{2}}{0.09499 - x} \approx \frac{x^{2}}{0.09499} = 1.470588 \times 10^{-11}$ $x = [\text{OH}^{-}] = 1.1819 \times 10^{-6} M \text{ (unrounded)}$ $[\text{H}_{3}\text{O}^{+}] = K_{w} / [\text{OH}^{-}] = (1.0 \times 10^{-14}) / (1.1819 \times 10^{-6}) = 8.4609527 \times 10^{-9} M \text{ (unrounded)}$ $p_{H} = -\log [\text{H}_{3}\text{O}^{+}] = -\log (8.4609527 \times 10^{-9} M) = 8.07258 = 8.07$ e) Moles NaOH excess = $(0.50 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) \left(\frac{0.1532 \text{ mol NaOH}}{1 \text{ L}}\right) = 7.66 \times 10^{-5} \text{ mol NaOH (unrounded)}$ $Volume of solution = (35.00 + 57.11488 + 0.50) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.09261 \text{ L}$ $[\text{OH}^{-}] = (7.66 \times 10^{-5} \text{ mol F}^{-}) / (0.09261 \text{ L}) = 8.271 \times 10^{-4} M \text{ OH}^{-} \text{ (unrounded)}$ The excess OH⁻ will predominate and essentially control the pH. $[\text{H}_{3}\text{O}^{+}] = K_{w} / [\text{OH}^{-}] = (1.0 \times 10^{-14}) / (8.271 \times 10^{-4}) = 1.2090436 \times 10^{-11} M \text{ (unrounded)}$ $p_{H} = -\log [\text{H}_{3}\text{O}^{+}] = -\log (1.2090436 \times 10^{-11} M) = 10.917558 = 10.92$

19.145 a) The formula is Hg₂Cl₂ which simplifies to the empirical formula **HgCl**.
b) The equilibrium is: Hg₂Cl₂(s)
$$\leftrightarrows$$
 Hg₂²⁺(aq) + 2 Cl⁻(aq)
 $K_{sp} = [Hg_2^{2+}][Cl^{-}]^2 = (S) (2S)^2 = 4S^3 = 1.5 \times 10^{-18}$
 $S = 7.2112478 \times 10^{-7} = 7.2 \times 10^{-7} M$
c) $[Hg_2^{2+}] = K_{sp} / [Cl^{-}]^2 = \frac{1.5 \times 10^{-18}}{1.5 \times 10^{-18}}$

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

$$= 8.9174129 \text{ x } 10^{-18} = 8.9 \text{ x } 10^{-18} M \text{ Hg}_2^{2+1}$$

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

$$Mass = \left(\frac{7.2112478 \text{ x } 10^{-7} \text{ mol } \text{Hg}_2\text{Cl}_2}{\text{L}}\right) \left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3}\right) \left(\frac{10^3 \text{ m}}{1 \text{ km}}\right)^3 (4900 \text{ km}^3) \left(\frac{472.1 \text{ g } \text{Hg}_2\text{Cl}_2}{1 \text{ mol } \text{Hg}_2\text{Cl}_2}\right)$$
$$= 1.6681707 \text{ x } 10^{12} = 1.7 \text{ x } 10^{12} \text{ g } \text{Hg}_2\text{Cl}_2$$

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

$$Mass = \left(\frac{8.9174129 \text{ x } 10^{-18} \text{ mol } \text{Hg}_2^{2+}}{\text{L}}\right) \left(\frac{1 \text{ mol } \text{Hg}_2\text{Cl}_2}{1 \text{ mol } \text{Hg}_2^{2+}}\right) \left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3}\right) \left(\frac{10^3 \text{ m}}{1 \text{ km}}\right)^3 (4900 \text{ km}^3) \left(\frac{472.1 \text{ g } \text{Hg}_2\text{Cl}_2}{1 \text{ mol } \text{Hg}_2\text{Cl}_2}\right) = 20.62856 = 21 \text{ g } \text{Hg}_2\text{Cl}_2$$

19.146 To find the volume of rain, first convert the inches to yards and find the volume in yd³. Then convert units to cm³ and on to L.

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

a) At pH = 4.20, [H₃O⁺] = 10^{-4.20} = 6.3095734 \text{ x } 10^{-5} M \text{ (unrounded)}
Mol H₃O⁺ = (6.3095734 x 10⁻⁵ M) (1.0279015 x 10⁶ L) = 64.8562 = **65 mol**
b) Volume = (10.0 \text{ acres}) \left(\frac{4.840 \text{ x } 10^3 \text{ yd}^2}{1 \text{ acre}}\right) \left(\frac{36 \text{ in}}{1 \text{ yd}}\right)^2 (10.0 \text{ ft}) \left(\frac{12 \text{ in}}{1 \text{ ft}}\right) \left(\frac{2.54 \text{ cm}}{1 \text{ in}}\right)^3 \left(\frac{1 \text{ mL}}{1 \text{ cm}^3}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)
= 1.23348 x 10⁸ L (unrounded)

Total volume of lake after rain = $1.23348 \times 10^8 \text{ L} + 1.0279015 \times 10^6 \text{ L} = 1.243759 \times 10^8 \text{ L}$ (unrounded) [H₃O⁺] = $64.8562 \text{ mol } \text{H}_3\text{O}^+ / 1.243759 \times 10^8 \text{ L} = 5.214531 \times 10^{-7} M$ pH = $-\log(5.214531 \times 10^{-7}) = 6.2827847 = 6.28$

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

$$Mass = (64.8562 \text{ mol } H_3O^+) \left(\frac{1 \text{ mol } HCO_3^-}{1 \text{ mol } H_3O^+}\right) \left(\frac{61.02 \text{ g } HCO_3^-}{1 \text{ mol } HCO_3^-}\right) = 3.97575 \text{ x } 10^3 = 4.0 \text{ x } 10^3 \text{ g } HCO_3^-$$

19.147 a) CaF₂ with K_{sp} = 3.2 x 10⁻¹¹ will precipitate before BaF₂ with K_{sp} = 1.5 x 10⁻⁶.
b) Add KF until [F⁻] is such that the CaF₂ precipitates but just lower than the concentration required to precipitate BaF₂.
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.

$$[F^{-}]^{2} = K_{sp} / [Ba^{2+}] = (1.5 \times 10^{-6}) / (0.0375) = 4.0 \times 10^{-6}$$

[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 CO₂, [CO₂], depends on how much CO₂(g) from the atmosphere can dissolve in pure

water. At 25°C and 1 atm CO₂, 88 mL of CO₂ can dissolve in 100 mL of H₂O. The number of moles of CO₂ in 88 mL of CO₂ is:

Moles CO₂ = PV / RT =
$$\frac{(1 \text{ atm})(88 \text{ mL})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) \left((273 + 25)\text{K}\right)} \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) \left(\frac{0.033\%}{100\%}\right)$$

= $1.186963 \times 10^{-6} \text{ mol CO}_2$ (unrounded)

Since air is not pure CO₂, account for the volume fraction of air (0.033 L / 100 L) when determining the moles. $[CO_2] = (1.186963 \times 10^6 \text{ mol } CO_2) / [(100 \text{ mL}) (10^3 \text{ L} / 1 \text{ mL})] = 1.186963 \times 10^5 M \text{ CO}_2 \text{ (unrounded)}$

$$K_{a1} = \frac{\left[H_{3}O^{+}\right]\left[HCO_{3}^{-}\right]}{\left[H_{2}CO_{3}\right]} = \frac{\left[H_{3}O^{+}\right]\left[HCO_{3}^{-}\right]}{\left[CO_{2}\right]} = 4.5 \times 10^{-7}$$

Let x = [H₃O⁺] = [HCO₃⁻]
$$\frac{\left[x\right]\left[x\right]}{\left[1.186963 \times 10^{-5} - x\right]} = 4.5 \times 10^{-7}$$

x² + 4.5 x 10⁻⁷ x - 5.341336 x 10⁻¹² = 0
x = 2.0970596 x 10⁻⁶ M = [H₃O⁺] (unrounded)
pH = -log(2.0970596 x 10⁻⁶) = 5.678389 = **5.68**

19.149 a) For H₂CO₃,

 $pK_{a} = -\log K_{a}$ $pK_{a1} = -\log 4.5 \times 10^{-7} = 6.3468 \text{ (unrounded)}$ $pK_{a2} = -\log 4.7 \times 10^{-11} = 10.3279 \text{ (unrounded)}$ $pK_{a1} = 6.35 \text{ and } pK_{a2} = 10.33. \text{ Since } pK_{a1} > pH < pK_{a2}, \text{ the base in the first dissociation (HCO_{3}^{-}) and the acid in the second dissociation (also HCO_{3}^{-}) will predominate.$ b) pH = pK_a + log [base] / [acid] $8.5 = 6.35 + \log [HCO_{3}^{-}] / [H_{2}CO_{3}]$ $[HCO_{3}^{-}] / [H_{2}CO_{3}] = 1.4125 \times 10^{2} = 1 \times 10^{2} M \text{ (unrounded) (8.5 limits the significant figures)}$ $pH = pK_{a} + \log [base] / [acid]$ $8.5 = 10.33 + \log [CO_{3}^{-2}] / [HCO_{3}^{-}]$ $[CO_{3}^{2^{-}}] / [HCO_{3}^{-}] = 1.4791 \times 10^{-2} = 1 \times 10^{-2} M \text{ (unrounded)}$

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 Pb²⁺ and Ca(EDTA)²⁻ before reaction based on mixing 100. mL of 0.10 *M* Na₂Ca(EDTA) with 1.5 L blood:

$$\begin{split} [\text{Pb}^{2+}] &= \left(\frac{120 \ \mu\text{g Pb}^{2+}}{100 \ \text{mL}}\right) \left(\frac{1 \ \text{mL}}{10^{-3} \ \text{L}}\right) \left(\frac{1.5 \ \text{L} \ \text{blood}}{1.6 \ \text{L} \ \text{mixture}}\right) \left(\frac{10^{-6} \ \text{g}}{1 \ \mu\text{g}}\right) \left(\frac{1 \ \text{mol Pb}^{2+}}{207.2 \ \text{g Pb}^{2+}}\right) = 5.4295366 \ \text{x} \ 10^{-6} \ M \ \text{Pb}^{2+} \ (\text{unrounded}) \\ \\ M_{\text{con}} V_{\text{con}} &= M_{\text{dil}} V_{\text{dil}} \\ &= [\text{Ca}(\text{EDTA})^{2-}] = M_{\text{con}} V_{\text{con}} / V_{\text{dil}} = [(0.10 \ M) \ (100 \ \text{mL}) \ (10^{-3} \ \text{L} / 1 \ \text{mL})] / (1.6 \ \text{L}) \\ &= 6.25 \ \text{x} \ 10^{-3} \ M \ (\text{unrounded}) \\ \end{split}$$
Set up a reaction table:
Concentration (M) [Ca(EDTA)]^{2-}(aq) + Pb^{2+}(aq) &\rightleftharpoons [Pb(EDTA)]^{2-}(aq) + Ca^{2+}(aq) \\ \text{Initial} & 6.25 \ \text{x} \ 10^{-3} \ \text{s} \ 5.4295366 \ \text{x} \ 10^{-6} \ 0 \ 0 \\ \end{aligned}
Change $-5.4295366 \ \text{x} \ 10^{-6} \ \text{s} \ 5.4295366 \ \text{x} \ 10^{-6} \ \text{s} \ 10^{-6} \ 1$

 $x = [Pb^{2+}] = 1.8883521 \times 10^{-16} M$ (unrounded) Convert concentration from M to us in 100 mI

The final concentration is **3.9** x 10^{-9} µg / 100 mL.

19.151
$$\operatorname{Co}^{2+}(aq) + \operatorname{EDTA}^{4-}(aq) \rightleftharpoons [\operatorname{Co}(\operatorname{EDTA})]^{2-}(aq)$$

 $K_{\rm f} = 10^{16.31} = 2.0417379 \times 10^{16} \text{ (unrounded)}$
 $K_{\rm f} = \frac{\left[\operatorname{Co}(\operatorname{EDTA})^{2-}\right]}{\left[\operatorname{CO}^{2+}\right]\left[\operatorname{EDTA}^{4-}\right]}$
Moles $\operatorname{Co}^{2+}(\operatorname{original}) = \left(\frac{0.048 \text{ mol } \operatorname{Co}^{2+}}{L}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (50.0 \text{ mL}) = 0.0024 \text{ mol } \operatorname{Co}^{2+}$
a) Moles EDTA added $= \left(\frac{0.050 \text{ mol } \operatorname{EDTA}^{4-}}{L}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (25.0 \text{ mL}) = 0.00125 \text{ mol } \operatorname{EDTA} \text{ (unrounded)}$

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 Co²⁺: Co²⁺ = (0.0024 - 0.00125) = 0.00115 mol Co²⁺ Total volume = (50.0 + 25.0) mL (10⁻³ L / 1 mL) = 0.0750 L $[Co^{2^+}] = (0.00115 mol Co^{2^+}) / (0.0750 L) = 0.015333 M Co^{2^+} (unrounded)$ $[Co(EDTA)^{2^-}] = (0.00125 mol [Co(EDTA)]^{2^-}) / (0.0750 L) = 0.016667 M (unrounded)$ To reach equilibrium the concentrations of the species involved are: [EDTA] = x $[Co^{2^+}] = 0.015333 + x$ $[Co(EDTA)^{2^-}] = 0.016667 - x$

$$K_{\rm f} = \frac{\left[{\rm Co}({\rm EDTA})^{2^{-}}\right]}{\left[{\rm Co}^{2^{+}}\right]\left[{\rm EDTA}^{4^{-}}\right]} = \frac{\left[0.016667 - x\right]}{\left[0.01533 + x\right]\left[x\right]} = \frac{\left[0.016667\right]}{\left[0.01533\right]\left[x\right]} = 2.0417379 \times 10^{16}$$

$$x = 5.3249468 \times 10^{-17} \, \text{(unrounded)}$$

$$\left[{\rm EDTA}\right] = 5.3 \times 10^{-17} \, M$$

$$\left[{\rm Co}^{2^{+}}\right] = 0.015 \, M$$
b) Moles EDTA added = $\left(\frac{0.050 \text{ mol EDTA}^{4^{-}}}{L}\right) \left(\frac{10^{-3} \, \text{L}}{1 \, \text{mL}}\right) (75.0 \, \text{mL}) = 0.00375 \, \text{mol EDTA} \, (\text{unrounded})$
The Co²⁺ is limiting so no Co²⁺ is left. The original moles Co²⁺ equals the moles of complex formed.
Moles EDTA remaining = (0.00375 - 0.0024) \, \text{mol = 0.00135 mol EDTA} (unrounded)
Total volume = $(50.0 + 75.0) \, \text{mL} \, (10^{3} \, \text{L} / 1 \, \text{mL}) = 0.1250 \, \text{L}$

$$\left[\text{EDTA}\right] = (0.00135 \, \text{mol EDTA}) / (0.1250 \, \text{L}) = 0.0108 \, M \, \text{EDTA} \, (\text{unrounded})$$

$$\left[\text{Co}(\text{EDTA})^{2^{-}}\right] = (0.0024 \, \text{mol [Co}(\text{EDTA})]^{2^{-}} / (0.1250 \, \text{L}) = 0.0192 \, M \, (\text{unrounded})$$
To reach equilibrium the concentrations of the species involved are:

$$\left[\text{EDTA}\right] = 0.0108 + x \quad \left[\text{Co}(\text{EDTA})^{2^{-}}\right] = 0.0192 - x$$

$$K_{\rm f} = \frac{\left[\text{Co}(\text{EDTA})^{2^{-}}\right]}{\left[\text{Co}^{2^{+}}\right]\left[\text{EDTA}^{4^{-}}\right]} = \frac{\left[0.0192 - x\right]}{\left[x\right]\left[0.0108 + x\right]} = \frac{\left[0.0192\right]}{\left[x\right]\left[0.0108\right]} = 2.0417379 \, x \, 10^{16} \, x = 8.7071792 \, x \, 10^{-17} \, (\text{unrounded})$$

$$\left[\text{EDTA}\right] = 0.0192 \, M \, (\text{Co}^{2^{+}}) = 8.7 \, x \, 10^{-17} \, M$$

19.152 The molarity of a saturated NaCl solution must be found. (317 g NaCl)(1 mol NaCl)

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

Determine the $K_{\rm sp}$ from the molarity just calculated.
 $K_{\rm sp} = [\operatorname{Na}^+][\operatorname{Cl}^-] = \operatorname{S}^2 = (5.42436687)^2 = 29.42375594 = 29.4$
Moles of Cl^- initially $= \left(\frac{5.4236687 \text{ mol NaCl}}{L}\right) (0.100 \text{ L}) \left(\frac{1 \text{ mol Cl}^-}{1 \text{ mol NaCl}}\right) = 0.54236687 \text{ mol Cl}^- \text{ (unrounded)}$

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

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

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

Volume of mixed solutions = $0.100 \text{ L} + (25.5 \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.1255 \text{ L}$ (unrounded) Molarity of Cl⁻ in mixture = $[(0.54236687 + 0.200175) \text{ mol Cl}^-] / (0.1255 \text{ L}) = 5.916668 M \text{ Cl}^- (unrounded)$ Molarity of Na⁺ in mixture = $(0.54236687 \text{ mol Na}^+) / (0.1255 \text{ L}) = 4.321648 M \text{ Na}^+$ (unrounded) Determine a Q value and compare this value to the K_{sp} to determine if precipitation will occur. $Q_{sp} = [Na^+][Cl^-] = (4.321648) (5.916668) = 25.569756 = 25.6$ Since $Q_{sp} < K_{sp}$, no NaCl will precipitate.

19.153 a) Ag⁺ ions come from the dissolution of AgCl(s)

$$K_{sp} = [Ag^{+}][Cl^{-}] = 1.8 \times 10^{-10}$$

$$[Ag^{+}] = \frac{1.8 \times 10^{-10}}{[Cl^{-}]}$$
AgCl(s) $\leftrightarrows Ag^{+}(aq) + Cl^{-}(aq)$

$$K_{sp} = 1.8 \times 10^{-10}$$

$$Ag^{+}(aq) + 2 Cl^{-}(aq) \leftrightarrows AgCl_{2}(aq)$$

$$K_{f} = 1.8 \times 10^{5}$$
AgCl(aq) + Cl^{-}(aq) $\leftrightarrows AgCl_{2}(aq)$

$$K = 3.24 \times 10^{-5} = \frac{[AgCl_{2}^{-}]}{[Cl^{-}]}$$

$$[AgCl_{2}^{-}] = (3.24 \times 10^{-5})[Cl^{-}] = (3.2 \times 10^{-5})[Cl^{-}]$$
b) $[Ag^{+}] = [AgCl_{2}^{-}]$

$$\frac{1.8 \times 10^{-10}}{[Cl^{-}]} = (3.24 \times 10^{-5})[Cl^{-}]$$

$$[Cl^{-}]^{2} = \frac{1.8 \times 10^{-10}}{3.24 \times 10^{-5}}$$

$$[Cl^{-}]^{2} = \frac{1.8 \times 10^{-10}}{3.24 \times 10^{-5}}$$

 $[Cl^-] = 2.3570226 \times 10^{-3} = 2.4 \times 10^{-3} M Cl^$ 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, AgCl₂⁻ 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) = $(7.6367532 \times 10^{-8} + 7.6367532 \times 10^{-8}) M = 1.52735 \times 10^{-7} = 1.5 \times 10^{-7} M$
19.154 $[H^+] = 10^{-9.5} = 3.1622776 \times 10^{-10} M H^+$ (unrounded)
pOH = 14.0 - pH = 14.0 - 9.5 = 4.5
 $[OH^-] = 10^{-4.5} = 3.1622776 \times 10^{-5} M OH^-$ (unrounded)
 $[HCO_3^-] = \left(\frac{65.0 \text{ mg HCO}_3^-}{L}\right) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right) \left(\frac{1 \text{ mol HCO}_3^{--}}{61.02 \text{ g HCO}_3^{--}}\right) = 1.0652245 \times 10^{-3} M HCO_3^-$ (unrounded)
 $[CO_3^{-2}] = \left(\frac{26.0 \text{ mg CO}_3^{-2}}{L}\right) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right) \left(\frac{1 \text{ mol CO}_3^{-2-}}{60.01 \text{ g CO}_3^{-2-}}\right) = 4.3326112 \times 10^{-4} M CO_3^{-2-}$ (unrounded)
Alkalinity = $[HCO_3^-] + 2[CO_3^{-2^-}] + [OH^-] + [H^+]$
Alkalinity = $(1.0652245 \times 10^{-3}) + 2(4.3326112 \times 10^{-4}) + (3.1622776 \times 10^{-5}) + (3.1622776 \times 10^{-10})$

19.155 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 $K_{sp} = [Ca^{2+}][CO_3^{2-}] = S^2 = 4.4 \times 10^{-9}$ $S = 6.6332495 \times 10^{-5} = 6.6 \times 10^{-5} M CaCO_3$ At 30°C $K_{sp} = [Ca^{2+}][CO_3^{2-}] = S^2 = 3.1 \times 10^{-9}$ $S = 5.5677643 \times 10^{-5} = 5.6 \times 10^{-5} M CaCO_3$

19.156 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.

19.157 Assume that pK_a is in the center of the range, and calculate the K_a from the average pK_a . Average pK_a (center of range) = (7.9 + 6.5) / 2 = 7.2 $K_a 10^{-7.2} = 6.3095734 \text{ x } 10^{-8} = 6 \text{ x } 10^{-8}$ There is only one digit after the decimal point in the pK_a values; thus, there is only one significant figure.

19.158 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. This is halfway to the equivalence point. Halfway to the equivalence point means that $pH = pK_a$ $pH = -\log 4.5 \ge 10^{-5} = 4.346787 = 4.35$

Box B

This is the equivalence point. Only A^{-} is present at a concentration of 0.10 M. The K_b for A⁻ is needed. $K_{\rm b} = K_{\rm w} / K_{\rm a} = 1.0 \text{ x } 10^{-14} / 4.5 \text{ x } 10^{-5} = 2.222 \text{ x } 10^{-10} \text{ (unrounded)}$ $A^{-}(aq) + H_2O(l) \leftrightarrows OH^{-}(aq) + HA(aq)$ 0.10 - x $K_{\rm b} = \frac{\left[\mathrm{HA}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{A}^{-}\right]} = 2.222 \text{ x } 10^{-10}$ $K_{\rm b} = \frac{[\mathbf{x}][\mathbf{x}]}{[0.10 - \mathbf{x}]} = 2.222 \text{ x } 10^{-10} \text{ Assume that } \mathbf{x} \text{ is small compared to } 0.10$ $K_{\rm b} = 2.222 \text{ x } 10^{-10} = \frac{({\rm x})({\rm x})}{(0.10)}$ $x = 4.7138095 \times 10^{-6} M OH^{-1}$ (unrounded) Check assumption: $(4.7138095 \times 10^{-6} / 0.10) \times 100\% = 0.005\%$ error, so the assumption is valid. $[H_3O]^+ = K_w / [OH^-] = (1.0 \times 10^{-14}) / (4.7138095 \times 10^{-6})$ = 2.1214264 x 10⁻⁹ M H₃O⁺ (unrounded) $pH = -log [H_3O^+] = -log (2.1214264 \times 10^{-9}) = 8.67337 = 8.67$ 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) $H_2O(l)$ $H_3O^+(aq) + A^-(aq)$ Initial 0.10 0 0 Change +x+x- X Equilibrium 0.10 - x

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

$$K_{a} = 4.5 \text{ x } 10^{-5} = \frac{(\text{H}_{3}\text{O}^{+})(\text{A}^{-})}{(\text{HA})}$$
$$K_{a} = 4.5 \text{ x } 10^{-5} = \frac{(\text{x})(\text{x})}{(0.10 - \text{x})}$$

Assume that x is small compared to 0.10.

$$K_{\rm a} = 4.5 \ {\rm x} \ 10^{-5} = \frac{({\rm x})({\rm x})}{(0.10)}$$

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

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

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

Box D

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

Use the Henderson-Hasselbalch equation for this buffer.

$$pH = pK_a + \log [A^-] / [HA]$$

 $pH = -log (4.5 \times 10^{-5}) + log 5 / 3 = 4.568636 = 4.57$

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**.

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

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

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

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**.