

CHAPTER 19 IONIC EQUILIBRIA IN AQUEOUS SYSTEMS

END-OF-CHAPTER PROBLEMS

- 19.1 The purpose of an acid-base buffer is to maintain a relatively constant pH in a solution.
- 19.2 The weak-acid component neutralizes added base and the weak-base component neutralizes added acid so that the pH of the buffer solution remains relatively constant. The components of a buffer do not neutralize one another when they are a conjugate acid-base pair.
- 19.3 The presence of an ion in common between two solutes will cause any equilibrium involving either of them to shift in accordance with Le Châtelier's principle. For example, addition of NaF to a solution of HF will cause the equilibrium
- $$\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$$
- to shift to the left, away from the excess of F^- , the common ion.
- 19.4 a) **Buffer 3** has equal, high concentrations of both HA and A^- . It has the highest buffering capacity.
b) **All** of the buffers have the same pH range. The practical buffer range is $\text{pH} = \text{p}K_a \pm 1$, and is independent of concentration.
c) **Buffer 2** has the greatest amount of weak base and can therefore neutralize the greatest amount of added acid.
- 19.5 A buffer is a mixture of a weak acid and its conjugate base (or weak base and its conjugate acid). The pH of a buffer decreases only slightly with added H_3O^+ because the added H_3O^+ reacts with the base of the buffer. The result is that the concentration of H_3O^+ does not change much from the original concentration, keeping the pH nearly constant.
- net
- 19.6 A buffer with a high capacity has a great resistance to pH change. A high buffer capacity results when the weak acid and weak base are both present at high concentration. Addition of 0.01 mol of HCl to a high capacity buffer will cause a smaller change in pH than with a low capacity buffer, since the ratio $[\text{HA}]/[\text{A}^-]$ will change less.
- 19.7 Only the **concentration of the buffer components (c)** has an effect on the buffer capacity. In theory, any conjugate pair (of any $\text{p}K_a$) can be used to make a high capacity buffer. With proper choice of components, it can be at any pH. The buffer range changes along with the buffer capacity, but does not determine it. A high capacity buffer will result when comparable quantities (i.e., buffer-component ratio < 10:1) of weak acid and weak base are dissolved so that their concentrations are relatively high.
- 19.8 The buffer-component ratio refers to the ratio of concentrations of the acid and base that make up the buffer. When this ratio is equal to 1, the buffer resists changes in pH with added acid to the same extent that it resists changes in pH with added base. The buffer range extends equally in both the acidic and basic direction. When the ratio shifts with higher [base] than [acid], the buffer is more effective at neutralizing added acid than base so the range extends further in the acidic than basic direction. The opposite is true for a buffer where [acid] > [base]. Buffers with a ratio equal to 1 have the greatest buffer range. The more the buffer-component ratio deviates from 1, the smaller the buffer range.
- 19.9 $\text{p}K_a$ (formic acid) = 3.74; $\text{p}K_a$ (acetic acid) = 4.74. Formic acid would be the better choice, since its $\text{p}K_a$ is closer to the desired pH of 3.5. If acetic acid were used, the buffer-component ratio would be far from 1:1 and the buffer's effectiveness would be lower. The NaOH serves to partially neutralize the acid and produce its conjugate base.
- 19.10 Plan: The buffer components are propanoic acid and propanoate ion, the concentrations of which are known. The sodium ion is a spectator ion and is ignored because it is not involved in the buffer. Write the propanoic acid-dissociation reaction and its K_a expression. Set up a reaction table in which x equals the amount of acid that

dissociates; solving for x will result in $[\text{H}_3\text{O}^+]$, from which the pH can be calculated. Alternatively, the pH can be calculated from the Henderson-Hasselbalch equation.

Solution:

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

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

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

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

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

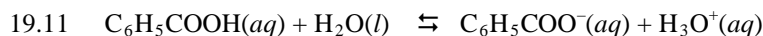
$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.57143 \times 10^{-6}) = 5.2540 = \mathbf{5.25}$$

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

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

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

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



$$K_a = 6.3 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{[x][0.28 + x]}{[0.33 - x]} = \frac{[x][0.28]}{[0.33]}$$

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

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

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

19.12 Plan: The buffer components phenol, $\text{C}_6\text{H}_5\text{OH}$, and phenolate ion, $\text{C}_6\text{H}_5\text{O}^-$, the concentrations of which are known. The sodium ion is a spectator ion and is ignored because it is not involved in the buffer. Write the $\text{C}_6\text{H}_5\text{OH}$ acid-dissociation reaction and its K_a expression. Set up a reaction table in which x equals the amount of acid that dissociates; solving for x will result in $[\text{H}_3\text{O}^+]$, from which the pH can be calculated. Alternatively, the pH can be calculated from the Henderson-Hasselbalch equation.

Solution:

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

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

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

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

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

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

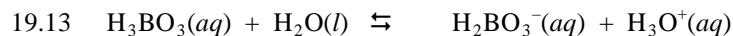
$$\text{pH} = -\log (9.23077 \times 10^{-11}) = 10.03476 = \mathbf{10.03}$$

Verify the pH using the Henderson-Hasselbalch equation:

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

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

$$\text{pH} = 10.03$$



$$K_a = 10^{-\text{p}K_a} = 10^{-9.24} = 5.7543994 \times 10^{-10}$$

$$K_a = 5.7543994 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{BO}_3^-]}{[\text{H}_3\text{BO}_3]} = \frac{[x][0.82 + x]}{[0.12 - x]} = \frac{[x][0.82]}{[0.12]}$$

$$x = [\text{H}_3\text{O}^+] = K_a \frac{[\text{H}_3\text{BO}_3]}{[\text{H}_2\text{BO}_3^-]} = (5.7543994 \times 10^{-10})(0.12/0.82) = 8.4210723 \times 10^{-11} \text{ M}$$

Check assumption: Percent error = $(8.4210723 \times 10^{-11}/0.12)100\% = 7.0 \times 10^{-8}\%$. The assumption is valid.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (8.4210723 \times 10^{-11}) = 10.0746326 = \mathbf{10.07}$$

Verify the pH using the Henderson-Hasselbalch equation.

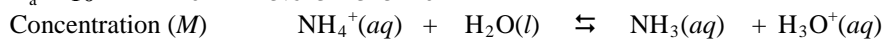
- 19.14 Plan: The buffer components ammonia, NH_3 , and ammonium ion, NH_4^+ , the concentrations of which are known. The chloride ion is a spectator ion and is ignored because it is not involved in the buffer. Write the NH_4^+ acid-dissociation reaction and its K_a expression. Set up a reaction table in which x equals the amount of acid that dissociates; solving for x will result in $[\text{H}_3\text{O}^+]$, from which the pH can be calculated. Alternatively, the pH can be calculated from the Henderson-Hasselbalch equation. The K_a of NH_4^+ will have to be calculated from the $\text{p}K_b$.

Solution:

$$14 = \text{p}K_a + \text{p}K_b$$

$$\text{p}K_a = 14 - \text{p}K_b = 14 - 4.75 = 9.25$$

$$K_a = 10^{-\text{p}K_a} = 10^{-9.25} = 5.62341325 \times 10^{-10}$$



Initial 0.15 — 0.25 0

Change — x — + x + x

Equilibrium 0.15 — x — 0.25 + x x

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

$$K_a = .62341325 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{[0.25 + x][\text{H}_3\text{O}^+]}{[0.15 - x]} = \frac{[0.25][\text{H}_3\text{O}^+]}{[0.15]}$$

$$X = [\text{H}_3\text{O}^+] = K_a \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = (5.62341325 \times 10^{-10})\left(\frac{0.15}{0.25}\right) = 3.374048 \times 10^{-10} \text{ M}$$

Check assumption: Percent error = $(3.374048 \times 10^{-10}/0.15)100\% = 2 \times 10^{-7}\%$. The assumption is valid.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [3.374048 \times 10^{-10}] = 9.4718 = \mathbf{9.47}$$

Verify the pH using the Henderson-Hasselbalch equation.

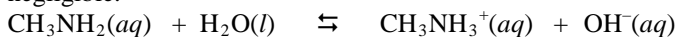
$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

$$\text{pH} = 9.25 + \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right) = 9.25 + \log\left(\frac{[0.25]}{[0.15]}\right)$$

$$\text{pH} = \mathbf{9.47}$$

$$19.15 \quad K_b = 10^{-pK_b} = 10^{-3.35} = 4.4668359 \times 10^{-4}$$

The base component is CH_3NH_2 and the acid component is CH_3NH_3^+ . Neglect Cl^- . Assume $+x$ and $-x$ are negligible.



$$K_b = 4.4668359 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{[0.60 + x][\text{OH}^-]}{[0.50 - x]} = \frac{[0.60][\text{OH}^-]}{[0.50]}$$

$$[\text{OH}^-] = K_b \frac{[\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]} = (4.4668359 \times 10^{-4})(0.50/0.60) = 3.7223632 \times 10^{-4} \text{ M}$$

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

$$p\text{OH} = -\log [\text{OH}^-] = -\log (3.7223632 \times 10^{-4}) = 3.429181254$$

$$p\text{H} = 14.00 - p\text{OH} = 14.00 - 3.429181254 = 10.57081875 = \mathbf{10.57}$$

Verify the pH using the Henderson-Hasselbalch equation.

- 19.16 Plan: Given the pH and K_a of an acid, the buffer-component ratio can be calculated from the Henderson-Hasselbalch equation. Convert K_a to pK_a .

Solution:

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

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

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

$$0.5539467 = \log \left(\frac{[\text{Pr}^-]}{[\text{HPr}]} \right) \quad \text{Raise each side to } 10^x.$$

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

$$19.17 \quad pK_a = -\log K_a = -\log (7.1 \times 10^{-4}) = 3.14874165$$

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

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

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

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

- 19.18 Plan: 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. Set up a reaction table that shows the stoichiometry of adding the strong base NaOH to the weak acid in the buffer. Calculate the new concentrations of the buffer components and use the Henderson-Hasselbalch equation to find the new pH.

Solution:

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

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

$$3.35 = \text{p}K_a - 0.1249387$$

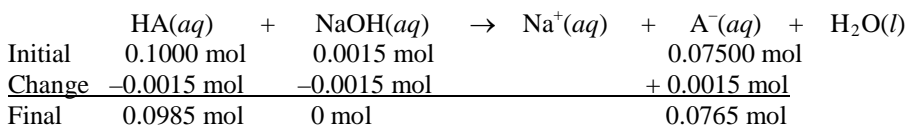
$$\text{p}K_a = 3.474939 = 3.47$$

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

$$\text{Moles of HA} = (0.5000 \text{ L}) \left(\frac{0.2000 \text{ mol HA}}{1 \text{ L}} \right) = 0.1000 \text{ mol HA}$$

$$\text{Moles of } A^- = (0.5000 \text{ L}) \left(\frac{0.1500 \text{ mol } A^-}{1 \text{ L}} \right) = 0.07500 \text{ mol } A^-$$

The reaction is:



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

Then:

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

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

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

$$\text{pH} = 3.474939 + \log \left(\frac{[0.153]}{[0.197]}\right) = 3.365164 = \mathbf{3.37}$$

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

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

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

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

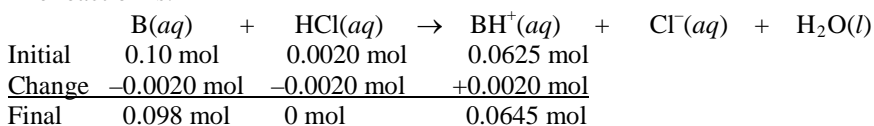
$$\text{p}K_a = 8.67588 = 8.68$$

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

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

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

The reaction is:



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

Then:

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

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

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

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

19.20 Plan: The hydrochloric acid will react with the sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, to form acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$. Calculate the number of moles of HCl and $\text{NaC}_2\text{H}_3\text{O}_2$. Set up a reaction table that shows the stoichiometry of the reaction of HCl and $\text{NaC}_2\text{H}_3\text{O}_2$. All of the HCl will be consumed to form $\text{HC}_2\text{H}_3\text{O}_2$, and the number of moles of $\text{C}_2\text{H}_3\text{O}_2^-$ will decrease. Find the new concentrations of $\text{NaC}_2\text{H}_3\text{O}_2$ and $\text{HC}_2\text{H}_3\text{O}_2$ and use the Henderson-Hasselbalch equation to find the pH of the buffer. Add 0.15 to find the pH of the buffer after the addition of the KOH. Use the Henderson-Hasselbalch equation to find the [base]/[acid] ratio needed to achieve that pH.

Solution:

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

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

	HCl	+	$\text{NaC}_2\text{H}_3\text{O}_2$	\rightarrow	$\text{HC}_2\text{H}_3\text{O}_2$	+	NaCl
Initial	0.092208 mol		0.200 mol		0 mol		
<u>Change</u>	<u>-0.092208 mol</u>		<u>-0.092208 mol</u>		<u>+0.092208 mol</u>		
Final	0 mol		0.107792 mol		0.092208 mol		

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

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

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

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

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

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

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

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

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

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

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

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

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

Given that $[C_2H_3O_2^-]/[HC_2H_3O_2] = 1.64162$ and $[HC_2H_3O_2] + [C_2H_3O_2^-] = 0.2840909 M$, solve for $[C_2H_3O_2^-]$ and substitute into the second equation.

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

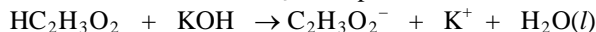
$$[HC_2H_3O_2] = 0.1075441 M \text{ and } [C_2H_3O_2^-] = 0.176547 M$$

$$\text{Moles of } C_2H_3O_2^- \text{ needed} = (0.176547 \text{ mol } C_2H_3O_2^-/L)(0.500 L) = 0.0882735 \text{ mol}$$

$$\text{Moles of } C_2H_3O_2^- \text{ initially} = (0.1531136 \text{ mol } C_2H_3O_2^-/L)(0.500 L) = 0.0765568 \text{ mol}$$

$$\text{This would require the addition of } (0.0882735 \text{ mol} - 0.0765568 \text{ mol}) = 0.0117167 \text{ mol } C_2H_3O_2^-$$

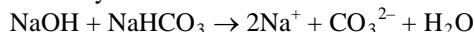
The KOH added reacts with $HC_2H_3O_2$ to produce additional $C_2H_3O_2^-$:



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

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

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



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

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

$$\text{Initial moles } HCO_3^- = \left(\frac{0.050 \text{ mol } HCO_3^-}{L} \right) \left(\frac{10^{-3} L}{1 \text{ mL}} \right) (50.0 \text{ mL}) = 0.0025 \text{ mol } HCO_3^-$$

	NaOH	+	NaHCO ₃	→	2Na ⁺	+	CO ₃ ²⁻	+	H ₂ O
Initial	0.00107 mol		0.0025 mol				0 mol		
Change	-0.00107 mol		-0.00107 mol				+0.00107 mol		
Final	0 mol		0.00143 mol				0.00107 mol		

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

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

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

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

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

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

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

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

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

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

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

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = 0.63401$$

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

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

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

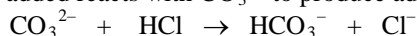
$$[\text{HCO}_3^-] = 0.025205019 \text{ M and } [\text{CO}_3^{2-}] = 0.015980234 \text{ M}$$

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

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

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

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



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

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

19.22 Plan: Select conjugate pairs with K_a values close to the desired $[\text{H}_3\text{O}^+]$.

Solution:

a) For $\text{pH} \approx 4.5$, $[\text{H}_3\text{O}^+] = 10^{-4.5} = 3.2 \times 10^{-5} \text{ M}$. Some good selections are the $\text{HOOC}(\text{CH}_2)_4\text{COOH}/\text{HOOC}(\text{CH}_2)_4\text{COOH}^-$ conjugate pair with K_a equal to 3.8×10^{-5} or $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}/\text{C}_6\text{H}_5\text{CH}_2\text{COO}^-$ conjugate pair with K_a equal to 4.9×10^{-5} . From the base list, the $\text{C}_6\text{H}_5\text{NH}_2/\text{C}_6\text{H}_5\text{NH}_3^+$ conjugate pair comes close with $K_a = K_w/K_b = 1.0 \times 10^{-14}/4.0 \times 10^{-10} = 2.5 \times 10^{-5}$.

b) For $\text{pH} \approx 7.0$, $[\text{H}_3\text{O}^+] = 10^{-7.0} = 1.0 \times 10^{-7} \text{ M}$. Two choices are the $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ conjugate pair with K_a of 6.3×10^{-8} and the $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$ conjugate pair with K_a of 1.1×10^{-7} .

19.23 Select conjugate pairs that have K_a or K_b values close to the desired $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$.

a) For $[\text{H}_3\text{O}^+] \approx 1 \times 10^{-9} \text{ M}$, the HOBr/OBr^- conjugate pair comes close with K_a equal to 2.3×10^{-9} . From the base list, the $\text{NH}_3/\text{NH}_4^+$ conjugate pair comes close with $K_a = K_w/K_b = 1.0 \times 10^{-14}/1.76 \times 10^{-5} = 5.7 \times 10^{-10}$.

b) For $[\text{OH}^-] \approx 3 \times 10^{-5} \text{ M}$, the $\text{NH}_3/\text{NH}_4^+$ conjugate pair comes close; also, it is possible to choose $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-14}/3 \times 10^{-5} = 3.3 \times 10^{-10}$; the $\text{C}_6\text{H}_5\text{OH}/\text{C}_6\text{H}_5\text{O}^-$ comes close with $K_a = 1.0 \times 10^{-10}$.

19.24 The value of the K_a from the Appendix: $K_a = 2.9 \times 10^{-8}$

$$\text{p}K_a = -\log(2.9 \times 10^{-8}) = 7.5376$$

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

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

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

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

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

The original moles of HClO and OCl^- are both $= (0.100 \text{ mol/L})(1.0 \text{ L}) = 0.100 \text{ mol}$

	NaOH	+	HClO	→	Na ⁺	+	ClO ⁻	+	H ₂ O
Initial	0.0050 mol		0.100 mol				0.100 mol		
Change	-0.0050 mol		-0.0050 mol				+ 0.0050 mol		
Final	0 mol		0.095 mol				0.105 mol		

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

19.25 Plan: Given the pH and K_a of an acid, the buffer-component ratio can be calculated from the Henderson-Hasselbalch equation. Convert K_a to $\text{p}K_a$.

Solution:

The value of the K_a from the Appendix: $K_a = 6.3 \times 10^{-8}$ (We are using K_{a2} since we are dealing with the equilibrium in which the second hydrogen ion is being lost.)

$$\text{p}K_a = -\log K_a = -\log(6.3 \times 10^{-8}) = 7.200659451$$

Use the Henderson-Hasselbalch equation:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}\right) \\ 7.40 &= 7.200659451 + \log\left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}\right) \\ 0.19934055 &= \log\left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}\right) \\ \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} &= 1.582486 = \mathbf{1.6} \end{aligned}$$

19.26 You need to know the $\text{p}K_a$ value for the indicator. Its transition range is approximately $\text{p}K_a \pm 1$. If the indicator is a diprotic acid, it will have two transition ranges, one for each of the two H_3O^+ ions lost.

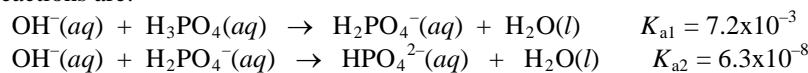
19.27 To see a distinct color in a mixture of two colors, you need one color to be about 10 times the intensity of the other. For this to take place, the concentration ratio $[\text{HIn}]/[\text{In}^-]$ needs to be greater than 10:1 or less than 1:10. This will occur when $\text{pH} = \text{p}K_a - 1$ or $\text{pH} = \text{p}K_a + 1$, respectively, giving a transition range of about two units.

19.28 The addition of an acid-base indicator does not affect the pH of the test solution because the concentration of indicator is very small.

19.29 The equivalence point in a titration is the point at which the number of moles of OH^- equals the number of moles of H_3O^+ (be sure to account for stoichiometric ratios, e.g., one mol of $\text{Ca}(\text{OH})_2$ produces two moles of OH^-). The end point is the point at which the added indicator changes color. If an appropriate indicator is selected, the end point 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 end point is reached first.

19.30 At the equivalence point, the slope of the titration curve is its maximum value.

19.31 a) The reactions are:



The correct order is **C, B, D, A**. Scene C shows the solution before the addition of any NaOH. Scene B is halfway to the first equivalence point; Scene D is halfway to the second equivalence point and Scene A is at end of the titration.

b) Scene B is the second scene in the correct order. This is halfway towards the first equivalence point when there are equal amounts of the acid and conjugate base, which constitutes a buffer.

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}\right)$$

$$\text{Determine the } \text{p}K_a \text{ using } \text{p}K_a = -\log(7.2 \times 10^{-3}) = 2.142668$$

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

- c) 10.00 mL of NaOH is required to reach the first half equivalence point. Therefore, an additional 10.00 mL of NaOH is required to reach the first equivalence point, for a total of 20 mL for the first equivalence point. An additional 20.00 mL of NaOH will be required to reach the second equivalence point where only HPO_4^{2-} remains. A total of **40.00 mL** of NaOH is required to reach Scene A.
- 19.32 a) The initial pH is lowest for the 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** in terms of initial pH.
 b) At the equivalence point, the moles of H_3O^+ equal the moles of OH^- , regardless of the type of titration. However, the strong acid–strong base equivalence point occurs at $\text{pH} = 7.00$ because the resulting cation-anion combination does not react with water. An example is the reaction $\text{NaOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{NaCl}$. Neither Na^+ nor Cl^- ions dissociate in water.
 The weak acid–strong base equivalence point occurs at $\text{pH} > 7$, 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 $\text{HCOOH} + \text{NaOH} \rightarrow \text{HCOO}^- + \text{H}_2\text{O} + \text{Na}^+$. The conjugate base, HCOO^- , reacts with water according to this reaction: $\text{HCOO}^- + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{OH}^-$.
 The strong acid–weak base equivalence point occurs at $\text{pH} < 7$, 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 $\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Cl}^-$. The conjugate acid, NH_4^+ , dissociates slightly in water: $\text{NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{H}_3\text{O}^+$.
 In rank order of pH at the equivalence point, **strong acid–weak base < strong acid–strong base < weak acid–strong base**.
- 19.33 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.
- 19.34 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. If equal values for concentration are put into the Henderson-Hasselbalch equation, the $[\text{base}]/[\text{acid}]$ ratio is 1, the log of 1 is 0, and the pH of the solution equals the $\text{p}K_a$ of the weak acid.
- $$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$
- $$\text{pH} = \text{p}K_a + \log 1$$
- $$\text{pH} = \text{p}K_a$$
- 19.35 Plan: Indicators have a pH range that is approximated by $\text{p}K_a \pm 1$. Find the $\text{p}K_a$ of the indicator by using the relationship $\text{p}K_a = -\log K_a$.
Solution:
 The $\text{p}K_a$ of cresol red is $-\log(3.5 \times 10^{-9}) = 8.5$, so the indicator changes color over an approximate range of 8.5 ± 1 or **7.5 to 9.5**.
- 19.36 Indicators have a pH range that is approximated by $\text{p}K_a \pm 1$. The $\text{p}K_a$ of ethyl red is $-\log(3.8 \times 10^{-6}) = 5.42$, so the indicator changes color over an approximate range of **4.4 to 6.4**.
- 19.37 Plan: Choose an indicator that changes color at a pH close to the pH of the equivalence point.
Solution:
 a) The equivalence point for a strong acid–strong base titration occurs at $\text{pH} = 7.0$. **Bromthymol blue** is an indicator that changes color around pH 7.
 b) The equivalence point for a weak acid–strong base is above pH 7. Estimate the pH at equivalence point from equilibrium calculations.

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

Concentration, <i>M</i>	COOH(<i>aq</i>) + H ₂ O(<i>l</i>)	⇌	HCOOH(<i>aq</i>) + OH ⁻ (<i>aq</i>)
Initial	0.050 <i>M</i>	—	0
Change	- <i>x</i>		+ <i>x</i>
Equilibrium	0.050 - <i>x</i>		<i>x</i>

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

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

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

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

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.7781496 = 8.2218504 = 8.22$$

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

- 19.38 a) Determine the K_a (of the conjugate acid) from the K_b for CH₃NH₂.

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

An acid-base titration of two components of equal concentration and at a 1:1 ratio gives a solution of the conjugates with half the concentration. In this case, the concentration of CH₃NH₃⁺ = 0.050 *M*.

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

$$x = [\text{H}_3\text{O}^+] = 1.0659972 \times 10^{-6} \text{ M}$$

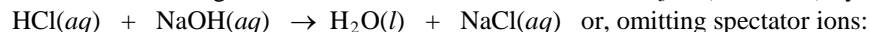
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.0659972 \times 10^{-6}) = 5.97224 = 5.97$$

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

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

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

- 19.39 Plan: The reaction occurring in the titration is the neutralization of H₃O⁺ (from HCl) by OH⁻ (from NaOH):



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

Solution:

The initial number of moles of HCl = (0.1000 mol HCl/L)(10⁻³ L/1 mL)(40.00 mL) = 4.000 × 10⁻³ mol HCl

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

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

- b) Determine the moles of NaOH added:

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

	HCl(<i>aq</i>)	+ NaOH(<i>aq</i>)	→	H ₂ O(<i>l</i>)	+ NaCl(<i>aq</i>)
Initial	4.000 × 10 ⁻³ mol	2.500 × 10 ⁻³ mol		—	0
Change	-2.500 × 10 ⁻³ mol	-2.500 × 10 ⁻³ mol		—	+2.500 × 10 ⁻³ mol
Final	1.500 × 10 ⁻³ mol	0			2.500 × 10 ⁻³ mol

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

The molarity of the excess HCl is (1.500 × 10⁻³ mol HCl)/(0.06500 L) = 0.023077 *M*

$$\text{pH} = -\log(0.023077) = \mathbf{1.6368}$$

- c) Determine the moles of NaOH added:

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

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

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

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

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

d) Determine the moles of NaOH added:

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

	$\text{HCl}(aq)$	+	$\text{NaOH}(aq)$	\rightarrow	$\text{H}_2\text{O}(l)$	+	$\text{NaCl}(aq)$
Initial	4.000×10^{-3} mol		3.990×10^{-3} mol		-		0
Change	-3.990×10^{-3} mol		-3.990×10^{-3} mol		-		$+3.990 \times 10^{-3}$ mol
Final	1.000×10^{-5} mol		0				3.900×10^{-3} mol

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

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

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

e) Determine the moles of NaOH added:

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

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

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

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

Determine the moles of NaOH added:

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

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

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

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

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

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

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

g) Determine the moles of NaOH added:

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

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

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

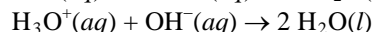
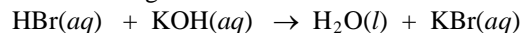
The volume of the solution at this point is $[(40.00 + 50.00) \text{ mL}](10^{-3} \text{ L/1 mL}) = 0.09000 \text{ L}$

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

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

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

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



For the titration of a strong base with a strong acid, the pH before the equivalence point depends on the excess concentration of base and the pH after the equivalence point depends on the excess concentration of acid. At the

equivalence point, there is not an excess of either acid or base so pH is 7.0. The equivalence point occurs when 30.00 mL of acid has been added.

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

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

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

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

b) Determine the moles of HBr added:

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

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

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

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

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

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

c) Determine the moles of HBr added:

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

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

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

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

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

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

d) Determine the moles of HBr added:

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

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

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

The molarity of the excess KOH is $(1.0 \times 10^{-5} \text{ mol KOH})/(0.05990 \text{ L}) = 0.000166945 \text{ M}$

$$\text{pOH} = -\log(0.000166945) = 3.7774266$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.7774266 = 10.2225734 = \mathbf{10.2}$$

e) Determine the moles of HBr added:

$$\text{Moles of added HBr} = (0.1000 \text{ mol HBr/L})(10^{-3} \text{ L/1 mL})(30.00 \text{ mL}) = 3.000 \times 10^{-3} \text{ mol HBr}$$

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

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

Determine the moles of HBr added:

$$\text{Moles of added HBr} = (0.1000 \text{ mol HBr/L})(10^{-3} \text{ L/1 mL})(30.10 \text{ mL}) = 3.010 \times 10^{-3} \text{ mol HBr}$$

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

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

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

$$\text{pH} = -\log(0.000166389) = 3.778875 = \mathbf{3.8}$$

g) Determine the moles of HBr added:

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

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

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

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

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

- 19.41 Plan: 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⁻.

Solution:

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

	HBuT	+	H ₂ O	⇌	H ₃ O ⁺	+	But ⁻
Initial	0.100 M				0		0
Change	-x				+x		+x
Equilibrium	0.100 - x				x		x

$$K_a = 1.54 \times 10^{-5} = \frac{[H_3O^+][But^-]}{[HBuT]} = \frac{x^2}{0.1000 - x} = \frac{x^2}{0.1000}$$

$$x = [H_3O^+] = 1.2409674 \times 10^{-3} M$$

$$pH = -\log [H_3O^+] = -\log (1.2409674 \times 10^{-3}) = 2.9062 = \mathbf{2.91}$$

b) The initial number of moles of HBuT = $(M)(V) = (0.1000 \text{ mol HBuT/L})(10^{-3} \text{ L/1 mL})(20.00 \text{ mL}) = 2.000 \times 10^{-3} \text{ mol HBuT}$

Determine the moles of NaOH added:

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

The NaOH will react with an equal amount of the acid, and $1.000 \times 10^{-3} \text{ mol HBuT}$ will remain. An equal number of moles of But⁻ will form.

	HBuT(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial	$2.000 \times 10^{-3} \text{ mol}$		$1.000 \times 10^{-3} \text{ mol}$		-		0		-
Change	$-1.000 \times 10^{-3} \text{ mol}$		$-1.000 \times 10^{-3} \text{ mol}$		-		$+1.000 \times 10^{-3} \text{ mol}$		-
Final	$1.000 \times 10^{-3} \text{ mol}$		0				$1.000 \times 10^{-3} \text{ mol}$		

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

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

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

Using a reaction table for the equilibrium reaction of HBuT:

	HBuT	+	H ₂ O	⇌	H ₃ O ⁺	+	But ⁻
Initial	0.03333 M		-		0		0.03333 M
Change	-x				+x		+x
Equilibrium	0.03333 - x				x		0.03333 + x

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

$$x = [H_3O^+] = 1.54 \times 10^{-5} M$$

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

c) Determine the moles of NaOH added:

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

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

	HBuT(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial	$2.000 \times 10^{-3} \text{ mol}$		$1.500 \times 10^{-3} \text{ mol}$		-		0		-
Change	$-1.500 \times 10^{-3} \text{ mol}$		$-1.500 \times 10^{-3} \text{ mol}$		-		$+1.500 \times 10^{-3} \text{ mol}$		-
Final	$5.000 \times 10^{-4} \text{ mol}$		0				$1.500 \times 10^{-3} \text{ mol}$		

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

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

The molarity of the But⁻ formed is $(1.500 \times 10^{-3} \text{ mol But}^-)/(0.03500 \text{ L}) = 0.042857 M$

Using a reaction table for the equilibrium reaction of HBuT:

	HBuT	+	H ₂ O	⇌	H ₃ O ⁺	+	But ⁻
Initial	0.0142857 M		-		0		0.042857 M
Change	-x				+x		+x
Equilibrium	0.0142857 - x				x		0.042857 + x

$$K_a = 1.54 \times 10^{-5} = \frac{[H_3O^+][But^-]}{[HBuT]} = \frac{x(0.042857 + x)}{0.0142857 - x} = \frac{x(0.042857)}{0.0142857}$$

$$x = [H_3O^+] = 5.1333 \times 10^{-6} M$$

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

d) Determine the moles of NaOH added:

Moles of added NaOH = (0.1000 mol NaOH/L)(10⁻³ L/1 mL)(19.00 mL) = 1.900x10⁻³ mol NaOH
 The NaOH will react with an equal amount of the acid, and 1.00x10⁻⁴ mol HBut will remain,
 and 1.900x10⁻³ moles of But⁻ will form.

	HBut(aq)	+ NaOH(aq)	→ H ₂ O(l)	+ But ⁻ (aq)	+ Na ⁺ (aq)
Initial	2.000x10 ⁻³ mol	1.900x10 ⁻³ mol	-	0	-
Change	-1.900x10 ⁻³ mol	-1.900x10 ⁻³ mol	-	+1.900x10 ⁻³ mol	-
Final	1.000x10 ⁻⁴ mol	0		1.900x10 ⁻³ mol	

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

The molarity of the excess HBut is (1.00x10⁻⁴ mol HBut)/(0.03900 L) = 0.0025641 M

The molarity of the But⁻ formed is (1.900x10⁻³ mol But⁻)/(0.03900 L) = 0.0487179 M

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+ H ₂ O	⇌ H ₃ O ⁺	+ But ⁻
Initial	0.0025641 M	-	0	0.0487179 M
Change	-x	-	+x	+x
Equilibrium	0.0025641 - x		+x	0.0487179 + x

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

$$x = [\text{H}_3\text{O}^+] = 8.1052632 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (8.1052632 \times 10^{-7}) = 6.09123 = \mathbf{6.09}$$

e) Determine the moles of NaOH added:

Moles of added NaOH = (0.1000 mol NaOH/L)(10⁻³ L/1 mL)(19.95 mL) = 1.995x10⁻³ mol NaOH
 The NaOH will react with an equal amount of the acid, and 5x10⁻⁶ mol HBut will remain,
 and 1.995x10⁻³ moles of But⁻ will form.

	HBut(aq)	+ NaOH(aq)	→ H ₂ O(l)	+ But ⁻ (aq)	+ Na ⁺ (aq)
Initial	2.000x10 ⁻³ mol	1.995x10 ⁻³ mol	-	0	-
Change	-1.995x10 ⁻³ mol	-1.995x10 ⁻³ mol	-	+1.995x10 ⁻³ mol	-
Final	5.000x10 ⁻⁶ mol	0		1.995x10 ⁻³ mol	

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

The molarity of the excess HBut is (5x10⁻⁶ mol HBut)/(0.03995 L) = 0.000125156 M

The molarity of the But⁻ formed is (1.995x10⁻³ mol But⁻)/(0.03995 L) = 0.0499374 M

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+ H ₂ O	⇌ H ₃ O ⁺	+ But ⁻
Initial	0.000125156 M	-	0	0.0499374 M
Change	-x	-	+x	+x
Equilibrium	0.000125156 - x		x	0.0499374 + x

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

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

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

f) Determine the moles of NaOH added:

Moles of added NaOH = (0.1000 mol NaOH/L)(10⁻³ L/1 mL)(20.00 mL) = 2.000x10⁻³ mol NaOH
 The NaOH will react with an equal amount of the acid, and 0 mol HBut will remain, and
 2.000x10⁻³ moles of But⁻ will form. This is the equivalence point.

	HBut(aq)	+ NaOH(aq)	→ H ₂ O(l)	+ But ⁻ (aq)	+ Na ⁺ (aq)
Initial	2.000x10 ⁻³ mol	2.000x10 ⁻³ mol	-	0	-
Change	-2.000x10 ⁻³ mol	-2.000x10 ⁻³ mol	-	+2.000x10 ⁻³ mol	-
Final	0	0		2.000x10 ⁻³ mol	

The K_b of But⁻ is now important.

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

The molarity of the But⁻ formed is (2.000x10⁻³ mol But⁻)/(0.04000 L) = 0.05000 M

$$K_b = K_w/K_a = (1.0 \times 10^{-14})/(1.54 \times 10^{-5}) = 6.49351 \times 10^{-10}$$

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

	But ⁻	+	H ₂ O	⇌	HBut	+	OH ⁻
Initial	0.05000 M		-		0		0
Change	-x		-		+x		+x
Equilibrium	0.05000 - x				x		x

$$K_b = 6.49351 \times 10^{-10} = \frac{[\text{HBut}][\text{OH}^-]}{[\text{But}^-]} = \frac{[x][x]}{[0.05000 - x]} = \frac{[x][x]}{[0.05000]}$$

$$[\text{OH}^-] = x = 5.6980304 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(5.6980304 \times 10^{-6}) = 5.244275238$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.244275238 = 8.7557248 = \mathbf{8.76}$$

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

Determine the moles of NaOH added:

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

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

	HBut(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial	2.000×10^{-3} mol		2.005×10^{-3} mol		-		0		-
Change	-2.000×10^{-3} mol		-2.000×10^{-3} mol		-		$+2.000 \times 10^{-3}$ mol		-
Final	0		5.000×10^{-6} mol				2.000×10^{-3} mol		

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

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

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

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

h) Determine the moles of NaOH added:

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

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

	HBut(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial	2.000×10^{-3} mol		2.500×10^{-3} mol		-		0		-
Change	-2.000×10^{-3} mol		-2.000×10^{-3} mol		-		$+2.000 \times 10^{-3}$ mol		-
Final	0		5.000×10^{-4} mol				2.000×10^{-3} mol		

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

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

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

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

19.42 This is a titration between a weak base and a strong acid. The pH before addition of the acid is dependent on the K_b of the base ($(\text{CH}_3\text{CH}_2)_3\text{N}$). Prior to reaching the equivalence point, the added acid reacts with base to form $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ 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^+ .

$$\begin{aligned} \text{The initial number of moles of } (\text{CH}_3\text{CH}_2)_3\text{N} &= (0.1000 \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{N/L})(10^{-3} \text{ L/1 mL})(20.00 \text{ mL}) \\ &= 2.000 \times 10^{-3} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{N} \end{aligned}$$

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

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

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

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

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

b) Determine the moles of HCl added:

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

The HCl will react with an equal amount of the base, and 1.000×10^{-3} mol $(\text{CH}_3\text{CH}_2)_3\text{N}$ will remain; an equal number of moles of $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ will form.

The volume of the solution at this point is $[(20.00 + 10.00) \text{ mL}](10^{-3} \text{ L/1 mL}) = 0.03000 \text{ L}$
 The molarity of the excess $(\text{CH}_3\text{CH}_2)_3\text{N}$ is $(1.000 \times 10^{-3} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{N}) / (0.03000 \text{ L}) = 0.03333 \text{ M}$
 The molarity of the $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ formed is $(1.000 \times 10^{-3} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{NH}^+) / (0.03000 \text{ L})$
 $= 0.03333 \text{ M}$

$$K_b = 5.2 \times 10^{-4} = \frac{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_3\text{N}]} = \frac{[x][0.03333 + x]}{[0.03333 - x]} = \frac{[x][0.03333]}{[0.03333]}$$

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

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

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

c) Determine the moles of HCl added:

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

The HCl will react with an equal amount of the base, and $5.00 \times 10^{-4} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{N}$ will remain; and $1.500 \times 10^{-3} \text{ moles of } (\text{CH}_3\text{CH}_2)_3\text{NH}^+$ will form.

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

The molarity of the excess $(\text{CH}_3\text{CH}_2)_3\text{N}$ is $(5.00 \times 10^{-4} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{N}) / (0.03500 \text{ L}) = 0.0142857 \text{ M}$

The molarity of the $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ formed is $(1.500 \times 10^{-3} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{NH}^+) / (0.03500 \text{ L})$
 $= 0.0428571 \text{ M}$

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

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

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

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

d) Determine the moles of HCl added:

Moles of added HCl = $(0.1000 \text{ mol HCl/L})(10^{-3} \text{ L/1 mL})(19.00 \text{ mL}) = 1.900 \times 10^{-3} \text{ mol HCl}$

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

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

The molarity of the excess $(\text{CH}_3\text{CH}_2)_3\text{N}$ is $(1.00 \times 10^{-4} \text{ mol } (\text{CH}_3\text{CH}_2)_3\text{N}) / (0.03900 \text{ L}) = 0.002564103 \text{ M}$

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

$$K_b = 5.2 \times 10^{-4} = \frac{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_3\text{N}]} = \frac{[x][0.0487179 + x]}{[0.002564103 - x]} = \frac{[x][0.0487179]}{[0.002564103]}$$

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

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

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

e) Determine the moles of HCl added:

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

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

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

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

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

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

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

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

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

f) Determine the moles of HCl added:

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

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

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

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

$$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (5.2 \times 10^{-4}) = 1.9231 \times 10^{-11}$$

$$K_a = 1.9231 \times 10^{-11} = \frac{[\text{H}_3\text{O}^+][(\text{CH}_3\text{CH}_2)_3\text{N}]}{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+]} = \frac{[x][x]}{[0.05000 - x]} = \frac{[x][x]}{[0.05000]}$$

$$x = [\text{H}_3\text{O}^+] = 9.80587 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.80587 \times 10^{-7}) = 6.0085 = \mathbf{6.01}$$

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

Determine the moles of HCl added:

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

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

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

The molarity of the excess H_3O^+ is $(5 \times 10^{-6} \text{ mol } \text{H}_3\text{O}^+) / (0.04005 \text{ L}) = 1.2484 \times 10^{-4} \text{ M}$

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

h) Determine the moles of HCl added:

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

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

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

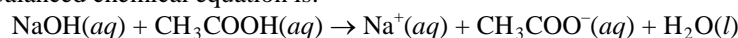
The molarity of the excess H_3O^+ is $(5.00 \times 10^{-4} \text{ mol } \text{H}_3\text{O}^+) / (0.04500 \text{ L}) = 1.1111 \times 10^{-2} \text{ M}$

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

19.43 Plan: Use $(M)(V)$ to find the initial moles of acid and then use the mole ratio in the balanced equation to find moles of base; dividing moles of base by the molarity of the base gives the volume. At the equivalence point, the conjugate base of the weak acid is present; set up a reaction table for the base dissociation in which x = the amount of dissociated base. Use the K_b expression to solve for x from which pOH and then pH is obtained.

Solution:

a) The balanced chemical equation is:



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

Volume (mL) of NaOH =

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

Determine the moles of initially CH_3COOH present:

$$\text{Moles of CH}_3\text{COOH} = \left(\frac{0.0520 \text{ mol CH}_3\text{COOH}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (42.2 \text{ mL}) = 0.0021944 \text{ mol CH}_3\text{COOH}$$

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

The NaOH will react with an equal amount of the acid, 0 mol CH_3COOH will remain, and 0.0021944 moles of CH_3COO^- will be formed.

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

Determine the liters of solution present at the equivalence point:

$$\text{Volume} = [(42.2 + 58.989247) \text{ mL}](10^{-3} \text{ L/1 mL}) = 0.101189247 \text{ L}$$

Concentration of CH_3COO^- at equivalence point:

$$\text{Molarity} = (0.0021944 \text{ mol } \text{CH}_3\text{COO}^-)/(0.101189247 \text{ L}) = 0.0216861 \text{ M}$$

Calculate K_b for CH_3COO^- : $K_a \text{ CH}_3\text{COOH} = 1.8 \times 10^{-5}$

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

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

	CH_3COO^-	+	H_2O	\rightleftharpoons	CH_3COOH	+	OH^-
Initial	0.0216861 M		-		0		0
Change	-x				+x		+x
Equilibrium	0.0216861 - x				x		x

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

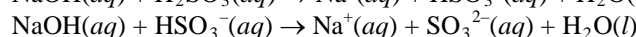
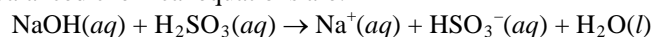
$$K_b = 5.556 \times 10^{-10} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{[x][x]}{[0.0216861 - x]} = \frac{[x][x]}{[0.0216861]}$$

$$[\text{OH}^-] = x = 3.471138 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(3.471138 \times 10^{-6}) = 5.459528$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.459528 = 8.54047 = \mathbf{8.54}$$

b) The balanced chemical equations are:



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 (mL) of NaOH =

$$\left(\frac{0.0850 \text{ mol } \text{H}_2\text{SO}_3}{\text{L}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(28.9 \text{ mL})\left(\frac{1 \text{ mol NaOH}}{1 \text{ mol } \text{H}_2\text{SO}_3}\right)\left(\frac{\text{L}}{0.0372 \text{ mol NaOH}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

$$= 66.034946 = \mathbf{66.0 \text{ mL NaOH}}$$

It will require an equal volume to reach the second equivalence point for a total of $2 \times 66.034946 = \mathbf{132.1 \text{ mL}}$.

Determine the moles of HSO_3^- produced:

$$\text{Moles of } \text{HSO}_3^- = \left(\frac{0.0850 \text{ mol } \text{H}_2\text{SO}_3}{\text{L}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(28.9 \text{ mL})\left(\frac{1 \text{ mol } \text{HSO}_3^{2-}}{1 \text{ mol } \text{H}_2\text{SO}_3}\right) = 0.0024565 \text{ mol } \text{HSO}_3^-$$

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

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

$$\text{Volume} = [(28.9 + 66.034946) \text{ mL}](10^{-3} \text{ L}/1 \text{ mL}) = 0.094934946 \text{ L}$$

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

$$\text{Volume} = [(28.9 + 66.034946 + 66.034946) \text{ mL}](10^{-3} \text{ L}/1 \text{ mL}) = 0.160969892 \text{ L}$$

Concentration of HSO_3^- at equivalence point:

$$\text{Molarity} = (0.0024565 \text{ moles } \text{HSO}_3^-)/(0.094934946 \text{ L}) = 0.0258756 \text{ M}$$

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

$$\text{Molarity} = (0.0024565 \text{ moles } \text{SO}_3^{2-})/(0.160969892 \text{ L}) = 0.0152606 \text{ M}$$

Calculate K_b for HSO_3^- : $K_a \text{ H}_2\text{SO}_3 = 1.4 \times 10^{-2}$

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

Calculate K_b for SO_3^{2-} : $K_a \text{ HSO}_3^- = 6.5 \times 10^{-8}$

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

For the first equivalence point:

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

	HSO_3^-	+	H_2O	\rightleftharpoons	H_2SO_3	+	OH^-
Initial	0.0258756 M				0		0
Change	-x				+x		+x
Equilibrium	0.0258756 - x				x		x

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

$$K_b = 7.142857 \times 10^{-13} = \frac{[\text{H}_2\text{SO}_3][\text{OH}^-]}{[\text{HSO}_3^-]} = \frac{[x][x]}{[0.0258756 - x]} = \frac{[x][x]}{[0.0258756]}$$

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

$$\text{pOH} = -\log(1.359506 \times 10^{-7}) = 6.8666189$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 6.8666189 = 7.13338 = \mathbf{7.13}$$

For the second equivalence point:

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

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

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

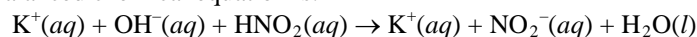
$$K_b = 1.53846 \times 10^{-7} = \frac{[\text{HSO}_3^-][\text{OH}^-]}{[\text{SO}_3^{2-}]} = \frac{[x][x]}{[0.0152606 - x]} = \frac{[x][x]}{[0.0152606]}$$

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

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

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.31467 = 9.68533 = \mathbf{9.69}$$

19.44 a) The balanced chemical equation is:



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

Volume (mL) of KOH =

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

$$= 15.5204 = \mathbf{15.5 \text{ mL KOH}}$$

Determine the moles of HNO_2 present:

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

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

The KOH will react with an equal amount of the acid, 0 mol HNO_2 will remain, and 0.0009126 moles of NO_2^- will be formed.

	$\text{HNO}_2(\text{aq})$	+	$\text{KOH}(\text{aq})$	\rightarrow	$\text{H}_2\text{O}(\text{l})$	+	$\text{NO}_2^-(\text{aq})$	+	$\text{K}^+(\text{aq})$
Initial	0.0009126 mol		0.0009126 mol		-		0		-
Change	-0.0009126 mol		-0.0009126 mol		-		+0.0009126 mol		-
Final	0		0				0.0009126 mol		

Determine the liters of solution present at the equivalence point:

$$\text{Volume} = [(23.4 + 15.5204) \text{ mL}](10^{-3} \text{ L}/1 \text{ mL}) = 0.0389204 \text{ L}$$

Concentration of NO_2^- at equivalence point:

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

Calculate K_b for NO_2^- :

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

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

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

	NO_2^-	+	H_2O	\rightleftharpoons	HNO_2	+	OH^-
Initial	0.023447858 M				0		0
Change	-x				+x		+x
Equilibrium	0.023447858 - x				x		x

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

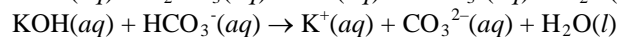
$$K_b = 1.40845 \times 10^{-11} = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} = \frac{[x][x]}{[0.023447858 - x]} = \frac{[x][x]}{[0.023447858]}$$

$$[\text{OH}^-] = x = 5.7468 \times 10^{-7} \text{ M}$$

$$\text{pOH} = -\log(5.7468 \times 10^{-7}) = 6.240574$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 6.240574 = 7.759426 = \mathbf{7.76}$$

b) The balanced chemical equations are:



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 (mL) of KOH =

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

$$= 38.248299 = \mathbf{38.2 \text{ mL KOH}}$$

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

Determine the moles of HCO_3^- produced:

$$\text{Moles} = \left(\frac{0.130 \text{ mol H}_2\text{CO}_3}{\text{L}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(17.3 \text{ mL})\left(\frac{1 \text{ mol HCO}_3^-}{1 \text{ mol H}_2\text{CO}_3}\right) = 0.002249 \text{ mol HCO}_3^-$$

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:

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

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

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

Concentration of HCO_3^- at equivalence point:

$$\text{Molarity} = (0.002249 \text{ mol HCO}_3^-)/(0.055548 \text{ L}) = 0.0404875 \text{ M}$$

Concentration of CO_3^{2-} at equivalence point:

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

Calculate K_b for HCO_3^- :

$$K_a \text{ H}_2\text{CO}_3 = 4.5 \times 10^{-7}$$

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

Calculate K_b for CO_3^{2-} :

$$K_a \text{ HCO}_3^- = 4.7 \times 10^{-11}$$

$$K_b = K_w/K_a = (1.0 \times 10^{-14})/(4.7 \times 10^{-11}) = 2.1276596 \times 10^{-4}$$

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

For the first equivalence point:

$$K_b = 2.222 \times 10^{-8} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} = \frac{[x][x]}{[0.0404875 - x]} = \frac{[x][x]}{[0.0404875]}$$

$$[\text{OH}^-] = x = 2.999387 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(2.999387 \times 10^{-5}) = 4.522967495$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.522967495 = 9.4770 = \mathbf{9.48}$$

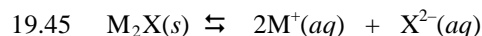
For the second equivalence point:

$$K_b = 2.1276596 \times 10^{-4} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{[x][x]}{[0.023977 - x]} = \frac{[x][x]}{[0.023977]}$$

$$[\text{OH}^-] = x = 2.2586477 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log(2.2586477 \times 10^{-3}) = 2.6461515$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.6461515 = 11.3538 = \mathbf{11.35}$$



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

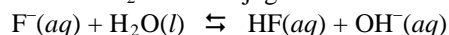
S = molar solubility = $5 \times 10^{-5} \text{ M}$

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

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

The actual K_{sp} is lower than the calculated value because the assumption that M_2X is a strong electrolyte (i.e., exists as $\text{M}^+ + \text{X}^{2-}$) is in error to some degree. There would be some (probably significant) amount of ion pairing to form $\text{MX}^-(aq)$, $\text{M}_2\text{X}(aq)$, etc., which reduces the effective concentrations of the ions.

19.46 Fluoride ion in BaF_2 is the conjugate base of the weak acid HF. The base hydrolysis reaction of fluoride ion

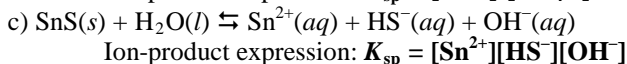
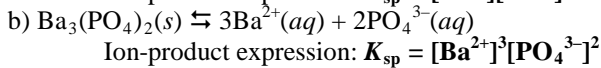
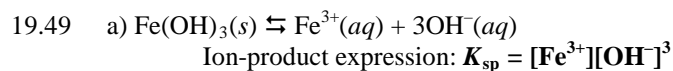
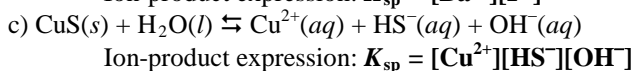
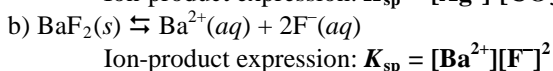
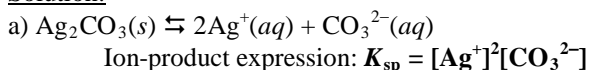


therefore is influenced by the pH of the solution. As the pH increases, $[\text{OH}^-]$ increases and the equilibrium shifts to the left to decrease $[\text{OH}^-]$ and increase $[\text{F}^-]$. As the pH decreases, $[\text{OH}^-]$ decreases and the equilibrium shifts to the right to increase $[\text{OH}^-]$ and decrease $[\text{F}^-]$. The changes in $[\text{F}^-]$ influence the solubility of BaF_2 . Chloride ion is the conjugate base of a strong acid so it does not react with water. Thus, its concentration is not influenced by pH, and solubility of BaCl_2 does not change with pH.

19.47 Consider the reaction $\text{AB}(s) \rightleftharpoons \text{A}^+(aq) + \text{B}^-(aq)$, where $Q_{\text{sp}} = [\text{A}^+][\text{B}^-]$. If $Q_{\text{sp}} > K_{\text{sp}}$, then there are more ions dissolved than expected at equilibrium, and the equilibrium shifts to the left and the compound AB precipitates. The excess ions precipitate as solid from the solution.

19.48 Plan: Write an equation that describes the solid compound dissolving to produce its ions. The ion-product expression follows the equation $K_{\text{sp}} = [\text{M}^{n+}]^p[\text{X}^{z-}]^q$ where p and q are the subscripts of the ions in the compound's formula.

Solution:



19.50 Plan: Write an equation that describes the solid compound dissolving in water and then write the ion-product expression. Write a reaction table, where S is the molar solubility of Ag_2CO_3 . Substitute the given solubility, S , into the ion-expression and solve for K_{sp} .

Solution:

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

$$S = [\text{Ag}_2\text{CO}_3] = 0.032 \text{ M so } [\text{Ag}^+] = 2S = 0.064 \text{ M and } [\text{CO}_3^{2-}] = S = 0.032 \text{ M}$$

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = (0.064)^2(0.032) = 1.31072 \times 10^{-4} = \mathbf{1.3 \times 10^{-4}}$$

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

Concentration (M)	$\text{ZnC}_2\text{O}_4(s)$	\rightleftharpoons	$\text{Zn}^{2+}(aq)$	+	$\text{C}_2\text{O}_4^{2-}(aq)$
Initial	—		0		0
Change	—		$+S$		$+S$
Equilibrium	—		S		S

$$S = [\text{ZnC}_2\text{O}_4] = 7.9 \times 10^{-3} \text{ M so } [\text{Zn}^{2+}] = [\text{C}_2\text{O}_4^{2-}] = S = 7.9 \times 10^{-3} \text{ M}$$

$$K_{\text{sp}} = [\text{Zn}^{2+}][\text{C}_2\text{O}_4^{2-}] = (7.9 \times 10^{-3})(7.9 \times 10^{-3}) = 6.241 \times 10^{-5} = \mathbf{6.2 \times 10^{-5}}$$

19.52 Plan: Write an equation that describes the solid compound dissolving in water and then write the ion-product expression. Write a reaction table, where S is the molar solubility of $\text{Ag}_2\text{Cr}_2\text{O}_7$. Substitute the given solubility, S , converted from mass/volume to molarity, into the ion-expression and solve for K_{sp} .

Solution:

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

$$\text{Molar solubility} = S = \left(\frac{8.3 \times 10^{-3} \text{ g Ag}_2\text{Cr}_2\text{O}_7}{100 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol Ag}_2\text{Cr}_2\text{O}_7}{431.8 \text{ g Ag}_2\text{Cr}_2\text{O}_7} \right) = 0.00019221862 \text{ M}$$

The equation for silver dichromate, $\text{Ag}_2\text{Cr}_2\text{O}_7$, is:

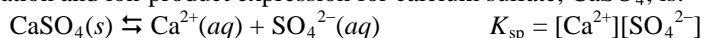
Concentration (M)	$\text{Ag}_2\text{Cr}_2\text{O}_7(s)$	\rightleftharpoons	$2\text{Ag}^+(aq)$	$+$	$\text{Cr}_2\text{O}_7^{2-}(aq)$
Initial	—		0		0
Change	—		$+2S$		$+S$
Equilibrium	—		$2S$		S

$$2S = [\text{Ag}^+] = 2(0.00019221862 M) = 0.00038443724 M$$

$$S = [\text{Cr}_2\text{O}_7^{2-}] = 0.00019221862 M$$

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{Cr}_2\text{O}_7^{2-}] = (2S)^2(S) = (0.00038443724)^2(0.00019221862) = 2.8408 \times 10^{-11} = \mathbf{2.8 \times 10^{-11}}$$

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



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

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

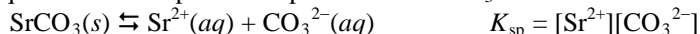
Since one mole of CaSO_4 dissociates to form one mole of Ca^{2+} , the concentration of Ca^{2+} is $S = 0.015350716 M$. The concentration of SO_4^{2-} is $S = 0.015350716 M$ because one mole of CaSO_4 dissociates to form one mole of SO_4^{2-} .

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

- 19.54 Plan: Write the equation that describes the solid compound dissolving in water and then write the ion-product expression. Set up a reaction table that expresses $[\text{Sr}^{2+}]$ and $[\text{CO}_3^{2-}]$ in terms of S , substitute into the ion-product expression, and solve for S . In part b), the $[\text{Sr}^{2+}]$ that comes from the dissolved $\text{Sr}(\text{NO}_3)_2$ must be included in the reaction table.

Solution:

- a) The equation and ion-product expression for SrCO_3 is:



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

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

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

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

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

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

Equilibrium $[\text{Sr}^{2+}] = 0.13 + S$ and equilibrium $[\text{CO}_3^{2-}] = S$ where S is the solubility of SrCO_3 .

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

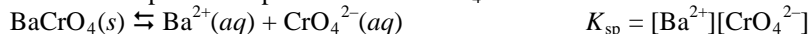
$$K_{\text{sp}} = 5.4 \times 10^{-10} = [\text{Sr}^{2+}][\text{CO}_3^{2-}] = (0.13 + S)S$$

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

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

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

- 19.55 The equation and ion-product expression for BaCrO_4 is:



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

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

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

- b) In $1.5 \times 10^{-3} M \text{Na}_2\text{CrO}_4$, the initial concentration of CrO_4^{2-} is $1.5 \times 10^{-3} M$.

Equilibrium $[\text{Ba}^{2+}] = S$ and equilibrium $[\text{CrO}_4^{2-}] = 1.5 \times 10^{-3} + S$ where S is the solubility of BaCrO_4 .

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

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

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

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

- 19.56 **Plan:** Write the equation that describes the solid compound dissolving in water and then write the ion-product expression. Set up a reaction table that expresses $[Ca^{2+}]$ and $[IO_3^-]$ in terms of S , substitute into the ion-product expression, and solve for S . The $[Ca^{2+}]$ that comes from the dissolved $Ca(NO_3)_2$ and the $[IO_3^-]$ that comes from $NaIO_3$ must be included in the reaction table.

Solution:

a) The equilibrium is: $Ca(IO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2IO_3^-(aq)$. From the Appendix, $K_{sp}(Ca(IO_3)_2) = 7.1 \times 10^{-7}$. 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)	$Ca(IO_3)_2(s)$	\rightleftharpoons	$Ca^{2+}(aq)$	+	$2IO_3^-(aq)$
Initial	—		0.060		0
Change	—		+S		+2S
Equilibrium	—		0.060 + S		2S

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

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

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

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

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

b) Write a reaction table that reflects an initial concentration of $IO_3^- = 0.060 M$. IO_3^- is the common ion.

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

The equilibrium concentration of Ca^{2+} is S , and the IO_3^- concentration is $0.060 + 2S$.

Assume that $0.060 + 2S \approx 0.060$

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

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

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

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

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

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

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

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

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

$$S = 3.099174 \times 10^{-4} = 3.1 \times 10^{-4} M$$

Check assumption: $(3.099174 \times 10^{-4} M) / (0.22 M) \times 100\% = 1.4\% < 5\%$, so the assumption is good.

S represents the molar solubility of $Ag_2SO_4(s)$: $\mathbf{3.1 \times 10^{-4} M}$.

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

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

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

Assume that $0.22 + S \approx 0.22$.

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

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

Check assumption: $(4.1286 \times 10^{-3} M) / (0.22 M) \times 100\% = 1.9\% < 5\%$, so the assumption is good. S represents the molar solubility of Ag_2SO_4 , so the molar solubility of Ag_2SO_4 is $4.1 \times 10^{-3} M$.

19.58 Plan: The larger the K_{sp} , the larger the molar solubility if the number of ions are equal.

Solution:

a) $\text{Mg}(\text{OH})_2$ with $K_{sp} = 6.3 \times 10^{-10}$ has higher molar solubility than $\text{Ni}(\text{OH})_2$ with $K_{sp} = 6 \times 10^{-16}$.

b) PbS with $K_{sp} = 3 \times 10^{-25}$ has higher molar solubility than CuS with $K_{sp} = 8 \times 10^{-34}$.

c) Ag_2SO_4 with $K_{sp} = 1.5 \times 10^{-5}$ has higher molar solubility than MgF_2 with $K_{sp} = 7.4 \times 10^{-9}$.

19.59 The larger the K_{sp} , the larger the molar solubility if the number of ions are equal.

a) SrSO_4 with $K_{sp} = 3.2 \times 10^{-7}$ has higher molar solubility than BaCrO_4 with $K_{sp} = 2.1 \times 10^{-10}$.

b) CaCO_3 with $K_{sp} = 3.3 \times 10^{-9}$ has higher molar solubility than CuCO_3 with $K_{sp} = 3 \times 10^{-12}$.

c) $\text{Ba}(\text{IO}_3)_2$ with $K_{sp} = 1.5 \times 10^{-9}$ has higher molar solubility than Ag_2CrO_4 with $K_{sp} = 2.6 \times 10^{-12}$.

19.60 Plan: If a compound contains an anion that is the weak conjugate base of a weak acid, the concentration of that anion, and thus the solubility of the compound, is influenced by pH.

Solution:

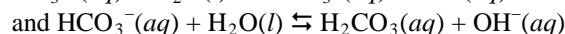
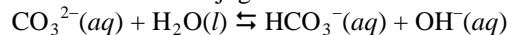
a) $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$

The chloride ion is the anion of a strong acid, so it does not react with H_3O^+ . The solubility is not affected by pH.

b) $\text{SrCO}_3(s) \rightleftharpoons \text{Sr}^{2+}(aq) + \text{CO}_3^{2-}(aq)$

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

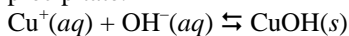
The carbonate ion is the conjugate base of a weak acid and will act as a base:



The H_2CO_3 will decompose to $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$. The gas will escape and further shift the equilibrium. Changes in pH will change the $[\text{CO}_3^{2-}]$, so the solubility of SrCO_3 is affected. **Solubility increases with addition of H_3O^+ (decreasing pH).** A decrease in pH will decrease $[\text{OH}^-]$, causing the base equilibrium to shift to the right which decreases $[\text{CO}_3^{2-}]$, causing the solubility equilibrium to shift to the right, dissolving more solid.

19.61 a) $\text{CuBr}(s) \rightleftharpoons \text{Cu}^+(aq) + \text{Br}^-(aq)$

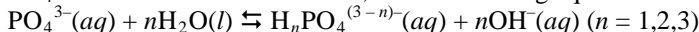
The bromide ion is the anion of a strong acid, so it does not react with H_3O^+ . At high pH the copper ion may precipitate.



b) $\text{Ca}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Ca}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$

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

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



Since these involve OH^- , the solubility will change with changing pH. **Solubility increases with addition of H_3O^+ (decreasing pH).** A decrease in pH will decrease $[\text{OH}^-]$, causing the base equilibrium to shift to the right which decreases $[\text{PO}_4^{3-}]$, causing the solubility equilibrium to shift to the right, dissolving more solid.

19.62 Plan: Find the initial molar concentrations of Cu^{2+} and OH^- . The molarity of the KOH is calculated by converting mass to moles and dividing by the volume. Put these concentrations in the ion-product expression, solve for Q_{sp} , and compare Q_{sp} with K_{sp} . If $Q_{sp} > K_{sp}$, precipitate forms.

Solution:

The equilibrium is: $\text{Cu}(\text{OH})_2(s) \rightleftharpoons \text{Cu}^{2+}(aq) + 2\text{OH}^-(aq)$. The ion-product expression is $K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2$ and, from the Appendix, K_{sp} equals 2.2×10^{-20} .

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

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

$$Q_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2 = (1.0 \times 10^{-3})(1.33666 \times 10^{-3})^2 = 1.786660 \times 10^{-9}$$

Q_{sp} is greater than K_{sp} ($1.8 \times 10^{-9} > 2.2 \times 10^{-20}$), so **Cu(OH)₂ will precipitate.**

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

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

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

$$Q_{sp} = [Pb^{2+}][Cl^-]^2 = (0.12)(2.3952 \times 10^{-4})^2 = 6.8843796 \times 10^{-9}$$

Q_{sp} is smaller than K_{sp} ($6.9 \times 10^{-9} < 1.7 \times 10^{-5}$), so **PbCl₂ will not precipitate.**

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

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

- $C_2O_4^{2-}$ The Ca^{2+} is limiting leaving 0 M, and after the reaction there will be $(0.01550 - 0.00025170) = 0.0152483 \text{ mol}$ of $C_2O_4^{2-}$ left in a total volume of $104 + 100.0 \text{ mL} = 204 \text{ mL}$.

$$[C_2O_4^{2-}] = \left(\frac{0.0152483 \text{ mol } C_2O_4^{2-}}{204 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.0747466 \text{ M } C_2O_4^{2-}$$

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

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

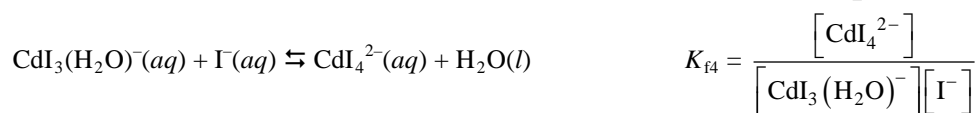
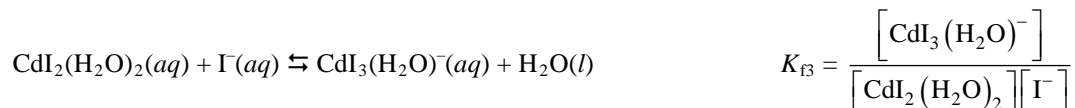
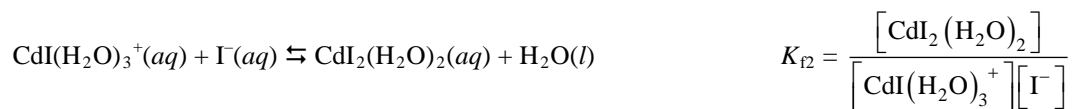
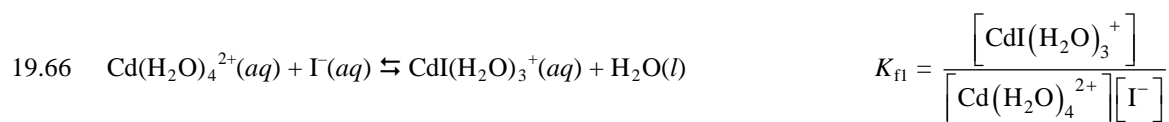
$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = (S)(0.0747466) = 2.3 \times 10^{-9}$$

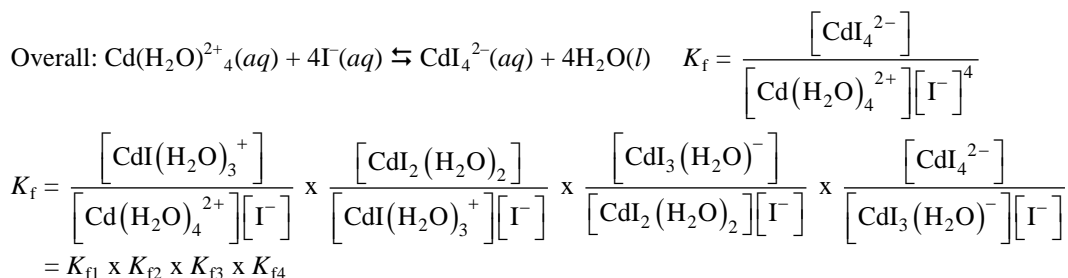
$$S = 3.07706 \times 10^{-8} = 3.1 \times 10^{-8}$$

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

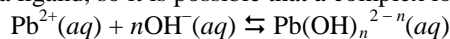
S represents both the molar solubility of Ca^{2+} and $CaC_2O_4 \cdot H_2O(s)$, so the concentration of Ca^{2+} is **$3.1 \times 10^{-8} \text{ M}$** .

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





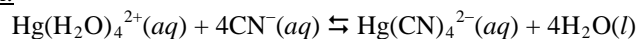
- 19.67 In the context of this equilibrium only, the increased solubility with added OH^- appears to be a violation of Le Châtelier's principle. Adding OH^- should cause the equilibrium to shift towards the left, decreasing the solubility of PbS . Before accepting this conclusion, other possible equilibria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



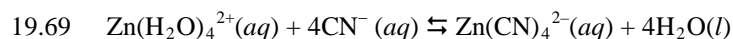
This decreases the concentration of Pb^{2+} , shifting the solubility equilibrium to the right to dissolve more PbS .

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

Solution:



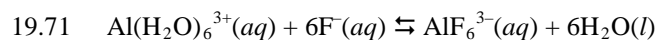
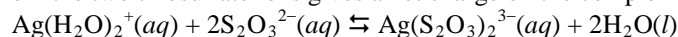
Note that both sides of the equation have the same "overall" charge of -2 . The mercury complex changes from $+2$ to -2 because water is a neutral *molecular* ligand, whereas cyanide is an *ionic* ligand.



- 19.70 Plan: In many cases, a hydrated metal complex (e.g., $\text{Ag(H}_2\text{O)}_4^+$) will exchange ligands when placed in a solution of another ligand (e.g., $\text{S}_2\text{O}_3^{2-}$).

Solution:

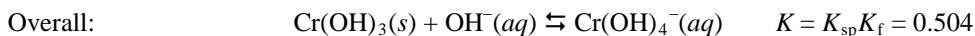
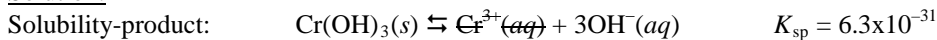
The two water ligands are replaced by two thiosulfate ion ligands. The $+1$ charge from the silver ion plus the -4 charge from the two thiosulfate ions gives a net charge on the complex ion of -3 .



- 19.72 Plan: Write the ion-product equilibrium reaction and the complex-ion equilibrium reaction. Add the two reactions to yield an overall reaction; multiply the two constants to obtain K_{overall} . Write a reaction table where

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

Solution:



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

Reaction table:

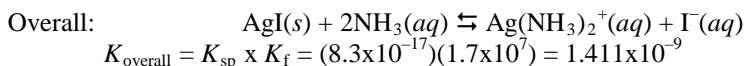
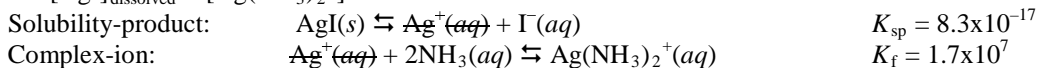
Concentration (M)	$\text{Cr(OH)}_3(s)$	$+$	$\text{OH}^-(aq)$	\rightleftharpoons	$\text{Cr(OH)}_4^-(aq)$
Initial	—		0.1		0
Change	—		$-S$		$+S$
Equilibrium	—		$0.1 - S$		S

Assume that $0.1 - S \approx 0.1$.

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

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

- 19.73 Write the ion-product equilibrium reaction and the complex-ion equilibrium reaction. Add the two reactions to yield an overall reaction; multiply the two constants to obtain K_{overall} . Write a reaction table where $S = [\text{AgI}]_{\text{dissolved}} = [\text{Ag}(\text{NH}_3)_2^+]$.



Reaction table:

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

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

$$K_{\text{overall}} = 1.411 \times 10^{-9} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{I}^-]}{[\text{NH}_3]^2} = \frac{[S][S]}{[2.5 - 2S]^2} = \frac{[S][S]}{[2.5]^2} \quad S = 9.3908 \times 10^{-5} = \mathbf{9.4 \times 10^{-5} M}$$

- 19.74 $\text{p}K_{\text{a}} = -\log K_{\text{a}} = -\log 6.3 \times 10^{-8} = 7.200659$. The K_{a} comes from Appendix C; it is $K_{\text{a}2}$ for phosphoric acid.

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

$$7.00 = 7.200659 + \log \left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)$$

$$-0.200659 = \log \left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)$$

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 0.63000$$

Since they are equimolar, $\frac{V_{\text{HPO}_4^{2-}}}{V_{\text{H}_2\text{PO}_4^-}} = 0.63000$

and $V_{\text{HPO}_4^{2-}} + V_{\text{H}_2\text{PO}_4^-} = 100. \text{ mL}$

so $(0.63000)V_{\text{H}_2\text{PO}_4^-} + V_{\text{H}_2\text{PO}_4^-} = 100. \text{ mL}$

$V_{\text{H}_2\text{PO}_4^-} = \mathbf{61 \text{ mL}}$ and $V_{\text{HPO}_4^{2-}} = \mathbf{39 \text{ mL}}$

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

- 19.76 H_2SO_4 is a strong acid and will be completely ionized: $\text{H}_2\text{SO}_4(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{SO}_4^{2-}(aq) + 2\text{H}_3\text{O}^+(aq)$. Calculate the moles of $\text{H}_3\text{O}^+(aq)$ from the H_2SO_4 in the $8.0 \times 10^3 \text{ lb}$ of water and then the amount of sodium acetate trihydrate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) that will be required to neutralize that amount of $\text{H}_3\text{O}^+(aq)$.

$$\text{Mass (g) of water} = (8.0 \times 10^3 \text{ lb water}) \left(\frac{1 \text{ kg}}{2.205 \text{ lb}} \right) \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) = 3.628118 \times 10^6 \text{ g H}_2\text{O}$$

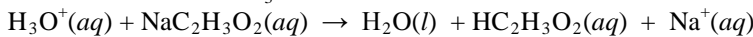
$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

$$10 \text{ ppm} = \frac{\text{mass of H}_2\text{SO}_4}{3.628118 \times 10^6 \text{ g}} \times 10^6$$

Mass (g) of $\text{H}_2\text{SO}_4 = 36.28118 \text{ g}$

$$\text{Moles of } \text{H}_3\text{O}^+ = (36.28118 \text{ g } \text{H}_2\text{SO}_4) \left(\frac{1 \text{ mol } \text{H}_2\text{SO}_4}{98.09 \text{ g } \text{H}_2\text{SO}_4} \right) \left(\frac{2 \text{ mol } \text{H}_3\text{O}^+}{1 \text{ mol } \text{H}_2\text{SO}_4} \right) = 0.7398 \text{ mol } \text{H}_3\text{O}^+$$

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



Mass (lb) of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ required to neutralize the $\text{H}_2\text{SO}_4 =$

$$\left(0.7398 \text{ mol } \text{H}_3\text{O}^+ \right) \left(\frac{1 \text{ mol } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}}{1 \text{ mol } \text{H}_3\text{O}^+} \right) \left(\frac{136.08 \text{ g } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}}{1 \text{ mol } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}} \right) \left(\frac{2.205 \text{ lb}}{1 \text{ kg}} \right) \\ = 0.22198 \text{ lb } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$$

Now consider the acetic acid. Calculate the amount of acetic acid in $8.0 \times 10^3 \text{ lb}$ or $3.628118 \times 10^6 \text{ g } \text{H}_2\text{O}$.

$$\text{Moles of acetic acid} = \left(3.628118 \times 10^6 \text{ g } \text{H}_2\text{O} \right) \left(\frac{0.015\%}{100\%} \right) \left(\frac{1 \text{ mol } \text{HC}_2\text{H}_3\text{O}_2}{60.05 \text{ g } \text{HC}_2\text{H}_3\text{O}_2} \right) = 9.0627 \text{ mol}$$

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

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

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

$$0.2553 = \log \left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[9.0627 \text{ mol}]} \right)$$

$$1.800 = \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[9.0627 \text{ mol}]}$$

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

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

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

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

- 19.77 Plan: 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 $[\text{Na}^+]$ and K_{sp} into the ion-product expression allows one to find $[\text{Ur}^-]$.

Solution:

Molar solubility of NaUr:

$$[\text{NaUr}] = \left(\frac{0.085 \text{ g } \text{NaUr}}{100. \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol } \text{NaUr}}{190.10 \text{ mol } \text{NaUr}} \right) = 4.4713309 \times 10^{-3} \text{ M } \text{NaUr}$$

$$4.4713309 \times 10^{-3} \text{ M } \text{NaUr} = [\text{Na}^+] = [\text{Ur}^-]$$

$$K_{\text{sp}} = [\text{Na}^+][\text{Ur}^-] = (4.4713309 \times 10^{-3})(4.4713309 \times 10^{-3}) = 1.99927998 \times 10^{-5} \text{ M}$$

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

$$K_{\text{sp}} = 1.99927998 \times 10^{-5} \text{ M} = [0.15][\text{Ur}^-]$$

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

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

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

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

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

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

- 19.79 Plan: Substitute the given molar solubility of KCl into the ion-product expression to find the K_{sp} of KCl. 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. Determine a Q_{sp} value to see if K_{sp} is exceeded. If $Q_{sp} < K_{sp}$, nothing will precipitate.

Solution:

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

The solubility of KCl is 3.7 M.

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

b) Find the moles of Cl^- :

Original moles from the KCl:

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

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

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

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

Original moles from the 12 M HCl in the second beaker:

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

This results in $(0.37 + 1.2) \text{ mol} = 1.57 \text{ mol Cl}^-$

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

After the mixing:

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

From 6.0 M HCl in the first beaker:

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

From 12 M HCl in the second beaker:

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

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

From 6.0 M HCl in the first beaker:

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

From 12 M HCl in the second beaker:

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

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

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

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

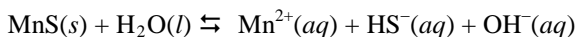
$$x = 0.08659785 = 0.09$$

This is the change in the molarity of each of the ions.

$$\text{Mass (g) of KCl} = \left(\frac{0.08659785 \text{ mol K}^+}{\text{L}} \right) (0.200 \text{ L}) \left(\frac{1 \text{ mol KCl}}{1 \text{ mol K}^+} \right) \left(\frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} \right) = 1.291174 = \mathbf{1 \text{ g KCl}}$$

- 19.80 Determine the solubility of MnS:

$$S = \left(\frac{4.7 \times 10^{-4} \text{ g MnS}}{100 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol MnS}}{87.01 \text{ g MnS}} \right) = 5.401677968 \times 10^{-5} \text{ M}$$



$$K_{sp} = [\text{Mn}^{2+}][\text{HS}^-][\text{OH}^-] = S^3 = (5.401677968 \times 10^{-5})^3 = 1.5761 \times 10^{-13} = \mathbf{1.6 \times 10^{-13}}$$

- 19.81 Plan: Use the Henderson-Hasselbalch equation to find the ratio of $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$ that will produce a buffer with a pH of 7.40 and a buffer of 7.20.

Solution:

a) $K_{a1} = 4.5 \times 10^{-7}$

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

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

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

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

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 11.30342352$$

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

b)
$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}\right)$$

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

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

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

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

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

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

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

$$K_{\text{sp}} = [\text{M}^{2+}][\text{Cl}^-]^2 = [1.2 \times 10^{-5}][4.0 \times 10^{-5}]^2 = 1.92 \times 10^{-14} = \mathbf{1.9 \times 10^{-14}}$$

b) M^{2+} is a common ion for $\text{M}(\text{NO}_3)_2$ and MCl_2 . If $\text{M}(\text{NO}_3)_2$ is added to the solution, $[\text{M}^{2+}]$ is increased and, according to Le Chatelier's principle, the solubility equilibrium will shift to the left, precipitating more MCl_2 . The number of Cl^- particles decreases, the mass of MCl_2 increases, and the K_{sp} value remains the same.

- 19.83 The equilibrium is: $\text{Ca}_5(\text{PO}_4)_3\text{OH}(s) \rightleftharpoons 5\text{Ca}^{2+}(aq) + 3\text{PO}_4^{3-}(aq) + \text{OH}^-(aq)$

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

$$S = 2.7166444 \times 10^{-5} = 2.7 \times 10^{-5} \text{ M}$$

$$\text{Solubility} = (2.7166444 \times 10^{-5} \text{ mol/L})(502.32 \text{ g/mol}) = 0.013646248 = \mathbf{0.014 \text{ g/L Ca}_5(\text{PO}_4)_3\text{OH}}$$

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

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

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

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

19.84 Plan: 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.

Solution:

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

19.85 Plan: 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.

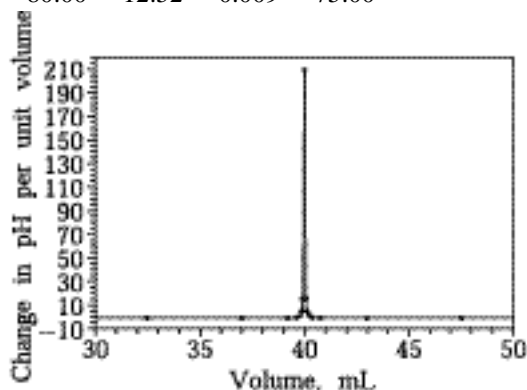
Solution:

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

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

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

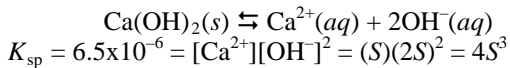
b)



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

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

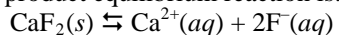
Determine the concentration of a saturated calcium hydroxide solution from the K_{sp} .



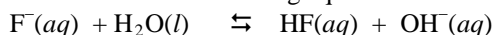
$$S = \sqrt[3]{\frac{6.5 \times 10^{-6}}{4}} = 0.01175667 = 0.012 \text{ M}$$

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

19.87 The ion-product equilibrium reaction is:



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



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

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

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

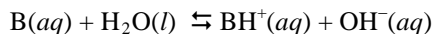
(IV) 0.01M HCl: H^+ ions remove OH^- ions from solution so the base equilibrium reaction shifts to the right, consuming F^- . This shifts the ion-product equilibrium to the right so that more CaF_2 dissolves in this solution than in pure water.

(V) 0.01M Ca(OH)_2 : Because of the common-ion effect, less CaF_2 would dissolve in this solution than in pure water. Additional OH^- ions shift the base equilibrium reaction to the left, producing more F^- . The additional F^- shifts the ion-product equilibrium to the left so less CaF_2 would dissolve.

a) **0.01M HCl**

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

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



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

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

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

$$\text{p}K_b = -\log \frac{[\text{BH}^+]}{[\text{B}]} + \text{pOH}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{BH}^+]}{[\text{B}]}$$

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

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

At 10°C

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

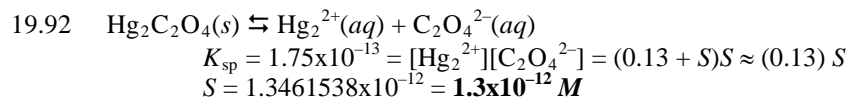
$$S = 6.6332496 \times 10^{-5} = \mathbf{6.6 \times 10^{-5} \text{ M CaCO}_3}$$

At 30°C

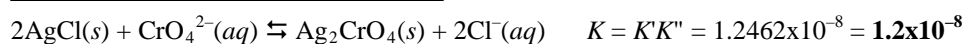
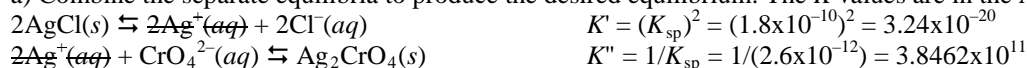
$$K_{sp} = 3.1 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = S^2$$

$$S = 5.5677644 \times 10^{-5} = \mathbf{5.6 \times 10^{-5} \text{ M CaCO}_3}$$

- 19.90 $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$
 $K_{\text{sp}} = 3.3 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = S^2$
 $S = [\text{Ca}^{2+}] = 5.7445626 \times 10^{-5} = \mathbf{5.7 \times 10^{-5} M}$
- 19.91 Refer to Figure 19.5. Litmus paper indicates the pH is below 7. The result from thymol blue, which turns yellow at a pH above 2.5, indicates that the pH is above 2.5. Bromphenol blue is the best indicator as it is green in a fairly narrow range of $3.5 < \text{pH} < 4$. Methyl red turns red below a pH of 4.3. Therefore, a reasonable estimate for the rainwater pH is **3.5 to 4**.



- 19.93 a) Combine the separate equilibria to produce the desired equilibrium. The K values are in the Appendix.



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.

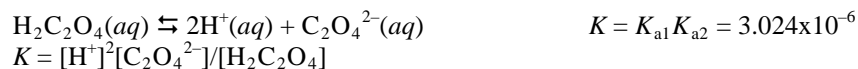
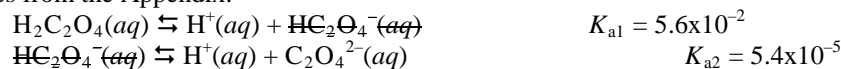
$K_{\text{sp}} = 1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-] = S^2$
 $S = [\text{Ag}^+] = 1.34164 \times 10^{-5} M = \mathbf{1.3 \times 10^{-5} M Ag^+}$

Use the K_{sp} for silver chromate.

$K_{\text{sp}} = 2.6 \times 10^{-12} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$
 $[\text{CrO}_4^{2-}] = (2.6 \times 10^{-12}) / (1.34164 \times 10^{-5})^2 = 0.01444 = 0.014 M$

If the chromate ion concentration exceeds 0.014 M, Ag_2CrO_4 will precipitate.

- 19.94 K values from the Appendix:



a) At pH = 5.5: $[\text{H}^+] = 10^{-5.5} = 3.162 \times 10^{-6} M$
 $[\text{C}_2\text{O}_4^{2-}] = K[\text{H}_2\text{C}_2\text{O}_4] / [\text{H}^+]^2 = (3.024 \times 10^{-6})(3.0 \times 10^{-13}) / (3.162 \times 10^{-6})^2$
 $[\text{C}_2\text{O}_4^{2-}] = 9.07359 \times 10^{-8} M$
 $Q = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$

$Q = (2.6 \times 10^{-3})(9.07359 \times 10^{-8}) = 2.3591 \times 10^{-10} = 2.4 \times 10^{-10} < K_{\text{sp}} = \mathbf{\text{No precipitate}}$

b) At pH = 7.0: $[\text{H}^+] = 10^{-7.0} = 1 \times 10^{-7} M$
 $[\text{C}_2\text{O}_4^{2-}] = K[\text{H}_2\text{C}_2\text{O}_4] / [\text{H}^+]^2 = (3.024 \times 10^{-6})(3.0 \times 10^{-13}) / (1 \times 10^{-7})^2$
 $[\text{C}_2\text{O}_4^{2-}] = 9.072 \times 10^{-5} M$

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

c) The higher pH would favor precipitation.

19.95 a) $K_a = 6.8 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{0.2500 - x} \approx \frac{x^2}{0.2500}$

$x = [\text{H}_3\text{O}^+] = 0.0130384 M$

$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.0130384 M) = 1.8847757 = \mathbf{1.88}$

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

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

$$\text{Moles of NaOH added} = ((57.11488 - 0.50) \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.1532 \text{ mol NaOH}}{1 \text{ L}} \right) = 8.6734 \times 10^{-3} \text{ mol NaOH}$$

Moles of F^- formed = moles NaOH

$$\text{Moles of HF remaining} = (8.750 \times 10^{-3} - 8.6734 \times 10^{-3}) \text{ mol} = 7.66 \times 10^{-5} \text{ mol HF}$$

$$\text{Volume of solution} = (35.00 + 57.11488 - 0.50)(10^{-3} \text{ L/1 mL}) = 0.091615 \text{ L}$$

$$[\text{HF}] = (7.66 \times 10^{-5} \text{ mol HF}) / (0.091615 \text{ L}) = 0.00083611 \text{ M HF}$$

$$[\text{F}^-] = (8.6734 \times 10^{-3} \text{ mol F}^-) / (0.091615 \text{ L}) = 0.09467 \text{ M F}^-$$

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

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

$$\text{pH} = 3.1675 + \log \left(\frac{[0.09467]}{[0.0008361]} \right)$$

$$\text{pH} = 5.2215 = \mathbf{5.22}$$

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

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

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

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

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

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (1.1819 \times 10^{-6}) = 8.4609527 \times 10^{-9} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (8.4609527 \times 10^{-9} \text{ M}) = 8.07258 = \mathbf{8.07}$$

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

$$\text{Volume of solution} = (35.00 + 57.11488 + 0.50)(10^{-3} \text{ L/1 mL}) = 0.092615 \text{ L}$$

$$[\text{OH}^-] = (7.66 \times 10^{-5} \text{ mol F}^-) / (0.092615 \text{ L}) = 8.271 \times 10^{-4} \text{ M OH}^-$$

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

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (8.271 \times 10^{-4}) = 1.2090436 \times 10^{-11} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.2090436 \times 10^{-11} \text{ M}) = 10.917558 = \mathbf{10.92}$$

- 19.96 **Plan:** Use the surface area of the lake and the depth of rain to find the volume of rain that falls. The amount of rain in inches must be converted to yards and multiplied by the lake's surface area to find the volume in yd^3 . Then convert units to cm^3 and on to L. The pH of the rain gives the molarity of H_3O^+ ; multiple that molarity by the volume of rain to find the moles of H_3O^+ in the rain. Use the surface area and depth of the lake to find the volume of water in the lake and add the volume of rain to find the total volume of lake water and rain water. Divide the moles of H_3O^+ in the rain by the total volume of lake and rain water to obtain the molarity of H_3O^+ in the lake/rain water mixture and find the pH. In part c, use the mole ratio between H_3O^+ and HCO_3^- to convert moles of H_3O^+ to moles of HCO_3^- and convert to mass of HCO_3^- .

Solution:

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

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

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

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

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

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

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

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

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

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

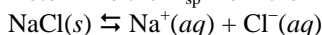
19.97 Plan: Convert the given solubility of NaCl from g/L to mol/L and use this solubility to find the K_{sp} of NaCl. Multiply the molarity of the HCl by the given volume to find the moles of added Cl^- . Use the molarity of Na^+ and the new molarity of Cl^- to determine a Q value to compare to the K_{sp} value.

Solution:

The molarity of a saturated NaCl solution must be found.

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

Determine the K_{sp} from the molarity just calculated.



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

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

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

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

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.

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

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

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

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

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

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

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

b) The equilibrium is: $\text{Hg}_2\text{Cl}_2(s) \rightleftharpoons \text{Hg}_2^{2+}(aq) + 2\text{Cl}^-(aq)$ $K_{\text{sp}} = 1.5 \times 10^{-18}$

$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (S)(2S)^2 = 4S^3 = 1.5 \times 10^{-18}$$

$$S = 7.2112479 \times 10^{-7} = \mathbf{7.2 \times 10^{-7} \text{ M}}$$

c) $[\text{Hg}_2^{2+}] = K_{\text{sp}} / [\text{Cl}^-]^2 =$

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

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

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

$$\text{Mass (g) of Hg}_2\text{Cl}_2 = \left(\frac{7.2112479 \times 10^{-7} \text{ mol Hg}_2\text{Cl}_2}{\text{L}} \right) \left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3} \right) \left(\frac{10^3 \text{ m}}{1 \text{ km}} \right)^3 (4900 \text{ km}^3) \left(\frac{472.1 \text{ g Hg}_2\text{Cl}_2}{1 \text{ mol Hg}_2\text{Cl}_2} \right)$$

$$= 1.6681708 \times 10^{12} = \mathbf{1.7 \times 10^{12} \text{ g Hg}_2\text{Cl}_2}$$

e) Use the value determined in part c).

Mass (g) of $\text{Hg}_2\text{Cl}_2 =$

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

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

19.99 Plan: A buffer contains a weak acid conjugate base pair. A K_a expression is used to calculate the pH of a weak acid while a K_b expression is used to calculate the pH of a weak base. The Henderson-Hasselbalch equation is used to calculate the pH when both the weak acid and conjugate base are present (a buffer).

Solution:

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) Scene A:

The amounts of HA and A^- are equal.

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

$$\text{pH} = \text{p}K_a + \log 1$$

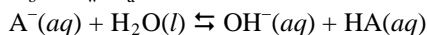
$$\text{pH} = \text{p}K_a = -\log (4.5 \times 10^{-5}) = 4.346787 = \mathbf{4.35}$$

Scene B:

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

The K_b for A^- is needed.

$$K_b = K_w/K_a = 1.0 \times 10^{-14}/4.5 \times 10^{-5} = 2.222 \times 10^{-10}$$



Initial:	0.10 M	0	0
Change:	-x	-x	-x
Equilibrium:	0.10 - x	x	x

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

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

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

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

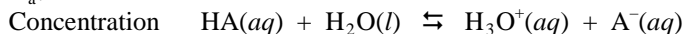
Check assumption: $(4.7138095 \times 10^{-6}/0.10) \times 100\% = 0.005\%$ error, so the assumption is valid.

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

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

Scene C:

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



Initial 0.10 M — 0 0

Change -x +x +x

Equilibrium 0.10 - x x x

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

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

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

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

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

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

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

Scene D:

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

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

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

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

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

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

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

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

c) The addition of Na_2Z would increase the Z^{2-} and shifts the equilibrium to the left, resulting in fewer ions of M^{2+} . There will be more Z^{2-} than M^{2+} . This occurs in box **C**.

d) Lowering the pH will protonate some Z^{2-} (the weak base CO_3^{2-}). This will decrease the Z^{2-} concentration and shift the equilibrium to the right, resulting in more M^{2+} . This occurs in box **A**.