

CHAPTER 17 IONIC EQUILIBRIA IN AQUEOUS SYSTEMS

CHEMICAL CONNECTIONS BOXED READING PROBLEMS

B17.2 Plan: Find the volume of the rain received by multiplying the surface area of the lake by the depth of rain. Find the volume of the lake before the rain. Express both volumes in litres. The pH of the rain is used to find the concentration (mol/L) of H^+ ; this concentration (mol/L) multiplied by the volume of rain gives the amount (mol) of H^+ . The amount (mol) of H^+ divided by the volume of the lake plus rain gives the concentration (mol/L) of H^+ and the pH of the lake.

Solution:

a) To find the volume of rain, multiply the surface area in square kilometers by the depth of rain. Convert the volume to cm^3 and then to L using the density of water.

$$\begin{aligned}\text{Volume (L) of rain} &= (0.040 \text{ km}^2) \left(\frac{1000 \text{ m}}{1 \text{ km}} \right)^2 \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^2 (25.4 \text{ mm}) \left(\frac{1 \text{ cm}}{10 \text{ mm}} \right) \left(\frac{1 \text{ mL}}{1 \text{ cm}^3} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \\ &= 1.016 \times 10^6 \text{ L}\end{aligned}$$

At pH = 4.20, $[\text{H}^+] = 10^{-4.20} = 6.3095734 \times 10^{-5} \text{ mol/L}$

$$\text{amount (mol) of } \text{H}^+ = (1.016 \times 10^6 \text{ L}) \left(\frac{6.3095734 \times 10^{-5} \text{ mol}}{\text{L}} \right) = 64.105266 = \mathbf{64 \text{ mol}}$$

$$\begin{aligned}\text{b) Volume (L) of the lake} &= (0.040 \text{ km}^2) \left(\frac{1000 \text{ m}}{1 \text{ km}} \right)^2 \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^2 (3.05 \text{ m}) \left(\frac{100 \text{ cm}}{1 \text{ m}} \right) \left(\frac{1 \text{ mL}}{1 \text{ cm}^3} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \\ &= 1.22 \times 10^8 \text{ L}\end{aligned}$$

Total volume of lake after rain = $1.22 \times 10^8 \text{ L} + 1.016 \times 10^6 \text{ L} = 1.23016 \times 10^8 \text{ L}$

$$[\text{H}^+] = \frac{\text{mol } \text{H}_3\text{O}^+}{\text{L}} = \frac{64.105266 \text{ mol}}{1.23016 \times 10^8 \text{ L}} = 5.211132 \times 10^{-7} \text{ mol/L}$$

pH = $-\log(5.211132 \times 10^{-7}) = 6.28307 = \mathbf{6.28}$

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

$$\begin{aligned}\text{Mass (g)} &= (64.105266 \text{ mol } \text{H}^+) \left(\frac{1 \text{ mol } \text{HCO}_3^-}{1 \text{ mol } \text{H}_3\text{O}^+} \right) \left(\frac{61.02 \text{ g } \text{HCO}_3^-}{1 \text{ mol } \text{HCO}_3^-} \right) \\ &= 3.9117 \times 10^3 = \mathbf{3.9 \times 10^3 \text{ g } \text{HCO}_3^-}\end{aligned}$$

END-OF-CHAPTER PROBLEMS

- 17.2 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.
- 17.7 The buffer-component ratio refers to the ratio of concentrations of the acid and base that make up the buffer. When this ratio is equal to 1, the buffer resists changes in pH with added acid to the same extent that it resists changes in pH with added base. The buffer range extends equally in both the acidic and basic direction. When the ratio shifts with higher [base] than [acid], the buffer is more effective at neutralizing added acid than base so the range extends further in the acidic than basic direction. The opposite is true for a buffer where [acid] > [base]. Buffers with a ratio equal to 1 have the greatest buffer range. The more the buffer-component ratio deviates from 1, the smaller the buffer range.

- 17.9 Plan: Remember that the weak-acid buffer component neutralizes added base and the weak-base buffer component neutralizes added acid.

Solution:

- a) The buffer-component ratio and pH **increase** with added base. The OH^- reacts with HA to decrease its concentration and increase [NaA]. The ratio $[\text{NaA}]/[\text{HA}]$ thus increases. The pH of the buffer will be more basic because the concentration of base, A^- , has increased and the concentration of acid, HA, decreased.
- b) Buffer-component ratio and pH **decrease** with added acid. The H_3O^+ reacts with A^- to decrease its concentration and increase [HA]. The ratio $[\text{NaA}]/[\text{HA}]$ thus decreases. The pH of the buffer will be more acidic because the concentration of base, A^- , has decreased and the concentration of acid, HA, increased.
- c) Buffer-component ratio and pH **increase** with the added sodium salt. The additional NaA increases the concentration of both NaA and HA, but the relative increase in [NaA] is greater. Thus, the ratio increases and the solution becomes more basic. Whenever base is added to a buffer, the pH always increases, but only slightly if the amount of base is not too large.
- d) Buffer-component ratio and pH **decrease**. The concentration of HA increases more than the concentration of NaA, so the ratio is less and the solution is more acidic.

- 17.11 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 $[\text{H}^+]$, from which the pH can be calculated. Alternatively, the pH can be calculated from the Henderson-Hasselbalch equation.

Solution:

Concentration (mol/L)	$\text{CH}_3\text{CH}_2\text{COOH}(aq) + \text{H}_2\text{O}(l)$	\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 . Check assumption: $0.15/1.3 \times 10^{-5} = 12\,000 > 400$, the assumption is justified.

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

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

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

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

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

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

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

- 17.13 Plan: The buffer components are HNO_2 and NO_2^- , the concentrations of which are known. The potassium ion is a spectator ion and is ignored because it is not involved in the buffer. Write the HNO_2 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 (mol/L)	$\text{HNO}_2(aq) + \text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq)$
Initial	0.55	—	0.75 0
Change	-x	—	+x +x
Equilibrium	$0.55 - x$	—	$0.75 + x$ x

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

$$K_a = 7.1 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{(x)(0.75 + x)}{(0.55 - x)} = \frac{(x)(0.75)}{(0.55)}$$

$$x = [\text{H}_3\text{O}^+] = K_a \frac{[\text{HNO}_2]}{[\text{NO}_2^-]} = (7.1 \times 10^{-4}) \frac{(0.55)}{(0.75)} = 5.2066667 \times 10^{-4} = \mathbf{5.2 \times 10^{-4} \text{ mol/L}}$$

Check assumption: Percent error = $(5.2066667 \times 10^{-4} / 0.55) 100\% = 0.095\%$. The assumption is valid.

$$\text{pH} = -\log [\text{H}^+] = -\log (5.2066667 \times 10^{-4}) = 3.28344 = \mathbf{3.28}$$

Using the Henderson-Hasselbalch equation instead:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right) \quad \text{p}K_a = -\log(7.1 \times 10^{-4}) = 3.149$$

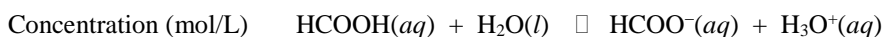
$$\text{pH} = 3.149 + \log \left(\frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \right) = 3.149 + \log \left(\frac{[0.75]}{[0.55]} \right)$$

$$\text{pH} = 3.2837 = 3.28$$

- 17.15 Plan: The buffer components are formic acid, HCOOH , and formate ion, HCOO^- , 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 HCOOH 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:

$$K_a = 10^{-\text{p}K_a} = 10^{-3.74} = 1.8197 \times 10^{-4}$$



$$\text{Initial} \quad 0.45 \quad \text{—} \quad 0.63 \quad 0$$

$$\text{Change} \quad -x \quad \text{—} \quad +x \quad +x$$

$$\text{Equilibrium} \quad 0.45 - x \quad \text{—} \quad 0.63 + x \quad x$$

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

$$K_a = 1.8197 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{(x)(0.63 + x)}{(0.45 - x)} = \frac{(x)(0.63)}{(0.45)}$$

$$x = [\text{H}_3\text{O}^+] = K_a \frac{[\text{HCOOH}]}{[\text{HCOO}^-]} = (1.8197 \times 10^{-4}) \frac{(0.45)}{(0.63)} = 1.29979 \times 10^{-4} = 1.3 \times 10^{-4} \text{ mol/L}$$

Check assumption: Percent error = $(1.29979 \times 10^{-4} / 0.45) 100\% = 0.029\%$. The assumption is valid.

$$\text{pH} = -\log [\text{H}^+] = -\log (1.29979 \times 10^{-4}) = 3.886127 = \mathbf{3.89}$$

Alternatively, using the Henderson-Hasselbalch equation.

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

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

$$\text{pH} = 3.8861 = 3.89$$

- 17.17 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:

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

Concentration (mol/L)	$C_6H_5OH(aq)$	$+ H_2O(l)$	\rightleftharpoons	$C_6H_5O^-(aq)$	$+ H_3O^+(aq)$
Initial	1.2	—		1.3	0
Change	-x	—		+x	+x
Equilibrium	1.2 - x	—		1.3 + x	x

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

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

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

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

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

Using the Henderson-Hasselbalch equation:

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

$$pH = 10.00 + \log \left(\frac{[C_6H_5O^-]}{[C_6H_5OH]} \right) = 10.00 + \log \left(\frac{[1.3]}{[1.2]} \right) = \mathbf{10.03}$$

- 17.19 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 $[H_3O^+]$, 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 pK_b .

Solution:

$$14 = pK_a + pK_b$$

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

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

Concentration (mol/L)	$NH_4^+(aq)$	$+ H_2O(l)$	\rightleftharpoons	$NH_3(aq)$	$+ H_3O^+(aq)$
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 .

$$K_a = 5.62341325 \times 10^{-10} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{(0.25 + x)[H_3O^+]}{(0.15 - x)} = \frac{(0.25)[H_3O^+]}{(0.15)}$$

$$X = [H_3O^+] = K_a \frac{[NH_4^+]}{[NH_3]} = (5.62341325 \times 10^{-10}) \left(\frac{0.15}{0.25} \right) = 3.374048 \times 10^{-10} \text{ mol/L}$$

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

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

Using the Henderson-Hasselbalch equation:

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

$$pH = 9.25 + \log \left(\frac{[NH_3]}{[NH_4^+]} \right) = 9.25 + \log \left(\frac{[0.25]}{[0.15]} \right) = \mathbf{9.47}$$

- 17.21 Plan: The buffer components are HCO_3^- from the salt KHCO_3 and CO_3^{2-} from the salt K_2CO_3 . Choose the K_a value that corresponds to the equilibrium with these two components. The potassium ion is a spectator ion and is ignored because it is not involved in the buffer. Write the 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:

a) K_{a1} refers to carbonic acid, H_2CO_3 , losing one proton to produce HCO_3^- . This is not the correct K_a because H_2CO_3 is not involved in the buffer. K_{a2} is the correct K_a to choose because it is the equilibrium constant for the loss of the second proton to produce CO_3^{2-} from HCO_3^- .

b) Set up the reaction table and use K_{a2} to calculate pH.

Concentration (mol/L)	$\text{HCO}_3^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{CO}_3^{2-}(aq)$	+	$\text{H}_3\text{O}^+(aq)$
Initial	0.22		—		0.37		0
Change	-x		—		+x		+x
Equilibrium	$0.22 - x$		—		$0.37 + x$		x

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

$$K_a = 4.7 \times 10^{-11} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(x)(0.37 + x)}{(0.22 - x)} = \frac{(x)(0.37)}{(0.22)}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = (4.7 \times 10^{-11}) \left(\frac{0.22}{0.37} \right) = 2.79459 \times 10^{-11} \text{ mol/L}$$

Check assumption: Percent error = $(2.79459 \times 10^{-11} / 0.22) 100\% = 1.3 \times 10^{-8}\%$. The assumption is valid.

$$\text{pH} = -\log [\text{H}^+] = -\log (2.79459 \times 10^{-11}) = 10.5537 = \mathbf{10.55}$$

Using the Henderson-Hasselbalch equation:

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

$$\text{pH} = 10.328 + \log \left(\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right) = 10.328 + \log \left(\frac{[0.37]}{[0.22]} \right)$$

$$\mathbf{\text{pH} = 10.55}$$

- 17.23 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:

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

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

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

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

$$\frac{[\text{EtCOO}^-]}{[\text{EtCOOH}]} = 3.5805 = \mathbf{3.6}$$

- 17.25 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:

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

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

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

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

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

- 17.27 Plan: 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. 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:

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

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

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

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

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

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

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

The reaction is:

	HA(aq)	+	NaOH(aq)	→	Na ⁺ (aq)	+	A ⁻ (aq)	+	H ₂ O(l)
Initial	0.1000 mol		0.0015 mol				0.07500 mol		
Change	-0.0015 mol		-0.0015 mol				+0.0015 mol		
Final	0.0985 mol		0 mol				0.0765 mol		

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

Then:

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

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

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

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

Note: Since the volume is identical for the conjugate base and acid, we can substitute the amount (moles) directly into the ratio (i.e., n_{A^-}/V divided by n_{HA}/V is the same as $n_{\text{A}^-}/n_{\text{HA}}$), i.e.,

$$\text{pH} = \text{p}K_a + \log\left(\frac{n_{\text{base}}}{n_{\text{acid}}}\right) = 3.474939 + \log\left(\frac{[0.0765]}{[0.0985]}\right) = 3.37$$

- 17.29 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 $Ba(OH)_2$ 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:

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

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

$$8.77 = pK_a + 0.3010299957$$

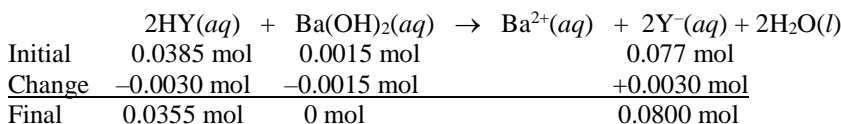
$$pK_a = 8.46897 = 8.47$$

Determine the amount (mol) of conjugate acid (HY) and conjugate base (Y^-) using $(c)(V) = \text{amount (mol)}$.

$$\text{amount (mol) of HY} = (0.350 \text{ L}) \left(\frac{0.110 \text{ mol HY}}{1 \text{ L}} \right) = 0.0385 \text{ mol HY}$$

$$\text{amount (mol) of } Y^- = (0.350 \text{ L}) \left(\frac{0.220 \text{ mol } Y^-}{1 \text{ L}} \right) = 0.077 \text{ mol } Y^-$$

The reaction is:



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

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

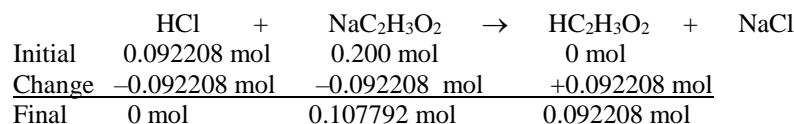
$$pH = 8.46897 + \log \left(\frac{[0.0800]}{[0.0355]} \right) = 8.82183 = \mathbf{8.82}$$

- 17.31 Plan: The hydrochloric acid will react with the sodium acetate, $NaC_2H_3O_2$, to form acetic acid, $HC_2H_3O_2$. Calculate the amount (mol) of HCl and $NaC_2H_3O_2$. Set up a reaction table that shows the stoichiometry of the reaction of HCl and $NaC_2H_3O_2$. All of the HCl will be consumed to form $HC_2H_3O_2$, and the amount (mol) of $C_2H_3O_2^-$ will decrease. Find the new concentrations of $NaC_2H_3O_2$ and $HC_2H_3O_2$ 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:

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

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



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

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

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

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

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

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

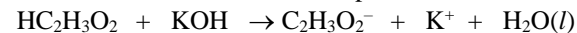
$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.1075441 \text{ mol/L and } [\text{C}_2\text{H}_3\text{O}_2^-] = 0.176547 \text{ mol/L}$$

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

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

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

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



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

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

- 17.33 Plan: Select conjugate pairs with K_a values close to the desired $[\text{H}^+]$. Convert pH to $[\text{H}^+]$ for easy comparison to K_a values in the Appendix. Determine an appropriate base by $[\text{OH}^-] = K_w/[\text{H}^+]$.

Solution:

a) For $\text{pH} \approx 4.5$, $[\text{H}^+] = 10^{-4.5} = 3.2 \times 10^{-5} \text{ mol/L}$. Some good selections are the $\text{HOOC}(\text{CH}_2)_4\text{COOH}/\text{HOOC}(\text{CH}_2)_4\text{COO}^-$ 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 $\text{pH} \approx 7.0$, $[\text{H}^+] = 10^{-7.0} = 1.0 \times 10^{-7} \text{ mol/L}$. 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} .

- 17.35 Plan: Select conjugate pairs with $\text{p}K_a$ values close to the desired pH. Convert pH to $[\text{H}^+]$ for easy comparison to K_a values in the Appendix. Determine an appropriate base by $[\text{OH}^-] = K_w/[\text{H}^+]$.

Solution:

a) For $\text{pH} \approx 3.5$ ($[\text{H}^+] = 10^{-\text{pH}} = 10^{-3.5} = 3.2 \times 10^{-4}$), the best selection is the $\text{HOCH}_2\text{CH}(\text{OH})\text{COOH}/\text{HOCH}_2\text{CH}(\text{OH})\text{COO}^-$ conjugate pair with a $K_a = 2.9 \times 10^{-4}$. The $\text{CH}_3\text{COOC}_6\text{H}_4\text{COOH}/\text{CH}_3\text{COOC}_6\text{H}_4\text{COO}^-$ pair, with $K_a = 3.6 \times 10^{-4}$, is also a good choice. The $[\text{OH}^-] = K_w/[\text{H}^+] = 1.0 \times 10^{-14}/3.2 \times 10^{-4} = 3.1 \times 10^{-11}$, results in no reasonable K_b values from the Appendix.

b) For $\text{pH} \approx 5.5$ ($[\text{H}^+] = 10^{-\text{pH}} = 3 \times 10^{-6}$), no K_{a1} gives an acceptable pair; the K_{a2} values for adipic acid, malonic acid, and succinic acid are reasonable. The $[\text{OH}^-] = K_w/[\text{H}^+] = 1.0 \times 10^{-14}/3 \times 10^{-6} = 3 \times 10^{-9}$; the K_b selection is $\text{C}_5\text{H}_5\text{N}/\text{C}_5\text{H}_5\text{NH}^+$.

- 17.38 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:
 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.)
 $pK_a = -\log K_a = -\log (6.3 \times 10^{-8}) = 7.200659451$
 Use the Henderson-Hasselbalch equation:
- $$pH = pK_a + \log \left(\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \right)$$
- $$7.40 = 7.200659451 + \log \left(\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \right)$$
- $$0.19934055 = \log \left(\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \right)$$
- $$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 1.582486 = \mathbf{1.6}$$
- 17.42 To see a distinct colour in a mixture of two colours, you need one colour to be about 10 times the intensity of the other. For this to take place, the concentration ratio $[HIn]/[In^-]$ needs to be greater than 10:1 or less than 1:10. This will occur when $pH = pK_a - 1$ or $pH = pK_a + 1$, respectively, giving a transition range of about two units.
- 17.44 The equivalence point in a titration is the point at which the amount (mol) of OH^- equals the amount (mol) of H_3O^+ (be sure to account for stoichiometric ratios, e.g., one mol of $Ca(OH)_2$ produces two moles of OH^-). The end point is the point at which the added indicator changes colour. 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 colour at a pH after the equivalence point means the equivalence point is reached first. However, if an indicator is selected that changes colour at a pH before the equivalence point, then the end point is reached first.
- 17.46 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 amount (mol) of H^+ equals the amount (mol) of OH^- , regardless of the type of titration. However, the strong acid–strong base equivalence point occurs at $pH = 7.00$ because the resulting cation-anion combination does not react with water. An example is the reaction $NaOH + HCl \rightarrow H_2O + NaCl$. Neither Na^+ nor Cl^- ions dissociate in water.
 The weak acid–strong base equivalence point occurs at $pH > 7$, because the anion of the weak acid is weakly basic, whereas the cation of the strong base does not react with water. An example is the reaction $HCOOH + NaOH \rightarrow HCOO^- + H_2O + Na^+$. The conjugate base, $HCOO^-$, reacts with water according to this reaction: $HCOO^- + H_2O \rightarrow HCOOH + OH^-$.
 The strong acid–weak base equivalence point occurs at $pH < 7$, because the anion of the strong acid does not react with water, whereas the cation of the weak base is weakly acidic. An example is the reaction $HCl + NH_3 \rightarrow NH_4^+ + Cl^-$. The conjugate acid, NH_4^+ , dissociates slightly in water: $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$.
 In rank order of pH at the equivalence point, strong acid–*weak base* < *strong acid*–strong base < *weak acid*–strong base.
- 17.48 At the very centre 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 $[base]/[acid]$ ratio is 1, the log of 1 is 0, and the pH of the solution equals the pK_a of the weak acid.
- $$pH = pK_a + \log \left(\frac{[base]}{[acid]} \right)$$
- $$pH = pK_a + \log 1$$

- 17.52 Plan: Indicators have a pH range that is approximated by $pK_a \pm 1$. Find the pK_a of the indicator by using the relationship $pK_a = -\log K_a$.

Solution:

The pK_a of cresol red is $-\log(3.5 \times 10^{-9}) = 8.5$, so the indicator changes colour over an approximate range of 8.5 ± 1 or **7.5 to 9.5**.

- 17.54 Plan: Choose an indicator that changes colour 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 pH = 7.0. **Bromthymol blue** is an indicator that changes colour 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 mol/L 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, mol/L	COOH(aq) + H ₂ O(l)	⇌	HCOOH(aq) + OH [−] (aq)
Initial	0.050 mol/L	—	0
Change	−x		+x
Equilibrium	0.050 − x		x

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

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

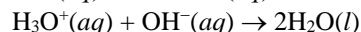
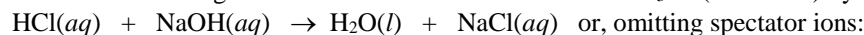
$$[\text{OH}^-] = x = 1.666673 \times 10^{-6} \text{ mol/L}$$

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

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

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

- 17.58 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 (c)(V) to determine the amount (mol) of acid and base. Note that the NaCl product is a neutral salt that does not affect the pH.

Solution:

The initial amount (mol) 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.

$$\text{pH} = -\log(0.1000 \text{ mol/L}) = \mathbf{1.0000}$$

b) Determine the amount (mol) of NaOH added:

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

	HCl(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	NaCl(aq)
Initial	4.000 × 10 ^{−3} mol		2.500 × 10 ^{−3} mol		—		0
Change	−2.500 × 10 ^{−3} mol		−2.500 × 10 ^{−3} mol		—		+2.500 × 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 concentration (mol/L) of the excess HCl is (1.500 × 10^{−3} mol HCl)/(0.06500 L) = 0.023077 mol/L

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

c) Determine the amount (mol) of NaOH added:

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



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

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

d) Determine the amount (mol) of NaOH added:

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

	HCl(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	NaCl(aq)
Initial	4.000×10^{-3} mol		3.990×10^{-3} mol		–		0
Change	-3.990×10^{-3} mol		-3.990×10^{-3} mol		–		$+3.990 \times 10^{-3}$ mol
Final	1.000×10^{-5} mol		0				3.900×10^{-3} mol

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

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

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

e) Determine the amount (mol) of NaOH added:

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

	HCl(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	NaCl(aq)
Initial	4.000×10^{-3} mol		4.000×10^{-3} mol		–		0
Change	-4.000×10^{-3} mol		-4.000×10^{-3} mol		–		$+4.000 \times 10^{-3}$ mol
Final	0		0				4.000×10^{-3} mol

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

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

Determine the amount (mol) of NaOH added:

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

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

	HCl(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	NaCl(aq)
Initial	4.000×10^{-3} mol		4.010×10^{-3} mol		–		0
Change	-4.000×10^{-3} mol		-4.000×10^{-3} mol		–		$+4.000 \times 10^{-3}$ mol
Final	0		1.000×10^{-5} mol				4.000×10^{-3} mol

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

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

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

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

g) Determine the amount (mol) of NaOH added:

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

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

	HCl(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	NaCl(aq)
Initial	4.000×10^{-3} mol		5.000×10^{-3} mol		–		0
Change	-4.000×10^{-3} mol		-4.000×10^{-3} mol		–		$+4.000 \times 10^{-3}$ mol
Final	0		1.000×10^{-3} mol				4.000×10^{-3} mol

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

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

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

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

17.60 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, amount (mol) acid = amount (mol) 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 [H₃O⁺] is dependent on the dissociation of butanoic acid:

	HBut	+	H ₂ O	⇌	H ₃ O ⁺	+	But ⁻
Initial	0.1000 mol/L				0		0
Change	-x				+x		+x
Equilibrium	0.1000 - x				x		x

$$K_a = 1.54 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x^2}{0.1000 - x} = \frac{x^2}{0.1000}$$

$$x = [\text{H}_3\text{O}^+] = 1.2409674 \times 10^{-3} \text{ mol/L}$$

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

b) The initial amount (mol) of HBut = (c)(V) = (0.1000 mol HBut/L)(10⁻³ L/1 mL)(20.00 mL)
= 2.000x10⁻³ mol HBut

Determine the amount (mol) of NaOH added:

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

The NaOH will react with an equal amount of the acid, and 1.000x10⁻³ mol HBut will remain. An equal amount (mol) of But⁻ will form.

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

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

The concentration (mol/L) of the excess HBut is (1.000x10⁻³ mol HBut)/(0.03000 L) = 0.03333 mol/L

The concentration (mol/L) of the But⁻ formed is (1.000x10⁻³ mol But⁻)/(0.03000 L) = 0.03333 mol/L

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H ₂ O	⇌	H ₃ O ⁺	+	But ⁻
Initial	0.03333 mol/L		-		0		0.03333 mol/L
Change	-x				+x		+x
Equilibrium	0.03333 - x				x		0.03333 + x

$$K_a = 1.54 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x(0.0333 + x)}{0.03333 - x} = \frac{x(0.03333)}{0.03333}$$

$$x = [\text{H}_3\text{O}^+] = 1.54 \times 10^{-5} \text{ mol/L}$$

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

c) Determine the amount (mol) of NaOH added:

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

The NaOH will react with an equal amount of the acid, and 5.00x10⁻⁴ mol HBut will remain, and 1.500x10⁻³ moles of But⁻ will form.

	HBut(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial	2.000x10 ⁻³ mol		1.500x10 ⁻³ mol		-		0		-
Change	-1.500x10 ⁻³ mol		-1.500x10 ⁻³ mol		-		+1.500x10 ⁻³ mol		-
Final	5.000x10 ⁻⁴ mol		0				1.500x10 ⁻³ mol		

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

The concentration (mol/L) of the excess HBut is (5.00x10⁻⁴ mol HBut)/(0.03500 L) = 0.0142857 mol/L

The concentration (mol/L) of the But⁻ formed is (1.500x10⁻³ mol But⁻)/(0.03500 L) = 0.042857 mol/L

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H ₂ O	⇌	H ₃ O ⁺	+	But ⁻
Initial	0.0142857 mol/L		-		0		0.042857 mol/L
Change	-x				+x		+x
Equilibrium	0.0142857 - x				x		0.042857 + x

$$K_a = 1.54 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x(0.042857 + x)}{0.0142857 - x} = \frac{x(0.042857)}{0.0142857}$$

$$x = [\text{H}_3\text{O}^+] = 5.1333 \times 10^{-6} \text{ mol/L}$$

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

d) Determine the amount (mol) of NaOH added:

$$\begin{aligned} \text{amount (mol) of added NaOH} &= (0.1000 \text{ mol NaOH/L})(10^{-3} \text{ L/1 mL})(19.00 \text{ mL}) \\ &= 1.900 \times 10^{-3} \text{ mol NaOH} \end{aligned}$$

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

	HBut(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial	2.000 × 10 ⁻³ mol		1.900 × 10 ⁻³ mol		—		0		—
Change	-1.900 × 10 ⁻³ mol		-1.900 × 10 ⁻³ mol		—		+1.900 × 10 ⁻³ mol		—
Final	1.000 × 10 ⁻⁴ mol		0				1.900 × 10 ⁻³ mol		

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 concentration (mol/L) of the excess HBut is $(1.00 \times 10^{-4} \text{ mol HBut})/(0.03900 \text{ L}) = 0.0025641 \text{ mol/L}$

The concentration (mol/L) of the But^- formed is $(1.900 \times 10^{-3} \text{ mol But}^-)/(0.03900 \text{ L}) = 0.0487179 \text{ mol/L}$

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H ₂ O	⇌	H ₃ O ⁺	+	But ⁻
Initial	0.0025641 mol/L		—		0		0.0487179 mol/L
Change	-x		—		+x		+x
Equilibrium	0.0025641 - x				+x		0.0487179 + x

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

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

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

e) Determine the amount (mol) of NaOH added:

$$\begin{aligned} \text{amount (mol) of added NaOH} &= (0.1000 \text{ mol NaOH/L})(10^{-3} \text{ L/1 mL})(19.95 \text{ mL}) \\ &= 1.995 \times 10^{-3} \text{ mol NaOH} \end{aligned}$$

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

	HBut(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial	2.000 × 10 ⁻³ mol		1.995 × 10 ⁻³ mol		—		0		—
Change	-1.995 × 10 ⁻³ mol		-1.995 × 10 ⁻³ mol		—		+1.995 × 10 ⁻³ mol		—
Final	5.000 × 10 ⁻⁶ mol		0				1.995 × 10 ⁻³ mol		

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

The concentration (mol/L) of the excess HBut is $(5 \times 10^{-6} \text{ mol HBut})/(0.03995 \text{ L}) = 0.000125156 \text{ mol/L}$

The concentration (mol/L) of the But^- formed is $(1.995 \times 10^{-3} \text{ mol But}^-)/(0.03995 \text{ L}) = 0.0499374 \text{ mol/L}$

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H ₂ O	⇌	H ₃ O ⁺	+	But ⁻
Initial	0.000125156 mol/L		—		0		0.0499374 mol/L
Change	-x		—		+x		+x
Equilibrium	0.000125156 - x				x		0.0499374 + x

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

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

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

f) Determine the amount (mol) of NaOH added:

$$\begin{aligned} \text{amount (mol) of added NaOH} &= (0.1000 \text{ mol NaOH/L})(10^{-3} \text{ L/1 mL})(20.00 \text{ mL}) \\ &= 2.000 \times 10^{-3} \text{ mol NaOH} \end{aligned}$$

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

	HBut(aq)	+	NaOH(aq)	→	H 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 concentration (mol/L) of the But⁻ formed is (2.000x10⁻³ mol But⁻)/(0.04000 L) = 0.05000 mol/L

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

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

	But ⁻	+	H ₂ O	⇌	HBut	+	OH ⁻
Initial	0.05000 mol/L		–		0		0
Change	–x		–		+x		+x
Equilibrium	0.05000 – x				x		x

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

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

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

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

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

Determine the amount (mol) of NaOH added:

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

The NaOH will react with an equal amount of the acid, 0 mol HBut will remain, and 5x10⁻⁶ moles of NaOH will be in excess. There will be 2.000x10⁻³ 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	2.000x10 ⁻³ mol		2.005x10 ⁻³ mol		–		0		–
Change	–2.000x10 ⁻³ mol		–2.000x10 ⁻³ mol		–		+2.000x10 ⁻³ mol		–
Final	0		5.000x10 ⁻⁶ mol				2.000x10 ⁻³ mol		

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

The concentration (mol/L) of the excess OH⁻ is (5x10⁻⁶ mol OH⁻)/(0.04005 L) = 1.2484x10⁻⁴ mol/L

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

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

h) Determine the amount (mol) of NaOH added:

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

The NaOH will react with an equal amount of the acid, 0 mol HBut will remain, and 5.00x10⁻⁴ moles of NaOH will be in excess.

	HBut(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial	2.000x10 ⁻³ mol		2.500x10 ⁻³ mol		–		0		–
Change	–2.000x10 ⁻³ mol		–2.000x10 ⁻³ mol		–		+2.000x10 ⁻³ mol		–
Final	0		5.000x10 ⁻⁴ mol				2.000x10 ⁻³ mol		

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

The concentration (mol/L) of the excess OH⁻ is (5.00x10⁻⁴ mol OH⁻)/(0.04500 L) = 1.1111x10⁻² mol/L

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

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

- 17.62 Plan: Use (c)(V) to find the initial amount (mol) of acid and then use the mole ratio in the balanced equation to find amount (mol) of base; dividing amount (mol) of base by the concentration (mol/L) 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 =

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

Determine the amount (mol) of initially CH_3COOH present:

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

At the equivalence point, 0.0021944 mol NaOH will be added so the amount (mol) acid = amount (mol) 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.

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

Determine the volume of solution in litre 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:

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

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 mol/L		–		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.

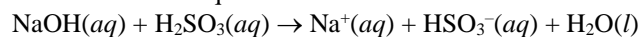
$$K_b = 5.556 \times 10^{-10} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{(x)(x)}{(0.0216861 - x)} = \frac{(x)(x)}{(0.0216861)}$$

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

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

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

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 =

$$\left(\frac{0.0850 \text{ mol H}_2\text{SO}_3}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (28.9 \text{ mL}) \left(\frac{1 \text{ mol NaOH}}{1 \text{ mol H}_2\text{SO}_3} \right) \left(\frac{\text{L}}{0.0372 \text{ mol NaOH}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$
$$= 66.034946 \text{ mL} = \mathbf{66.0 \text{ mL NaOH}}$$

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

Determine the amount (mol) of HSO_3^- produced:

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

An equal amount (mol) of SO_3^{2-} will be present at the second equivalence point.

Determine the volume of solution in litre present at the first equivalence point:

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

Determine the volume of solution in litre present at the second equivalence point:

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

Concentration of HSO_3^- at equivalence point:

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

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

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

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 mol/L				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.

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

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

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

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

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 mol/L				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.

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

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

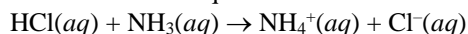
$$\text{pOH} = -\log(4.84539 \times 10^{-5}) = 4.31467$$

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

- 17.64 **Plan:** Use $(c)(V)$ to find the initial amount (mol) of base and then use the mole ratio in the balanced equation to find amount (mol) of acid; dividing amount (mol) of acid by the concentration (mol/L) of the acid gives the volume. At the equivalence point, the conjugate acid of the weak base is present; set up a reaction table for the acid dissociation in which x = the amount of dissociated acid. Use the K_a expression to solve for x from which pH is obtained.

Solution:

a) The balanced chemical equation is:



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

Volume (mL) of HCl =

$$\left(\frac{0.234 \text{ mol } \text{NH}_3}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (65.5 \text{ mL}) \left(\frac{1 \text{ mol HCl}}{1 \text{ mol } \text{NH}_3} \right) \left(\frac{\text{L}}{0.125 \text{ mol HCl}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 122.616 \text{ mL} = \mathbf{123 \text{ mL HCl}}$$

Determine the amount (mol) of NH_3 present:

$$\text{amount (mol)} = \left(\frac{0.234 \text{ mol NH}_3}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (65.5 \text{ mL}) = 0.015327 \text{ mol NH}_3$$

At the equivalence point, 0.015327 mol HCl will be added so the amount (mol) acid = amount (mol) base.

The HCl will react with an equal amount of the base, 0 mol NH_3 will remain, and 0.015327 moles of NH_4^+ will be formed.

	HCl(aq)	+	$\text{NH}_3(\text{aq})$	\rightarrow	$\text{NH}_4^+(\text{aq})$	+	$\text{Cl}^-(\text{aq})$
Initial	0.015327 mol		0.015327 mol		0		–
Change	–0.015327 mol		–0.015327 mol		+0.015327 mol		–
Final	0		0		0.015327 mol		

Determine the volume of solution in litre present at the equivalence point:

$$\text{Volume} = [(65.5 + 122.616) \text{ mL}](10^{-3} \text{ L/1 mL}) = 0.188116 \text{ L}$$

Concentration of NH_4^+ at equivalence point:

$$\text{concentration (mol/L)} = (0.015327 \text{ mol NH}_4^+) / (0.188116 \text{ L}) = 0.081476 \text{ mol/L}$$

Calculate K_a for NH_4^+ :

$$K_b \text{ NH}_3 = 1.76 \times 10^{-5}$$

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

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

	NH_4^+	+	H_2O	\rightleftharpoons	NH_3	+	H_3O^+
Initial	0.081476 mol/L		–		0		0
Change	–x				+x		+x
Equilibrium	0.081476 – x				x		x

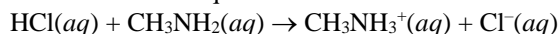
Determine the hydrogen ion concentration from the K_a , and then determine the pH.

$$K_a = 5.6818 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{(x)(x)}{(0.081476 - x)} = \frac{(x)(x)}{(0.081476)}$$

$$x = [\text{H}_3\text{O}^+] = 6.803898 \times 10^{-6} \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (6.803898 \times 10^{-6}) = 5.1672 = \mathbf{5.17}$$

b) The balanced chemical equation is:



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

$$\begin{aligned} \text{Volume (mL) of HCl} &= \left(\frac{1.11 \text{ mol CH}_3\text{NH}_2}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (21.8 \text{ mL}) \left(\frac{1 \text{ mol HCl}}{1 \text{ mol CH}_3\text{NH}_2} \right) \left(\frac{\text{L}}{0.125 \text{ mol HCl}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ &= 193.584 \text{ mL} = \mathbf{194 \text{ mL HCl}} \end{aligned}$$

Determine the amount (mol) of CH_3NH_2 present:

$$\text{amount (mol)} = \left(\frac{1.11 \text{ mol CH}_3\text{NH}_2}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (21.8 \text{ mL}) = 0.024198 \text{ mol CH}_3\text{NH}_2$$

At the equivalence point, 0.024198 mol HCl will be added so the amount (mol) acid = amount (mol) base.

The HCl will react with an equal amount of the base, 0 mol CH_3NH_2 will remain, and 0.024198 moles of CH_3NH_3^+ will be formed.

	HCl(aq)	+	$\text{CH}_3\text{NH}_2(\text{aq})$	\rightarrow	$\text{CH}_3\text{NH}_3^+(\text{aq})$	+	$\text{Cl}^-(\text{aq})$
Initial	0.024198 mol		0.024198 mol		0		–
Change	–0.024198 mol		–0.024198 mol		+0.024198 mol		–
Final	0		0		0.024198 mol		

Determine the volume of solution in litre present at the equivalence point:

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

Concentration of CH_3NH_3^+ at equivalence point:

$$\text{concentration (mol/L)} = (0.024198 \text{ mol CH}_3\text{NH}_3^+) / (0.215384 \text{ L}) = 0.1123482 \text{ mol/L}$$

Calculate K_a for CH_3NH_3^+ :

$$K_b \text{ CH}_3\text{NH}_2 = 4.4 \times 10^{-4}$$

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

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

	CH_3NH_3^+	+	H_2O	\rightleftharpoons	CH_3NH_2	+	H_3O^+
Initial	0.1123482 mol/L		—		0		0
Change	—x				+x		+x
Equilibrium	0.1123482 — x				x		x

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

$$K_a = 2.2727 \times 10^{-11} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]} = \frac{(x)(x)}{(0.1123482 - x)} = \frac{(x)(x)}{(0.1123482)}$$

$$x = [\text{H}_3\text{O}^+] = 1.5979 \times 10^{-6} \text{ mol/L}$$

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

- 17.72 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.

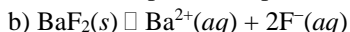
- 17.74 Consider the reaction $\text{AB}(s) \rightleftharpoons \text{A}^+(aq) + \text{B}^-(aq)$, where $Q_{\text{sp}} = [\text{A}^+][\text{B}^-]$. If $Q_{\text{sp}} > K_{\text{sp}}$, then there are more ions dissolved than expected at equilibrium, and the equilibrium shifts to the left and the compound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

- 17.75 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.

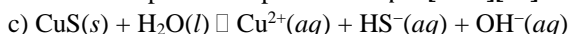
Solution:



$$\text{Ion-product expression: } K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$$



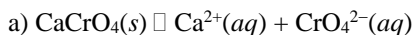
$$\text{Ion-product expression: } K_{\text{sp}} = [\text{Ba}^{2+}][\text{F}^-]^2$$



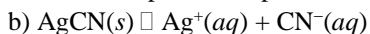
$$\text{Ion-product expression: } K_{\text{sp}} = [\text{Cu}^{2+}][\text{HS}^-][\text{OH}^-]$$

- 17.77 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.

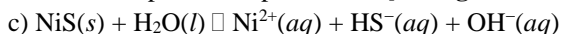
Solution:



$$\text{Ion-product expression: } K_{\text{sp}} = [\text{Ca}^{2+}][\text{CrO}_4^{2-}]$$



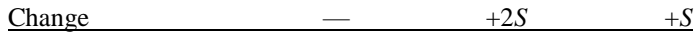
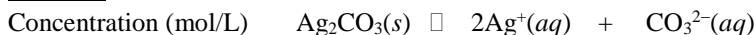
$$\text{Ion-product expression: } K_{\text{sp}} = [\text{Ag}^+][\text{CN}^-]$$



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

- 17.79 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:



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

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

- 17.81 **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 concentration (mol/L), 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 mol/L is:

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

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

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

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

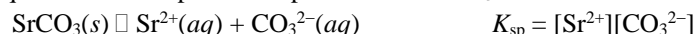
$$S = [\text{Cr}_2\text{O}_7^{2-}] = 0.00019221862 \text{ mol/L}$$

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

- 17.83 **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 (mol/L)	$\text{SrCO}_3(s)$	\rightleftharpoons	$\text{Sr}^{2+}(aq)$	$+ \text{CO}_3^{2-}(aq)$
Initial	—		0	0
Change	—		$+S$	$+S$
Equilibrium	—		S	S

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

$$S = 2.32379 \times 10^{-5} = \mathbf{2.3 \times 10^{-5} \text{ mol/L}}$$

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

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

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

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

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

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

$$S = 4.1538 \times 10^{-9} = \mathbf{4.2 \times 10^{-9} \text{ mol/L}}$$

- 17.85 **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 $[\text{Ca}^{2+}]$ and $[\text{IO}_3^-]$ in terms of S , substitute into the ion-product expression, and solve for S . The $[\text{Ca}^{2+}]$ that comes from the dissolved $\text{Ca}(\text{NO}_3)_2$ and the $[\text{IO}_3^-]$ that comes from NaIO_3 must be included in the reaction table.

Solution:

a) The equilibrium is: $\text{Ca}(\text{IO}_3)_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{IO}_3^-(aq)$. From the Appendix, $K_{sp}(\text{Ca}(\text{IO}_3)_2) = 7.1 \times 10^{-7}$.

Write a reaction table that reflects an initial concentration of $\text{Ca}^{2+} = 0.060 \text{ mol/L}$. In this case, Ca^{2+} is the common ion.

Concentration (mol/L)	$\text{Ca}(\text{IO}_3)_2(s)$	\rightleftharpoons	$\text{Ca}^{2+}(aq)$	$+ 2\text{IO}_3^-(aq)$
Initial	—		0.060	0

Change	—	+S	+2S
Equilibrium	—	0.060 + S	2S

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

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

$$S = 1.71998 \times 10^{-3} = 1.7 \times 10^{-3} \text{ mol/L}$$

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

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

b) Write a reaction table that reflects an initial concentration of $\text{IO}_3^- = 0.060 \text{ mol/L}$. IO_3^- is the common ion.

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

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

Assume that $0.060 + 2S \approx 0.060$

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

$$S = 1.97222 \times 10^{-4} = 2.0 \times 10^{-4} \text{ mol/L}$$

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

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

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

Solution:

a) **Mg(OH)₂** with $K_{sp} = 6.3 \times 10^{-10}$ has higher molar solubility than Ni(OH)_2 with $K_{sp} = 6 \times 10^{-16}$.

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

c) **Ag₂SO₄** with $K_{sp} = 1.5 \times 10^{-5}$ has higher molar solubility than MgF_2 with $K_{sp} = 7.4 \times 10^{-9}$.

17.89 Plan: The larger the K_{sp} , the more water soluble the compound if the number of ions are equal.

Solution:

a) **CaSO₄** with $K_{sp} = 2.4 \times 10^{-5}$ is more water soluble than BaSO_4 with $K_{sp} = 1.1 \times 10^{-10}$.

b) **Mg₃(PO₄)₂** with $K_{sp} = 5.2 \times 10^{-24}$ is more water soluble than $\text{Ca}_3(\text{PO}_4)_2$ with $K_{sp} = 1.2 \times 10^{-29}$.

c) **PbSO₄** with $K_{sp} = 1.6 \times 10^{-8}$ is more water soluble than AgCl with $K_{sp} = 1.8 \times 10^{-10}$.

17.91 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:

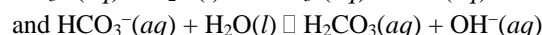
a) $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$

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:



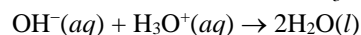
The H_2CO_3 will decompose to $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$. The gas will escape and further shift the equilibrium. Changes in pH will change the $[\text{CO}_3^{2-}]$, so the solubility of SrCO_3 is affected. **Solubility increases with addition of H_3O^+ (decreasing pH).** A decrease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

17.93 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:

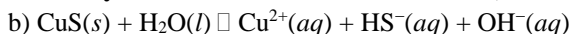
a) $\text{Fe(OH)}_2(s) \rightleftharpoons \text{Fe}^{2+}(aq) + 2\text{OH}^-(aq)$

The hydroxide ion reacts with added H_3O^+ :



The added H_3O^+ consumes the OH^- , driving the equilibrium toward the right to dissolve more $\text{Fe}(\text{OH})_2$.

Solubility increases with addition of H_3O^+ (decreasing pH).



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

- 17.95 **Plan:** Find the initial molar concentrations of Cu^{2+} and OH^- . The concentration (mol/L) of the KOH is calculated by converting mass to the amount (mol) 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 $Q_{\text{sp}} > K_{\text{sp}}$, 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 $K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^-]^2$ and, from the Appendix, K_{sp} equals 2.2×10^{-20} .

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

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

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

Q_{sp} is greater than K_{sp} ($1.8 \times 10^{-9} > 2.2 \times 10^{-20}$), so **$\text{Cu}(\text{OH})_2$ will precipitate.**

- 17.97 **Plan:** Find the initial molar concentrations of Ba^{2+} and IO_3^- . The concentration (mol/L) of the BaCl_2 is calculated by converting mass to amount (mol) 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 $Q_{\text{sp}} > K_{\text{sp}}$, precipitate forms.

Solution:

The equilibrium is: $\text{Ba}(\text{IO}_3)_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2\text{IO}_3^-(aq)$. The ion-product expression is $K_{\text{sp}} = [\text{Ba}^{2+}][\text{IO}_3^-]^2$ and, from the Appendix, K_{sp} equals 1.5×10^{-9} .

$$[\text{Ba}^{2+}] = \left(\frac{7.5 \text{ mg BaCl}_2}{500. \text{ mL}} \right) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol BaCl}_2}{208.2 \text{ g BaCl}_2} \right) \left(\frac{1 \text{ mol Ba}^{2+}}{1 \text{ mol BaCl}_2} \right) = 7.204611 \times 10^{-5} \text{ mol/L Ba}^{2+}$$

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

$$Q_{\text{sp}} = [\text{Ba}^{2+}][\text{IO}_3^-]^2 = (7.204611 \times 10^{-5})(0.023)^2 = 3.81124 \times 10^{-8}$$

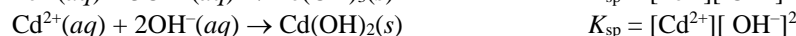
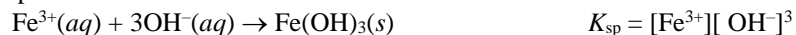
Since $Q_{\text{sp}} > K_{\text{sp}}$ ($3.8 \times 10^{-8} > 1.5 \times 10^{-9}$), **$\text{Ba}(\text{IO}_3)_2$ will precipitate.**

- 17.100 **Plan:** When $\text{Fe}(\text{NO}_3)_3$ and $\text{Cd}(\text{NO}_3)_2$ mix with NaOH , the insoluble compounds $\text{Fe}(\text{OH})_3$ and $\text{Cd}(\text{OH})_2$ form. The compound with the smaller value of K_{sp} precipitates first. Calculate the initial concentrations of Fe^{3+} and Cd^{2+} from the dilution formula $c_{\text{conc}}V_{\text{conc}} = c_{\text{dil}}V_{\text{dil}}$. Use the ion-product expressions to find the minimum OH^- concentration required to cause precipitation of each compound.

Solution:

a) **$\text{Fe}(\text{OH})_3$** will precipitate first because its K_{sp} (1.6×10^{-39}) is smaller than the K_{sp} for $\text{Cd}(\text{OH})_2$ at 7.2×10^{-15} .

The precipitation reactions are:



The concentrations of Fe^{3+} and Cd^{2+} in the mixed solution are found from $c_{\text{conc}}V_{\text{conc}} = c_{\text{dil}}V_{\text{dil}}$

$$[\text{Fe}^{3+}] = [(0.50 \text{ mol/L})(50.0 \text{ mL})]/[(50.0 + 125) \text{ mL}] = 0.142857 \text{ mol/L Fe}^{3+}$$

$$[\text{Cd}^{2+}] = [(0.25 \text{ mol/L})(125 \text{ mL})]/[(50.0 + 125) \text{ mL}] = 0.178571 \text{ mol/L Cd}^{2+}$$

The hydroxide ion concentration required to precipitate the metal ions comes from the metal ion concentrations and the K_{sp} .

$$[\text{OH}^-]_{\text{Fe}} = \sqrt[3]{\frac{K_{\text{sp}}}{[\text{Fe}^{3+}]}} = \sqrt[3]{\frac{1.6 \times 10^{-39}}{0.142857}} = 2.237 \times 10^{-13} = 2.2 \times 10^{-13} \text{ mol/L}$$

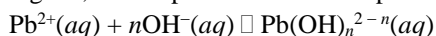
$$[\text{OH}^-]_{\text{Cd}} = \sqrt{\frac{K_{\text{sp}}}{[\text{Cd}^{2+}]}} = \sqrt{\frac{7.2 \times 10^{-15}}{0.178571}} = 2.0079864 \times 10^{-7} = 2.0 \times 10^{-7} \text{ mol/L}$$

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

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

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

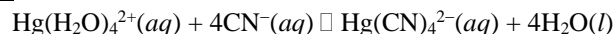
- 17.103 In the context of this equilibrium only, the increased solubility with added OH^- appears to be a violation of Le Châtelier's principle. Adding OH^- should cause the equilibrium to shift towards the left, decreasing the solubility of PbS. Before accepting this conclusion, other possible equilibria 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.

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

Solution:

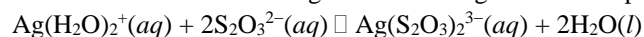


Note that both sides of the equation have the same "overall" charge of -2 . The mercury complex changes from $+2$ to -2 because water is a neutral *molecular* ligand, whereas cyanide is an *ionic* ligand.

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

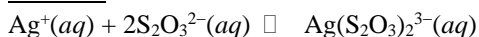
Solution:

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 .



- 17.108 Plan: Write the formation reaction and the K_f expression. The initial concentrations of Ag^+ and $\text{S}_2\text{O}_3^{2-}$ may be determined from $c_{\text{conc}}V_{\text{conc}} = c_{\text{dil}}V_{\text{dil}}$. Set up a reaction table and use the limiting reactant to find the amounts of species in the mixture, assuming a complete reaction. A second reaction table is then written, with x representing the amount of complex ion that dissociates. Use the K_f expression to solve for x .

Solution:



$$[\text{Ag}^+] = (0.044 \text{ mol/L})(25.0 \text{ mL}) / ((25.0 + 25.0) \text{ mL}) = 0.022 \text{ mol/L Ag}^+$$

$$[\text{S}_2\text{O}_3^{2-}] = (0.57 \text{ mol/L})(25.0 \text{ mL}) / ((25.0 + 25.0) \text{ mL}) = 0.285 \text{ mol/L S}_2\text{O}_3^{2-}$$

The reaction gives:

Concentration (mol/L)	$\text{Ag}^+(\text{aq})$	+	$2\text{S}_2\text{O}_3^{2-}(\text{aq})$	\rightarrow	$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(\text{aq})$	
Initial	0.022		0.285		0	
Change	-0.022		-2(0.022)		+0.022	1:2:1 mole ratio
Equilibrium	0		0.241		0.022	

To reach equilibrium:

Concentration (mol/L)	$\text{Ag}^+(\text{aq})$	+	$2\text{S}_2\text{O}_3^{2-}(\text{aq})$	\rightleftharpoons	$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(\text{aq})$
Initial	0		0.241		0.022
Change	+x		+2x		-x

$$\text{Equilibrium} \quad +x \quad \quad \quad 0.241 + 2x \quad \quad \quad 0.022 - x$$

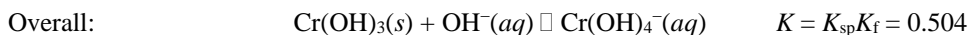
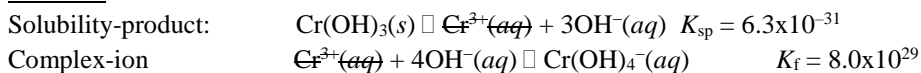
K_f is large, so $[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] \approx 0.022 \text{ mol/L}$ and $[\text{S}_2\text{O}_3^{2-}]_{\text{equil}} \approx 0.241 \text{ mol/L}$

$$K_f = 4.7 \times 10^{13} = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^2} = \frac{(0.022)}{(x)(0.022)^2}$$

$$x = [\text{Ag}^+] = 8.0591778 \times 10^{-15} = \mathbf{8.1 \times 10^{-15} \text{ mol/L}}$$

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

Solution:



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

Reaction table:

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

Assume that $0.1 - S \approx 0.1$.

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

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

- 17.112 Plan: First, calculate the initial amount (mol) of Zn^{2+} and CN^- , then set up reaction table assuming that the reaction first goes to completion, and then calculate back to find the reactant concentrations.

Solution:

The complex formation equilibrium is:



$$\text{amount (mol) of } \text{Zn}^{2+} = (0.84 \text{ g ZnCl}_2) \left(\frac{1 \text{ mol ZnCl}_2}{136.31 \text{ g ZnCl}_2} \right) \left(\frac{1 \text{ mol Zn}^{2+}}{1 \text{ mol ZnCl}_2} \right) = 0.0061624 \text{ mol Zn}^{2+}$$

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

The Zn^{2+} is limiting because the amount (mol) of this ion is significantly smaller, thus, $[\text{Zn}^{2+}] = 0$.

$$\text{amount (mol) of } \text{CN}^- \text{ reacting} = (0.0061624 \text{ mol Zn}^{2+}) \left(\frac{4 \text{ mol CN}^-}{1 \text{ mol Zn}^{2+}} \right) = 0.0246496 \text{ mol CN}^-$$

amount (mol) of CN^- remaining are: $0.03675 - 0.0246496 = 0.0121004 \text{ mol CN}^-$

$$[\text{CN}^-] = \frac{(0.0121004 \text{ mol CN}^-)}{(245 \text{ mL})} \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.0493894 \text{ mol/L CN}^-$$

The Zn^{2+} will produce an equal amount (mol) of the complex with the concentration:

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

Concentration (mol/L)	$\text{Zn}^{2+}(aq)$	$+$	$4\text{CN}^-(aq)$	\rightleftharpoons	$\text{Zn}(\text{CN})_4^{2-}(aq)$
Initial	0		0.0493894		0.025153
Change	$+x$		$+4x$		$-x$
Equilibrium	x		$0.0493894 + 4x$		$0.025153 - x$

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

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

$$x = 1.006481 \times 10^{-16} = 1.0 \times 10^{-16}$$

$$[\text{Zn}^{2+}] = \mathbf{1.0 \times 10^{-16} \text{ mol/L Zn}^{2+}}$$

$$[\text{Zn}(\text{CN})_4^{2-}] = 0.025153 - x = 0.025153 - 1.0 \times 10^{-16} = 0.025153 = \mathbf{0.025 \text{ mol/L Zn}(\text{CN})_4^{2-}}$$

$$[\text{CN}^-] = 0.0493894 + 4x = 0.0493894 + 4(1.0 \times 10^{-16}) = 0.0493894 = \mathbf{0.049 \text{ mol/L CN}^-}$$

- 17.114 Plan: The NaOH will react with the benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, to form the conjugate base benzoate ion, $\text{C}_6\text{H}_5\text{COO}^-$. Calculate the amount (mol) of NaOH and $\text{C}_6\text{H}_5\text{COOH}$. Set up a reaction table that shows the stoichiometry of the reaction of NaOH and $\text{C}_6\text{H}_5\text{COOH}$. Since NaOH is a limiting reagent, all of the NaOH will be consumed to form $\text{C}_6\text{H}_5\text{COO}^-$, and the amount (mol) of $\text{C}_6\text{H}_5\text{COOH}$ will decrease. Find the new amount (mol) of $\text{C}_6\text{H}_5\text{COOH}$ and $\text{C}_6\text{H}_5\text{COO}^-$ and use the Henderson-Hasselbalch equation to find the pH of this buffer. Once the pH of the benzoic acid/benzoate buffer is known, the Henderson-Hasselbalch equation can be used to find the ratio of formate ion and formic acid that will produce a buffer of that same pH. From the ratio, the volumes of HCOOH and NaOH are calculated.

Solution:

The K_a for benzoic acid is 6.3×10^{-5} (from the Appendix). The $\text{p}K_a$ is $-\log(6.3 \times 10^{-5}) = 4.201$. The reaction of benzoic acid with sodium hydroxide is:



$$\text{amount (mol) of C}_6\text{H}_5\text{COOH} = \left(\frac{0.200 \text{ mol C}_6\text{H}_5\text{COOH}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (475 \text{ mL}) = 0.0950 \text{ mol C}_6\text{H}_5\text{COOH}$$

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

NaOH is the limiting reagent:

The reaction table gives:

	$\text{C}_6\text{H}_5\text{COOH}(aq) + \text{NaOH}(aq) \rightarrow \text{Na}^+(aq) + \text{C}_6\text{H}_5\text{COO}^-(aq) + \text{H}_2\text{O}(l)$			
Initial	0.0950 mol	0.050 mol	—	0
Reacting	-0.050 mol	-0.050 mol		+0.050 mol
Final	0.045 mol	0 mol		0.050 mol

Calculating the pH from the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left(\frac{n_{\text{C}_6\text{H}_5\text{COO}^-}}{n_{\text{C}_6\text{H}_5\text{COOH}}} \right) = 4.201 + \log \left(\frac{0.050}{0.045} \right) = 4.24676 = 4.2$$

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

The formate to formic acid ratio may now be determined:

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

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

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

$$\left(\frac{n_{\text{HCOO}^-}}{n_{\text{HCOOH}}} \right) = 3.177313$$

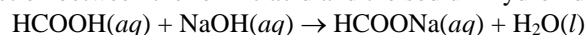
$$n_{\text{HCOO}^-} = 3.177313 \times n_{\text{HCOOH}} \quad (\text{eqn 1})$$

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

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

$$V_a + V_b = 0.500 \text{ L} \quad (\text{eqn 2})$$

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



The amount (mol) of NaOH added equal the amount (mol) of HCOOH reacted and the amount (mol) of HCOONa formed.

$$\text{amount (mol) NaOH} = (2.00 \text{ mol NaOH/L})(V_b) = 2.00V_b \text{ mol}$$

$$\text{Total amount (mol) HCOOH} = (0.200 \text{ mol HCOOH/L})(V_a) = 0.200V_a \text{ mol}$$

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

$$\text{amount (mol) of HCOOH remaining after the reaction} = (0.200V_a - 2.00V_b) \text{ mol} \quad (\text{eqn 3})$$

$$\text{amount (mol) of HCOO}^- = \text{amount (mol) of HCOONa} = \text{amount (mol) of NaOH} = 2.00 V_b \quad (\text{eqn 4})$$

Using these amounts (mol) and the mole ratio determined for the buffer gives:

$$\text{amount (mol) of HCOO}^- = 3.177313 \text{ mol HCOOH} \quad \text{Substituting equations 3 and 4 into 1 gives:}$$

$$2.00V_b \text{ mol} = 3.177313(0.200V_a - 2.00V_b) \text{ mol}$$

$$2.00V_b = 0.6354626V_a - 6.354626V_b$$

$$8.354626 V_b = 0.6354626 V_a \quad (\text{eqn 5})$$

Rearranging equation 2 gives $V_a = (0.500 - V_b) \text{ L}$ (eqn 2b)

Substituting equation 2b into equation 5 gives:

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

Solving for V_b :

$$8.354626 V_b = 0.3177313 - 0.6354626 V_b$$

$$8.9900886 V_b = 0.3177313$$

$$V_b = 0.0353424 = \mathbf{0.035 \text{ L NaOH}}$$

Substituting V_b into equation 2b:

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

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

- 17.116 Plan: A formate buffer contains formate (HCOO^-) as the base and formic acid (HCOOH) as the acid. The Henderson-Hasselbalch equation gives the component ratio, $[\text{HCOO}^-]/[\text{HCOOH}]$. The ratio is used to find the volumes of acid and base required to prepare the buffer.

Solution:

From the Appendix, the K_a for formic acid is 1.8×10^{-4} and the $\text{p}K_a = -\log(1.8 \times 10^{-4}) = 3.7447$.

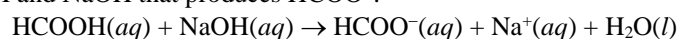
$$\text{a) } \text{pH} = \text{p}K_a + \log\left(\frac{[\text{HCOO}^-]}{[\text{HCOOH}]}\right)$$

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

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

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

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



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

$$[\text{HCOOH}] = (1.0 \text{ mol / L HCOOH}) \left(\frac{x \text{ L HCOOH}}{0.700 \text{ L solution}} \right) -$$

$$(1.0 \text{ mol / L NaOH}) \left(\frac{(0.700 - x) \text{ L NaOH}}{0.700 \text{ L solution}} \right) \left(\frac{1 \text{ mol HCOO}^-}{1 \text{ mol NaOH}} \right)$$

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

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

Solving for x:

$$x = 0.46751 = 0.468 \text{ L}$$

Mixing **0.468 L of 1.0 mol/L HCOOH** and $0.700 - 0.468 = \mathbf{0.232 \text{ L of 1.0 mol/L NaOH}}$ gives a buffer of pH 3.74.

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

$$[\text{HCOOH}] = (1.0 \text{ mol / L HCOOH}) \left(\frac{0.468 \text{ L HCOOH}}{0.700 \text{ L solution}} \right) -$$

$$(1.0 \text{ mol / L NaOH}) \left(\frac{0.232 \text{ L NaOH}}{0.700 \text{ L solution}} \right) \left(\frac{1 \text{ mole HCOO}^-}{1 \text{ mole NaOH}} \right) = 0.33714 \text{ mol/L} = \mathbf{0.34 \text{ mol/L HCOOH}}$$

- 17.119 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:

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

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

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

When $[\text{Na}^+] = 0.15 \text{ mol/L}$:

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

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

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

- 17.122 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 amount (mol) originally present and the amount (mol) 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 mol/L.

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

b) Find the amount (mol) of Cl^- :

Original amount (mol) from the KCl:

amount (mol) of K^+ = amount (mol) 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 amount (mol) from the 6.0 mol/L HCl in the first beaker:

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

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

Original amount (mol) from the 12 mol/L HCl in the second beaker:

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

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

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

After the mixing:

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

From 6.0 mol/L HCl in the first beaker:

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

From 12 mol/L HCl in the second beaker:

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

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

From 6.0 mol/L HCl in the first beaker:

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

From 12 mol/L HCl in the second beaker:

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

The mass of KCl that will precipitate when 12 mol/L HCl is added:

Equal amounts of K and Cl will precipitate. Let x be the concentration (mol/L) change.

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

$$x = 0.08659785 = 0.09$$

This is the change in the concentration (mol/L) of each of the ions.

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

- 17.125 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:

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

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

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

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

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

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

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

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

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

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

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

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

- 17.126 Plan: The buffer components will be TRIS, $(\text{HOCH}_2)_3\text{CNH}_2$, and its conjugate acid TRISH⁺, $(\text{HOCH}_2)_3\text{CNH}_3^+$. The conjugate acid is formed from the reaction between TRIS and HCl. Since HCl is the limiting reactant in this problem, the concentration of conjugate acid will equal the starting concentration of HCl, 0.095 mol/L. The concentration of TRIS is the initial concentration minus the amount reacted. Once the concentrations of the TRIS-TRISH⁺ acid-base pair are known, the Henderson-Hasselbalch equation can be used to find the pH.

Solution:

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

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

	$(\text{HOCH}_2)_3\text{CNH}_2(aq) + \text{HCl}(aq) \rightleftharpoons (\text{HOCH}_2)_3\text{CNH}_3^+(aq) + \text{Cl}^-(aq)$			
Initial	0.354961 mol	0.095 mol	0	0
Reacting	-0.095 mol	-0.095 mol	+0.095 mol	—
Final	0.259961 mol	0 mol	0.095 mol	

Since there is 1.00 L of solution, the amount (mol) of TRIS and TRISH⁺ equal their concentrations (mol/L).

$$\text{p}K_a \text{ of TRISH}^+ = 14 - \text{p}K_b = 14 - 5.91 = 8.09$$

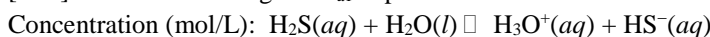
$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{TRIS}]}{[\text{TRISH}^+]} \right) = 8.09 + \log \left(\frac{[0.259961]}{[0.095]} \right) = 8.527185 = \mathbf{8.53}$$

- 17.128 Zinc sulfide, ZnS, is much less soluble than manganese sulfide, MnS. Convert ZnCl_2 and MnCl_2 to ZnS and MnS by saturating the solution with H_2S ; $[\text{H}_2\text{S}]_{\text{sat'd}} = 0.10 \text{ mol/L}$. Adjust the pH so that the greatest amount of ZnS will precipitate and not exceed the solubility of MnS as determined by $K_{\text{sp}}(\text{MnS})$.

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

$$[\text{Mn}^{2+}] = [\text{MnCl}_2] = 0.020 \text{ mol/L}$$

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



Initial	0.10 mol/L	0	0
Reacting	-x	+x	+x
Final	0.10 - x	x	x

$$K_{\text{a1}} = 9 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{(0.10 - x)} \quad \text{Assume } 0.10 - x = 0.10.$$

$$[\text{H}_3\text{O}^+][\text{HS}^-] = 9 \times 10^{-9}$$

$$[\text{HS}^-] = 9 \times 10^{-9} / [\text{H}_3\text{O}^+]$$

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

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

$$K_{\text{sp}}(\text{MnS}) = [\text{Mn}^{2+}](9 \times 10^{-9} / [\text{H}_3\text{O}^+])[\text{OH}^-] = 3 \times 10^{-11}$$

Substituting $K_w / [\text{H}_3\text{O}^+]$ for $[\text{OH}^-]$:

$$K_{sp}(\text{MnS}) = 3 \times 10^{-11} = [\text{Mn}^{2+}] \left(\frac{9 \times 10^{-9}}{[\text{H}_3\text{O}^+]} \right) \left(\frac{K_w}{[\text{H}_3\text{O}^+]} \right)$$

$$3 \times 10^{-11} \times [\text{H}_3\text{O}^+]^2 = [\text{Mn}^{2+}] (9 \times 10^{-9}) (K_w)$$

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{[\text{Mn}^{2+}] (9 \times 10^{-9}) K_w}{3 \times 10^{-11}}} = \sqrt{\frac{(0.020) (9 \times 10^{-9}) (1.0 \times 10^{-14})}{3 \times 10^{-11}}} = 2.4494897 \times 10^{-7}$$

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

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

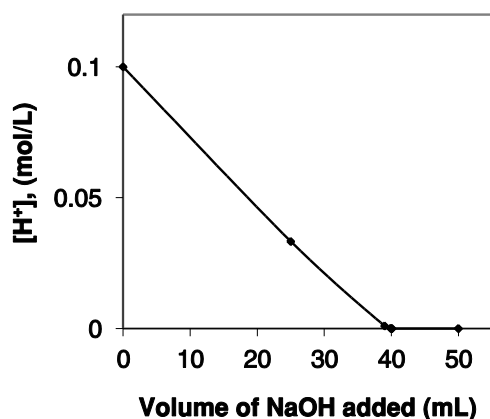
- 17.132 Plan: An indicator changes colour when the buffer-component ratio of the two forms of the indicator changes from a value greater than 1 to a value less than 1. The pH at which the ratio equals 1 is equal to $\text{p}K_a$. The midpoint in the pH range of the indicator is a good estimate of the $\text{p}K_a$ of the indicator.

Solution:

$$\text{p}K_a = (3.4 + 4.8)/2 = 4.1$$

$$K_a = 10^{-4.1} = 7.943 \times 10^{-5} = \mathbf{8 \times 10^{-5}}$$

17.133



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

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

Solution:

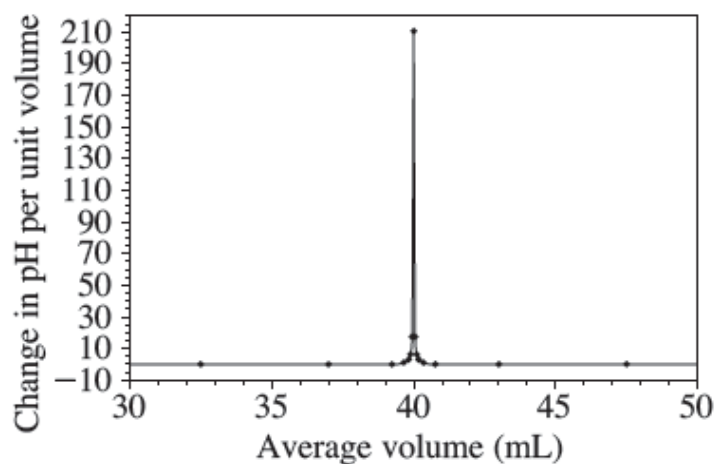
a) Example calculation: For the first two lines of data: $\Delta\text{pH} = 1.22 - 1.00 = 0.22$; $\Delta V = 10.00 - 0.00 = 10.00$

$$\frac{\Delta\text{pH}}{\Delta V} = \frac{0.22}{10.00} = 0.022$$

$$V_{\text{average}}(\text{mL}) = (0.00 + 10.00)/2 = 5.00$$

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

b)



- 17.136 Use HLac to indicate lactic acid and Lac^- to indicate the lactate ion. The Henderson-Hasselbalch equation gives the pH of the buffer. Determine the final concentrations of the buffer components from $c_{\text{conc}}V_{\text{conc}} = c_{\text{dil}}V_{\text{dil}}$. Determine the $\text{p}K_{\text{a}}$ of the acid from the K_{a} .

$$\text{p}K_{\text{a}} = -\log K_{\text{a}} = -\log (1.38 \times 10^{-4}) = 3.86012$$

Determine the concentration (mol/L) of the diluted buffer component as $c_{\text{dil}} = c_{\text{conc}}V_{\text{conc}}/V_{\text{dil}}$.

$$[\text{HLac}] = [(0.85 \text{ M}) (225 \text{ mL})] / [(225 + 435) \text{ mL}] = 0.28977 \text{ mol/L HLac}$$

$$[\text{Lac}^-] = [(0.68 \text{ M}) (435 \text{ mL})] / [(225 + 435) \text{ mL}] = 0.44818 \text{ mol/L Lac}^-$$

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

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

- 17.142 Plan: To determine which species are present from a buffer system of a polyprotic acid, check the $\text{p}K_a$ values for the one that is closest to the pH of the buffer. The two components involved in the equilibrium associated with this K_a are the principle species in the buffer. Use the Henderson-Hasselbalch equation to find the ratio of the phosphate species that will produce a buffer with a pH of 7.4.

Solution:

For carbonic acid, $\text{p}K_{a1} [-\log (8 \times 10^{-7}) = 6.1]$ is closer to the pH of 7.4, so H_2CO_3 and HCO_3^- are the species present. For phosphoric acid, $\text{p}K_{a2} [-\log (2.3 \times 10^{-7}) = 6.6]$ is closest to the pH, so H_2PO_4^- and HPO_4^{2-} are the principle species present.



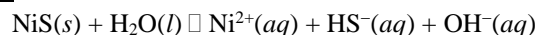
$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)$$

$$7.4 = 6.6383 + \log \left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)$$

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 5.77697 = \mathbf{5.8}$$

- 17.143 Plan: Mercury sulfide, HgS , is much less soluble than nickel sulfide, NiS . Adjust the pH so that the greatest amount of HgS will precipitate and not exceed the solubility of NiS as determined by K_{sp} of NiS . Determine the minimum pH needed to cause the initial precipitation of NiS . Use the K_a expression for H_2S to express $[\text{HS}^-]$ in terms of $[\text{H}_3\text{O}^+]$; use the K_w expression for water to express $[\text{OH}^-]$ in terms of $[\text{H}_3\text{O}^+]$.

Solution:



$$K_{sp}(\text{NiS}) = 3 \times 10^{-16} = [\text{Ni}^{2+}][\text{HS}^-][\text{OH}^-]$$

$[\text{Ni}^{2+}] = 0.15 \text{ mol/L}$, so $[\text{HS}^-]$ and $[\text{OH}^-]$ must be found.

From $[\text{H}_2\text{S}] = 0.050 \text{ mol/L}$ and K_{a1} in the Appendix:



$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{(0.050 - x)} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{(0.050)} = 9 \times 10^{-8}$$

$$[\text{HS}^-][\text{H}_3\text{O}^+] = 4.5 \times 10^{-9} \text{ or } [\text{HS}^-] = 4.5 \times 10^{-9} / [\text{H}_3\text{O}^+]$$

$$[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+]$$

$$K_{sp}(\text{NiS}) = 3 \times 10^{-16} = [\text{Ni}^{2+}][\text{HS}^-][\text{OH}^-]$$

$$K_{sp}(\text{NiS}) = 3 \times 10^{-16} = (0.15) \left(\frac{4.5 \times 10^{-9}}{[\text{H}_3\text{O}^+]} \right) \left(\frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]} \right)$$

$$3 \times 10^{-16} = \frac{(0.15)(4.5 \times 10^{-9})(1.0 \times 10^{-14})}{([\text{H}_3\text{O}^+])^2}$$

$$[\text{H}_3\text{O}^+]^2 = [(0.15)(4.5 \times 10^{-9})(1.0 \times 10^{-14})] / (3 \times 10^{-16}) = 2.25 \times 10^{-8}$$

$$[\text{H}_3\text{O}^+] = 1.5 \times 10^{-4} \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1.5 \times 10^{-4} \text{ mol/L}) = 3.8239 = \mathbf{3.8}$$

- 17.145 Plan: Find the amount (mol) of quinidine initially present in the sample by dividing its mass in grams by the molar mass. Use the molar ratio between quinidine and HCl to find the amount (mol) of HCl that would react with the

amount (mol) of quinidine and subtract the reacted HCl from the initial amount (mol) of HCl to find the excess. Use the molar ratio between HCl and NaOH to find the volume of NaOH required to react with the excess HCl. Then use the molar ratio between NaOH and quinidine to find the volume of NaOH required to react with the quinidine.

Solution:

a) To find the concentration of HCl after neutralizing the quinidine, calculate the concentration of quinidine and the amount of HCl required to neutralize it, remembering that the mole ratio for the neutralization is 2 mol HCl/1 mol quinidine.

$$\begin{aligned}\text{amount (mol) of quinidine} &= (33.85 \text{ mg quinidine}) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left(\frac{1 \text{ mol quinidine}}{324.41 \text{ g quinidine}} \right) \\ &= 1.0434327 \times 10^{-4} \text{ mol quinidine}\end{aligned}$$

$$\begin{aligned}\text{amount (mol) of HCl excess} &= (6.55 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.150 \text{ mol HCl}}{\text{L}} \right) \\ &\quad - (1.0434327 \times 10^{-4} \text{ mol quinidine}) \left(\frac{2 \text{ mol HCl}}{1 \text{ mol quinidine}} \right) = 7.7381346 \times 10^{-4} \text{ mol HCl}\end{aligned}$$

$$\begin{aligned}\text{Volume (mL) of NaOH needed} &= (7.7381346 \times 10^{-4} \text{ mol HCl}) \left(\frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} \right) \left(\frac{1 \text{ L}}{0.0133 \text{ mol NaOH}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ &= 58.18146 \text{ mL} = \mathbf{58.2 \text{ mL NaOH solution}}\end{aligned}$$

b) Use the amount (mol) of quinidine and the concentration of the NaOH to determine the volume in millilitre.

$$\begin{aligned}\text{Volume} &= (1.0434327 \times 10^{-4} \text{ mol quinidine}) \left(\frac{1 \text{ mol NaOH}}{1 \text{ mol quinidine}} \right) \left(\frac{1 \text{ L}}{0.0133 \text{ mol NaOH}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ &= 7.84536 \text{ mL} = \mathbf{7.85 \text{ mL NaOH solution}}\end{aligned}$$

c) When quinidine (QNN) is first acidified, it has the general form QNH^+NH^+ . At the first equivalence point, one of the acidified nitrogen atoms has completely reacted, leaving a singly protonated form, QNNH^+ . This form of quinidine can react with water as either an acid or a base, so both must be considered. If the concentration of quinidine at the first equivalence point is greater than K_{b1} , then the $[\text{OH}^-]$ at the first equivalence point can be estimated as:

$$\begin{aligned}[\text{OH}^-] &= \sqrt{K_{b1}K_{b2}} = \sqrt{(4.0 \times 10^{-6})(1.0 \times 10^{-10})} = 2.0 \times 10^{-8} \text{ mol/L} \\ [\text{H}_3\text{O}^+] &= K_w/[\text{OH}^-] = (1.0 \times 10^{-14})/(2.0 \times 10^{-8}) = 5.0 \times 10^{-7} \text{ mol/L} \\ \text{pH} &= -\log [\text{H}^+] = -\log (5.0 \times 10^{-7} \text{ mol/L}) = 6.3010 = \mathbf{6.30}\end{aligned}$$

- 17.147 Plan: The Henderson-Hasselbalch equation demonstrates that the pH changes when the ratio of acid to base in the buffer changes ($\text{p}K_a$ is constant at a given temperature).

Solution:

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

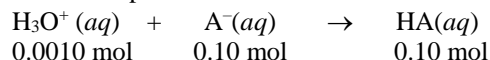
The pH of the A^-/HA buffer cannot be calculated because the identity of "A" and, thus, the value of $\text{p}K_a$ are unknown. However, the change in pH can be described:

$$\Delta \text{pH} = \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)_{\text{final}} - \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)_{\text{initial}}$$

Since both $[\text{HA}]$ and $[\text{A}^-] = 0.10 \text{ mol/L}$, $\log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)_{\text{initial}} = 0$ because $[\text{HA}] = [\text{A}^-]$, and $\log (1) = 0$

So the change in pH is equal to the concentration ratio of base to acid after the addition of H_3O^+ .

Consider the buffer prior to addition to the medium.



$$\begin{array}{ccc} \frac{-0.0010 \text{ mol}}{0} & \frac{-0.0010 \text{ mol}}{0.099 \text{ mol}} & \frac{+0.0010 \text{ mol}}{0.101 \text{ mol}} \end{array}$$

When 0.0010 mol H_3O^+ is added to 1 L of the undiluted buffer, the $[\text{A}^-]/[\text{HA}]$ ratio changes from 0.10/0.10 to (0.099)/(0.101). The change in pH is:

$$\Delta\text{pH} = \log(0.099/0.101) = -0.008686$$

If the undiluted buffer changes 0.009 pH units with addition of 0.0010 mol H_3O^+ , how much can the buffer be diluted and still not change by 0.05 pH units ($\Delta\text{pH} < 0.05$)?

Let x = fraction by which the buffer can be diluted. Assume 0.0010 mol H_3O^+ is added to 1 L.

$$\log \frac{[\text{base}]}{[\text{acid}]} = \log \left(\frac{(0.10x - 0.0010)}{(0.10x + 0.0010)} \right) = -0.05$$

$$\left(\frac{(0.10x - 0.0010)}{(0.10x + 0.0010)} \right) = 10^{-0.05} = 0.89125$$

$$0.10x - 0.0010 = 0.89125(0.10x + 0.0010)$$

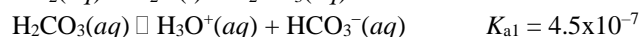
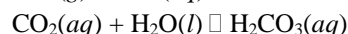
$$x = 0.173908 = 0.17$$

The buffer concentration can be decreased by a factor of 0.17, or **170 mL** of buffer can be diluted to 1 L of medium. At least this amount should be used to adequately buffer the pH change.

- 17.151 Plan: Use the ideal gas law to calculate the amount (mol) of CO_2 dissolved in water. Use the K_a expression for H_2CO_3 to find the $[\text{H}_3\text{O}^+]$ associated with that CO_2 concentration.

Solution:

Carbon dioxide dissolves in water to produce H_3O^+ ions:



The molar concentration of CO_2 , $[\text{CO}_2]$, depends on how much $\text{CO}_2(g)$ from the atmosphere can dissolve in pure water. Since air is not pure CO_2 , account for the volume fraction of air (0.033 L/100 L) when determining the amount (mol).

$$\text{Volume (L) of } \text{CO}_2 = (88 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.033\%}{100\%} \right) = 2.904 \times 10^{-5} \text{ L } \text{CO}_2$$

$$\text{amount (mol) of dissolved } \text{CO}_2 = \frac{PV}{RT} = \frac{(1 \text{ bar})(2.904 \times 10^{-5} \text{ L})}{\left(0.08314 \frac{\text{bar} \cdot \text{L}}{\text{mol} \cdot \text{K}} \right) ((273 + 25) \text{ K})} = 1.172115 \times 10^{-6} \text{ mol } \text{CO}_2$$

$$[\text{CO}_2] = (1.172115 \times 10^{-6} \text{ mol } \text{CO}_2) / [(100 \text{ mL})(10^{-3} \text{ L/1 mL})] = 1.172115 \times 10^{-5} \text{ mol/L } \text{CO}_2$$

$$K_{a1} = 4.5 \times 10^{-7} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad \text{Let } x = [\text{H}_3\text{O}^+] = [\text{HCO}_3^-]$$

$$4.5 \times 10^{-7} = \frac{(x)(x)}{(1.172115 \times 10^{-5} - x)} \quad \text{Check assumption: } 1.172115 \times 10^{-5} / 4.5 \times 10^{-7} = 26 < 400$$

The assumption is not justified and it is necessary to use the quadratic equation.

$$4.5 \times 10^{-7} = \frac{(x)(x)}{(1.172115 \times 10^{-5} - x)}$$

$$x^2 + 4.5 \times 10^{-7}x - 5.27452 \times 10^{-12} = 0$$

$$a = 1$$

$$b = 4.5 \times 10^{-7}$$

$$c = -5.27452 \times 10^{-12}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(4.5 \times 10^{-7}) \pm \sqrt{(4.5 \times 10^{-7})^2 - 4(1)(-5.27452 \times 10^{-12})}}{2(1)}$$

$$x = 2.0826276 \times 10^{-6} \text{ mol/L} = [\text{H}^+]$$

$$\text{pH} = -\log(2.0826276 \times 10^{-6}) = 5.68139 = \mathbf{5.68}$$

- 17.153 Initial concentrations of Pb^{2+} and $\text{Ca}(\text{EDTA})^{2-}$ before reaction based on mixing 100. mL of 0.10 mol/L $\text{Na}_2\text{Ca}(\text{EDTA})$ with 1.5 L blood:

$$[\text{Pb}^{2+}] = \left(\frac{120 \mu\text{g Pb}^{2+}}{100 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1.5 \text{ L blood}}{1.6 \text{ L mixture}} \right) \left(\frac{10^{-6} \text{ g}}{1 \mu\text{g}} \right) \left(\frac{1 \text{ mol Pb}^{2+}}{207.2 \text{ g Pb}^{2+}} \right) = 5.42953668 \times 10^{-6} \text{ mol/L Pb}^{2+}$$

$$c_{\text{conc}} V_{\text{conc}} = c_{\text{dil}} V_{\text{dil}}$$

$$[\text{Ca}(\text{EDTA})^{2-}] = c_{\text{conc}} V_{\text{conc}} / V_{\text{dil}} = [(0.10 \text{ mol/L} (100 \text{ mL}) (10^{-3} \text{ L/1 mL})) / (1.6 \text{ L})]$$

$$= 6.25 \times 10^{-3} \text{ mol/L}$$

Set up a reaction table assuming the reaction goes to completion:

Concentration (mol/L)	$[\text{Ca}(\text{EDTA})]^{2-}(\text{aq})$	+	$\text{Pb}^{2+}(\text{aq})$	\rightleftharpoons	$[\text{Pb}(\text{EDTA})]^{2-}(\text{aq})$	+	$\text{Ca}^{2+}(\text{aq})$
Initial	6.25×10^{-3}		$5.42953668 \times 10^{-6}$		0		0
React	$-5.42953668 \times 10^{-6}$		$-5.42953668 \times 10^{-6}$		$+5.42953668 \times 10^{-6}$		$+5.42953668 \times 10^{-6}$
	6.24457×10^{-3}		0		$5.42953668 \times 10^{-6}$		$5.42953668 \times 10^{-6}$

Now set up a reaction table for the equilibrium process:

Concentration (mol/L)	$[\text{Ca}(\text{EDTA})]^{2-}(\text{aq})$	+	$\text{Pb}^{2+}(\text{aq})$	\rightleftharpoons	$[\text{Pb}(\text{EDTA})]^{2-}(\text{aq})$	+	$\text{Ca}^{2+}(\text{aq})$
Initial	6.24457×10^{-3}		0		$5.42953668 \times 10^{-6}$		$5.42953668 \times 10^{-6}$
Change	+x		+x		-x		-x
Equilibrium	$6.24457 \times 10^{-3} + x$		x		$5.4295366 \times 10^{-6} - x$		$5.4295366 \times 10^{-6} - x$

Assuming that x is much smaller than all the numerical quantities and hence the change caused by x is negligible,:

$$K_c = 2.5 \times 10^7 = \frac{[\text{Pb}(\text{EDTA})^{2-}][\text{Ca}^{2+}]}{[\text{Ca}(\text{EDTA})^{2-}][\text{Pb}^{2+}]} = \frac{(5.42953668 \times 10^{-6})(5.42953668 \times 10^{-6})}{(6.24457 \times 10^{-3})(x)}$$

$$x = [\text{Pb}^{2+}] = 1.8883522 \times 10^{-16} \text{ mol/L}$$

$$\text{Mass } (\mu\text{g}) \text{ of } \text{Pb}^{2+} \text{ in } 100 \text{ mL} = \left(\frac{1.8883522 \times 10^{-16} \text{ mol Pb}^{2+}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100 \text{ mL}) \left(\frac{207.2 \text{ g Pb}^{2+}}{1 \text{ mol Pb}^{2+}} \right) \left(\frac{1 \mu\text{g}}{10^{-6} \text{ g}} \right)$$

$$= 3.9126658 \times 10^{-9} \mu\text{g Pb}^{2+}$$

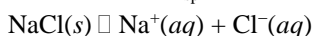
The final concentration is $\mathbf{3.9 \times 10^{-9} \mu\text{g/100 mL}}$.

- 17.155 Plan: Convert the solubility of NaCl from g/L to mol/l (concentration). Use the solubility to find the K_{sp} value for NaCl. Find the amount (mol) of Na^+ and Cl^- in the original solution; find the amount (mol) of added Cl^- (from the added HCl). The concentration (mol/L) of the Na^+ and Cl^- ions are then found by dividing amount (mol) of each by the total volume after mixing. Using the concentrations (mol/L) of the two ions, determine a Q value and compare this value to the K_{sp} to determine if precipitation will occur.

Solution:

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

Determine the K_{sp} from the concentration (mol/L) just calculated.



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

$$\text{amount (mol) of } \text{Cl}^- \text{ initially} = \left(\frac{5.42436687 \text{ mol NaCl}}{\text{L}} \right) (0.100 \text{ L}) \left(\frac{1 \text{ mol Cl}^-}{1 \text{ mol NaCl}} \right) = 0.542436687 \text{ mol Cl}^-$$

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

$$\text{amount (mol) of } \text{Cl}^- \text{ added} = \left(\frac{8.65 \text{ mol HCl}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (28.5 \text{ mL}) \left(\frac{1 \text{ mol Cl}^-}{1 \text{ mol HCl}} \right) = 0.246525 \text{ mol Cl}^-$$

0.100 L of saturated solution contains 0.542 mol each Na^+ and Cl^- , to which you are adding 0.246525 mol of additional Cl^- from HCl.

Volume of mixed solutions = 0.100 L + (28.5 mL)(10⁻³ L/mL) = 0.1285 L
 concentration (mol/L) of Cl⁻ in mixture = [(0.542436687 + 0.246525) mol Cl⁻]/(0.1285 L) = 6.13978 mol/L Cl⁻
 concentration (mol/L) of Na⁺ in mixture = (0.542436687 mol Na⁺)/(0.1285 L) = 4.22130 mol/L Na⁺
 Determine a Q value and compare this value to the K_{sp} to determine if precipitation will occur.

$$Q_{sp} = [\text{Na}^+][\text{Cl}^-] = (4.22130)(6.13978) = 25.9179 = 25.9$$

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

- 17.156 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.

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

$$\text{pH} = \text{p}K_a + \log 1$$

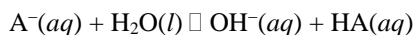
$$\text{pH} = \text{p}K_a = -\log (4.5 \times 10^{-5}) = 4.346787 = \mathbf{4.35}$$

Scene B:

Only A⁻ is present at a concentration of 0.10 mol/L.

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 mol/L	0	0
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Change:	-x	-x	-x
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Equilibrium:	0.10 - x	x	x
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$$K_b = 2.222 \times 10^{-10} = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$K_b = 2.222 \times 10^{-10} = \frac{(x)(x)}{(0.10 - x)} \quad \text{Assume that } x \text{ is small compared to } 0.10$$

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

$$x = 4.7138095 \times 10^{-6} \text{ mol/L OH}^-$$

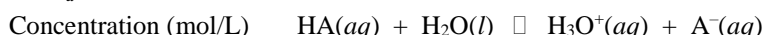
Check assumption: $(4.7138095 \times 10^{-6}/0.10) \times 100\% = 0.005\%$ error, so the assumption is valid.

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

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

Scene C:

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



Initial	0.10 mol/L	—	0	0
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Change	-x	+x	+x
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Equilibrium	0.10 - x	x	x
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(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.

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

Scene D:

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

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

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**.