

CHAPTER 8

APPLICATIONS OF AQUEOUS EQUILIBRIA

Buffers

15. Only the third beaker represents a buffer solution. A weak acid and its conjugate base must both be present in large quantities in order to have a buffer solution. This is only the case in the third beaker. The first beaker represents a beaker full of strong acid which is 100% dissociated. The second beaker represents a weak acid solution. In a weak acid solution, only a small fraction of the acid is dissociated. In this representation, 1/10 of the weak acid has dissociated. The only B^- present in this beaker is from the dissociation of the weak acid. A buffer solution has B^- added from another source.
16. A buffer solution is a solution containing a weak acid plus its conjugate base or a weak base plus its conjugate acid. Solution c contains a weak acid (HOCl) plus its conjugate base (OCl^-), so it is a buffer. Solution e is also a buffer solution. It contains a weak base (H_2NNH_2) plus its conjugate acid ($H_2NNH_3^+$).

Solution a contains a strong acid (HBr) and a weak acid (HOBr). Solution b contains a strong acid ($HClO_4$) and a strong base (RbOH). Solution d contains a strong base (KOH) and a weak base ($HONH_2$).

17. $pH = pK_a + \log \frac{[base]}{[acid]}$; when $[acid] > [base]$, then $\frac{[base]}{[acid]} < 1$ and $\log \left(\frac{[base]}{[acid]} \right) < 0$.

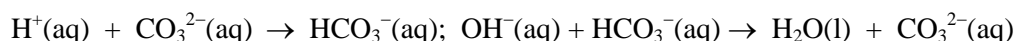
From the Henderson-Hasselbalch equation, if the log term is negative, then $pH < pK_a$. When one has more acid than base in a buffer, the pH will be on the acidic side of the pK_a value; that is, the pH is at a value lower than the pK_a value. When one has more base than acid in a buffer ($[conjugate\ base] > [weak\ acid]$), then the log term in the Henderson-Hasselbalch equation is positive, resulting in $pH > pK_a$. When one has more base than acid in a buffer, the pH is on the basic side of the pK_a value; that is, the pH is at a value greater than the pK_a value. The other scenario you can run across in a buffer is when $[acid] = [base]$. Here, the log term is equal to zero, and $pH = pK_a$.

18. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$; taking the $-\log$ of the K_b expression:

$$-\log K_b = -\log[OH^-] - \log \frac{[NH_4^+]}{[NH_3]}, \quad -\log[OH^-] = -\log K_b + \log \frac{[NH_4^+]}{[NH_3]}$$

$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]} \quad \text{or} \quad pOH = pK_b + \log \frac{[acid]}{[base]}$$

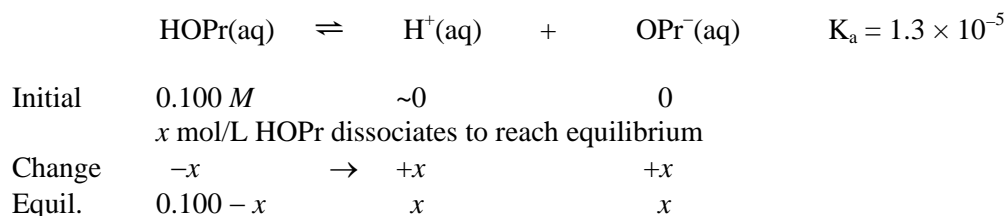
19. A buffer solution is one that resists a change in its pH when either hydroxide ions or protons (H^+) are added. Any solution that contains a weak acid and its conjugate base or a weak base and its conjugate acid is classified as a buffer. The pH of a buffer depends on the $[\text{base}]/[\text{acid}]$ ratio. When H^+ is added to a buffer, the weak base component of the buffer reacts with the H^+ and forms the acid component of the buffer. Even though the concentrations of the acid and base components of the buffer change some, the ratio of $[\text{base}]/[\text{acid}]$ does not change that much. This translates into a pH that doesn't change much. When OH^- is added to a buffer, the weak acid component is converted into the base component of the buffer. Again, the $[\text{base}]/[\text{acid}]$ ratio does not change a lot (unless a large quantity of OH^- is added), so the pH does not change much.



20. When $[\text{HA}] = [\text{A}^-]$ (or $[\text{BH}^+] = [\text{B}]$) for a buffer, the pH of the solution is equal to the pK_a value for the acid component of the buffer ($\text{pH} = \text{pK}_a$ because $[\text{H}^+] = \text{K}_a$). A best buffer has equal concentrations of the acid and base components so it is equally efficient at absorbing H^+ and OH^- . For a $\text{pH} = 4.00$ buffer, we would choose the acid component having a K_a close to $10^{-4.00} = 1.0 \times 10^{-4}$ ($\text{pH} = \text{pK}_a$ for a best buffer). For a $\text{pH} = 10.00$ buffer, we would want the acid component of the buffer to have a K_a close to $10^{-10.00} = 1.0 \times 10^{-10}$. Of course, we can have a buffer solution made from a weak base and its conjugate acid. For a $\text{pH} = 10.00$ buffer, our conjugate acid should have $\text{K}_a \approx 1.0 \times 10^{-10}$, which translates into a K_b value of the base close to 1.0×10^{-4} ($\text{K}_b = \text{K}_w/\text{K}_a$ for conjugate acid-base pairs).

The capacity of a buffer is a measure of how much strong acid or strong base the buffer can neutralize. All the buffers listed have the same pH ($= \text{pK}_a = 4.74$) because they all have a 1 : 1 concentration ratio between the weak acid and the conjugate base. The 1.0 M buffer has the greatest capacity; the 0.01 M buffer the least capacity. In general, the larger the concentrations of weak acid and conjugate base, the greater is the buffer capacity, that is, the more strong acid or strong base that can be neutralized with little pH change.

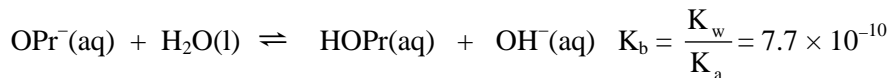
21. a. This is a weak acid problem. Let $\text{HC}_3\text{H}_5\text{O}_2 = \text{HOPr}$ and $\text{C}_3\text{H}_5\text{O}_2^- = \text{OPr}^-$.



$$\text{K}_a = 1.3 \times 10^{-5} = \frac{[\text{H}^+][\text{OPr}^-]}{[\text{HOPr}]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$$x = [\text{H}^+] = 1.1 \times 10^{-3} \text{ M}; \quad \text{pH} = 2.96; \quad \text{assumptions good by the 5\% rule.}$$

b. This is a weak base problem.



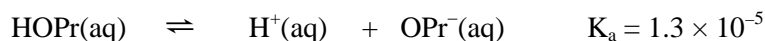
Initial	0.100 M	0	~0
	x mol/L OPr^- reacts with H_2O to reach equilibrium		
Change	$-x$	\rightarrow $+x$	$+x$
Equil.	$0.100 - x$	x	x

$$K_b = 7.7 \times 10^{-10} = \frac{[\text{HOPr}][\text{OH}^-]}{[\text{OPr}^-]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$$x = [\text{OH}^-] = 8.8 \times 10^{-6} \text{ M}; \text{ pOH} = 5.06; \text{ pH} = 8.94; \text{ assumptions good.}$$

c. Pure H_2O , $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$; $\text{pH} = 7.00$

d. This solution contains a weak acid and its conjugate base. This is a buffer solution. We will solve for the pH through the weak acid equilibrium reaction.



Initial	0.100 M	~0	0.100 M
	x mol/L HOPr dissociates to reach equilibrium		
Change	$-x$	\rightarrow $+x$	$+x$
Equil.	$0.100 - x$	x	$0.100 + x$

$$1.3 \times 10^{-5} = \frac{(0.100 + x)(x)}{0.100 - x} \approx \frac{(0.100)(x)}{0.100} = x = [\text{H}^+]$$

$$[\text{H}^+] = 1.3 \times 10^{-5} \text{ M}; \text{ pH} = 4.89; \text{ assumptions good.}$$

Alternately, we can use the Henderson-Hasselbalch equation to calculate the pH of buffer solutions.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = \text{p}K_a + \log \left(\frac{0.100}{0.100} \right) = \text{p}K_a = -\log(1.3 \times 10^{-5}) = 4.89$$

The Henderson-Hasselbalch equation will be valid when an assumption of the type $0.1 + x \approx 0.1$ that we just made in this problem is valid. From a practical standpoint, this will almost always be true for useful buffer solutions. If the assumption is not valid, the solution will have such a low buffering capacity it will not be of any use to control the pH. *Note:* The Henderson-Hasselbalch equation can only be used to solve for the pH of buffer solutions.

22. a. We have a weak acid ($\text{HOPr} = \text{HC}_3\text{H}_5\text{O}_2$) and a strong acid (HCl) present. The amount of H^+ donated by the weak acid will be negligible. To prove it let's consider the weak acid equilibrium reaction:

	$\text{HOPr} \rightleftharpoons \text{H}^+ + \text{OPr}^-$	$K_a = 1.3 \times 10^{-5}$
Initial	0.100 M x mol/L HOPr dissociates to reach equilibrium	0.020 M 0
Change	$-x$ →	$+x$ $+x$
Equil.	$0.100 - x$	$0.020 + x$ x

$[\text{H}^+] = 0.020 + x \approx 0.020\text{ M}$; $\text{pH} = 1.70$; assumption good ($x = 6.5 \times 10^{-5}$ is $\ll 0.020$).

Note: The H^+ contribution from the weak acid HOPr was negligible. The pH of the solution can be determined by only considering the amount of strong acid present.

- b. Added H^+ reacts completely with the best base present, OPr^- .

	$\text{OPr}^- + \text{H}^+ \rightarrow \text{HOPr}$	
Before	0.100 M 0.020 M	0
Change	-0.020 →	$+0.020$
After	0.080 0	0.020 M

Reacts completely

After reaction, a weak acid, HOPr, and its conjugate base, OPr^- , are present. This is a buffer solution. Using the Henderson-Hasselbalch equation where $\text{p}K_a = -\log(1.3 \times 10^{-5}) = 4.89$:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.89 + \log \frac{(0.080)}{(0.020)} = 5.49; \text{ assumptions good.}$$

- c. This is a strong acid problem. $[\text{H}^+] = 0.020\text{ M}$; $\text{pH} = 1.70$
- d. Added H^+ reacts completely with the best base present, OPr^- .

	$\text{OPr}^- + \text{H}^+ \rightarrow \text{HOPr}$	
Before	0.100 M 0.020 M	0.100 M
Change	-0.020 →	$+0.020$
After	0.080 0	0.120

Reacts completely

A buffer solution results (weak acid + conjugate base). Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.89 + \log \frac{(0.080)}{(0.120)} = 4.71; \text{ assumptions good.}$$

23. a. OH^- will react completely with the best acid present, HOPr.

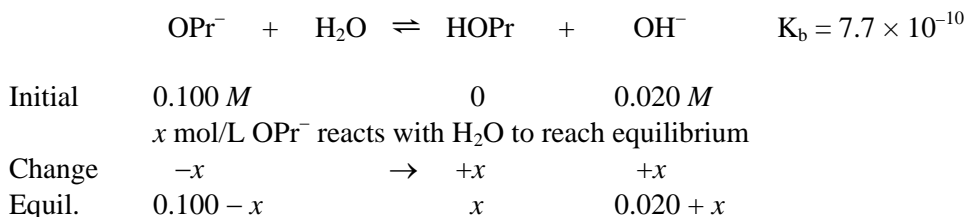
	$\text{HOPr} + \text{OH}^- \rightarrow \text{OPr}^- + \text{H}_2\text{O}$	
Before	0.100 M 0.020 M	0
Change	-0.020 →	$+0.020$
After	0.080 0	0.020

Reacts completely

A buffer solution results after the reaction. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.89 + \log \frac{(0.020)}{(0.080)} = 4.29; \text{ assumptions good.}$$

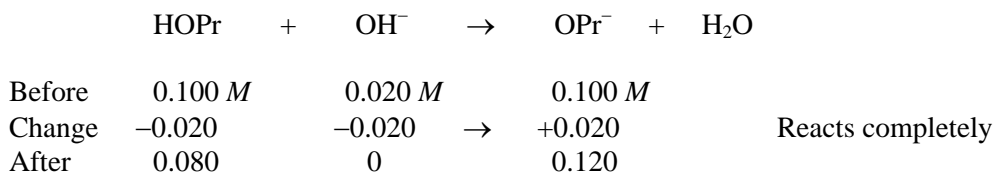
- b. We have a weak base and a strong base present at the same time. The amount of OH^- added by the weak base will be negligible. To prove it, let's consider the weak base equilibrium:



$[\text{OH}^-] = 0.020 + x \approx 0.020 \text{ M}$; $\text{pOH} = 1.70$; $\text{pH} = 12.30$; assumption good.

Note: The OH^- contribution from the weak base OPr^- was negligible ($x = 3.9 \times 10^{-9} \text{ M}$ as compared to 0.020 M OH^- from the strong base). The pH can be determined by only considering the amount of strong base present.

- c. This is a strong base in water. $[\text{OH}^-] = 0.020 \text{ M}$; $\text{pOH} = 1.70$; $\text{pH} = 12.30$
- d. OH^- will react completely with HOPr , the best acid present.



Using the Henderson-Hasselbalch equation to solve for the pH of the resulting buffer solution:

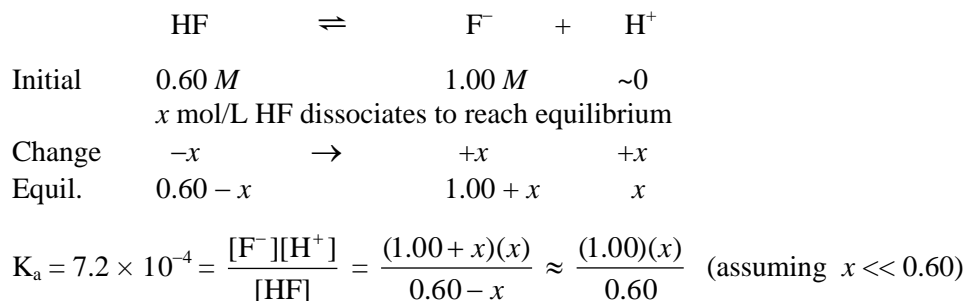
$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.89 + \log \frac{(0.120)}{(0.080)} = 5.07; \text{ assumptions good.}$$

24. Consider all the results to Exercises 21, 22, and 23:

Solution	Initial pH	After Added H^+	After Added OH^-
a	2.96	1.70	4.29
b	8.94	5.49	12.30
c	7.00	1.70	12.30
d	4.89	4.71	5.07

The solution in Exercise 21d is a buffer; it contains both a weak acid ($\text{HC}_3\text{H}_5\text{O}_2$) and a weak base ($\text{C}_3\text{H}_5\text{O}_2^-$). Solution d shows the greatest resistance to changes in pH when either a strong acid or a strong base is added, which is the primary property of buffers.

25. Major species: HF, F⁻, K⁺, and H₂O. K⁺ has no acidic or basic properties. This is a solution containing a weak acid and its conjugate base. This is a buffer solution. One appropriate equilibrium reaction you can use is the K_a reaction of HF, which contains both HF and F⁻. However, you could also use the K_b reaction for F⁻ and come up with the same answer. Alternately, you could use the Henderson-Hasselblach equation to solve for the pH. For this problem, we will use the K_a reaction and set up an ICE table to solve for the pH.



$$x = [H^+] = 0.60 \times (7.2 \times 10^{-4}) = 4.3 \times 10^{-4} \text{ M; assumptions good.}$$

$$\text{pH} = -\log(4.3 \times 10^{-4}) = 3.37$$

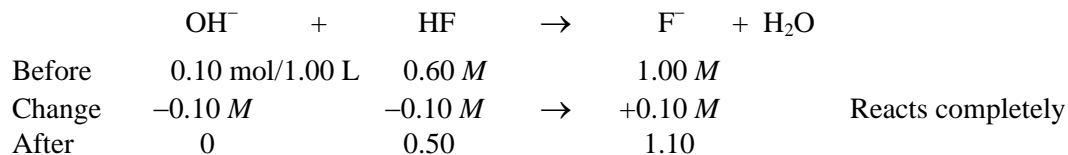
26. Major species: HONH₂ (K_b = 1.1 × 10⁻⁸), HONH₃⁺, Cl⁻, and H₂O; Cl⁻ has no acidic/basic properties. We have a weak base and its conjugate acid present at the same time in solution. We have a buffer solution. To solve for the pH of a buffer, one can set up an ICE table using the K_a reaction for HONH₃⁺, or set up an ICE table using the K_b reaction for HONH₂, or use the Henderson-Hasselbalch equation. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = -\log \left(\frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} \right) + \log \frac{[\text{HONH}_2]}{[\text{HONH}_3^+]}$$

$$\text{pH} = -\log(9.1 \times 10^{-7}) + \log \left(\frac{0.100}{0.100} \right) = 6.04 + 0.00 = 6.04$$

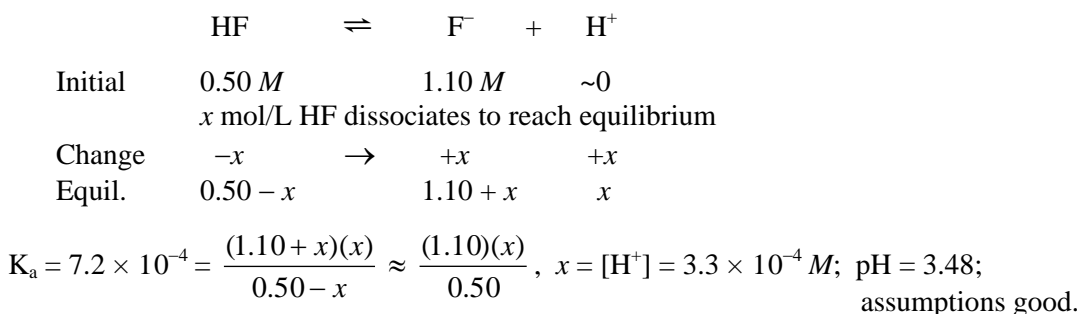
Note that pH = pK_a for a buffer solution when [weak base] = [conjugate acid].

27. Major species after NaOH added: HF, F⁻, K⁺, Na⁺, OH⁻, and H₂O. The OH⁻ from the strong base will react with the best acid present (HF). Any reaction involving a strong base is assumed to go to completion. Because all species present are in the same volume of solution, we can use molarity units to do the stoichiometry part of the problem (instead of moles). The stoichiometry problem is:



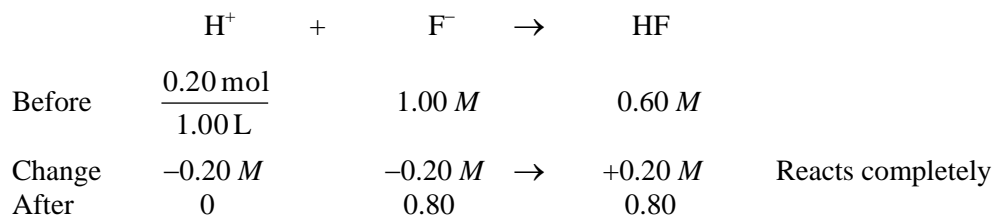
After all the OH⁻ reacts, we are left with a solution containing a weak acid (HF) and its conjugate base (F⁻). This is what we call a buffer problem. We will solve this buffer problem

using the K_a equilibrium reaction. One could also use the K_b equilibrium reaction or use the Henderson-Hasselbalch equation to solve for the pH.

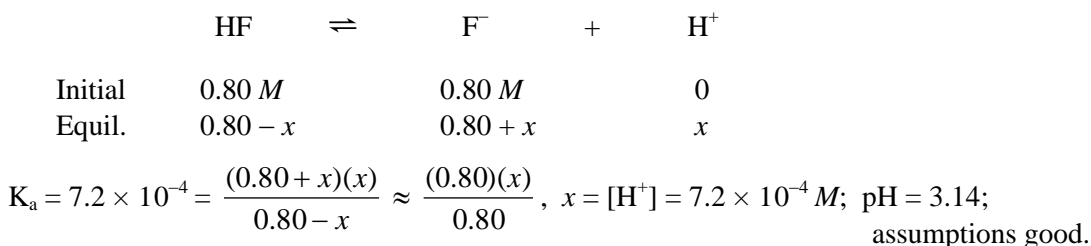


Note: The added NaOH to this buffer solution changes the pH only from 3.37 to 3.48. If the NaOH were added to 1.0 L of pure water, the pH would change from 7.00 to 13.00.

Major species after HCl added: HF, F⁻, H⁺, K⁺, Cl⁻, and H₂O; the added H⁺ from the strong acid will react completely with the best base present (F⁻).

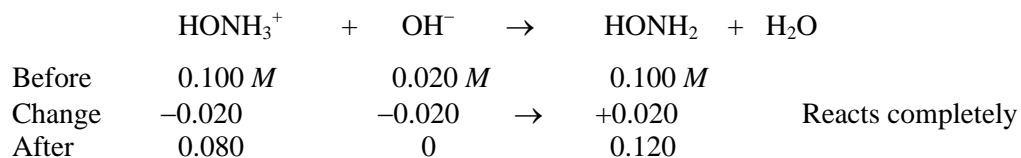


After all the H⁺ has reacted, we have a buffer solution (a solution containing a weak acid and its conjugate base). Solving the buffer problem:



Note: The added HCl to this buffer solution changes the pH only from 3.37 to 3.14. If the HCl were added to 1.0 L of pure water, the pH would change from 7.00 to 0.70.

28. Major species: H₂O, Cl⁻, Na⁺, HONH₂, HONH₃⁺, and OH⁻; the added strong base dominates the initial reaction mixture. Let the OH⁻ react completely with the best acid present (HONH₃⁺).



A buffer solution results. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}; \quad \text{pK}_a = -\log \left(\frac{K_w}{K_{b, \text{HONH}_2}} \right) = -\log \left(\frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} \right) = 6.04$$

$$\text{pH} = 6.04 + \log \frac{[\text{HONH}_2]}{[\text{HONH}_3^+]} = 6.04 + \log \frac{(0.120)}{(0.080)} = 6.04 + 0.18 = 6.22$$

Major species: H_2O , Cl^- , HONH_2 , HONH_3^+ , and H^+ ; the added strong acid dominates the initial reaction mixture. Let the H^+ react completely with HONH_2 , the best base present.

	HONH_2	+	H^+	\rightarrow	HONH_3^+	
Before	0.100 M		0.020 M		0.100 M	
Change	-0.020		-0.020	\rightarrow	+0.020	Reacts completely
After	0.080		0		0.120	

A buffer solution results after reaction. Using the Henderson-Hasselbalch equation:

$$\text{pH} = 6.04 + \log \frac{[\text{HONH}_2]}{[\text{HONH}_3^+]} = 6.04 + \log \frac{(0.080)}{(0.120)} = 6.04 - 0.18 = 5.86$$

$$29. \quad \text{C}_5\text{H}_5\text{NH}^+ \rightleftharpoons \text{H}^+ + \text{C}_5\text{H}_5\text{N} \quad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}$$

$$\text{pK}_a = -\log(5.9 \times 10^{-6}) = 5.23$$

We will use the Henderson-Hasselbalch equation to calculate the concentration ratio necessary for each buffer.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}, \quad \text{pH} = 5.23 + \log \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]}$$

$$\text{a.} \quad 4.50 = 5.23 + \log \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]}$$

$$\log \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} = -0.73$$

$$\frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} = 10^{-0.73} = 0.19$$

$$\text{b.} \quad 5.00 = 5.23 + \log \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]}$$

$$\log \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} = -0.23$$

$$\frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} = 10^{-0.23} = 0.59$$

$$\text{c. } 5.23 = 5.23 + \log \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} \quad \text{d. } 5.50 = 5.23 + \log \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]}$$

$$\frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} = 10^{0.0} = 1.0 \quad \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} = 10^{0.27} = 1.9$$

$$30. \quad \text{pH} = \text{pK}_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]}, \quad 3.55 = -\log(4.0 \times 10^{-4}) + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]}$$

$$3.55 = 3.40 + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]}, \quad \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} = 10^{0.15} = 1.4$$

Let x = volume (L) HNO_2 solution needed, then $1.00 - x$ = volume of NaNO_2 solution needed to form this buffer solution.

$$\frac{[\text{NO}_2^-]}{[\text{HNO}_2]} = 1.4 = \frac{(1.00 - x) \times \frac{0.50 \text{ mol NaNO}_2}{\text{L}}}{x \times \frac{0.50 \text{ mol HNO}_2}{\text{L}}} = \frac{0.50 - (0.50)x}{(0.50)x}$$

$$(0.70)x = 0.50 - (0.50)x, \quad (1.20)x = 0.50, \quad x = 0.42 \text{ L}$$

We need 0.42 L of 0.50 M HNO_2 and $1.00 - 0.42 = 0.58$ L of 0.50 M NaNO_2 to form a pH = 3.55 buffer solution.

$$31. \quad \text{K}_a \text{ for } \text{H}_2\text{NNH}_3^+ = \text{K}_w/\text{K}_b, \text{H}_2\text{NNH}_2 = 1.0 \times 10^{-14}/3.0 \times 10^{-6} = 3.3 \times 10^{-9}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{H}_2\text{NNH}_2]}{[\text{H}_2\text{NNH}_3^+]} = -\log(3.3 \times 10^{-9}) + \log \left(\frac{0.40}{0.80} \right) = 8.48 + (-0.30) = 8.18$$

$\text{pH} = \text{pK}_a$ for a buffer when $[\text{acid}] = [\text{base}]$. Here, the acid (H_2NNH_3^+) concentration needs to decrease, while the base (H_2NNH_2) concentration needs to increase in order for $[\text{H}_2\text{NNH}_3^+] = [\text{H}_2\text{NNH}_2]$. Both of these changes are accomplished by adding a strong base (like NaOH) to the original buffer. The added OH^- from the strong base converts the acid component of the buffer into the conjugate base. Here, the reaction is $\text{H}_2\text{NNH}_3^+ + \text{OH}^- \rightarrow \text{H}_2\text{NNH}_2 + \text{H}_2\text{O}$. Because a strong base is reacting, the reaction is assumed to go to completion. The following set-up determines the number of moles of $\text{OH}^-(x)$ that must be added so that $\text{mol H}_2\text{NNH}_3^+ = \text{mol H}_2\text{NNH}_2$. When $\text{mol acid} = \text{mol base}$ in a buffer, then $[\text{acid}] = [\text{base}]$ and $\text{pH} = \text{pK}_a$.

	H_2NNH_3^+	+	OH^-	\rightarrow	H_2NNH_2	+	H_2O	
Before	1.0 L \times 0.80 mol/L		x		1.0 L \times 0.40 mol/L			
Change	$-x$		$-x$	\rightarrow	$+x$			Reacts completely
After	$0.80 - x$		0		$0.40 + x$			

We want $\text{mol H}_2\text{NNH}_3^+ = \text{mol H}_2\text{NNH}_2$. So:

$$0.80 - x = 0.40 + x, \quad 2x = 0.40, \quad x = 0.20 \text{ mol OH}^-$$

When 0.20 mol OH^- is added to the initial buffer, mol H_2NNH_3^+ is decreased to 0.60 mol, while mol H_2NNH_2 is increased to 0.60 mol. Therefore, 0.20 mol of NaOH must be added to the initial buffer solution in order to produce a solution where $\text{pH} = \text{pK}_a$.

$$32. \quad [\text{H}^+] \text{ added} = \frac{0.010 \text{ mol}}{0.2500 \text{ L}} = 0.040 \text{ M}; \text{ the added } \text{H}^+ \text{ reacts completely with } \text{NH}_3 \text{ to form } \text{NH}_4^+.$$

a.	NH_3	+	H^+	\rightarrow	NH_4^+	
	Before		0.050 M		0.040 M	0.15 M
	Change		-0.040	\rightarrow	-0.040	+0.040
	After		0.010		0	0.19

Reacts completely

A buffer solution still exists after H^+ reacts completely. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = -\log(5.6 \times 10^{-10}) + \log \left(\frac{0.010}{0.19} \right) = 9.25 + (-1.28) = 7.97$$

b.	NH_3	+	H^+	\rightarrow	NH_4^+	
	Before		0.50 M		0.040 M	1.50 M
	Change		-0.040	\rightarrow	-0.040	+0.040
	After		0.46		0	1.54

Reacts completely

A buffer solution still exists. $\text{pH} = \text{pK}_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}, \quad 9.25 + \log \left(\frac{0.46}{1.54} \right) = 8.73$

Note: The two buffers differ in their capacity and not their initial pH (both buffers had an initial $\text{pH} = 8.77$). Solution b has the greatest capacity since it has the largest concentrations of weak acid and conjugate base. Buffers with greater capacities will be able to absorb more added H^+ or OH^- .

$$33. \quad [\text{HC}_7\text{H}_5\text{O}_2] = \frac{21.5 \text{ g HC}_7\text{H}_5\text{O}_2 \times \frac{1 \text{ mol HC}_7\text{H}_5\text{O}_2}{122.12 \text{ g}}}{0.2000 \text{ L}} = 0.880 \text{ M}$$

$$[\text{C}_7\text{H}_5\text{O}_2^-] = \frac{37.7 \text{ g NaC}_7\text{H}_5\text{O}_2 \times \frac{1 \text{ mol NaC}_7\text{H}_5\text{O}_2}{144.10 \text{ g}} \times \frac{1 \text{ mol C}_7\text{H}_5\text{O}_2^-}{\text{mol NaC}_7\text{H}_5\text{O}_2}}{0.2000 \text{ L}} = 1.31 \text{ M}$$

We have a buffer solution since we have both a weak acid and its conjugate base present at the same time. One can use the K_a reaction or the K_b reaction to solve. We will use the K_a reaction for the acid component of the buffer.

	$\text{HC}_7\text{H}_5\text{O}_2$	\rightleftharpoons	H^+	+	$\text{C}_7\text{H}_5\text{O}_2^-$
Initial	0.880 M		~0		1.31 M
	x mol/L of $\text{HC}_7\text{H}_5\text{O}_2$ dissociates to reach equilibrium				
Change	-x	\rightarrow	+x		+x
Equil.	0.880 - x		x		1.31 + x

$$K_a = 6.4 \times 10^{-5} = \frac{x(1.31+x)}{0.880-x} \approx \frac{x(1.31)}{0.880}, \quad x = [\text{H}^+] = 4.3 \times 10^{-5} M$$

$$\text{pH} = -\log(4.3 \times 10^{-5}) = 4.37; \text{ assumptions good.}$$

Alternatively, we can use the Henderson-Hasselbalch equation to calculate the pH of buffer solutions.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = \text{p}K_a + \log \frac{[\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]}$$

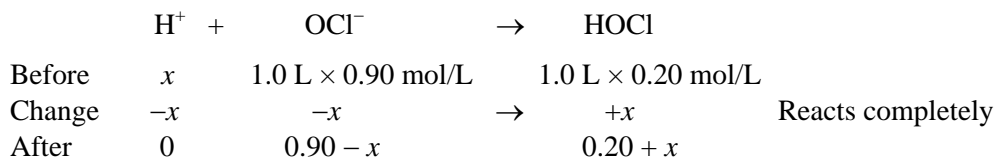
$$\text{pH} = -\log(6.4 \times 10^{-5}) + \log \left(\frac{1.31}{0.880} \right) = 4.19 + 0.173 = 4.36$$

Within round-off error, this is the same answer we calculated solving the equilibrium problem using the K_a reaction.

The Henderson-Hasselbalch equation will be valid when an assumption of the type $1.31 + x \approx 1.31$ that we just made in this problem is valid. From a practical standpoint, this will almost always be true for useful buffer solutions. If the assumption is not valid, the solution will have such a low buffering capacity that it will be of no use to control the pH. *Note:* The Henderson-Hasselbalch equation can only be used to solve for the pH of buffer solutions.

$$34. \quad \text{pH} = \text{p}K_a + \log \frac{[\text{OCl}^-]}{[\text{HOCl}]} = -\log(3.5 \times 10^{-8}) + \log \left(\frac{0.90}{0.20} \right) = 7.46 + 0.65 = 8.11$$

$\text{pH} = \text{p}K_a$ when $[\text{HOCl}] = [\text{OCl}^-]$ (or when mol HOCl = mol OCl^-). Here, the moles of the base component of the buffer must decrease, while the moles of the acid component of the buffer must increase in order to achieve a solution where $\text{pH} = \text{p}K_a$. Both of these changes occur when a strong acid (like HCl) is added. Let $x = \text{mol H}^+$ added from the strong acid HCl.



We want mol HOCl = mol OCl^- . Therefore:

$$0.90 - x = 0.20 + x, \quad 2x = 0.70, \quad x = 0.35 \text{ mol H}^+$$

When 0.35 mol H^+ is added, mol OCl^- is decreased to 0.55 mol, while the mol HOCl is increased to 0.55 mol. Therefore, 0.35 mol of HCl must be added to the original buffer solution in order to produce a solution where $\text{pH} = \text{p}K_a$.

$$35. \quad \text{pH} = \text{p}K_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}; \quad \text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

Because the buffer components, $\text{C}_2\text{H}_3\text{O}_2^-$ and $\text{HC}_2\text{H}_3\text{O}_2$, are both in the same volume of water, the concentration ratio of $[\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2]$ will equal the mole ratio of $\text{mol C}_2\text{H}_3\text{O}_2^-/\text{mol HC}_2\text{H}_3\text{O}_2$.

$$5.00 = 4.74 + \log \frac{\text{mol C}_2\text{H}_3\text{O}_2^-}{\text{mol HC}_2\text{H}_3\text{O}_2}; \quad \text{mol HC}_2\text{H}_3\text{O}_2 = 0.5000 \text{ L} \times \frac{0.200 \text{ mol}}{\text{L}} = 0.100 \text{ mol}$$

$$0.26 = \log \frac{\text{mol C}_2\text{H}_3\text{O}_2^-}{0.100 \text{ mol}}, \quad \frac{\text{mol C}_2\text{H}_3\text{O}_2^-}{0.100 \text{ mol}} = 10^{0.26} = 1.8, \quad \text{mol C}_2\text{H}_3\text{O}_2^- = 0.18 \text{ mol}$$

$$\text{Mass NaC}_2\text{H}_3\text{O}_2 = 0.18 \text{ mol NaC}_2\text{H}_3\text{O}_2 \times \frac{82.03 \text{ g}}{\text{mol}} = 15 \text{ g NaC}_2\text{H}_3\text{O}_2$$

36. Added OH^- converts $\text{HC}_2\text{H}_3\text{O}_2$ into $\text{C}_2\text{H}_3\text{O}_2^-$: $\text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^- \rightarrow \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O}$

From this reaction, the moles of $\text{C}_2\text{H}_3\text{O}_2^-$ produced equal the moles of OH^- added. Also, the total concentration of acetic acid plus acetate ion must equal 2.0 M (assuming no volume change on addition of NaOH). Summarizing for each solution:

$$[\text{C}_2\text{H}_3\text{O}_2^-] + [\text{HC}_2\text{H}_3\text{O}_2] = 2.0 \text{ M} \text{ and } [\text{C}_2\text{H}_3\text{O}_2^-] \text{ produced} = [\text{OH}^-] \text{ added}$$

a. $\text{pH} = \text{pK}_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$; for $\text{pH} = \text{pK}_a$, $\log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 0$

Therefore, $\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.0$ and $[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{HC}_2\text{H}_3\text{O}_2]$.

Because $[\text{C}_2\text{H}_3\text{O}_2^-] + [\text{HC}_2\text{H}_3\text{O}_2] = 2.0 \text{ M}$:

$$[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{HC}_2\text{H}_3\text{O}_2] = 1.0 \text{ M} = [\text{OH}^-] \text{ added}$$

To produce a $1.0 \text{ M C}_2\text{H}_3\text{O}_2^-$ solution, we need to add 1.0 mol of NaOH to 1.0 L of the $2.0 \text{ M HC}_2\text{H}_3\text{O}_2$ solution. The resulting solution will have $\text{pH} = \text{pK}_a = 4.74$.

b. $4.00 = 4.74 + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$, $\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 10^{-0.74} = 0.18$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.18[\text{HC}_2\text{H}_3\text{O}_2] \text{ or } [\text{HC}_2\text{H}_3\text{O}_2] = 5.6[\text{C}_2\text{H}_3\text{O}_2^-]$$

Because $[\text{C}_2\text{H}_3\text{O}_2^-] + [\text{HC}_2\text{H}_3\text{O}_2] = 2.0 \text{ M}$:

$$[\text{C}_2\text{H}_3\text{O}_2^-] + 5.6[\text{C}_2\text{H}_3\text{O}_2^-] = 2.0 \text{ M}, \quad [\text{C}_2\text{H}_3\text{O}_2^-] = \frac{2.0}{6.6} = 0.30 \text{ M} = [\text{OH}^-] \text{ added}$$

We need to add 0.30 mol of NaOH to 1.0 L of $2.0 \text{ M HC}_2\text{H}_3\text{O}_2$ solution to produce $0.30 \text{ M C}_2\text{H}_3\text{O}_2^-$. The resulting solution will have $\text{pH} = 4.00$.

c. $5.00 = 4.74 + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$, $\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 10^{0.26} = 1.8$

$$1.8[\text{HC}_2\text{H}_3\text{O}_2] = [\text{C}_2\text{H}_3\text{O}_2^-] \text{ or } [\text{HC}_2\text{H}_3\text{O}_2] = 0.56[\text{C}_2\text{H}_3\text{O}_2^-]$$

$$1.56[\text{C}_2\text{H}_3\text{O}_2^-] = 2.0 \text{ M}, [\text{C}_2\text{H}_3\text{O}_2^-] = 1.3 \text{ M} = [\text{OH}^-] \text{ added}$$

We need to add 1.3 mol of NaOH to 1.0 L of 2.0 M $\text{HC}_2\text{H}_3\text{O}_2$ to produce a solution with pH = 5.00.

37. When H^+ is added, it converts $\text{C}_2\text{H}_3\text{O}_2^-$ into $\text{HC}_2\text{H}_3\text{O}_2$: $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}^+ \rightarrow \text{HC}_2\text{H}_3\text{O}_2$. From this reaction, the moles of $\text{HC}_2\text{H}_3\text{O}_2$ produced must equal the moles of H^+ added and the total concentration of acetate ion + acetic acid must equal 1.0 M (assuming no volume change). Summarizing for each solution:

$$[\text{C}_2\text{H}_3\text{O}_2^-] + [\text{HC}_2\text{H}_3\text{O}_2] = 1.0 \text{ M} \text{ and } [\text{HC}_2\text{H}_3\text{O}_2] = [\text{H}^+] \text{ added}$$

a. $\text{pH} = \text{pK}_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$; for pH = pK_a, $[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{HC}_2\text{H}_3\text{O}_2]$.

For this to be true, $[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{HC}_2\text{H}_3\text{O}_2] = 0.50 \text{ M} = [\text{H}^+] \text{ added}$, which means that 0.50 mol of HCl must be added to 1.0 L of the initial solution to produce a solution with pH = pK_a.

b. $4.20 = 4.74 + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$, $\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 10^{-0.54} = 0.29$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.29[\text{HC}_2\text{H}_3\text{O}_2]; 0.29[\text{HC}_2\text{H}_3\text{O}_2] + [\text{HC}_2\text{H}_3\text{O}_2] = 1.0 \text{ M}$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.78 \text{ M} = [\text{H}^+] \text{ added}$$

0.78 mol of HCl must be added to produce a solution with pH = 4.20.

c. $5.00 = 4.74 + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$, $\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 10^{0.26} = 1.8$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 1.8[\text{HC}_2\text{H}_3\text{O}_2]; 1.8[\text{HC}_2\text{H}_3\text{O}_2] + [\text{HC}_2\text{H}_3\text{O}_2] = 1.0 \text{ M}$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.36 \text{ M} = [\text{H}^+] \text{ added}$$

0.36 mol of HCl must be added to produce a solution with pH = 5.00.

38. $50.0 \text{ g NH}_4\text{Cl} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} = 0.935 \text{ mol NH}_4\text{Cl}$ added to 1.00 L; $[\text{NH}_4^+] = 0.935 \text{ M}$

Using the Henderson Hasselbalch equation to solve for the pH of this buffer solution:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = -\log(5.6 \times 10^{-10}) + \log \left(\frac{0.75}{0.935} \right) = 9.25 - 0.096 = 9.15$$

39. a. pK_b for $C_6H_5NH_2 = -\log(3.8 \times 10^{-10}) = 9.42$; pK_a for $C_6H_5NH_3^+ = 14.00 - 9.42 = 4.58$

$$pH = pK_a + \log \frac{[C_6H_5NH_2]}{[C_6H_5NH_3^+]}, \quad 4.20 = 4.58 + \log \frac{0.50 M}{[C_6H_5NH_3^+]}$$

$$-0.38 = \log \frac{0.50 M}{[C_6H_5NH_3^+]}, \quad [C_6H_5NH_3^+] = [C_6H_5NH_3Cl] = 1.2 M$$

- b. $4.0 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} = 0.10 \text{ mol OH}^-$; $[OH^-] = \frac{0.10 \text{ mol}}{1.0 \text{ L}} = 0.10 M$

	$C_6H_5NH_3^+$	+	OH^-	\rightarrow	$C_6H_5NH_2$	+	H_2O
Before	1.2 M		0.10 M		0.50 M		
Change	-0.10		-0.10	\rightarrow	+0.10		
After	1.1		0		0.60		

A buffer solution exists. $pH = 4.58 + \log \left(\frac{0.60}{1.1} \right) = 4.32$

40. $pH = pK_a + \log \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}, \quad 4.00 = -\log(1.8 \times 10^{-5}) + \log \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$

$$\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 0.18; \text{ this is also equal to the mole ratio between } C_2H_3O_2^- \text{ and } HC_2H_3O_2.$$

Let x = volume of 1.00 M $HC_2H_3O_2$ and y = volume of 1.00 M $NaC_2H_3O_2$

$$x + y = 1.00 \text{ L}, \quad x = 1.00 - y$$

$$x(1.00 \text{ mol/L}) = \text{mol } HC_2H_3O_2; \quad y(1.00 \text{ mol/L}) = \text{mol } NaC_2H_3O_2 = \text{mol } C_2H_3O_2^-$$

$$\text{Thus: } \frac{y}{x} = 0.18 \text{ or } \frac{y}{1.00 - y} = 0.18; \text{ solving: } y = 0.15 \text{ L, so } x = 1.00 - 0.15 = 0.85 \text{ L.}$$

We need 850 mL of 1.00 M $HC_2H_3O_2$ and 150 mL of 1.00 M $NaC_2H_3O_2$ to produce a buffer solution at $pH = 4.00$.

41. a. $pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}, \quad 7.15 = -\log(6.2 \times 10^{-8}) + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$

$$7.15 = 7.21 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}, \quad \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 10^{-0.06} = 0.9, \quad \frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = \frac{1}{0.9} = 1.1 \approx 1$$

- b. A best buffer has approximately equal concentrations of weak acid and conjugate base, so $pH \approx pK_a$ for a best buffer. The pK_a value for a $H_3PO_4/H_2PO_4^-$ buffer is $-\log(7.5 \times 10^{-3}) = 2.12$. A pH of 7.15 is too high for a $H_3PO_4/H_2PO_4^-$ buffer to be effective. At this high of pH , there would be so little H_3PO_4 present that we could hardly consider it a buffer; this solution would not be effective in resisting pH changes, especially when a strong base is added.

$$42. \quad \text{pH} = \text{pK}_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}, \quad 7.40 = -\log(4.3 \times 10^{-7}) + \log \frac{[\text{HCO}_3^-]}{0.0012}$$

$$\log \frac{[\text{HCO}_3^-]}{0.0012} = 7.40 - 6.37 = 1.03, \quad \frac{[\text{HCO}_3^-]}{0.0012} = 10^{1.03}, \quad [\text{HCO}_3^-] = 1.3 \times 10^{-2} M$$

$$43. \quad \text{At pH} = 7.40: \quad 7.40 = -\log(4.3 \times 10^{-7}) + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$\log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 7.40 - 6.37 = 1.03, \quad \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{1.03}, \quad \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = 10^{-1.03} = 0.093$$

$$\text{At pH} = 7.35: \quad \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 7.35 - 6.37 = 0.98, \quad \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{0.98}$$

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = 10^{-0.98} = 0.10$$

The $[\text{H}_2\text{CO}_3] : [\text{HCO}_3^-]$ concentration ratio must increase from 0.093 to 0.10 in order for the onset of acidosis to occur.

44. Because we have added two solutions together, the concentration of each reagent has changed. What hasn't changed is the moles or millimoles of each reagent. Let's determine the millimoles of each reagent present by multiplying the volume in milliliters by the molarity in units of mmol/mL.

$$100.0 \text{ mL} \times 0.100 M = 10.0 \text{ mmol NaF}; \quad 100.0 \text{ mL} \times 0.025 M = 2.5 \text{ mmol HCl}$$

$\text{H}^+ + \text{F}^- \rightarrow \text{HF}$; 2.5 mmol H^+ converts 2.5 mmol F^- into 2.5 mmol HF. After the reaction, a buffer solution results containing 2.5 mmol HF and $(10.0 - 2.5 =) 7.5$ mmol F^- in 200.0 mL of solution.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{F}^-]}{[\text{HF}]} = 3.14 + \log \left(\frac{7.5 \text{ mmol}/200.0 \text{ mL}}{2.5 \text{ mmol}/200.0 \text{ mL}} \right) = 3.62; \quad \text{assumptions good.}$$

45. A best buffer has large and equal quantities of weak acid and conjugate base. Because $[\text{acid}] = [\text{base}]$ for a best buffer, $\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} = \text{pK}_a + 0 = \text{pK}_a$ ($\text{pH} \approx \text{pK}_a$ for a best buffer).

The best acid choice for a $\text{pH} = 7.00$ buffer would be the weak acid with a pK_a close to 7.0 or $\text{K}_a \approx 1 \times 10^{-7}$. HOCl is the best choice in Table 7.2 ($\text{K}_a = 3.5 \times 10^{-8}$; $\text{pK}_a = 7.46$). To make this buffer, we need to calculate the $[\text{base}]/[\text{acid}]$ ratio.

$$7.00 = 7.46 + \log \frac{[\text{base}]}{[\text{acid}]}, \quad \frac{[\text{OCl}^-]}{[\text{HOCl}]} = 10^{-0.46} = 0.35$$

Any OCl^-/HOCl buffer in a concentration ratio of 0.35 : 1 will have a $\text{pH} = 7.00$. One possibility is $[\text{NaOCl}] = 0.35 \text{ M}$ and $[\text{HOCl}] = 1.0 \text{ M}$.

46. For a $\text{pH} = 5.00$ buffer, we want an acid with a pK_a close to 5.00. For a conjugate acid-base pair, $14.00 = \text{pK}_a + \text{pK}_b$. So for a $\text{pH} = 5.00$ buffer, we want the base to have a pK_b close to $(14.0 - 5.0 =) 9.0$ or a K_b close to 1×10^{-9} . The best choice in Table 7.3 is pyridine ($\text{C}_5\text{H}_5\text{N}$) with $K_b = 1.7 \times 10^{-9}$.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}; \quad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}$$

$$5.00 = -\log(5.9 \times 10^{-6}) + \log \frac{[\text{base}]}{[\text{acid}]}, \quad \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} = 10^{-0.23} = 0.59$$

There are many possibilities to make this buffer. One possibility is a solution of $[\text{C}_5\text{H}_5\text{N}] = 0.59 \text{ M}$ and $[\text{C}_5\text{H}_5\text{NHCl}] = 1.0 \text{ M}$. The pH of this solution will be 5.00 because the base to acid concentration ratio is 0.59 : 1.

47. a. No; a solution of a strong acid (HNO_3) and its conjugate base (NO_3^-) is not generally considered a buffer solution.
- b. No; two acids are present (HNO_3 and HF), so it is not a buffer solution.
- c. H^+ reacts completely with F^- . Since equal volumes are mixed, the initial concentrations in the mixture are 0.10 M HNO_3 and 0.20 M NaF .

	H^+	+	F^-	\rightarrow	HF	
Before	0.10 M		0.20 M		0	
Change	-0.10		-0.10	\rightarrow	+0.10	Reacts completely
After	0		0.10		0.10	

After H^+ reacts completely, a buffer solution results; that is, a weak acid (HF) and its conjugate base (F^-) are both present in solution in large quantities.

- d. No; a strong acid (HNO_3) and a strong base (NaOH) do not form buffer solutions. They will neutralize each other to form H_2O .
48. The reaction $\text{OH}^- + \text{CH}_3\text{NH}_3^+ \rightarrow \text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$ goes to completion for solutions a, c, and d (no reaction occurs between the species in solution b because both species are bases). After the OH^- reacts completely, there must be both CH_3NH_3^+ and CH_3NH_2 in solution for it to be a buffer. The important components of each solution (after the OH^- reacts completely) is(are):

- a. $0.05 \text{ M CH}_3\text{NH}_2$ (no CH_3NH_3^+ remains, no buffer)
- b. 0.05 M OH^- and $0.1 \text{ M CH}_3\text{NH}_2$ (two bases present, no buffer)

- c. 0.05 M OH^- and $0.05\text{ M CH}_3\text{NH}_2$ (too much OH^- added, no CH_3NH_3^+ remains, no buffer)
- d. $0.05\text{ M CH}_3\text{NH}_2$ and $0.05\text{ M CH}_3\text{NH}_3^+$ (a buffer solution results)

Only the combination in mixture d results in a buffer. Note that the concentrations are halved from the initial values. This is so because equal volumes of two solutions were added together, which halves the concentrations.

49. Using regular procedures, $\text{pH} = \text{pK}_a = -\log(1.6 \times 10^{-7}) = 6.80$ since $[\text{A}^-]_0 = [\text{HA}]_0$ in this buffer solution. However, the pH is very close to that of neutral water, so maybe we need to consider the H^+ contribution from water. Another problem with this answer is that $x (= [\text{H}^+])$ is not small as compared with $[\text{HA}]_0$ and $[\text{A}^-]_0$, which was assumed when solving using the regular procedures. Because the concentrations of the buffer components are less than 10^{-6} M , let us use the expression for the exact treatment of buffers to solve.

$$\text{K}_a = 1.6 \times 10^{-7} = \frac{[\text{H}^+] \left([\text{A}^-]_0 + \frac{[\text{H}^+]^2 - \text{K}_w}{[\text{H}^+]} \right)}{[\text{HA}]_0 - \frac{[\text{H}^+]^2 - \text{K}_w}{[\text{H}^+]}} = \frac{[\text{H}^+] \left(5.0 \times 10^{-7} + \frac{[\text{H}^+]^2 - (1.0 \times 10^{-14})}{[\text{H}^+]} \right)}{5.0 \times 10^{-7} - \frac{[\text{H}^+]^2 - (1.0 \times 10^{-14})}{[\text{H}^+]}}$$

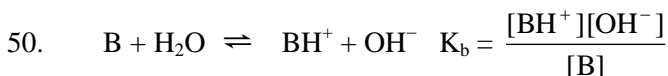
Solving exactly requires solving a cubic equation. Instead, we will use the method of successive approximations where our initial guess for $[\text{H}^+] = 1.6 \times 10^{-7}\text{ M}$ (the value obtained using the regular procedures).

$$1.6 \times 10^{-7} = \frac{[\text{H}^+] \left(5.0 \times 10^{-7} + \frac{(1.6 \times 10^{-7})^2 - (1.0 \times 10^{-14})}{1.6 \times 10^{-7}} \right)}{5.0 \times 10^{-7} - \frac{(1.6 \times 10^{-7})^2 - (1.0 \times 10^{-14})}{1.6 \times 10^{-7}}}, \quad [\text{H}^+] = 1.1 \times 10^{-7}$$

We continue the process using 1.1×10^{-7} as our estimate for $[\text{H}^+]$. This gives $[\text{H}^+] = 1.5 \times 10^{-7}$. We continue the process until we get a self consistent answer. After three more iterations, we converge on $[\text{H}^+] = 1.3 \times 10^{-7}\text{ M}$. Solving for the pH:

$$\text{pH} = -\log(1.3 \times 10^{-7}) = 6.89$$

Note that if we were to solve this problem exactly (using the quadratic formula) while ignoring the H^+ contribution from water, the answer comes out to $[\text{H}^+] = 1.0 \times 10^{-7}\text{ M}$. We get a significantly different answer when we consider the H^+ contribution from H_2O .



The equation for the exact treatment of B/BHCl type buffers would be analogous to the equation for HA/NaA type buffers. The equation is:

$$K_b = \frac{[\text{OH}^-] \left([\text{BH}^+]_0 + \frac{[\text{OH}^-]^2 - K_w}{[\text{OH}^-]} \right)}{[\text{B}]_0 - \frac{[\text{OH}^-]^2 - K_w}{[\text{OH}^-]}}$$

Solving the buffer problem using the regular procedures:



Initial $1.0 \times 10^{-4} M$ $1.0 \times 10^{-5} M$ ~ 0
 x mol/L of HONH₂ reacts with H₂O to reach equilibrium

Change $-x$ $+x$ $+x$

Equil. $1.0 \times 10^{-4} - x$ $1.0 \times 10^{-5} + x$ x

$$K_b = 1.1 \times 10^{-8} = \frac{[\text{HONH}_3^+][\text{OH}^-]}{[\text{HONH}_2]} = \frac{(1.0 \times 10^{-5} + x)x}{(1.0 \times 10^{-4} - x)} \approx \frac{(1.0 \times 10^{-5})x}{1.0 \times 10^{-4}}$$

(Assuming $x \ll 1.0 \times 10^{-5}$.)

$x = [\text{OH}^-] = 1.1 \times 10^{-7} M$; assumption that $x \ll 1.0 \times 10^{-5}$ is good (x is 1.1% of 1.0×10^{-5}).

In the regular procedure to solve the buffer problem, the problem reduced down to the expression:

$$K_b = \frac{[\text{HONH}_3^+]_0[\text{OH}^-]}{[\text{HONH}_2]_0}$$

This expression holds if x is negligible as compared to $[\text{HONH}_3^+]_0$ and $[\text{HONH}_2]_0$ as it was in this problem. Now we want to know if we need to worry about the contribution of OH⁻ from water. From the equation for the exact treatment of buffers, if $([\text{OH}^-]^2 - K_w) / [\text{OH}^-]$ is much less than $[\text{HONH}_3^+]_0$ and $[\text{HONH}_2]_0$, then the exact equation reduces to:

$$K_b = \frac{[\text{OH}^-][\text{HONH}_3^+]_0}{[\text{HONH}_2]_0}$$

This is the same expression we ended up with to solve the problem using the regular procedures. Checking the neglected term using the $[\text{OH}^-]$ calculated above:

$$\frac{[\text{OH}^-]^2 - K_w}{[\text{OH}^-]} = \frac{(1.1 \times 10^{-7})^2 - (1.0 \times 10^{-14})}{1.1 \times 10^{-7}} = 1.9 \times 10^{-8}$$

This is indeed much smaller than $[\text{HONH}_3^+]_0$ and $[\text{HONH}_2]_0$ (1.9×10^{-8} is 0.19% of 1.0×10^{-5}). So for this problem we would calculate the same $[\text{OH}^-]$ using the exact equation as we calculated using the regular procedures. In general, we only need to use the exact equation when the buffering materials have a concentration of $10^{-6} M$ or less.

51. To solve for $[\text{KOCl}]$, we need to use the equation derived in Section 8.3 of the text on the exact treatment of buffered solutions. The equation is:

$$K_a = \frac{[\text{H}^+] \left([\text{A}^-]_0 + \frac{[\text{H}^+]^2 - K_w}{[\text{H}^+]} \right)}{[\text{HA}]_0 - \frac{[\text{H}^+]^2 - K_w}{[\text{H}^+]}}$$

Because $\text{pH} = 7.20$, $[\text{H}^+] = 10^{-7.20} = 6.3 \times 10^{-8} M$.

$$K_a = 3.5 \times 10^{-8} = \frac{6.3 \times 10^{-8} \left([\text{OCl}^-] + \frac{(6.3 \times 10^{-8})^2 - (1.0 \times 10^{-14})}{6.3 \times 10^{-8}} \right)}{1.0 \times 10^{-6} - \frac{(6.3 \times 10^{-8})^2 - (1.0 \times 10^{-14})}{6.3 \times 10^{-8}}}$$

$$3.5 \times 10^{-8} = \frac{6.3 \times 10^{-8}([\text{OCl}^-] - 9.57 \times 10^{-8})}{(1.0 \times 10^{-6}) + (9.57 \times 10^{-8})} \quad (\text{Carrying extra significant figures.})$$

$$3.83 \times 10^{-14} = 6.3 \times 10^{-8}([\text{OCl}^-] - 9.57 \times 10^{-8}), \quad [\text{OCl}^-] = [\text{KOCl}] = 7.0 \times 10^{-7} M$$

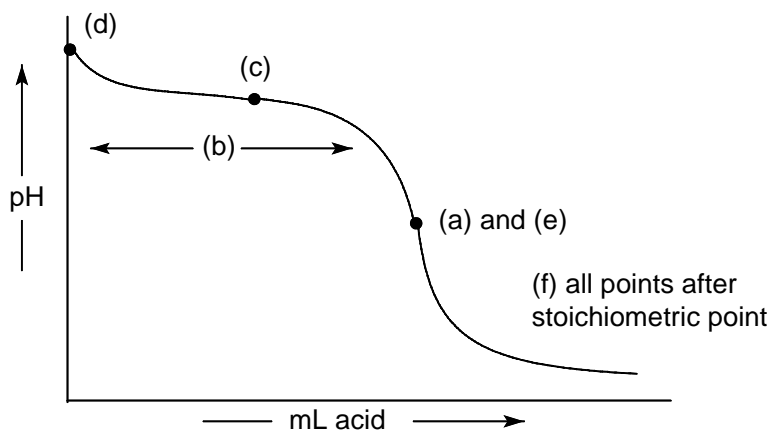
Acid-Base Titrations

52. Let's review the strong acid-strong base titration using the example (case study) covered in Section 8.5 of the text. The example used was the titration of 50.0 mL of 0.200 M HNO_3 titrated by 0.100 M NaOH. See Fig. 8.1 for the titration curve. Here are the important points.
- Initially, before any strong base has been added. Major species: H^+ , NO_3^- , and H_2O . To determine the pH, determine the $[\text{H}^+]$ in solution after the strong acid has completely dissociated, as we always do for strong acid problems.
 - After some strong base has been added, up to the equivalence point. For our example, this is from just after 0.00 mL NaOH added up to just before 100.0 mL NaOH added. Major species before any reaction: H^+ , NO_3^- , Na^+ , OH^- , and H_2O . Na^+ and NO_3^- have no acidic or basic properties. In this region, the OH^- from the strong base reacts with some of the H^+ from the strong acid to produce water ($\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$). As is always the case when something strong reacts, we assume the reaction goes to completion. Major species after reaction: H^+ , NO_3^- , Na^+ , and H_2O : To determine the pH of the solution, we first determine how much of the H^+ is neutralized by the OH^- . Then we determine the excess $[\text{H}^+]$ and take the $-\log$ of this quantity to determine pH. From 0.1 to 99.9 mL NaOH added, the excess H^+ from the strong acid determines the pH.

- c. The equivalence point (100.0 mL NaOH added). Major species before reaction: H^+ , NO_3^- , Na^+ , OH^- , and H_2O . Here, we have added just enough OH^- to neutralize all of the H^+ from the strong acid (moles OH^- added = moles H^+ present). After the stoichiometry reaction ($\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$), both H^+ and OH^- have run out (this is the definition of the equivalence point). Major species after reaction: Na^+ , NO_3^- , and H_2O . All we have in solution are some ions with no acidic or basic properties (NO_3^- and Na^+ in H_2O). The $\text{pH} = 7.00$ at the equivalence point of a strong acid-strong base titration.
- d. Past the equivalence point (volume of NaOH added > 100.0 mL). Major species before reaction H^+ , NO_3^- , Na^+ , OH^- , and H_2O . After the stoichiometry reaction goes to completion ($\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$), we have excess OH^- present. Major species after reaction: OH^- , Na^+ , NO_3^- , and H_2O . We determine the excess $[\text{OH}^-]$ and convert this into the pH . After the equivalence point, the excess OH^- from the strong base determines the pH .

See Fig. 8.2 for a titration curve of a strong base by a strong acid. The stoichiometry problem is still the same, $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$, but what is in excess after this reaction goes to completion is the reverse of the strong acid-strong base titration. The pH up to just before the equivalence point is determined by the excess OH^- present. At the equivalence point, $\text{pH} = 7.00$ because we have added just enough H^+ from the strong acid to react with all the OH^- from the strong base (moles of base present = moles of acid added). Past the equivalence point, the pH is determined by the excess H^+ present. As can be seen from Figs. 8.1 and 8.2, both strong by strong titrations have $\text{pH} = 7.00$ at the equivalence point, but the curves are the reverse of each other before and after the equivalence point.

53.



$\text{B} + \text{H}^+ \rightarrow \text{BH}^+$; added H^+ from the strong acid converts the weak base B into its conjugate acid BH^+ . Initially, before any H^+ is added (point d), B is the dominant species present. After H^+ is added, both B and BH^+ are present, and a buffered solution results (region b). At the equivalence point (points a and e), exactly enough H^+ has been added to convert all the weak base present initially into its conjugate acid BH^+ . Past the equivalence point (region f), excess H^+ is present. For the answer to b, we included almost the entire buffer region. The maximum buffer region is around the halfway point to equivalence (point c), where $[\text{B}] = [\text{BH}^+]$. Here, $\text{pH} = \text{pK}_a$, which is a characteristic of a best buffer.

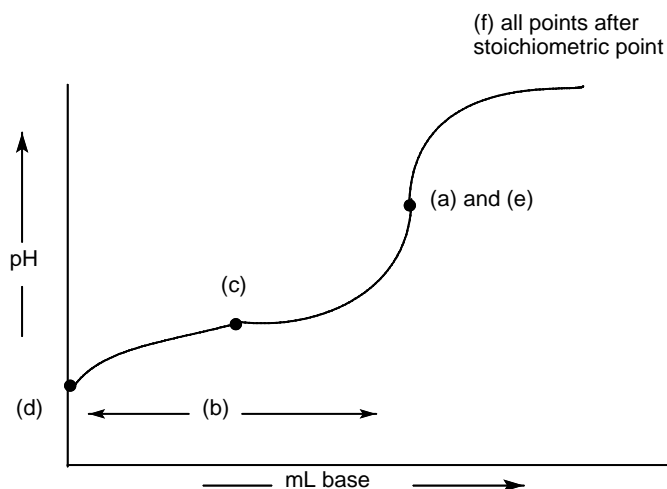
54. a. The red plot is the pH curve for the strong acid and the blue plot is the pH curve for the weak acid. The pH at the equivalence point is 7.00 for the strong acid-strong base titration, while the pH is greater than 7.00 if a weak acid is titrated. Another point one could look at is the initial point. Because both acids have the same concentration, the strong acid curve will be at the lowest initial pH. Actually, any point at any volume up to the equivalence point for the strong acid plot will have a lower pH than the weak acid plot (assuming equal concentrations and volumes). Another difference would be the pH at the halfway point to equivalence. For the weak acid titration, the pH of solution equals the pK_a value for the weak acid at the halfway point to equivalence; this is not the case when a strong acid is titrated.
- b. A buffer is a solution that resists pH change. From this definition, both titrations have regions where the pH doesn't change much on addition of strong base, so both could be labeled to have buffer regions. However, we don't normally include strong acids as a component of buffer solutions. Strong acids certainly can absorb added OH^- by reacting with it to form water. But when more strong acid is added, the H^+ concentration increases steadily; there is nothing present in a strong acid solution to react with added H^+ .
- This is not the case in the weak acid-strong base titration. After some OH^- has been added, some weak acid is converted into its conjugate base. We now have a typical buffer solution because there are significant amounts of weak acid and conjugate base present at the same time. The buffer region extends from a little past the initial point in the titration up to just a little before the equivalence point. This entire region is a buffer region because both the weak acid and conjugate base are present in significant quantities in this region.
- c. True; $HA + OH^- \rightarrow A^- + H_2O$; both reactions have the same neutralization reaction. In both cases, the equivalence point is reached when enough OH^- has been added to exactly react with the acid present initially. Because all acid concentrations and volumes are the same, we have equal moles of each acid which requires the same moles of OH^- to reach the equivalence point. Therefore, each acid requires the same volume of 0.10 M NaOH to reach the equivalence point.
- d. False; the pH for the strong acid-strong base titration will be 7.00 at the equivalence point. The pH for the weak acid-strong base titration will be greater than 7.00 at the equivalence point. In both titrations, the major species present at the equivalence points are Na^+ , H_2O , and the conjugate base of the acid titrated. Because the conjugate base of a strong acid has no basic characteristics, $pH = 7.00$ at the equivalence point. However, the conjugate base of a weak acid is a weak base. A weak base is present at the equivalence point of a weak acid-strong base titration, so the pH is basic ($pH > 7.0$).
55. a. Let's call the acid HB, which is a weak acid. When HB is present in the beakers, it exists in the undissociated form, making it a weak acid. A strong acid would exist as separate H^+ and B^- ions.
- b. Beaker a contains 4 HB molecules and 2 B^- ions, beaker b contains 6 B^- ions, beaker c contains 6 HB molecules, beaker d contains 6 B^- and 6 OH^- ions, and beaker e contains 3 HB molecules and 3 B^- ions. $HB + OH^- \rightarrow B^- + H_2O$; this is the neutralization reaction that occurs when OH^- is added. We start off the titration with a beaker full of weak acid (beaker c). When some OH^- is added, we convert some weak acid HB into its conjugate

base B^- (beaker a). At the halfway point to equivalence, we have converted exactly one-half of the initial amount of acid present into its conjugate base (beaker e). We finally reach the equivalence point when we have added just enough OH^- to convert all of the acid present initially into its conjugate base (beaker b). Past the equivalence point, we have added an excess of OH^- , so we have excess OH^- present as well as the conjugate base of the acid produced from the neutralization reaction (beaker d). The order of the beakers from start to finish is:

beaker c \rightarrow beaker a \rightarrow beaker e \rightarrow beaker b \rightarrow beaker d

- c. $pH = pK_a$ when a buffer solution is present that has equal concentrations of the weak acid and conjugate base. This is beaker e.
- d. The equivalence point is when just enough OH^- has been added to exactly react with all of the acid present initially. This is beaker b.
- e. Past the equivalence, the pH is dictated by the concentration of excess OH^- added from the strong base. We can ignore the amount of hydroxide added by the weak conjugate base that is also present. This is beaker d.

56.

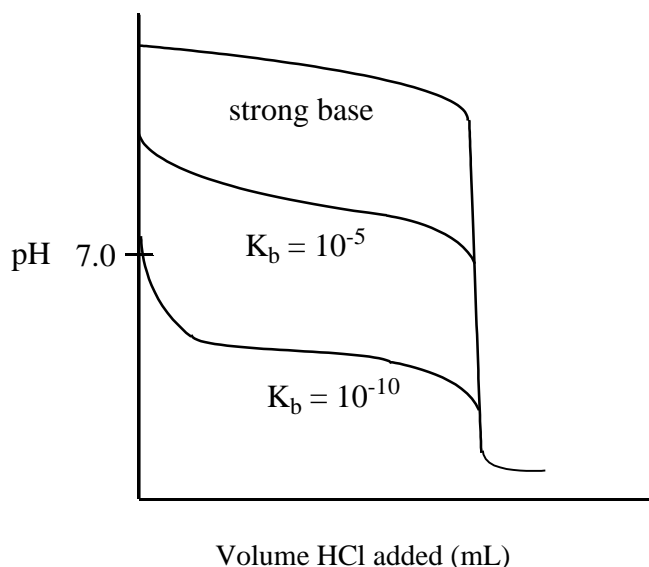


$HA + OH^- \rightarrow A^- + H_2O$; added OH^- from the strong base converts the weak acid HA into its conjugate base A^- . Initially before any OH^- is added (point d), HA is the dominant species present. After OH^- is added, both HA and A^- are present, and a buffer solution results (region b). At the equivalence point (points a and e), exactly enough OH^- has been added to convert all the weak acid HA into its conjugate base A^- . Past the equivalence point (region f), excess OH^- is present. For the answer to part b, we included almost the entire buffer region. The maximum buffer region (or the region which is the best buffer solution) is around the halfway point to equivalence (point c). At this point, enough OH^- has been added to convert exactly one-half of the weak acid present initially into its conjugate base, so $[HA] = [A^-]$ and $pH = pK_a$. A best buffer has about equal concentrations of weak acid and conjugate base present.

57. a. Because all acids are the same initial concentration, the pH curve with the highest pH at 0 mL of NaOH added will correspond to the titration of the weakest acid. This is curve f.
- b. The pH curve with the lowest pH at 0 mL of NaOH added will correspond to the titration of the strongest acid. This is pH curve a.

The best point to look at to differentiate a strong acid from a weak acid titration (if initial concentrations are not known) is the equivalence point pH. If the pH = 7.00, the acid titrated is a strong acid; if the pH is greater than 7.00, the acid titrated is a weak acid.

- c. For a weak acid-strong base titration, the pH at the halfway point to equivalence is equal to the pK_a value. The pH curve, which represents the titration of an acid with $K_a = 1.0 \times 10^{-6}$, will have a $pH = -\log(1 \times 10^{-6}) = 6.0$ at the halfway point. The equivalence point, from the plots, occurs at 50 mL NaOH added, so the halfway point is 25 mL. Plot d has a $pH \approx 6.0$ at 25 mL of NaOH added, so the acid titrated in this pH curve (plot d) has $K_a \approx 1 \times 10^{-6}$.
58. The three key points to emphasize in your sketch are the initial pH, the pH at the halfway point to equivalence, and the pH at the equivalence point. For all the weak bases titrated, $pH = pK_a$ at the halfway point to equivalence (50.0 mL HCl added) because $[weak\ base] = [conjugate\ acid]$ at this point. Here, the weak base with $K_b = 1 \times 10^{-5}$ has a conjugate acid with $K_a = 1 \times 10^{-9}$, so $pH = 9.0$ at the halfway point. The weak base with $K_b = 1 \times 10^{-10}$ has a $pH = 4.0$ at the halfway point to equivalence. For the initial pH, the strong base has the highest pH (most basic), whereas the weakest base has the lowest pH (least basic). At the equivalence point (100.0 mL HCl added), the strong base titration has $pH = 7.0$. The weak bases titrated have acidic pH's because the conjugate acids of the weak bases titrated are the major species present. The weakest base has the strongest conjugate acid so its pH will be lowest (most acidic) at the equivalence point.



59. Titration i is a strong acid titrated by a strong base. The pH is very acidic until just before the equivalence point; at the equivalence point, $\text{pH} = 7.00$; and past the equivalence the pH is very basic. Titration ii is a strong base titrated by a strong acid. Here the pH is very basic until just before the equivalence point; at the equivalence point, $\text{pH} = 7.00$; and past the equivalence point, the pH is very acidic. Titration iii is a weak base titrated by a strong acid. The pH starts out basic because a weak base is present. However, the pH will not be as basic as in titration ii, where a strong base is titrated. The pH drops as HCl is added; then at the halfway point to equivalence, $\text{pH} = \text{p}K_a$. Because $K_b = 4.4 \times 10^{-4}$ for CH_3NH_2 , CH_3NH_3^+ has $K_a = K_w/K_b = 2.3 \times 10^{-11}$ and $\text{p}K_a = 10.64$. So, at the halfway point to equivalence for this weak base-strong acid titration, $\text{pH} = 10.64$. The pH continues to drop as HCl is added; then at the equivalence point the pH is acidic ($\text{pH} < 7.00$) because the only important major species present is a weak acid (the conjugate acid of the weak base). Past the equivalence point the pH becomes more acidic as excess HCl is added. Titration iv is a weak acid titrated by a strong base. The pH starts off acidic, but not nearly as acidic as the strong acid titration (i). The pH increases as NaOH is added; then, at the halfway point to equivalence, $\text{pH} = \text{p}K_a$ for $\text{HF} = -\log(7.2 \times 10^{-4}) = 3.14$. The pH continues to increase past the halfway point; then at the equivalence point, the pH is basic ($\text{pH} > 7.0$) because the only important major species present is a weak base (the conjugate base of the weak acid). Past the equivalence point, the pH becomes more basic as excess NaOH is added.
- All require the same volume of titrant to reach the equivalence point. At the equivalence point for all these titrations, moles acid = moles base ($M_A V_A = M_B V_B$). Because all the molarities and volumes are the same in the titrations, the volume of titrant will be the same (50.0 mL titrant added to reach equivalence point).
 - Increasing initial pH: $i < iv < iii < ii$; the strong acid titration has the lowest pH, the weak acid titration is next, followed by the weak base titration, with the strong base titration having the highest pH.
 - $i < iv < iii < ii$; the strong acid titration has the lowest pH at the halfway point to equivalence, and the strong base titration has the highest halfway point pH. For the weak acid titration, $\text{pH} = \text{p}K_a = 3.14$, and for the weak base titration, $\text{pH} = \text{p}K_a = 10.64$.
 - Equivalence point pH: $iii < ii = i < iv$; the strong-by-strong titrations have $\text{pH} = 7.00$ at the equivalence point. The weak base titration has an acidic pH at the equivalence point, and a weak acid titration has a basic equivalence point pH.

The only different answer when the weak acid and weak base are changed would be for part c. This is for the halfway point to equivalence, where $\text{pH} = \text{p}K_a$.

$$\text{HOC}_6\text{H}_5; K_a = 1.6 \times 10^{-10}, \text{p}K_a = -\log(1.6 \times 10^{-10}) = 9.80$$

$$\text{C}_5\text{H}_5\text{NH}^+, K_a = \frac{K_w}{K_{b, \text{C}_5\text{H}_5\text{N}}} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}, \text{p}K_a = 5.23$$

From the pK_a values, the correct ordering at the halfway point to equivalence would be $i < iii < iv < ii$. Note that for the weak base-strong acid titration using C_5H_5N , the pH is acidic at the halfway point to equivalence, whereas the weak acid-strong base titration using HOC_6H_5 is basic at the halfway point to equivalence. This is fine; this will always happen when the weak base titrated has a $K_b < 1 \times 10^{-7}$ (so K_a of the conjugate acid is greater than 1×10^{-7}) and when the weak acid titrated has a $K_a < 1 \times 10^{-7}$ (so K_b of the conjugate base is greater than 1×10^{-7}).

60. $HA + OH^- \rightarrow A^- + H_2O$; it takes 25.0 mL of 0.100 M NaOH to reach the equivalence point where $\text{mmol HA} = \text{mmol OH}^- = 25.0 \text{ mL}(0.100 \text{ M}) = 2.50 \text{ mmol}$. At the equivalence point, some HCl is added. The H^+ from the strong acid reacts to completion with the best base present, A^- .

	H^+	+	A^-	\rightarrow	HA
Before	$13.0 \text{ mL} \times 0.100 \text{ M}$		2.5 mmol		0
Change	-1.3 mmol		-1.3 mmol		+1.3 mmol
After	0		1.2 mmol		1.3 mmol

A buffer solution is present after the H^+ has reacted completely.

$$pH = pK_a + \log \frac{[A^-]}{[HA]}, \quad 4.7 = pK_a + \log \left(\frac{1.2 \text{ mmol}/V_T}{1.3 \text{ mmol}/V_T} \right)$$

Because the log term will be negative [$\log(1.2/1.3) = -0.035$], the pK_a value of the acid must be greater than 4.7.

61. This is a strong acid ($HClO_4$) titrated by a strong base (KOH). Added OH^- from the strong base will react completely with the H^+ present from the strong acid to produce H_2O .

a. Only strong acid present. $[H^+] = 0.200 \text{ M}$; $pH = 0.699$

b. $\text{mmol OH}^- \text{ added} = 10.0 \text{ mL} \times \frac{0.100 \text{ mmol OH}^-}{\text{mL}} = 1.00 \text{ mmol OH}^-$

$$\text{mmol H}^+ \text{ present} = 40.0 \text{ mL} \times \frac{0.200 \text{ mmol H}^+}{\text{mL}} = 8.0 \text{ mmol H}^+$$

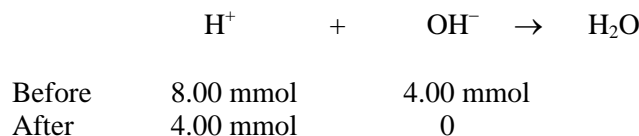
Note: The units millimoles are usually easier numbers to work with. The units for molarity are moles per liter but are also equal to millimoles per milliliter.

	H^+	+	OH^-	\rightarrow	H_2O
Before	8.00 mmol		1.00 mmol		
Change	-1.00 mmol		-1.00 mmol		Reacts completely
After	7.00 mmol		0		

$$\text{The excess H}^+ \text{ determines the pH. } [H^+]_{\text{excess}} = \frac{7.00 \text{ mmol H}^+}{40.0 \text{ mL} + 10.0 \text{ mL}} = 0.140 \text{ M}$$

$$pH = -\log(0.140) = 0.854$$

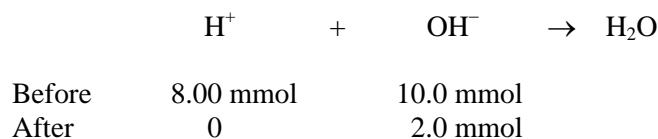
c. $\text{mmol OH}^- \text{ added} = 40.0 \text{ mL} \times 0.100 \text{ M} = 4.00 \text{ mmol OH}^-$



$$[\text{H}^+]_{\text{excess}} = \frac{4.00 \text{ mmol}}{(40.0 + 40.0) \text{ mL}} = 0.0500 \text{ M}; \text{ pH} = 1.301$$

d. $\text{mmol OH}^- \text{ added} = 80.0 \text{ mL} \times 0.100 \text{ M} = 8.00 \text{ mmol OH}^-$; this is the equivalence point because we have added just enough OH^- to react with all the acid present. For a strong acid-strong base titration, $\text{pH} = 7.00$ at the equivalence point because only neutral species are present (K^+ , ClO_4^- , H_2O).

e. $\text{mmol OH}^- \text{ added} = 100.0 \text{ mL} \times 0.100 \text{ M} = 10.0 \text{ mmol OH}^-$



Past the equivalence point, the pH is determined by the excess OH^- present.

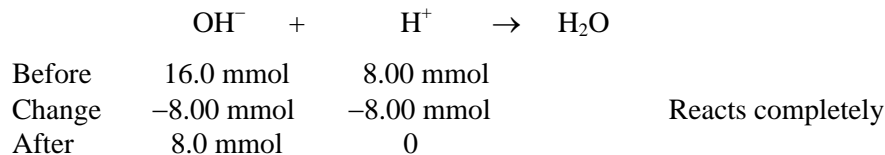
$$[\text{OH}^-]_{\text{excess}} = \frac{2.0 \text{ mmol}}{(40.0 + 100.0) \text{ mL}} = 0.014 \text{ M}; \text{ pOH} = 1.85; \text{ pH} = 12.15$$

62. This is a strong base, $\text{Ba}(\text{OH})_2$, titrated by a strong acid, HCl . The added strong acid will neutralize the OH^- from the strong base. As is always the case when a strong acid and/or strong base reacts, the reaction is assumed to go to completion.

a. Only a strong base is present, but it breaks up into two moles of OH^- ions for every mole of $\text{Ba}(\text{OH})_2$. $[\text{OH}^-] = 2 \times 0.100 \text{ M} = 0.200 \text{ M}$; $\text{pOH} = 0.699$; $\text{pH} = 13.301$

b. $\text{mmol OH}^- \text{ present} = 80.0 \text{ mL} \times \frac{0.100 \text{ mmol Ba}(\text{OH})_2}{\text{mL}} \times \frac{2 \text{ mmol OH}^-}{\text{mmol Ba}(\text{OH})_2}$
 $= 16.0 \text{ mmol OH}^-$

$$\text{mmol H}^+ \text{ added} = 20.0 \text{ mL} \times \frac{0.400 \text{ mmol H}^+}{\text{mL}} = 8.00 \text{ mmol H}^+$$



$$[\text{OH}^-]_{\text{excess}} = \frac{8.0 \text{ mmol OH}^-}{80.0 \text{ mL} + 20.0 \text{ mL}} = 0.080 \text{ M}; \text{ pOH} = 1.10; \text{ pH} = 12.90$$

c. $\text{mmol H}^+ \text{ added} = 30.0 \text{ mL} \times 0.400 \text{ M} = 12.0 \text{ mmol H}^+$

	OH^-	+	H^+	\rightarrow	H_2O
Before	16.0 mmol		12.0 mmol		
After	4.0 mmol		0		

$$[\text{OH}^-]_{\text{excess}} = \frac{4.0 \text{ mmol OH}^-}{(80.0 + 30.0) \text{ mL}} = 0.036 \text{ M}; \text{ pOH} = 1.44; \text{ pH} = 12.56$$

d. $\text{mmol H}^+ \text{ added} = 40.0 \text{ mL} \times 0.400 \text{ M} = 16.0 \text{ mmol H}^+$; this is the equivalence point. Because the H^+ will exactly neutralize the OH^- from the strong base, all we have in solution is Ba^{2+} , Cl^- , and H_2O . All are neutral species, so $\text{pH} = 7.00$.

e. $\text{mmol H}^+ \text{ added} = 80.0 \text{ mL} \times 0.400 \text{ M} = 32.0 \text{ mmol H}^+$

	OH^-	+	H^+	\rightarrow	H_2O
Before	16.0 mmol		32.0 mmol		
After	0		16.0 mmol		

$$[\text{H}^+]_{\text{excess}} = \frac{16.0 \text{ mmol H}^+}{(80.0 + 80.0) \text{ mL}} = 0.100 \text{ M}; \text{ pH} = 1.000$$

63. This is a weak acid ($\text{HC}_2\text{H}_3\text{O}_2$) titrated by a strong base (KOH).

a. Only weak acid is present. Solving the weak acid problem:

	$\text{HC}_2\text{H}_3\text{O}_2$	\rightleftharpoons	H^+	+	$\text{C}_2\text{H}_3\text{O}_2^-$
Initial	0.200 M		~0		0
	$x \text{ mol/L HC}_2\text{H}_3\text{O}_2 \text{ dissociates to reach equilibrium}$				
Change	$-x$	\rightarrow	$+x$		$+x$
Equil.	$0.200 - x$		x		x

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.200 - x} \approx \frac{x^2}{0.200}, \quad x = [\text{H}^+] = 1.9 \times 10^{-3} \text{ M}$$

$\text{pH} = 2.72$; assumptions good.

b. The added OH^- will react completely with the best acid present, $\text{HC}_2\text{H}_3\text{O}_2$.

$$\text{mmol HC}_2\text{H}_3\text{O}_2 \text{ present} = 100.0 \text{ mL} \times \frac{0.200 \text{ mmol HC}_2\text{H}_3\text{O}_2}{\text{mL}} = 20.0 \text{ mmol HC}_2\text{H}_3\text{O}_2$$

$$\text{mmol OH}^- \text{ added} = 50.0 \text{ mL} \times \frac{0.100 \text{ mmol OH}^-}{\text{mL}} = 5.00 \text{ mmol OH}^-$$

	$\text{HC}_2\text{H}_3\text{O}_2$	+	OH^-	\rightarrow	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O	
Before	20.0 mmol		5.00 mmol		0			
Change	-5.00 mmol		-5.00 mmol	\rightarrow	+5.00 mmol			Reacts completely
After	15.0 mmol		0		5.00 mmol			

After reaction of all the strong base, we have a buffer solution containing a weak acid ($\text{HC}_2\text{H}_3\text{O}_2$) and its conjugate base ($\text{C}_2\text{H}_3\text{O}_2^-$). We will use the Henderson-Hasselbalch equation to solve for the pH.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = -\log(1.8 \times 10^{-5}) + \log \left(\frac{5.00 \text{ mmol}/V_T}{15.0 \text{ mmol}/V_T} \right), \text{ where } V_T = \text{total volume}$$

$$\text{pH} = 4.74 + \log \left(\frac{5.00}{15.0} \right) = 4.74 + (-0.477) = 4.26$$

Note that the total volume cancels in the Henderson-Hasselbalch equation. For the [base]/[acid] term, the mole ratio equals the concentration ratio because the components of the buffer are always in the same volume of solution.

- c. mmol OH^- added = $100.0 \text{ mL} \times (0.100 \text{ mmol OH}^-/\text{mL}) = 10.0 \text{ mmol OH}^-$; the same amount (20.0 mmol) of $\text{HC}_2\text{H}_3\text{O}_2$ is present as before (it doesn't change). As before, let the OH^- react to completion, then see what is remaining in solution after this reaction.

	$\text{HC}_2\text{H}_3\text{O}_2$	+	OH^-	\rightarrow	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O	
Before	20.0 mmol		10.0 mmol		0			
After	10.0 mmol		0		10.0 mmol			

A buffer solution results after reaction. Because $[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{HC}_2\text{H}_3\text{O}_2] = 10.0 \text{ mmol}/\text{total volume}$, $\text{pH} = \text{pK}_a$. This is always true at the halfway point to equivalence for a weak acid-strong base titration, $\text{pH} = \text{pK}_a$.

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

- d. mmol OH^- added = $150.0 \text{ mL} \times 0.100 \text{ M} = 15.0 \text{ mmol OH}^-$. Added OH^- reacts completely with the weak acid.

	$\text{HC}_2\text{H}_3\text{O}_2$	+	OH^-	\rightarrow	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O	
Before	20.0 mmol		15.0 mmol		0			
After	5.0 mmol		0		15.0 mmol			

We have a buffer solution after all the OH^- reacts to completion. Using the Henderson-Hasselbalch equation:

$$\text{pH} = 4.74 + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 4.74 + \log \left(\frac{15.0 \text{ mmol}}{5.0 \text{ mmol}} \right)$$

$$\text{pH} = 4.74 + 0.48 = 5.22$$

- e. mmol OH^- added = $200.00 \text{ mL} \times 0.100 \text{ M} = 20.0 \text{ mmol OH}^-$; as before, let the added OH^- react to completion with the weak acid; then see what is in solution after this reaction.

	$\text{HC}_2\text{H}_3\text{O}_2$	+	OH^-	\rightarrow	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O
Before	20.0 mmol		20.0 mmol		0		
After	0		0		20.0 mmol		

This is the equivalence point. Enough OH^- has been added to exactly neutralize all the weak acid present initially. All that remains that affects the pH at the equivalence point is the conjugate base of the weak acid ($\text{C}_2\text{H}_3\text{O}_2^-$). This is a weak base equilibrium problem.

	$\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O}$	\rightleftharpoons	$\text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^-$	$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$
Initial	20.0 mmol/300.0 mL		0	$K_b = 5.6 \times 10^{-9}$
	$x \text{ mol/L C}_2\text{H}_3\text{O}_2^- \text{ reacts with H}_2\text{O to reach equilibrium}$			
Change	$-x$	\rightarrow	$+x$	$+x$
Equil.	$0.0667 - x$		x	x

$$K_b = 5.6 \times 10^{-9} = \frac{x^2}{0.0667 - x} \approx \frac{x^2}{0.0667}, \quad x = [\text{OH}^-] = 6.1 \times 10^{-6} \text{ M}$$

pOH = 5.21; pH = 8.79; assumptions good.

- f. mmol OH^- added = $250.0 \text{ mL} \times 0.100 \text{ M} = 25.0 \text{ mmol OH}^-$

	$\text{HC}_2\text{H}_3\text{O}_2$	+	OH^-	\rightarrow	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O
Before	20.0 mmol		25.0 mmol		0		
After	0		5.0 mmol		20.0 mmol		

After the titration reaction, we have a solution containing excess OH^- and a weak base $\text{C}_2\text{H}_3\text{O}_2^-$. When a strong base and a weak base are both present, assume that the amount of OH^- added from the weak base will be minimal; that is, the pH past the equivalence point is determined by the amount of excess strong base.

$$[\text{OH}^-]_{\text{excess}} = \frac{5.0 \text{ mmol}}{100.0 \text{ mL} + 250.0 \text{ mL}} = 0.014 \text{ M}; \quad \text{pOH} = 1.85; \quad \text{pH} = 12.15$$

64. This is a weak base (H_2NNH_2) titrated by a strong acid (HNO_3). To calculate the pH at the various points, let the strong acid react completely with the weak base present; then see what is in solution.

- a. Only a weak base is present. Solve the weak base equilibrium problem.

	$\text{H}_2\text{NNH}_2 + \text{H}_2\text{O}$	\rightleftharpoons	$\text{H}_2\text{NNH}_3^+ + \text{OH}^-$
Initial	0.100 M		0
Equil.	$0.100 - x$		x

$$K_b = 3.0 \times 10^{-6} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}, \quad x = [\text{OH}^-] = 5.5 \times 10^{-4} M$$

pOH = 3.26; pH = 10.74; assumptions good.

b. mmol H_2NNH_2 present = $100.0 \text{ mL} \times \frac{0.100 \text{ mmol H}_2\text{NNH}_2}{\text{mL}} = 10.0 \text{ mmol H}_2\text{NNH}_2$

mmol H^+ added = $20.0 \text{ mL} \times \frac{0.200 \text{ mmol H}^+}{\text{mL}} = 4.00 \text{ mmol H}^+$

	H_2NNH_2	+	H^+	\rightarrow	H_2NNH_3^+	
Before	10.0 mmol		4.00 mmol		0	
Change	-4.00 mmol		-4.00 mmol	\rightarrow	+4.00 mmol	Reacts completely
After	6.0 mmol		0		4.00 mmol	

A buffer solution results after the titration reaction. Solving using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}; \quad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-6}} = 3.3 \times 10^{-9}$$

$$\text{pH} = -\log(3.3 \times 10^{-9}) + \log \left(\frac{6.0 \text{ mmol} / V_T}{4.00 \text{ mmol} / V_T} \right), \quad \text{where } V_T = \text{total volume, which cancels.}$$

$$\text{pH} = 8.48 + \log(1.5) = 8.48 + 0.18 = 8.66$$

c. mmol H^+ added = $25.0 \text{ mL} \times 0.200 M = 5.00 \text{ mmol H}^+$

	H_2NNH_2	+	H^+	\rightarrow	H_2NNH_3^+
Before	10.0 mmol		5.00 mmol		0
After	5.0 mmol		0		5.00 mmol

This is the halfway point to equivalence where $[\text{H}_2\text{NNH}_3^+] = [\text{H}_2\text{NNH}_2]$. At this point, $\text{pH} = \text{p}K_a$ (which is characteristic of the halfway point for any weak base-strong acid titration).

$$\text{pH} = -\log(3.3 \times 10^{-9}) = 8.48$$

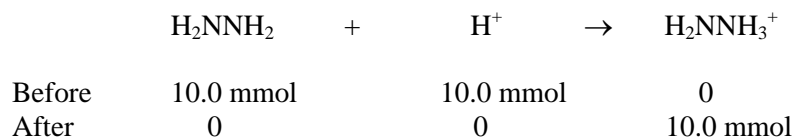
d. mmol H^+ added = $40.0 \text{ mL} \times 0.200 M = 8.00 \text{ mmol H}^+$

	H_2NNH_2	+	H^+	\rightarrow	H_2NNH_3^+
Before	10.0 mmol		8.00 mmol		0
After	2.0 mmol		0		8.00 mmol

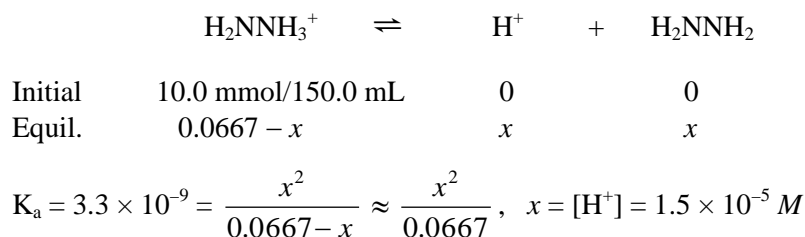
A buffer solution results.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 8.48 + \log \left(\frac{2.0 \text{ mmol}/V_T}{8.00 \text{ mmol}/V_T} \right) = 8.48 + (-0.60) = 7.88$$

e. $\text{mmol H}^+ \text{ added} = 50.0 \text{ mL} \times 0.200 \text{ M} = 10.0 \text{ mmol H}^+$

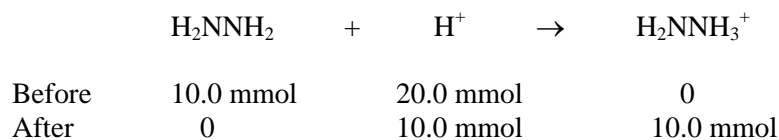


As is always the case in a weak base-strong acid titration, the pH at the equivalence point is acidic because only a weak acid (H_2NNH_3^+) is present. Solving the weak acid equilibrium problem:



pH = 4.82; assumptions good.

f. $\text{mmol H}^+ \text{ added} = 100.0 \text{ mL} \times 0.200 \text{ M} = 20.0 \text{ mmol H}^+$

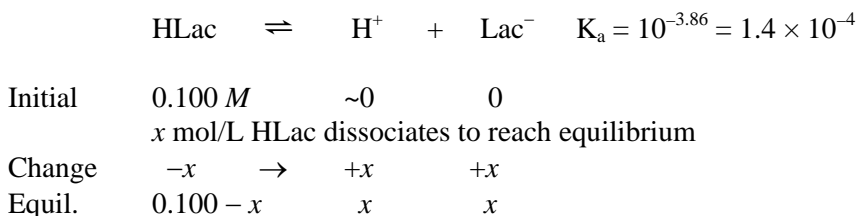


Two acids are present past the equivalence point, but the excess H^+ will determine the pH of the solution since H_2NNH_3^+ is a weak acid.

$$[\text{H}^+]_{\text{excess}} = \frac{10.0 \text{ mmol}}{100.0 \text{ mL} + 100.0 \text{ mL}} = 0.0500 \text{ M}; \text{ pH} = 1.301$$

65. We will do sample calculations for the various parts of the titration. All results are summarized in Table 8.1 at the end of Exercise 68.

At the beginning of the titration, only the weak acid $\text{HC}_3\text{H}_5\text{O}_3$ is present. Let $\text{HLac} = \text{HC}_3\text{H}_5\text{O}_3$ and $\text{Lac}^- = \text{C}_3\text{H}_5\text{O}_3^-$.



$$1.4 \times 10^{-4} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}, \quad x = [\text{H}^+] = 3.7 \times 10^{-3} \text{ M}; \quad \text{pH} = 2.43; \quad \text{assumptions good.}$$

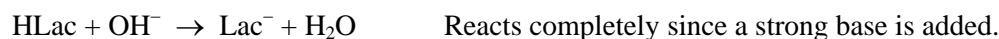
Up to the stoichiometric point, we calculate the pH using the Henderson-Hasselbalch equation. This is the buffer region. For example, at 4.0 mL of NaOH added:

$$\text{initial mmol HLac present} = 25.0 \text{ mL} \times \frac{0.100 \text{ mmol}}{\text{mL}} = 2.50 \text{ mmol HLac}$$

$$\text{mmol OH}^- \text{ added} = 4.0 \text{ mL} \times \frac{0.100 \text{ mmol}}{\text{mL}} = 0.40 \text{ mmol OH}^-$$

Note: The units millimoles are usually easier numbers to work with. The units for molarity are moles per liter but are also equal to millimoles per milliliter.

The 0.40 mmol of added OH^- converts 0.40 mmol HLac to 0.40 mmol Lac^- according to the equation:



$$\text{mmol HLac remaining} = 2.50 - 0.40 = 2.10 \text{ mmol}; \quad \text{mmol Lac}^- \text{ produced} = 0.40 \text{ mmol}$$

We have a buffer solution. Using the Henderson-Hasselbalch equation where $\text{pK}_a = 3.86$:

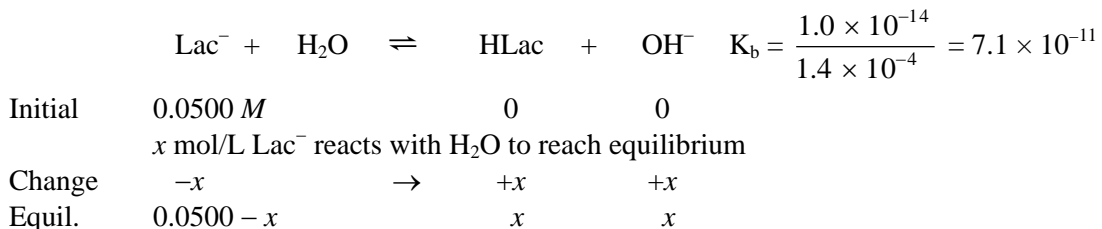
$$\text{pH} = \text{pK}_a + \log \frac{[\text{Lac}^-]}{[\text{HLac}]} = 3.86 + \log \frac{(0.40)}{(2.10)} \quad \text{(Total volume cancels, so we can use use the ratio of moles or millimoles.)}$$

$$\text{pH} = 3.86 - 0.72 = 3.14$$

Other points in the buffer region are calculated in a similar fashion. Perform a stoichiometry problem first, followed by a buffer problem. The buffer region includes all points up to and including 24.9 mL OH^- added.

At the stoichiometric point (25.0 mL OH^- added), we have added enough OH^- to convert all of the HLac (2.50 mmol) into its conjugate base (Lac^-). All that is present is a weak base. To determine the pH, we perform a weak base calculation.

$$[\text{Lac}^-]_0 = \frac{2.50 \text{ mmol}}{25.0 \text{ mL} + 25.0 \text{ mL}} = 0.0500 \text{ M}$$



$$K_b = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500} = 7.1 \times 10^{-11}$$

$x = [\text{OH}^-] = 1.9 \times 10^{-6} \text{ M}$; $\text{pOH} = 5.72$; $\text{pH} = 8.28$; assumptions good.

Past the stoichiometric point, we have added more than 2.50 mmol of NaOH. The pH will be determined by the excess OH^- ion present. An example of this calculation follows.

$$\text{At 25.1 mL: } \text{OH}^- \text{ added} = 25.1 \text{ mL} \times \frac{0.100 \text{ mmol}}{\text{mL}} = 2.51 \text{ mmol OH}^-$$

2.50 mmol OH^- neutralizes all the weak acid present. The remainder is excess OH^- .

$$\text{Excess OH}^- = 2.51 - 2.50 = 0.01 \text{ mmol OH}^-$$

$$[\text{OH}^-]_{\text{excess}} = \frac{0.01 \text{ mmol}}{(25.0 + 25.1) \text{ mL}} = 2 \times 10^{-4} \text{ M}; \text{ pOH} = 3.7; \text{ pH} = 10.3$$

All results are listed in Table 8.1 at the end of the solution to Exercise 68.

66. Results for all points are summarized in Table 8.1 at the end of the solution to Exercise 68. At the beginning of the titration, we have a weak acid problem:

	HOPr	\rightleftharpoons	H^+	+	OPr ⁻	HOPr = $\text{HC}_3\text{H}_5\text{O}_2$ OPr ⁻ = $\text{C}_3\text{H}_5\text{O}_2^-$
Initial	0.100 M		~0		0	
	x mol/L HOPr acid dissociates to reach equilibrium					
Change	- x	\rightarrow	+ x		+ x	
Equil.	$0.100 - x$		x		x	

$$K_a = \frac{[\text{H}^+][\text{OPr}^-]}{[\text{HOPr}]} = 1.3 \times 10^{-5} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$x = [\text{H}^+] = 1.1 \times 10^{-3} \text{ M}$; $\text{pH} = 2.96$; assumptions good.

The buffer region is from 4.0 to 24.9 mL of OH^- added. We will do a sample calculation at 24.0 mL OH^- added.

$$\text{Initial mmol HOPr present} = 25.0 \text{ mL} \times \frac{0.100 \text{ mmol}}{\text{mL}} = 2.50 \text{ mmol HOPr}$$

$$\text{mmol OH}^- \text{ added} = 24.0 \text{ mL} \times \frac{0.100 \text{ mmol}}{\text{mL}} = 2.40 \text{ mmol OH}^-$$

The added strong base converts HOPr into OPr⁻.

	HOPr	+	OH ⁻	→	OPr ⁻	+	H ₂ O	
Before	2.50 mmol		2.40 mmol		0			
Change	-2.40		-2.40	→	+2.40			Reacts completely
After	0.10 mmol		0		2.40 mmol			

A buffer solution results. Using the Henderson-Hasselbalch equation where $pK_a = -\log(1.3 \times 10^{-5}) = 4.89$:

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.89 + \log \frac{[\text{OPr}^-]}{[\text{HOPr}]}$$

$$pH = 4.89 + \log \left(\frac{2.40}{0.10} \right) = 4.89 + 1.38 = 6.27 \quad (\text{Volume cancels, so we can use the millimole ratio in the log term.})$$

All points in the buffer region 4.0 mL to 24.9 mL are calculated this way. See Table 8.1 at the end of Exercise 68 for all the results.

At the stoichiometric point (25.0 mL KOH added), only a weak base (OPr⁻) is present:

	OPr ⁻	+	H ₂ O	⇌	OH ⁻	+	HOPr
Initial	$\frac{2.50 \text{ mmol}}{50.0 \text{ mL}} = 0.0500 \text{ M}$				0		0
	<i>x</i> mol/L OPr ⁻ reacts with H ₂ O to reach equilibrium						
Change	- <i>x</i>			→	+ <i>x</i>		+ <i>x</i>
Equil.	0.0500 - <i>x</i>				<i>x</i>		<i>x</i>

$$K_b = \frac{[\text{OH}^-][\text{HOPr}]}{[\text{OPr}^-]} = \frac{K_w}{K_a} = 7.7 \times 10^{-10} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}$$

$$x = 6.2 \times 10^{-6} \text{ M} = [\text{OH}^-], \quad pOH = 5.21, \quad pH = 8.79; \quad \text{assumptions good.}$$

Beyond the stoichiometric point, the pH is determined by the excess strong base added. The results are the same as those in Exercise 65 (see Table 8.1).

For example at 26.0 mL KOH added:

$$[\text{OH}^-] = \frac{2.60 \text{ mmol} - 2.50 \text{ mmol}}{(25.0 + 26.0) \text{ mL}} = 2.0 \times 10^{-3} \text{ M}; \quad pOH = 2.70; \quad pH = 11.30$$

67. At beginning of the titration, only the weak base NH₃ is present. As always, solve for the pH using the K_b reaction for NH₃.

	NH ₃	+	H ₂ O	⇌	NH ₄ ⁺	+	OH ⁻	K _b = 1.8 × 10 ⁻⁵
Initial	0.100 M				0		~0	
Equil.	0.100 - <i>x</i>				<i>x</i>		<i>x</i>	

$$K_b = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} = 1.8 \times 10^{-5}$$

$x = [\text{OH}^-] = 1.3 \times 10^{-3} \text{ M}$; $\text{pOH} = 2.89$; $\text{pH} = 11.11$; assumptions good.

In the buffer region (4.0 – 24.9 mL), we can use the Henderson-Hasselbalch equation:

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}; \text{p}K_a = 9.25; \text{pH} = 9.25 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

We must determine the amounts of NH_3 and NH_4^+ present after the added H^+ reacts completely with the NH_3 . For example, after 8.0 mL HCl added:

$$\text{initial mmol NH}_3 \text{ present} = 25.0 \text{ mL} \times \frac{0.100 \text{ mmol}}{\text{mL}} = 2.50 \text{ mmol NH}_3$$

$$\text{mmol H}^+ \text{ added} = 8.0 \text{ mL} \times \frac{0.100 \text{ mmol}}{\text{mL}} = 0.80 \text{ mmol H}^+$$

Added H^+ reacts with NH_3 to completion: $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$

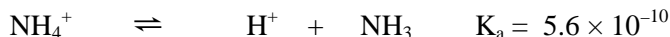
mmol NH_3 remaining = $2.50 - 0.80 = 1.70$ mmol; mmol NH_4^+ produced = 0.80 mmol

$$\text{pH} = 9.25 + \log \frac{1.70}{0.80} = 9.58 \text{ (Mole ratios can be used since the total volume cancels.)}$$

Other points in the buffer region are calculated in similar fashion. Results are summarized in Table 8.1 at the end of Exercise 68.

At the stoichiometric point (25.0 mL H^+ added), just enough HCl has been added to convert all the weak base (NH_3) into its conjugate acid (NH_4^+). Perform a weak acid calculation.

$$[\text{NH}_4^+]_0 = 2.50 \text{ mmol}/50.0 \text{ mL} = 0.0500 \text{ M}$$



Initial 0.0500 M 0 0

Equil. 0.0500 - x x x

$$5.6 \times 10^{-10} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}, \quad x = [\text{H}^+] = 5.3 \times 10^{-6} \text{ M}; \text{pH} = 5.28; \text{assumptions good.}$$

Beyond the stoichiometric point, the pH is determined by the excess H^+ . For example, at 28.0 mL of H^+ added:

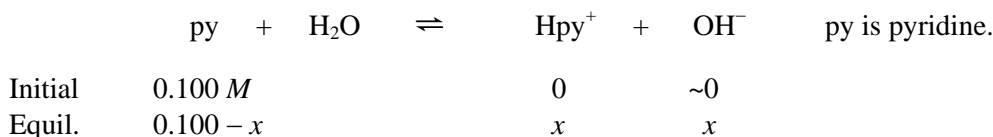
$$\text{H}^+ \text{ added} = 28.0 \text{ mL} \times \frac{0.100 \text{ mmol}}{\text{mL}} = 2.80 \text{ mmol H}^+$$

$$\text{Excess H}^+ = 2.80 \text{ mmol} - 2.50 \text{ mmol} = 0.30 \text{ mmol excess H}^+$$

$$[\text{H}^+]_{\text{excess}} = \frac{0.30 \text{ mmol}}{(25.0 + 28.0) \text{ mL}} = 5.7 \times 10^{-3} \text{ M}; \text{ pH} = 2.24$$

All results are summarized in Table 8.1 at the end of Exercise 68.

68. Initially, a weak base problem:



$$K_b = \frac{[\text{Hpy}^+][\text{OH}^-]}{[\text{py}]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} \approx 1.7 \times 10^{-9}$$

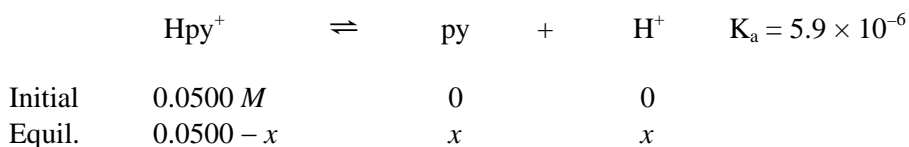
$$x = [\text{OH}^-] = 1.3 \times 10^{-5} \text{ M}; \text{ pOH} = 4.89; \text{ pH} = 9.11; \text{ assumptions good.}$$

Buffer region (4.0 – 24.5 mL): Added H⁺ reacts completely with py: py + H⁺ → Hpy⁺. Determine the moles (or millimoles) of py and Hpy⁺ after reaction, then use the Henderson-Hasselbalch equation to solve for the pH.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}; \text{ p}K_a = 5.23; \text{ pH} = 5.23 + \log \frac{[\text{py}]}{[\text{Hpy}^+]}$$

Results in the buffer region are summarized in Table 8.1, which follows this problem. See Exercise 67 for a similar sample calculation.

At the stoichiometric point (25.0 mL H⁺ added), this is a weak acid problem since just enough H⁺ has been added to convert all the weak base into its conjugate acid. The initial concentration of [Hpy⁺] = 0.0500 M.

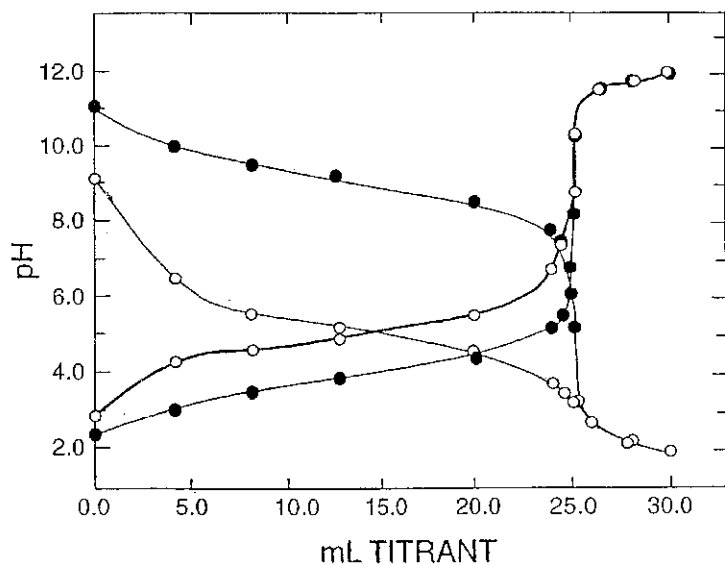


$$5.9 \times 10^{-6} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}, \quad x = [\text{H}^+] = 5.4 \times 10^{-4} \text{ M}; \text{ pH} = 3.27; \text{ assumptions good.}$$

Beyond the equivalence point, the pH determination is made by calculating the concentration of excess H⁺. See Exercise 8.67 for an example. All results are summarized in Table 8.1 on the next page.

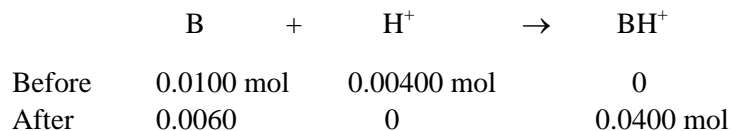
Table 8.1 Summary of pH Results for Exercises 65 – 68 (Graph follows)

Titrant mL	Exercise 65	Exercise 66	Exercise 67	Exercise 68
0.0	2.43	2.96	11.11	9.11
4.0	3.14	4.17	9.97	5.95
8.0	3.53	4.56	9.58	5.56
12.5	3.86	4.89	9.25	5.23
20.0	4.46	5.49	8.65	4.63
24.0	5.24	6.27	7.87	3.85
24.5	5.6	6.6	7.6	3.5
24.9	6.3	7.3	6.9	-
25.0	8.28	8.79	5.28	3.27
25.1	10.3	10.3	3.7	-
26.0	11.30	11.30	2.71	2.71
28.0	11.75	11.75	2.24	2.25
30.0	11.96	11.96	2.04	2.04



69. Mol H^+ added = $0.0400 \text{ L} \times 0.100 \text{ mol/L} = 0.00400 \text{ mol H}^+$

The added strong acid reacts to completion with the weak base to form the conjugate acid of the weak base and H_2O . Let B = weak base:



After the H^+ reacts to completion, we have a buffer solution. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}, \quad 8.00 = \text{pK}_a + \log \frac{(0.0060/V_T)}{(0.00400/V_T)}, \quad \text{where } V_T = \text{total volume of solution}$$

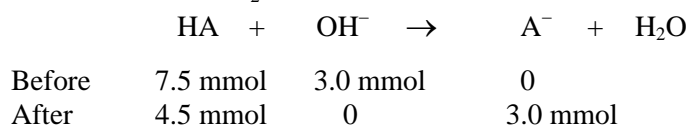
$$\text{pK}_a = 8.00 - \log \frac{(0.0060)}{(0.00400)} = 8.00 - 0.18, \quad \text{pK}_a = 7.82$$

For a conjugate acid-base pair, $\text{pK}_a + \text{pK}_b = 14.00$, so:

$$\text{pK}_b = 14.00 - 7.82 = 6.18; \quad K_b = 10^{-6.18} = 6.6 \times 10^{-7}$$

70. $75.0 \text{ mL} \times \frac{0.10 \text{ mmol}}{\text{mL}} = 7.5 \text{ mmol HA}; \quad 30.0 \text{ mL} \times \frac{0.10 \text{ mmol}}{\text{mL}} = 3.0 \text{ mmol OH}^- \text{ added}$

The added strong base reacts to completion with the weak acid to form the conjugate base of the weak acid and H_2O .



A buffer results after the OH^- reacts to completion. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}, \quad 5.50 = \text{pK}_a + \log \left(\frac{3.0 \text{ mmol}/105.0 \text{ mmol}}{4.5 \text{ mmol}/105.0 \text{ mmol}} \right)$$

$$\text{pK}_a = 5.50 - \log(3.0/4.5) = 5.50 - (-0.18) = 5.68; \quad K_a = 10^{-5.68} = 2.1 \times 10^{-6}$$

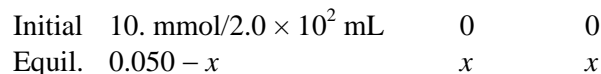
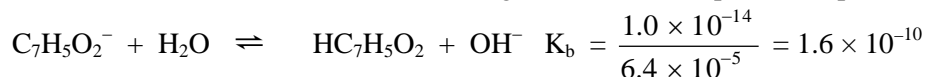
71. a. This is a weak acid-strong base titration. At the halfway point to equivalence, $[\text{weak acid}] = [\text{conjugate base}]$, so $\text{pH} = \text{pK}_a$ (always for a weak acid-strong base titration).

$$\text{pH} = -\log(6.4 \times 10^{-5}) = 4.19$$

mmol $\text{HC}_7\text{H}_5\text{O}_2$ present = $100.0 \text{ mL} \times 0.10 \text{ M} = 10. \text{ mmol HC}_7\text{H}_5\text{O}_2$. For the equivalence point, 10. mmol of OH^- must be added. The volume of OH^- added to reach the equivalence point is:

$$10. \text{ mmol OH}^- \times \frac{1 \text{ mL}}{0.10 \text{ mmol OH}^-} = 1.0 \times 10^2 \text{ mL OH}^-$$

At the equivalence point, 10. mmol of $\text{HC}_7\text{H}_5\text{O}_2$ is neutralized by 10. mmol of OH^- to produce 10. mmol of $\text{C}_7\text{H}_5\text{O}_2^-$. This is a weak base. The total volume of the solution is $100.0 \text{ mL} + 1.0 \times 10^2 \text{ mL} = 2.0 \times 10^2 \text{ mL}$. Solving the weak base equilibrium problem:



$$K_b = 1.6 \times 10^{-10} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}, \quad x = [\text{OH}^-] = 2.8 \times 10^{-6} \text{ M}$$

$\text{pOH} = 5.55$; $\text{pH} = 8.45$; assumptions good.

- b. At the halfway point to equivalence for a weak base-strong acid titration, $\text{pH} = \text{pK}_a$ because $[\text{weak base}] = [\text{conjugate acid}]$.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-4}} = 1.8 \times 10^{-11}; \text{pH} = \text{pK}_a = -\log(1.8 \times 10^{-11}) = 10.74$$

For the equivalence point (mmol acid added = mmol base present):

$$\text{mmol C}_2\text{H}_5\text{NH}_2 \text{ present} = 100.0 \text{ mL} \times 0.10 \text{ M} = 10. \text{ mmol C}_2\text{H}_5\text{NH}_2$$

$$\text{mL H}^+ \text{ added} = 10. \text{ mmol H}^+ \times \frac{1 \text{ mL}}{0.20 \text{ mmol H}^+} = 50. \text{ mL H}^+$$

The strong acid added completely converts the weak base into its conjugate acid. Therefore, at the equivalence point, $[\text{C}_2\text{H}_5\text{NH}_3^+]_0 = 10. \text{ mmol}/(100.0 + 50.) \text{ mL} = 0.067 \text{ M}$. Solving the weak acid equilibrium problem:



Initial	0.067 M	0	0
Equil.	0.067 - x	x	x

$$K_a = 1.8 \times 10^{-11} = \frac{x^2}{0.067 - x} \approx \frac{x^2}{0.067}, \quad x = [\text{H}^+] = 1.1 \times 10^{-6} \text{ M}$$

$\text{pH} = 5.96$; assumptions good.

- c. In a strong acid-strong base titration, the halfway point has no special significance other than that exactly one-half of the original amount of acid present has been neutralized.

$$\text{mmol H}^+ \text{ present} = 100.0 \text{ mL} \times 0.50 \text{ M} = 50. \text{ mmol H}^+$$

$$\text{mL OH}^- \text{ added} = 25 \text{ mmol OH}^- \times \frac{1 \text{ mL}}{0.25 \text{ mmol}} = 1.0 \times 10^2 \text{ mL OH}^-$$



Before	50. mmol	25 mmol
After	25 mmol	0

$$[\text{H}^+]_{\text{excess}} = \frac{25 \text{ mmol}}{(100.0 + 1.0 \times 10^2) \text{ mL}} = 0.13 \text{ M}; \text{pH} = 0.89$$

At the equivalence point of a strong acid-strong base titration, only neutral species are present (Na^+ , Cl^- , and H_2O), so the $\text{pH} = 7.00$.

Indicators

72. An acid-base indicator marks the end point of a titration by changing color. Acid-base indicators are weak acids themselves. We abbreviate the acid form of an indicator as HIn and the conjugate base form as In^- . The reason there is a color change with indicators is that the HIn form has one color associated with it, whereas the In^- form has a different color associated with it. Which form dominates in solution and dictates the color is determined by the pH of the solution. The related equilibrium is $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$. In a very acidic solution, there are lots of H^+ ions present, which drives the indicator equilibrium to the left. The HIn form dominates, and the color of the solution is the color due to the HIn form. In a very basic solution, H^+ has been removed from solution. This drives the indicator equilibrium to the right, and the In^- form dominates. In very basic solutions, the solution takes on the color of the In^- form. In between very acidic and very basic solutions, there is a range of pH values where the solution has significant amounts of both the HIn and In^- forms present. This is where the color change occurs, and we want this pH to be close to the stoichiometric point of the titration. The pH at which the color change occurs is determined by the K_a of the indicator.

Equivalence point: when enough titrant has been added to react exactly with the substance in the solution being titrated. Endpoint: when the indicator changes color. We want the indicator to tell us when we have reached the equivalence point. We can detect the endpoint visually and assume that it is the equivalence point for doing stoichiometric calculations. They don't have to be as close as 0.01 pH units since, at the equivalence point, the pH is changing very rapidly with added titrant. The range over which an indicator changes color only needs to be close to the pH of the equivalence point.

The two forms of an indicator are different colors. The HIn form has one color and the In^- form has another color. To see only one color, that form must be in an approximately tenfold excess or greater over the other form. When the ratio of the two forms is less than 10, both colors are present. To go from $[\text{HIn}]/[\text{In}^-] = 10$ to $[\text{HIn}]/[\text{In}^-] = 0.1$ requires a change of 2 pH units (a 100-fold decrease in $[\text{H}^+]$) as the indicator changes from the HIn color to the In^- color.

From Figure 8.8, thymol blue has three colors associated with it: orange, yellow, and blue. In order for this to happen, thymol blue must be a diprotic acid. The H_2In form has the orange color, the HIn^- form has the yellow color, and the In^{2-} form has the blue color associated with it. Thymol blue cannot be monoprotic; monoprotic indicators only have two colors associated with them (either the HIn color or the In^- color).

73. The color of the indicator will change over the approximate range of $\text{pH} = \text{p}K_a \pm 1 = 5.3 \pm 1$. Therefore, the useful pH range of methyl red where it changes color would be about 4.3 (red) to 6.3 (yellow). Note that at $\text{pH} < 4.3$, the HIn form of the indicator dominates, and the color of the solution is the color of HIn (red). At $\text{pH} > 6.3$, the In^- form of the indicator dominates, and the color of the solution is the color of In^- (yellow). In titrating a weak acid with base, we start off with an acidic solution with $\text{pH} < 4.3$, so the color would change from red to reddish orange at $\text{pH} \approx 4.3$. In titrating a weak base with acid, the color change would be

from yellow to yellowish orange at $\text{pH} \approx 6.3$. Only a weak base-strong acid titration would have an acidic pH at the equivalence point, so only in this type of titration would the color change of methyl red indicate the approximate endpoint.

74. a. yellow b. green (Both yellow and blue forms are present.)
c. yellow d. blue
75. When choosing an indicator, we want the color change of the indicator to occur approximately at the pH of the equivalence point. Since the pH generally changes very rapidly at the equivalence point, we don't have to be exact. This is especially true for strong acid-strong base titrations. The following are some indicators where the color change occurs at about the pH of the equivalence point.

<u>Exercise</u>	<u>pH at Eq. Pt.</u>	<u>Indicator</u>
61	7.00	bromthymol blue or phenol red
63	8.79	o-cresolphthalein or phenolphthalein
76. <u>Exercise</u>	<u>pH at Eq. Pt.</u>	<u>Indicator</u>
62	7.00	bromthymol blue or phenol red
64	4.82	bromcresol green
77. <u>Exercise</u>	<u>pH at Eq. Pt.</u>	<u>Indicator</u>
65	8.28	o-cresolphthalein or phenolphthalein
67	5.28	bromcresol green
78. <u>Exercise</u>	<u>pH at Eq. Pt.</u>	<u>Indicator</u>
66	8.79	o-cresolphthalein or phenolphthalein
68	3.27	2,4-dinitrophenol

The titration in Exercise 68 will be very difficult to mark the equivalence point. The pH break at the equivalence point is very small.

79. $\text{HIn} \rightleftharpoons \text{In}^- + \text{H}^+ \quad K_a = \frac{[\text{In}^-][\text{H}^+]}{[\text{HIn}]} = 1.0 \times 10^{-9}$
- a. In a very acid solution, the HIn form dominates, so the solution will be yellow.
- b. The color change occurs when the concentration of the more dominant form is approximately ten times as great as the less dominant form of the indicator.
- $$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{10}{1}; \quad K_a = 1.0 \times 10^{-9} = \left(\frac{1}{10}\right)[\text{H}^+], \quad [\text{H}^+] = 1 \times 10^{-8} \text{ M}; \quad \text{pH} = 8.0 \text{ at color change}$$
- c. This is way past the equivalence point (100.0 mL OH^- added), so the solution is very basic and the In^- form of the indicator dominates. The solution will be blue.

80. For bromcresol green, the resulting green color indicates that both HIn and In⁻ are present in significant amounts. This occurs when pH ≈ pK_a of the indicator. From results of the bromcresol green indicator, pH ≈ 5.0 ([H⁺] ≈ 1 × 10⁻⁵). Note that the results of the first two indicators are inconclusive.

HX ⇌ H⁺ + X⁻; from the typical weak acid setup: [H⁺] = [X⁻] ≈ 1 × 10⁻⁵ M, [HX] ≈ 0.01 M

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{(1 \times 10^{-5})^2}{0.01} = 1 \times 10^{-8}$$

81. pH > 5 for bromcresol green to be blue. pH < 8 for thymol blue to be yellow. The pH is between 5 and 8.

82. HIn ⇌ In⁻ + H⁺ $K_a = \frac{[In^-][H^+]}{[HIn]} = 10^{-3.00} = 1.0 \times 10^{-3}$

At 7.00% conversion of HIn into In⁻, [In⁻]/[HIn] = 7.00/93.00.

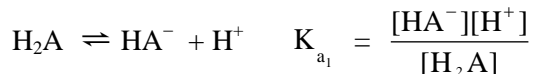
$$K_a = 1.0 \times 10^{-3} = \frac{[In^-]}{[HIn]} \times [H^+] = \frac{7.00}{93.00} \times [H^+], \quad [H^+] = 1.3 \times 10^{-2} \text{ M}, \quad \text{pH} = 1.89$$

The color of the base form will start to show when the pH is increased to 1.89.

Polyprotic Acid Titrations

83. The first titration plot (from 0 – 100.0 mL) corresponds to the titration of H₂A by OH⁻. The reaction is H₂A + OH⁻ → HA⁻ + H₂O. After all the H₂A has been reacted, the second titration (from 100.0 – 200.0 mL) corresponds to the titration of HA⁻ by OH⁻. The reaction is HA⁻ + OH⁻ → A²⁻ + H₂O.
- At 100.0 mL of NaOH, just enough OH⁻ has been added to react completely with all of the H₂A present (mol OH⁻ added = mol H₂A present initially). From the balanced equation, the mol of HA⁻ produced will equal the mol of H₂A present initially. Because mol of HA⁻ present at 100.0 mL OH⁻ added equals the mol of H₂A present initially, exactly 100.0 mL more of NaOH must be added to react with all of the HA⁻. The volume of NaOH added to reach the second equivalence point equals 100.0 mL + 100.0 mL = 200.0 mL.
 - H₂A + OH⁻ → HA⁻ + H₂O is the reaction occurring from 0 – 100.0 mL NaOH added.
 - No reaction has taken place, so H₂A and H₂O are the major species.
 - Adding OH⁻ converts H₂A into HA⁻. The major species between 0 mL and 100.0 mL NaOH added are H₂A, HA⁻, H₂O, and Na⁺.
 - At 100.0 mL NaOH added, mol of OH⁻ = mol H₂A, so all of the H₂A present initially has been converted into HA⁻. The major species are HA⁻, H₂O, and Na⁺.
 - Between 100.0 and 200.0 mL NaOH added, the OH⁻ converts HA⁻ into A²⁻. The major species are HA⁻, A²⁻, H₂O, and Na⁺.

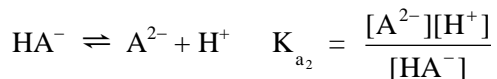
- v. At the second equivalence point (200.0 mL), just enough OH^- has been added to convert all of the HA^- into A^{2-} . The major species are A^{2-} , H_2O , and Na^+ .
- vi. Past 200.0 mL NaOH added, excess OH^- is present. The major species are OH^- , A^{2-} , H_2O , and Na^+ .
- c. 50.0 mL of NaOH added corresponds to the first halfway point to equivalence. Exactly one-half of the H_2A present initially has been converted into its conjugate base HA^- , so $[\text{H}_2\text{A}] = [\text{HA}^-]$ in this buffer solution.



When $[\text{HA}^-] = [\text{H}_2\text{A}]$, then $K_{a_1} = [\text{H}^+]$ or $\text{p}K_{a_1} = \text{pH}$.

Here, $\text{pH} = 4.0$, so $\text{p}K_{a_1} = 4.0$ and $K_{a_1} = 10^{-4.0} = 1 \times 10^{-4}$.

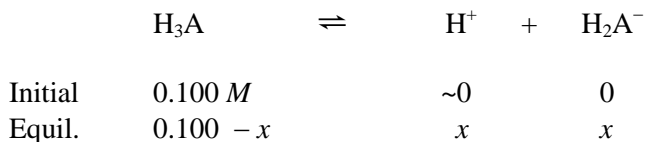
150.0 mL of NaOH added correspond to the second halfway point to equivalence, where $[\text{HA}^-] = [\text{A}^{2-}]$ in this buffer solution.



When $[\text{A}^{2-}] = [\text{HA}^-]$, then $K_{a_2} = [\text{H}^+]$ or $\text{p}K_{a_2} = \text{pH}$.

Here, $\text{pH} = 8.0$, so $\text{p}K_{a_2} = 8.0$ and $K_{a_2} = 10^{-8.0} = 1 \times 10^{-8}$.

84. a. Because $K_{a_1} \gg K_{a_2} \gg K_{a_3}$, the initial pH is determined by H_3A . Consider only the first dissociation.



$$K_{a_1} = \frac{[\text{H}^+][\text{H}_2\text{A}^-]}{[\text{H}_3\text{A}]} = \frac{x^2}{0.100 - x} = 1.5 \times 10^{-4} \approx \frac{x^2}{0.100}, \quad x = 3.9 \times 10^{-3}$$

$[\text{H}^+] = 3.9 \times 10^{-3} \text{ M}$; $\text{pH} = 2.41$; assumptions good.

- b. $10.0 \text{ mL} \times 1.00 \text{ M} = 10.0 \text{ mmol NaOH}$. Began with $100.0 \text{ mL} \times 0.100 \text{ M} = 10.0 \text{ mmol H}_3\text{A}$. Added OH^- converts H_3A into H_2A^- . This takes us to the first stoichiometric point where the amphoteric H_2A^- is the major species present.

$$\text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2} = \frac{3.82 + 7.52}{2} = 5.67$$

- c. $25.0 \text{ mL} \times 1.00 \text{ M} = 25.0 \text{ mmol NaOH}$ added. After OH^- reacts completely, the mixture contains 5.0 mmol HA^{2-} and 5.0 mmol A^{3-} .

$$K_{a_3} = \frac{[\text{H}^+][\text{A}^{3-}]}{[\text{HA}^{2-}]}; \text{ because } [\text{A}^{3-}] = [\text{HA}^{2-}], [\text{H}^+] = K_{a_3}; \text{ pH} = \text{p}K_{a_3} = 11.30$$

This is the third halfway point to equivalence; assumptions good.

85. $\frac{0.200 \text{ g}}{165.0 \text{ g/mol}} = 1.212 \times 10^{-3} \text{ mol} = 1.212 \text{ mmol H}_3\text{A}$ (carrying extra sig. figs.)

- a. $10.50 \text{ mL} \times 0.0500 \text{ M} = 0.525 \text{ mmol OH}^-$ added; $\text{H}_3\text{A} + \text{OH}^- \rightarrow \text{H}_2\text{A}^- + \text{H}_2\text{O}$;
 $1.212 - 0.525 = 0.687 \text{ mmol H}_3\text{A}$ remains after OH^- reacts completely and $0.525 \text{ mmol H}_2\text{A}^-$ formed. Solving the buffer problem using the K_{a_1} reaction gives:

$$K_{a_1} = \frac{(10^{-3.73})\left(\frac{0.525}{60.50} + 10^{-3.73}\right)}{\frac{0.687}{60.50} - 10^{-3.73}} = 1.5 \times 10^{-4}; \text{ p}K_{a_1} = -\log(1.5 \times 10^{-4}) = 3.82$$

First stoichiometric point: $\text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2} = 5.19 = \frac{3.82 + \text{p}K_{a_2}}{2}$

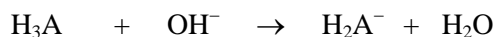
$$\text{p}K_{a_2} = 6.56; K_{a_2} = 10^{-6.56} = 2.8 \times 10^{-7}$$

Second stoichiometric point: $\text{pH} = \frac{\text{p}K_{a_2} + \text{p}K_{a_3}}{2}, 8.00 = \frac{6.56 + \text{p}K_{a_3}}{2}$

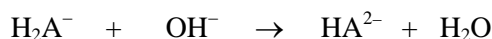
$$\text{p}K_{a_3} = 9.44; K_{a_3} = 10^{-9.44} = 3.6 \times 10^{-10}$$

- b. $1.212 \text{ mmol H}_3\text{A} = 0.0500 \text{ M OH}^- \times V_{\text{OH}^-}, V_{\text{OH}^-} = 24.2 \text{ mL}$; 24.2 mL of OH^- are necessary to reach the first stoichiometric point. It will require 60.5 mL to reach the third halfway point to equivalence, where $\text{pH} = \text{p}K_{a_3} = 9.44$. The pH at 59.0 mL of NaOH added should be a little lower than 9.44 .

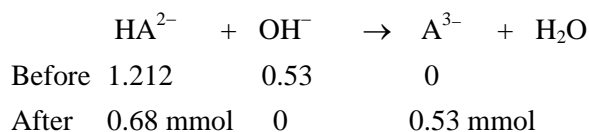
- c. 59.0 mL of $0.0500 \text{ M OH}^- = 2.95 \text{ mmol OH}^-$ added



Before	1.212 mmol	2.95 mmol	0
After	0	1.74	1.212



Before	1.212	1.74	0
After	0	0.53	1.212



Use the K_{a_3} reaction to solve for the $[\text{H}^+]$ in this buffer solution and make the normal assumptions.

$$K_{a_3} = 3.6 \times 10^{-10} = \frac{\left(\frac{0.53 \text{ mmol}}{109 \text{ mL}}\right)[\text{H}^+]}{\left(\frac{0.68 \text{ mmol}}{109 \text{ mL}}\right)}, \quad [\text{H}^+] = 4.6 \times 10^{-10} \text{ M}; \quad \text{pH} = 9.34$$

Assumptions good.

86. $100.0 \text{ mL} \times 0.100 \text{ M} = 10.0 \text{ mmol H}_3\text{A}$ initially

a. $100.0 \text{ mL} \times 0.0500 \text{ mmol/mL} = 5.00 \text{ mmol OH}^-$ added

This is the first halfway point to equivalence, where $[\text{H}_3\text{A}] = [\text{H}_2\text{A}^-]$ and $\text{pH} = \text{p}K_{a_1}$.

$\text{pH} = -\log(5.0 \times 10^{-4}) = 3.30$; assumptions good.

b. Since $\text{p}K_{a_2} = 8.00$, a buffer mixture of H_2A^- and HA^{2-} can produce a $\text{pH} = 8.67$ solution.

$$8.67 = 8.00 + \log \frac{[\text{HA}^{2-}]}{[\text{H}_2\text{A}^-]}, \quad \frac{[\text{HA}^{2-}]}{[\text{H}_2\text{A}^-]} = 10^{+0.67} = 4.7$$

Both species are in the same volume, so the mole ratio also equals 4.7. Let $n = \text{mmol}$:

$$\frac{n_{\text{HA}^{2-}}}{n_{\text{H}_2\text{A}^-}} = 4.7, \quad n_{\text{HA}^{2-}} = (4.7)n_{\text{H}_2\text{A}^-}; \quad n_{\text{HA}^{2-}} + n_{\text{H}_2\text{A}^-} = 10.0 \text{ mmol (mole balance)}$$

$$(5.7)n_{\text{H}_2\text{A}^-} = 10.0 \text{ mmol}, \quad n_{\text{H}_2\text{A}^-} = 1.8 \text{ mmol}; \quad n_{\text{HA}^{2-}} = 8.2 \text{ mmol}$$

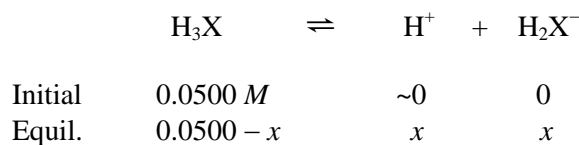
To reach this point, we must add a total of 18.2 mmol NaOH. 10.0 mmol OH^- converts all of the 10.0 mmol H_3A into H_2A^- . The next 8.2 mmol OH^- converts 8.2 mmol H_2A^- into 8.2 mmol HA^{2-} , leaving 1.8 mmol H_2A^- .

$$18.2 \text{ mmol} = 0.0500 \text{ M} \times V, \quad V = 364 \text{ mL NaOH}$$

Note: Normal buffer assumptions are good.

87. $100.0 \text{ mL} \times 0.0500 \text{ M} = 5.00 \text{ mmol H}_3\text{X}$ initially

a. Because $K_{a_1} \gg K_{a_2} \gg K_{a_3}$, pH initially is determined by H_3X equilibrium reaction.

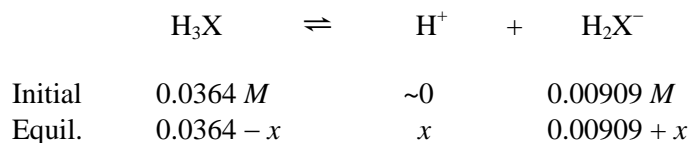


$$K_{a_1} = 1.0 \times 10^{-3} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}, \quad x = 7.1 \times 10^{-3}; \quad \text{assumption poor.}$$

Using the quadratic formula:

$$x^2 + (1.0 \times 10^{-3})x - 5.0 \times 10^{-5} = 0, \quad x = 6.6 \times 10^{-3} \text{ M} = [\text{H}^+]; \quad \text{pH} = 2.18$$

- b. 1.00 mmol OH^- added converts H_3X into H_2X^- . After this reaction goes to completion, 4.00 mmol H_3X and 1.00 mmol H_2X^- are in a total volume of 110.0 mL. Solving the buffer problem:



$$K_{a_1} = 1.0 \times 10^{-3} = \frac{x(0.00909 + x)}{0.0364 - x}; \quad \text{assumption that } x \text{ is small does not work here.}$$

Using the quadratic formula and carrying extra significant figures:

$$x^2 + (1.01 \times 10^{-2})x - 3.64 \times 10^{-5} = 0, \quad x = 2.8 \times 10^{-3} \text{ M} = [\text{H}^+]; \quad \text{pH} = 2.55$$

- c. 2.50 mmol OH^- added results in 2.50 mmol H_3X and 2.50 mmol H_2X^- after OH^- reacts completely with H_3X . This is the first halfway point to equivalence. $\text{pH} = \text{p}K_{a_1} = 3.00$; assumptions good (5% error).
- d. 5.00 mmol OH^- added results in 5.00 mmol H_2X^- after OH^- reacts completely with H_3X . This is the first stoichiometric point.

$$\text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2} = \frac{3.00 + 7.00}{2} = 5.00$$

- e. 6.00 mmol OH^- added results in 4.00 mmol H_2X^- and 1.00 mmol HX^{2-} after OH^- reacts completely with H_3X and then reacts completely with H_2X^- .

Using the $\text{H}_2\text{X}^- \rightleftharpoons \text{H}^+ + \text{HX}^{2-}$ reaction:

$$\text{pH} = \text{p}K_{a_2} + \log \frac{[\text{HX}^{2-}]}{[\text{H}_2\text{X}^-]} = 7.00 - \log(1.00/4.00) = 6.40; \quad \text{assumptions good.}$$

- f. 7.50 mmol KOH added results in 2.50 mmol H_2X^- and 2.50 mmol HX^{2-} after OH^- reacts completely. This is the second halfway point to equivalence.

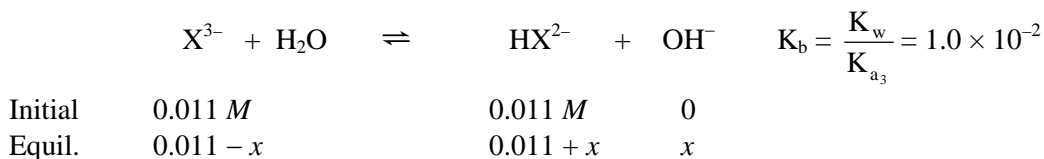
$\text{pH} = \text{p}K_{a_2} = 7.00$; assumptions good.

- g. 10.0 mmol OH^- added results in 5.0 mmol HX^{2-} after OH^- reacts completely. This is the second stoichiometric point.

$$\text{pH} = \frac{\text{p}K_{a_2} + \text{p}K_{a_3}}{2} = \frac{7.00 + 12.00}{2} = 9.50$$

- h. 12.5 mmol OH^- added results in 2.5 mmol HX^{2-} and 2.5 mmol X^{3-} after OH^- reacts completely with H_3X first, then H_2X^- , and finally HX^{2-} . This is the third halfway point to equivalence. Usually $\text{pH} = \text{p}K_{a_3}$ but normal assumptions don't hold. We must solve for the pH exactly.

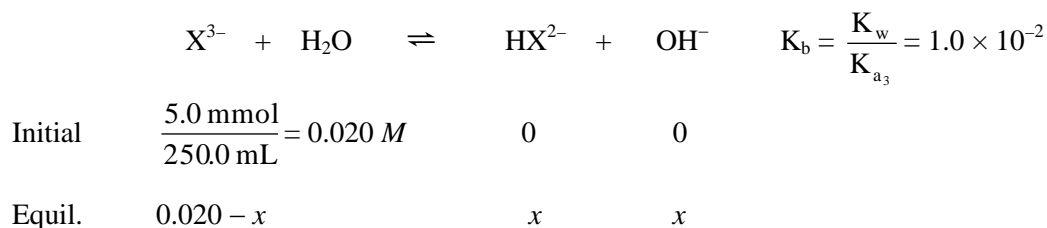
$$[\text{X}^{3-}] = [\text{HX}^{2-}] = 2.5 \text{ mmol}/225.0 \text{ mL} = 1.1 \times 10^{-2} \text{ M}$$



$$K_b = 1.0 \times 10^{-2} = \frac{x(0.011 + x)}{0.011 - x}; \text{ using the quadratic formula:}$$

$$x^2 + (2.1 \times 10^{-2})x - 1.1 \times 10^{-4} = 0, \quad x = 4.3 \times 10^{-3} \text{ M} = \text{OH}^-; \quad \text{pH} = 11.63$$

- i. 15.0 mmol OH^- added results in 5.0 mmol X^{3-} after OH^- reacts completely. This is the third stoichiometric point.



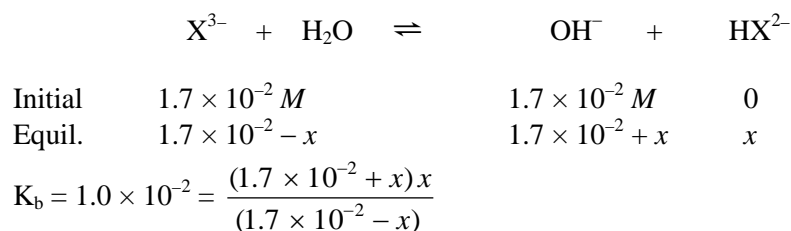
$$K_b = \frac{x^2}{0.020 - x}, \quad 1.0 \times 10^{-2} \approx \frac{x^2}{0.020}, \quad x = 1.4 \times 10^{-2}; \quad \text{assumption poor.}$$

$$\text{Using the quadratic formula: } x^2 + (1.0 \times 10^{-2})x - 2.0 \times 10^{-4} = 0$$

$$x = [\text{OH}^-] = 1.0 \times 10^{-2} \text{ M}; \quad \text{pH} = 12.00$$

- j. 20.0 mmol OH^- added results in 5.0 mmol X^{3-} and 5.0 mmol OH^- excess after OH^- reacts completely. Because K_b for X^{3-} is fairly large for a weak base, we have to worry about the OH^- contribution from X^{3-} .

$$[\text{X}^{3-}] = [\text{OH}^-] = 5.0 \text{ mmol}/300.0 \text{ mL} = 1.7 \times 10^{-2} \text{ M}$$



Using the quadratic formula: $x^2 + (2.7 \times 10^{-2})x - 1.7 \times 10^{-4} = 0$, $x = 5.3 \times 10^{-3} M$

$[\text{OH}^-] = (1.7 \times 10^{-2}) + x = (1.7 \times 10^{-2}) + (5.3 \times 10^{-3}) = 2.2 \times 10^{-2} M$; $\text{pH} = 12.34$

88. $50.0 \text{ mL} \times (0.10 \text{ mmol H}_2\text{A/mL}) = 5.0 \text{ mmol H}_2\text{A}$ initially

To reach the first equivalence point, 5.0 mmol OH^- must be added. This occurs after addition of 50.0 mL of 0.10 M NaOH. At the first equivalence point for a diprotic acid, $\text{pH} = (\text{pK}_{a_1} + \text{pK}_{a_2})/2 = 8.00$. Addition of 25.0 mL of 0.10 M NaOH will be the first halfway point to equivalence, where $[\text{H}_2\text{A}] = [\text{HA}^-]$ and $\text{pH} = \text{pK}_{a_1} = 6.70$. Solving for the K_a values:

$$\text{pK}_{a_1} = 6.70, \text{K}_{a_1} = 10^{-6.70} = 2.0 \times 10^{-7}$$

$$\frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} = 8.00, \frac{6.70 + \text{pK}_{a_2}}{2} = 8.00, \text{pK}_{a_2} = 9.30, \text{K}_{a_2} = 10^{-9.30} = 5.0 \times 10^{-10}$$

89. a. Na^+ is present in all solutions. The added H^+ from HCl reacts completely with CO_3^{2-} to convert it into HCO_3^- . After all CO_3^{2-} is reacted (after point C, the first equivalence point), H^+ then reacts completely with the next best base present, HCO_3^- . Point E represents the second equivalence point. The major species present at the various points after H^+ reacts completely follow.

A. $\text{CO}_3^{2-}, \text{H}_2\text{O}, \text{Na}^+$

B. $\text{CO}_3^{2-}, \text{HCO}_3^-, \text{H}_2\text{O}, \text{Cl}^-, \text{Na}^+$

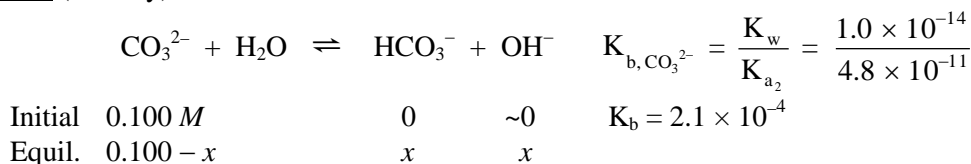
C. $\text{HCO}_3^-, \text{H}_2\text{O}, \text{Cl}^-, \text{Na}^+$

D. $\text{HCO}_3^-, \text{CO}_2 (\text{H}_2\text{CO}_3), \text{H}_2\text{O}, \text{Cl}^-, \text{Na}^+$

E. $\text{CO}_2 (\text{H}_2\text{CO}_3), \text{H}_2\text{O}, \text{Cl}^-, \text{Na}^+$

F. H^+ (excess), $\text{CO}_2 (\text{H}_2\text{CO}_3), \text{H}_2\text{O}, \text{Cl}^-, \text{Na}^+$

b. Point A (initially):



$$\text{K}_b = 2.1 \times 10^{-4} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$x = 4.6 \times 10^{-3} M = [\text{OH}^-]$; $\text{pH} = 11.66$; assumptions good.

Point B: The first halfway point where $[\text{CO}_3^{2-}] = [\text{HCO}_3^-]$.

$$\text{pH} = \text{pK}_{a_2} = -\log(4.8 \times 10^{-11}) = 10.32; \text{ assumptions good.}$$

Point C: First equivalence point (25.00 mL of 0.100 M HCl added). The amphoteric HCO_3^- is the major acid-base species present.

$$\text{pH} = \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2}; \text{ pK}_{a_1} = -\log(4.3 \times 10^{-7}) = 6.37$$

$$\text{pH} = \frac{6.37 + 10.32}{2} = 8.35$$

Point D: The second halfway point where $[\text{HCO}_3^-] = [\text{H}_2\text{CO}_3]$.

$$\text{pH} = \text{pK}_{a_1} = 6.37; \text{ assumptions good.}$$

Point E: This is the second equivalence point, where all of the CO_3^{2-} present initially has been converted into H_2CO_3 by the added strong acid. 50.0 mL HCl added.

$$[\text{H}_2\text{CO}_3] = 2.50 \text{ mmol}/75.0 \text{ mL} = 0.0333 \text{ M}$$



Initial	0.0333 M	0	0
Equil.	0.0333 - x	x	x

$$K_{a_1} = 4.3 \times 10^{-7} = \frac{x^2}{0.0333 - x} \approx \frac{x^2}{0.0333}$$

$$x = [\text{H}^+] = 1.2 \times 10^{-4} \text{ M}; \text{ pH} = 3.92; \text{ assumptions good.}$$

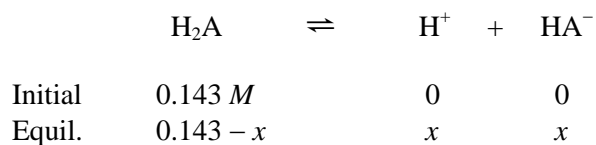
90. a. $\text{HA}^- \rightleftharpoons \text{H}^+ + \text{A}^{2-}$ $K_a = 1 \times 10^{-8}$; when $[\text{HA}^-] = [\text{A}^{2-}]$, $\text{pH} = \text{pK}_{a_2} = 8.00$.

The titration reaction is $\text{A}^{2-} + \text{H}^+ \rightarrow \text{HA}^-$ (goes to completion). Begin with 100.0 mL \times 0.200 mmol/mL = 20.0 mmol A^{2-} . We need to convert 10.0 mmol A^{2-} into HA^- by adding 10.0 mmol H^+ . This will produce a solution where $[\text{HA}^-] = [\text{A}^{2-}]$ and $\text{pH} = \text{pK}_{a_2} = 8.00$.

$$10.0 \text{ mmol} = 1.00 \text{ mmol/mL} \times V, \quad V = 10.0 \text{ mL HCl}$$

- b. At the second stoichiometric point, all A^{2-} is converted into H_2A . This requires 40.0 mmol HCl, which is 40.0 mL of 1.00 M HCl.

$$[\text{H}_2\text{A}]_0 = \frac{20.0 \text{ mmol}}{140.0 \text{ mL}} = 0.143 \text{ M}; \text{ because } K_{a_1} \gg K_{a_2}, \text{ H}_2\text{A} \text{ is the major source of } \text{H}^+.$$



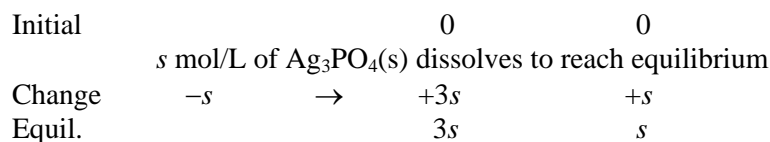
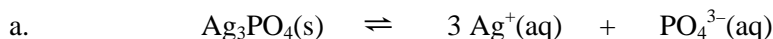
$$K_{a_1} = \frac{x^2}{0.143 - x}, 1.0 \times 10^{-3} \approx \frac{x^2}{0.143}, x = 0.012 \text{ M}; \text{ check assumptions:}$$

$$\frac{0.012}{0.143} \times 100 = 8.4\%; \text{ can't neglect } x. \text{ Using successive approximations:}$$

$$x = 0.0115 \text{ (carrying extra sig. figs.); } [\text{H}^+] = 0.0115 \text{ M and pH} = 1.94$$

Solubility Equilibria

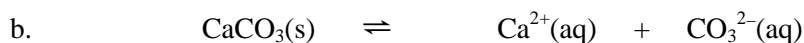
91. $\text{MX(s)} \rightleftharpoons \text{M}^{n+}(\text{aq}) + \text{X}^{n-}(\text{aq})$ $K_{\text{sp}} = [\text{M}^{n+}][\text{X}^{n-}]$; the K_{sp} reaction always refers to a solid breaking up into its ions. The representations all show 1 : 1 salts, i.e., the formula of the solid contains 1 cation for every 1 anion (either +1 and -1, or +2 and -2, or +3 and -3). The solution with the largest number of ions (largest $[\text{M}^{n+}]$ and $[\text{X}^{n-}]$) will have the largest K_{sp} value. From the representations, the second beaker has the largest number of ions present, so this salt has the largest K_{sp} value. Conversely, the third beaker, with the fewest number of hydrated ions, will have the smallest K_{sp} value.
92. K_{sp} values can only be compared directly to determine relative solubilities when the salts produce the same number of ions (have the same stoichiometry). Here, Ag_2S and CuS do not produce the same number of ions when they dissolve, so each has a different mathematical relationship between the K_{sp} value and the molar solubility. To determine which salt has the larger molar solubility, you must do the actual calculations and compare the two molar solubility values.
93. In our setups, s = solubility in mol/L. Because solids do not appear in the K_{sp} expression, we do not need to worry about their initial or equilibrium amounts.



$$K_{\text{sp}} = 1.8 \times 10^{-18} = [\text{Ag}^+]^3[\text{PO}_4^{3-}] = (3s)^3(s) = 27s^4$$

$$27s^4 = 1.8 \times 10^{-18}, s = (6.7 \times 10^{-20})^{1/4} = 1.6 \times 10^{-5} \text{ mol/L} = \text{molar solubility}$$

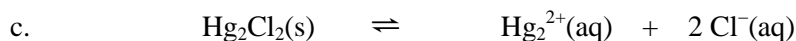
$$\frac{1.6 \times 10^{-5} \text{ mol Ag}_3\text{PO}_4}{\text{L}} \times \frac{418.7 \text{ g Ag}_3\text{PO}_4}{\text{mol Ag}_3\text{PO}_4} = 6.7 \times 10^{-3} \text{ g/L}$$



Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		s	s

$$K_{\text{sp}} = 8.7 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = s^2, \quad s = 9.3 \times 10^{-5} \text{ mol/L}$$

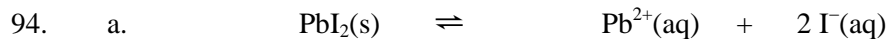
$$\frac{9.3 \times 10^{-5} \text{ mol}}{\text{L}} \times \frac{100.1 \text{ g}}{\text{mol}} = 9.3 \times 10^{-3} \text{ g/L}$$



Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		s	$2s$

$$K_{\text{sp}} = 1.1 \times 10^{-18} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (s)(2s)^2 = 4s^3, \quad s = 6.5 \times 10^{-7} \text{ mol/L}$$

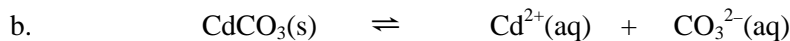
$$\frac{6.5 \times 10^{-7} \text{ mol}}{\text{L}} \times \frac{472.1 \text{ g}}{\text{mol}} = 3.1 \times 10^{-4} \text{ g/L}$$



Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		s	$2s$

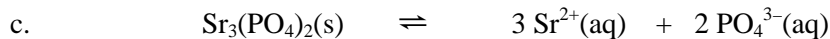
$$K_{\text{sp}} = 1.4 \times 10^{-8} = [\text{Pb}^{2+}][\text{I}^-]^2 = s(2s)^2 = 4s^3$$

$$s = (1.4 \times 10^{-8}/4)^{1/3} = 1.5 \times 10^{-3} \text{ mol/L} = \text{molar solubility}$$



Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		s	s

$$K_{\text{sp}} = 5.2 \times 10^{-12} = [\text{Cd}^{2+}][\text{CO}_3^{2-}] = s^2, \quad s = 2.3 \times 10^{-6} \text{ mol/L}$$

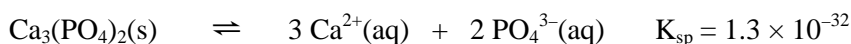


Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		$3s$	$2s$

$$K_{\text{sp}} = 1 \times 10^{-31} = [\text{Sr}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3s)^3(2s)^2 = 108s^5, \quad s = 2 \times 10^{-7} \text{ mol/L}$$

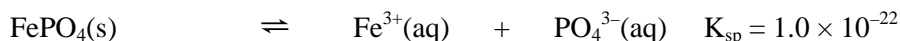
95. a. Because both solids dissolve to produce three ions in solution, we can compare values of K_{sp} to determine relative solubility. Because the K_{sp} for CaF_2 is the smallest, $\text{CaF}_2(\text{s})$ has the smallest molar solubility.

- b. We must calculate molar solubilities because each salt yields a different number of ions when it dissolves.



Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		$3s$	$2s$

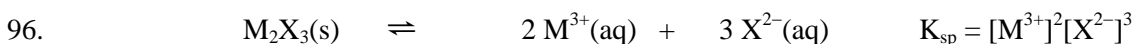
$$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3s)^3(2s)^2 = 108s^5, \quad s = (1.3 \times 10^{-32}/108)^{1/5} = 1.6 \times 10^{-7} \text{ mol/L}$$



Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		s	s

$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{PO}_4^{3-}] = s^2, \quad s = \sqrt{1.0 \times 10^{-22}} = 1.0 \times 10^{-11} \text{ mol/L}$$

FePO_4 has the smallest molar solubility.

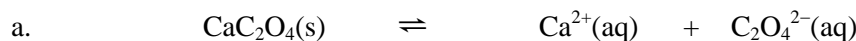


Initial	$s = \text{solubility (mol/L)}$	0	0
	$s \text{ mol/L of } \text{M}_2\text{X}_3(\text{s}) \text{ dissolves to reach equilibrium}$		
Change	$-s$	\rightarrow	$+2s$
Equil.			$+3s$
			$2s$
			$3s$

$$K_{\text{sp}} = (2s)^2(3s)^3 = 108s^5; \quad s = \frac{3.60 \times 10^{-7} \text{ g}}{\text{L}} \times \frac{1 \text{ mol } \text{M}_2\text{X}_3}{288 \text{ g}} = 1.25 \times 10^{-9} \text{ mol/L}$$

$$K_{\text{sp}} = 108(1.25 \times 10^{-9})^5 = 3.30 \times 10^{-43}$$

97. In our setup, s = solubility of the ionic solid in mol/L. This is defined as the maximum amount of a salt that can dissolve. Because solids do not appear in the K_{sp} expression, we do not need to worry about their initial and equilibrium amounts.



Initial		0	0
	$s \text{ mol/L of } \text{CaC}_2\text{O}_4(\text{s}) \text{ dissolves to reach equilibrium}$		
Change	$-s$	\rightarrow	$+s$
Equil.			$+s$
			s

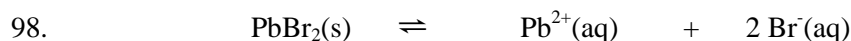
$$\text{From the problem, } s = \frac{6.1 \times 10^{-3} \text{ g}}{\text{L}} \times \frac{1 \text{ mol } \text{CaC}_2\text{O}_4}{128.10 \text{ g}} = 4.8 \times 10^{-5} \text{ mol/L.}$$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (s)(s) = s^2, \quad K_{\text{sp}} = (4.8 \times 10^{-5})^2 = 2.3 \times 10^{-9}$$



Initial		0	0
	<i>s</i> mol/L of BiI ₃ (s) dissolves to reach equilibrium		
Change	- <i>s</i>	→	+3 <i>s</i>
Equil.		<i>s</i>	3 <i>s</i>

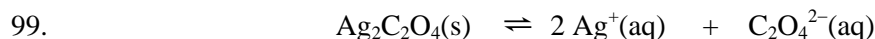
$$K_{\text{sp}} = [\text{Bi}^{3+}][\text{I}^{-}]^3 = (s)(3s)^3 = 27s^4, \quad K_{\text{sp}} = 27(1.32 \times 10^{-5})^4 = 8.20 \times 10^{-19}$$



Initial		0	0
	<i>s</i> mol/L of PbBr ₂ (s) dissolves to reach equilibrium		
Change	- <i>s</i>	→	+2 <i>s</i>
Equil.		<i>s</i>	2 <i>s</i>

From the problem, $s = [\text{Pb}^{2+}] = 2.14 \times 10^{-2} \text{ M}$. So:

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Br}^{-}]^2 = s(2s)^2 = 4s^3, \quad K_{\text{sp}} = 4(2.14 \times 10^{-2})^3 = 3.92 \times 10^{-5}$$



Initial	<i>s</i> = solubility (mol/L)	0	0
Equil.		2 <i>s</i>	<i>s</i>

From problem, $[\text{Ag}^{+}] = 2s = 2.2 \times 10^{-4} \text{ M}$, $s = 1.1 \times 10^{-4} \text{ M}$

$$K_{\text{sp}} = [\text{Ag}^{+}]^2[\text{C}_2\text{O}_4^{2-}] = (2s)^2(s) = 4s^3 = 4(1.1 \times 10^{-4})^3 = 5.3 \times 10^{-12}$$

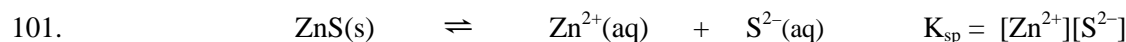


Initial	<i>s</i> = solubility (mol/L)	0	0.20 <i>M</i>
Equil.		<i>s</i>	0.20 + 3 <i>s</i>

$$K_{\text{sp}} = [\text{Ce}^{3+}][\text{IO}_3^{-}]^3 = s(0.20 + 3s)^3$$

From the problem, $s = 4.4 \times 10^{-8} \text{ mol/L}$; solving for K_{sp} :

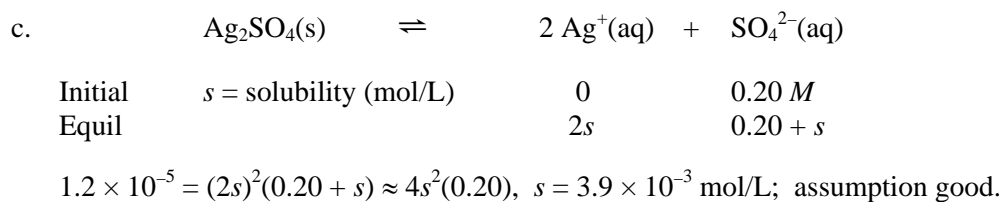
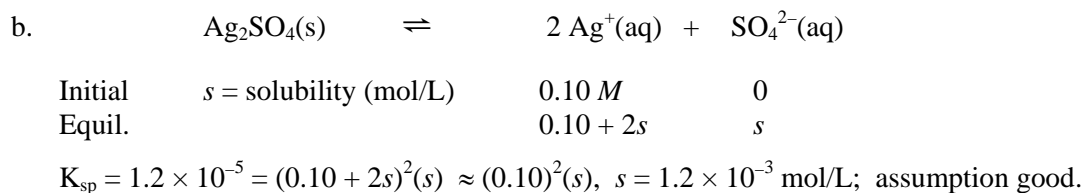
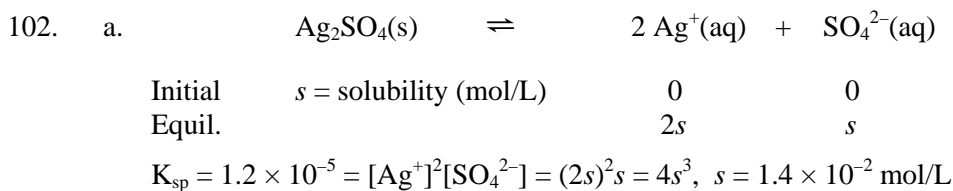
$$K_{\text{sp}} = (4.4 \times 10^{-8}) \times [0.20 + 3(4.4 \times 10^{-8})]^3 = 3.5 \times 10^{-10}$$



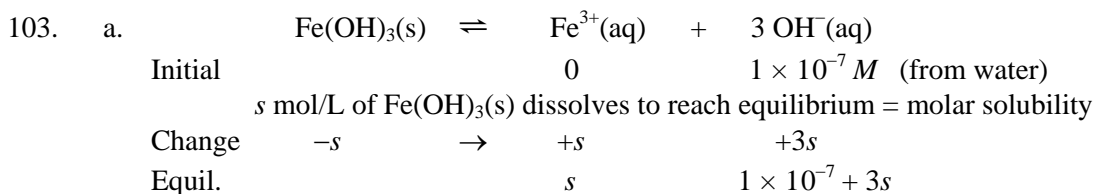
Initial	<i>s</i> = solubility (mol/L)	0.050 <i>M</i>	0
Equil.		0.050 + <i>s</i>	<i>s</i>

$$K_{sp} = 2.5 \times 10^{-22} = (0.050 + s)(s) \approx (0.050)s, \quad s = 5.0 \times 10^{-21} \text{ mol/L}; \quad \text{assumption good.}$$

$$\text{Mass ZnS that dissolves} = 0.3000 \text{ L} \times \frac{5.0 \times 10^{-21} \text{ mol ZnS}}{\text{L}} \times \frac{97.45 \text{ g ZnS}}{\text{mol}} = 1.5 \times 10^{-19} \text{ g}$$

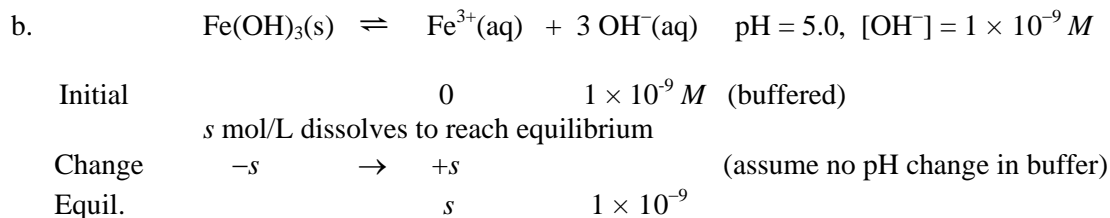


Note: Comparing the solubilities in parts b and c to part a illustrates that the solubility of a salt decreases when a common ion is present.

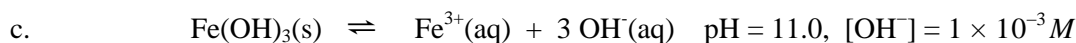


$$K_{sp} = 4 \times 10^{-38} = [\text{Fe}^{3+}][\text{OH}^-]^3 = (s)(1 \times 10^{-7} + 3s)^3 \approx s(1 \times 10^{-7})^3$$

$$s = 4 \times 10^{-17} \text{ mol/L}; \quad \text{assumption good } (3s \ll 1 \times 10^{-7})$$



$$K_{sp} = 4 \times 10^{-38} = [\text{Fe}^{3+}][\text{OH}^-]^3 = (s)(1 \times 10^{-9})^3, \quad s = 4 \times 10^{-11} \text{ mol/L} = \text{molar solubility}$$

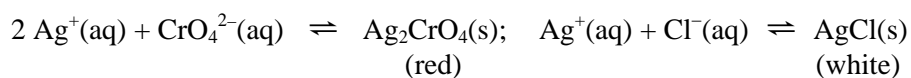


Initial		0	0.001 M	(buffered)
		<i>s</i> mol/L dissolves to reach equilibrium		
Change	- <i>s</i>	→	+ <i>s</i>	(assume no pH change)
Equil.			<i>s</i>	0.001

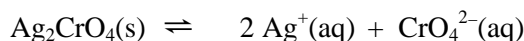
$$K_{\text{sp}} = 4 \times 10^{-38} = [\text{Fe}^{3+}][\text{OH}^{-}]^3 = (s)(0.001)^3, \quad s = 4 \times 10^{-29} \text{ mol/L} = \text{molar solubility}$$

Note: As $[\text{OH}^{-}]$ increases, solubility decreases. This is the common ion effect.

104. The relevant equations are:



In the first test tube, Ag^{+} and NO_3^{-} ions are present. As CrO_4^{2-} is added, the red precipitate Ag_2CrO_4 forms, leaving some Ag^{+} and CrO_4^{2-} in equilibrium with the red precipitate (Na^{+} and NO_3^{-} spectator ions are also present). As Cl^{-} is added, the white precipitate AgCl forms, lowering the concentration of Ag^{+} . As Ag^{+} is removed, the equilibrium of the first equation above is shifted to the left to produce more Ag^{+} , resulting in the dissolution of the red precipitate [$\text{Ag}_2\text{CrO}_4(\text{s})$]. As more of the CrO_4^{2-} ion goes into solution, the solution turns yellow due to the presence of the yellow $\text{CrO}_4^{2-}(\text{aq})$ ion. Because $\text{AgCl}(\text{s})$ forms in preference to $\text{Ag}_2\text{CrO}_4(\text{s})$, AgCl is less soluble than Ag_2CrO_4 . This can be verified by calculating the molar solubilities from the K_{sp} values given in Table 8.5 of the text.



Initial		0	0
Change	- <i>s</i>	→	+2 <i>s</i> + <i>s</i>
Equil.			2 <i>s</i> <i>s</i>

$$(2s)^2(s) = K_{\text{sp}} = 9.0 \times 10^{-12}, \quad s = \text{molar solubility} = 1.3 \times 10^{-4} \text{ mol/L}$$



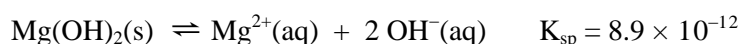
Initial		0	0
Change	- <i>s</i>	→	+ <i>s</i> + <i>s</i>
Equil.			<i>s</i> <i>s</i>

$$s^2 = K_{\text{sp}} = 1.6 \times 10^{-10}, \quad s = 1.3 \times 10^{-5} \text{ mol/L}; \quad \text{Ag}_2\text{CrO}_4(\text{s}) \text{ is more soluble than } \text{AgCl}(\text{s}).$$

105. a. AgF b. $\text{Pb}(\text{OH})_2$ c. $\text{Sr}(\text{NO}_2)_2$ d. $\text{Ni}(\text{CN})_2$

All these salts have anions that are bases. The anions of the other choices are conjugate bases of strong acids. They have no basic properties in water and, therefore, do not have solubilities that depend on pH.

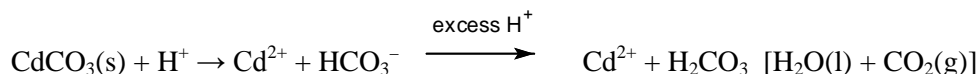
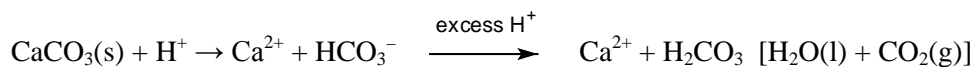
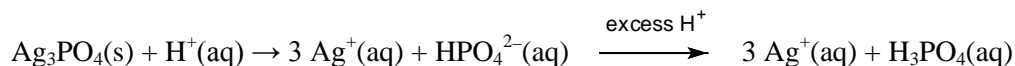
106. For 99% of the Mg^{2+} to be removed, we need, at equilibrium, $[\text{Mg}^{2+}] = 0.01(0.052 \text{ M})$. Using the K_{sp} equilibrium constant, calculate the $[\text{OH}^-]$ required to reach this reduced $[\text{Mg}^{2+}]$.



$$8.9 \times 10^{-12} = [\text{Mg}^{2+}][\text{OH}^-]^2 = [0.01(0.052 \text{ M})][\text{OH}^-]^2, \quad [\text{OH}^-] = 1.3 \times 10^{-4} \text{ M} \text{ (extra sig. fig.)}$$

$\text{pOH} = -\log(1.3 \times 10^{-4}) = 3.89$; $\text{pH} = 10.11$; at a $\text{pH} = 10.1$, 99% of the Mg^{2+} in seawater will be removed as $\text{Mg}(\text{OH})_2(\text{s})$.

107. If the anion in the salt can act as a base in water, then the solubility of the salt will increase as the solution becomes more acidic. Added H^+ will react with the base, forming the conjugate acid. As the basic anion is removed, more of the salt will dissolve to replenish the basic anion. The salts with basic anions are Ag_3PO_4 , CaCO_3 , CdCO_3 and $\text{Sr}_3(\text{PO}_4)_2$. Hg_2Cl_2 and PbI_2 do not have any pH dependence because Cl^- and I^- are terrible bases (the conjugate bases of a strong acids).



108. From Table 8.5, K_{sp} for $\text{NiCO}_3 = 1.4 \times 10^{-7}$ and K_{sp} for $\text{CuCO}_3 = 2.5 \times 10^{-10}$. From the K_{sp} values, CuCO_3 will precipitate first because it has the smaller K_{sp} value and will be least soluble. For $\text{CuCO}_3(\text{s})$, precipitation begins when:

$$[\text{CO}_3^{2-}] = \frac{K_{\text{sp}, \text{CuCO}_3}}{[\text{Cu}^{2+}]} = \frac{2.5 \times 10^{-10}}{0.25 \text{ M}} = 1.0 \times 10^{-9} \text{ M CO}_3^{2-}$$

For $\text{NiCO}_3(\text{s})$ to precipitate:

$$[\text{CO}_3^{2-}] = \frac{K_{\text{sp}, \text{NiCO}_3}}{[\text{Ni}^{2+}]} = \frac{1.4 \times 10^{-7}}{0.25 \text{ M}} = 5.6 \times 10^{-7} \text{ M CO}_3^{2-}$$

Determining the $[\text{Cu}^{2+}]$ when $\text{NiCO}_3(\text{s})$ begins to precipitate:

$$[\text{Cu}^{2+}] = \frac{K_{\text{sp}, \text{CuCO}_3}}{[\text{CO}_3^{2-}]} = \frac{2.5 \times 10^{-10}}{5.6 \times 10^{-7} \text{ M}} = 4.5 \times 10^{-4} \text{ M Cu}^{2+}$$

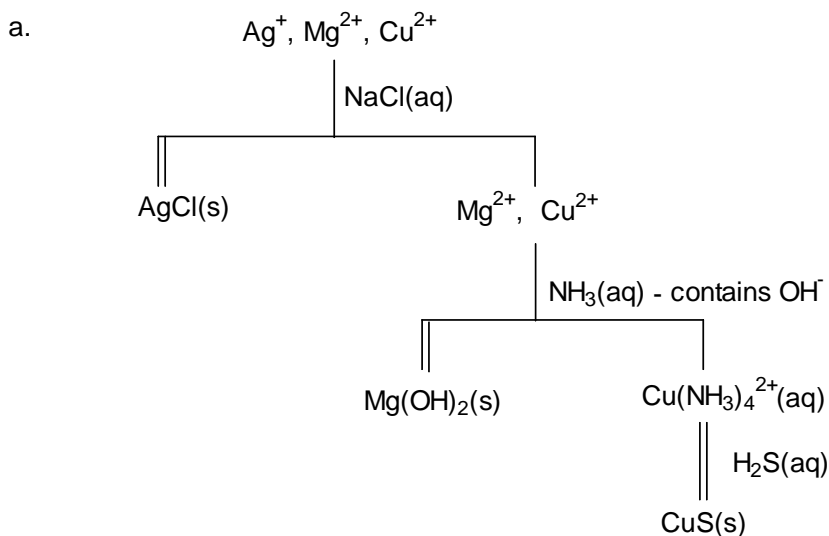
For successful separation, 1% Cu^{2+} or less of the initial amount of Cu^{2+} ($0.25 M$) must be present before $\text{NiCO}_3(\text{s})$ begins to precipitate. The percent of Cu^{2+} present when $\text{NiCO}_3(\text{s})$ begins to precipitate is:

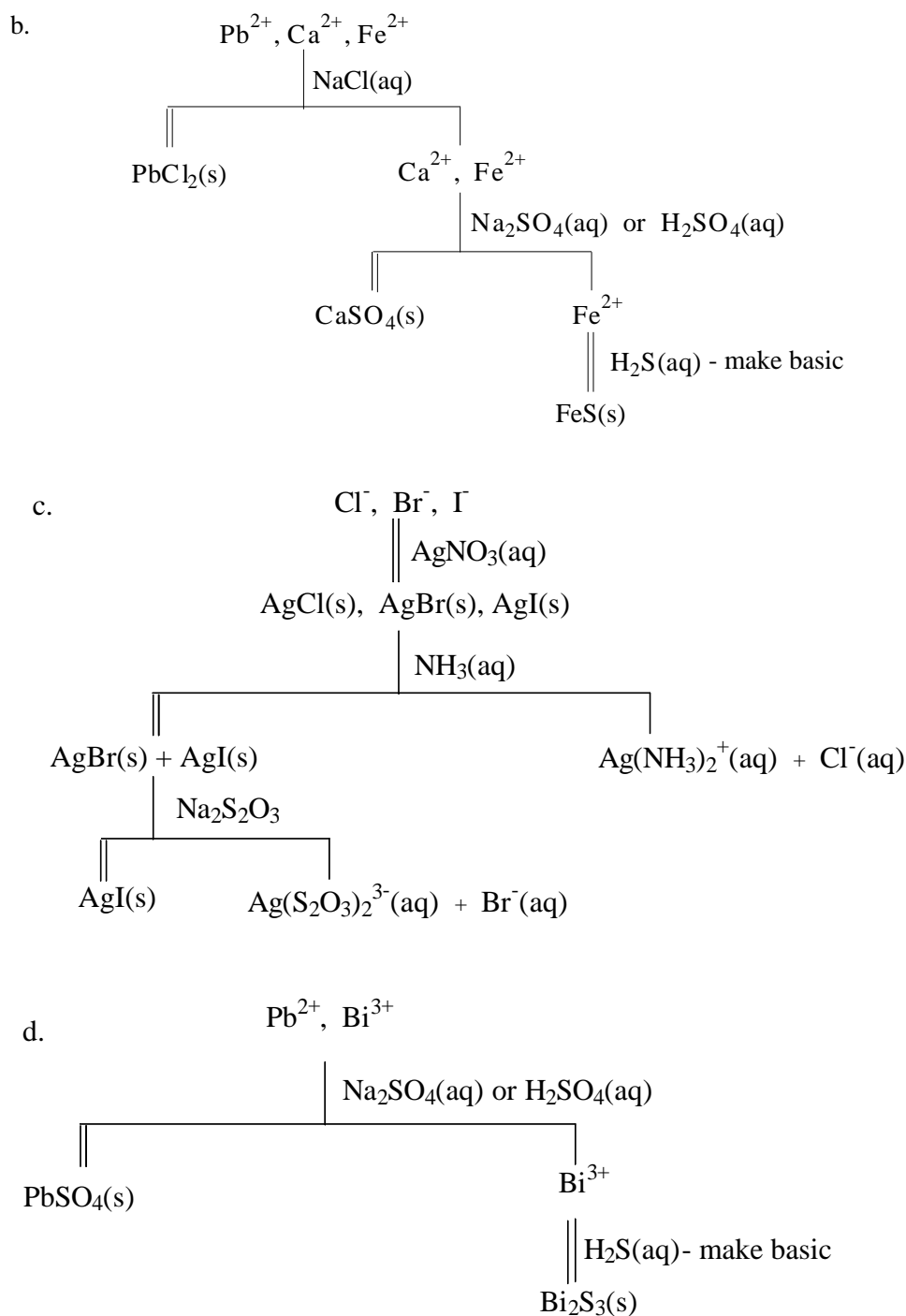
$$\frac{4.5 \times 10^{-4} M}{0.25 M} \times 100 = 0.18\% \text{ Cu}^{2+}$$

Because less than 1% Cu^{2+} remains of the initial amount, the metals can be separated through slow addition of $\text{Na}_2\text{CO}_3(\text{aq})$.

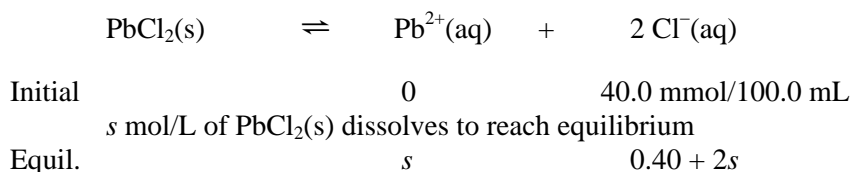
109. S^{2-} is a very basic anion and reacts significantly with H^+ to form HS^- ($\text{S}^{2-} + \text{H}^+ \rightleftharpoons \text{HS}^-$). Thus, the actual concentration of S^{2-} in solution depends on the amount of H^+ present. In basic solutions, little H^+ is present, which shifts the above equilibrium to the left. In basic solutions, the S^{2-} concentration is relatively high. So, in basic solutions, a wider range of sulfide salts will precipitate. However, in acidic solutions, added H^+ shifts the equilibrium to the right resulting in a lower S^{2-} concentration. In acidic solutions, only the least soluble sulfide salts will precipitate out of solution.
110. Unlike $\text{AgCl}(\text{s})$, $\text{PbCl}_2(\text{s})$ shows a significant increase in solubility with an increase in temperature. Hence add NaCl to the solution containing the metal ion to form the chloride salt precipitate, and then heat the solution. If the precipitate dissolves, then PbCl_2 is present, and the metal ion is Pb^{2+} . If the precipitate does not dissolve with an increase in temperature, then AgCl is the precipitate, and Ag^+ is the metal ion present.

111.





112. $50.0 \text{ mL} \times 0.10 \text{ M} = 5.0 \text{ mmol Pb}^{2+}$; $50.0 \text{ mL} \times 1.0 \text{ M} = 50. \text{ mmol Cl}^-$. For this solution, $Q > K_{\text{sp}}$, so PbCl_2 precipitates. Assume precipitation of $\text{PbCl}_2(\text{s})$ is complete. 5.0 mmol Pb^{2+} requires $10. \text{ mmol of Cl}^-$ for complete precipitation, which leaves $40. \text{ mmol Cl}^-$ in excess. Now let some of the $\text{PbCl}_2(\text{s})$ re-dissolve to establish equilibrium.



$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2, 1.6 \times 10^{-5} = s(0.40 + 2s)^2 \approx s(0.40)^2$$

$$s = 1.0 \times 10^{-4} \text{ mol/L}; \text{ assumption good.}$$

At equilibrium:

$$[\text{Pb}^{2+}] = s = 1.0 \times 10^{-4} \text{ mol/L and } [\text{Cl}^{-}] = 0.40 + 2s, 0.40 + 2(1.0 \times 10^{-4}) = 0.40 \text{ M}$$

$$113. [\text{BaBr}_2]_0 = \frac{0.150 \text{ L}(1.0 \times 10^{-4} \text{ mol/L})}{0.250 \text{ L}} = 6.0 \times 10^{-5} \text{ M}$$

$$[\text{K}_2\text{C}_2\text{O}_4]_0 = \frac{0.100 \text{ L}(6.0 \times 10^{-4} \text{ mol/L})}{0.250 \text{ L}} = 2.4 \times 10^{-4} \text{ M}$$

$$Q = [\text{Ba}^{2+}]_0[\text{C}_2\text{O}_4^{2-}]_0 = (6.0 \times 10^{-5})(2.4 \times 10^{-4}) = 1.5 \times 10^{-8} \text{ M}$$

Because $Q < K_{\text{sp}}$, BaC₂O₄(s) will not precipitate. The final concentration of ions will be:

$$[\text{Ba}^{2+}] = 6.0 \times 10^{-5} \text{ M}, [\text{Br}^{-}] = 1.2 \times 10^{-4} \text{ M}$$

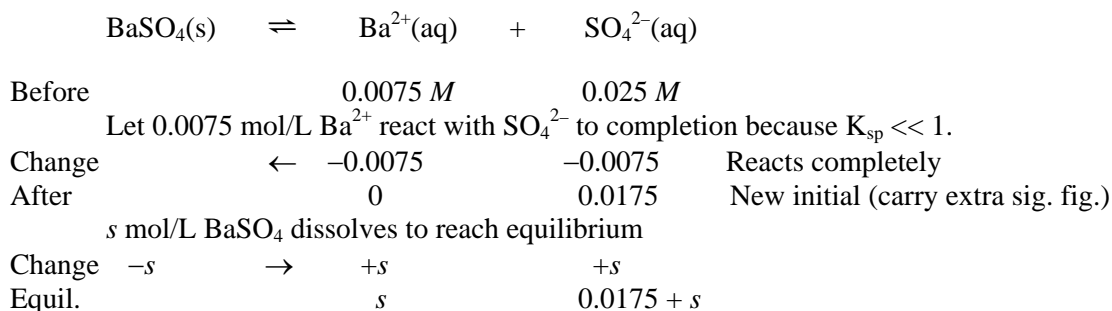
$$[\text{K}^{+}] = 4.8 \times 10^{-4} \text{ M}, [\text{C}_2\text{O}_4^{2-}] = 2.4 \times 10^{-4} \text{ M}$$

$$114. [\text{Ba}^{2+}]_0 = \frac{75.0 \text{ mL} \times \frac{0.020 \text{ mmol}}{\text{mL}}}{200. \text{ mL}} = 7.5 \times 10^{-3} \text{ M}$$

$$[\text{SO}_4^{2-}]_0 = \frac{125 \text{ mL} \times \frac{0.040 \text{ mmol}}{\text{mL}}}{200. \text{ mL}} = 2.5 \times 10^{-2} \text{ M}$$

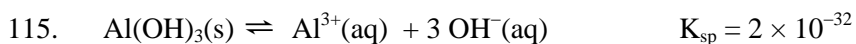
$$Q = [\text{Ba}^{2+}]_0[\text{SO}_4^{2-}]_0 = (7.5 \times 10^{-3})(2.5 \times 10^{-2}) = 1.9 \times 10^{-4} > K_{\text{sp}} (1.5 \times 10^{-9})$$

A precipitate of BaSO₄(s) will form.



$$K_{sp} = 1.5 \times 10^{-9} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (s)(0.0175 + s) \approx s(0.0175)$$

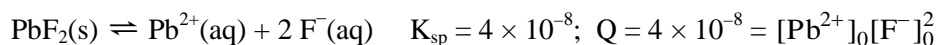
$$s = 8.6 \times 10^{-8} \text{ mol/L}; [\text{Ba}^{2+}] = 8.6 \times 10^{-8} \text{ M}; [\text{SO}_4^{2-}] = 0.018 \text{ M}; \text{ assumption good.}$$



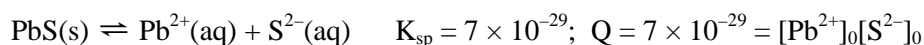
$$Q = 2 \times 10^{-32} = [\text{Al}^{3+}]_0[\text{OH}^{-}]_0^3 = (0.2)[\text{OH}^{-}]_0^3, [\text{OH}^{-}]_0 = 4.6 \times 10^{-11} \text{ (carrying extra sig. fig.)}$$

$\text{pOH} = -\log(4.6 \times 10^{-11}) = 10.3$; when the pOH of the solution equals 10.3, $K_{sp} = Q$. For precipitation, we want $Q > K_{sp}$. This will occur when $[\text{OH}^{-}]_0 > 4.6 \times 10^{-11}$ or when $\text{pOH} < 10.3$. Because $\text{pH} + \text{pOH} = 14.00$, precipitation of $\text{Al}(\text{OH})_3(\text{s})$ will begin when $\text{pH} > 3.7$ because this corresponds to a solution with $\text{pOH} < 10.3$.

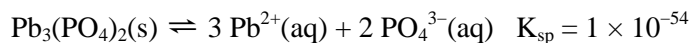
116. For each lead salt, we will calculate the $[\text{Pb}^{2+}]_0$ necessary for $Q = K_{sp}$. Any $[\text{Pb}^{2+}]_0$ greater than this value will cause precipitation of the salt ($Q > K_{sp}$).



$$[\text{Pb}^{2+}]_0 = \frac{4 \times 10^{-8}}{(1 \times 10^{-4})^2} = 4 \text{ M}$$



$$[\text{Pb}^{2+}]_0 = \frac{7 \times 10^{-29}}{1 \times 10^{-4}} = 7 \times 10^{-25} \text{ M}$$



$$Q = 1 \times 10^{-54} = [\text{Pb}^{2+}]_0^3[\text{PO}_4^{3-}]_0^2$$

$$[\text{Pb}^{2+}]_0 = \left[\frac{1 \times 10^{-54}}{(1 \times 10^{-4})^2} \right]^{1/3} = 5 \times 10^{-16} \text{ M}$$

From the calculated $[\text{Pb}^{2+}]_0$, the least soluble salt is $\text{PbS}(\text{s})$, and it will form first. $\text{Pb}_3(\text{PO}_4)_2(\text{s})$ will form second, and $\text{PbF}_2(\text{s})$ will form last because it requires the largest $[\text{Pb}^{2+}]_0$ in order for precipitation to occur.

117. $\text{Ag}_3\text{PO}_4(\text{s}) \rightleftharpoons 3 \text{Ag}^{+}(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$; when Q is greater than K_{sp} , precipitation will occur. We will calculate the $[\text{Ag}^{+}]_0$ necessary for $Q = K_{sp}$. Any $[\text{Ag}^{+}]_0$ greater than this calculated number will cause precipitation of $\text{Ag}_3\text{PO}_4(\text{s})$. In this problem, $[\text{PO}_4^{3-}]_0 = [\text{Na}_3\text{PO}_4]_0 = 1.0 \times 10^{-5} \text{ M}$.

$$K_{sp} = 1.8 \times 10^{-18}; \quad Q = 1.8 \times 10^{-18} = [\text{Ag}^{+}]_0^3[\text{PO}_4^{3-}]_0 = [\text{Ag}^{+}]_0^3(1.0 \times 10^{-5} \text{ M})$$

$$[\text{Ag}^+]_0 = \left(\frac{1.8 \times 10^{-18}}{1.0 \times 10^{-5}} \right)^{1/3}, \quad [\text{Ag}^+]_0 = 5.6 \times 10^{-5} M$$

When $[\text{Ag}^+]_0 = [\text{AgNO}_3]_0$ is greater than $5.6 \times 10^{-5} M$, $\text{Ag}_3\text{PO}_4(\text{s})$ will precipitate.

Complex Ion Equilibria

118. $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightleftharpoons \text{AgCl}(\text{s})$, white ppt.; $\text{AgCl}(\text{s}) + 2 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 $\text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightleftharpoons \text{AgBr}(\text{s}) + 2 \text{NH}_3(\text{aq})$, pale yellow ppt. = $\text{AgBr}(\text{s})$
 $\text{AgBr}(\text{s}) + 2 \text{S}_2\text{O}_3^{2-}(\text{aq}) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(\text{aq}) + \text{Br}^-(\text{aq})$
 $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{AgI}(\text{s}) + 2 \text{S}_2\text{O}_3^{2-}(\text{aq})$, yellow ppt. = $\text{AgI}(\text{s})$

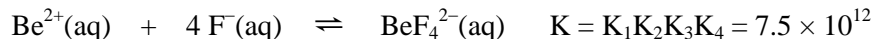
The least soluble salt (smallest K_{sp} value) must be AgI because it forms in the presence of Cl^- and Br^- . The most soluble salt (largest K_{sp} value) must be AgCl because it forms initially but never re-forms. The order of K_{sp} values is $K_{\text{sp}}(\text{AgCl}) > K_{\text{sp}}(\text{AgBr}) > K_{\text{sp}}(\text{AgI})$.

The order of formation constants is $K_f[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] > K_f[\text{Ag}(\text{NH}_3)_2^+]$ because addition of $\text{S}_2\text{O}_3^{2-}$ causes the $\text{AgBr}(\text{s})$ precipitate to dissolve, but the presence of NH_3 was unable to prevent $\text{AgBr}(\text{s})$ from forming. This assumes concentrations are about equal.

119. $\text{Hg}^{2+}(\text{aq}) + 2 \text{I}^-(\text{aq}) \rightarrow \text{HgI}_2(\text{s})$, orange ppt; $\text{HgI}_2(\text{s}) + 2 \text{I}^-(\text{aq}) \rightarrow \text{HgI}_4^{2-}(\text{aq})$
Soluble complex ion
120. $\text{Mn}^{2+} + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{MnC}_2\text{O}_4 \quad K_1 = 7.9 \times 10^3$
 $\text{MnC}_2\text{O}_4 + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{Mn}(\text{C}_2\text{O}_4)_2^{2-} \quad K_2 = 7.9 \times 10^1$
-
- $\text{Mn}^{2+}(\text{aq}) + 2 \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightleftharpoons \text{Mn}(\text{C}_2\text{O}_4)_2^{2-}(\text{aq}) \quad K_f = K_1K_2 = 6.2 \times 10^5$

121. $[\text{Be}^{2+}]_0 = 5.0 \times 10^{-5} M$ and $[\text{F}^-]_0 = 4.0 M$ because equal volumes of each reagent are mixed, so all concentrations given in the problem are diluted by a factor of one-half.

Because the K values are large, assume all reactions go to completion, and then solve an equilibrium problem.



Before	$5.0 \times 10^{-5} M$	$4.0 M$	0
After	0	$4.0 M$	$5.0 \times 10^{-5} M$
Equil.	x	$4.0 + 4x$	$5.0 \times 10^{-5} - x$

$$K = 7.5 \times 10^{12} = \frac{[\text{BeF}_4^{2-}]}{[\text{Be}^{2+}][\text{F}^-]^4} = \frac{5.0 \times 10^{-5} - x}{x(4.0 + 4x)^4} \approx \frac{5.0 \times 10^{-5}}{x(4.0)^4}$$

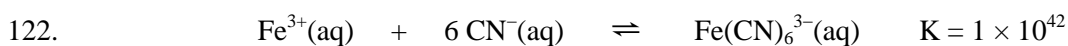
$$x = [\text{Be}^{2+}] = 2.6 \times 10^{-20} M; \text{ assumptions good. } [\text{F}^-] = 4.0 M; [\text{BeF}_4^{2-}] = 5.0 \times 10^{-5} M$$

Now use the stepwise K values to determine the other concentrations.

$$K_1 = 7.9 \times 10^4 = \frac{[\text{BeF}^+]}{[\text{Be}^{2+}][\text{F}^-]} = \frac{[\text{BeF}^+]}{(2.6 \times 10^{-20})(4.0)}, \quad [\text{BeF}^+] = 8.2 \times 10^{-15} M$$

$$K_2 = 5.8 \times 10^3 = \frac{[\text{BeF}_2]}{[\text{BeF}^+][\text{F}^-]} = \frac{[\text{BeF}_2]}{(8.2 \times 10^{-15})(4.0)}, \quad [\text{BeF}_2] = 1.9 \times 10^{-10} M$$

$$K_3 = 6.1 \times 10^2 = \frac{[\text{BeF}_3^-]}{[\text{BeF}_2][\text{F}^-]} = \frac{[\text{BeF}_3^-]}{(1.9 \times 10^{-10})(4.0)}, \quad [\text{BeF}_3^-] = 4.6 \times 10^{-7} M$$



Initial	0	2.0 M		0.090 mol/0.60 L = 0.15 M
	$x \text{ mol/L Fe}(\text{CN})_6^{3-}$ dissociates to reach equilibrium			
Change	+x	+6x	←	-x
Equil.	x	2.0 + 6x		0.15 - x

$$K = 1 \times 10^{42} = \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}^{3+}][\text{CN}^-]^6} = \frac{(0.15 - x)}{(x)(2.0 + 6x)^6}, \quad 1 \times 10^{42} \approx \frac{0.15}{x(2.0)^6}$$

$x = [\text{Fe}^{3+}] = 2 \times 10^{-45} M$; $[\text{Fe}(\text{CN})_6^{3-}] = 0.15 M - x = 0.15 M$; assumptions good.

123. $\frac{65 \text{ g KI}}{0.500 \text{ L}} \times \frac{1 \text{ mol KI}}{166.0 \text{ g KI}} = 0.78 M \text{ KI}$

The formation constant for HgI_4^{2-} is an extremely large number. Because of this, we will let the Hg^{2+} and I^- ions present initially react to completion and then solve an equilibrium problem to determine the Hg^{2+} concentration.

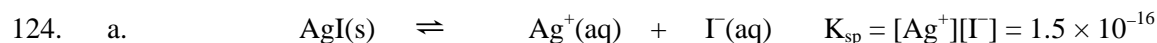


Before	0.010 M	0.78 M		0
Change	-0.010	-0.040	→	+0.010
After	0	0.74		0.010
	$x \text{ mol/L HgI}_4^{2-}$ dissociates to reach equilibrium			
Change	+x	+4x	←	-x
Equil.	x	0.74 + 4x		0.010 - x

$$K = 1.0 \times 10^{30} = \frac{[\text{HgI}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4} = \frac{(0.010 - x)}{(x)(0.74 + 4x)^4}; \quad \text{making usual assumptions:}$$

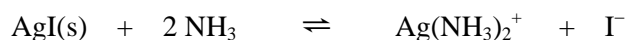
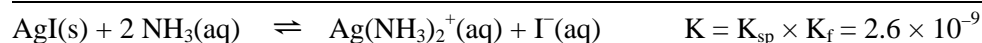
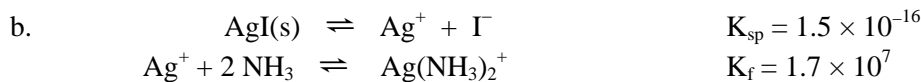
$$1.0 \times 10^{30} \approx \frac{(0.010)}{(x)(0.74)^4}, \quad x = [\text{Hg}^{2+}] = 3.3 \times 10^{-32} M; \quad \text{assumptions good.}$$

Note: $3.3 \times 10^{-32} \text{ mol/L}$ corresponds to one Hg^{2+} ion per $5 \times 10^7 \text{ L}$. It is very reasonable to approach the equilibrium in two steps. The reaction does essentially go to completion.



Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		s	s

$$K_{\text{sp}} = 1.5 \times 10^{-16} = s^2, \quad s = 1.2 \times 10^{-8} \text{ mol/L}$$



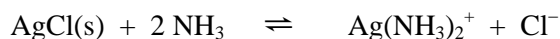
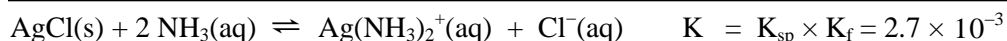
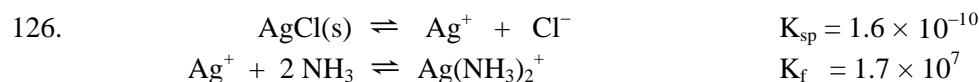
Initial	3.0 M	0	0
	$s \text{ mol/L of AgI(s) dissolves to reach equilibrium} = \text{molar solubility}$		
Equil.	$3.0 - 2s$	s	s

$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{I}^-]}{[\text{NH}_3]^2} = \frac{s^2}{(3.0 - 2s)^2}, \quad 2.6 \times 10^{-9} \approx \frac{s^2}{(3.0)^2}, \quad s = 1.5 \times 10^{-4} \text{ mol/L}$$

Assumption good.

- c. The presence of NH_3 increases the solubility of AgI . Added NH_3 removes Ag^+ from solution by forming the complex ion, $\text{Ag}(\text{NH}_3)_2^+$. As Ag^+ is removed, more AgI(s) will dissolve to replenish the Ag^+ concentration.

125. Test tube 1: Added Cl^- reacts with Ag^+ to form a silver chloride precipitate. The net ionic equation is $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl(s)}$. Test tube 2: Added NH_3 reacts with Ag^+ ions to form a soluble complex ion, $\text{Ag}(\text{NH}_3)_2^+$. As this complex ion forms, Ag^+ is removed from the solution, which causes the AgCl(s) to dissolve. When enough NH_3 is added, all the silver chloride precipitate will dissolve. The equation is $\text{AgCl(s)} + 2 \text{NH}_3(\text{aq}) \rightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Cl}^-(\text{aq})$. Test tube 3: Added H^+ reacts with the weak base, NH_3 , to form NH_4^+ . As NH_3 is removed from the $\text{Ag}(\text{NH}_3)_2^+$ complex ion, Ag^+ ions are released to solution and can then react with Cl^- to re-form AgCl(s) . The equations are $\text{Ag}(\text{NH}_3)_2^+(\text{aq}) + 2 \text{H}^+(\text{aq}) \rightarrow \text{Ag}^+(\text{aq}) + 2 \text{NH}_4^+(\text{aq})$, and $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl(s)}$.



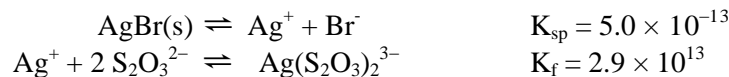
Initial	1.0 M	0	0
	$s \text{ mol/L of AgCl(s) dissolves to reach equilibrium} = \text{molar solubility}$		
Equil.	$1.0 - 2s$	s	s

$$K = 2.7 \times 10^{-3} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = \frac{s^2}{(1.0 - 2s)^2}; \text{ taking the square root:}$$

$$\frac{s}{1.0 - 2s} = (2.7 \times 10^{-3})^{1/2} = 5.2 \times 10^{-2}, \quad s = 4.7 \times 10^{-2} \text{ mol/L}$$

In pure water, the solubility of $\text{AgCl}(s)$ is $(1.6 \times 10^{-10})^{1/2} = 1.3 \times 10^{-5} \text{ mol/L}$. Notice how the presence of NH_3 increases the solubility of $\text{AgCl}(s)$ by over a factor of 3500.

127.



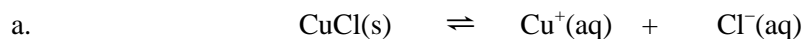
	$\text{AgBr}(s)$	$+ 2 \text{S}_2\text{O}_3^{2-}(\text{aq})$	\rightleftharpoons	$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(\text{aq})$	$+ \text{Br}^-(\text{aq})$
Initial		0.500 M		0	0
	$s \text{ mol/L AgBr}(s)$ dissolves to reach equilibrium				
Change	-s	-2s	→	+s	+s
Equil.		0.500 - 2s		s	s

$$K = \frac{s^2}{(0.500 - 2s)^2} = 14.5; \text{ taking the square root of both sides:}$$

$$\frac{s}{0.500 - 2s} = 3.81, \quad s = 1.91 - (7.62)s, \quad s = 0.222 \text{ mol/L}$$

$$1.00 \text{ L} \times \frac{0.222 \text{ mol AgBr}}{\text{L}} \times \frac{187.8 \text{ g AgBr}}{\text{mol AgBr}} = 41.7 \text{ g AgBr} = 42 \text{ g AgBr}$$

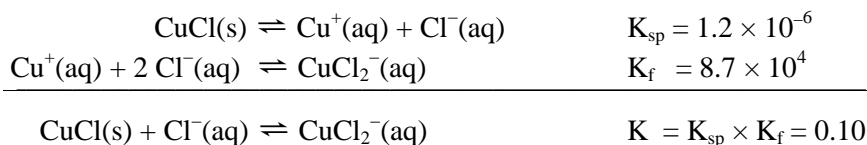
128.



Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		s	s

$$K_{\text{sp}} = 1.2 \times 10^{-6} = [\text{Cu}^+][\text{Cl}^-] = s^2, \quad s = 1.1 \times 10^{-3} \text{ mol/L}$$

b. Cu^+ forms the complex ion CuCl_2^- in the presence of Cl^- . We will consider both the K_{sp} reaction and the complex ion reaction at the same time.

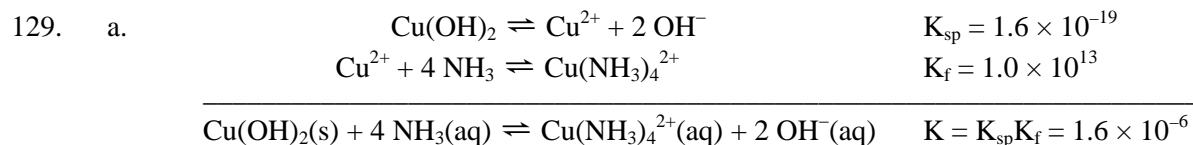




Initial	0.10 M	0	
Equil.	0.10 - s	s	where s = solubility of CuCl(s) in mol/L

$$K = 0.10 = \frac{[\text{CuCl}_2^-]}{[\text{Cl}^-]} = \frac{s}{0.10 - s}, \quad 1.0 \times 10^{-2} - (0.10)s = s$$

$$(1.10)s = 1.0 \times 10^{-2}, \quad s = 9.1 \times 10^{-3} \text{ mol/L}$$



Initial	5.0 M	0	0.0095 M
	<i>s</i> mol/L Cu(OH) ₂ dissolves to reach equilibrium		
Equil.	5.0 - 4 <i>s</i>	<i>s</i>	0.0095 + 2 <i>s</i>

$$K = 1.6 \times 10^{-6} = \frac{[\text{Cu(NH}_3)_4^{2+}][\text{OH}^-]^2}{[\text{NH}_3]^4} = \frac{s(0.0095 + 2s)^2}{(5.0 - 4s)^4}$$

If *s* is small: $1.6 \times 10^{-6} = \frac{s(0.0095)^2}{(5.0)^4}$, $s = 11. \text{ mol/L}$

Assumptions are not good. We will solve the problem by successive approximations.

$$s_{\text{calc}} = \frac{1.6 \times 10^{-6}(5.0 - 4s_{\text{guess}})^4}{(0.0095 + 2s_{\text{guess}})^2}; \quad \text{the results from six trials are:}$$

$$s_{\text{guess}}: \quad 0.10, 0.050, 0.060, 0.055, 0.056$$

$$s_{\text{calc}}: \quad 1.6 \times 10^{-2}, 0.071, 0.049, 0.058, 0.056$$

Thus the solubility of Cu(OH)₂ is 0.056 mol/L in 5.0 M NH₃.

Additional Exercises

130. 50.0 mL × 0.100 M = 5.00 mmol NaOH initially

At pH = 10.50, pOH = 3.50, $[\text{OH}^-] = 10^{-3.50} = 3.2 \times 10^{-4} \text{ M}$

$$\text{mmol OH}^- \text{ remaining} = 3.2 \times 10^{-4} \text{ mmol/mL} \times 73.75 \text{ mL} = 2.4 \times 10^{-2} \text{ mmol}$$

$$\text{mmol OH}^- \text{ that reacted} = 5.00 - 0.024 = 4.98 \text{ mmol}$$

Because the weak acid is monoprotic, 23.75 mL of the weak acid solution contains 4.98 mmol HA.

$$[\text{HA}]_0 = \frac{4.98 \text{ mmol}}{23.75 \text{ mL}} = 0.210 \text{ M}$$

131. $\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$, where HA = acetylsalicylic acid

$$\text{mmol HA present} = 27.36 \text{ mL OH}^- \times \frac{0.5106 \text{ mmol OH}^-}{\text{mL OH}^-} \times \frac{1 \text{ mmol HA}}{\text{mmol OH}^-} = 13.97 \text{ mmol HA}$$

$$\text{Molar mass of HA} = \frac{2.51 \text{ g HA}}{13.97 \times 10^{-3} \text{ mol HA}} = 180. \text{ g/mol}$$

To determine the K_a value, use the pH data. After complete neutralization of acetylsalicylic acid by OH^- , we have 13.97 mmol of A^- produced from the neutralization reaction. A^- will react completely with the added H^+ and re-form acetylsalicylic acid HA.

$$\text{mmol H}^+ \text{ added} = 15.44 \text{ mL} \times \frac{0.4524 \text{ mmol H}^+}{\text{mL}} = 6.985 \text{ mmol H}^+$$

	A^-	+	H^+	\rightarrow	HA	
Before	13.97 mmol		6.985 mmol		0	
Change	-6.985		-6.985	\rightarrow	+6.985	Reacts completely
After	6.985 mmol		0		6.985 mmol	

We have back titrated this solution to the halfway point to equivalence, where $\text{pH} = \text{p}K_a$ (assuming HA is a weak acid). This is true because after H^+ reacts completely, equal milliliters of HA and A^- are present, which only occurs at the halfway point to equivalence. Assuming acetylsalicylic acid is a weak acid, then $\text{pH} = \text{p}K_a = 3.48$. $K_a = 10^{-3.48} = 3.3 \times 10^{-4}$.

132. In the final solution: $[\text{H}^+] = 10^{-2.15} = 7.1 \times 10^{-3} \text{ M}$

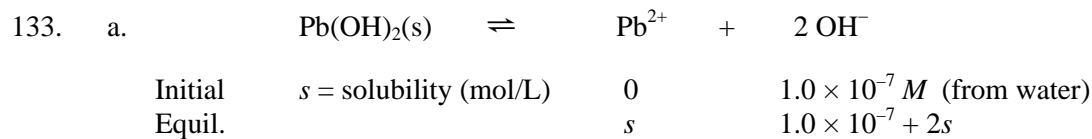
$$\text{Beginning mmol HCl} = 500.0 \text{ mL} \times 0.200 \text{ mmol/mL} = 100. \text{ mmol HCl}$$

$$\text{Amount of HCl that reacts with NaOH} = 1.50 \times 10^{-2} \text{ mmol/mL} \times V$$

$$\frac{7.1 \times 10^{-3} \text{ mmol}}{\text{mL}} = \frac{\text{final mmol H}^+}{\text{total volume}} = \frac{100. - 0.0150V}{500.0 + V}$$

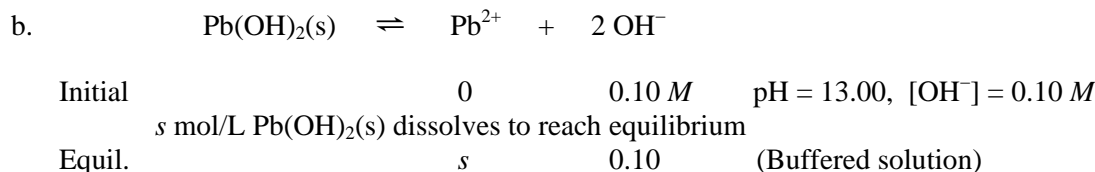
$$3.6 + (7.1 \times 10^{-3})V = 100. - (1.50 \times 10^{-2})V, (2.21 \times 10^{-2})V = 100. - 3.6$$

$$V = 4.36 \times 10^3 \text{ mL} = 4.36 \text{ L} = 4.4 \text{ L NaOH}$$



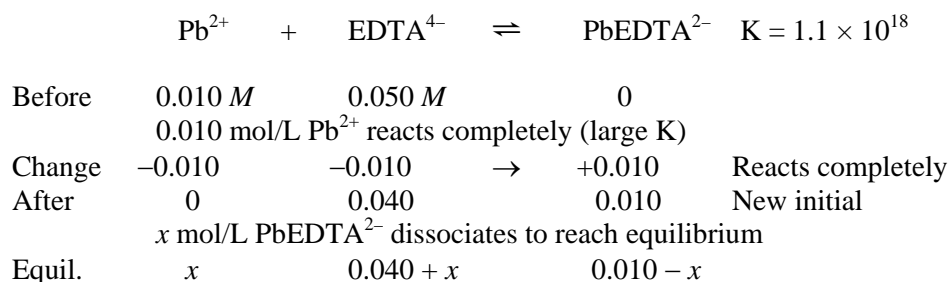
$$K_{\text{sp}} = 1.2 \times 10^{-15} = [\text{Pb}^{2+}][\text{OH}^-]^2 = s(1.0 \times 10^{-7} + 2s)^2 \approx s(2s)^2 = 4s^3$$

$$s = [\text{Pb}^{2+}] = 6.7 \times 10^{-6} \text{ M}; \text{ assumption is good by the 5\% rule.}$$



$$1.2 \times 10^{-15} = (s)(0.10)^2, \quad s = [\text{Pb}^{2+}] = 1.2 \times 10^{-13} \text{ M}$$

c. We need to calculate the Pb²⁺ concentration in equilibrium with EDTA⁴⁻. Since K is large for the formation of PbEDTA²⁻, let the reaction go to completion, and then solve an equilibrium problem to get the Pb²⁺ concentration.

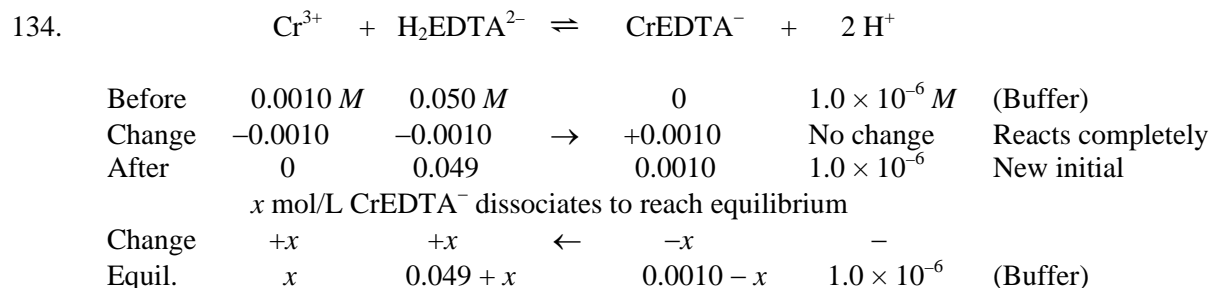


$$1.1 \times 10^{18} = \frac{(0.010 - x)}{(x)(0.040 + x)} \approx \frac{0.010}{x(0.040)}, \quad x = [\text{Pb}^{2+}] = 2.3 \times 10^{-19} \text{ M}; \text{ assumptions good.}$$

Now calculate the solubility quotient for Pb(OH)₂ to see if precipitation occurs. The concentration of OH⁻ is 0.10 M since we have a solution buffered at pH = 13.00.

$$Q = [\text{Pb}^{2+}]_0[\text{OH}^-]_0^2 = (2.3 \times 10^{-19})(0.10)^2 = 2.3 \times 10^{-21} < K_{\text{sp}} (1.2 \times 10^{-15})$$

Pb(OH)₂(s) will not form since Q is less than K_{sp}.



$$K_f = 1.0 \times 10^{23} = \frac{[\text{CrEDTA}^-][\text{H}^+]^2}{[\text{Cr}^{3+}][\text{H}_2\text{EDTA}^{2-}]} = \frac{(0.0010-x)(1.0 \times 10^{-6})^2}{(x)(0.049+x)}$$

$$1.0 \times 10^{23} \approx \frac{(0.0010)(1.0 \times 10^{-12})}{x(0.049)}, \quad x = [\text{Cr}^{3+}] = 2.0 \times 10^{-37} \text{ M}; \quad \text{assumptions good.}$$

135. $\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$; let C_0 = initial concentration of $\text{HC}_2\text{H}_3\text{O}_2$

$$\text{From normal weak acid setup: } K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{[\text{H}^+]^2}{C_0 - [\text{H}^+]}$$

$$[\text{H}^+] = 10^{-2.68} = 2.1 \times 10^{-3} \text{ M}; \quad 1.8 \times 10^{-5} = \frac{(2.1 \times 10^{-3})^2}{C_0 - (2.1 \times 10^{-3})}, \quad C_0 = 0.25 \text{ M}$$

$$25.0 \text{ mL} \times 0.25 \text{ mmol/mL} = 6.3 \text{ mmol HC}_2\text{H}_3\text{O}_2$$

$$\text{Need } 6.3 \text{ mmol KOH} = V_{\text{KOH}} \times 0.0975 \text{ mmol/mL}, \quad V_{\text{KOH}} = 65 \text{ mL}$$

136. $[\text{X}^-]_0 = 5.00 \text{ M}$ and $[\text{Cu}^+]_0 = 1.0 \times 10^{-3} \text{ M}$ since equal volumes of each reagent are mixed.

Because the K values are large, assume that the reaction goes completely to CuX_3^{2-} ; then solve an equilibrium problem.

	Cu^+	+	3 X^-	\rightleftharpoons	CuX_3^{2-}	$K = K_1K_2K_3 = 1.0 \times 10^9$
Before	$1.0 \times 10^{-3} \text{ M}$		5.00 M		0	
After	0		$5.00 - 3(10^{-3}) = 5.00$		1.0×10^{-3}	
Equil.	x		$5.00 + 3x$		$1.0 \times 10^{-3} - x$	

$$K = \frac{(1.0 \times 10^{-3} - x)}{x(5.00 + 3x)^3}, \quad 1.0 \times 10^9 \approx \frac{1.0 \times 10^{-3}}{x(5.00)^3}, \quad x = [\text{Cu}^+] = 8.0 \times 10^{-15} \text{ M}; \quad \text{assumptions good.}$$

$$[\text{CuX}_3^{2-}] = 1.0 \times 10^{-3} - 8.0 \times 10^{-15} = 1.0 \times 10^{-3} \text{ M}$$

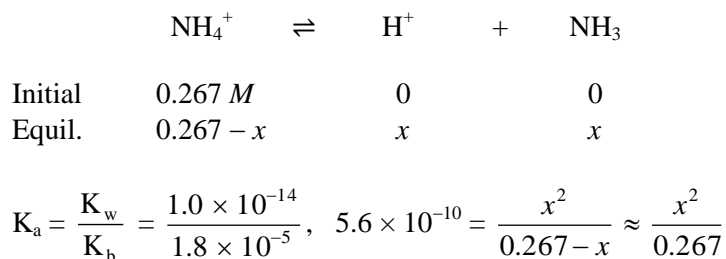
$$K_3 = \frac{[\text{CuX}_3^{2-}]}{[\text{CuX}_2^-][\text{X}^-]}, \quad 1.0 \times 10^3 = \frac{(1.0 \times 10^{-3})}{[\text{CuX}_2^-](5.00)}, \quad [\text{CuX}_2^-] = 2.0 \times 10^{-7} \text{ M}$$

Summarizing:

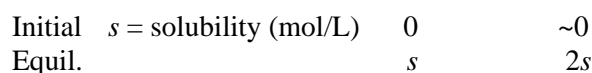
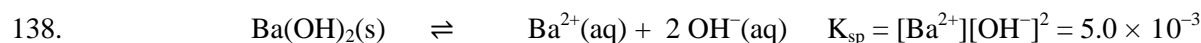
$$\begin{aligned} [\text{CuX}_3^{2-}] &= 1.0 \times 10^{-3} \text{ M} && \text{(answer a)} \\ [\text{CuX}_2^-] &= 2.0 \times 10^{-7} \text{ M} && \text{(answer b)} \\ [\text{Cu}^{2+}] &= 8.0 \times 10^{-15} \text{ M} && \text{(answer c)} \end{aligned}$$

137. $0.400 \text{ mol/L} \times V_{\text{NH}_3} = \text{mol NH}_3 = \text{mol NH}_4^+$ after reaction with HCl at the equivalence point.

At the equivalence point: $[\text{NH}_4^+]_0 = \frac{\text{mol NH}_4^+}{\text{total volume}} = \frac{0.400 \times V_{\text{NH}_3}}{1.50 \times V_{\text{NH}_3}} = 0.267 \text{ M}$

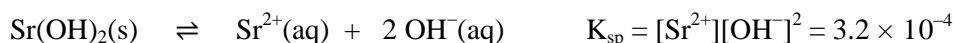


$x = [\text{H}^+] = 1.2 \times 10^{-5} \text{ M}$; pH = 4.92; assumptions good.



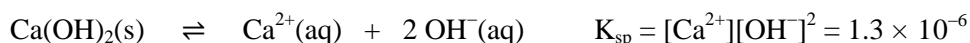
$K_{\text{sp}} = 5.0 \times 10^{-3} = s(2s)^2 = 4s^3$, $s = 0.11 \text{ mol/L}$; assumption good.

$[\text{OH}^-] = 2s = 2(0.11) = 0.22 \text{ mol/L}$; pOH = 0.66, pH = 13.34



$K_{\text{sp}} = 3.2 \times 10^{-4} = 4s^3$, $s = 0.043 \text{ mol/L}$; assumption good.

$[\text{OH}^-] = 2(0.043) = 0.086 \text{ M}$; pOH = 1.07, pH = 12.93



$K_{\text{sp}} = 1.3 \times 10^{-6} = 4s^3$, $s = 6.9 \times 10^{-3} \text{ mol/L}$; assumption good.

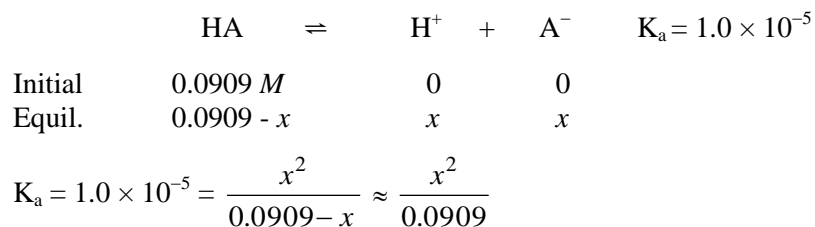
$[\text{OH}^-] = 2(6.9 \times 10^{-3}) = 1.4 \times 10^{-2} \text{ mol/L}$; pOH = 1.85, pH = 12.15

139. A best buffer is when $\text{pH} \approx \text{pK}_a$; these solutions have about equal concentrations of weak acid and conjugate base. Therefore, choose combinations that yield a buffer where $\text{pH} \approx \text{pK}_a$; that is, look for acids whose pK_a is closest to the pH.

- a. Potassium fluoride + HCl will yield a buffer consisting of HF ($\text{pK}_a = 3.14$) and F^- .
- b. Benzoic acid + NaOH will yield a buffer consisting of benzoic acid ($\text{pK}_a = 4.19$) and benzoate anion.

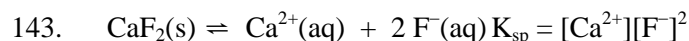
- c. Sodium acetate + acetic acid ($pK_a = 4.74$) is the best choice for $pH = 5.0$ buffer since acetic acid has a pK_a value closest to 5.0.
- d. HOCl and NaOH: This is the best choice to produce a conjugate acid-base pair with $pH = 7.0$. This mixture would yield a buffer consisting of HOCl ($pK_a = 7.46$) and OCl^- . Actually, the best choice for a $pH = 7.0$ buffer is an equimolar mixture of ammonium chloride and sodium acetate. NH_4^+ is a weak acid ($K_a = 5.6 \times 10^{-10}$), and $C_2H_3O_2^-$ is a weak base ($K_b = 5.6 \times 10^{-10}$). A mixture of the two will give a buffer at $pH = 7.0$ because the weak acid and weak base are the same strengths (K_a for $NH_4^+ = K_b$ for $C_2H_3O_2^-$). $NH_4C_2H_3O_2$ is commercially available, and its solutions are used for $pH = 7.0$ buffers.
- e. Ammonium chloride + NaOH will yield a buffer consisting of NH_4^+ ($pK_a = 9.26$) and NH_3 .
140. a. $1.00 \text{ L} \times 0.100 \text{ mol/L} = 0.100 \text{ mol HCl}$ added to reach stoichiometric point.
The 10.00-g sample must have contained 0.100 mol of NaA. $\frac{10.00 \text{ g}}{0.100 \text{ mol}} = 100. \text{ g/mol}$
- b. 500.0 mL of HCl added represents the halfway point to equivalence. Thus $pH = pK_a = 5.00$ and $K_a = 1.0 \times 10^{-5}$. At the equivalence point, enough H^+ has been added to convert all the A^- present initially into HA. The concentration of HA at the equivalence point is:

$$[HA]_0 = \frac{0.100 \text{ mol}}{1.10 \text{ L}} = 0.0909 \text{ M}$$

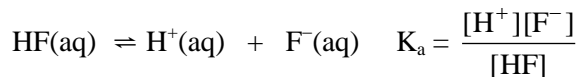


$$x = 9.5 \times 10^{-4} \text{ M} = [H^+]; \text{ pH} = 3.02; \text{ assumptions good.}$$

141. K_{a_3} is so small (4.8×10^{-13}) that a break is not seen at the third stoichiometric point.
142. We will see only the first stoichiometric point in the titration of salicylic acid because K_{a_2} is so small. For adipic acid, the K_a values are fairly close to each other. Both protons will be titrated almost simultaneously, giving us only one break. The stoichiometric points will occur when 1 mol of OH^- is added per mole of salicylic acid present and when 2 mol of OH^- is added per mole of adipic acid present. Thus the 25.00-mL volume corresponded to the titration of salicylic acid, and the 50.00-mL volume corresponded to the titration of adipic acid.



We need to determine the F^{-} concentration present in a 1.0 M HF solution. Solving the weak acid equilibrium problem:



Initial	1.0 M	~0	0
Equil.	1.0 - x	x	x

$$K_{\text{a}} = 7.2 \times 10^{-4} = \frac{x(x)}{1.0 - x} \approx \frac{x^2}{1.0}, \quad x = [\text{F}^{-}] = 2.7 \times 10^{-2} \text{ M}; \quad \text{assumption good.}$$

Next, calculate the Ca^{2+} concentration necessary for $Q = K_{\text{sp, CaF}_2}$.

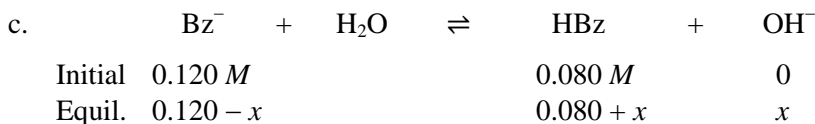
$$Q = [\text{Ca}^{2+}]_0[\text{F}^{-}]_0^2, \quad 4.0 \times 10^{-11} = [\text{Ca}^{2+}]_0(2.7 \times 10^{-2})^2, \quad [\text{Ca}^{2+}]_0 = 5.5 \times 10^{-8} \text{ mol/L}$$

$$\begin{aligned} \text{Mass Ca}(\text{NO}_3)_2 &= 1.0 \text{ L} \times \frac{5.5 \times 10^{-8} \text{ mol Ca}^{2+}}{\text{L}} \times \frac{1 \text{ mol Ca}(\text{NO}_3)_2}{\text{mol Ca}^{2+}} \times \frac{164.10 \text{ g Ca}(\text{NO}_3)_2}{\text{mol}} \\ &= 9.0 \times 10^{-6} \text{ g Ca}(\text{NO}_3)_2 \end{aligned}$$

For precipitation of $\text{CaF}_2(\text{s})$ to occur, we need $Q > K_{\text{sp}}$. When $9.0 \times 10^{-6} \text{ g Ca}(\text{NO}_3)_2$ has been added to 1.0 L of solution, $Q = K_{\text{sp}}$. So precipitation of $\text{CaF}_2(\text{s})$ will begin to occur when just more than $9.0 \times 10^{-6} \text{ g Ca}(\text{NO}_3)_2$ has been added.

144. a. $\text{pH} = \text{p}K_{\text{a}} = -\log(6.4 \times 10^{-5}) = 4.19$ since $[\text{HBz}] = [\text{Bz}^{-}]$, where $\text{HBz} = \text{C}_6\text{H}_5\text{CO}_2\text{H}$ and $[\text{Bz}^{-}] = \text{C}_6\text{H}_5\text{CO}_2^{-}$.
- b. $[\text{Bz}^{-}]$ will increase to 0.120 M and $[\text{HBz}]$ will decrease to 0.080 M after OH^{-} reacts completely with HBz. The Henderson-Hasselbalch equation is derived from the K_{a} dissociation reaction.

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{Bz}^{-}]}{[\text{HBz}]}, \quad \text{pH} = 4.19 + \log \frac{(0.120)}{(0.080)} = 4.37; \quad \text{assumptions good.}$$



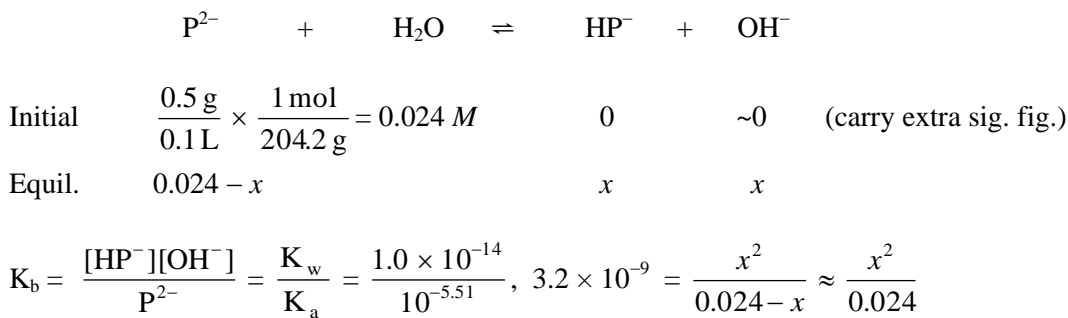
$$K_{\text{b}} = \frac{K_{\text{w}}}{K_{\text{a}}} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-5}} = \frac{(0.080 + x)(x)}{(0.120 - x)} \approx \frac{(0.080)(x)}{0.120}$$

$$x = [\text{OH}^{-}] = 2.34 \times 10^{-10} \text{ M} \quad (\text{carrying extra sig. fig.}); \quad \text{assumptions good.}$$

$$\text{pOH} = 9.63; \quad \text{pH} = 4.37$$

d. We get the same answer. Both equilibria involve the two major species, benzoic acid and benzoate anion. Both equilibria must hold true. K_b is related to K_a by K_w and $[\text{OH}^-]$ is related to $[\text{H}^+]$ by K_w , so all constants are interrelated.

145. At the equivalence point, P^{2-} is the major species. P^{2-} is a weak base in water because it is the conjugate base of a weak acid.

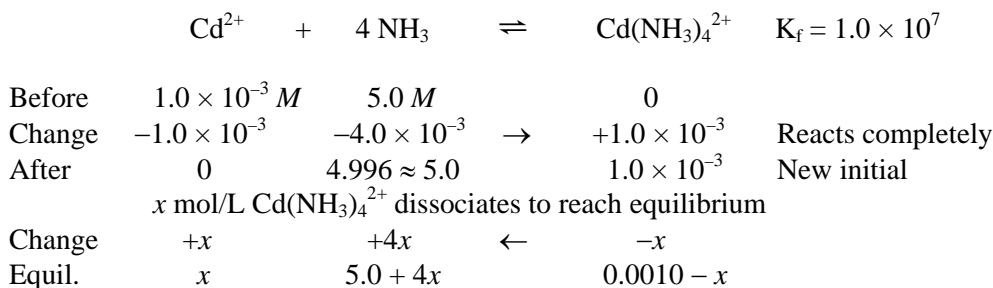


$$x = [\text{OH}^-] = 8.8 \times 10^{-6} \text{ M}; \quad \text{pOH} = 5.1; \quad \text{pH} = 8.9; \quad \text{assumptions good.}$$

Phenolphthalein would be the best indicator for this titration because it changes color at $\text{pH} \approx 9$ (from acid color to base color).

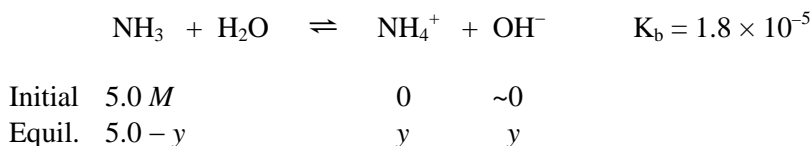
146. $1.0 \text{ mL} \times \frac{1.0 \text{ mmol}}{\text{mL}} = 1.0 \text{ mmol Cd}^{2+}$ added to the ammonia solution

Thus $[\text{Cd}^{2+}]_0 = 1.0 \times 10^{-3} \text{ mol/L}$. We will first calculate the equilibrium Cd^{2+} concentration using the complex ion equilibrium, and then determine if this Cd^{2+} concentration is large enough to cause precipitation of $\text{Cd}(\text{OH})_2(\text{s})$.



$$K_f = 1.0 \times 10^7 = \frac{(0.0010 - x)}{(x)(5.0 + 4x)^4} \approx \frac{(0.0010)}{(x)(5.0)^4}$$

$x = [\text{Cd}^{2+}] = 1.6 \times 10^{-13} \text{ M}$; assumptions good. This is the maximum $[\text{Cd}^{2+}]$ possible. Now we will determine if $\text{Cd}(\text{OH})_2(\text{s})$ forms at this concentration of Cd^{2+} . In 5.0 M NH_3 we can calculate the pH:



$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{y^2}{5.0 - y} \approx \frac{y^2}{5.0}, \quad y = [\text{OH}^-] = 9.5 \times 10^{-3} \text{ M}; \quad \text{assumptions good.}$$

We now calculate the value of the solubility quotient, Q:

$$Q = [\text{Cd}^{2+}][\text{OH}^-]^2 = (1.6 \times 10^{-13})(9.5 \times 10^{-3})^2$$

$$Q = 1.4 \times 10^{-17} < K_{sp}(5.9 \times 10^{-15}); \quad \text{therefore, no precipitate forms.}$$

$$147. \quad \text{NaOH added} = 50.0 \text{ mL} \times \frac{0.500 \text{ mmol}}{\text{mL}} = 25.0 \text{ mmol NaOH}$$

$$\text{NaOH left unreacted} = 31.92 \text{ mL HCl} \times \frac{0.289 \text{ mmol}}{\text{mL}} \times \frac{1 \text{ mmol NaOH}}{\text{mmol HCl}} = 9.22 \text{ mmol NaOH}$$

$$\text{NaOH reacted with aspirin} = 25.0 - 9.22 = 15.8 \text{ mmol NaOH}$$

$$15.8 \text{ mmol NaOH} \times \frac{1 \text{ mmol aspirin}}{2 \text{ mmol NaOH}} \times \frac{180.2 \text{ mg}}{\text{mmol}} = 1420 \text{ mg} = 1.42 \text{ g aspirin}$$

$$\text{Purity} = \frac{1.42 \text{ g}}{1.427 \text{ g}} \times 100 = 99.5\%$$

Here, a strong base is titrated by a strong acid. The equivalence point will be at pH = 7.0. Bromthymol blue would be the best indicator since it changes color at pH \approx 7 (from base color to acid color). See Fig. 8.8 of the text.

148. i. This is the result when you have a salt that breaks up into two ions. Examples of these salts (but not all) include AgCl, SrSO₄, BaCrO₄, and ZnCO₃.
- ii. This is the result when you have a salt that breaks up into three ions, either two cations and one anion or one cation and two anions. Some examples are SrF₂, Hg₂I₂, and Ag₂SO₄.
- iii. This is the result when you have a salt that breaks up into four ions, either three cations and one anion (Ag₃PO₄) or one cation and three anions (ignoring the hydroxides, there are no examples of this type of salt in Table 8.5).
- iv. This is the result when you have a salt that breaks up into five ions, either three cations and two anions [Sr₃(PO₄)₂] or two cations and three anions (no examples of this type of salt are in Table 8.5).
149. a. The optimum pH for a buffer is when pH = pK_a. At this pH a buffer will have equal neutralization capacity for both added acid and base. As shown next, because the pK_a for TRISH⁺ is 8.1, the optimal buffer pH is about 8.1.

$$K_b = 1.19 \times 10^{-6}; \quad K_a = K_w/K_b = 8.40 \times 10^{-9}; \quad \text{p}K_a = -\log(8.40 \times 10^{-9}) = 8.076$$

$$\text{b. } \text{pH} = \text{pK}_a + \log \frac{[\text{TRIS}]}{[\text{TRISH}^+]}, \quad 7.00 = 8.076 + \log \frac{[\text{TRIS}]}{[\text{TRISH}^+]}$$

$$\frac{[\text{TRIS}]}{[\text{TRISH}^+]} = 10^{-1.08} = 0.083 \quad (\text{at pH} = 7.00)$$

$$9.00 = 8.076 + \log \frac{[\text{TRIS}]}{[\text{TRISH}^+]}, \quad \frac{[\text{TRIS}]}{[\text{TRISH}^+]} = 10^{0.92} = 8.3 \quad (\text{at pH} = 9.00)$$

$$\text{c. } \frac{50.0 \text{ g TRIS}}{2.0 \text{ L}} \times \frac{1 \text{ mol}}{121.14 \text{ g}} = 0.206 \text{ M} = 0.21 \text{ M} = [\text{TRIS}]$$

$$\frac{65.0 \text{ g TRISHCl}}{2.0 \text{ L}} \times \frac{1 \text{ mol}}{157.60 \text{ g}} = 0.206 \text{ M} = 0.21 \text{ M} = [\text{TRISHCl}] = [\text{TRISH}^+]$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{TRIS}]}{[\text{TRISH}^+]} = 8.076 + \log \frac{(0.21)}{(0.21)} = 8.08$$

The amount of H^+ added from HCl is: $(0.50 \times 10^{-3} \text{ L}) \times 12 \text{ mol/L} = 6.0 \times 10^{-3} \text{ mol H}^+$

The H^+ from HCl will convert TRIS into TRISH^+ . The reaction is:

	TRIS	+	H^+	→	TRISH ⁺	
Before	0.21 M		$\frac{6.0 \times 10^{-3}}{0.2005} = 0.030 \text{ M}$		0.21 M	
Change	-0.030		-0.030	→	+0.030	Reacts completely
After	0.18		0		0.24	

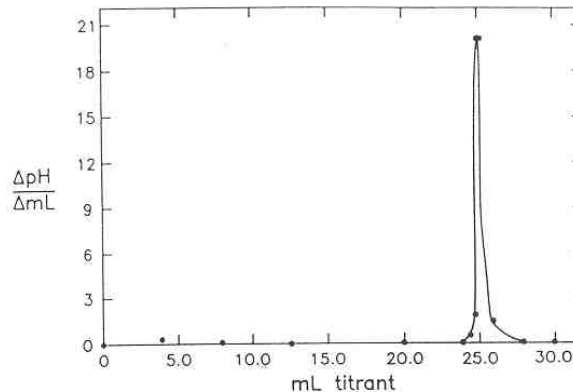
Now use the Henderson-Hasselbalch equation to solve this buffer problem.

$$\text{pH} = 8.076 + \log \left(\frac{0.18}{0.24} \right) = 7.95$$

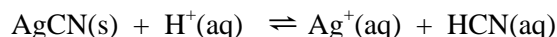
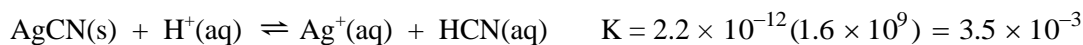
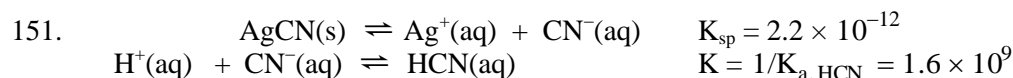
$$150. \quad \text{At 4.0 mL NaOH added: } \left| \frac{\Delta \text{pH}}{\Delta \text{mL}} \right| = \left| \frac{2.43 - 3.14}{0 - 4.0} \right| = 0.18$$

The other points are calculated in a similar fashion. The results are summarized and plotted on the following page. As can be seen from the plot, the advantage of this approach is that it is much easier to accurately determine the location of the equivalence point.

mL	pH	$ \Delta\text{pH}/\Delta\text{mL} $
0	2.43	—
4.0	3.14	0.18
8.0	3.53	0.098
12.5	3.86	0.073
20.0	4.46	0.080
24.0	5.24	0.20
24.5	5.6	0.7
24.9	6.3	2
25.0	8.28	20
25.1	10.3	20
26.0	11.30	1
28.0	11.75	0.23
30.0	11.96	0.11



Challenge Problems



Initial	1.0 M	0	0
	<i>s</i> mol/L AgCN(<i>s</i>) dissolves to reach equilibrium		
Equil.	1.0 - <i>s</i>	<i>s</i>	<i>s</i>

$$3.5 \times 10^{-3} = \frac{[\text{Ag}^+][\text{HCN}]}{[\text{H}^+]} = \frac{s(s)}{1.0 - s} \approx \frac{s^2}{1.0}, \quad s = 5.9 \times 10^{-2}$$

Assumption fails the 5% rule (*s* is 5.9% of 1.0 M). Using the method of successive approximations:

$$3.5 \times 10^{-3} = \frac{s^2}{1.0 - 0.059}, \quad s = 5.7 \times 10^{-2}$$

$$3.5 \times 10^{-3} = \frac{s^2}{1.0 - 0.057}, \quad s = 5.7 \times 10^{-2} \text{ (consistent answer)}$$

The molar solubility of AgCN(*s*) in 1.0 M H⁺ is 5.7×10^{-2} mol/L.

152. a. V_1 corresponds to the titration reaction of $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$; V_2 corresponds to the titration reaction of $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3$.

Here, there are two sources of HCO_3^- : NaHCO₃ and the titration of Na₂CO₃, so $V_2 > V_1$.

- b. V_1 corresponds to two titration reactions: $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$ and $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$.

V_2 corresponds to just one titration reaction: $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3$.

Here, $V_1 > V_2$ due to the presence of OH^- , which is titrated in the V_1 region.

- c. $0.100 \text{ mmol HCl/mL} \times 18.9 \text{ mL} = 1.89 \text{ mmol H}^+$; Because the first stoichiometric point only involves the titration of Na_2CO_3 by H^+ , 1.89 mmol of CO_3^{2-} has been converted into HCO_3^- . The sample contains $1.89 \text{ mmol Na}_2\text{CO}_3 \times 105.99 \text{ mg/mmol} = 2.00 \times 10^2 \text{ mg} = 0.200 \text{ g Na}_2\text{CO}_3$.

The second stoichiometric point involves the titration of HCO_3^- by H^+ .

$$\frac{0.100 \text{ mmol H}^+}{\text{mL}} \times 36.7 \text{ mL} = 3.67 \text{ mmol H}^+ = 3.67 \text{ mmol HCO}_3^-$$

1.89 mmol NaHCO_3 came from the first stoichiometric point of the Na_2CO_3 titration.

$3.67 - 1.89 = 1.78 \text{ mmol HCO}_3^-$ came from NaHCO_3 in the original mixture.

$$1.78 \text{ mmol NaHCO}_3 \times 84.01 \text{ mg NaHCO}_3/\text{mmol} = 1.50 \times 10^2 \text{ mg NaHCO}_3 = 0.150 \text{ g NaHCO}_3$$

$$\text{Mass \% Na}_2\text{CO}_3 = \frac{0.200 \text{ g}}{(0.200 + 0.150) \text{ g}} \times 100 = 57.1\% \text{ Na}_2\text{CO}_3$$

$$\text{Mass \% NaHCO}_3 = \frac{0.150 \text{ g}}{0.350 \text{ g}} \times 100 = 42.9\% \text{ NaHCO}_3$$

153. a. $200.0 \text{ mL} \times 0.250 \text{ mmol Na}_3\text{PO}_4/\text{mL} = 50.0 \text{ mmol Na}_3\text{PO}_4$

$$135.0 \text{ mL} \times 1.000 \text{ mmol HCl/mL} = 135.0 \text{ mmol HCl}$$

$$100.0 \text{ mL} \times 0.100 \text{ mmol NaCN/mL} = 10.0 \text{ mmol NaCN}$$

Let H^+ from the HCl react to completion with the bases in solution. In general, react the strongest base first and so on. Here, 110.0 mmol of HCl reacts to convert all CN^- to HCN and all PO_4^{3-} to H_2PO_4^- . At this point 10.0 mmol HCN, 50.0 mmol H_2PO_4^- , and 25.0 mmol HCl are in solution. The remaining HCl reacts completely with H_2PO_4^- , converting 25.0 mmol to H_3PO_4 . The final solution contains 25.0 mmol H_3PO_4 , $(50.0 - 25.0 =) 25.0 \text{ mmol H}_2\text{PO}_4^-$, and 10.0 mmol HCN. HCN ($K_a = 6.2 \times 10^{-10}$) is a much weaker acid than either H_3PO_4 ($K_{a1} = 7.5 \times 10^{-3}$) or H_2PO_4^- ($K_{a2} = 6.2 \times 10^{-8}$), so ignore it. We have a buffer solution. Principal equilibrium reaction is:



Initial	25.0 mmol/435.0 mL	0	25.0/435.0
Equil.	$0.0575 - x$	x	$0.0575 + x$

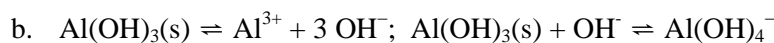
$$K_{a_1} = 7.5 \times 10^{-3} = \frac{x(0.0575 + x)}{0.0575 - x}; \text{ normal assumptions don't hold here.}$$

Using the quadratic formula and carrying extra sig. figs.:

$$x^2 + (0.0650)x - 4.31 \times 10^{-4} = 0, \quad x = 0.0061 \text{ M} = [\text{H}^+]; \quad \text{pH} = 2.21$$

b. $[\text{HCN}] = \frac{10.0 \text{ mmol}}{435.0 \text{ mL}} = 2.30 \times 10^{-2} \text{ M}$; HCN dissociation will be minimal.

154. a. In very acidic solutions, the reaction that occurs to increase the solubility is $\text{Al}(\text{OH})_3(\text{s}) + 3\text{H}^+ \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$. In very basic solutions, the reaction that occurs to increase solubility is $\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow \text{Al}(\text{OH})_4^-(\text{aq})$.



$$S = \text{solubility} = \text{total Al}^{3+} \text{ concentration} = [\text{Al}^{3+}] + [\text{Al}(\text{OH})_4^-]$$

$$[\text{Al}^{3+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^3} = K_{\text{sp}} \times \frac{[\text{H}^+]^3}{K_{\text{w}}^3}, \text{ because } [\text{OH}^-]^3 = (K_{\text{w}}/[\text{H}^+])^3$$

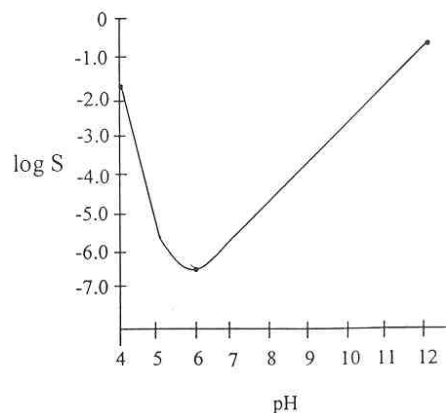
$$\frac{[\text{Al}(\text{OH})_4^-]}{[\text{OH}^-]} = K; \quad [\text{OH}^-] = \frac{K_{\text{w}}}{[\text{H}^+]}; \quad [\text{Al}(\text{OH})_4^-] = K[\text{OH}^-] = \frac{KK_{\text{w}}}{[\text{H}^+]}$$

$$S = [\text{Al}^{3+}] + [\text{Al}(\text{OH})_4^-] = [\text{H}^+]^3 K_{\text{sp}}/K_{\text{w}}^3 + KK_{\text{w}}/[\text{H}^+]$$

c. $K_{\text{sp}} = 2 \times 10^{-32}$; $K_{\text{w}} = 1.0 \times 10^{-14}$; $K = 40.0$

$$S = \frac{[\text{H}^+]^3 (2 \times 10^{-32})}{(1.0 \times 10^{-14})^3} + \frac{40.0(1.0 \times 10^{-14})}{[\text{H}^+]} = [\text{H}^+]^3 (2 \times 10^{10}) + \frac{4.0 \times 10^{-13}}{[\text{H}^+]}$$

pH	solubility (S, mol/L)	log S
4.0	2×10^{-2}	-1.7
5.0	2×10^{-5}	-4.7
6.0	4.2×10^{-7}	-6.38
7.0	4.0×10^{-6}	-5.40
8.0	4.0×10^{-5}	-4.40
9.0	4.0×10^{-4}	-3.40
10.0	4.0×10^{-3}	-2.40
11.0	4.0×10^{-2}	-1.40
12.0	4.0×10^{-1}	-0.40



As expected, the solubility of $\text{Al}(\text{OH})_3(\text{s})$ is increased by very acidic solutions and by very basic solutions.

$$155. \quad \text{mmol HC}_3\text{H}_5\text{O}_2 \text{ present initially} = 45.0 \text{ mL} \times \frac{0.750 \text{ mmol}}{\text{mL}} = 33.8 \text{ mmol HC}_3\text{H}_5\text{O}_2$$

$$\text{mmol C}_3\text{H}_5\text{O}_2^- \text{ present initially} = 55.0 \text{ mL} \times \frac{0.700 \text{ mmol}}{\text{mL}} = 38.5 \text{ mmol C}_3\text{H}_5\text{O}_2^-$$

The initial pH of the buffer is:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = -\log(1.3 \times 10^{-5}) + \log \frac{\frac{38.5 \text{ mmol}}{100.0 \text{ mL}}}{\frac{33.8 \text{ mmol}}{100.0 \text{ mL}}} = 4.89 + \log \frac{38.5}{33.8} = 4.95$$

Note: Because the buffer components are in the same volume of solution, we can use the mole (or millimole) ratio in the Henderson-Hasselbalch equation to solve for pH instead of using the concentration ratio of $[\text{C}_3\text{H}_5\text{O}_2^-]/[\text{HC}_3\text{H}_5\text{O}_2]$. The total volume always cancels for buffer solutions.

When NaOH is added, the pH will increase, and the added OH^- will convert $\text{HC}_3\text{H}_5\text{O}_2$ into $\text{C}_3\text{H}_5\text{O}_2^-$. The pH after addition of OH^- increases by 2.5%, so the resulting pH is:

$$4.95 + 0.025(4.95) = 5.07$$

At this pH, a buffer solution still exists, and the millimole ratio between $\text{C}_3\text{H}_5\text{O}_2^-$ and $\text{HC}_3\text{H}_5\text{O}_2$ is:

$$\text{pH} = \text{pK}_a + \log \frac{\text{mmol C}_3\text{H}_5\text{O}_2^-}{\text{mmol HC}_3\text{H}_5\text{O}_2}, \quad 5.07 = 4.89 + \log \frac{\text{mmol C}_3\text{H}_5\text{O}_2^-}{\text{mmol HC}_3\text{H}_5\text{O}_2}$$

$$\frac{\text{mmol C}_3\text{H}_5\text{O}_2^-}{\text{mmol HC}_3\text{H}_5\text{O}_2} = 10^{0.18} = 1.5$$

Let x = mmol OH^- added to increase pH to 5.07. Because OH^- will essentially react to completion with $\text{HC}_3\text{H}_5\text{O}_2$, the setup to the problem using millimoles is:

	$\text{HC}_3\text{H}_5\text{O}_2$	+	OH^-	→	$\text{C}_3\text{H}_5\text{O}_2^-$	
Before	33.8 mmol		x mmol		38.5 mmol	
Change	$-x$		$-x$	→	$+x$	Reacts completely
After	$33.8 - x$		0		$38.5 + x$	

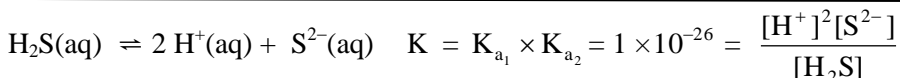
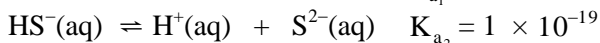
$$\frac{\text{mmol C}_3\text{H}_5\text{O}_2^-}{\text{mmol HC}_3\text{H}_5\text{O}_2} = 1.5 = \frac{38.5 + x}{33.8 - x}, \quad 1.5(33.8 - x) = 38.5 + x, \quad x = 4.9 \text{ mmol OH}^- \text{ added}$$

The volume of NaOH necessary to raise the pH by 2.5% is:

$$4.9 \text{ mmol NaOH} \times \frac{1 \text{ mL}}{0.10 \text{ mmol NaOH}} = 49 \text{ mL}$$

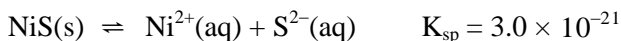
49 mL of 0.10 M NaOH must be added to increase the pH by 2.5%.

156. $K_{\text{sp}} = [\text{Ni}^{2+}][\text{S}^{2-}] = 3 \times 10^{-21}$



Because K is very small, only a tiny fraction of the H_2S will react. At equilibrium, $[\text{H}_2\text{S}] = 0.10 \text{ M}$ and $[\text{H}^+] = 1 \times 10^{-3}$.

$$[\text{S}^{2-}] = \frac{K[\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{(1 \times 10^{-26})(0.10)}{(1 \times 10^{-3})^2} = 1 \times 10^{-21} \text{ M}$$



Precipitation of NiS will occur when $Q > K_{\text{sp}}$. We will calculate $[\text{Ni}^{2+}]$ for $Q = K_{\text{sp}}$.

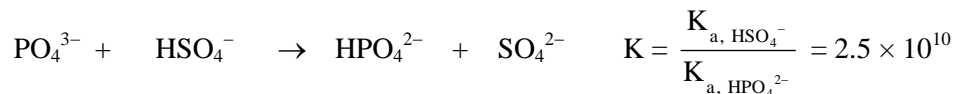
$$Q = K_{\text{sp}} = [\text{Ni}^{2+}][\text{S}^{2-}] = 3.0 \times 10^{-21}, \quad [\text{Ni}^{2+}] = \frac{3.0 \times 10^{-21}}{1 \times 10^{-21}} = 3 \text{ M} = \text{maximum concentration}$$

157. Major species PO_4^{3-} , H^+ , HSO_4^- , H_2O , and Na^+ ; let the best base (PO_4^{3-}) react with the best acid (H^+). Assume the reaction goes to completion because H^+ is reacting. Note that the concentrations are halved when equal volumes of the two reagents are mixed.



Before	0.25 M	0.050 M	0
After	0.20 M	0	0.050 M

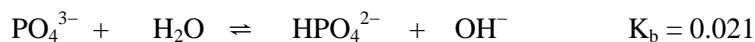
Major species: PO_4^{3-} , HPO_4^{2-} , HSO_4^- , H_2O , and Na^+ ; react the best base (PO_4^{3-}) with the best acid (HSO_4^-). Because K for this reaction is very large, assume the reaction goes to completion.



Before	0.20 M	0.050 M	0.050 M	0
After	0.15 M	0	0.100 M	0.050 M

Major species: PO_4^{3-} , HPO_4^{2-} , SO_4^{2-} (a very weak base with $K_{\text{b}} = 8.3 \times 10^{-13}$), H_2O , and Na^+ ; because the best base present (PO_4^{3-}) and best acid present (HPO_4^{2-}) are conjugate acid-base pairs, a buffer solution exists. Because K_{b} for PO_4^{3-} is a relatively large value ($K_{\text{b}} = K_{\text{w}}/K_{\text{a}, \text{HPO}_4^{2-}} = 0.021$), the usual assumptions that the amount of base that reacts to each

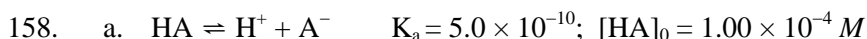
equilibrium is negligible compared with the initial concentration of base will not hold. Solve exactly using the K_b reaction for PO_4^{3-} .



Initial	0.15 M		0.100 M	0
Change	-x	→	+x	+x
Equil.	0.15 - x		0.100 + x	x

$$K_b = 0.021 = \frac{(0.100 + x)(x)}{0.15 - x}; \text{ using quadratic equation:}$$

$$x = [\text{OH}^-] = 0.022 \text{ M}; \text{ pOH} = 1.66; \text{ pH} = 12.34$$

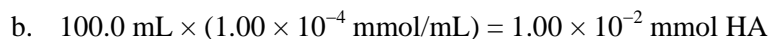


Because this is a dilute solution of a very weak acid, H_2O cannot be ignored as a source of H^+ .

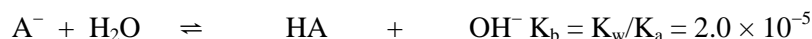
$$\text{From Section 7.9 of text, try: } [\text{H}^+] = (K_a[\text{HA}]_0 + K_w)^{1/2} = 2.4 \times 10^{-7} \text{ M}; \text{ pH} = 6.62$$

Check assumption:

$$\frac{[\text{H}^+]^2 - K_w}{[\text{H}^+]} = 2.0 \times 10^{-7} \ll 1.0 \times 10^{-4}; \text{ assumption good. pH} = 6.62$$



$5.00 \text{ mL} \times (1.00 \times 10^{-3} \text{ mmol/mL}) = 5.00 \times 10^{-3} \text{ mmol NaOH}$ added; let OH^- react completely with HA. After reaction, $5.0 \times 10^{-3} \text{ mmol HA}$ and $5.00 \times 10^{-3} \text{ mmol A}^-$ are in 105.0 mL. $[\text{A}^-]_0 = [\text{HA}]_0 = 5.00 \times 10^{-3} \text{ mmol}/105.0 \text{ mL} = 4.76 \times 10^{-5} \text{ M}$



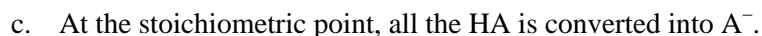
Initial	$4.76 \times 10^{-5} \text{ M}$		$4.76 \times 10^{-5} \text{ M}$	0
Equil.	$4.76 \times 10^{-5} - x$		$4.76 \times 10^{-5} + x$	x

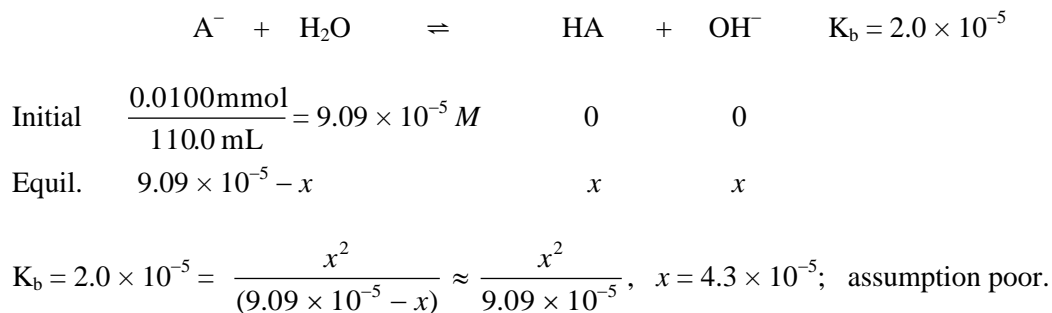
$$K_b = 2.0 \times 10^{-5} = \frac{(4.76 \times 10^{-5} + x)x}{(4.76 \times 10^{-5} - x)}; \text{ x will not be small compared to } 4.76 \times 10^{-5}.$$

Using the quadratic formula and carrying extra sig. figs.:

$$x^2 + (6.76 \times 10^{-5})x - 9.52 \times 10^{-10} = 0$$

$$x = [\text{OH}^-] = 1.2 \times 10^{-5} \text{ M}; \text{ pOH} = 4.92; \text{ pH} = 9.08$$

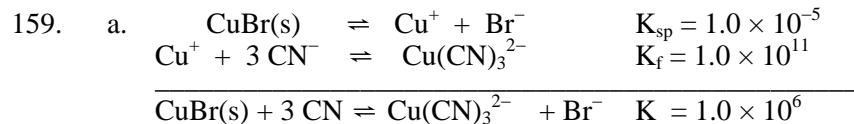




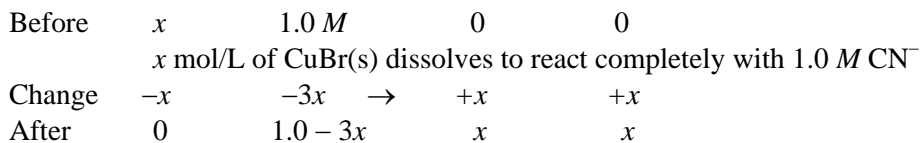
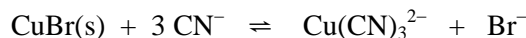
Using the quadratic formula and carrying extra sig. figs.:

$$x^2 + (2.0 \times 10^{-5})x - (1.82 \times 10^{-9}) = 0, \quad x = 3.4 \times 10^{-5} M = [\text{OH}^-]$$

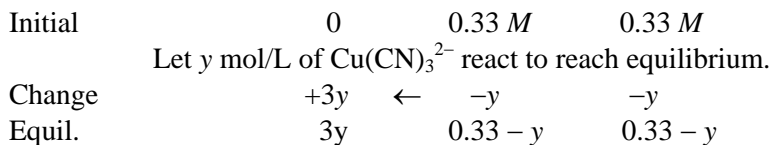
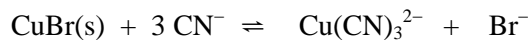
pOH = 4.47; pH = 9.53; assumption to ignore H₂O contribution to OH⁻ is good.



Because K is large, assume that enough CuBr(s) dissolves to completely use up the 1.0 M CN⁻; then solve the back equilibrium problem to determine the equilibrium concentrations.



For reaction to go to completion, $1.0 - 3x = 0$ and $x = 0.33$ mol/L. Now solve the back equilibrium problem.



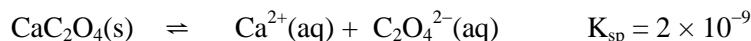
$$K = 1.0 \times 10^6 = \frac{(0.33 - y)^2}{(3y)^3} \approx \frac{(0.33)^2}{27y^3}, \quad y = 1.6 \times 10^{-3} M; \quad \text{assumptions good.}$$

Of the initial 1.0 M CN⁻, only $3(1.6 \times 10^{-3}) = 4.8 \times 10^{-3} M$ is present at equilibrium. Indeed, enough CuBr(s) did dissolve to essentially remove the initial 1.0 M CN⁻. This amount, 0.33 mol/L, is the solubility of CuBr(s) in 1.0 M NaCN.

$$\text{b. } [\text{Br}^-] = 0.33 - y = 0.33 - 1.6 \times 10^{-3} = 0.33 \text{ M}$$

$$\text{c. } [\text{CN}^-] = 3y = 3(1.6 \times 10^{-3}) = 4.8 \times 10^{-3} \text{ M}$$

160. Solubility in pure water:

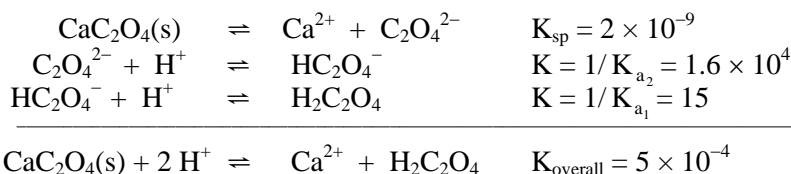


$$\text{Initial} \quad s = \text{solubility (mol/L)} \quad 0 \quad 0$$

$$\text{Equil.} \quad s \quad s$$

$$K_{\text{sp}} = s^2 = 2 \times 10^{-9}, \quad s = \text{solubility} = 4.47 \times 10^{-5} = 4 \times 10^{-5} \text{ mol/L}$$

Solubility in 0.10 M H⁺:



$$\text{Initial} \quad 0.10 \text{ M} \quad 0 \quad 0$$

s mol/L of CaC₂O₄(s) dissolves to reach equilibrium

$$\text{Equil.} \quad 0.10 - 2s \quad s \quad s$$

$$5 \times 10^{-4} = \frac{s^2}{(0.10 - 2s)^2}, \quad \frac{s}{0.10 - 2s} = (5 \times 10^{-4})^{1/2}, \quad s = 2 \times 10^{-3} \text{ mol/L}$$

$$\frac{\text{Solubility in } 0.10 \text{ M H}^+}{\text{Solubility in pure water}} = \frac{2 \times 10^{-3} \text{ mol/L}}{4 \times 10^{-5} \text{ mol/L}} = 50$$

CaC₂O₄(s) is 50 times more soluble in 0.10 M H⁺ than in pure water. This increase in solubility is due to the weak base properties of C₂O₄²⁻.

161. H₃A: pK_{a1} = 3.00, pK_{a2} = 7.30, pK_{a3} = 11.70

The pH at the second stoichiometric point is:

$$\text{pH} = \frac{\text{pK}_{\text{a}_2} + \text{pK}_{\text{a}_3}}{2} = \frac{7.30 + 11.70}{2} = 9.50$$

Thus to reach a pH of 9.50, we must go to the second stoichiometric point. 100.0 mL × 0.0500 M = 5.00 mmol H₃A initially. To reach the second stoichiometric point, we need 10.0 mmol OH⁻ = 1.00 mmol/mL × V_{NaOH}. Solving for V_{NaOH}:

$$V_{\text{NaOH}} = 10.0 \text{ mL (to reach pH} = 9.50)$$

pH = 4.00 is between the first halfway point to equivalence ($\text{pH} = \text{pK}_{a_1} = 3.00$) and the first stoichiometric point ($\text{pH} = \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} = 5.15$).

This is the buffer region controlled by $\text{H}_3\text{A} \rightleftharpoons \text{H}_2\text{A}^- + \text{H}^+$.

$$\text{pH} = \text{pK}_{a_1} + \log \frac{[\text{H}_2\text{A}^-]}{[\text{H}_3\text{A}]}, \quad 4.00 = 3.00 + \log \frac{[\text{H}_2\text{A}^-]}{[\text{H}_3\text{A}]}, \quad \frac{[\text{H}_2\text{A}^-]}{[\text{H}_3\text{A}]} = 10.$$

Because both species are in the same volume, the mole ratio also equals 10. Let $n = \text{mmol}$:

$$\frac{n_{\text{H}_2\text{A}^-}}{n_{\text{H}_3\text{A}}} = 10. \text{ and } n_{\text{H}_2\text{A}^-} + n_{\text{H}_3\text{A}} = 5.00 \text{ mmol (mole balance)}$$

$$11n_{\text{H}_3\text{A}} = 5.00, \quad n_{\text{H}_3\text{A}} = 0.45 \text{ mmol}; \quad n_{\text{H}_2\text{A}^-} = 4.55 \text{ mmol}$$

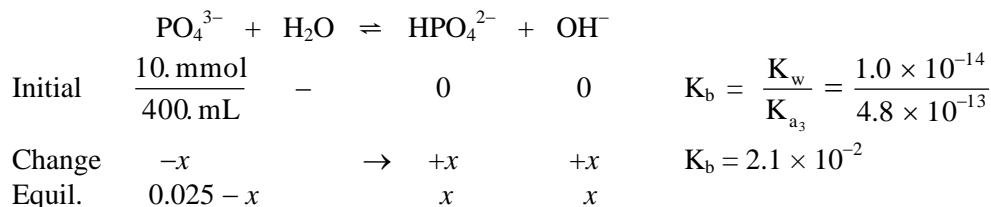
We need to add 4.55 mmol OH^- to get 4.55 mmol H_2A^- from the original H_3A present.

$$4.55 \text{ mmol} = 1.00 \text{ mmol/mL} \times V_{\text{NaOH}}, \quad V_{\text{NaOH}} = 4.55 \text{ mL of NaOH (to reach pH} = 4.00)$$

Note: Normal buffer assumptions are good.

162. a. At the third halfway point, $\text{pH} = \text{pK}_{a_3} = -\log(4.8 \times 10^{-13}) = 12.32$.

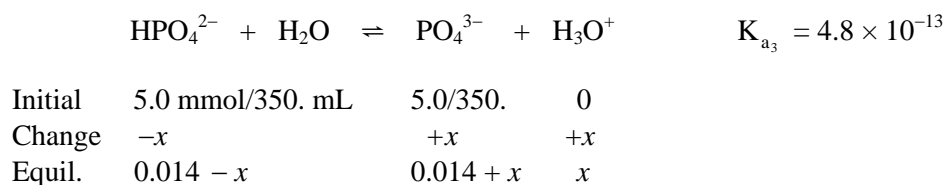
b. At third equivalence point, the reaction is:



$$\frac{x^2}{0.025 - x} = 2.1 \times 10^{-2}; \text{ using the quadratic equation:}$$

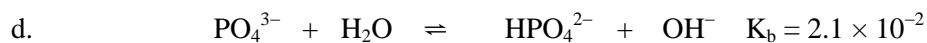
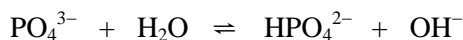
$$x = 1.5 \times 10^{-2} \text{ M} = [\text{OH}^-]; \quad \text{pOH} = 1.82; \quad \text{pH} = 12.18$$

b. The pH at the third halfway point must be more acidic (lower pH) than the pH at the third equivalence point. Therefore, the pH at the third halfway point cannot equal 12.32. In part a we assumed that x was negligible:



$$\frac{(0.014+x)(x)}{(0.014-x)} \approx \frac{(0.014)(x)}{(0.014)}, \quad x = 4.8 \times 10^{-13} M$$

This looks fine, but this is a situation where we must use the K_b reaction for the weak base PO_4^{3-} to solve for the pH. The $[\text{OH}^-]$ in solution is not negligible compared to 0.014 M , so the usual assumptions don't hold here. The usual buffer assumptions don't hold in very acidic or very basic solutions. In this very basic solution, we must use the K_b reaction and the quadratic equation:



Initial	0.014 M	–	0.014 M	0
Change	– x	–	+ x	+ x
Equil.	0.014 – x	–	0.014 + x	x

$$\frac{(0.014+x)(x)}{(0.014-x)} = 2.1 \times 10^{-2}; \text{ using the quadratic equation:}$$

$$x = [\text{OH}^-] = 7.0 \times 10^{-3} M; \quad \text{pOH} = 2.15; \quad \text{pH} = 11.85$$

This pH answer makes more sense because it is below the pH at the third equivalence point calculated in part b of this problem (pH = 12.18).

163. a. Best acid will react with the best base present, so the dominate equilibrium is:



Because initially $[\text{NH}_4^+]_0 = [\text{X}^-]_0$ and $[\text{NH}_3]_0 = [\text{HX}]_0 = 0$, at equilibrium $[\text{NH}_4^+] = [\text{X}^-]$ and $[\text{NH}_3] = [\text{HX}]$. Therefore:

$$K_{\text{eq}} = \frac{K_{\text{a}, \text{NH}_4^+}}{K_{\text{a}, \text{HX}}} = \frac{[\text{HX}]^2}{[\text{X}^-]^2}$$

The K_a expression for HX is: $K_{\text{a}, \text{HX}} = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$, $\frac{[\text{HX}]}{[\text{X}^-]} = \frac{[\text{H}^+]}{K_{\text{a}, \text{HX}}}$

Substituting into the K_{eq} expression: $K_{\text{eq}} = \frac{K_{\text{a}, \text{NH}_4^+}}{K_{\text{a}, \text{HX}}} = \frac{[\text{HX}]^2}{[\text{X}^-]^2} = \left(\frac{[\text{H}^+]}{K_{\text{a}, \text{HX}}} \right)^2$

Rearranging: $[\text{H}^+]^2 = K_{\text{a}, \text{NH}_4^+} \times K_{\text{a}, \text{HX}}$, or taking the $-\log$ of both sides:

$$\text{pH} = \frac{\text{p}K_{\text{a, NH}_4^+} + \text{p}K_{\text{a, HX}}}{2}$$

b. Ammonium formate = $\text{NH}_4(\text{HCO}_2)$

$$K_{\text{a, NH}_4^+} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}, \text{p}K_{\text{a}} = 9.25; K_{\text{a, HCO}_2\text{H}} = 1.8 \times 10^{-4}, \text{p}K_{\text{a}} = 3.74$$

$$\text{pH} = \frac{\text{p}K_{\text{a, NH}_4^+} + \text{p}K_{\text{a, HCO}_2\text{H}}}{2} = \frac{9.25 + 3.74}{2} = 6.50$$

Ammonium acetate = $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$; $K_{\text{a, HC}_2\text{H}_3\text{O}_2} = 1.8 \times 10^{-5}$; $\text{p}K_{\text{a}} = 4.74$

$$\text{pH} = \frac{9.25 + 4.74}{2} = 7.00$$

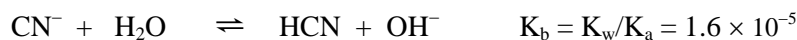
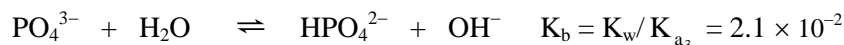
Ammonium bicarbonate = $\text{NH}_4(\text{HCO}_3)$; $K_{\text{a, H}_2\text{CO}_3} = 4.3 \times 10^{-7}$; $\text{p}K_{\text{a}} = 6.37$

$$\text{pH} = \frac{9.25 + 6.37}{2} = 7.81$$

c. $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{HC}_2\text{H}_3\text{O}_2(\text{aq})$

164. Major species: PO_4^{3-} , OH^- , H^+ , CN^- , Na^+ , K^+ , Cl^- , H_2O
 5.00 mmol 5.00 mmol 15.0 mmol 7.50 mmol

PO_4^{3-} and CN^- are weak bases.



One of the keys to this problem is to recognize that $\text{p}K_{\text{a}_2}$ for $\text{H}_3\text{PO}_4 = 7.21$ [$-\log(6.2 \times 10^{-8}) = 7.21$]. The K_{a_2} reaction for H_3PO_4 is:

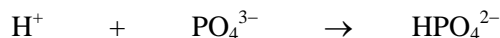


The pH of the final solution will equal 7.21 when we have a buffer solution with $[\text{H}_2\text{PO}_4^-] = [\text{HPO}_4^{2-}]$. Let's see what is in solution after we let the best acid and best base react. In each of the following reactions, something strong is reacting, so we assume the reactions go to completion. The first reaction to run to completion is $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$.



Before	15.0 mmol	5.00 mmol
After	10.0 mmol	0

The next best base present is PO_4^{3-} .



Before	10.0 mmol	5.00 mmol	0
After	5.0 mmol	0	5.00 mmol

The next best base present is CN^- .

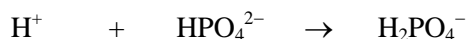


Before	5.0 mmol	7.50 mmol	0
After	0	2.5 mmol	5.0 mmol

We need to add 2.5 mmol H^+ to convert all the CN^- into HCN; then all that remains is 5.00 mmol HPO_4^{2-} and 7.5 mmol HCN (a very weak acid with $K_a = 6.2 \times 10^{-10}$). From here, we would need to add another 2.5 mmol H^+ in order to convert one-half the HPO_4^{2-} present into its conjugate acid so that $[\text{HPO}_4^{2-}] = [\text{H}_2\text{PO}_4^-]$ and $\text{pH} = \text{p}K_{a_2} = 7.21$. Adding 5.0 mmol H^+ to the original solution:



Before	5.0 mmol	2.5 mmol	5.0 mmol
After	2.5 mmol	0	7.5 mmol

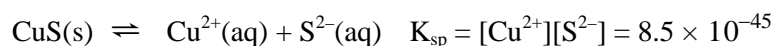


Before	2.5 mmol	5.00 mmol	0
After	0	2.5 mmol	2.5 mmol

After 5.0 mmol H^+ (HNO_3) is added to the original mixture, we are left with $[\text{HPO}_4^{2-}] = [\text{H}_2\text{PO}_4^-]$ so that $\text{pH} = \text{p}K_{a_2} = 7.21$. Note that HCN, with $K_a = 6.2 \times 10^{-10}$, is too weak of an acid to interfere with the $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffer.

$$\text{Volume HNO}_3 = 5.0 \text{ mmol HNO}_3 \times \frac{1 \text{ mL}}{0.100 \text{ mmol HNO}_3} = 50. \text{ mL HNO}_3$$

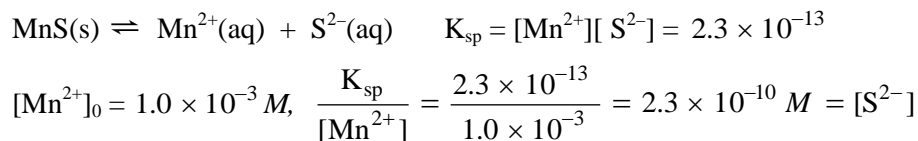
165. We need to determine $[\text{S}^{2-}]_0$ that will cause precipitation of CuS(s) but not MnS(s) . For CuS(s) :



$$[\text{Cu}^{2+}]_0 = 1.0 \times 10^{-3} \text{ M}, \quad \frac{K_{\text{sp}}}{[\text{Cu}^{2+}]_0} = \frac{8.5 \times 10^{-45}}{1.0 \times 10^{-3}} = 8.5 \times 10^{-42} \text{ M} = [\text{S}^{2-}]$$

This $[S^{2-}]$ represents the concentration that we must exceed to cause precipitation of CuS because if $[S^{2-}]_0 > 8.5 \times 10^{-42} M$, $Q > K_{sp}$.

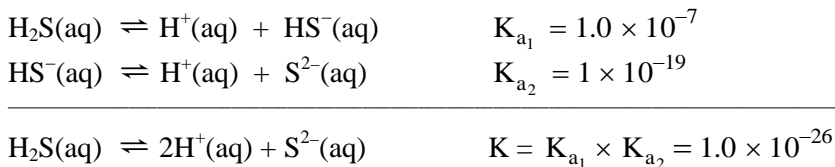
For $MnS(s)$:



This value of $[S^{2-}]$ represents the largest concentration of sulfide that can be present without causing precipitation of MnS . That is, for this value of $[S^{2-}]$, $Q = K_{sp}$, and no precipitation of MnS occurs. However, for any $[S^{2-}]_0 > 2.3 \times 10^{-10} M$, $MnS(s)$ will form.

We must have $[S^{2-}]_0 > 8.5 \times 10^{-42} M$ to precipitate CuS , but $[S^{2-}]_0 < 2.3 \times 10^{-10} M$ to prevent precipitation of MnS .

The question asks for a pH that will precipitate $CuS(s)$ but not $MnS(s)$. We need to first choose an initial concentration of S^{2-} that will do this. Let's choose $[S^{2-}]_0 = 1.0 \times 10^{-10} M$ because this will clearly cause $CuS(s)$ to precipitate but is still less than the $[S^{2-}]_0$ required for $MnS(s)$ to precipitate. The problem now is to determine the pH necessary for a $0.1 M H_2S$ solution to have $[S^{2-}] = 1.0 \times 10^{-10} M$. Let's combine the K_{a_1} and K_{a_2} equations for H_2S to determine the required $[H^+]$.

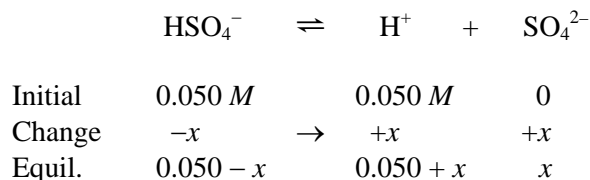


$$1 \times 10^{-26} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{[H^+]^2(1 \times 10^{-10})}{0.10}, \quad [H^+] = 3 \times 10^{-9} M$$

$pH = -\log(3 \times 10^{-9}) = 8.5$. So, if $pH = 8.5$, $[S^{2-}] = 1 \times 10^{-10} M$, which will cause precipitation of $CuS(s)$ but not $MnS(s)$.

Note: Any pH less than 8.7 would be a correct answer to this problem.

166. a. Major species: H^+ , HSO_4^- , $H_2C_6H_6O_6$, and H_2O ; HSO_4^- is the best acid, with H_2O as the best base.

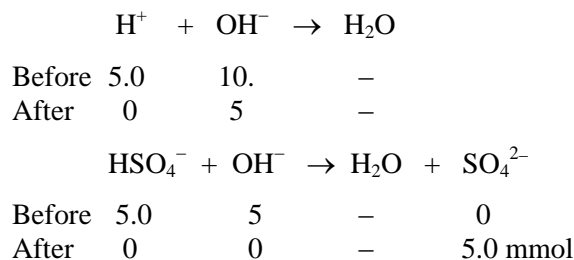


$$\frac{(0.050 + x)(x)}{(0.050 - x)} = 1.2 \times 10^{-2}; \text{ we must use the quadratic equation.}$$

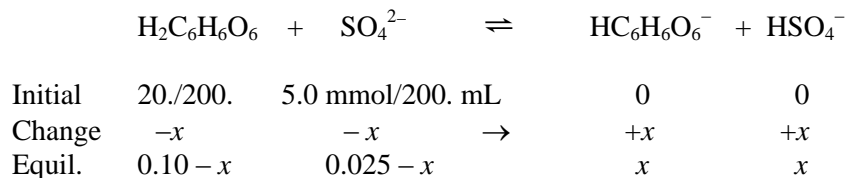
$$x = 8.5 \times 10^{-3} M, [\text{H}^+] = 0.050 + (8.5 \times 10^{-3}) = 5.85 \times 10^{-2} M, \text{pH} = 1.23$$

- b. Major species: H^+ , HSO_4^- , $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$, OH^- , Na^+ , H_2O
 5.0 mmol 5.0 mmol 20. mmol 10. mmol

React OH^- to completion. React the best base with the best acid.



After we have let OH^- react to completion, the best acid remaining is $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$, and the best base remaining is SO_4^{2-} . React these two together.



$$K = \frac{K_{a_1, \text{H}_2\text{C}_6\text{H}_6\text{O}_6}}{K_{a_2, \text{H}_2\text{SO}_4}} = 6.6 \times 10^{-3}; \frac{x^2}{(0.10 - x)(0.025 - x)} = 6.6 \times 10^{-3}$$

Using the quadratic equation, $x = 3.7 \times 10^{-3} M$.

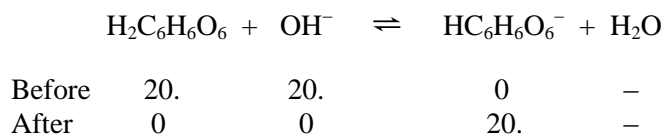
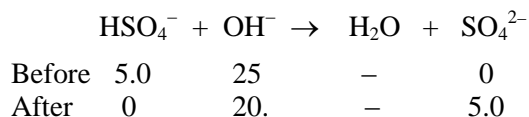
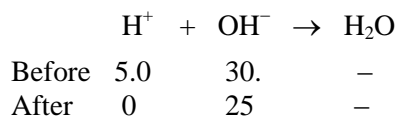
Use either K_{a_1} for $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$ or K_{a_2} for H_2SO_4 to calculate $[\text{H}^+]$.

$$\text{For example, } 7.9 \times 10^{-5} = \frac{[\text{H}^+][\text{HC}_6\text{H}_6\text{O}_6^-]}{[\text{H}_2\text{C}_6\text{H}_6\text{O}_6]} = \frac{[\text{H}^+](0.0037)}{(0.10 - 0.0037)}$$

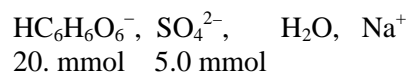
$$[\text{H}^+] = 2.1 \times 10^{-3} M, \text{pH} = 2.68$$

- c. Major species: H^+ , HSO_4^- , $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$, OH^- , Na^+ , H_2O
 5.0 mmol 5.0 mmol 20. mmol 30. mmol

React OH^- to completion first. React the best acid with the best base.



After we let all of the OH^- react completely, the major species are:



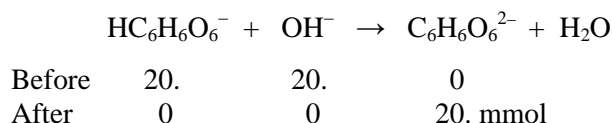
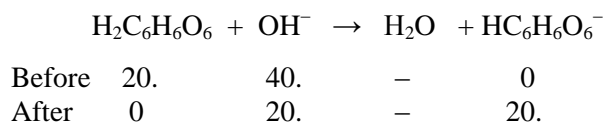
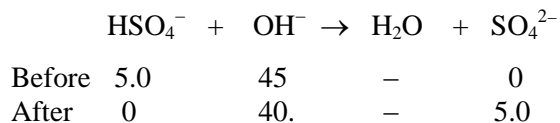
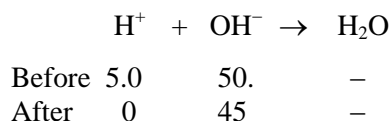
$\text{HC}_6\text{H}_6\text{O}_6^-$ is the best acid as well as the best base present (amphoteric species).

Dominant reaction: $\text{HC}_6\text{H}_6\text{O}_6^- + \text{HC}_6\text{H}_6\text{O}_6^- \rightleftharpoons \text{H}_2\text{C}_6\text{H}_6\text{O}_6 + \text{C}_6\text{H}_6\text{O}_6^{2-}$

$$\text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2} = \frac{4.10 + 11.80}{2} = 7.95$$

d. Major species: H^+ , HSO_4^- , $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$, OH^- , Na^+ , H_2O
 5.0 mmol 5.0 mmol 20. mmol 50. mmol

React OH^- first to completion. React the best acid with the best base.

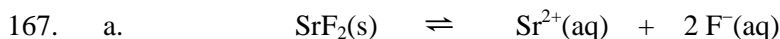


After all the OH^- reacts completely, we have a solution of the weak base $\text{C}_6\text{H}_6\text{O}_6^{2-}$ (SO_4^{2-} is a much weaker base than $\text{C}_6\text{H}_6\text{O}_6^{2-}$, so we can ignore it). Solving the weak base problem.

	$\text{C}_6\text{H}_6\text{O}_6^{2-}$	+	H_2O	\rightleftharpoons	$\text{HC}_6\text{H}_6\text{O}_6^-$	+	OH^-
Initial	20. mmol/600. mL				0		0
Change	$-x$			\rightarrow	$+x$		$+x$
Equil.	$0.033 - x$				x		x

$$K_b = \frac{K_w}{K_{a_2}} = 6.3 \times 10^{-3} = \frac{x^2}{0.033 - x}$$

Using the quadratic equation: $x = [\text{OH}^-] = 1.2 \times 10^{-2} \text{ M}$; $\text{pOH} = 1.92$, $\text{pH} = 12.08$



Initial	0	0
	$s \text{ mol/L SrF}_2$ dissolves to reach equilibrium	
Equil.	s	$2s$

$$[\text{Sr}^{2+}][\text{F}^-]^2 = K_{\text{sp}} = 7.9 \times 10^{-10} = 4s^3, \quad s = 5.8 \times 10^{-4} \text{ mol/L in pure water}$$

b. Greater, because some of the F^- would react with water:



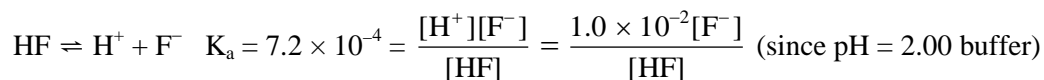
This lowers the concentration of F^- , forcing more SrF_2 to dissolve.



Let $s = \text{solubility} = [\text{Sr}^{2+}]$; then $2s = \text{total F}^- \text{ concentration}$.

Since F^- is a weak base, some of the F^- is converted into HF . Therefore:

$$\text{total F}^- \text{ concentration} = 2s = [\text{F}^-] + [\text{HF}]$$

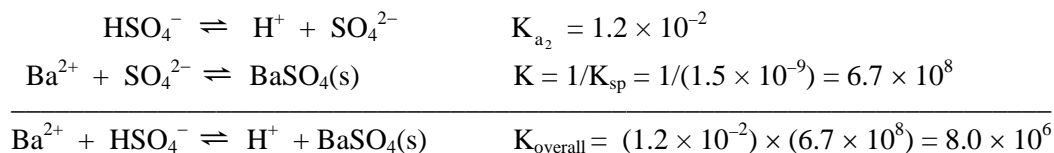


$$7.2 \times 10^{-2} = \frac{[\text{F}^-]}{[\text{HF}]}, \quad [\text{HF}] = 14[\text{F}^-]; \quad \text{Solving:}$$

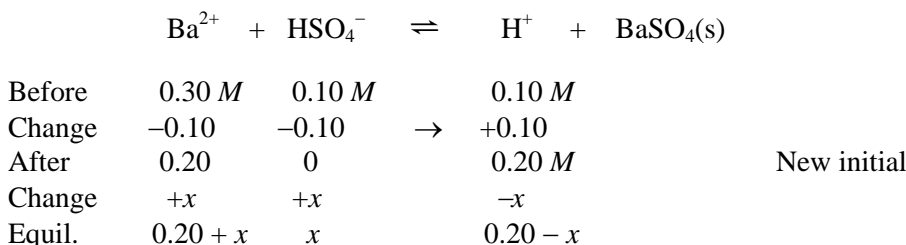
$$[\text{Sr}^{2+}] = s; \quad 2s = [\text{F}^-] + [\text{HF}] = [\text{F}^-] + 14[\text{F}^-], \quad 2s = 15[\text{F}^-], \quad [\text{F}^-] = 2s/15$$

$$K_{\text{sp}} = 7.9 \times 10^{-10} = [\text{Sr}^{2+}][\text{F}^-]^2 = (s) \left(\frac{2s}{15} \right)^2, \quad s = 3.5 \times 10^{-3} \text{ mol/L in pH} = 2.00 \text{ solution}$$

168. Major species: H^+ , HSO_4^- , Ba^{2+} , NO_3^- , and H_2O ; Ba^{2+} will react with the SO_4^{2-} produced from the K_a reaction for HSO_4^- .



Because K_{overall} is so large, the reaction essentially goes to completion. Because H_2SO_4 is a strong acid, $[\text{HSO}_4^-]_0 = [\text{H}^+]_0 = 0.10 \text{ M}$.



$$K = 8.0 \times 10^6 = \frac{0.20 - x}{(0.20 + x)x} \approx \frac{0.20}{0.20(x)}, \quad x = 1.3 \times 10^{-7} \text{ M}; \text{ assumptions good.}$$

$$[\text{H}^+] = 0.20 - 1.3 \times 10^{-7} = 0.20 \text{ M}; \quad \text{pH} = -\log(0.20) = 0.70$$

$$[\text{Ba}^{2+}] = 0.20 + 1.3 \times 10^{-7} = 0.20 \text{ M}$$

From the initial reaction essentially going to completion, 1.0 L(0.10 mol HSO_4^-/L) = 0.10 mol HSO_4^- reacted; this will produce 0.10 mol $\text{BaSO}_4(\text{s})$. Only 1.3×10^{-7} mol of this dissolves to reach equilibrium, so 0.10 mol $\text{BaSO}_4(\text{s})$ is produced.

$$0.10 \text{ mol BaSO}_4 \times \frac{233.4 \text{ g BaSO}_4}{\text{mol}} = 23 \text{ g BaSO}_4 \text{ produced}$$

169. For HOCl , $K_a = 3.5 \times 10^{-8}$ and $\text{p}K_a = -\log(3.5 \times 10^{-8}) = 7.46$. This will be a buffer solution because the pH is close to the $\text{p}K_a$ value.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{OCl}^-]}{[\text{HOCl}]}, \quad 8.00 = 7.46 + \log \frac{[\text{OCl}^-]}{[\text{HOCl}]}, \quad \frac{[\text{OCl}^-]}{[\text{HOCl}]} = 10^{0.54} = 3.5$$

1.00 L \times 0.0500 M = 0.0500 mol HOCl initially. Added OH^- converts HOCl into OCl^- . The total moles of OCl^- and HOCl must equal 0.0500 mol. Solving where n = moles:

$$n_{\text{OCl}^-} + n_{\text{HOCl}} = 0.0500 \text{ and } n_{\text{OCl}^-} = (3.5)n_{\text{HOCl}}$$

$$(4.5)n_{\text{HOCl}} = 0.0500, \quad n_{\text{HOCl}} = 0.011 \text{ mol}; \quad n_{\text{OCl}^-} = 0.039 \text{ mol}$$

Need to add 0.039 mol NaOH to produce 0.039 mol OCl^- .

$0.039 \text{ mol} = V \times 0.0100 \text{ M}$, $V = 3.9 \text{ L NaOH}$; *note*: Normal buffer assumptions hold.

170. $50.0 \text{ mL} \times 0.100 \text{ M} = 5.00 \text{ mmol H}_2\text{SO}_4$; $30.0 \text{ mL} \times 0.100 \text{ M} = 3.00 \text{ mmol HOCl}$

$25.0 \text{ mL} \times 0.200 \text{ M} = 5.00 \text{ mmol NaOH}$; $10.0 \text{ mL} \times 0.150 \text{ M} = 1.50 \text{ mmol KOH}$

$25.0 \text{ mL} \times 0.100 \text{ M} = 2.50 \text{ mmol Ba(OH)}_2 = 5.00 \text{ mmol OH}^-$; we've added 11.50 mmol OH^- total.

Let OH^- react completely with the best acid present (H_2SO_4).

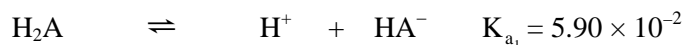
$10.00 \text{ mmol OH}^- + 5.00 \text{ mmol H}_2\text{SO}_4 \rightarrow 10.00 \text{ mmol H}_2\text{O} + 5.00 \text{ mmol SO}_4^{2-}$

OH^- still remains after reacting completely with H_2SO_4 . OH^- will then react with the next best acid (HOCl). The remaining 1.50 mmol OH^- will convert 1.50 mmol HOCl into 1.50 mmol OCl^- , resulting in a solution with 1.50 mmol OCl^- and $(3.00 - 1.50 =) 1.50 \text{ mmol HOCl}$. The major species at this point are HOCl , OCl^- , SO_4^{2-} , and H_2O plus cations that don't affect pH. SO_4^{2-} is an extremely weak base ($K_b = 8.3 \times 10^{-13}$). We have a buffer solution composed of HOCl and OCl^- . Because $[\text{HOCl}] = [\text{OCl}^-]$:

$[\text{H}^+] = K_a = 3.5 \times 10^{-8} \text{ M}$; $\text{pH} = 7.46$; assumptions good.

Marathon Problem

171. a. Because $K_{a_1} \gg K_{a_2}$, the amount of H^+ contributed by the K_{a_2} reaction will be negligible. The $[\text{H}^+]$ donated by the K_{a_1} reaction is $10^{-2.06} = 8.7 \times 10^{-3} \text{ M H}^+$.



Initial $[\text{H}_2\text{A}]_0$ ~ 0 0 $[\text{H}_2\text{A}]_0 = \text{initial concentration}$

Equil. $[\text{H}_2\text{A}]_0 - x$ x x

$$K_{a_1} = 5.90 \times 10^{-2} = \frac{x^2}{[\text{H}_2\text{A}]_0 - x} = \frac{(8.7 \times 10^{-3})^2}{[\text{H}_2\text{A}]_0 - 8.7 \times 10^{-3}}, \quad [\text{H}_2\text{A}]_0 = 1.0 \times 10^{-2} \text{ M}$$

$$\text{Mol H}_2\text{A present initially} = 0.250 \text{ L} \times \frac{1.0 \times 10^{-2} \text{ mol H}_2\text{A}}{\text{L}} = 2.5 \times 10^{-3} \text{ mol H}_2\text{A}$$

$$\text{Molar mass H}_2\text{A} = \frac{0.225 \text{ g H}_2\text{A}}{2.5 \times 10^{-3} \text{ mol H}_2\text{A}} = 90. \text{ g/mol}$$

b. $\text{H}_2\text{A} + 2 \text{ OH}^- \rightarrow \text{A}^{2-} + \text{H}_2\text{O}$; at the second equivalence point, the added OH^- has converted all the H_2A into A^{2-} , so A^{2-} is the major species present that determines the pH. The millimoles of A^{2-} present at the equivalence point equal the millimoles of H_2A present initially (2.5 mmol), and the millimoles of OH^- added to reach the second equivalence point are $2(2.5 \text{ mmol}) = 5.0 \text{ mmol OH}^-$ added. The only information we need

now in order to calculate the K_{a_2} value is the volume of Ca(OH)_2 added in order to reach the second equivalent point. We will use the K_{sp} value for Ca(OH)_2 to help solve for the volume of Ca(OH)_2 added.



Initial	$s = \text{solubility (mol/L)}$	0	~ 0
Equil.		s	$2s$

$$K_{sp} = 1.3 \times 10^{-6} = (s)(2s)^2 = 4s^3, \quad s = 6.9 \times 10^{-3} \text{ M Ca(OH)}_2; \quad \text{assumptions good.}$$

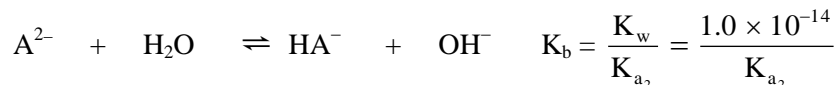
The volume of Ca(OH)_2 required to deliver 5.0 mmol OH^- (the amount of OH^- necessary to reach the second equivalence point) is:

$$\begin{aligned} 5.0 \text{ mmol OH}^- \times \frac{1 \text{ mmol Ca(OH)}_2}{2 \text{ mmol OH}^-} \times \frac{1 \text{ mL}}{6.9 \times 10^{-3} \text{ mmol Ca(OH)}_2} \\ = 362 \text{ mL} = 360 \text{ mL Ca(OH)}_2 \end{aligned}$$

At the second equivalence point, the total volume of solution is:

$$250. \text{ mL} + 360 \text{ mL} = 610 \text{ mL}$$

Now we can solve for K_{a_2} using the pH data at the second equivalence point. Because the only species present that has any effect on pH is the weak base A^{2-} , the setup to the problem requires the K_b reaction for A^{2-} .



Initial	$\frac{2.5 \text{ mmol}}{610 \text{ mmol}}$	0	0
Equil.	$4.1 \times 10^{-3} \text{ M} - x$	x	x

$$K_b = \frac{1.0 \times 10^{-14}}{K_{a_2}} = \frac{x^2}{4.1 \times 10^{-3} - x}$$

From the problem: $\text{pH} = 7.96$, so $[\text{OH}^-] = 10^{-6.04} = 9.1 \times 10^{-7} \text{ M} = x$

$$K_b = \frac{1.0 \times 10^{-14}}{K_{a_2}} = \frac{(9.1 \times 10^{-7})^2}{(4.1 \times 10^{-3}) - (9.1 \times 10^{-7})} = 2.0 \times 10^{-10}; \quad K_{a_2} = 5.0 \times 10^{-5}$$

Note: The amount of OH^- donated by the weak base HA^- will be negligible because the K_b value for A^{2-} is more than a 1000 times the K_b value for HA^- . In addition, because the pH is less than 8.0 at the second equivalence point, the amount of OH^- added by H_2O may need to be considered. Using the equation derived in Exercise 7.139, we get the same K_{a_2} value as calculated above by ignoring the OH^- contribution from H_2O .