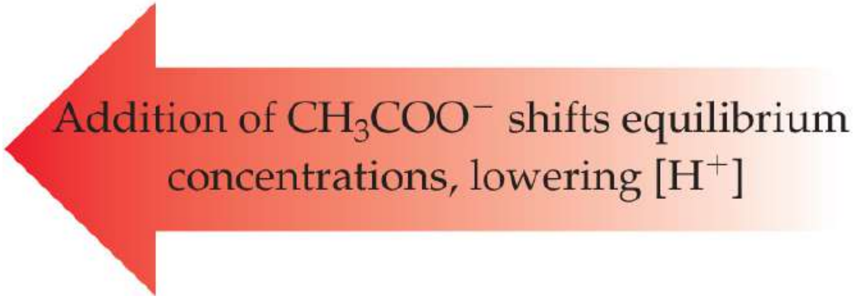
Chapter 17
Additional Aspects of Aqueous Equilibria

17.1 The Common Ion Effect

Effect of Acetate on the Acetic Acid Equilibrium

- Acetic acid is a weak acid:
- $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$
- Sodium acetate is a strong electrolyte:
- $NaCH_3COO(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq)$
- The presence of acetate from sodium acetate in an acetic acid solution will shift the equilibrium, according to LeChâtelier's Principle:
- $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$



Addition of CH_3COO^- shifts equilibrium concentrations, lowering $[H^+]$

The Common-Ion Effect

- “Whenever a weak electrolyte and a strong electrolyte containing a common ion are together in solution, the weak electrolyte ionizes less than it would if it were alone in solution.”
- This affects acid–base equilibria.
- We will also see (later in the chapter) how it affects solubility.

Sample Exercise 17.1

- What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?
- $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

1) $K_a = [H^+][CH_3COO^-]/[CH_3COOH] = 1.8 \times 10^{-5}$

2)

	$[CH_3COOH]$ (M)	$[H^+]$ (M)	$[CH_3COO^-]$ (M)
Initial Concentration (M)	0.30	0	0.30
Change in Concentration (M)	$-x$	$+x$	$+x$
Equilibrium Concentration (M)	$0.30 - x$	x	$0.30 + x$

Example (completed)

4) $1.8 \times 10^{-5} = (x)(0.30 + x)/(0.30 - x)$

Assume that adding or subtracting x from 0.30 will not change 0.30 enough to matter and the equation becomes

$1.8 \times 10^{-5} = (x)(0.30)/(0.30)$

which results in: $x = 1.8 \times 10^{-5} = [H^+]$

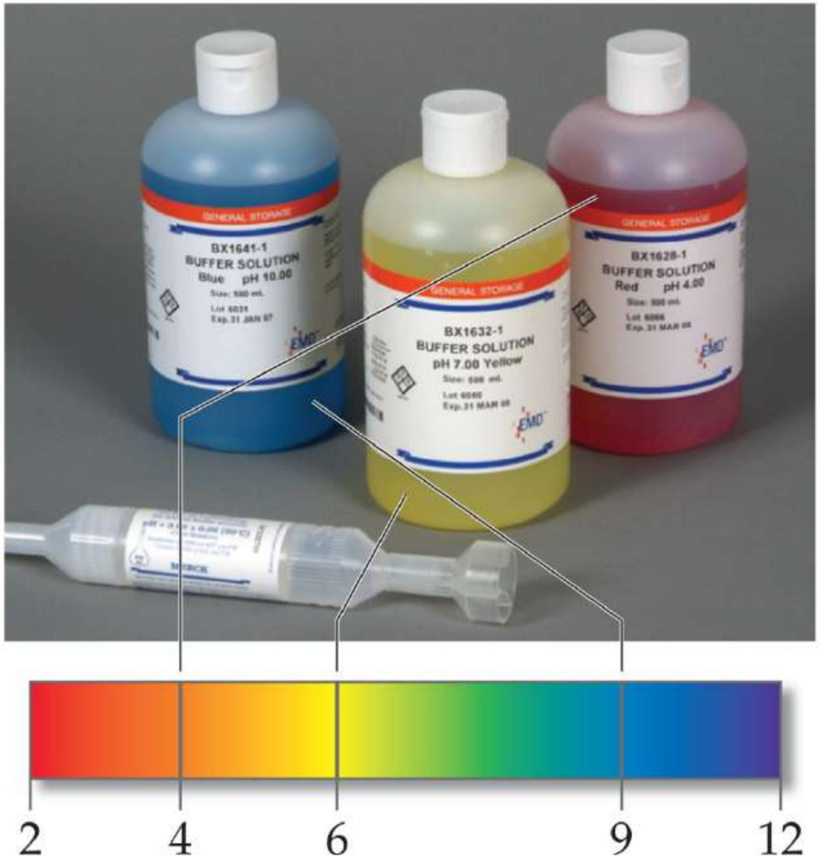
So: $\text{pH} = -\log[H^+] = 4.74$

17.1 Give It Some Thought

- If solutions of $NH_4Cl(aq)$ and $NH_3(aq)$ are mixed, which ions in the resulting solution are spectator ions in any acid-base chemistry occurring in the solution?
- What equilibrium reaction determines $[OH^-]$ and, therefore, the pH of the solution?

17.2 Buffered Solutions

Buffers



- Solutions of a weak conjugate acid–base pair that resist drastic changes in pH are called **buffers**.
- These solutions contain relatively high concentrations (10^{-3} *M* or more) of both the acid and base. Their concentrations are approximately equal.

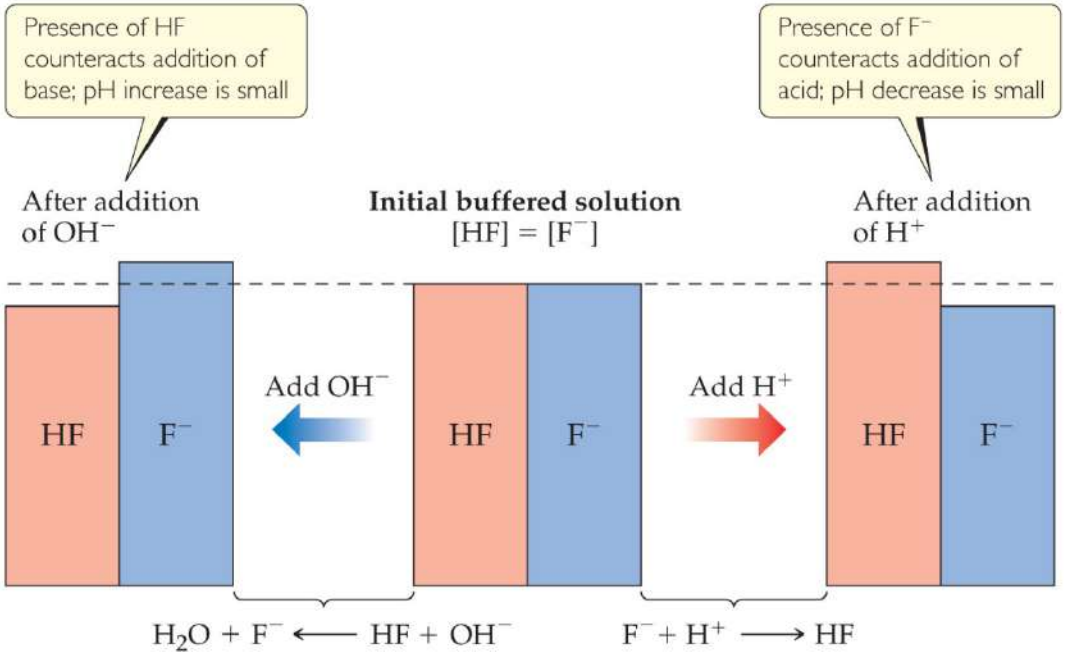
Ways to Make a Buffer

1) Mix a weak acid and a salt of its conjugate base or a weak base and a salt of its conjugate acid.
2) Add strong acid and partially neutralize a weak base or add strong base and partially neutralize a weak acid.

17.2 Give It Some Thought

- Which of the following conjugate acid-base pairs will not function as a buffer and explain:
  - C_2H_5COOH and $C_2H_5COO^-$
  - HCO_3^- and CO_3^{2-}
  - HNO_3 and NO_3^-

How a Buffer Works



- Adding a small amount of acid or base only slightly neutralizes one component of the buffer, so the pH doesn’t change much.

17.2 Give It Some Thought

- What happens when NaOH is added to a buffer composed of CH_3COOH and CH_3COO^-?
- What happens when HCl is added to this buffer?

Calculating the pH of a Buffer

- For a weak acid: $K_a = [H^+][A^-]/[HA]$
- Take –log of both sides:

$$-\log K_a = -\log[H^+] + -\log([A^-]/[HA])$$

- Rearrange:

$$-\log[H^+] = -\log K_a + \log([A^-]/[HA])$$

- Which is:

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

- This equation is known as the **Henderson–Hasselbalch equation**. This applies only to buffers.

Sample Exercise 17.3

What is the pH of a buffer that is 0.12 *M* in lactic acid, $CH_3CH(OH)COOH$, and 0.10 *M* in sodium lactate? K_a for lactic acid is 1.4×10^{-4}.

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

$= -\log(1.4 \times 10^{-4}) + \log[(0.10\ M)/(0.12\ M)]$

$= 3.85 + (-0.08) = 3.77$

Practice Exercise 1

If the pH of a buffer solution is equal to the pK_a of the acid in the buffer, what does this tell you about the relative concentrations of the acid and conjugate base forms of the buffer components?

(a) The acid concentration must be zero.

(b) The base concentration must be zero.

(c) The acid and base concentrations must be equal.

(d) The acid and base concentrations must be equal to the K_a.

(e) The base concentration must be 2.3 times as large as the acid concentration.

Practice Exercise 2

- Calculate the pH of a buffer composed of 0.12 *M* benzoic acid and 0.20 *M* sodium benzoate. The K_a of benzoic acid is 6.3 x 10^{-5}.

Practice Exercise 1

A buffer is made with sodium acetate (CH_3COONa) and acetic acid (CH_3COOH); the K_a for acetic acid is 1.80×10^{-5}. The pH of the buffer is 3.98. What is the ratio of the equilibrium concentration of sodium acetate to that of acetic acid?

(a) –0.760

(b) 0.174

(c) 0.840

(d) 5.75

(e) Not enough information is given.

Practice Exercise 2

Calculate the final, equilibrium pH of a buffer that initially contains 6.50×10^{-4} M HOCl and 7.50×10^{-4} M NaOCl. The K_a of HOCl is 3.0×10^{-5}.

Sample Exercise 17.5 Preparing a Buffer

How many moles of NH_4Cl must be added to 2.0 L of 0.10 *M* NH_3 to form a buffer whose pH is 9.00? (Assume that the addition of NH_4Cl does not change the volume of the solution.)

Practice Exercise 1

Calculate the number of grams of ammonium chloride that must be added to 2.00 L of a 0.500 *M* ammonia solution to obtain a buffer of pH = 9.20. Assume the volume of the solution does not change as the solid is added. K_b for ammonia is 1.80×10^{-5}.

(a) 60.7 g
(b) 30.4 g
(c) 1.52 g
(d) 0.568 g
(e) 1.59×10^{-5} g

Practice Exercise 2

Calculate the concentration of sodium benzoate that must be present in a 0.20 *M* solution of benzoic acid (C_6H_5COOH) to produce a pH of 4.00.

Buffer Capacity

- The amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree
- Using the Henderson–Hasselbalch equation, pH will be the same for a conjugate acid–base pair of 1 *M* each or 0.1 *M* each; however, the buffer which is 1 *M* can neutralize more acid or base before the pH changes.

pH Range

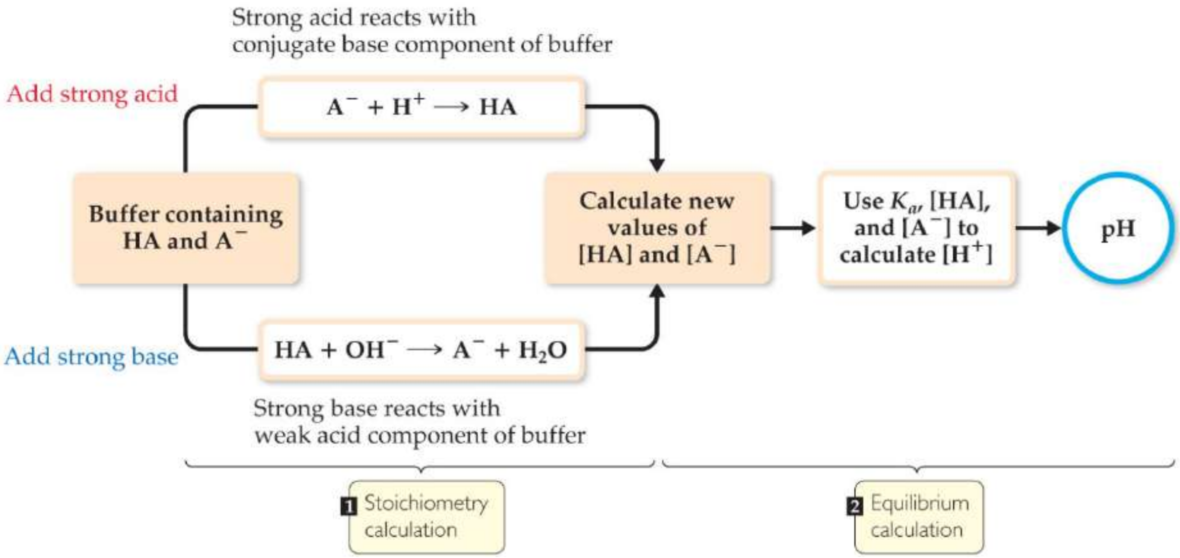
- The range of pH values over which a buffer system works effectively
- Optimal pH: where pH = pK_a([HA] = [A^-])
- If one concentration is more than 10 times the other, the buffering action is poor; this means that the pH range of a buffer is usually ±1 pH unit from pK_a.

17.2 Give It Some Thought

- The K_a values for nitrous acid (HNO_2) and hypochlorous (HClO) acid are 4.5×10^{-4} and 3.0×10^{-8}, respectively. Which one would be more suitable for use in a solution buffered at pH = 7.0? What other substances would be needed to make the buffer?

Addition of a Strong Acid or a Strong Base to a Buffer

1) Adding of the strong acid or base is a neutralization reaction; calculate like stoichiometry problem to find [HA] and $[A^-]$ when *all* of the added acid or base reacts.
2) Use the Henderson–Hasselbalch equation to find pH.



Strong acid reacts with conjugate base component of buffer

Add strong acid

$A^- + H^+ \longrightarrow HA$

Buffer containing HA and A^-

Calculate new values of [HA] and $[A^-]$

Use K_a, [HA], and $[A^-]$ to calculate $[H^+]$

pH

Add strong base

$HA + OH^- \longrightarrow A^- + H_2O$

Strong base reacts with weak acid component of buffer

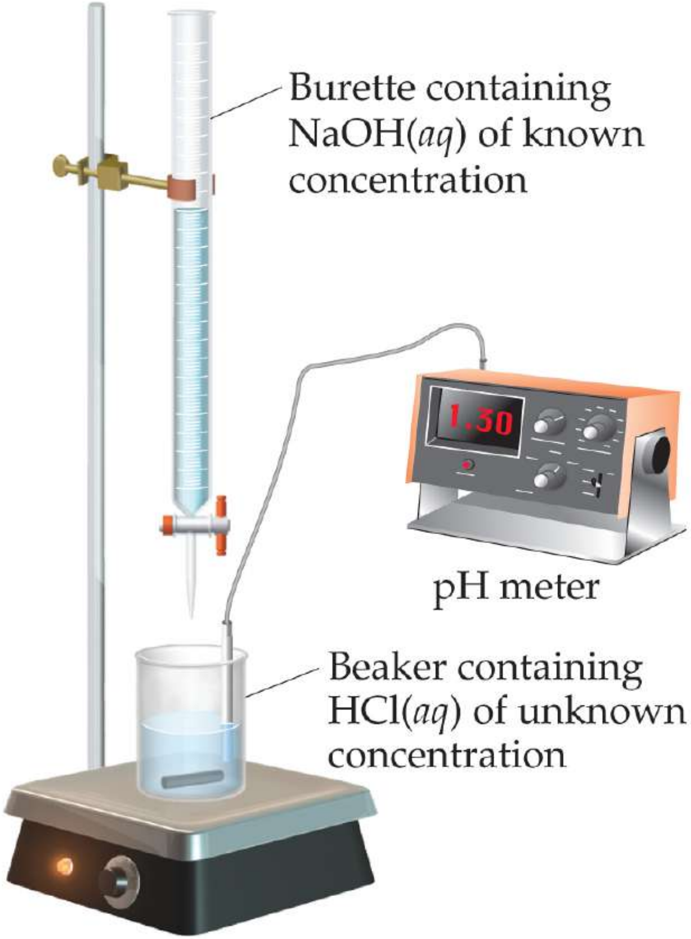
1 Stoichiometry calculation

2 Equilibrium calculation

17.3 Acid-Base Titrations

Titration

- In this technique, an acid (or base) solution of known concentration is slowly added to a base (or acid) solution of unknown concentration.
- A pH meter or indicators are used to determine when the solution has reached the **equivalence point**: The amount of acid equals that of base.



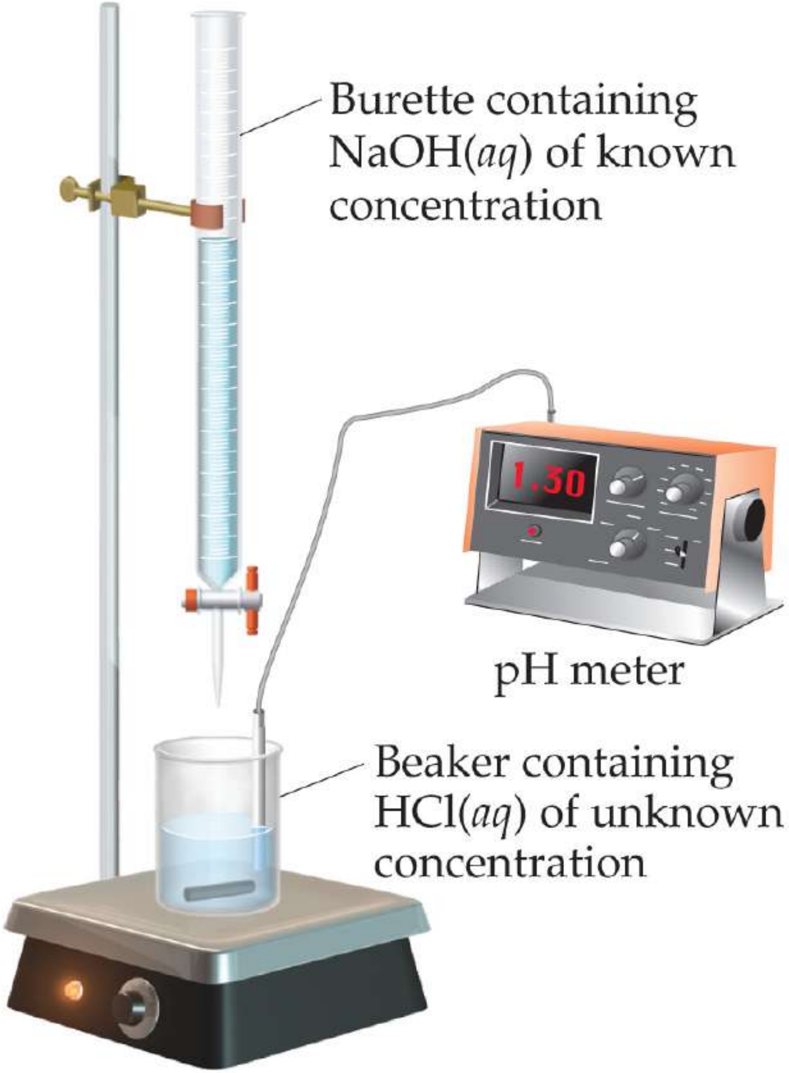
In which direction do you expect the pH to change as NaOH is added to the HCl solution?

a. No change

b. Increase

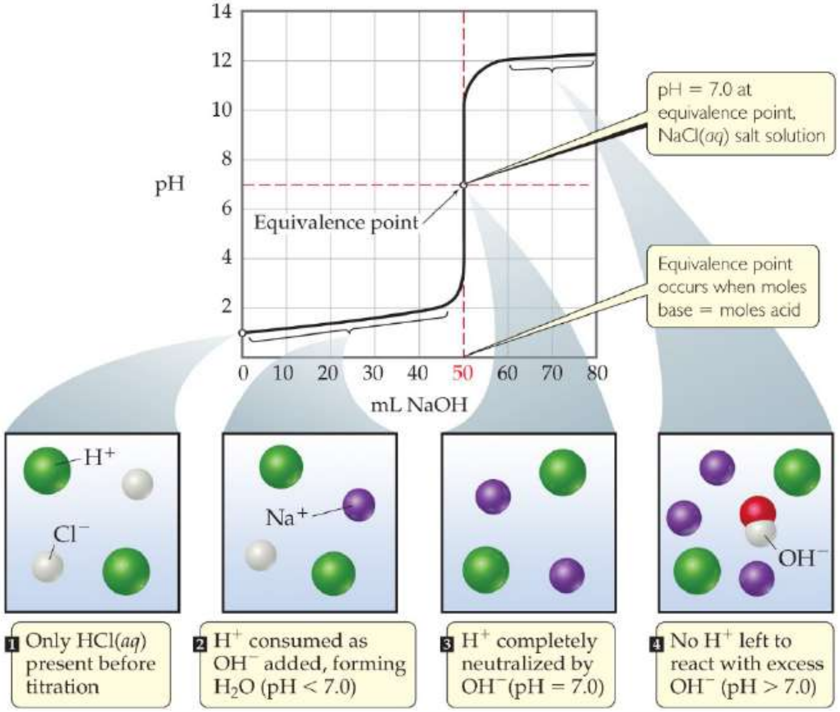
c. Decrease

d. Need volumes and molarities to answer the question



Titration of a Strong Acid with a Strong Base

- From the start of the titration to near the equivalence point, the pH goes up slowly.
- Just before (and after) the equivalence point, the pH rises rapidly.
- At the equivalence point, pH = 7.
- As more base is added, the pH again levels off.



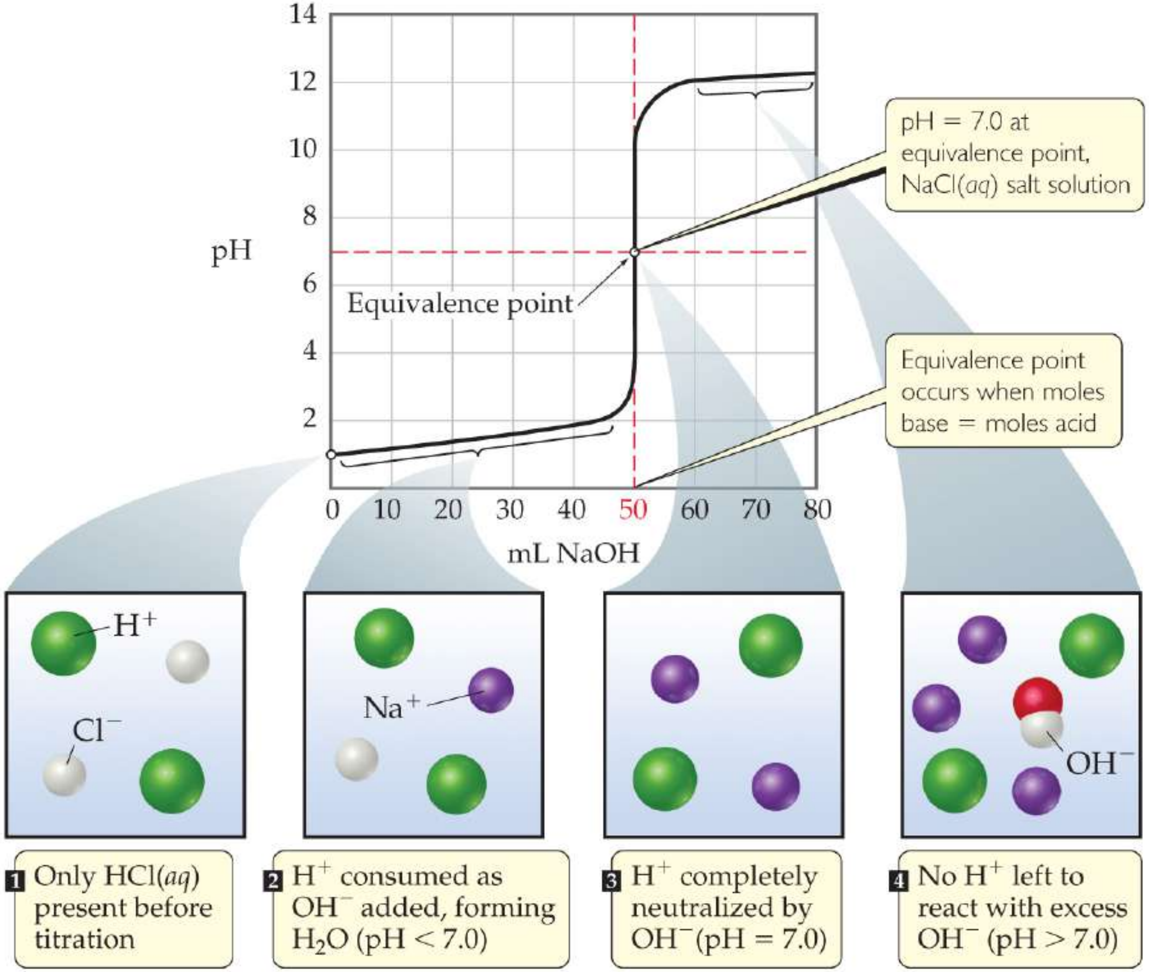
What volume of NaOH(*aq*) would be needed to reach the equivalence point if the concentration of the added base were 0.200 *M*?

a. 100.00 mL

b. 50.00 mL

c. 25.00 mL

d. 12.50 mL



Sample Exercise 17.7

Calculate the pH when **(a)** 49.0 mL and **(b)** 51.0 mL of 0.100 *M* NaOH solution have been added to 50.0 mL of 0.100 *M* HCl solution.

Practice Exercise 1

An acid–base titration is performed: 250.0 mL of an unknown concentration of HCl (*aq*) is titrated to the equivalence point with 36.7 mL of a 0.1000 *M* aqueous solution of NaOH. Which of the following statements is *not* true of this titration?

(a) The HCl solution is less concentrated than the NaOH solution.

(b) The pH is less than 7 after adding 25 mL of NaOH solution.

(c) The pH at the equivalence point is 7.00. **(d)** If an additional 1.00 mL of NaOH solution is added beyond the equivalence point, the pH of the solution is more than 7.00.

(e) At the equivalence point, the OH^- concentration in the solution is 3.67×10^{-3} *M*.

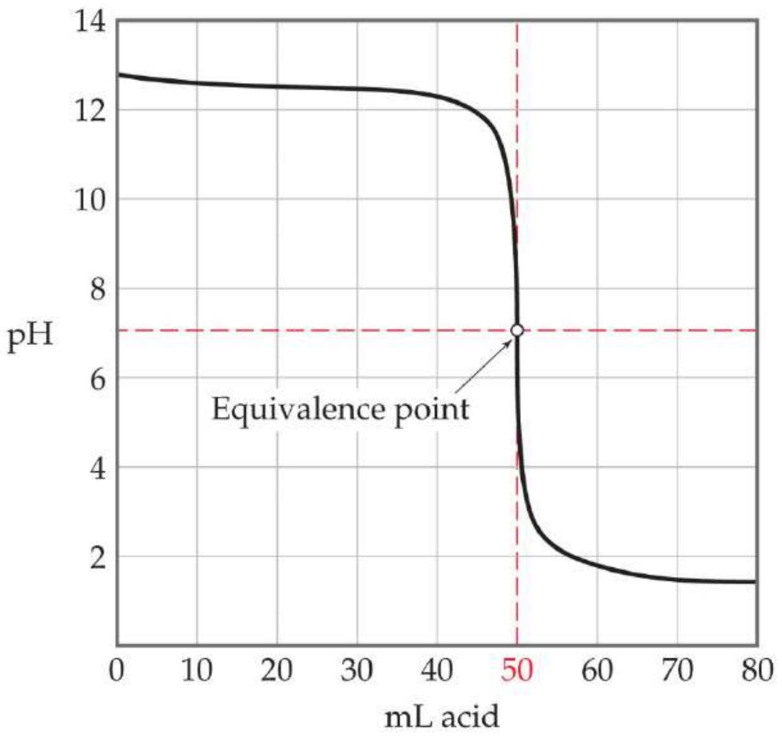
Practice Exercise 2

Calculate the pH when the following quantities of 0.100 *M* HNO_3 have been added to 25.0 mL of 0.100 *M* KOH solution: **(a)** 24.9 mL, **(b)** 25.1 mL.

17.3 Give It Some Thought

What is the pH at the equivalence point when 0.10 M HNO_3 is added to a solution containing 0.30 g of KOH?

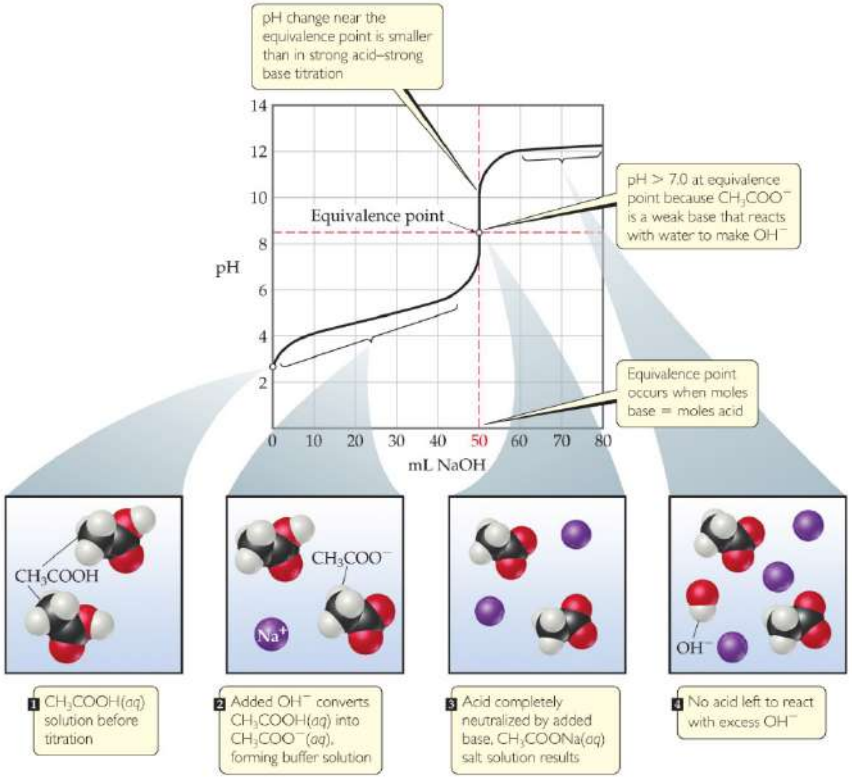
Titration of a Strong Base with a Strong Acid



- It looks like you “flipped over” the strong acid being titrated by a strong base.
- Start with a high pH (basic solution); the pH = 7 at the equivalence point; low pH to end.

Titration of a Weak Acid with a Strong Base

- Use K_a to find initial pH.
- Find the pH in the “buffer region” using stoichiometry followed by the Henderson–Hasselbalch equation.
- At the equivalence point the pH is >7. Use the conjugate base of the weak acid to determine the pH.
- As more base is added, the pH levels off. This is exactly the same as for strong acids.



pH change near the equivalence point is smaller than in strong acid–strong base titration

pH > 7.0 at equivalence point because CH_3COO^- is a weak base that reacts with water to make OH^-

Equivalence point occurs when moles base = moles acid

1 $CH_3COOH(aq)$ solution before titration

2 Added OH^- converts $CH_3COOH(aq)$ into $CH_3COO^-(aq)$, forming buffer solution

3 Acid completely neutralized by added base, $CH_3COONa(aq)$ salt solution results

4 No acid left to react with excess OH^-

If the acetic acid being titrated here were replaced by hydrochloric acid, would the amount of base needed to reach the equivalence point change? Would the pH at the equivalence point change?

a. The volume of base does not change but the equivalence point pH increases.

b. The volume of base increases but the equivalence point pH does not change.

c. The volume of base decreases and the equivalence point pH does not change.

d. The volume of base does not change but the equivalence point pH decreases.

Sample Exercise 17.8 Calculating pH for a Weak Acid–Strong Base Titration

Calculate the pH of the solution formed when 45.0 mL of 0.100 *M* NaOH is added to 50.0 mL of 0.100 *M* CH_3COOH ($K_a = 1.8 \times 10^{-5}$).

Practice Exercise 1

You can figure out the pK_a of a weak acid just by thinking about the definition of K_a and looking at the right place on the titration curve! Which of the following choices is the best way to do this?

(a) At the equivalence point, pH = pK_a.

(b) Halfway to the equivalence point, pH = pK_a.

(c) Before any base is added, pH = pK_a.

(d) At the top of the graph with excess base added, pH = pK_a.

Practice Exercise 2

(a) Calculate the pH in the solution formed by adding 10.0 mL of 0.050 *M* NaOH to 40.0 mL of 0.0250 *M* benzoic acid (C_6H_5COOH, $K_a = 6.3 \times 10^{-5}$) .

(b) Calculate the pH in the solution formed by adding 10.0 mL of 0.100 *M* HCl to 20.0 mL of 0.100 *M* NH_3.

Sample Exercise 17.9 Calculating the pH at the Equivalence Point

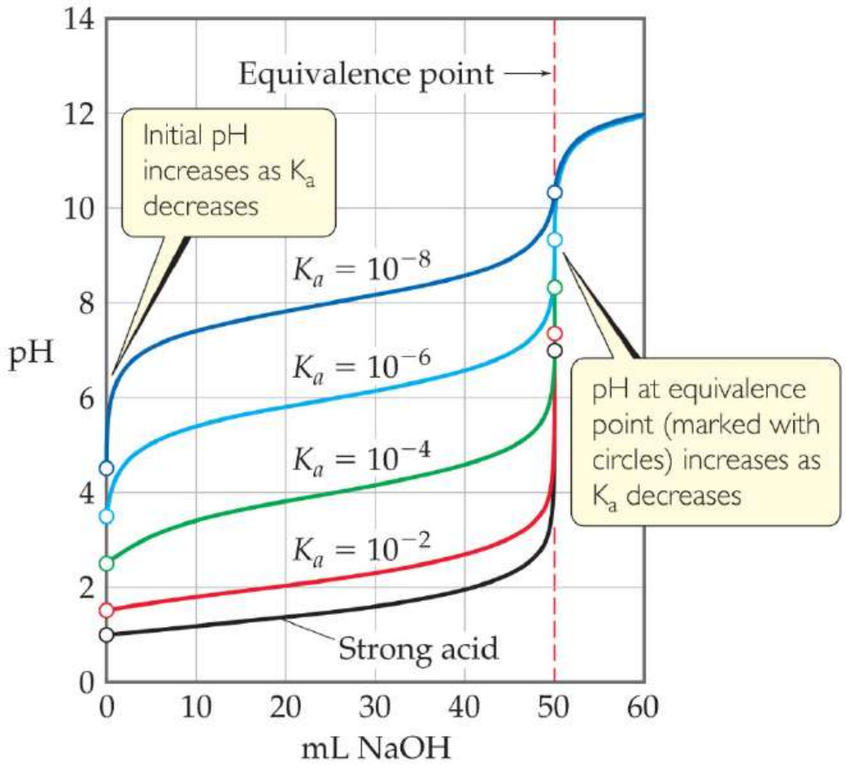
Calculate the pH at the equivalence point in the titration of 50.0 mL of 0.100 *M* CH_3COOH with 0.100 *M* NaOH.

Practice Exercise 2

Calculate the pH at the equivalence point when **(a)** 40.0 mL of 0.025 *M* benzoic acid (C_6H_5COOH, $K_a = 6.3 \times 10^{-5}$) is titrated with 0.050 *M* NaOH; **(b)** 40.0 mL of 0.100 *M* NH_3 is titrated with 0.100 *M* HCl.

Ways That a Weak Acid Titration Differs from a Strong Acid Titration

1) A solution of weak acid has a higher initial pH than a strong acid.
2) The pH change near the equivalence point is smaller for a weak acid. (This is at least partly due to the buffer region.)
3) The pH at the equivalence point is greater than 7 for a weak acid.

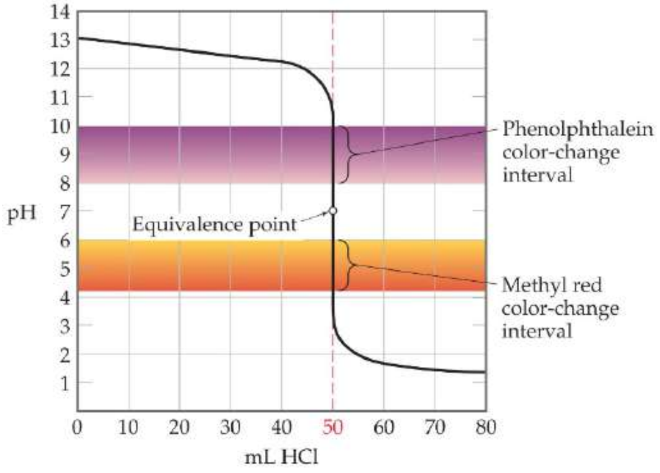


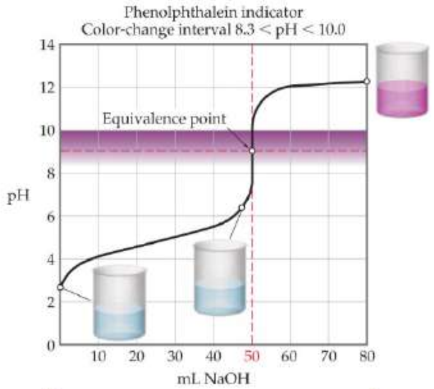
17.3 Give It Some Thought

- Explain why the following is true: The pH at the equivalence point is greater than 7 for a weak acid.

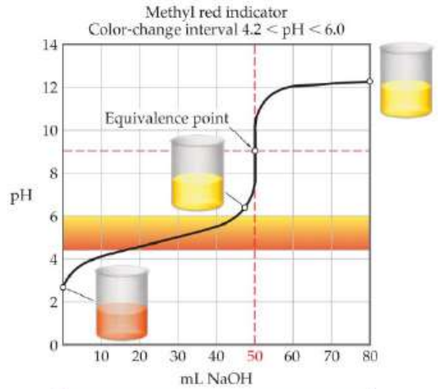
Use of Indicators

- Indicators are weak acids that have a different color than their conjugate base form.
- Each indicator has its own pH range over which it changes color.
- An indicator can be used to find the equivalence point in a titration as long as it changes color in the small volume change region where the pH rapidly changes.



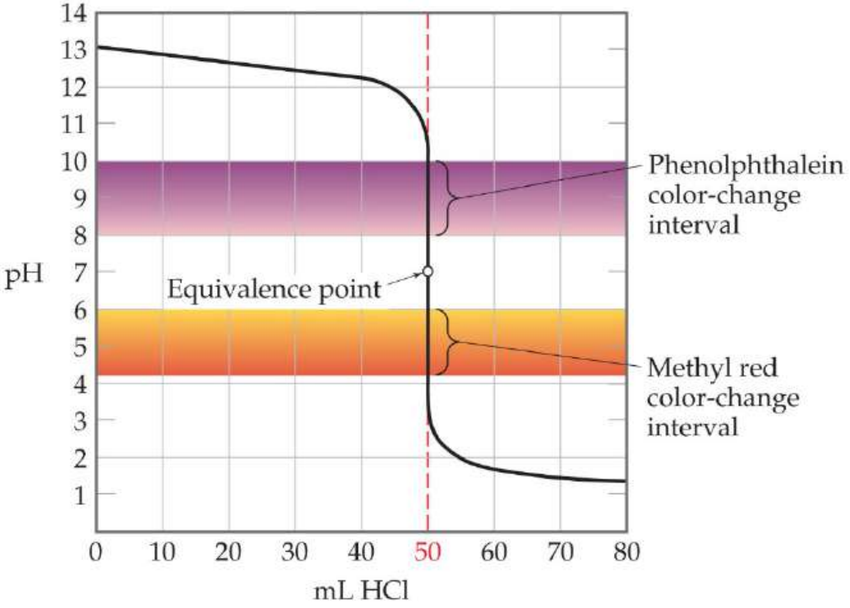


Suitable indicator for titration of a weak acid with a strong base because equivalence point falls within the color-change interval



Unsatisfactory indicator for titration of a weak acid with a strong base because color changes before reaching equivalence point

Is methyl red a suitable indicator when you are titrating a strong acid with a strong base? Explain your answer.



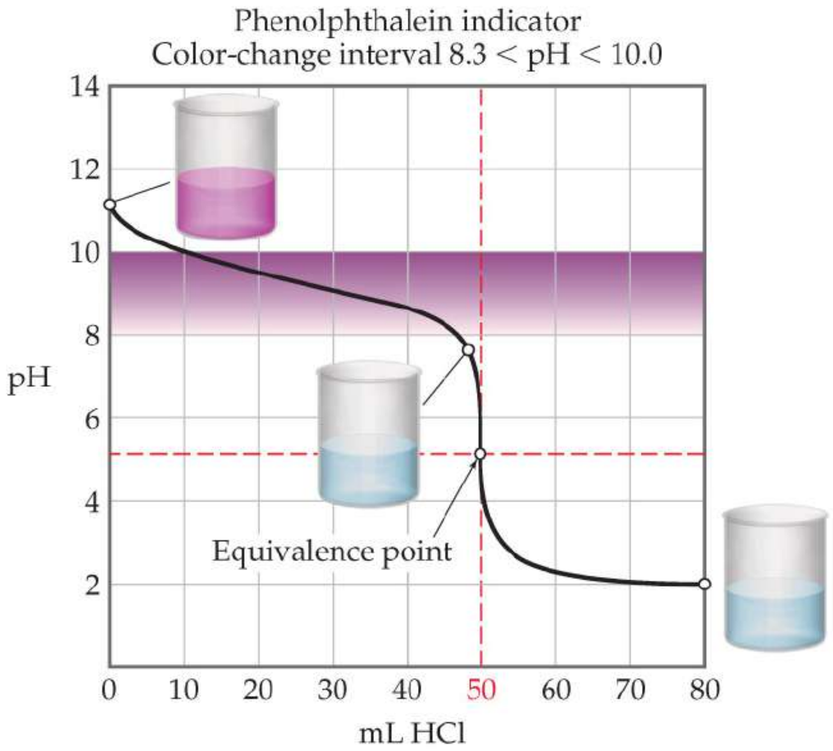
a. No, methyl red does not change equivalence point.

b. No methyl red's color change is not sharp and gives only a rough estimate of the equivalence point pH.

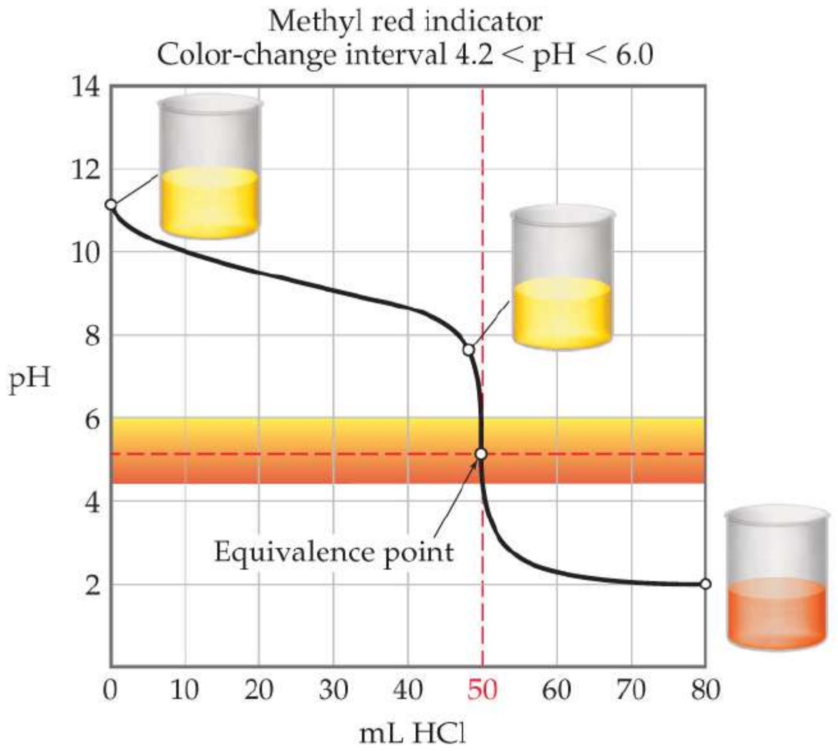
c. Yes, methyl red changes color in the pH region between 4 and 6 in a steeply sloping region.

d. Yes, methyl red changes color in the pH region between 8 and 10 in a steeply sloping region.

Indicator Choice Can Be Critical!



Unsatisfactory indicator for titration of a weak base with a strong acid because color changes before reaching equivalence point



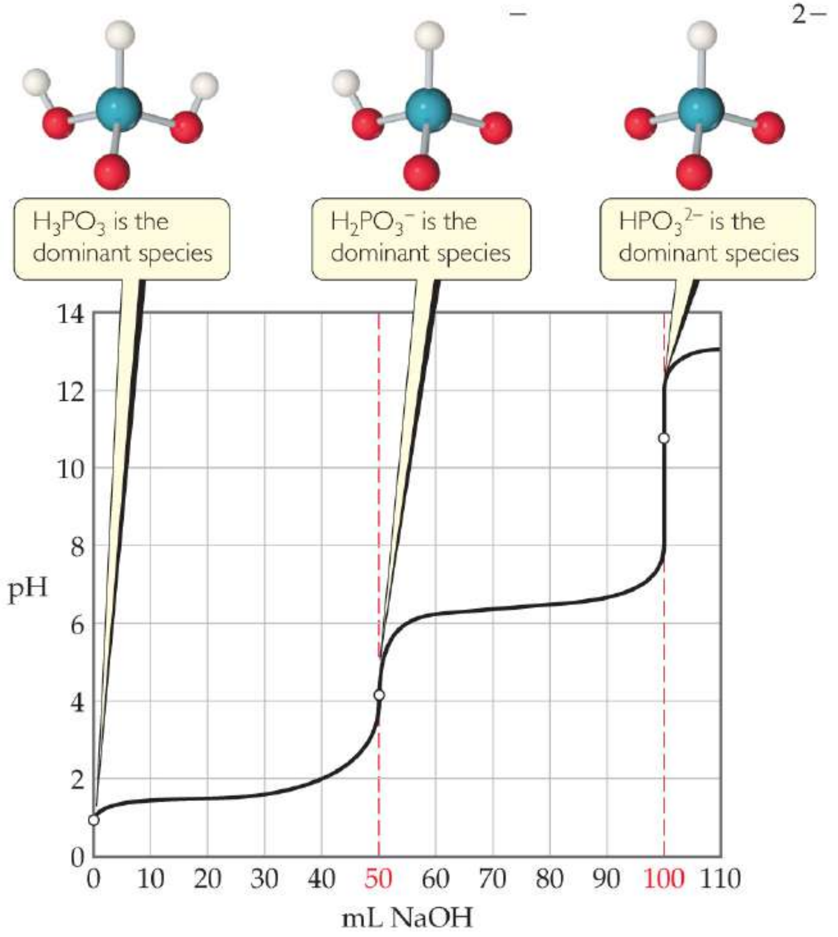
Suitable indicator for titration of a weak base with a strong acid because equivalence point falls within the color-change interval

17.3 Give It Some Thought

- Why is the choice of indicator more crucial for a weak acid-strong base titration than for a strong acid-strong base titration?

Titrations of Polyprotic Acids

- When a polyprotic acid is titrated with a base, there is an equivalence point for each dissociation.
- Using the Henderson–Hasselbalch equation,
we can see that *half* way to each equivalence point gives us the pK_a for that step.



17.3 Give It Some Thought

- Sketch an approximate titration curve for the titration of Na_2CO_3 with HCl.

17.4 Solubility Equilibria

Solubility Equilibria

- Because ionic compounds are strong electrolytes, they dissociate completely to the extent that they dissolve.
- When an equilibrium equation is written, the solid is the reactant and the ions in solution are the products.
- The equilibrium constant expression is called the **solubility-product constant**. It is represented as K_{sp}.

Solubility Product

- For example:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

- The equilibrium constant expression is

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

- Another example:

$$Ba_3(PO_4)_2(s) \rightleftharpoons 3\,Ba^{2+}(aq) + 2\,PO_4^{3-}(aq)$$

- The equilibrium constant expression is

$$K_{sp} = [Ba^{2+}]^3[PO_4^{3-}]^2$$

Sample Exercise 17.10 Writing Solubility–Product (K_{sp}) Expressions

Write the expression for the solubility-product constant for CaF_2, the corresponding K_{sp} value is 3.9×10^{-11}.

Practice Exercise 1

Which of these expressions correctly expresses the solubility-product constant for Ag_3PO_4 in water?

(a) $[Ag][PO_4]$

(b) $[Ag^+][PO_4^{3-}]$

(c) $[Ag^+]^3[PO_4^{3-}]$

(d) $[Ag^+][PO_4^{3-}]^3$

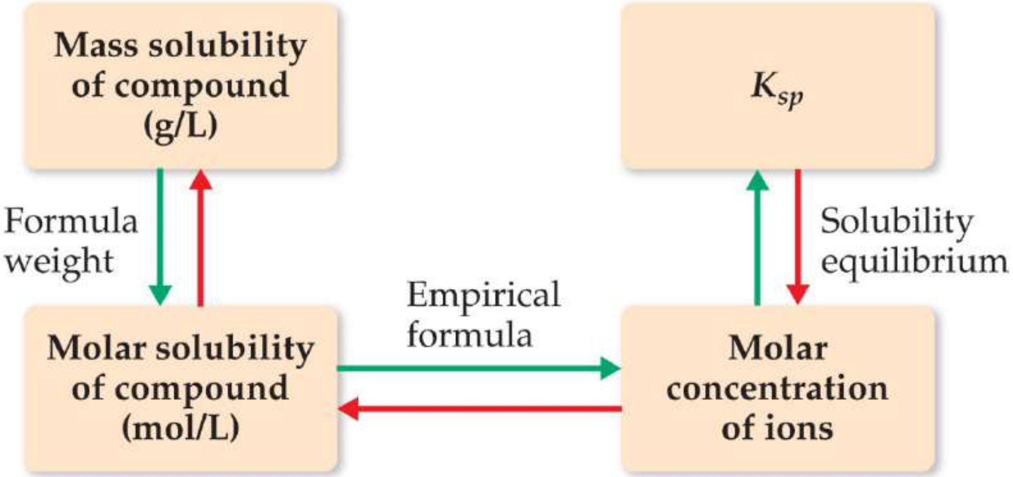
(e) $[Ag^+]^3[PO_4^{3-}]^3$

Practice Exercise 2

- Give the solubility-product-constant expressions and the values of the solubility-product constants for the following compounds:
  - A) barium carbonate ($K_{sp} = 5.0 \times 10^{-9}$)
  - B) silver sulfate ($K_{sp} = 1.5 \times 10^{-5}$)

Solubility vs. Solubility Product

- K_{sp} is *not* the same as solubility.
- Solubility is the quantity of a substance that dissolves to form a saturated solution
- Common units for solubility:
  - Grams per liter (g/L)
  - Moles per liter (mol/L)



Mass solubility of compound (g/L)

K_{sp}

Formula weight

Solubility equilibrium

Empirical formula

Molar solubility of compound (mol/L)

Molar concentration of ions

17.3 Give It Some Thought

- Without doing a calculation, predict which of the following compounds will have the greatest molar solubility in water:
  - AgCl ($K_{sp} = 1.8 \times 10^{-10}$)
  - AgBr ($K_{sp} = 5.0 \times 10^{-13}$)
  - AgI ($K_{sp} = 8.3 \times 10^{-17}$)

Sample Exercise 17.11 Calculating K_{sp} from Solubility

Solid silver chromate is added to pure water at 25 ºC. Some of the solid remains undissolved at the bottom of the flask. The mixture is stirred for several days to ensure that equilibrium is achieved between the undissolved $Ag_2CrO_4(s)$ and the solution. Analysis of the equilibrated solution shows that its silver ion concentration is 1.3×10^{-4} *M*. Assuming that Ag_2CrO_4 dissociates completely in water and that there are no other important equilibria involving the Ag^+ or $CrO4^{2-}$ ions in the solution, calculate K_{sp} for this compound.

Practice Exercise 1

You add 10.0 grams of solid copper(II) phosphate, $Cu_3(PO_4)_2$, to a beaker and then add 100.0 mL of water to the beaker at $T = 298$ K. The solid does not appear to dissolve. You wait a long time, with occasional stirring and eventually measure the equilibrium concentration of $Cu^{2+}(aq)$ in the water to be 5.01×10^{-8} M. What is the K_{sp} of copper(II) phosphate?

(a) 5.01×10^{-8} **(b)** 2.50×10^{-15}

(c) 4.20×10^{-15} **(d)** 3.16×10^{-37}

(e) 1.40×10^{-37}

Practice Exercise 2

A saturated solution of $Mg(OH)_2$ in contact with undissolved solid is prepared at 25 ºC. The pH of the solution is found to be 10.17. Assuming that $Mg(OH)_2$ dissociates completely in water and that there are no other simultaneous equilibria involving the Mg^{2+} or OH^- ions in the solution, calculate K_{sp} for this compound.

Sample Exercise 17.12

- The K_{sp} for CaF_2 is 3.9×10^{-11} at 25 °C. What is its molar solubility?
- Follow the same format as before:

1) $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$

2) $K_{sp} = [Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$

3)

	$CaF_2(s)$	$[Ca^{2+}]$ (*M*)	$[F^-]$ (*M*)
Initial concentration (*M*)	---	0	0
Change in concentration (*M*)	---	$+x$	$+2x$
Equilibrium concentration (*M*)	---	x	$2x$

Example (completed)

4) Solve: Substitute the equilibrium concentration values from the table into the solubility-product equation:

$3.9 \times 10^{-11} = (x)\,(2x)^2 = 4x^3$

$x = 2.1 \times 10^{-4}\ M$

(If you want the answer in g/L, multiply by molar mass; this would give 0.016 g/L.)

Practice Exercise 1

Of the five salts listed below, which has the highest concentration of its cation in water? Assume that all salt solutions are saturated and that the ions do not undergo any additional reactions in water.

(a) lead (II) chromate, $K_{sp} = 2.8 \times 10^{-13}$

(b) cobalt(II) hydroxide, $K_{sp} = 1.3 \times 10^{-15}$

(c) cobalt(II) sulfide, $K_{sp} = 5 \times 10^{-22}$

(d) chromium(III) hydroxide, $K_{sp} = 1.6 \times 10^{-30}$

(e) silver sulfide, $K_{sp} = 6 \times 10^{-51}$

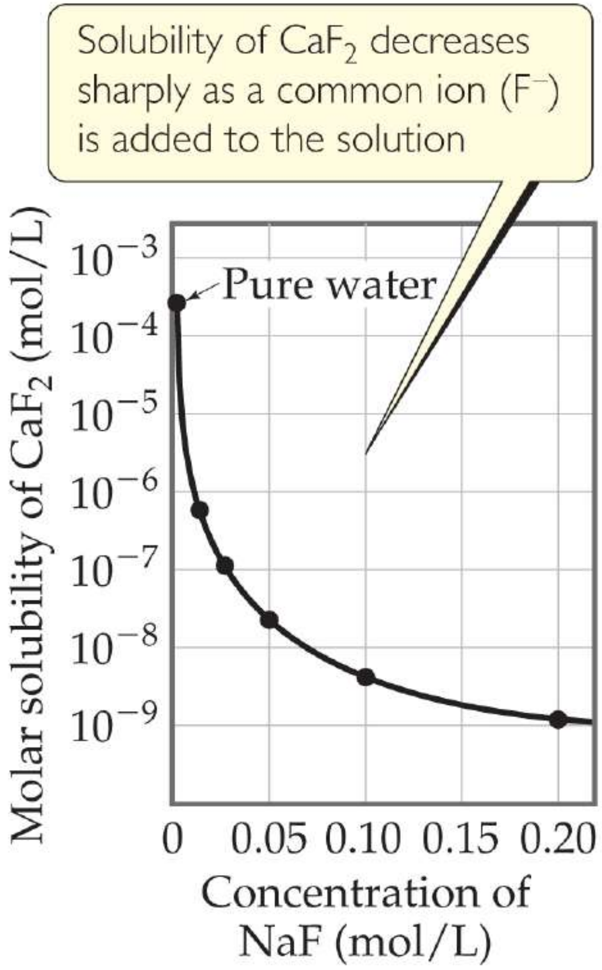
Practice Exercise 2

The K_{sp} for LaF_3 is 2×10^{-19}. What is the solubility of LaF_3 in water in moles per liter?

17.5 Factors that Affect Solubility

Factors Affecting Solubility

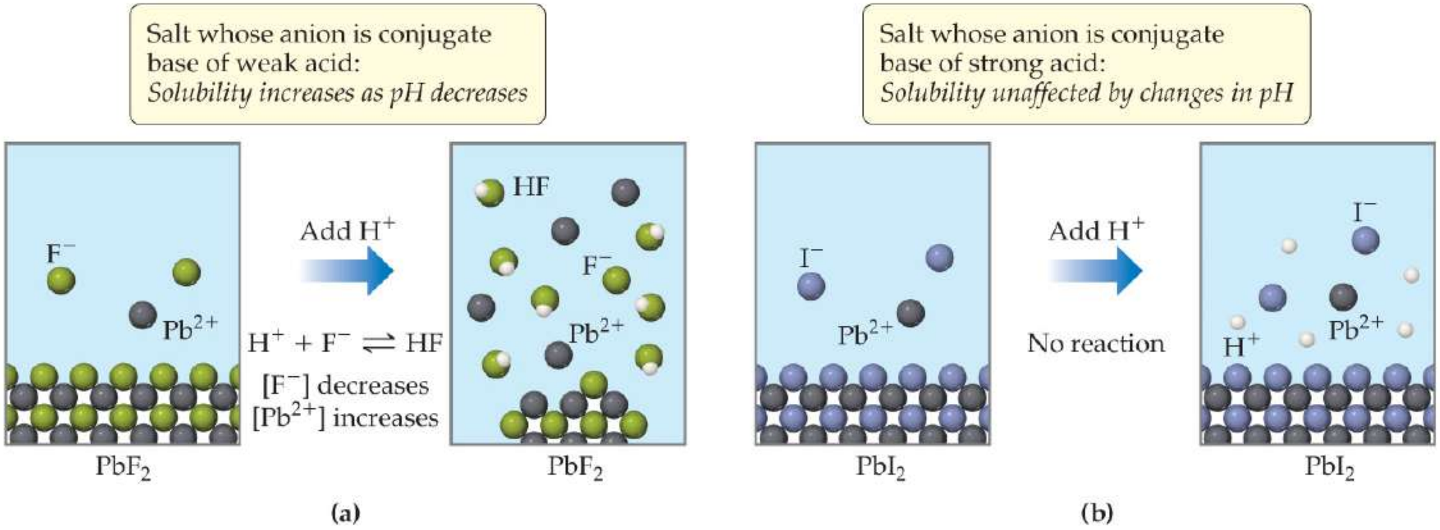
- The Common-Ion Effect
  - If one of the ions in a solution equilibrium is already dissolved in the solution, the solubility of the salt will decrease.
  - If either calcium ions or fluoride ions are present, then calcium fluoride will be less soluble.



Solubility of CaF_2 decreases sharply as a common ion (F^-) is added to the solution

Factors Affecting Solubility

- pH: If a substance has a basic anion, it will be more soluble in an acidic solution.
- Remember that buffers control pH. When a buffer is used, there is *no change* in concentration of hydroxide ion!



Sample Exercise 17.14 Predicting the Effect of Acid on Solubility

Which of the following substances will be more soluble in acidic solution than in basic solution:

(a) $Ni(OH)_2(s)$

(b) $CaCO_3(s)$

(c) $BaF_2(s)$

(d) $AgCl(s)$

Practice Exercise 2

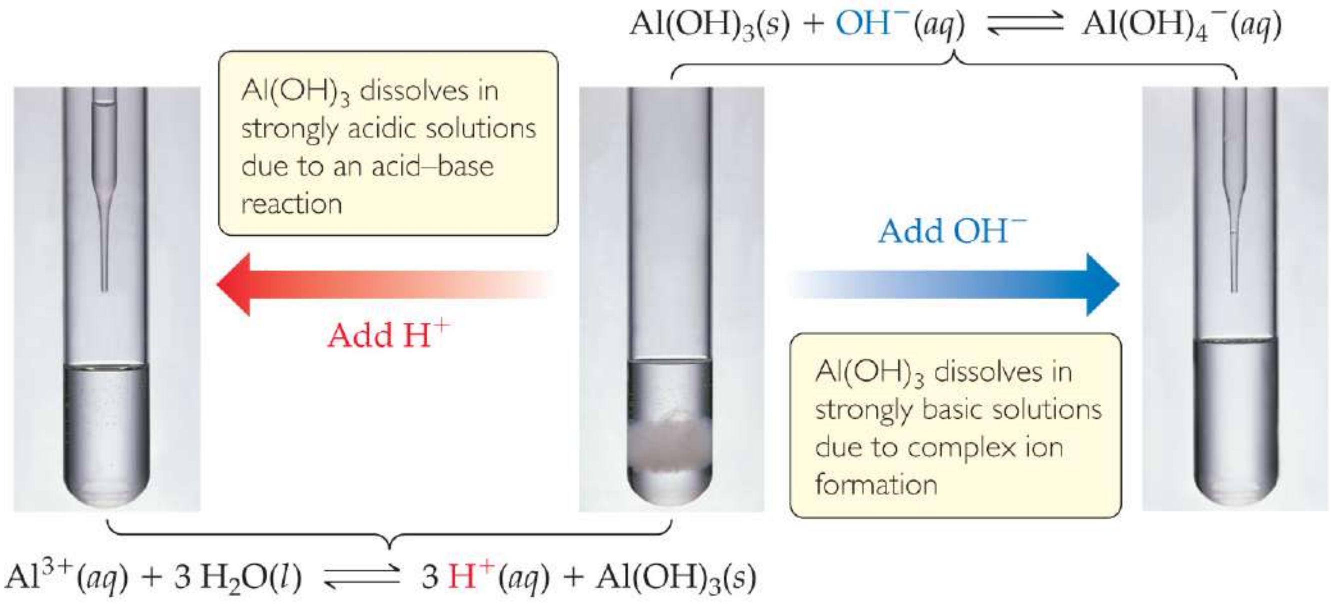
Write the net ionic equation for the reaction of the following copper(II) compounds with acid:

(a) CuS

(b) $Cu(N_3)_2$

Amphoterism and Solubility

- **Amphoteric oxides and hydroxides** are soluble in strong acids or base, because they can act either as acids or bases.
- Examples are oxides and hydroxides of Al^{3+}, Cr^{3+}, Zn^{2+}, and Sn^{2+}.



$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$

$Al(OH)_3$ dissolves in strongly acidic solutions due to an acid–base reaction

Add H^+

Add OH^-

$Al(OH)_3$ dissolves in strongly basic solutions due to complex ion formation

$Al^{3+}(aq) + 3\,H_2O(l) \rightleftharpoons 3\,H^+(aq) + Al(OH)_3(s)$

17.5 Give It Some Thought

- What is the difference between an amphoteric substance and an amphiprotic substance?

17.6 Precipitation and Separation of Ions

Will a Precipitate Form?

- To decide, we calculate the reaction quotient, Q, and compare it to the solubility product constant, K_{sp}.
  - If $Q = K_{sp}$, the system is at equilibrium and the solution is saturated.
  - If $Q < K_{sp}$, more solid can dissolve, so no precipitate forms.
  - If $Q > K_{sp}$, a precipitate will form.

Sample Exercise 17.16 Predicting Whether a Precipitate Will Form

Will a precipitate form when 0.10 L of 8.0×10^{-3} *M* $Pb(NO_3)_2$ is added to 0.40 L of 5.0×10^{-3} *M* Na_2SO_4?

Practice Exercise 2

Will a precipitate form when 0.050 L of 2.0×10^{-2} *M* NaF is mixed with 0.010 L of 1.0×10^{-2} *M* $Ca(NO_3)_2$?

Practice Exercise 1

Under what conditions does an ionic compound precipitate from a solution of the constituent ions?

(a) always

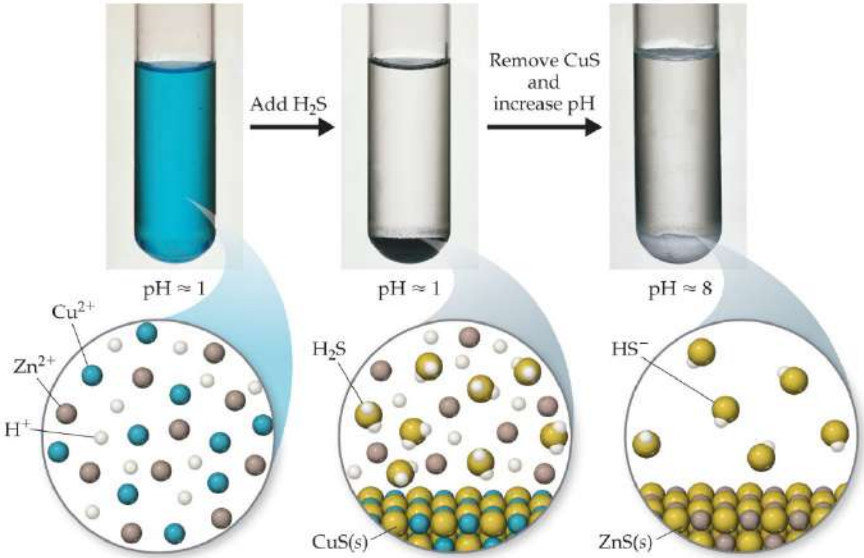
(b) when $Q = K_{sp}$

(c) when Q exceeds K_{sp}

(d) when Q is less than K_{sp}

(e) never, if it is very soluble.

What would happen if the pH were raised to 8 first and then H_2S were added?



Solution containing $Zn^{2+}(aq)$ and $Cu^{2+}(aq)$

When H_2S is added to a solution whose pH exceeds 0.6, CuS precipitates

After CuS is removed, the pH is increased, allowing ZnS to precipitate

a. ZnS and CuS both precipitate and separating the two ions is no longer feasible using given procedures.

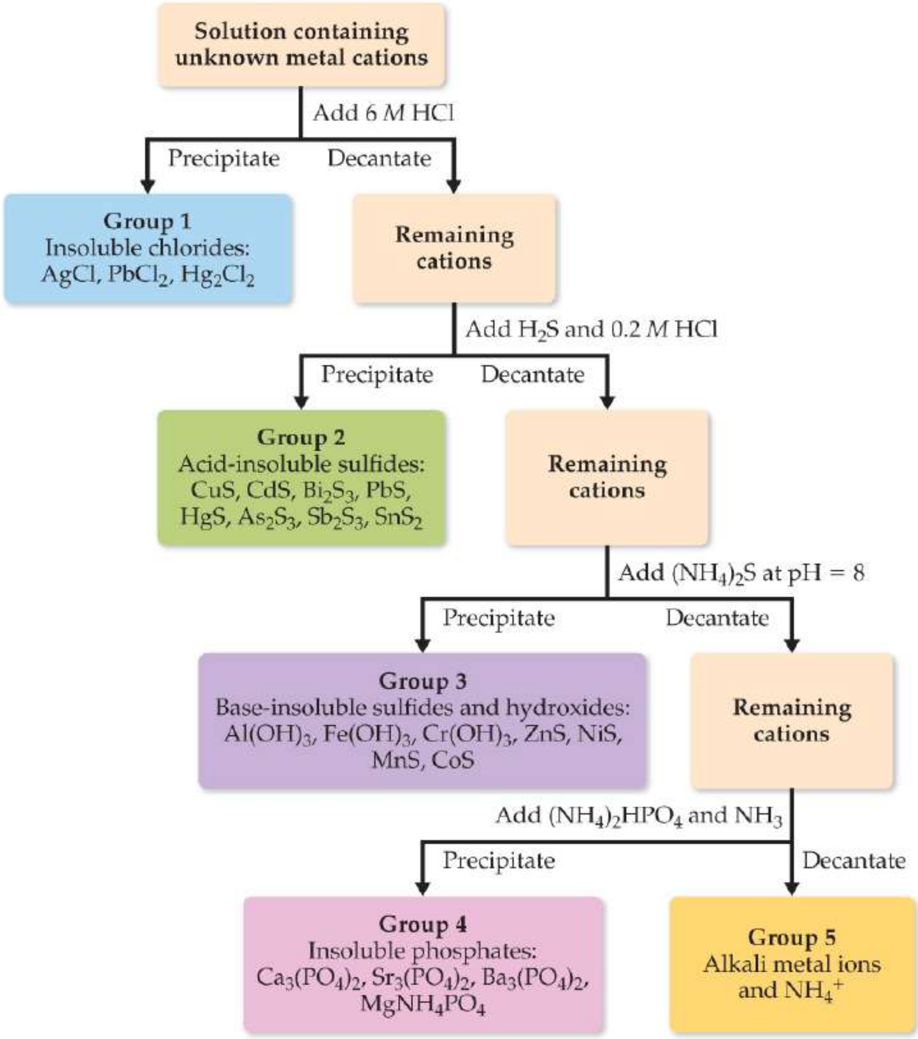
b. ZnS precipitates and separating the two ions is still feasible using given procedures.

c. CuS precipitates and separating the two ions is still feasible using given procedures.

d. No change in observations and ability to separate the two ions.

17.7 Qualitative Analysis for Metallic Elements

Selective Precipitation of Ions



Solution containing unknown metal cations

Add 6 *M* HCl

Precipitate / Decantate

Group 1
Insoluble chlorides:
$AgCl$, $PbCl_2$, Hg_2Cl_2

Remaining cations

Add H_2S and 0.2 *M* HCl

Precipitate / Decantate

Group 2
Acid-insoluble sulfides:
CuS, CdS, Bi_2S_3, PbS, HgS, As_2S_3, Sb_2S_3, SnS_2

Remaining cations

Add $(NH_4)_2S$ at pH = 8

Precipitate / Decantate

Group 3
Base-insoluble sulfides and hydroxides:
$Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$, ZnS, NiS, MnS, CoS

Remaining cations

Add $(NH_4)_2HPO_4$ and NH_3

Precipitate / Decantate

Group 4
Insoluble phosphates:
$Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ba_3(PO_4)_2$, $MgNH_4PO_4$

Group 5
Alkali metal ions and NH_4^+

One can use differences in solubilities of salts to separate ions in a mixture. This has been used for qualitative analysis of the presence of ions in a solution.

If a solution contained a mixture of Cu^{2+} and Zn^{2+} ions, would this separation scheme work? After which step would the first precipitate be observed?

a. No, both would precipitate in step 1 and subsequently are not easily separated.

b. No, both would precipitate in step 2 and subsequently are not easily separated.

c. Yes, ZnS precipitates in step 1 and CuS in step 4.

d. Yes, CuS precipitates in step 2 and Zn^{2+} remains in solution.

Sample Integrative Exercise

- A sample of 1.25 L of HCl gas at 21ºC and 9.50 atm is bubbled through 0.500 L of 0.150 M NH_3 solution. Calculate the pH of the resulting solution assuming that all the HCl dissolves and that the volume of the solution remains 0.500 L.