

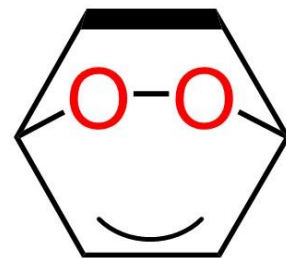
# CHEM103

## General Chemistry

### Chapter 17: Additional Aspects of Aqueous Equilibria



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# Homeworks 15-16

## Homework 15

**Due date: 7th Dec. (Wed)**

## Homework 16

**Due date: 14th Dec. (Wed)**

# Review on Chapter 16

Arrhenius/Brønsted/Lewis acids & bases

Conjugate acids and bases

Amphiprotic, autoionization, ion product constant ( $K_w$ )

Acid and base strength (pH), acid dissociation constant ( $K_a$  or  $pK_a$ ), base dissociation constant ( $K_b$  or  $pK_b$ ), percent ionization

Polyprotic acids, binary acids, oxyacids, zwitterion

# Outline of Chapter 17

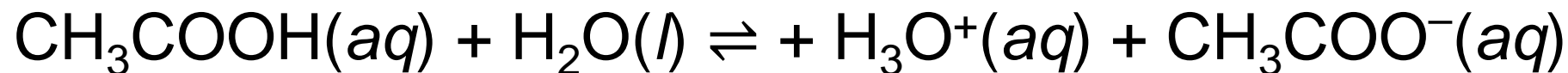
The common-ion effect

Buffer solution, Henderson–Hasselbalch equation

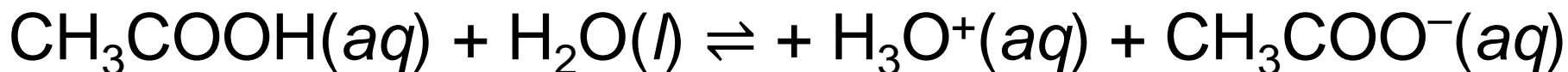
Solubility equilibria, solubility-product constant ( $K_{sp}$ ),  
complex ion formation, amphotericism

# The Common-Ion Effect (同离子效应)

- Acetic acid is a weak acid:



- The **addition of acetate** from a **strong electrolyte** sodium acetate in an acetic acid solution will **shift the left side** of the equilibrium, according to Le Châtelier's Principle:



Addition of  $\text{CH}_3\text{COO}^-$  shifts equilibrium concentrations, lowering  $[\text{H}^+]$

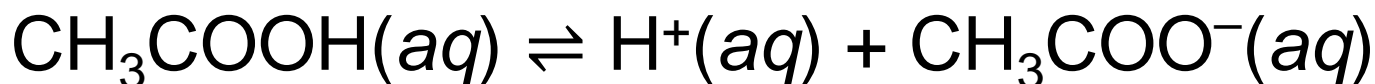
Acids  
and  
Bases

# The Common-Ion Effect (同离子效应)

- “The extent of **ionization** of a **weak electrolyte** is **decreased** by **adding** to the solution a **strong electrolyte** that has an **ion in common** with the weak electrolyte.”
- This affects acid–base **equilibria**.
- This also affects **solubility**.

# An Acid–Base Example

- 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?



$$K_a = [\text{H}^+][\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}] = 1.8 \times 10^{-5}$$



Initial ( <i>M</i> )	0.30	0	0.30
Change ( <i>M</i> )	$-x$	$+x$	$+x$
Equilibrium ( <i>M</i> )	$(0.30 - x)$	$x$	$(0.30 + x)$

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

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

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



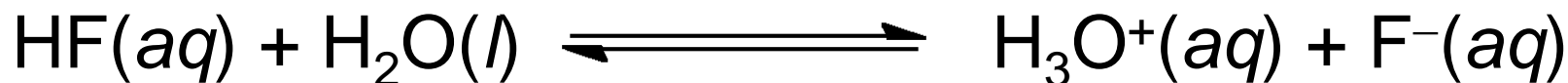
$$x = 1.8 \times 10^{-5} = [\text{H}^+]$$

So,

$$\text{pH} = -\log[\text{H}^+] = 4.74 \text{ (4.7)}$$



Calculate the fluoride ion concentration and pH of a solution that is 0.20 *M* in HF and 0.10 *M* in HCl. ( $K_a$  for HF is  $6.8 \times 10^{-4}$ )



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4}$$



Initial ( <i>M</i> )	0.20	0.10	0
Change ( <i>M</i> )	$-x$	$+x$	$+x$
Equilibrium ( <i>M</i> )	$(0.20 - x)$	$(0.10 + x)$	$x$

Because HCl, a strong acid, is also present, the initial  $[\text{H}_3\text{O}^+]$  is not 0, but rather 0.10 *M*.



Initial ( <i>M</i> )	0.20	0.10	0
Change ( <i>M</i> )	$-x$	$+x$	$+x$
Equilibrium ( <i>M</i> )	$(0.20 - x)$	$(0.10 + x)$	$x$

$$6.8 \times 10^{-4} = \frac{(0.10)(x)}{(0.20)}$$

$$x = 1.4 \times 10^{-3}$$

$$[\text{F}^-] = x = 1.4 \times 10^{-3}$$

$$[\text{H}_3\text{O}^+] = 0.10 + x = 0.10 + 1.4 \times 10^{-3} = 0.10 \text{ M}$$

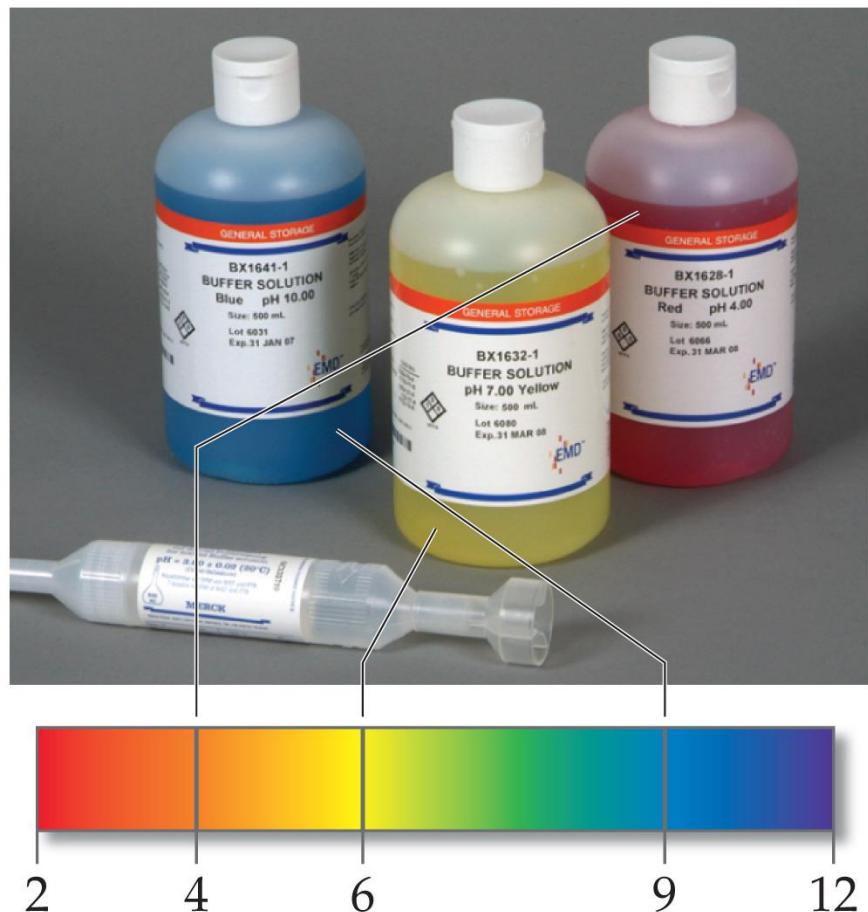
$$\text{pH} = 1.00$$

# Buffers

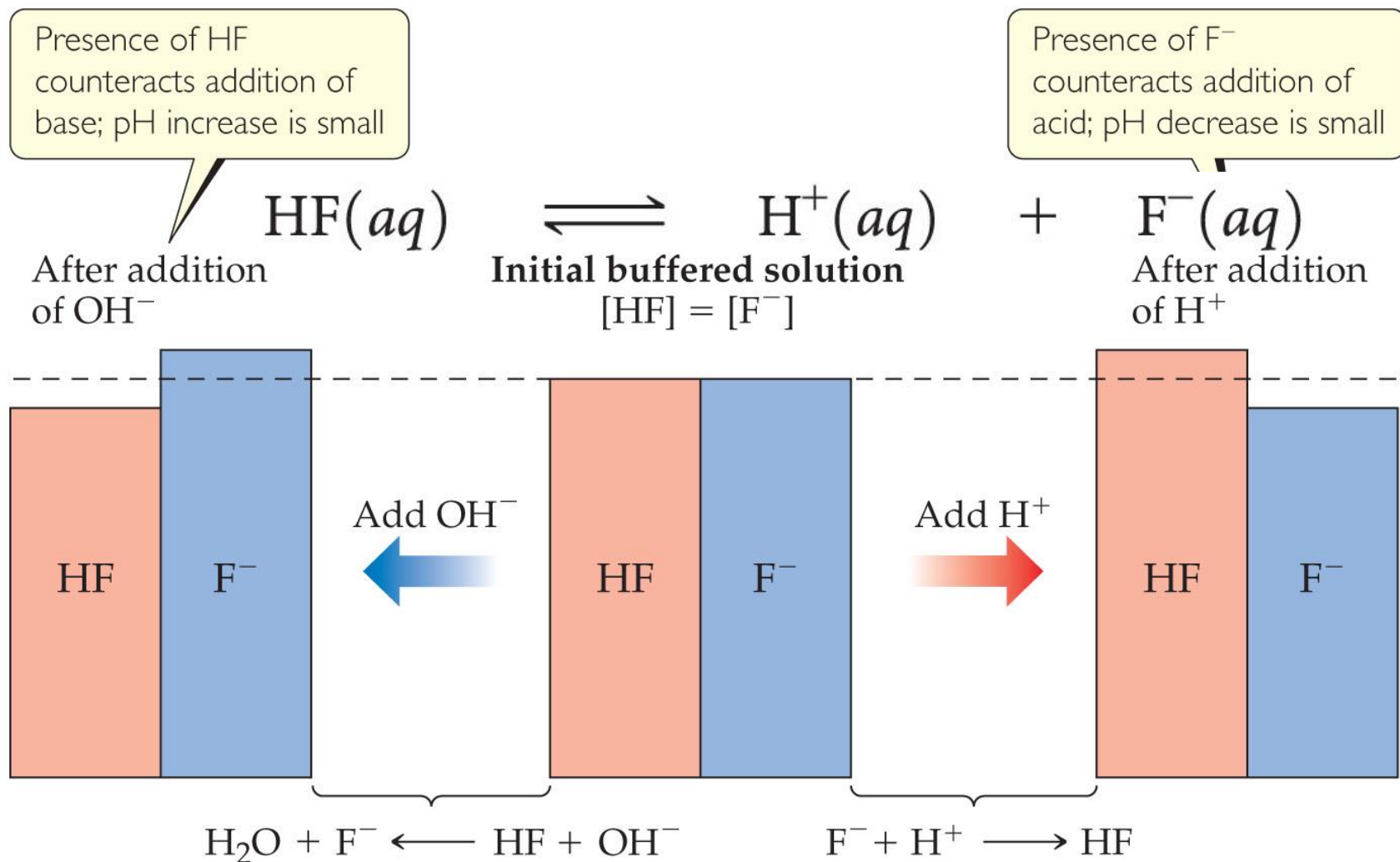
- Solutions of a weak conjugate acid–base pair that resist drastic changes in pH are called buffer solutions (缓冲溶液).

- These solutions contain relatively high concentrations ( $10^{-3}$  M or more) of both the acid and base. Their concentrations are approximately equal.

Acids  
and  
Bases



# 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.

# Calculating the pH of a Buffer

- For a weak acid:

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

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

- Rearrange:

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

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log([\text{A}^-]/[\text{HA}]) \\ &= \text{p}K_a + \log([\text{base}]/[\text{acid}])\end{aligned}$$

- This equation is known as the **Henderson–Hasselbalch equation**.

# Henderson–Hasselbalch Equation

What is the pH of a buffer that is 0.12 *M* in lactic acid, CH<sub>3</sub>CH(OH)COOH, and 0.10 *M* in sodium lactate? *K<sub>a</sub>* for lactic acid is  $1.4 \times 10^{-4}$ .

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

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

$$= 3.85 + (-0.08) = 3.77$$

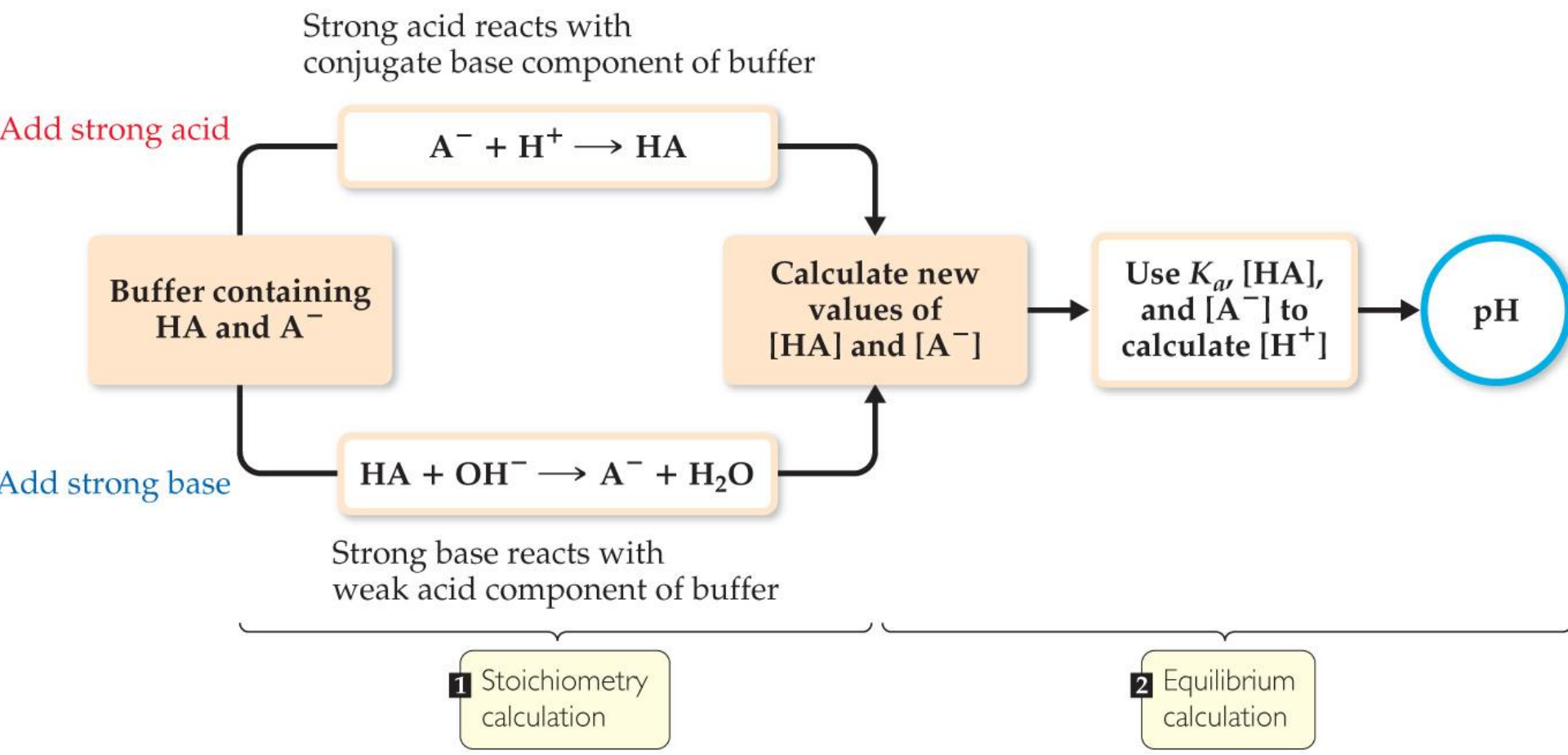
# Buffer Capacity & pH Range

- The **amount of acid or base** the buffer can neutralize before the pH begins to **change** to an appreciable degree.
- The buffer capacity depends on the **amount of acid and base** used to prepare the buffer.
- The range of pH values over which a buffer system works effectively.
- It is best to **choose an acid with a  $pK_a$  close to the desired pH.**

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

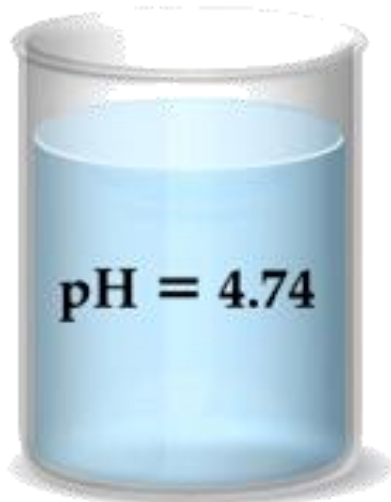
# Addition of a Strong Acid or Base to a Buffer

- Calculate  $[HA]$  and  $[A^-]$  by assuming **all** of the added **strong acid or base** reacts with a buffer.
- Use the Henderson–Hasselbalch equation to determine the new pH of the solution.

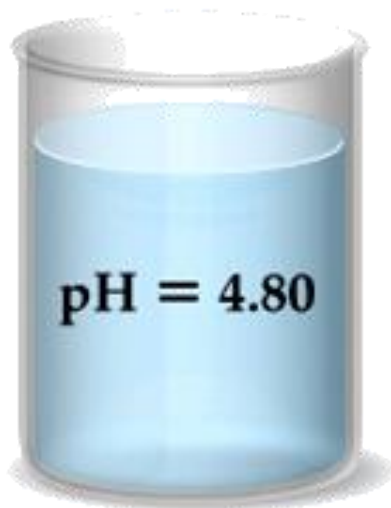




1.000 L buffer  
0.300 M  $\text{CH}_3\text{COOH}$   
0.300 M  $\text{CH}_3\text{COO}^-$



Add 5.0 mL of  
4.0 M  $\text{NaOH(aq)}$



pH increases by  
0.06 pH units

1.000 L  $\text{H}_2\text{O}$



Add 5.0 mL of  
4.0 M  $\text{NaOH(aq)}$



pH increases by  
5.30 pH units

Effect of adding  
a strong base to  
a buffered  
solution & to  
water

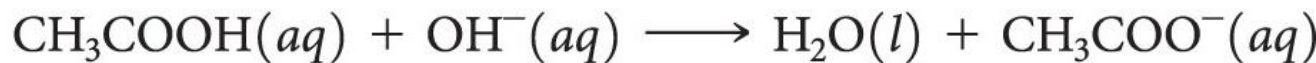
Acids

and

Bases

# Example

A buffer is made by adding 0.300 mol  $\text{C}_2\text{H}_3\text{O}_2\text{H}$  and 0.300 mol  $\text{C}_2\text{H}_3\text{O}_2\text{Na}$  to enough water to make 1.00 L of solution. The pH of the buffer is 4.74. Calculate the pH after 0.020 mol of NaOH is added.



Before reaction (mol)	0.300	0.020	—	0.300
Change (limiting reactant) (mol)	−0.020	−0.020	—	+0.020
After reaction (mol)	0.280	0	—	0.320

Use the Henderson–Hasselbalch equation:

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

Since this is a buffer, the volume for each concentration is the same, so the ratio of molarity can be calculated using a ratio of moles.

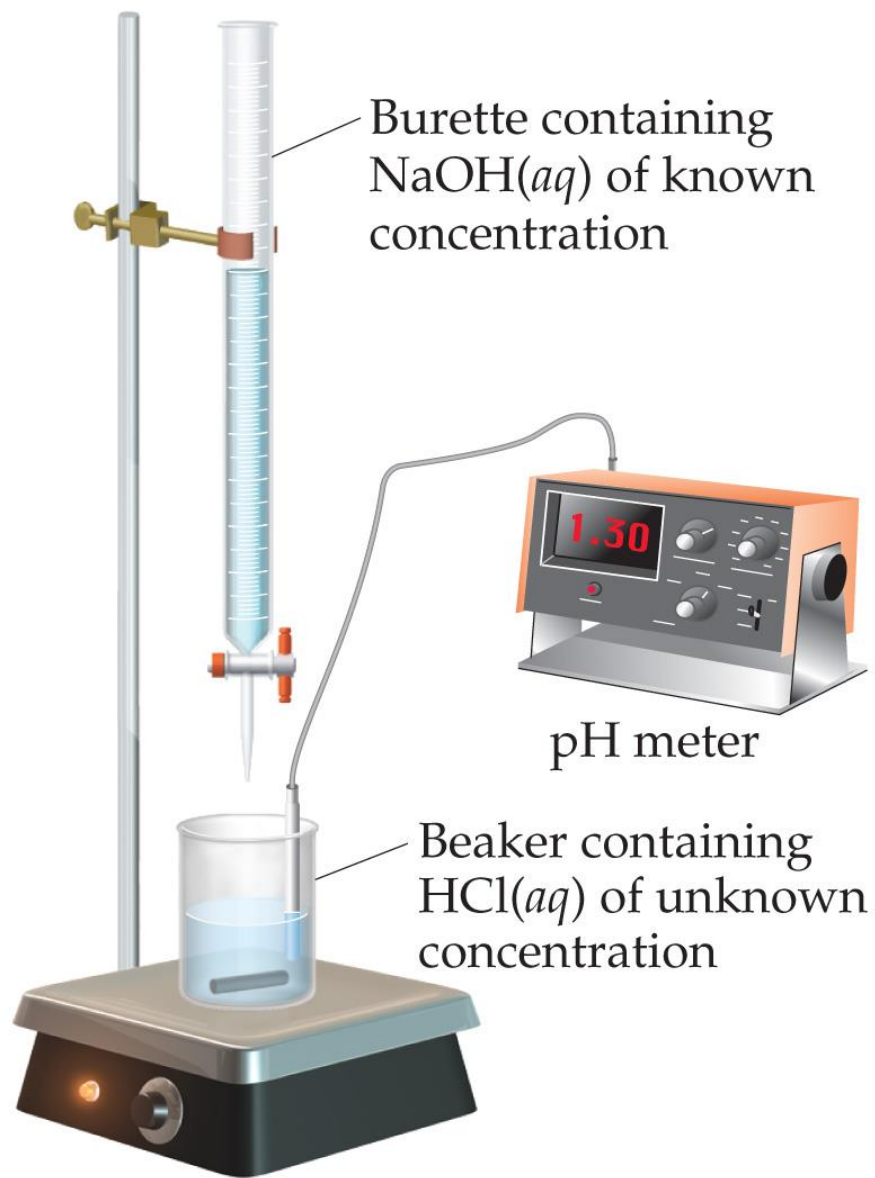
$$\text{pH} = \text{p}K_a + \log(n_{\text{HA}}/n_{\text{A}^-})$$

$$\text{pH} = 4.74 + \log(0.320/0.280) = 4.80$$

# Titration

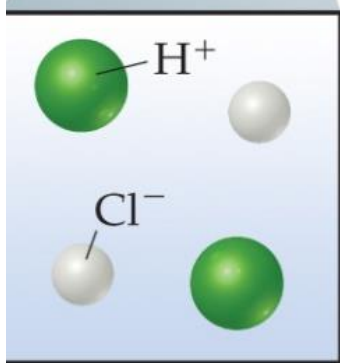
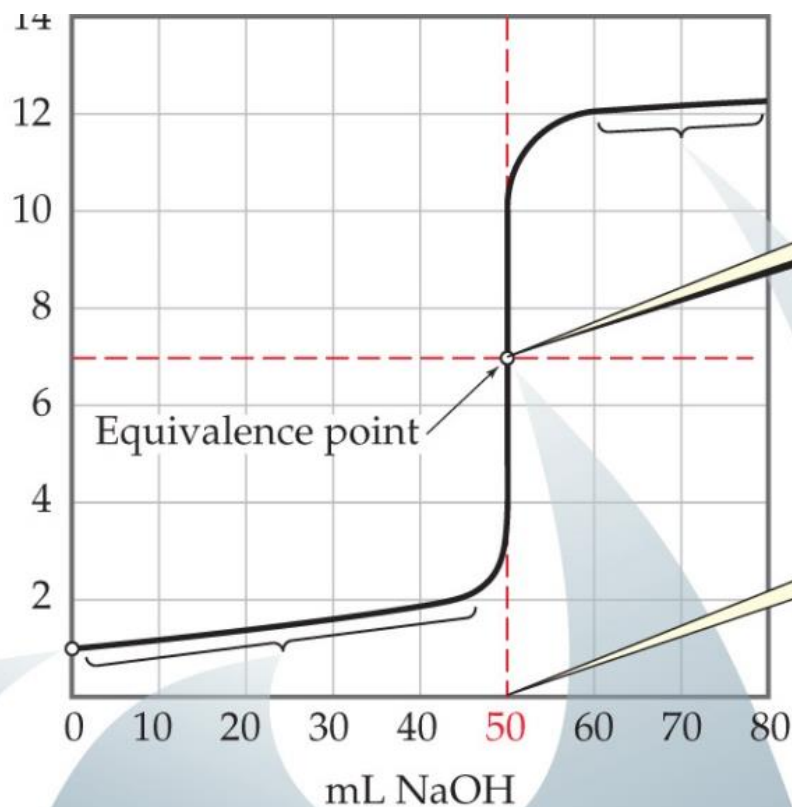
- In this technique, an acid (or base) solution of known concentration is slowly added to a base (or acid) solution of unknown concentration.

- 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 (if 1:1 ratio).

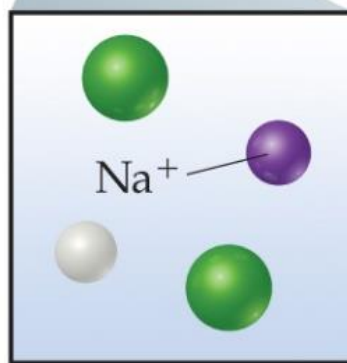


# Titration of a Strong Acid with a Strong Base

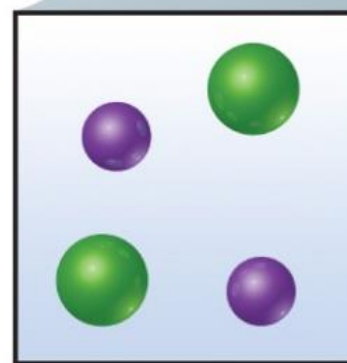
- From the start to near the equivalence point, the pH goes up slowly.



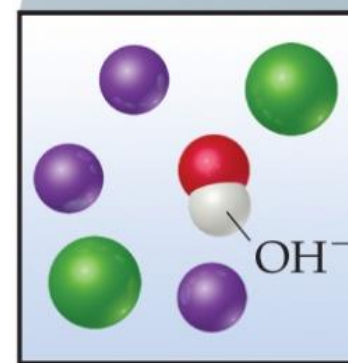
1 Only  $\text{HCl}(aq)$  present before titration



2  $\text{H}^+$  consumed as  $\text{OH}^-$  added, forming  $\text{H}_2\text{O}$  ( $\text{pH} < 7.0$ )



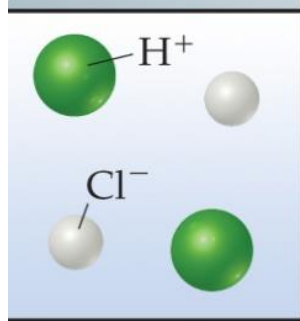
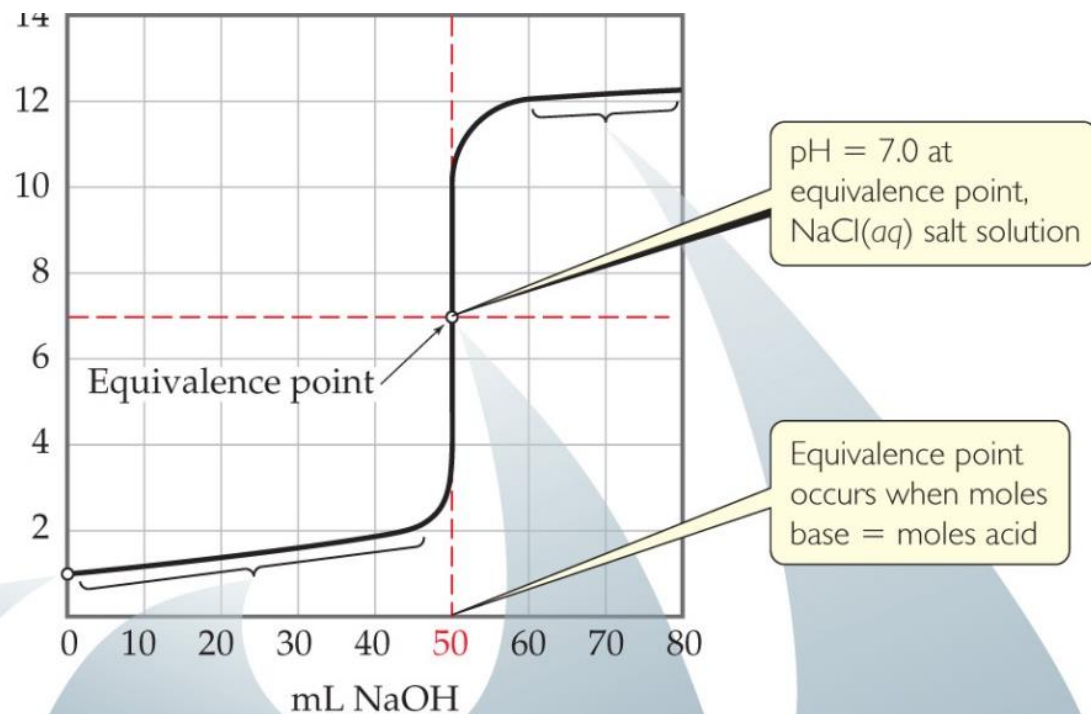
3  $\text{H}^+$  completely neutralized by  $\text{OH}^-$  ( $\text{pH} = 7.0$ )



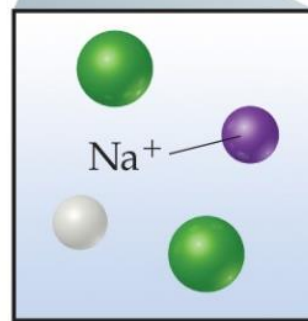
4 No  $\text{H}^+$  left to react with excess  $\text{OH}^-$  ( $\text{pH} > 7.0$ )

- Just before and after the equivalence point ( $\text{pH} = 7$ ), the pH rises rapidly.
- At the equivalence point, moles acid = moles base, & the solution contains only water and the salt.

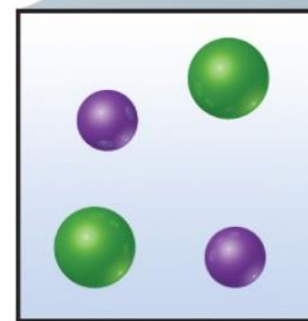
- As more base is added, the pH again levels off.



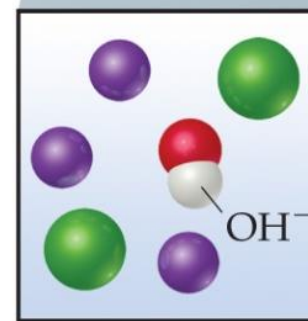
1 Only HCl(aq) present before titration



2  $\text{H}^+$  consumed as  $\text{OH}^-$  added, forming  $\text{H}_2\text{O}$  ( $\text{pH} < 7.0$ )



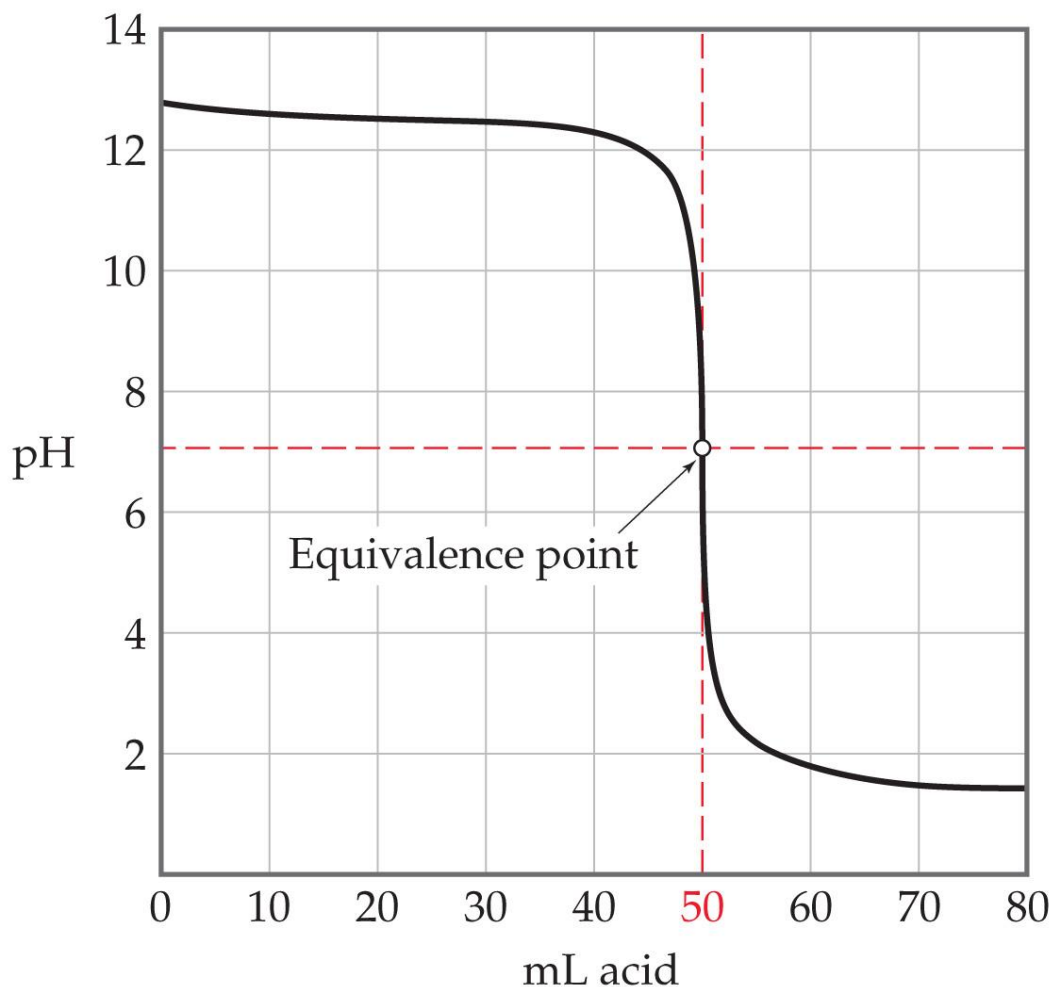
3  $\text{H}^+$  completely neutralized by  $\text{OH}^-$  ( $\text{pH} = 7.0$ )



4 No  $\text{H}^+$  left to react with excess  $\text{OH}^-$  ( $\text{pH} > 7.0$ )



# Titration of a Strong Base with a Strong Acid



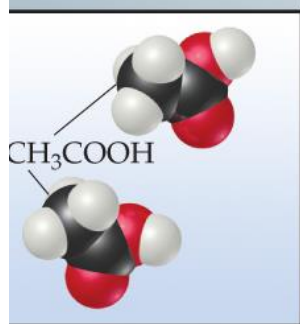
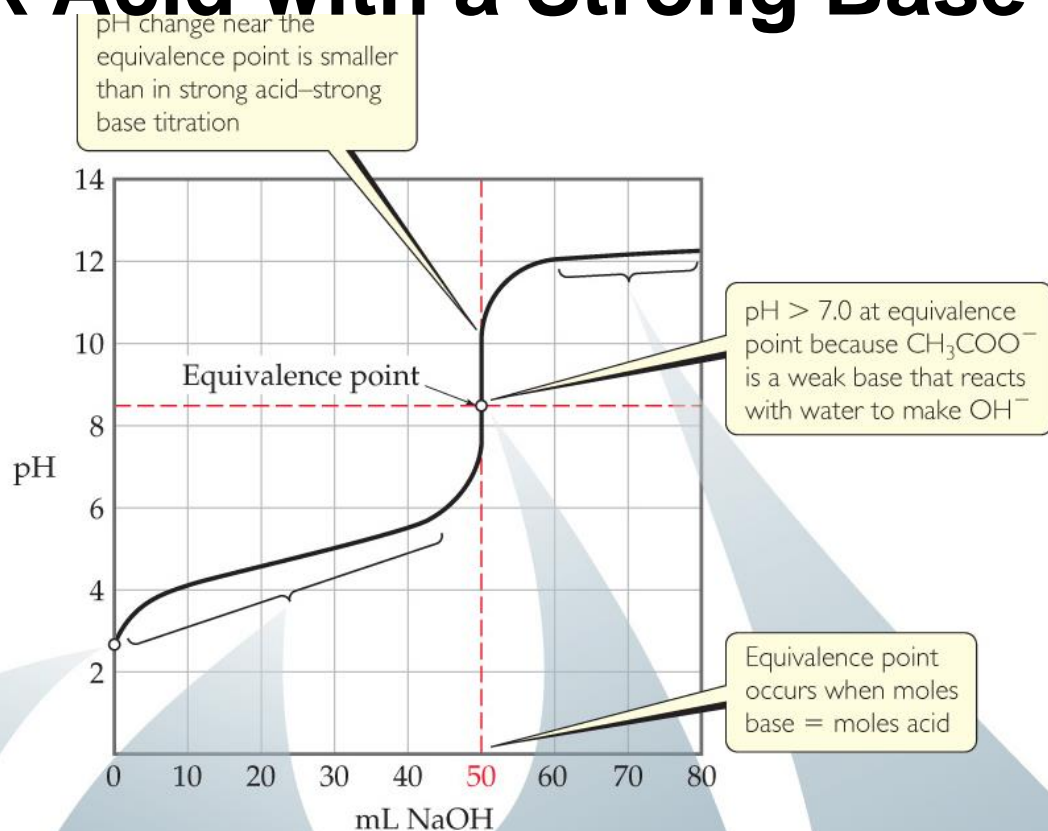
- Looks like you “flipped over” the strong acid being titrated by a strong base.

- Start with a high pH (basic solution); the **pH = 7** at the equivalence point; low pH to end.

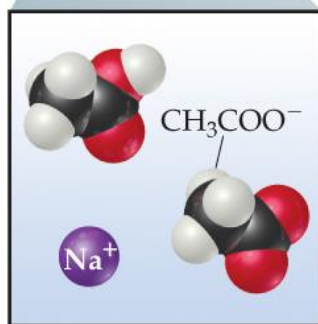
Acids  
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# Titration of a Weak Acid with a Strong Base

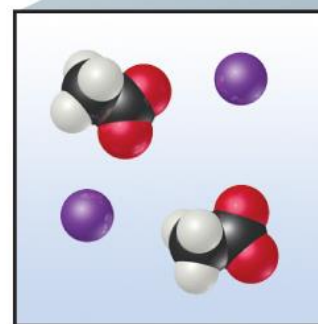
- At the equivalence point the pH is **>7**.
- Use the conjugate base of the weak acid to determine the pH.
- As more base is added, the pH levels off. This is same as for strong acids.



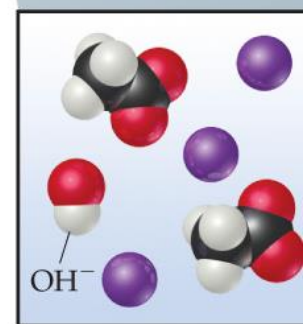
1  $\text{CH}_3\text{COOH}(aq)$  solution before titration



2 Added  $\text{OH}^-$  converts  $\text{CH}_3\text{COOH}(aq)$  into  $\text{CH}_3\text{COO}^-(aq)$ , forming buffer solution

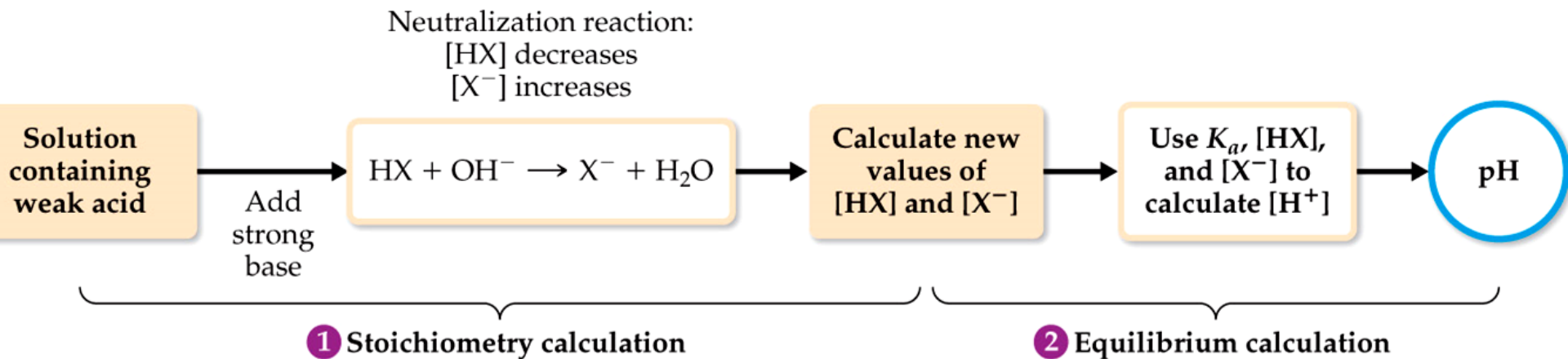


3 Acid completely neutralized by added base,  $\text{CH}_3\text{COONa}(aq)$  salt solution results



4 No acid left to react with excess  $\text{OH}^-$



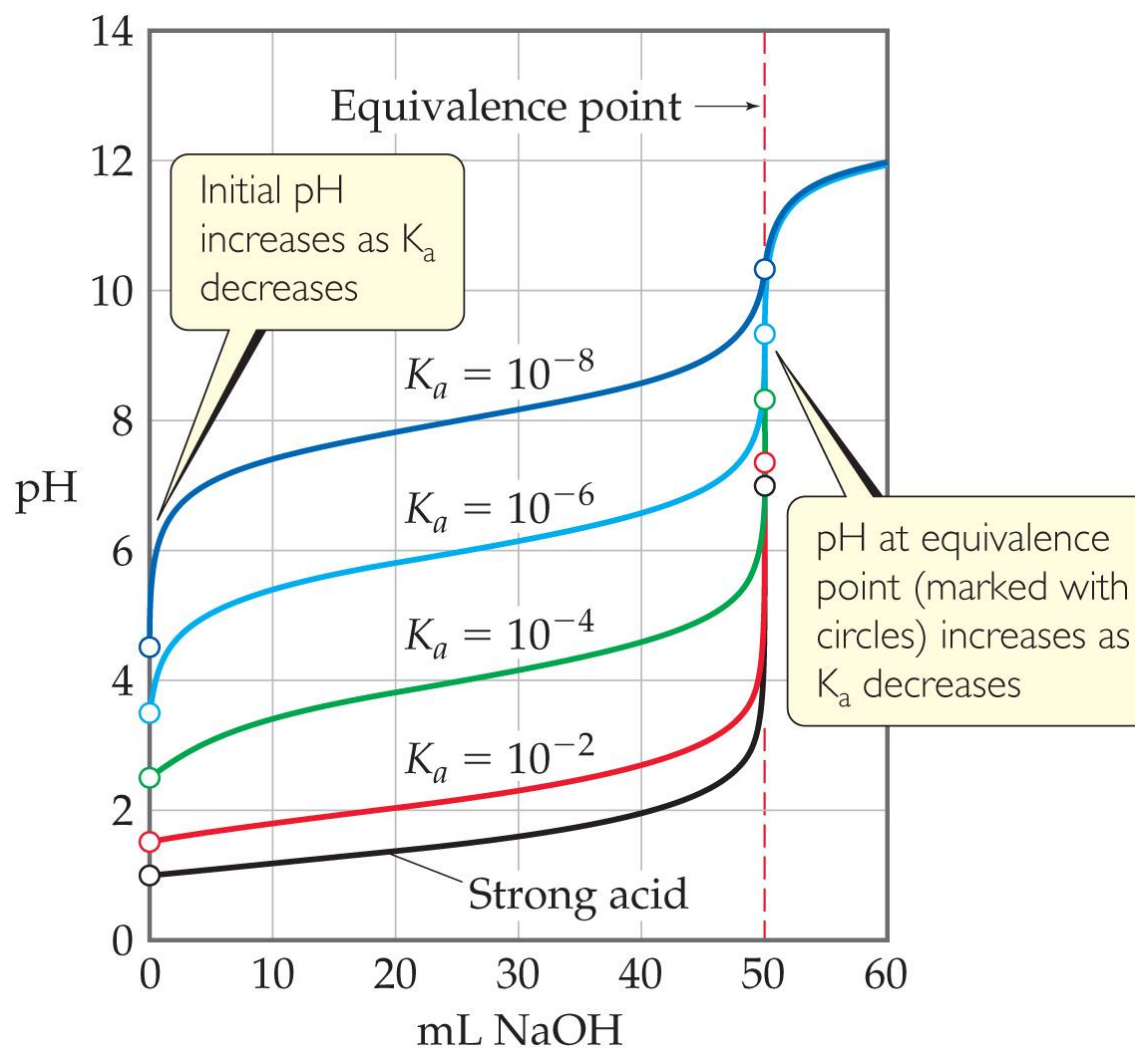


- Use  $K_a$  to find initial pH.
- Find the pH in the “buffer region” using stoichiometry followed by the Henderson–Hasselbalch equation.
- At each point below the equivalence point, the pH of the solution during titration is determined from the amounts of the acid and its conjugate base present at that particular time.
- Phenolphthalein is commonly used as an indicator in these titrations.

1) A solution of weak acid has a higher initial pH than a strong acid.

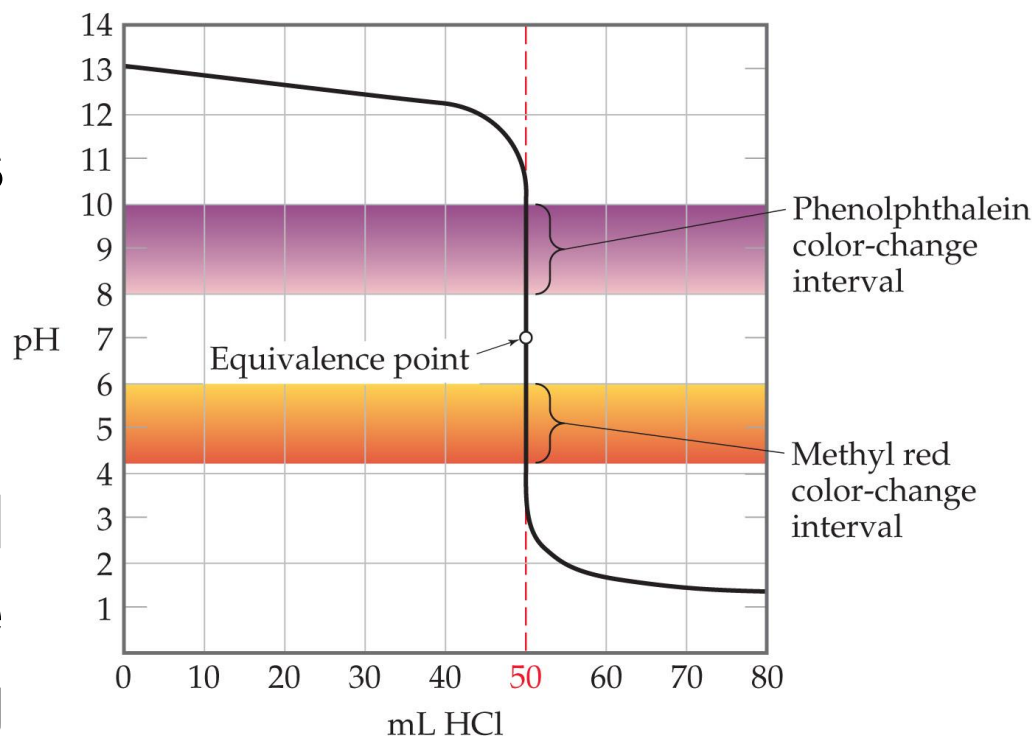
2) The **pH change** near the equivalence point is **smaller for a weak acid** (at least partly due to the buffer region).

3) The pH at the equivalence point is **greater than 7 for a weak acid**.



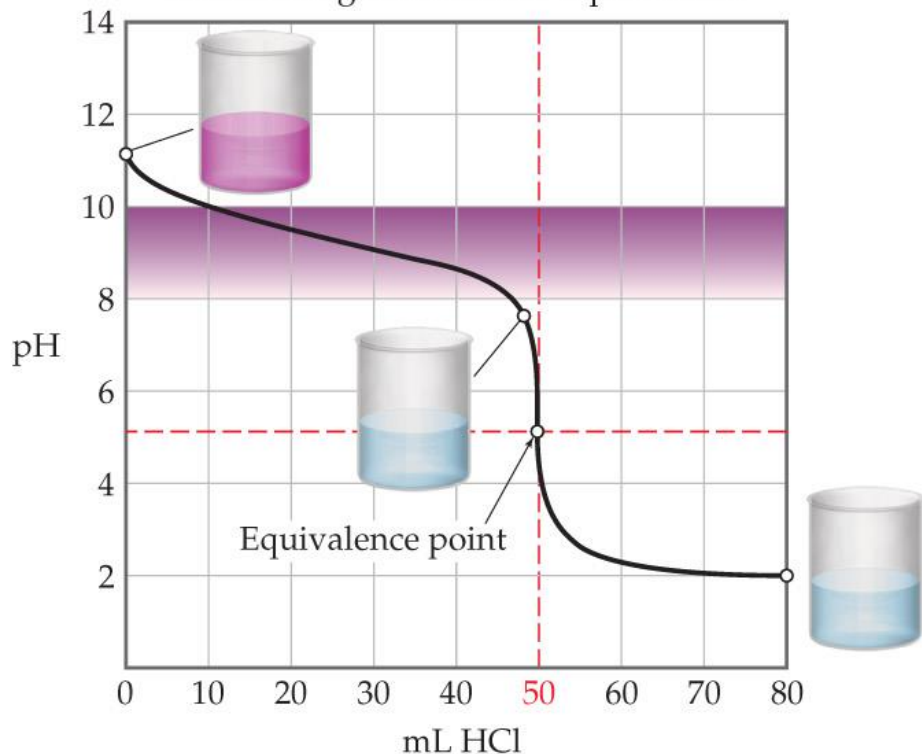
# Use of Indicators

- 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.**



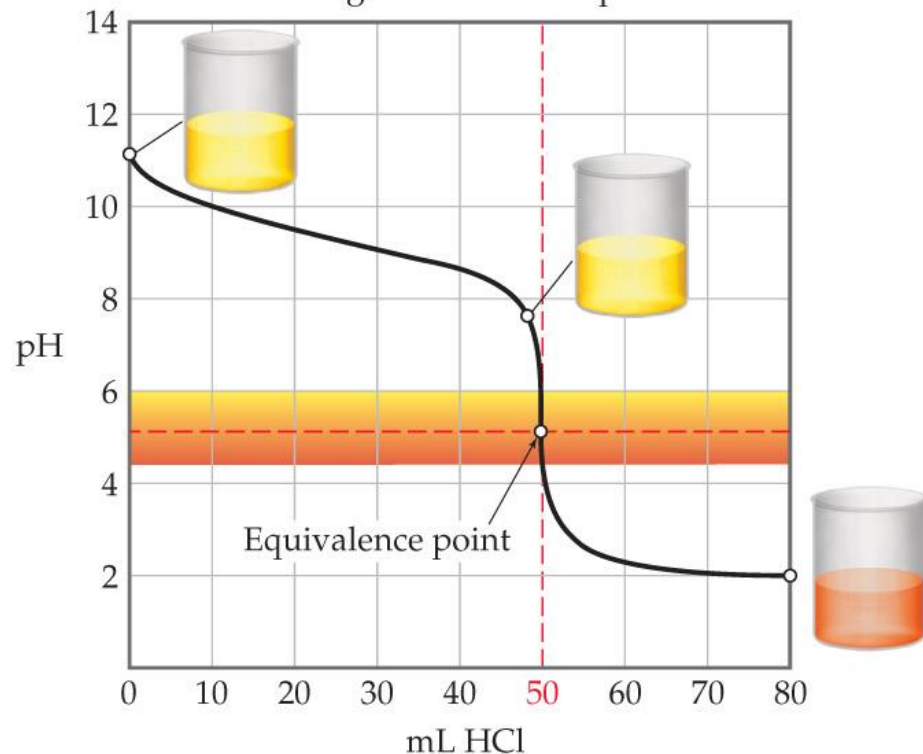
# Indicator Choice Can Be Critical!

Phenolphthalein indicator  
Color-change interval  $8.3 < \text{pH} < 10.0$



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

Methyl red indicator  
Color-change interval  $4.2 < \text{pH} < 6.0$



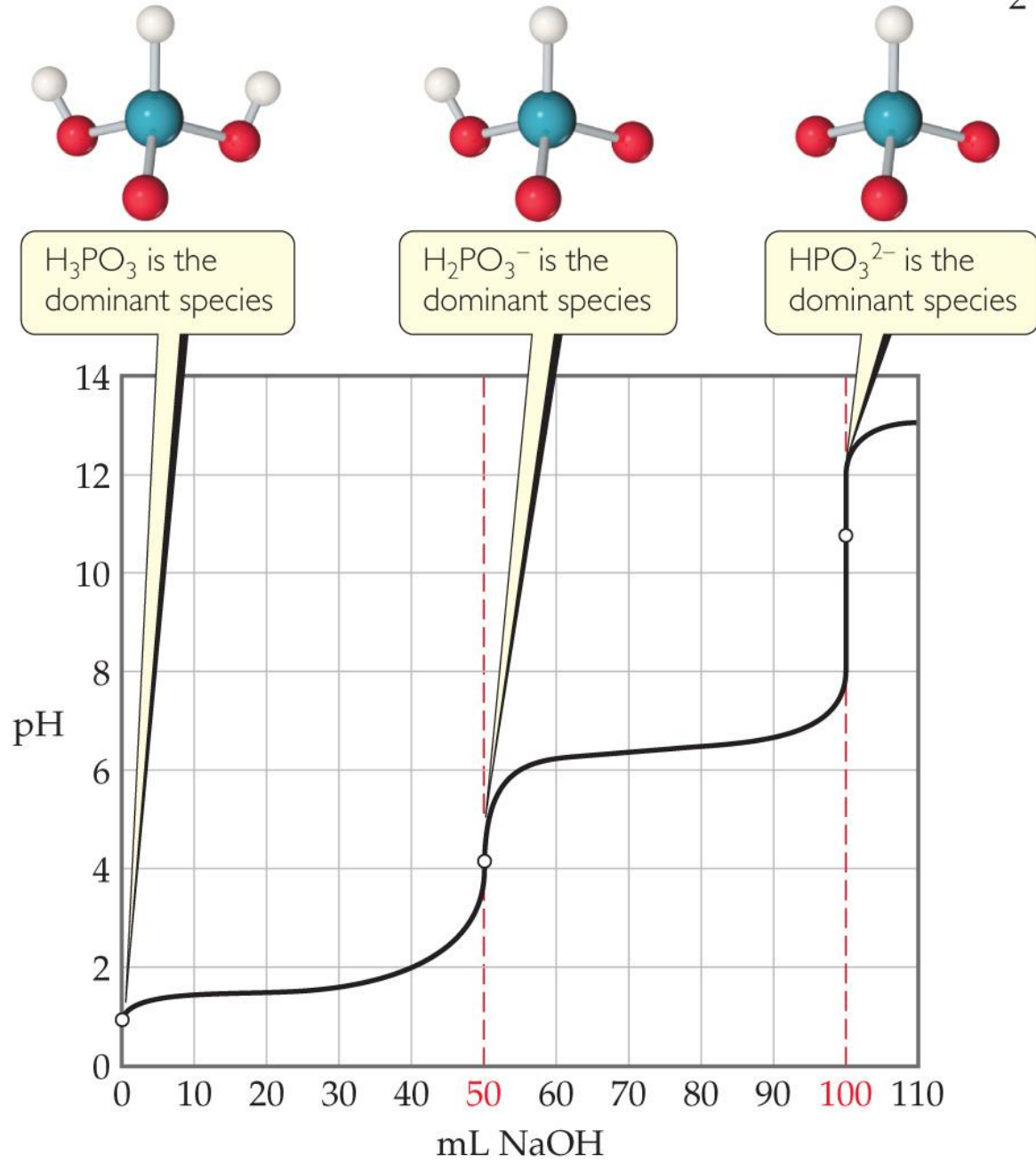
Suitable indicator for titration of a weak base with a strong acid because equivalence point falls within the color-change interval

- The pH at the equivalence point in these titrations is  $< 7$ , so using phenolphthalein would not be a good idea.
- Methyl red is the indicator of choice.



# Titration of Polyprotic Acids

- When a polyprotic acid is titrated with a base, there is an equivalence point for each dissociation.



If solutions of  $\text{NH}_4\text{Cl}(\text{aq})$  and  $\text{NH}_3(\text{aq})$  are mixed, which ions in the resulting solution are spectator ions in any acid–base chemistry occurring in the solution? What equilibrium reaction determines  $[\text{OH}^-]$  and, therefore, the pH of the solution?

(a)

- A. There are no spectator ions.
- B.  $\text{Cl}^-$
- C. Both  $\text{NH}_4^+$  and  $\text{Cl}^-$
- D.  $\text{NH}_4^+$

(b)

- A.  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
- B.  $\text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{HCl}(\text{l})$
- C.  $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$
- D.  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq})$

Which of these conjugate acid–base pairs will *not* function as a buffer:  $\text{C}_2\text{H}_5\text{COOH}$  and  $\text{C}_2\text{H}_5\text{COO}^-$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , or  $\text{HNO}_3$  and  $\text{NO}_3^-$ ? Explain.

- A. All listed pairs will not function as buffers.
- B.  $\text{HCHO}_2$  and  $\text{CHO}_2^-$  will not work as a buffer because  $\text{HCHO}_2$  is a weak acid and  $\text{CHO}_2^-$  is a spectator ion.
- C.  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  will not work as a buffer because  $\text{HCO}_3^-$  is a weak acid and  $\text{HCO}_3^-$  is a spectator ion.
- D.  $\text{HNO}_3$  and  $\text{NO}_3^-$  will not work as a buffer because  $\text{HNO}_3$  is a strong acid and  $\text{NO}_3^-$  is a spectator ion.



- a. What happens when NaOH is added to a buffer composed of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$ ?
- b. What happens when HCl is added to this buffer?

(a)

- A. There is no reaction because  $\text{C}_2\text{H}_3\text{O}_2^-$  and  $\text{C}_2\text{H}_3\text{O}_2\text{H}$  form a buffer.
- B. The NaOH reacts with  $\text{C}_2\text{H}_3\text{O}_2^-$  converting some of it into  $\text{C}_2\text{H}_3\text{O}_2\text{H}$ .
- C. The NaOH reacts with  $\text{C}_2\text{H}_3\text{O}_2\text{H}$  converting some of it into  $\text{C}_2\text{H}_3\text{O}_2^-$ .
- D. The NaOH is neutralized and all concentrations ( $\text{C}_2\text{H}_3\text{O}_2\text{H}$  and  $\text{C}_2\text{H}_3\text{O}_2^-$ ) remain unchanged.



- a. What happens when NaOH is added to a buffer composed of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$ ?
- b. What happens when HCl is added to this buffer?

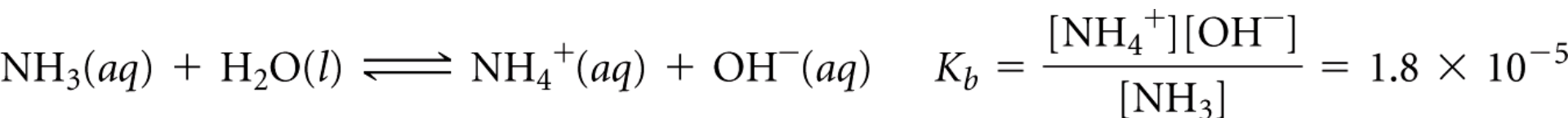
(b)

- A. There is no reaction because  $\text{C}_2\text{H}_3\text{O}_2^-$  and  $\text{C}_2\text{H}_3\text{O}_2\text{H}$  form a buffer.
- B. The HCl reacts with  $\text{C}_2\text{H}_3\text{O}_2^-$  converting some of it into  $\text{C}_2\text{H}_3\text{O}_2\text{H}$ .
- C. The HCl is neutralized and all concentrations ( $\text{C}_2\text{H}_3\text{O}_2\text{H}$  and  $\text{C}_2\text{H}_3\text{O}_2^-$ ) remain unchanged.
- D. The HCl reacts with  $\text{C}_2\text{H}_3\text{O}_2\text{H}$  converting some of it into  $\text{C}_2\text{H}_3\text{O}_2^-$ .

The  $K_a$  values for nitrous acid ( $\text{HNO}_2$ ) and hypochlorous ( $\text{HClO}$ ) acid are  $4.5 \times 10^{-4}$  and  $3.0 \times 10^{-8}$ , respectively. Which one would be more suitable for use in a solution buffered at  $\text{pH} = 7.0$ ? What other substance would be needed to make the buffer?

- A.  $\text{HClO}$  because it is a stronger weak acid. A salt containing  $\text{ClO}^-$  is also needed.
- B.  $\text{HNO}_2$  because it is a stronger weak acid. A salt containing  $\text{NO}_2^-$  is also needed.
- C.  $\text{HClO}$  because its  $\text{p}K_a$  is closer to  $\text{pH} = 7.0$ . A salt containing  $\text{ClO}^-$  is also needed.
- D.  $\text{HNO}_2$  because its  $\text{p}K_a$  is closer to  $\text{pH} = 7.0$ . A salt containing  $\text{NO}_2^-$  is also needed.

How many moles of  $\text{NH}_4\text{Cl}$  must be added to 2.0 L of 0.10 M  $\text{NH}_3$  to form a buffer whose pH is 9.00? (Assume that the addition of  $\text{NH}_4\text{Cl}$  does not change the volume of the solution.)



What is the pH at the equivalence point when 0.10  $M$   $\text{HNO}_3$  is used to titrate a volume of solution containing 0.30 g of  $\text{KOH}$ ?

- A.  $\text{pH} = 4.2$
- B.  $\text{pH} = 7.0$
- C.  $\text{pH} = 8.2$
- D.  $\text{pH} = 9.8$

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.

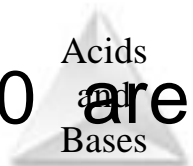
B. The volume of base increases but the equivalence point pH does not change.

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.

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

- A. The nearly vertical equivalence point portion of the titration curve is large for a weak acid-strong base titration, and fewer indicators undergo their color change so quickly because the change is difficult to monitor.
- B. The nearly vertical equivalence point portion of the titration curve is smaller for a weak acid-strong base titration, and fewer indicators undergo their color change within this narrow range.
- C. Many indicators do not change colors at the equivalence points of weak acid-strong base titrations.
- D. Equivalence points at pH's other than 7.00 are difficult to determine.



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<sub>3</sub>COOH ( $K_a = 1.8 \times 10^{-5}$ ).

For HCN,  $K_a = 4.9 \times 10^{-10}$ . What is the pH of a buffer solution in which  $[\text{HCN}] = 0.100 \text{ M} = [\text{KCN}]$  ?

- a. 4.7
- b. 7.0
- c. 9.3
- d. 14.0

For HCN,  $K_a = 4.9 \times 10^{-10}$ .  $[\text{HCN}] = 0.100 \text{ M}$ ,  $[\text{KCN}] = 0.200 \text{ M}$ , pH of buffer solution = \_\_\_\_\_.

- a. 7.0
- b. 9.0
- c. 9.3
- d. 9.6



For HCN,  $K_a = 4.9 \times 10^{-10}$ .  $[\text{HCN}] = 1.00 \text{ M}$ ,  $[\text{KCN}] = 0.100 \text{ M}$ , pH of buffer solution = \_\_\_\_\_.

- a. 7.0
- b. 8.3
- c. 9.0
- d. 9.3

When titrating a weak base with a strong acid, a good indicator to use would be

- a. methyl red (color change at pH = 5).
- b. bromothymol blue (change at pH = 7).
- c. phenolphthalein (change at pH = 9).
- d. None of the above

When titrating a weak acid with a strong base, a good indicator to use would be

- a. methyl red (color change at  $\text{pH} = 5$ ).
- b. bromothymol blue (change at  $\text{pH} = 7$ ).
- c. phenolphthalein (change at  $\text{pH} = 9$ ).
- d. None of the above

Which of the following mixtures could be used to prepare an effective buffer solution?

- a.  $\text{HCl}$  and  $\text{KCl}$
- b.  $\text{HNO}_3$  and  $\text{KNO}_3$
- c.  $\text{HCl}$  and  $\text{NH}_4\text{Cl}$
- d.  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$

# Solubility Equilibria

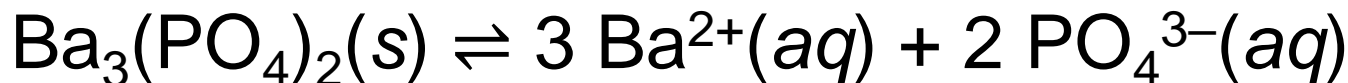
- Consider the equilibrium in **a saturated solution** of  $\text{BaSO}_4$  in water. An equilibrium equation can be expressed (**ions in solution: the products**):



- The equilibrium constant expression is called the **solubility-product constant**. It is represented as  $K_{sp}$ .

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

- Another example:

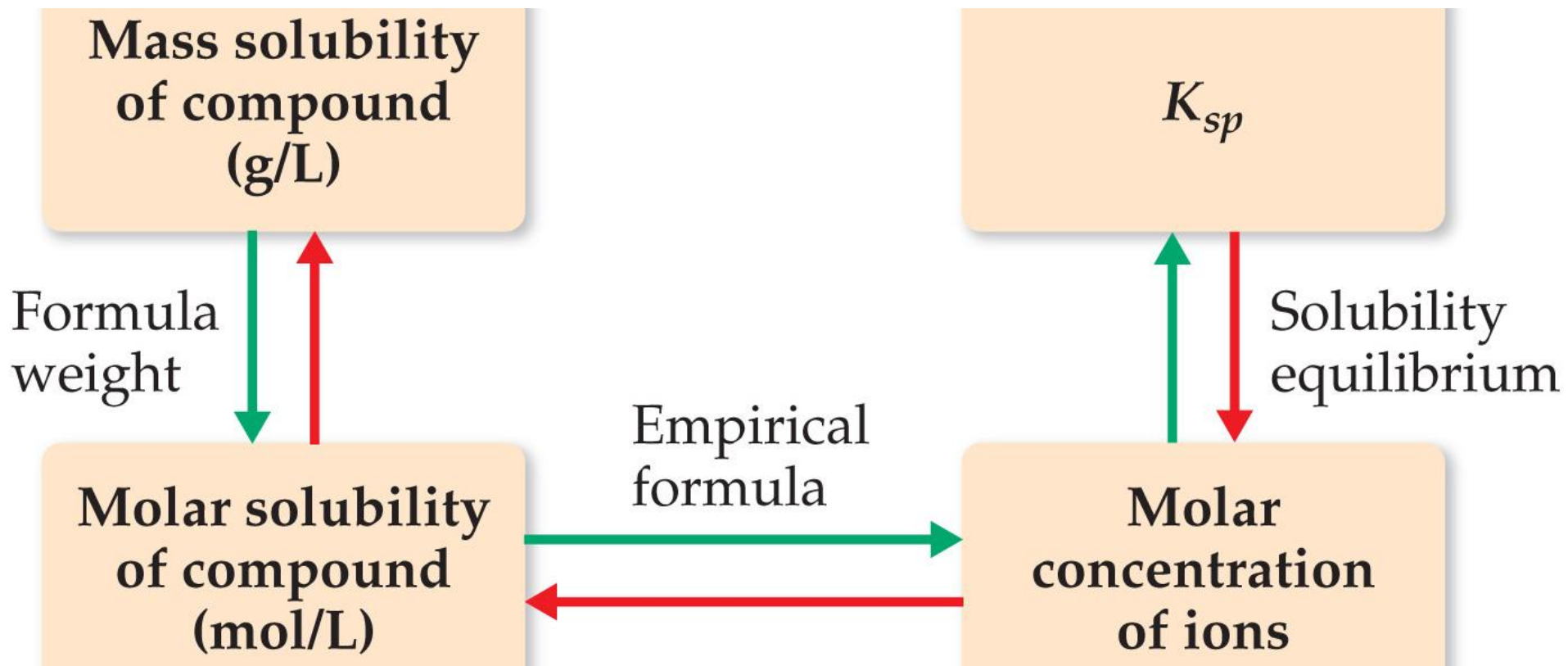


- The equilibrium constant expression is

$$K_{sp} = [\text{Ba}^{2+}]^3[\text{PO}_4^{3-}]^2$$

# 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** and is generally expressed as the mass of solute dissolved in 1 L (g/L) or 100 mL (g/mL) of solution, or in mol/L (**M**).



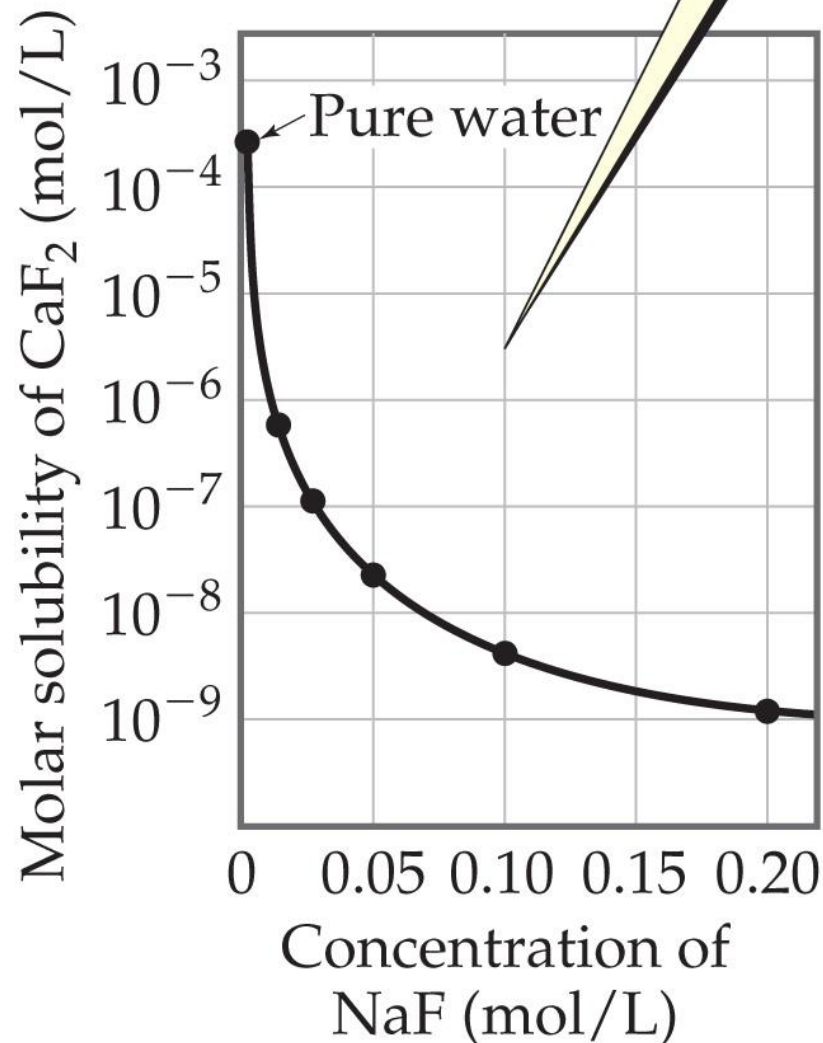
# Factors Affecting Solubility

- The **Common-Ion Effect**:

1) If one of the ions in a solution equilibrium is already dissolved in the solution, the **solubility of the salt** will **decrease**.

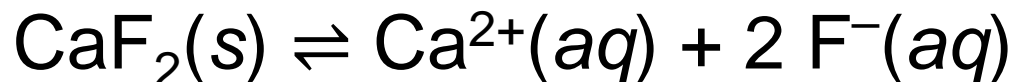
2) If either calcium ions or fluoride ions are present, then calcium fluoride will be less soluble.

Solubility of  $\text{CaF}_2$  decreases sharply as a common ion ( $\text{F}^-$ ) is added to the solution



# Calculating Solubility from $K_{sp}$

- The  $K_{sp}$  for  $\text{CaF}_2$  is  $3.9 \times 10^{-11}$  at  $25^\circ\text{C}$ . What is its molar solubility?



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

	$\text{CaF}_2(s)$	$\rightleftharpoons$	$\text{Ca}^{2+}(aq)$	+	$2 \text{F}^{-}(aq)$
Initial concentration ( $M$ )	—		0		0
Change ( $M$ )	—		$+x$		$+2x$
Equilibrium concentration ( $M$ )	—		$x$		$2x$

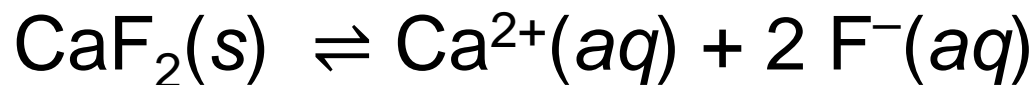
$$3.9 \times 10^{-11} = (x)(2x)^2 = 4x^3$$

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

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

# Calculating Solubility with a Common Ion

What is the molar solubility of  $\text{CaF}_2$  in  $0.010\text{ M}$   $\text{Ca}(\text{NO}_3)_2$ ?



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

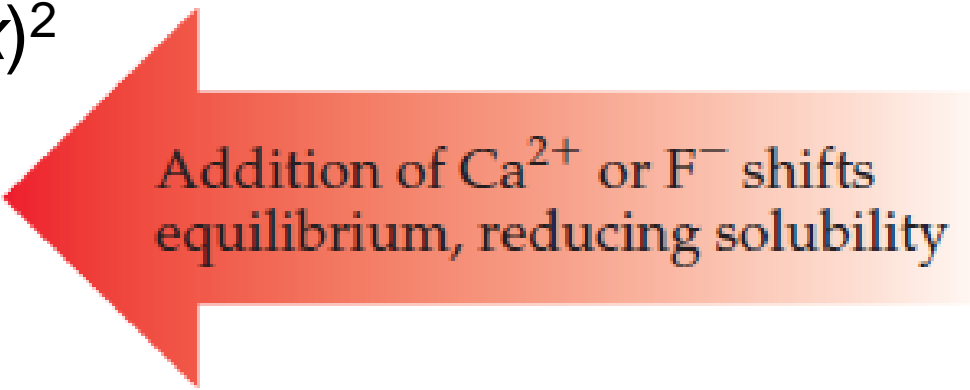
	$\text{CaF}_2(\text{s})$	$\rightleftharpoons$	$\text{Ca}^{2+}(\text{aq})$	$+$	$2\text{F}^{-}(\text{aq})$
Initial Concentration ( $M$ )	—		0.010		0
Change ( $M$ )	—		$+x$		$+2x$
Equilibrium Concentration ( $M$ )	—		$(0.010 + x)$		$2x$

$$3.9 \times 10^{-11} = (0.010 + x)(2x)^2$$

Assuming  $x \ll 0.010$ ,

$$3.9 \times 10^{-11} = (0.010)(2x)^2$$

$$x = 3.1 \times 10^{-5}\text{ M}$$

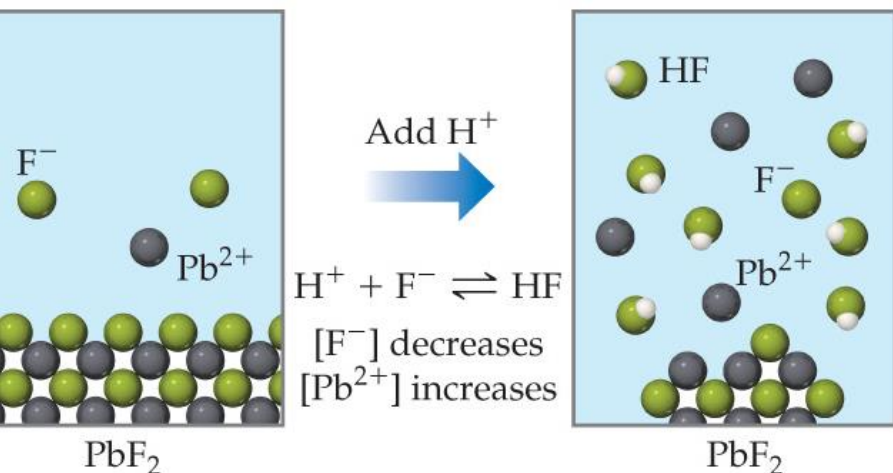


Addition of  $\text{Ca}^{2+}$  or  $\text{F}^{-}$  shifts equilibrium, reducing solubility

# Factors Affecting Solubility

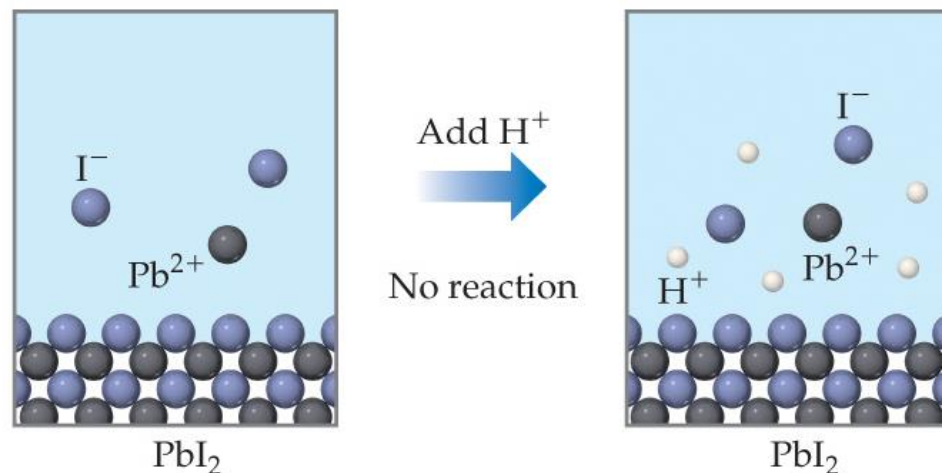
- **pH**: If a **substance** has a **basic** anion, it will be more **soluble** in an **acidic solution**.
- Remember that buffers control pH. When a buffer is used, there is *no change* in concentration of hydroxide ion!

Salt whose anion is conjugate base of weak acid:  
*Solubility increases as pH decreases*



(a)

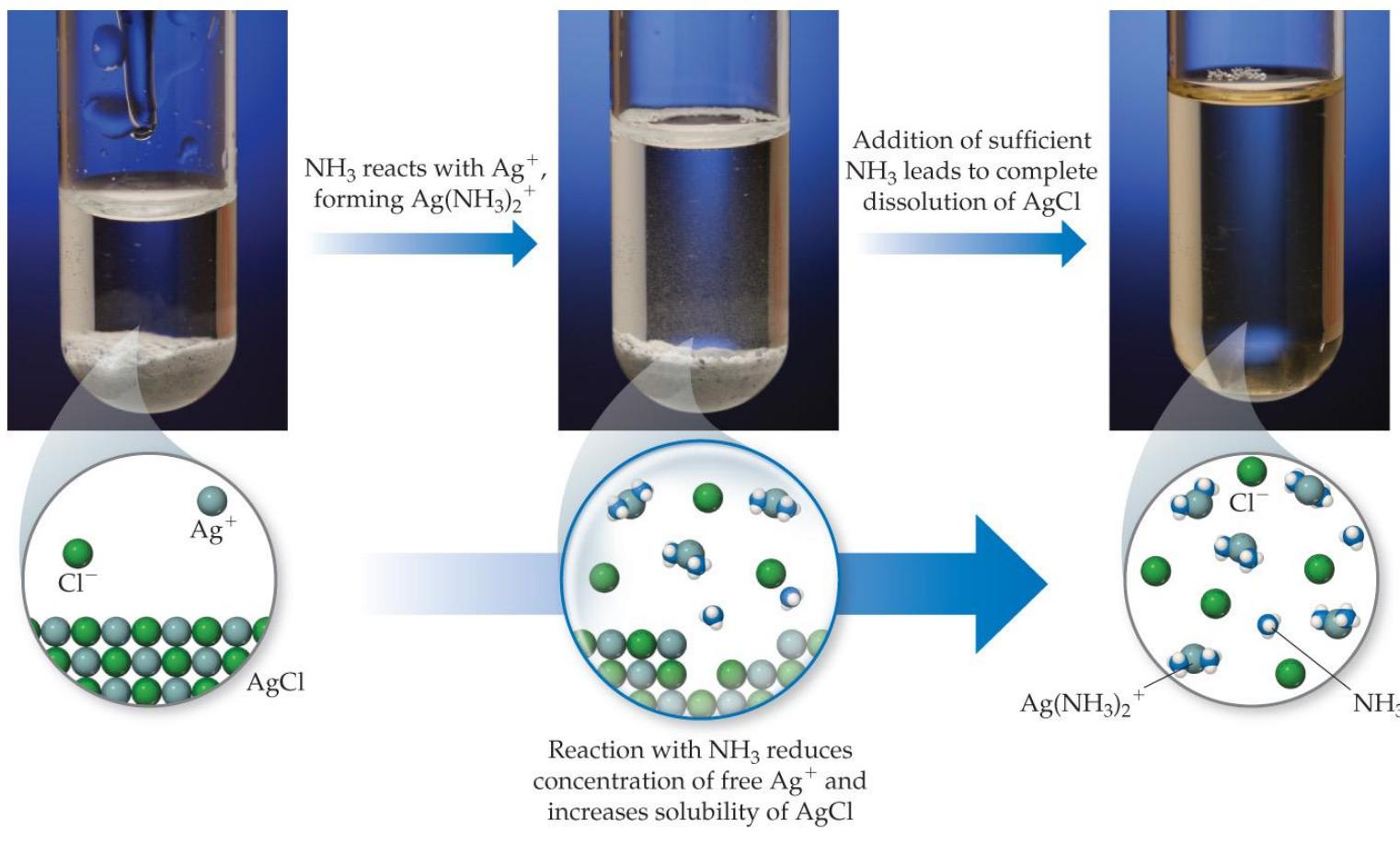
Salt whose anion is conjugate base of strong acid:  
*Solubility unaffected by changes in pH*

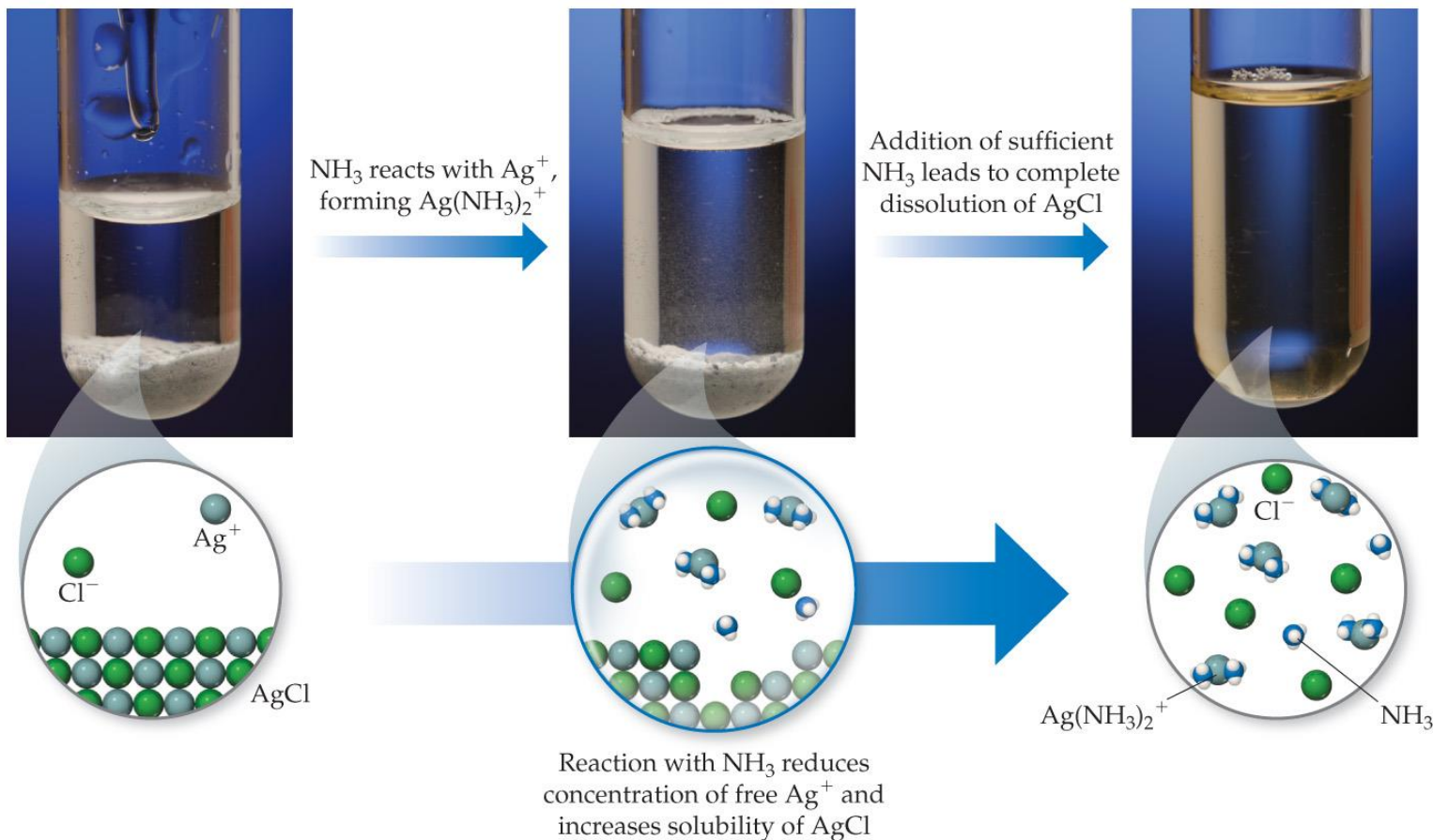


(b)



- **Complex Ion Formation:** Metal ions can act as Lewis acids and form **complex ions** (络离子) with Lewis bases in the solvent.
- The **formation** of these **complex ions** increases the **solubility** of these salts.



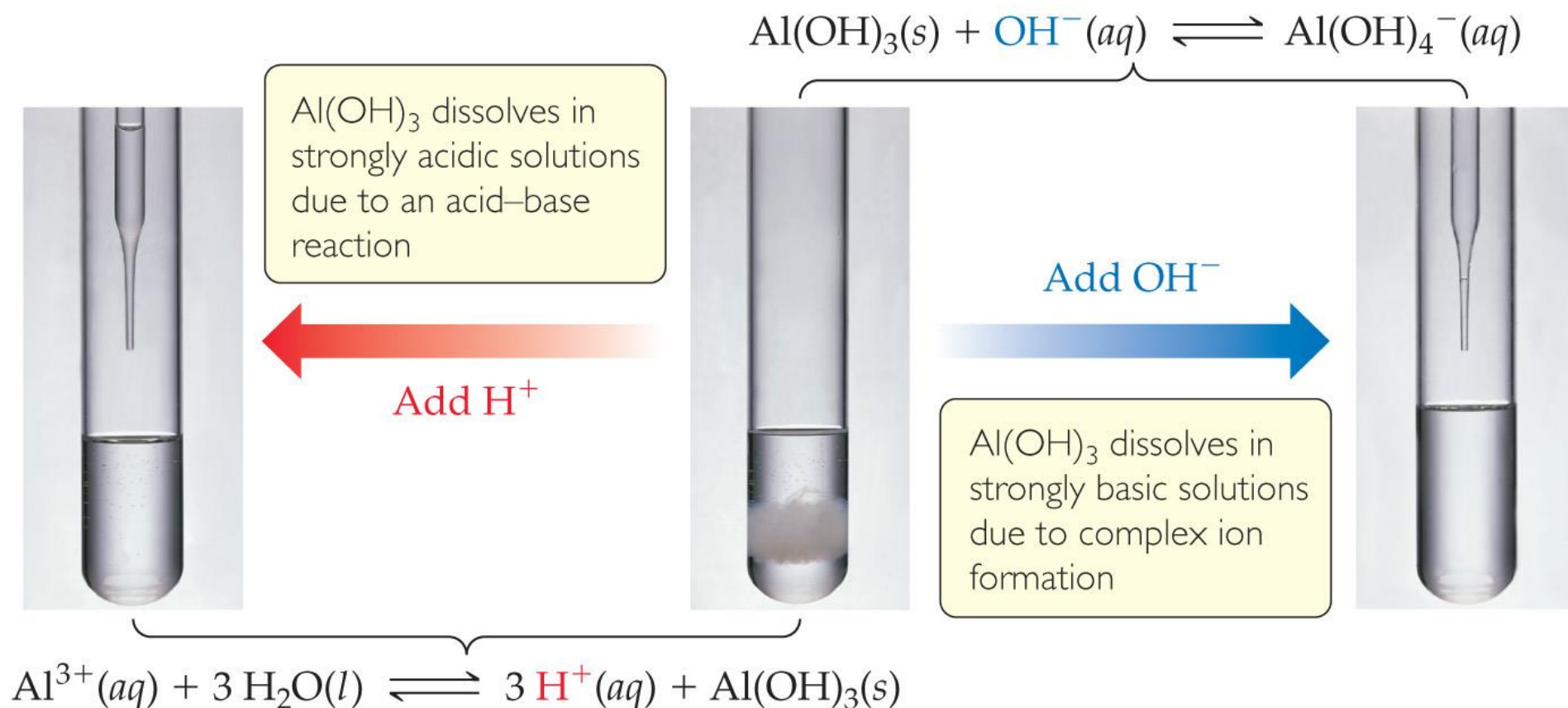


- Silver chloride is insoluble. It has a  $K_{sp}$  of  $1.6 \times 10^{-10}$ .
- In the presence of  $\text{NH}_3$ , the solubility greatly increases because  **$\text{Ag}^+$  will form complex ions with  $\text{NH}_3$ .**

**Table 17.1 Formation Constants for Some Metal Complex Ions in Water at 25 °C**

Complex Ion	$K_f$	Equilibrium Equation
$\text{Ag}(\text{NH}_3)_2^+$	$1.7 \times 10^7$	$\text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$
$\text{Ag}(\text{CN})_2^-$	$1 \times 10^{21}$	$\text{Ag}^+(aq) + 2 \text{CN}^-(aq) \rightleftharpoons \text{Ag}(\text{CN})_2^-(aq)$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	$2.9 \times 10^{13}$	$\text{Ag}^+(aq) + 2 \text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq)$
$\text{CdBr}_4^{2-}$	$5 \times 10^3$	$\text{Cd}^{2+}(aq) + 4 \text{Br}^-(aq) \rightleftharpoons \text{CdBr}_4^{2-}(aq)$
$\text{Cr}(\text{OH})_4^-$	$8 \times 10^{29}$	$\text{Cr}^{3+}(aq) + 4 \text{OH}^-(aq) \rightleftharpoons \text{Cr}(\text{OH})_4^-(aq)$
$\text{Co}(\text{SCN})_4^{2-}$	$1 \times 10^3$	$\text{Co}^{2+}(aq) + 4 \text{SCN}^-(aq) \rightleftharpoons \text{Co}(\text{SCN})_4^{2-}(aq)$
$\text{Cu}(\text{NH}_3)_4^{2+}$	$5 \times 10^{12}$	$\text{Cu}^{2+}(aq) + 4 \text{NH}_3(aq) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(aq)$
$\text{Cu}(\text{CN})_4^{2-}$	$1 \times 10^{25}$	$\text{Cu}^{2+}(aq) + 4 \text{CN}^-(aq) \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}(aq)$
$\text{Ni}(\text{NH}_3)_6^{2+}$	$1.2 \times 10^9$	$\text{Ni}^{2+}(aq) + 6 \text{NH}_3(aq) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(aq)$
$\text{Fe}(\text{CN})_6^{4-}$	$1 \times 10^{35}$	$\text{Fe}^{2+}(aq) + 6 \text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}(aq)$
$\text{Fe}(\text{CN})_6^{3-}$	$1 \times 10^{42}$	$\text{Fe}^{3+}(aq) + 6 \text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}(aq)$

- **Amphoterism** (酸碱两性现象): 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  **$\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Sn}^{2+}$** .

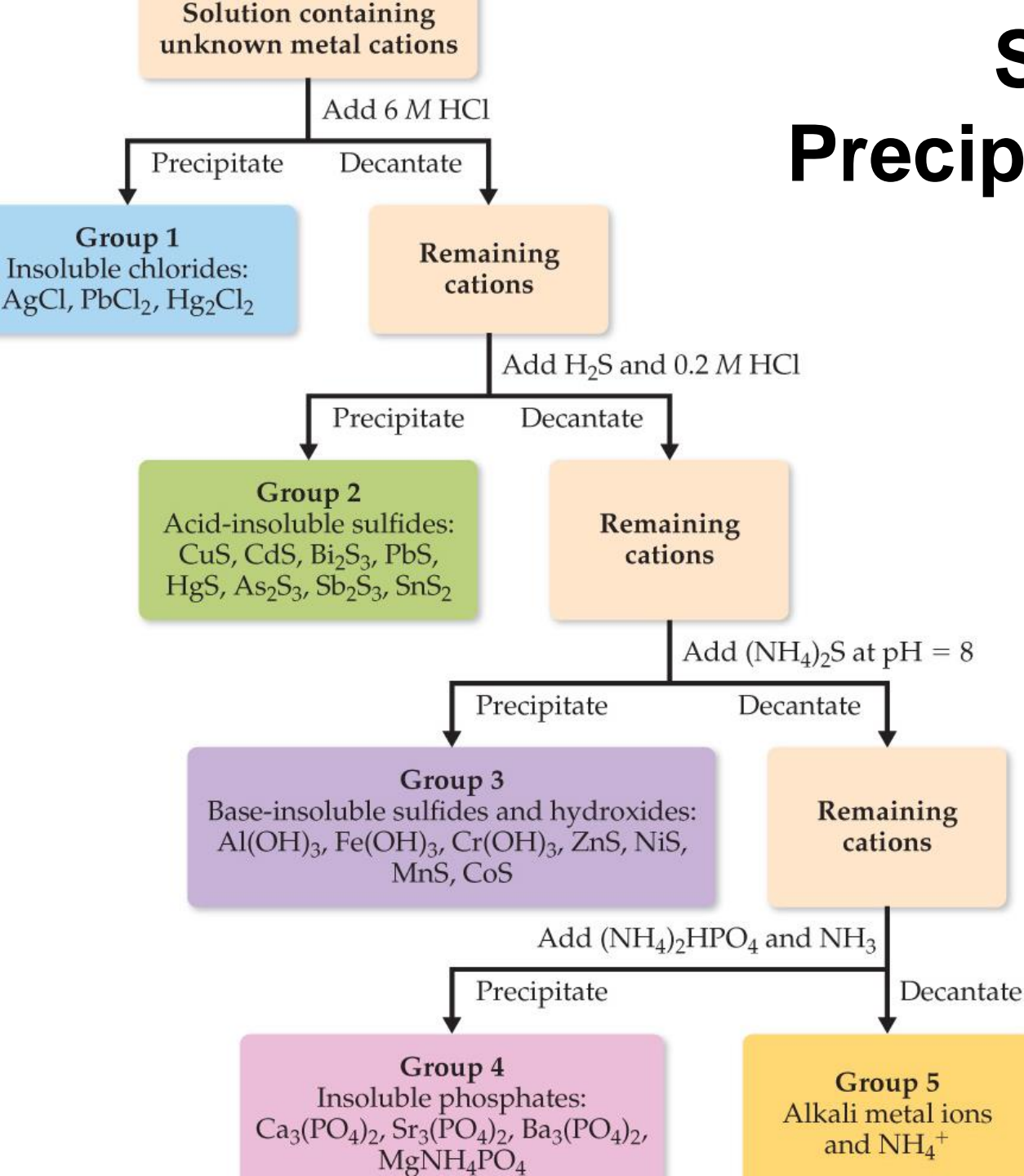


# Will a Precipitate Form?

- 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**.



# Selective Precipitation of Ions



- 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.

Acids  
and  
Bases

Mixture of  
cations A,B,C



Add 1st  
precipitating  
agent



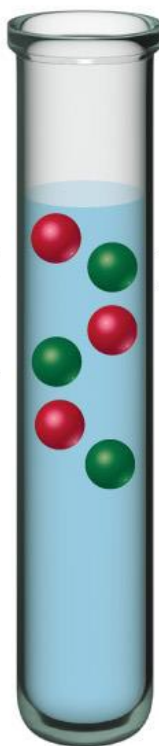
Cation A  
removed



Decant  
liquid



Cations  
B,C



Add 2nd  
precipitating  
agent



Cation B  
removed



Decant  
liquid



Cation  
C



Cation A ●

Cation B ●

Cation C ●

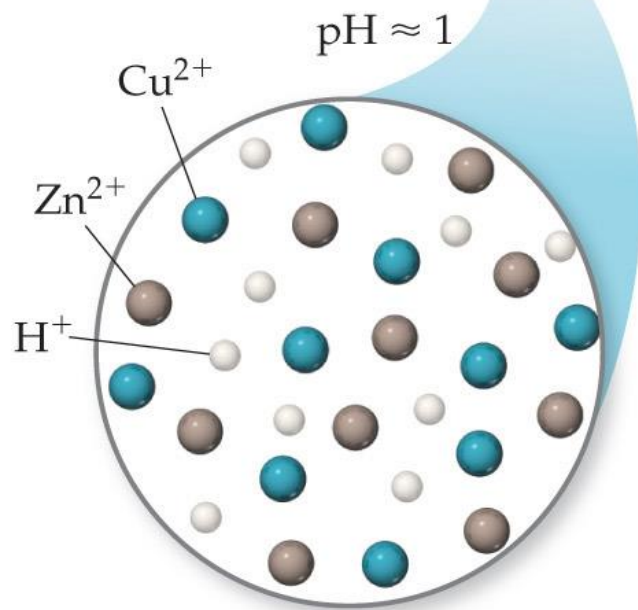
Acids  
and  
Bases



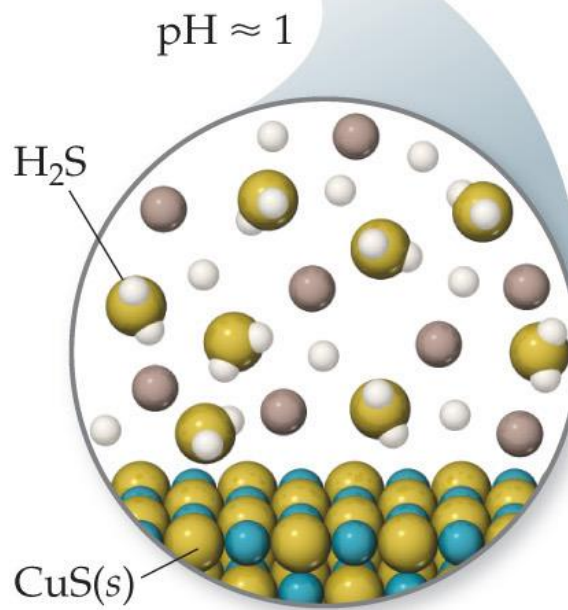
Add  $\text{H}_2\text{S}$



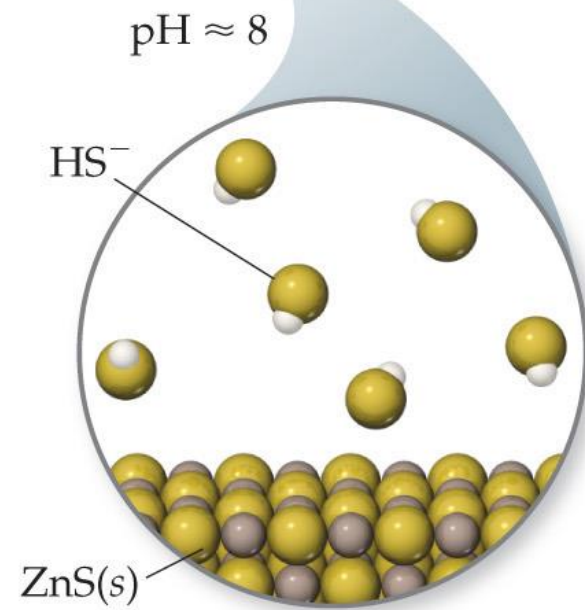
Remove  $\text{CuS}$   
and  
increase pH



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



When  $\text{H}_2\text{S}$  is added to a  
solution whose pH exceeds 0.6,  
 $\text{CuS}$  precipitates



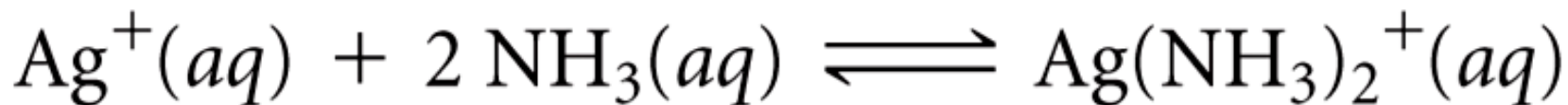
After  $\text{CuS}$  is removed, the pH  
is increased, allowing  $\text{ZnS}$  to  
precipitate



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

- A. AgI is the most soluble of the three.
- B. AgBr is the most soluble of the three.
- C. AgCl is the most soluble of the three.
- D. All of the compounds are totally insoluble based on their small  $K_{sp}$  values.

Calculate the concentration of  $\text{Ag}^+$  present in solution at equilibrium when concentrated ammonia is added to a  $0.010\text{ M}$  solution of  $\text{AgNO}_3$  to give an equilibrium concentration of  $[\text{NH}_3] = 0.20\text{ M}$ . Neglect the small volume change that occurs when  $\text{NH}_3$  is added.



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

- A. Amphoteric substances are acids whereas amphiprotic substances are acids.
- B. Amphoteric substances are bases whereas amphiprotic substances are acids.
- C. Amphoteric substances can act both as an acid and a base whereas amphiprotic substances are acids.
- D. Amphoteric substances can act both as an acid and a base whereas amphiprotic substances can accept or donate a proton.

Does a precipitate form when 0.10 L of  $8.0 \times 10^{-3} \text{ M}$   $\text{Pb}(\text{NO}_3)_2$  is added to 0.40 L of  $5.0 \times 10^{-3} \text{ M}$   $\text{Na}_2\text{SO}_4$ ?  
 $\text{PbSO}_4$  has a  $K_{sp}$  of  $6.3 \times 10^{-7}$

If a solution contained a mixture of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  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,  $\text{ZnS}$  precipitates in step 1 and  $\text{CuS}$  in step 4.

D. Yes,  $\text{CuS}$  precipitates in step 2 and  $\text{Zn}^{2+}$  remains in solution.

If a precipitate forms when HCl is added to an aqueous solution, what conclusions can you draw about the contents of the solution?

- A. The solution definitely contains either  $\text{Pb}^{2+}$  or  $\text{Hg}_2^{2+}$  cation.
- B. The solution definitely contains the  $\text{Ag}^+$  cation.
- C. The solution must contain one or more of the following cations:  $\text{Cu}^{2+}$ ,  $\text{Bi}^{3+}$ , or  $\text{Cd}^{2+}$ .
- D. The solution must contain one or more of the following cations:  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$  or  $\text{Hg}_2^{2+}$ .

Adding bromide ion to a saturated aqueous solution of \_\_\_\_\_ decreases its solubility in water.

- a.  $\text{BaSO}_4$
- b.  $\text{Li}_2\text{CO}_3$
- c.  $\text{PbS}$
- d.  $\text{AgBr}$

For  $\text{BaCO}_3$ ,  $K_{\text{sp}} = 5.0 \times 10^{-9}$ . What is  $[\text{Ba}^{2+}]$  in a saturated aqueous solution of  $\text{BaCO}_3$ ?

- a.  $7.1 \times 10^{-5} \text{ M}$
- b.  $1.0 \times 10^{-8} \text{ M}$
- c.  $2.5 \times 10^{-9} \text{ M}$
- d.  $5.0 \times 10^{-9} \text{ M}$

For  $\text{BaF}_2$ ,  $K_{\text{sp}} = 1.7 \times 10^{-6}$ . What is  $[\text{Ba}^{2+}]$  in a saturated aqueous solution of  $\text{BaF}_2$ ?

- a.  $1.7 \times 10^{-6} \text{ M}$
- b.  $3.4 \times 10^{-6} \text{ M}$
- c.  $7.6 \times 10^{-3} \text{ M}$
- d.  $1.5 \times 10^{-2} \text{ M}$

For  $\text{BaF}_2$ ,  $K_{\text{sp}} = 1.7 \times 10^{-6}$ . What is  $[\text{F}^{1-}]$  in a saturated aqueous solution of  $\text{BaF}_2$ ?

- a.  $1.7 \times 10^{-6} \text{ M}$
- b.  $5.7 \times 10^{-5} \text{ M}$
- c.  $7.6 \times 10^{-3} \text{ M}$
- d.  $1.5 \times 10^{-2} \text{ M}$



For  $\text{BaF}_2$ ,  $K_{\text{sp}} = 1.7 \times 10^{-6}$ . If KF is added to a saturated solution so that  $[\text{F}^{1-}] = 0.10 \text{ M}$ , what is  $[\text{Ba}^{2+}]$ ?

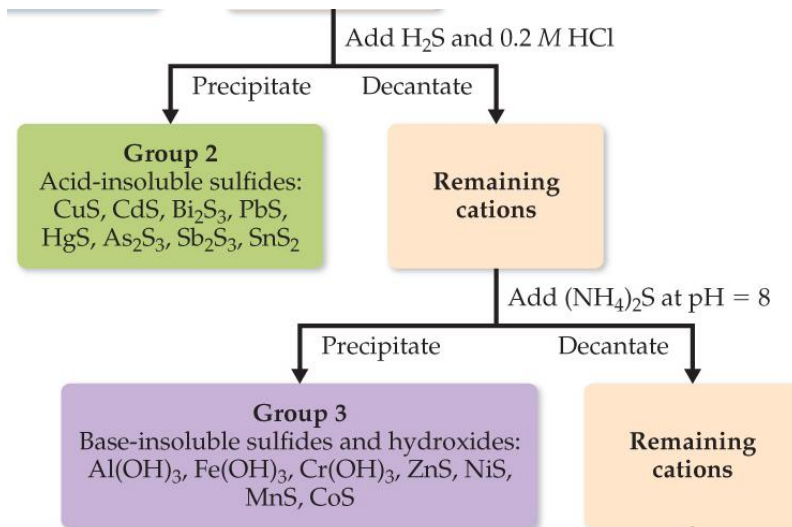
- a.  $1.7 \times 10^{-6} \text{ M}$
- b.  $1.7 \times 10^{-5} \text{ M}$
- c.  $1.7 \times 10^{-4} \text{ M}$
- d.  $1.7 \times 10^{-3} \text{ M}$

Silver bromide is insoluble in water, but dissolves in aqueous ammonia, due to the formation of \_\_\_\_\_.

- a.  $\text{Ag}(\text{NH}_3)_2^{1+}$
- b.  $\text{Ag}(\text{NH}_3)^{2+}$
- c.  $\text{NH}_3\text{Br}^{1-}$
- d.  $\text{NH}_4\text{Br}$

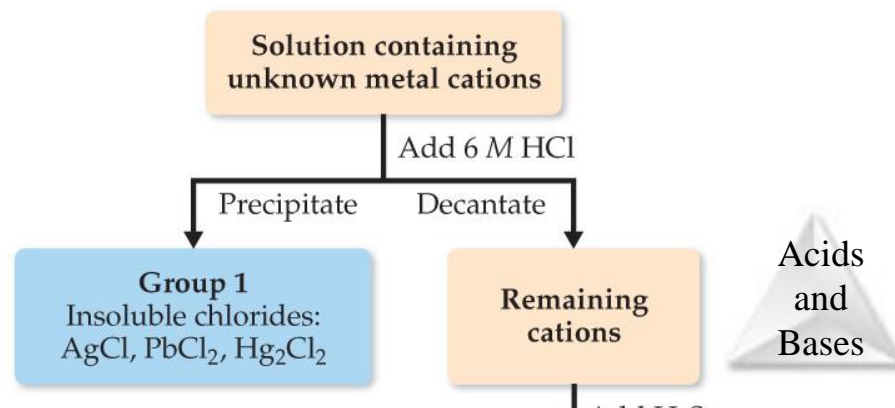
Which ion will precipitate first when sulfide ion is added to a solution containing all of the ions below?

- a.  $\text{Hg}^{2+}$
- b.  $\text{Pb}^{2+}$
- c.  $\text{Zn}^{2+}$
- d.  $\text{Cd}^{2+}$



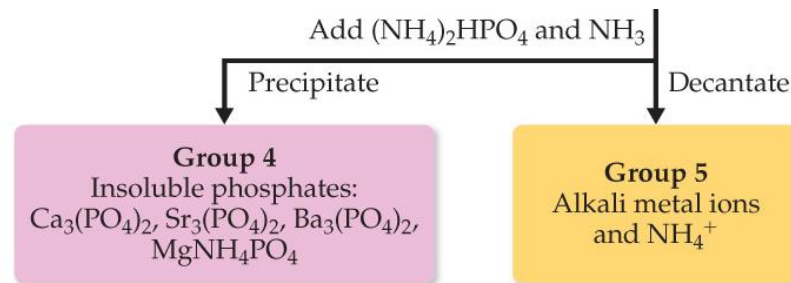
Which ion will precipitate when  $\text{HCl}$  is added to a solution containing all of the ions below?

- a.  $\text{Zn}^{2+}$
- b.  $\text{Pb}^{2+}$
- c.  $\text{Al}^{3+}$
- d.  $\text{Ba}^{2+}$



Which ion will precipitate when phosphate ion is added to a solution containing all of the ions below?

- a.  $\text{K}^{1+}$
- b.  $\text{Ba}^{2+}$
- c.  $\text{Na}^{1+}$
- d.  $\text{NH}_4^{1+}$



# Summary of Chapter 17

The common-ion effect

Buffer solution, Henderson–Hasselbalch equation

Solubility equilibria, solubility-product constant ( $K_{sp}$ ),  
Complex ion formation, amphotericism

**Thank You for Your  
Attention!  
Any Questions?**

