

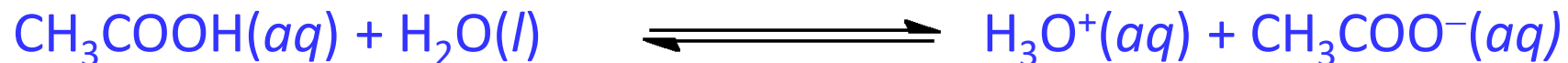
# **Chapter 17**

## **Additional Aspects of Aqueous Equilibria**

**By Zhen-Yu Wu**

## ➤ The Common-Ion Effect

- Consider a solution of acetic acid:



- If acetate ion is added to the solution, Le Châtelier says the equilibrium will shift to the left.

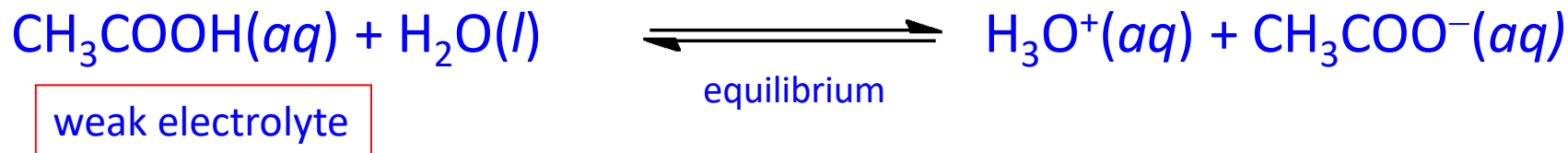
- Common-ion effect

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.

# ➤ The Common-Ion Effect

- “The extent of ionization of a weak electrolyte is decreased in the solution by adding a strong electrolyte that has an ion in **common** with the weak electrolyte.”

在弱电解质溶液中加入跟该电解质有相同离子的强电解质，可以降低弱电解质的电离度，这种叫做**同离子效应**



Addition of  $\text{CH}_3\text{COO}^-$  shifts equilibrium to the left, reducing  $[\text{H}_3\text{O}^+]$

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)

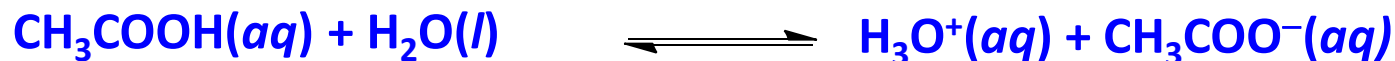
☒ A.  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

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.  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq})$

## ➤ The Salt Effect (盐效应)



Addition of NaCl: shift to right

往弱电解质的溶液中加入与弱电解质没有相同离子的强电解质时，由于溶液中离子总浓度增大，离子间相互牵制作用增强，使得弱电解质解离的阴、阳离子结合形成分子的机会减小，从而使弱电解质分子浓度减小，离子浓度相应增大，解离度增大，这种效应称为**盐效应**(salt effect)。

(这里必须注意：在发生同离子效应时，由于也外加了强电解质，所以也伴随有盐效应的发生，只是这时同离子效应远大于盐效应，所以可以忽略盐效应的影响)

## ➤ The Common-Ion Effect

- Calculate the fluoride ion concentration and pH of a solution that is 0.20 *M* in HF and 0.10 *M* in HCl.

Given:  $K_a$  for HF is  $6.8 \times 10^{-4}$ .

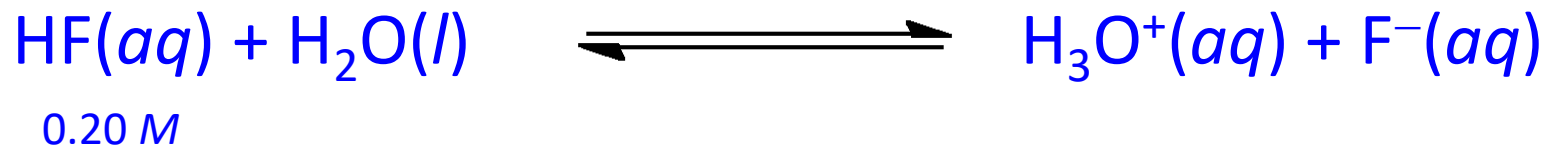
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4}$$

$K_a$ : acid-dissociation constant 酸解离常数

$K_b$ : base-dissociation constant 碱解离常数

$K_w$ : water-dissociation constant 水解离常数

## ➤ The Common-Ion Effect

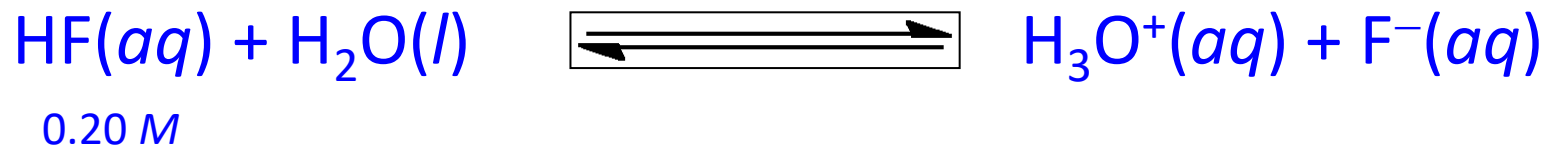


Because HCl, a strong acid, is also present, the initial  $[\text{H}_3\text{O}^+]$  is not 0, but rather 0.10 M.



	[HF], M	[H <sub>3</sub> O <sup>+</sup> ], M	[F <sup>-</sup> ], M
Initially	0.20	0.10	0
Change			
At equilibrium			

## ➤ The Common-Ion Effect



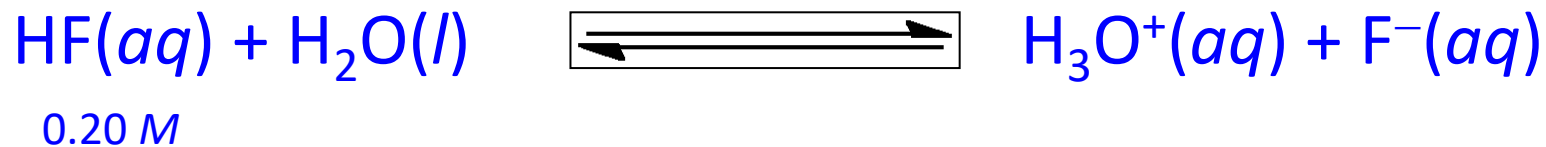
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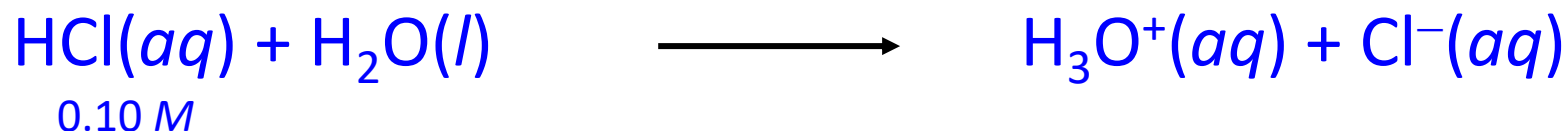
	[HF], M	[H <sub>3</sub> O <sup>+</sup> ], M	[F <sup>-</sup> ], M
Initially	0.20	0.10	0
Change	-x	+x	+x
At equilibrium			



## ➤ The Common-Ion Effect



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



	[HF], M	[H <sub>3</sub> O <sup>+</sup> ], M	[F <sup>-</sup> ], M
Initially	0.20	0.10	0
Change	-x	+x	+x
At equilibrium	0.20 - x ≈ 0.20	0.10 + x ≈ 0.10	x

## ➤ The Common-Ion Effect

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

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

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

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

## ➤ The Common-Ion Effect

□ Therefore,  $[F^-] = x = 1.4 \times 10^{-3}$

$$[H_3O^+] = 0.10 + x = 0.10 + 1.4 \times 10^{-3} = 0.10 \text{ M}$$

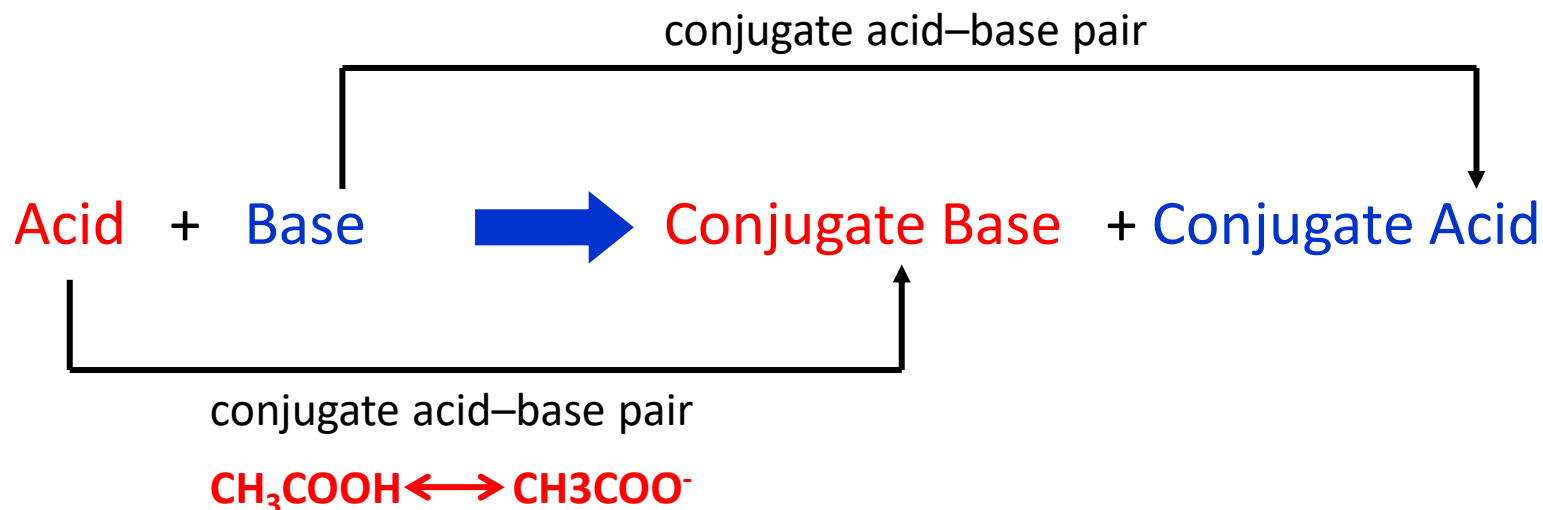
So,

$$\text{pH} = -\log (0.10)$$

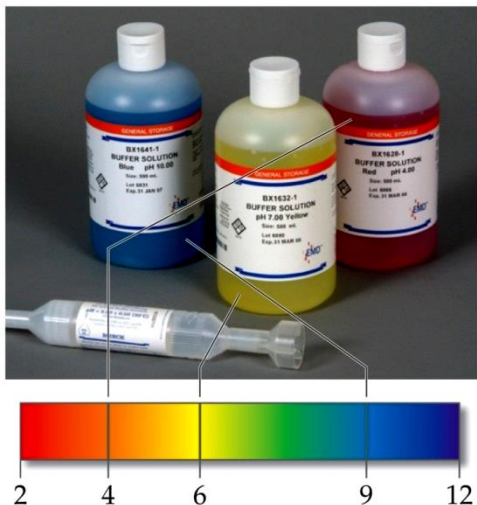
$$\text{pH} = 1.00$$

# ➤ Conjugate Acid and Base

- ❑ Conjugate acids and conjugate bases are characterized as the acids and bases that lose or gain protons.
- ❑ In an acid-base reaction, an acid plus a base reacts to form a conjugate base plus a conjugate acid.



# ➤ Buffers (缓冲液)



□ **缓冲溶液 (buffered solutions)** : Solutions that contain a weak conjugate acid–base pair, resist drastic changes in pH when small amounts of strong acid or strong base are added to them.

□ 是一种能抵抗外加少量强酸强碱而维持溶液pH基本不变的溶液

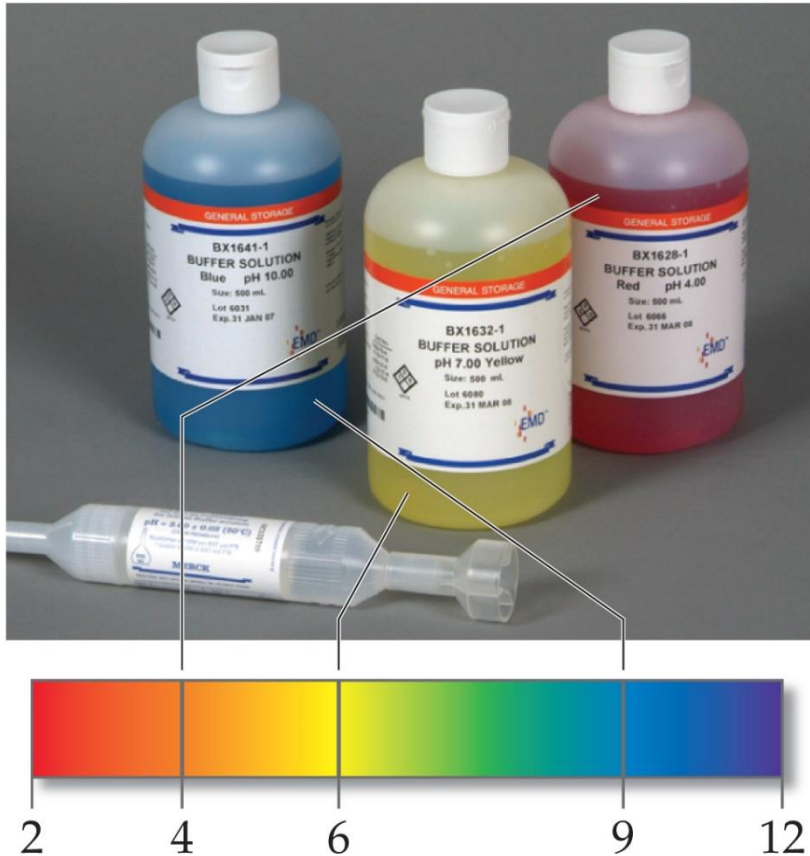
□ Buffers are solutions of a weak conjugate acid–base pair.

弱酸和它的盐 ( $\text{HAc} \cdots \text{NaAc}$ ) ; 弱碱和它的盐 ( $\text{NH}_3 \cdot \text{H}_2\text{O} \cdots \text{NH}_4\text{Cl}$ )

多元弱酸的酸式盐及其对应的次级盐; ( $\text{NaH}_2\text{PO}_4 \cdots \text{Na}_2\text{HPO}_4$ ) 的水溶液组成。

□ They are particularly resistant to pH changes, even when strong acid or base is added.

# 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**.

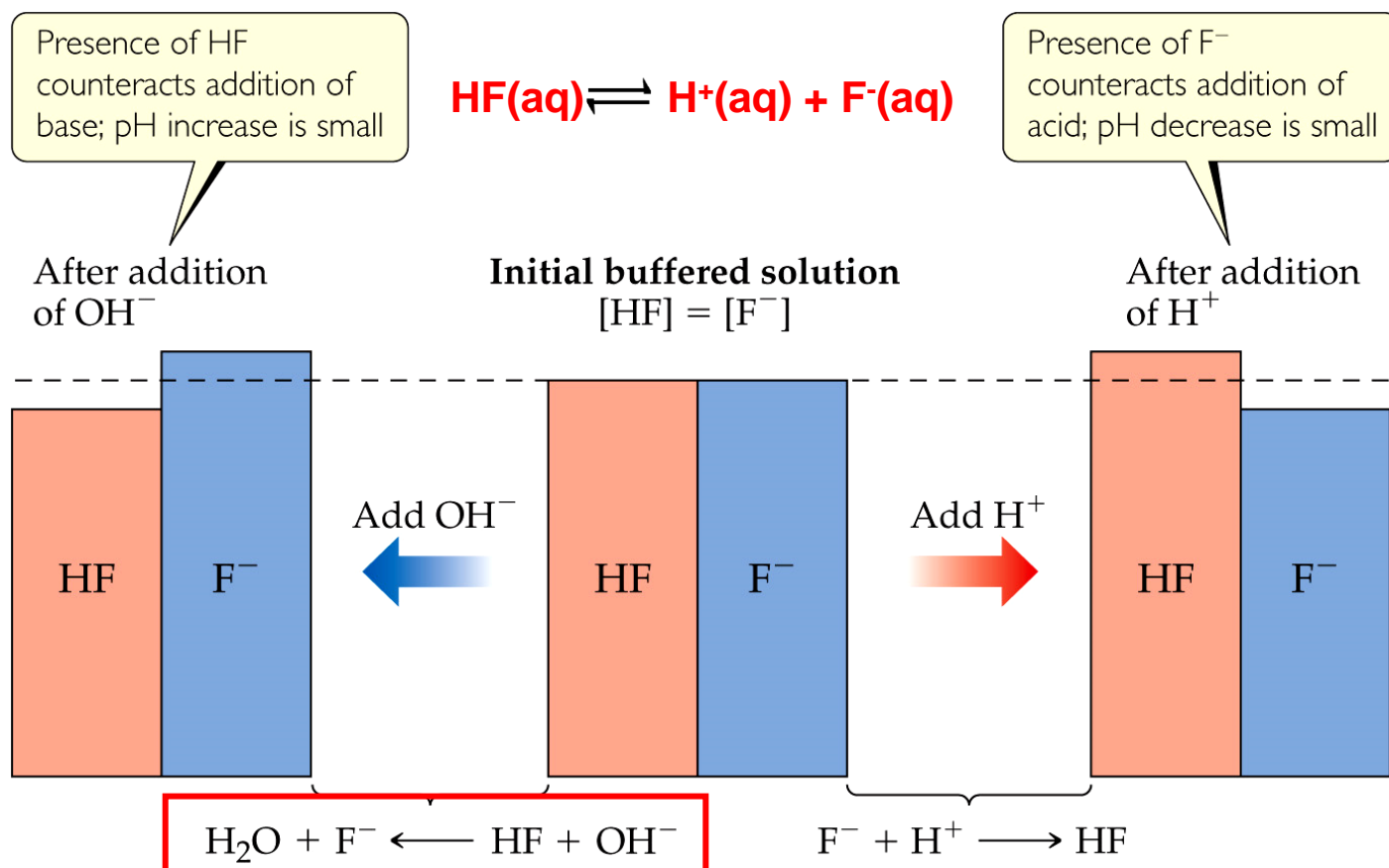
Which of these conjugate acid–base pairs will *not* function as a buffer:  $\text{C}_2\text{H}_5\text{COOH}$  and  $\text{C}_2\text{H}_5\text{COO}^-$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , or  $\text{HNO}_3$  and  $\text{NO}_3^-$ ? Explain.

- 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.

# ➤ Buffers

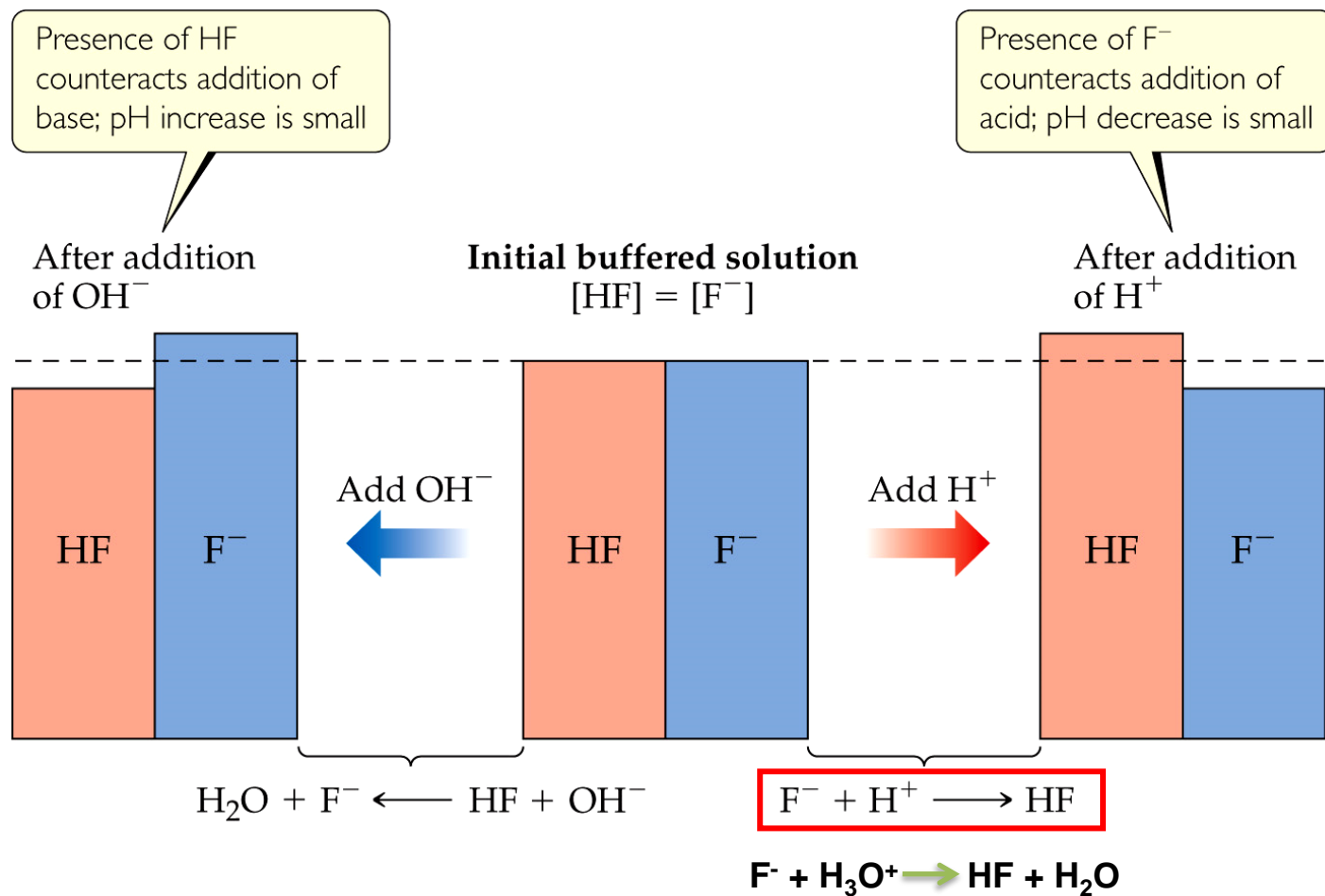
- ❑ If a small amount of hydroxide ( $\text{OH}^-$ ) is added to an equimolar solution of HF in NaF, for example, the HF reacts with the  $\text{OH}^-$  to make  $\text{F}^-$  and water.





# ➤ Buffers

- Similarly, if acid is added, the  $F^-$  reacts with it to form HF and water.



- 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  $\text{C}_2\text{H}_3\text{OO}^-$  and  $\text{C}_2\text{H}_3\text{OOH}$  form a buffer.
- B. The NaOH reacts with  $\text{C}_2\text{H}_3\text{OO}^-$  converting some of it into  $\text{C}_2\text{H}_3\text{OOH}$ .
- C.

 The NaOH reacts with  $\text{C}_2\text{H}_3\text{OOH}$  converting some of it into  $\text{C}_2\text{H}_3\text{OO}^-$ .
- D. The NaOH is neutralized and all concentrations ( $\text{C}_2\text{H}_3\text{OOH}$  and  $\text{C}_2\text{H}_3\text{OO}^-$ ) remain unchanged.

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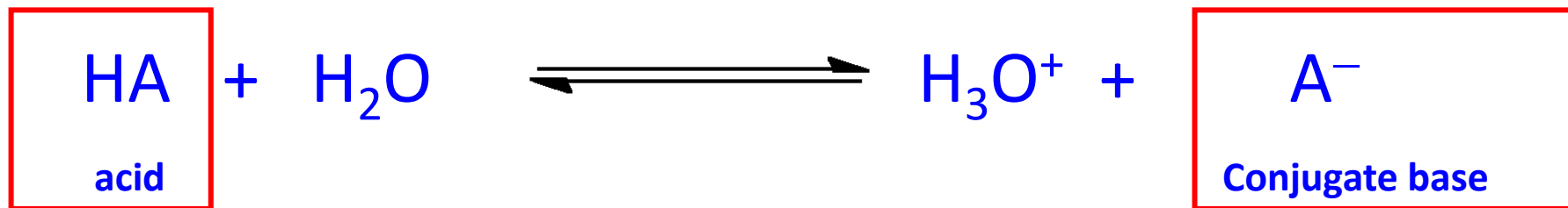
(b)

- A. There is no reaction because  $\text{C}_2\text{H}_3\text{OO}^-$  and  $\text{C}_2\text{H}_3\text{OOH}$  form a buffer.
- B.

 The HCl reacts with  $\text{C}_2\text{H}_3\text{OO}^-$  converting some of it into  $\text{C}_2\text{H}_3\text{OOH}$ .
- C. The HCl is neutralized and all concentrations ( $\text{C}_2\text{H}_3\text{OOH}$  and  $\text{C}_2\text{H}_3\text{OO}^-$ ) remain unchanged.
- D. The HCl reacts with  $\text{C}_2\text{H}_3\text{OOH}$  converting some of it into  $\text{C}_2\text{H}_3\text{OO}^-$ .

## ➤ Buffer Calculations

- Consider the equilibrium constant expression for the dissociation of a generic acid, HA:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

## ➤ Buffer Calculations

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Rearranging slightly, this becomes

$$K_a = [\text{H}_3\text{O}^+] \frac{[\text{A}^-]}{[\text{HA}]}$$

Taking the negative log of both side, we get

$$\begin{array}{c} \text{p}K_a \nearrow \\ -\log K_a = -\log [\text{H}_3\text{O}^+] + \left( -\log \frac{[\text{A}^-]}{[\text{HA}]} \right) \\ \text{pH} \nearrow \end{array} \quad \begin{array}{c} \text{base} \nearrow \\ \frac{[\text{A}^-]}{[\text{HA}]} \\ \text{acid} \nearrow \end{array}$$

## ➤ Buffer Calculations

- So  $pK_a = pH - \log \frac{[\text{base}]}{[\text{acid}]}$

- Rearranging, this becomes

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

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

亨德森-哈塞尔巴尔赫方程

## ➤ Henderson–Hasselbalch Equation

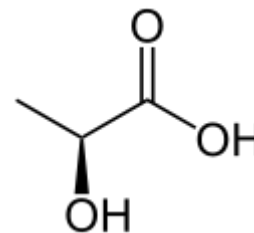
- What is the pH of a buffer that is 0.12 *M* in lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$  (lactic acid 乳酸), and 0.10 *M* in sodium lactate?  $K_a$  for lactic acid is  $1.4 \times 10^{-4}$ .

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

$$\text{pH} = -\log (1.4 \times 10^{-4}) + \log \frac{(0.10)}{(0.12)}$$

$$\text{pH} = 3.85 + (-0.08)$$

$$\text{pH} = 3.77$$



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  $\text{pH} = 7.0$ ?

- 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.

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

**hypochlorite**  
**nitrite**



## ➤ Buffer Capacity

- ❑ The amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree.
- ❑ It depends on the amount of acid and based used to prepare the buffer.

Capacity



1 L solution of 0.1 M  $\text{CH}_3\text{COOH}$  + 0.1 M  $\text{CH}_3\text{COONa}$

1 L solution of 1 M  $\text{CH}_3\text{COOH}$  + 1 M  $\text{CH}_3\text{COONa}$

## ➤ pH Range

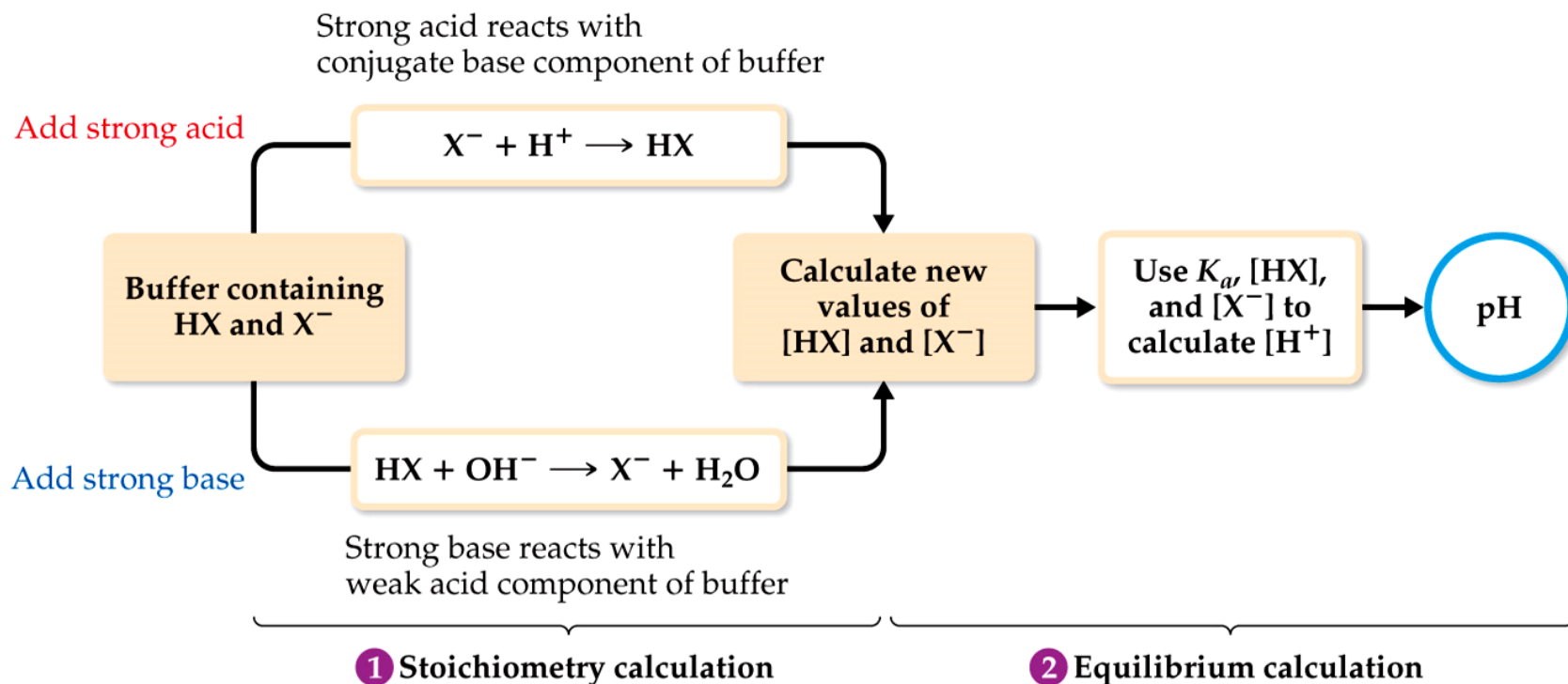
- ❑ The **pH range** is the range of pH values over which a buffer system works effectively.
- ❑ It is best to choose an acid with a  $pK_a$  close to the desired pH.
- ❑ Buffers usually have a usable range within  $\pm 1$  pH unit of  $pK_a$ .

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

(酸或碱和盐浓度相等时，缓冲液的缓冲效率为最高，比例相差越大，缓冲效率越低，缓冲液的一般有效缓冲范围为  $\text{pH} = \text{p}K_a \pm 1$ )

# ➤ When Strong Acids or Bases Are Added to a Buffer

- it is safe to assume that all of the strong acid or base is consumed in the reaction.



## ➤ Calculating pH Changes in Buffers

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

Before the reaction, since

$$\text{no. of mol } \text{C}_2\text{H}_3\text{OOH} = \text{no. of mol } \text{C}_2\text{H}_3\text{OO}^-$$

$$\text{pH} = \text{p}K_a = 4.74$$

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

## ➤ Calculating pH Changes in Buffers

The 0.020 mol NaOH will react with 0.020 mol of the acetic acid:



	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$	$\text{OH}^-$
Before reaction	0.300 mol	0.300 mol	0.020 mol
After reaction			

## ➤ Calculating pH Changes in Buffers

The 0.020 mol NaOH will react with 0.020 mol of the acetic acid:



	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$	$\text{OH}^-$
Before reaction	0.300 mol	0.300 mol	0.020 mol
After reaction	0.280 mol	0.320 mol	0.000 mol

## ➤ Calculating pH Changes in Buffers

- Now use the Henderson–Hasselbalch equation to calculate the new pH:



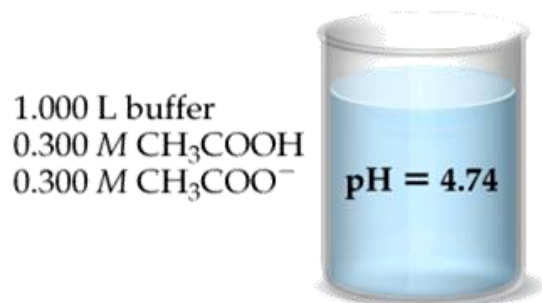
$$\text{pH} = 4.74 + \log \frac{(0.320)}{(0.280)}$$

$$\text{pH} = 4.74 + 0.06$$

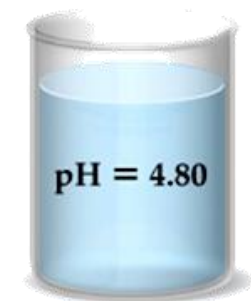
$$\text{pH} = 4.80$$

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

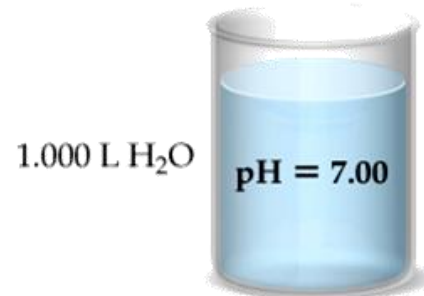
➤ **Effect of adding a strong base to a buffered solution and to water**



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



**pH increases by  
0.06 pH units**



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

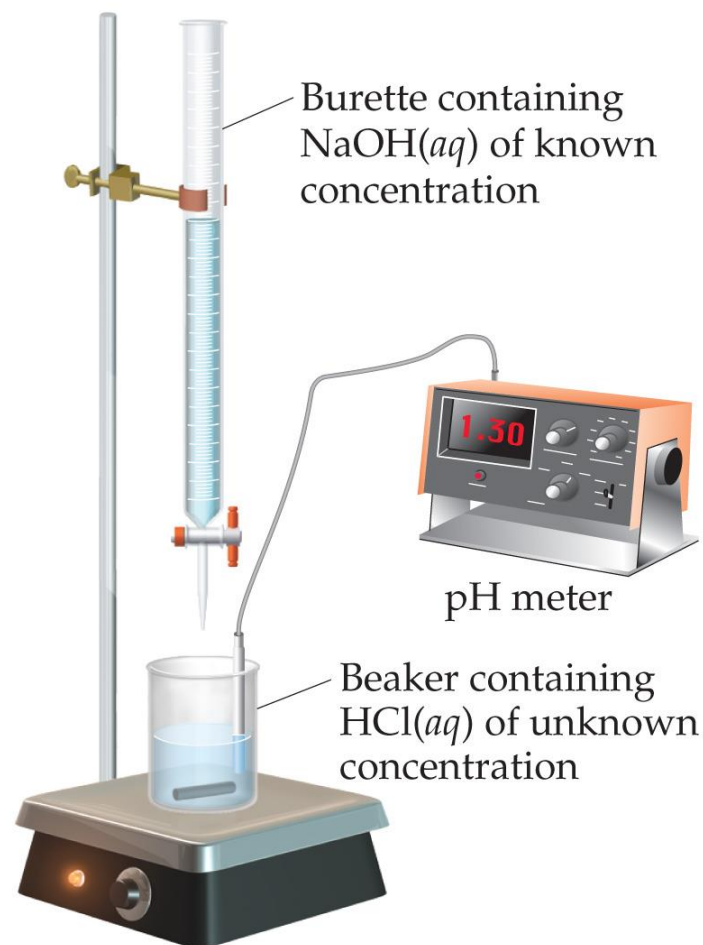


**pH increases by  
5.30 pH units**



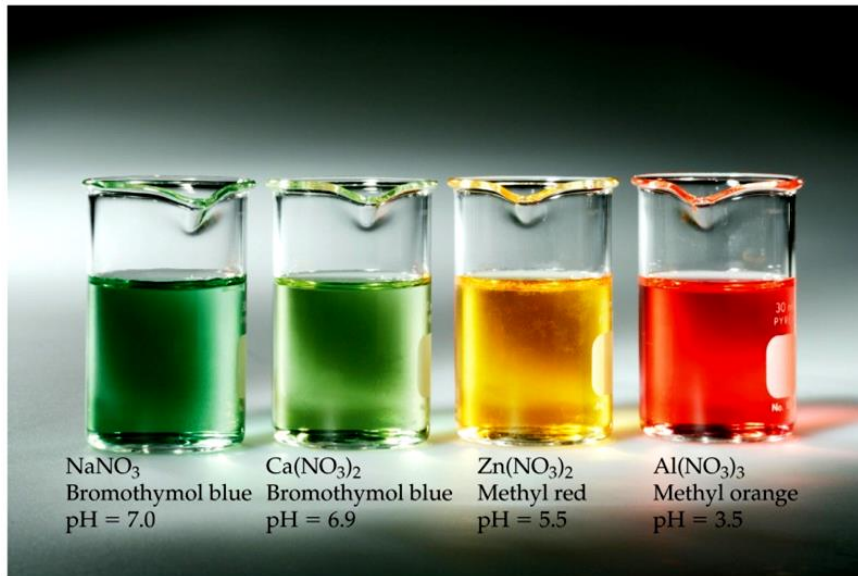
# Titration

- 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.



# ➤ Titration

- A pH meter or indicators are used to determine when the solution has reached the **equivalence point**, at which the **stoichiometric amount** of acid equals that of base.



在滴定反应中，当加入的标准溶液与待测组分按反应式的**化学计量关系**恰好反应完全时，反应到达了化学计量点（**等当点**）。

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 KOH?

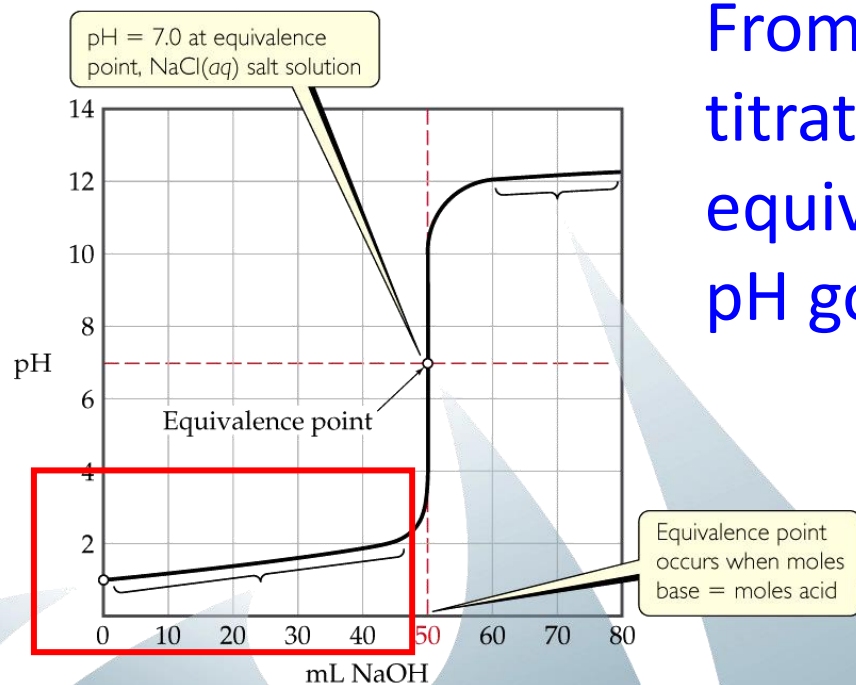
A. pH = 4.2

☒ B. pH = 7.0

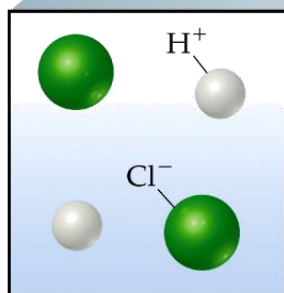
C. pH = 8.2

D. pH = 9.8

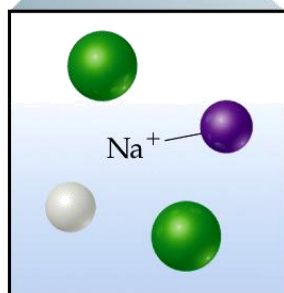
# ➤ Titration of a Strong Acid with a Strong Base



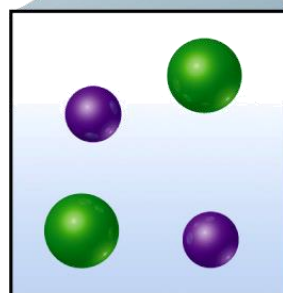
From the start of the titration to near the equivalence point, the pH goes up slowly.



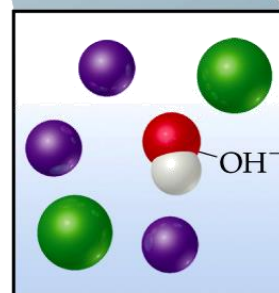
Only HCl(aq) present before titration



H<sup>+</sup> consumed as OH<sup>-</sup> added, forming H<sub>2</sub>O (pH < 7.0)



H<sup>+</sup> completely neutralized by OH<sup>-</sup> (pH = 7.0)



No H<sup>+</sup> left to react with excess OH<sup>-</sup> (pH > 7.0)

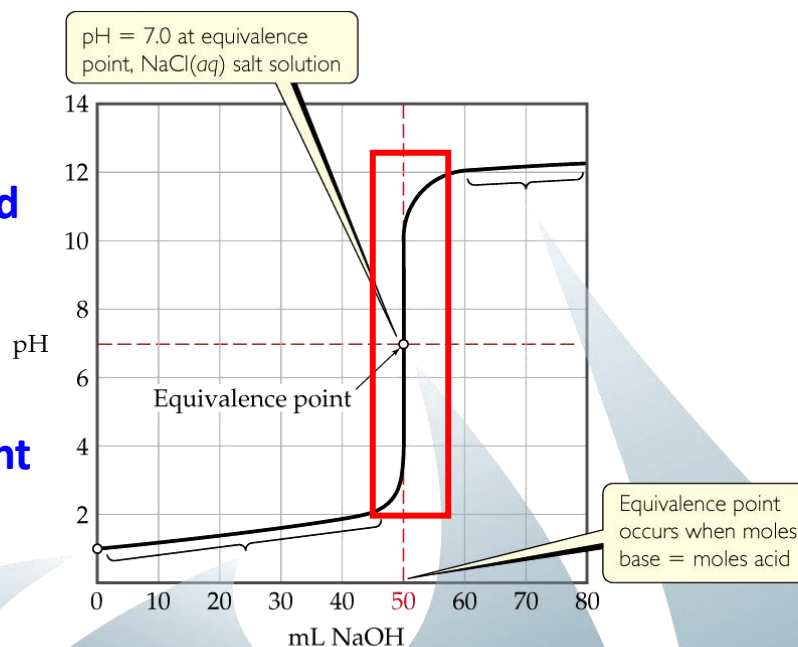
# ➤ Titration of a Strong Acid with a Strong Base

a. Initial pH:

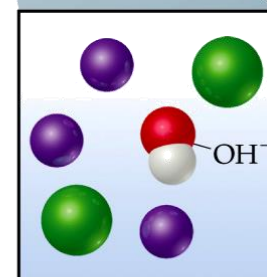
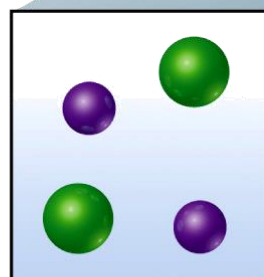
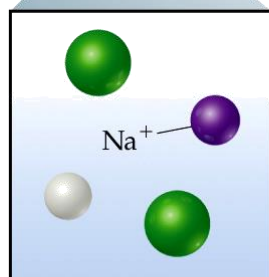
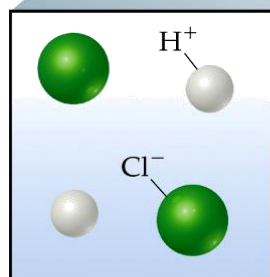
b. Between initial pH and equivalence point

c. Equivalence point

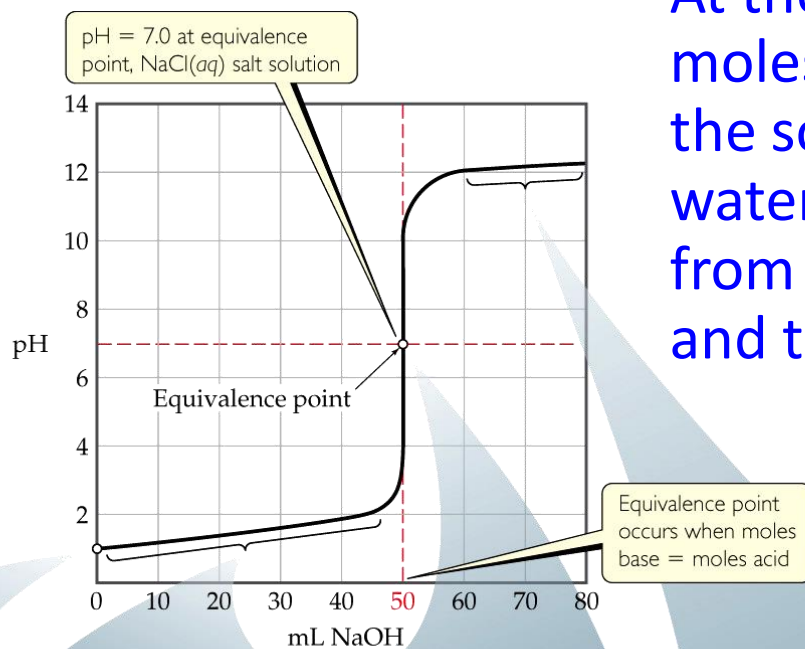
d. After equivalence point



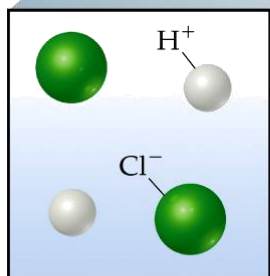
Just before (and after) the equivalence point, the pH increases rapidly.



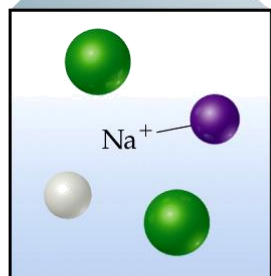
# ➤ Titration of a Strong Acid with a Strong Base



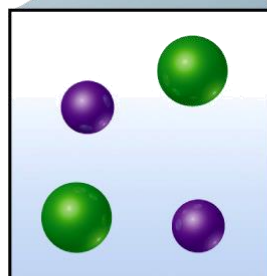
At the equivalence point, moles acid = moles base, and the solution contains only water and the salt from the cation of the base and the anion of the acid.



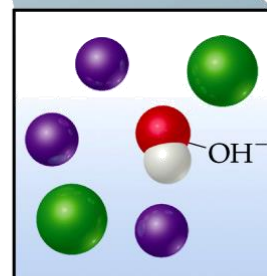
Only  $\text{HCl(aq)}$  present before titration



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

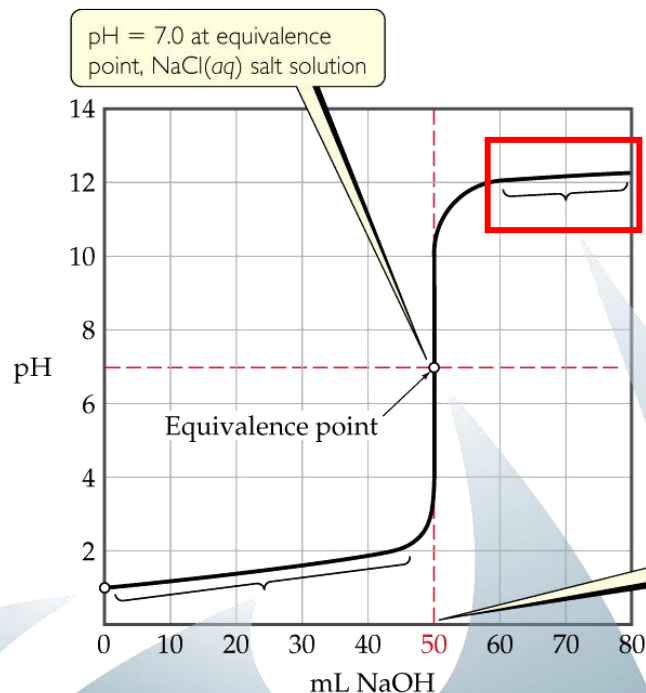


$\text{H}^+$  completely neutralized by  $\text{OH}^-$  ( $\text{pH} = 7.0$ )

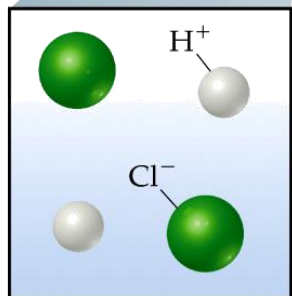


No  $\text{H}^+$  left to react with excess  $\text{OH}^-$  ( $\text{pH} > 7.0$ )

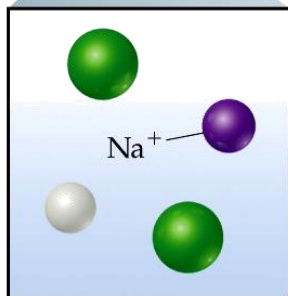
# ➤ Titration of a Strong Acid with a Strong Base



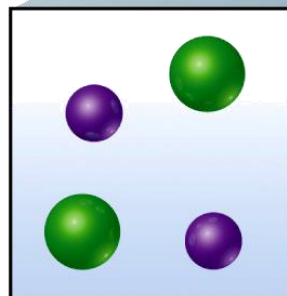
As more base is added, the increase in pH again levels off.



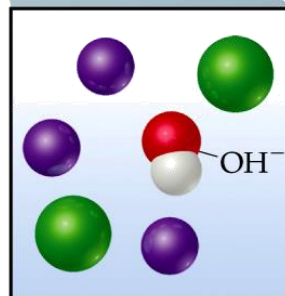
Only HCl(aq) present before titration



H<sup>+</sup> consumed as OH<sup>-</sup> added, forming H<sub>2</sub>O (pH < 7.0)



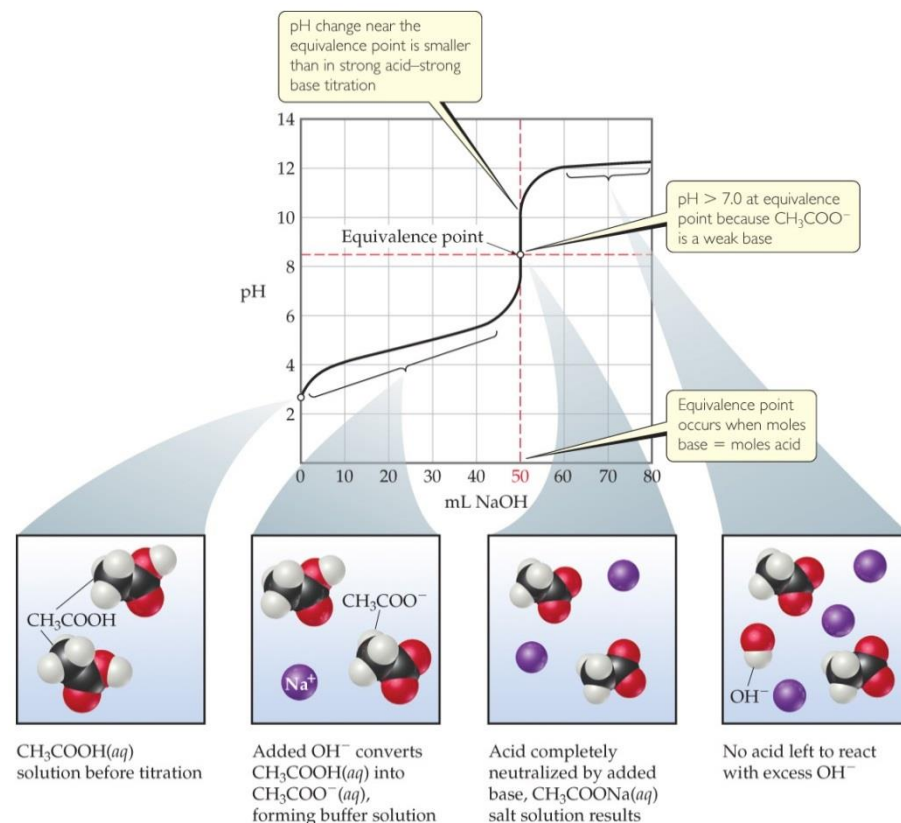
H<sup>+</sup> completely neutralized by OH<sup>-</sup> (pH = 7.0)



No H<sup>+</sup> left to react with excess OH<sup>-</sup> (pH > 7.0)

# ➤ Titration of a Weak Acid with a Strong Base

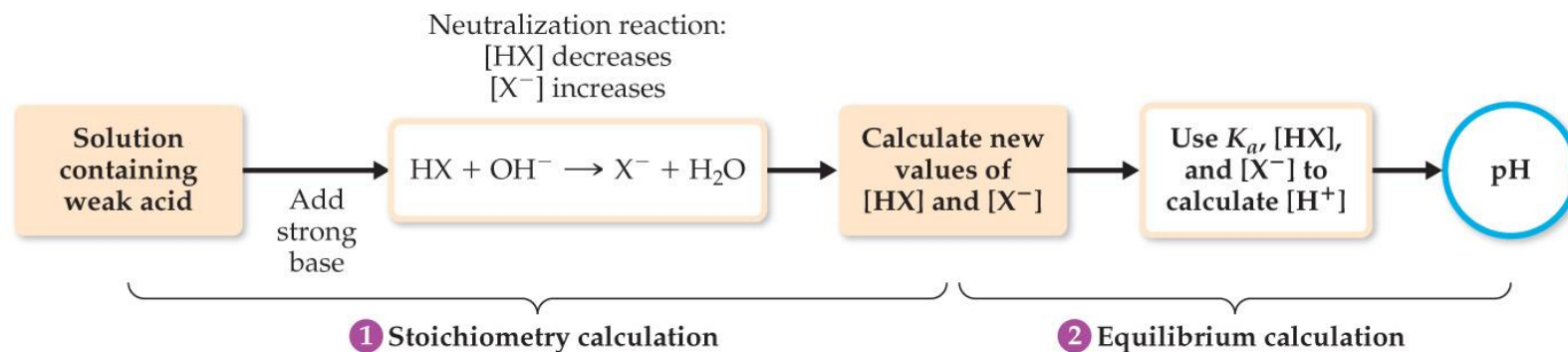
- ❑ Unlike in the previous case, the conjugate base of the acid affects the pH when it is formed.
- ❑ At the equivalence point the pH is  $>7$ .
- ❑ Phenolphthalein(酚酞) is commonly used as an indicator in these titrations.



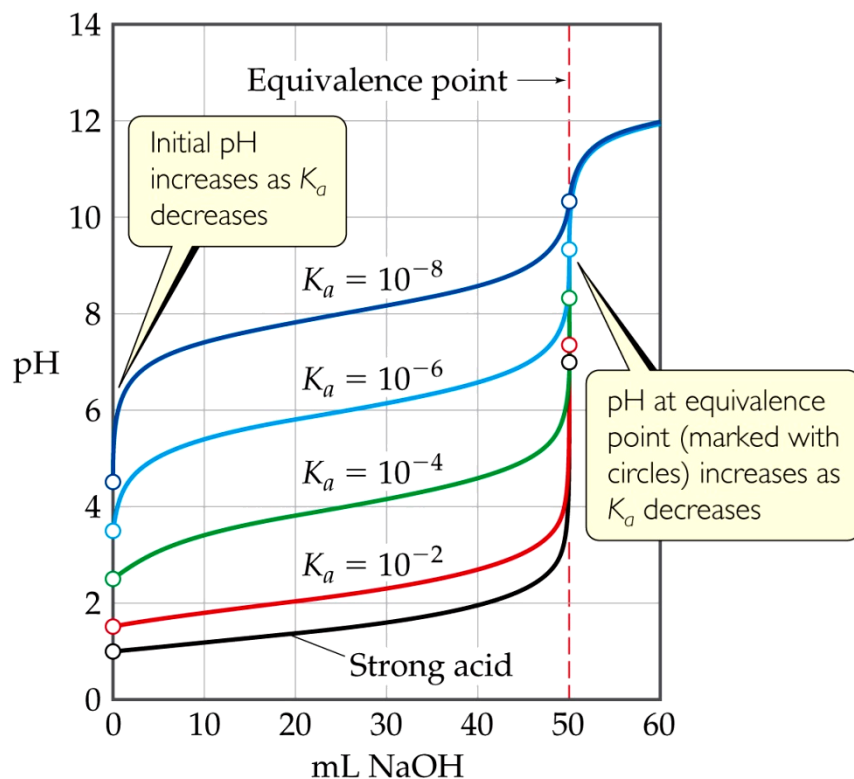


# ➤ Titration of a Weak Acid with a Strong Base

- 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.

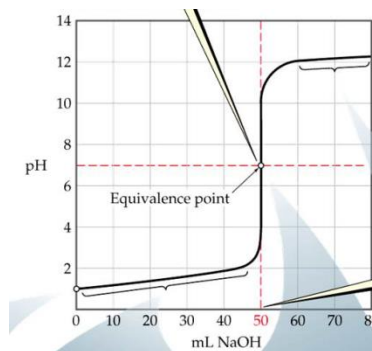


# ➤ Titration of a Weak Acid with a Strong Base



- ❑ With weaker acids, the initial pH is higher and pH changes near the equivalence point are less drastic
- ❑ When  $pK_a$  is 10, it is virtually impossible to determine the equivalence point because the change is too small

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



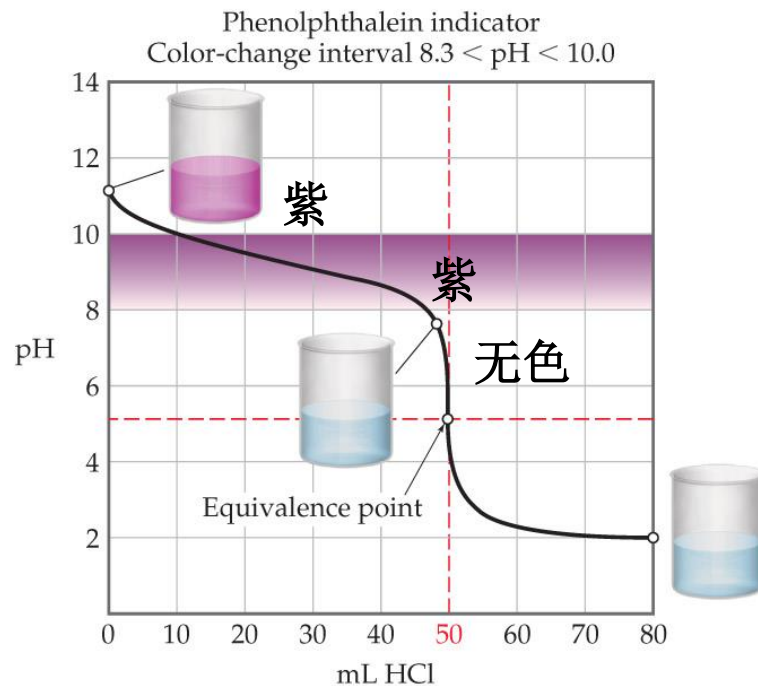
Why is the choice of indicator more crucial for a weak acid–strong base titration than for a strong acid–strong base titration?

- 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.

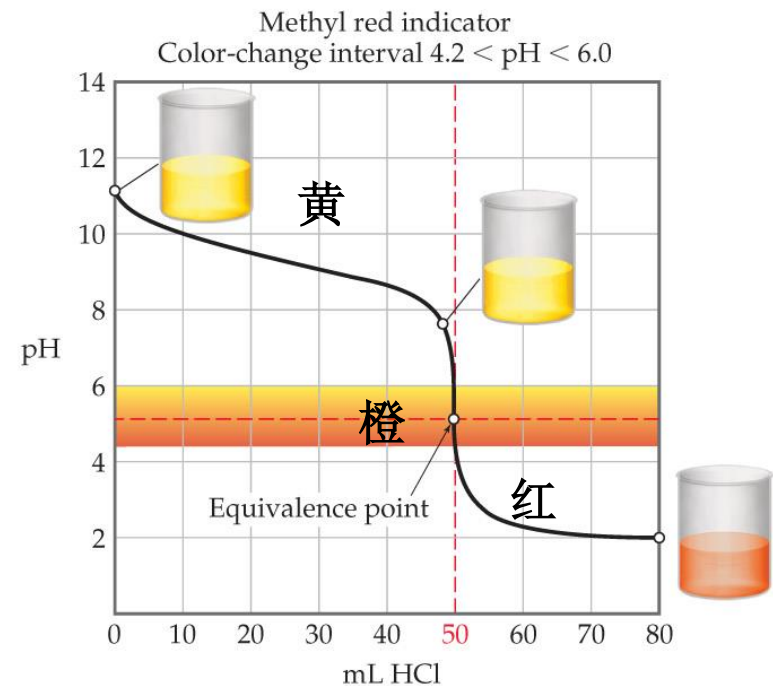
 The nearly vertical equivalence point portion of the titration curve is smaller for a weak acid-strong base titration, and fewer indicators undergo their color change within this narrow range.
- C. Many indicators do not change colors at the equivalence points of weak acid-strong base titrations.
- D.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

# ➤ Titration of a Weak Base with a Strong Acid

- ❑ 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.



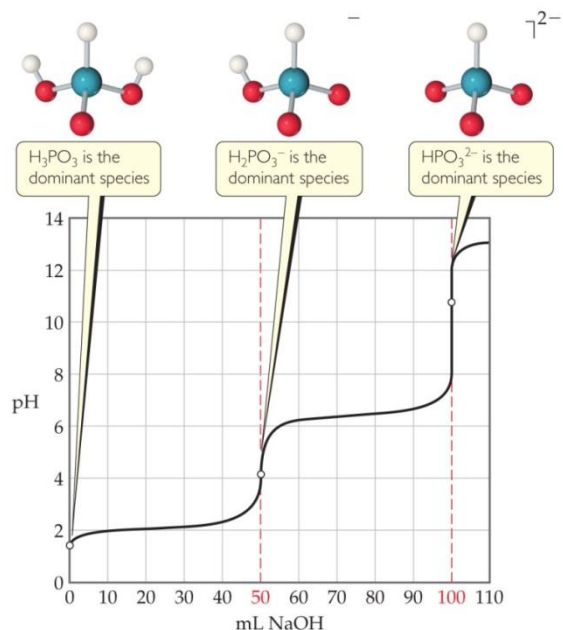
Unsatisfactory indicator because color changes before reaching equivalence point



Suitable indicator because equivalence point falls within the color-change interval

# ➤ Titrations of Polyprotic Acids

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



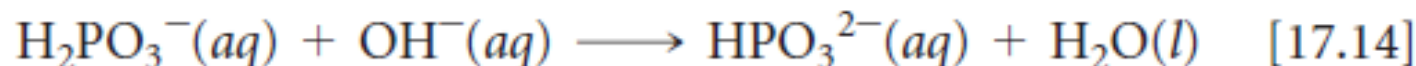
**Two equivalence points**

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

25 mL NaOH: pH = 2.5,  $\text{p}K_{a1} = 2.5$

75 mL NaOH: pH = 6.5,  $\text{p}K_{a2} = 6.5$

50.0 mL, 0.1 M  $\text{H}_3\text{PO}_3$  + 0.1 M NaOH



# ➤ **Titrating with an Acid–Base Indicator**

## ❑ **Optimally**

An indicator should change color at the equivalence point in a titration.

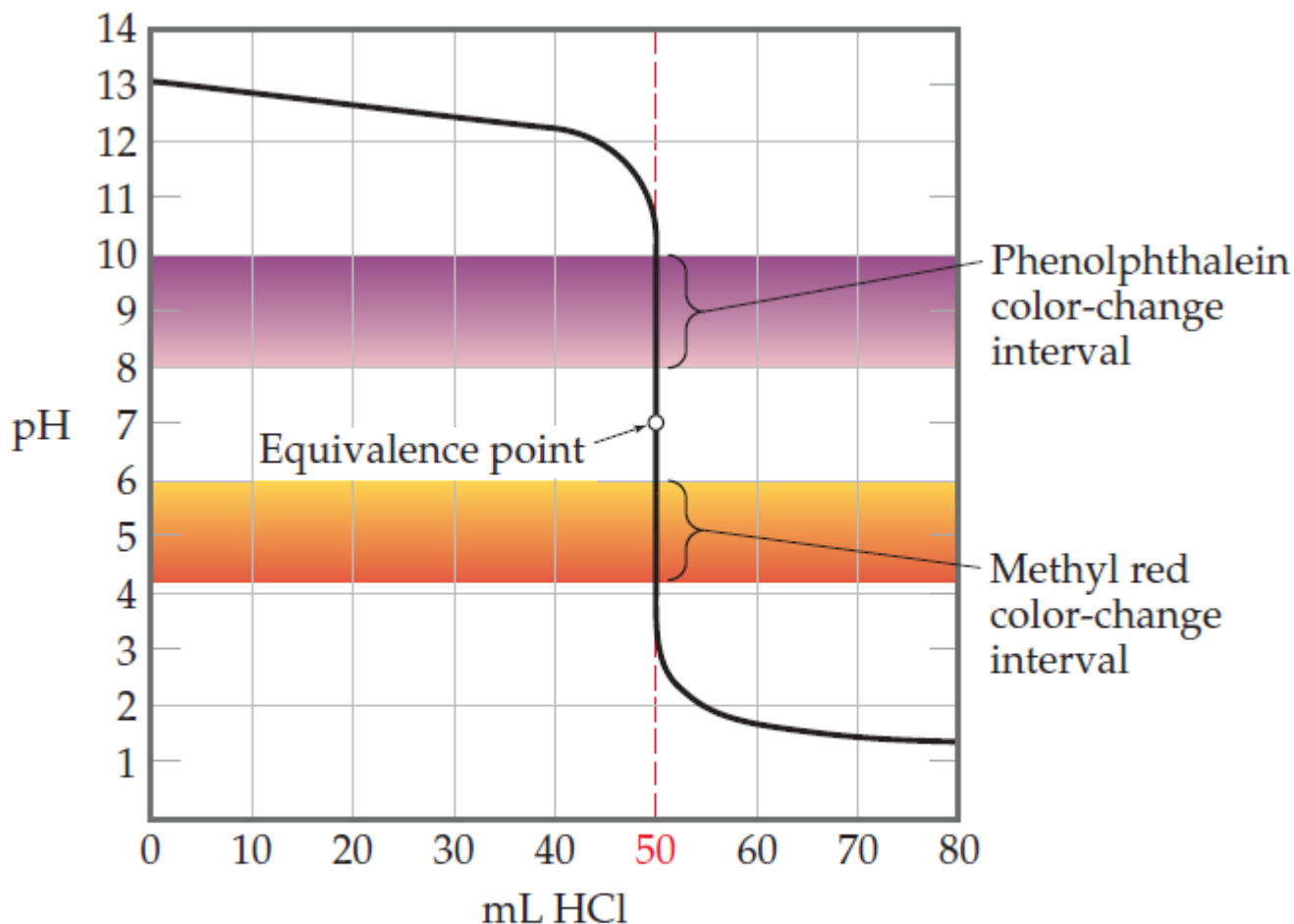
## ❑ **In practice**

An indicator need not precisely mark the equivalence point.

## ❑ **How to make a good choice ?**

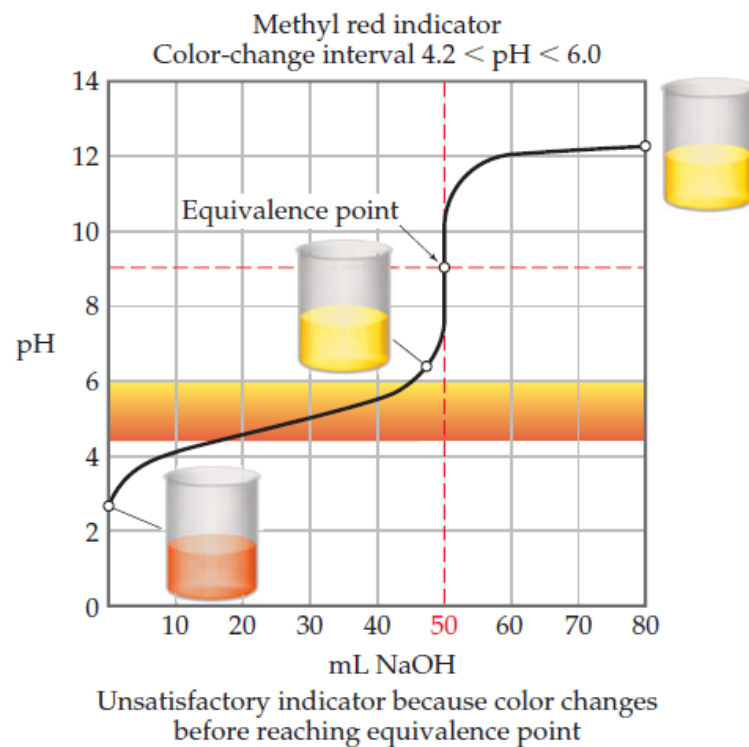
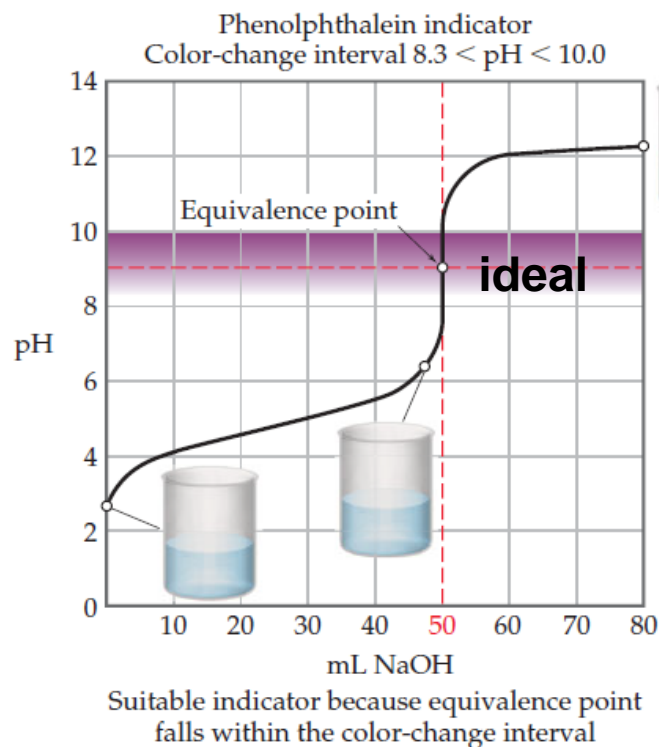
An indicator beginning and ending its color change (end point) anywhere on the rapid-rise portion of the titration curve gives a sufficiently accurate measure of the titrant volume needed to reach the equivalence point

- when you are titrating a strong acid with a strong base: Is methyl red a suitable indicator?



▲ **FIGURE 17.13** Using color indicators for titration of a strong base with a strong acid. Both phenolphthalein and methyl red change color in the rapid-rise portion of the titration curve.

## ➤ Titration weak acid with strong base

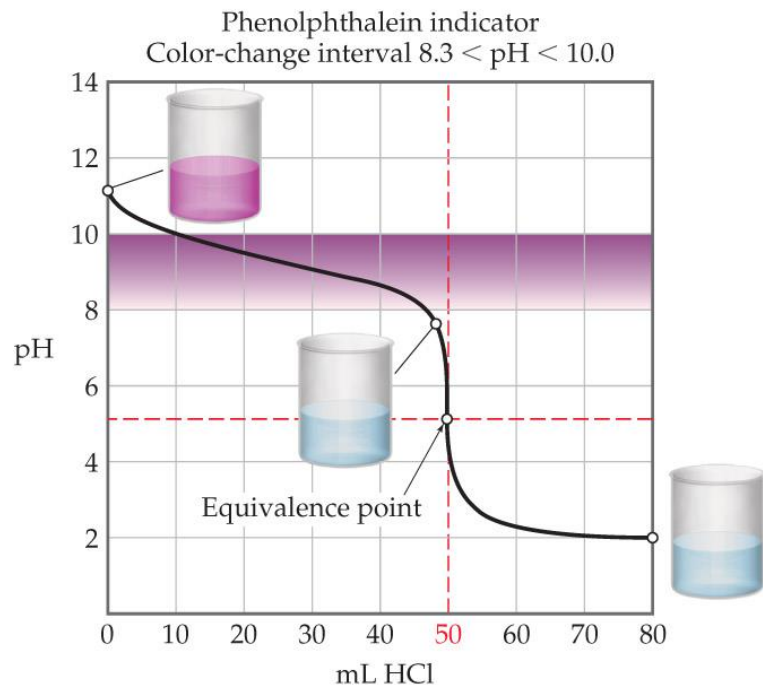


▲ FIGURE 17.14 Good and poor indicators for titration of a weak acid with a strong base.

- The pH at the equivalence point in these titrations is  $>7$ , so using phenolphthalein would be a good idea.

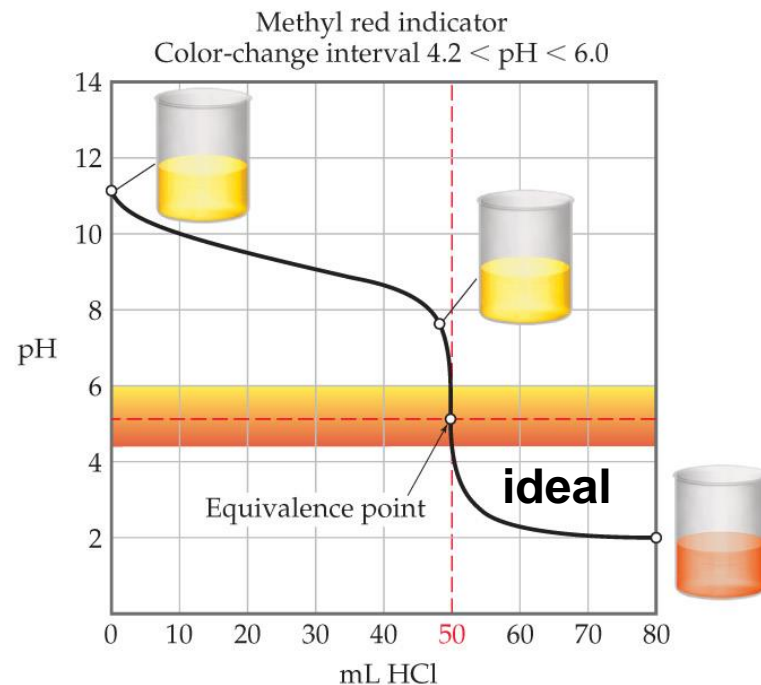


## ➤ Titration weak base with strong acid



Unsatisfactory indicator because color changes before reaching equivalence point

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Suitable indicator because equivalence point falls within the color-change interval

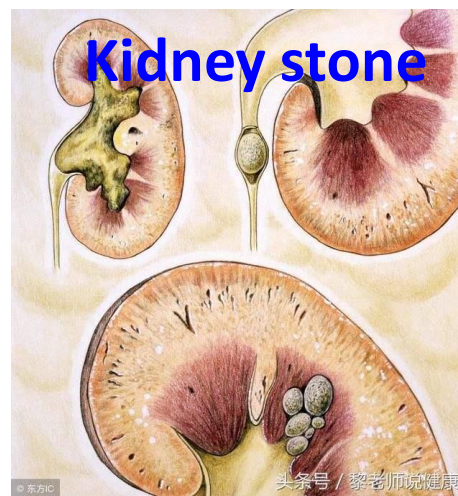
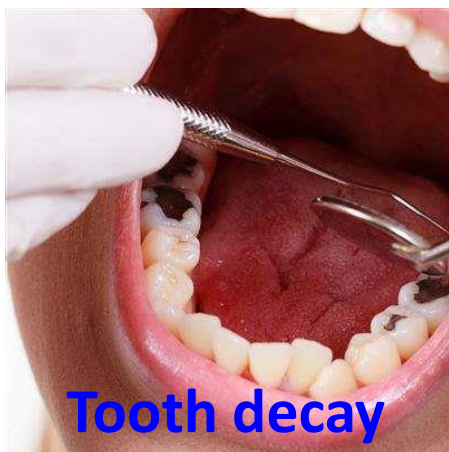
- ❑ The pH at the equivalence point in these titrations is  $< 7$ , so using phenolphthalein would not be a good idea.
- ❑ Methyl red is the indicator of choice.

## ➤ Solubility Equilibria

- Consider the equilibrium that exists in a saturated solution of  $\text{BaSO}_4$  in water:



Dissolution (溶解) and precipitation (沉淀)



## ➤ Solubility Products

- Consider the equilibrium that exists in a saturated solution of  $\text{BaSO}_4$  in water:



The equilibrium constant expression for this equilibrium is

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

where the equilibrium constant,  $K_{sp}$ , is called the **solubility product (溶度积)**.

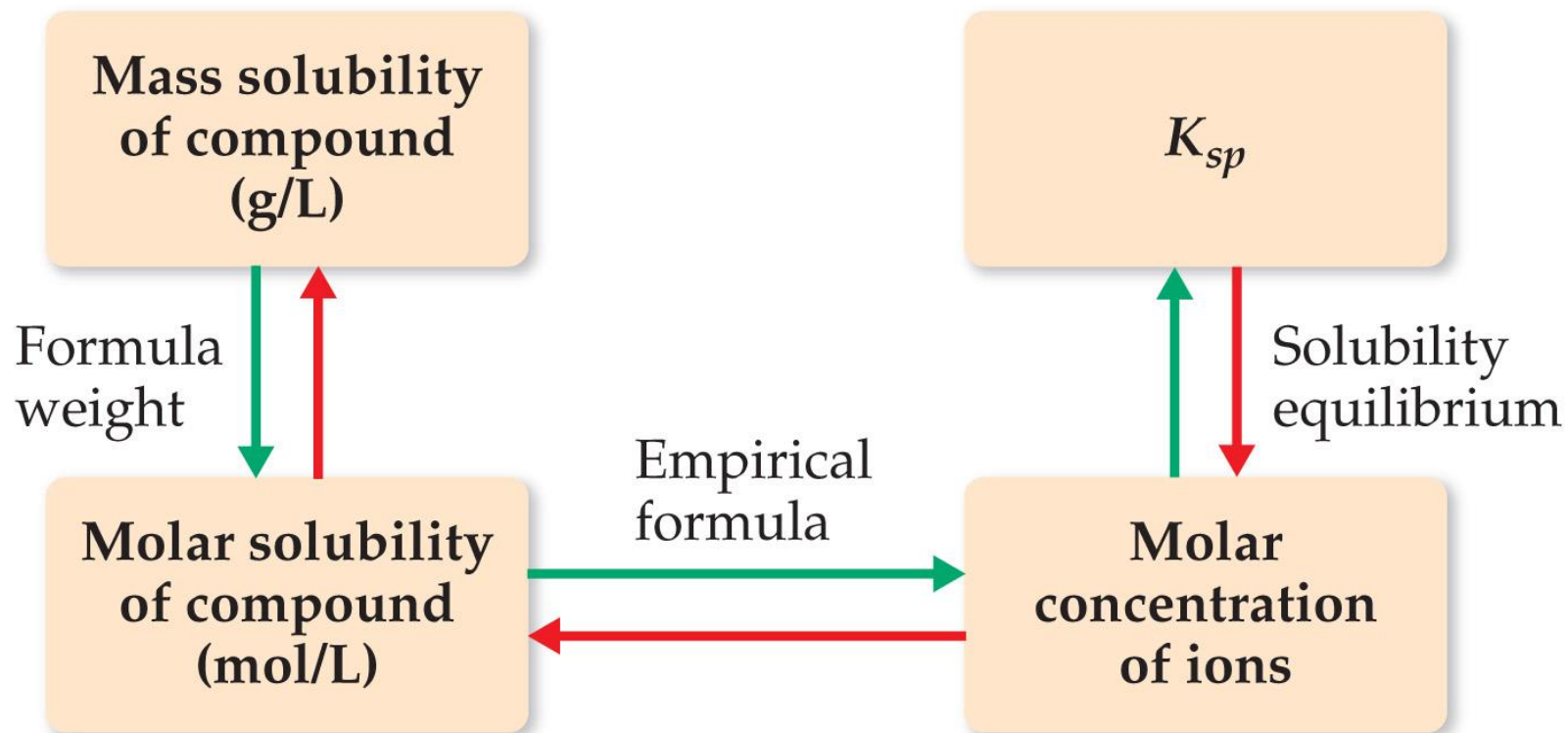
在一定温度下难溶电解质饱和溶液中相应的离子之浓度的乘积，其中各离子浓度的**幂次**与它在该电解质电离方程式中的系数相同。

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.

## ➤ Solubility Products

- ❑  $K_{sp}$  is *not* the same as solubility.
- ❑ Solubility is generally expressed as the mass of solute dissolved in 1 L (g/L) or (g/mL) of solution, or in mol/L ( $M$ ).



## ➤ LIMITATIONS OF SOLUBILITY PRODUCTS

Ion concentrations calculated from  $K_{sp}$  values sometimes deviate appreciably from those found experimentally

- ❑ due to electrostatic interactions between ions in solution, which can lead to ion pairs. (These interactions increase in magnitude both as the concentrations of the ions increase and as their charges increase.
- ❑ ignoring other equilibrium that occur simultaneously in the solution



- ❑ ionic compounds only dissociate partially when they dissolve (When  $\text{MgF}_2$  dissolves, it yields not only

$\text{Mg}^{2+}$  and  $\text{F}^{-}$  ion but also  $\text{MgF}^{+}$

## ➤ Factors Affecting Solubility

### □ The Common-Ion Effect

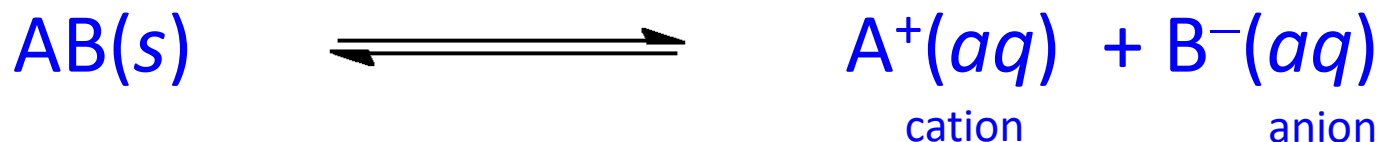
- If one of the ions in a solution equilibrium is already dissolved in the solution, the equilibrium will shift to the left and the solubility of the salt will decrease:



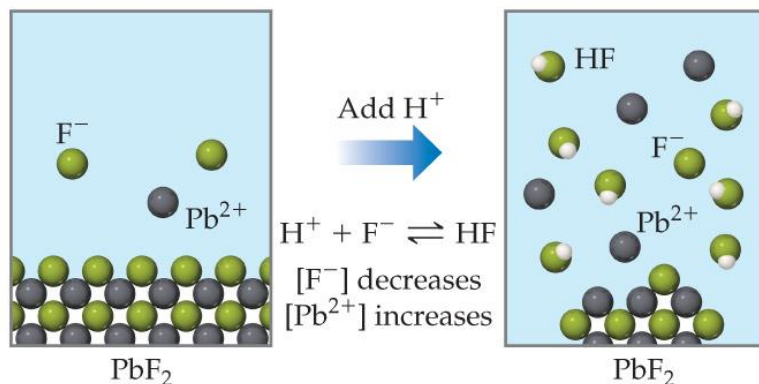
# ➤ Factors Affecting Solubility

## □ pH **Henderson–Hasselbalch**

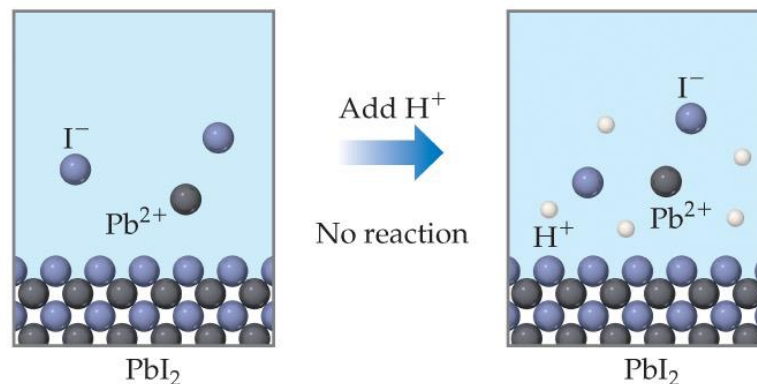
- If a substance has a basic anion, it will be more soluble in an acidic solution.
- Substances with acidic cation are more soluble in basic solutions.



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



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





# ➤ Factors Affecting Solubility

## □ Complex Ions (络离子)

- Metal ions can act as Lewis acids to form complex ions with Lewis bases in the solvent.

TABLE 17.1 • Formation Constants for Some Metal Complex Ions in Water at 25 °C

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

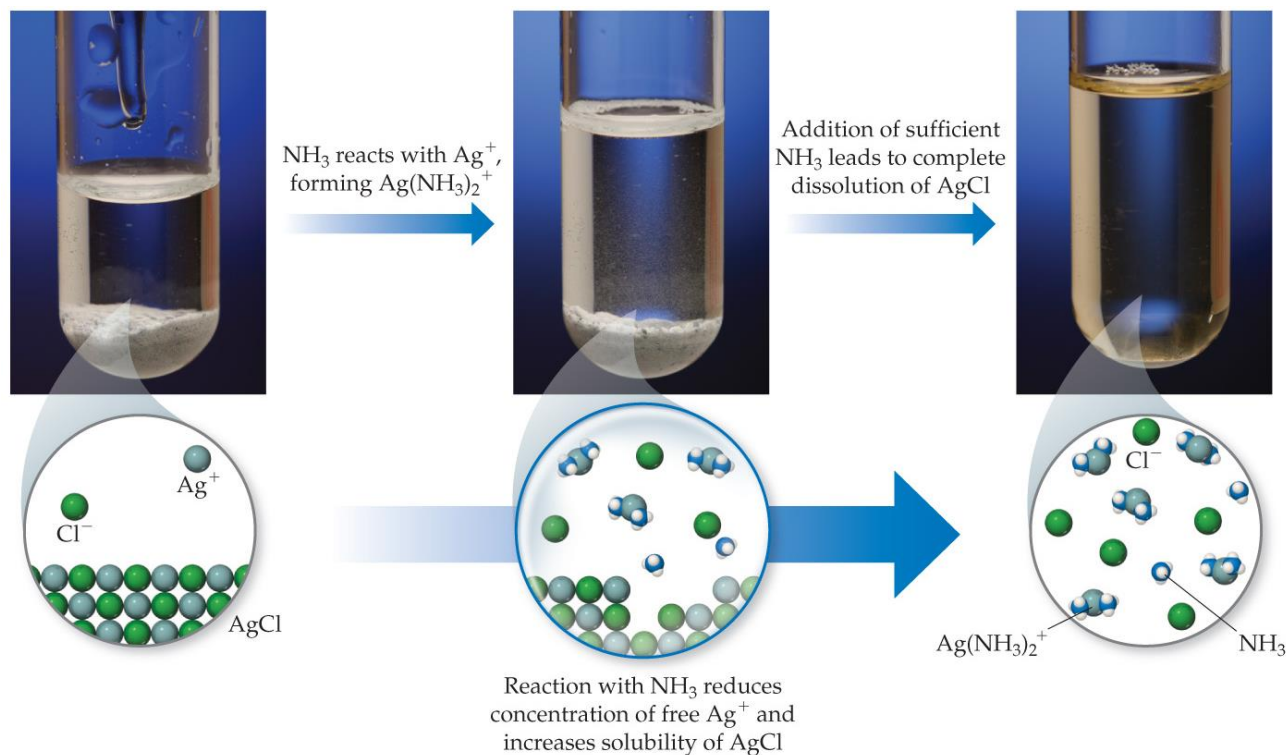
Formation  
constant

$$K_f = [\text{Ag}(\text{NH}_3)_2^+]/[\text{Ag}^+][\text{NH}_3]^2$$

# ➤ Factors Affecting Solubility

## ❑ Complex Ions

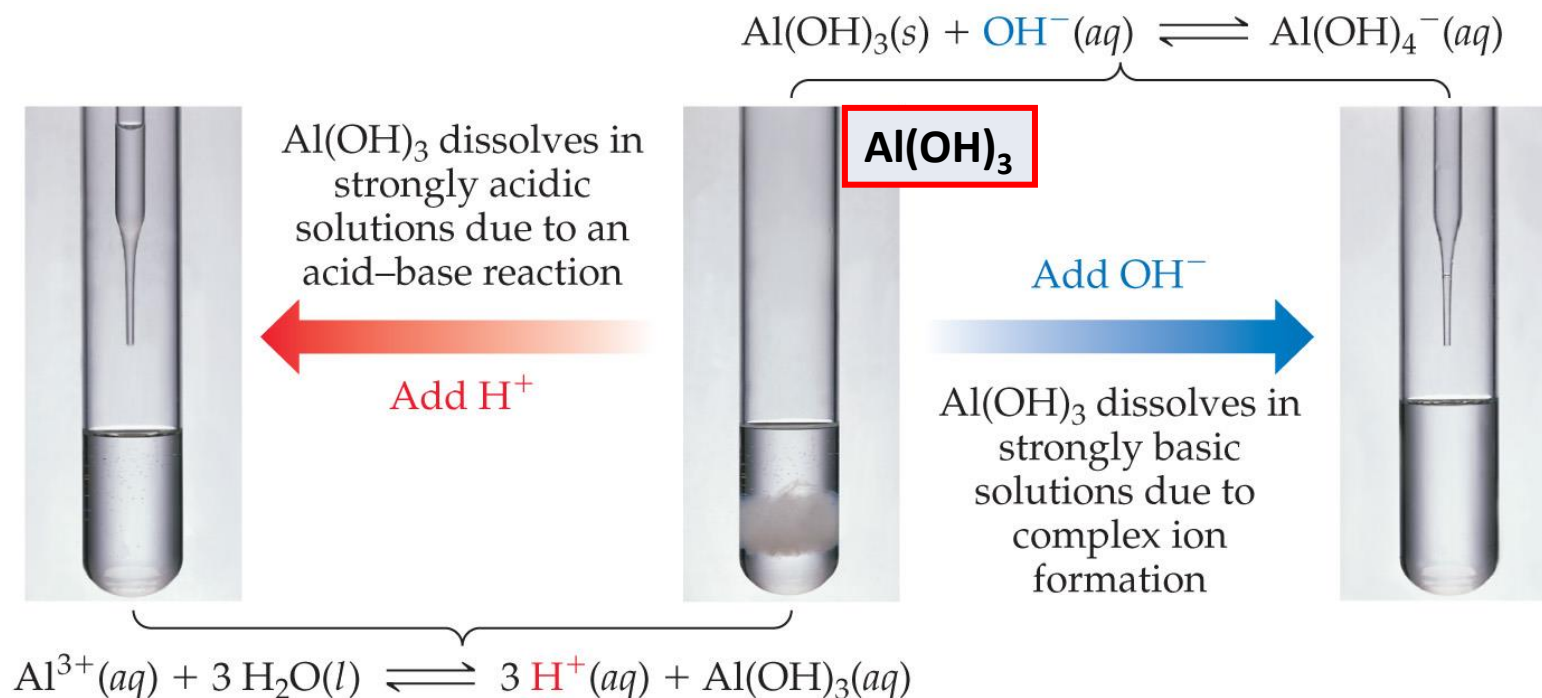
The formation of these complex ions increases the solubility of these salts.



# ➤ Factors Affecting Solubility

## □ Amphoterism (两性)

- Amphoteric metal oxides and hydroxides are soluble in strong acid or base, because they can act either as acids or bases.
- Examples of such cations are  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Sn}^{2+}$ .

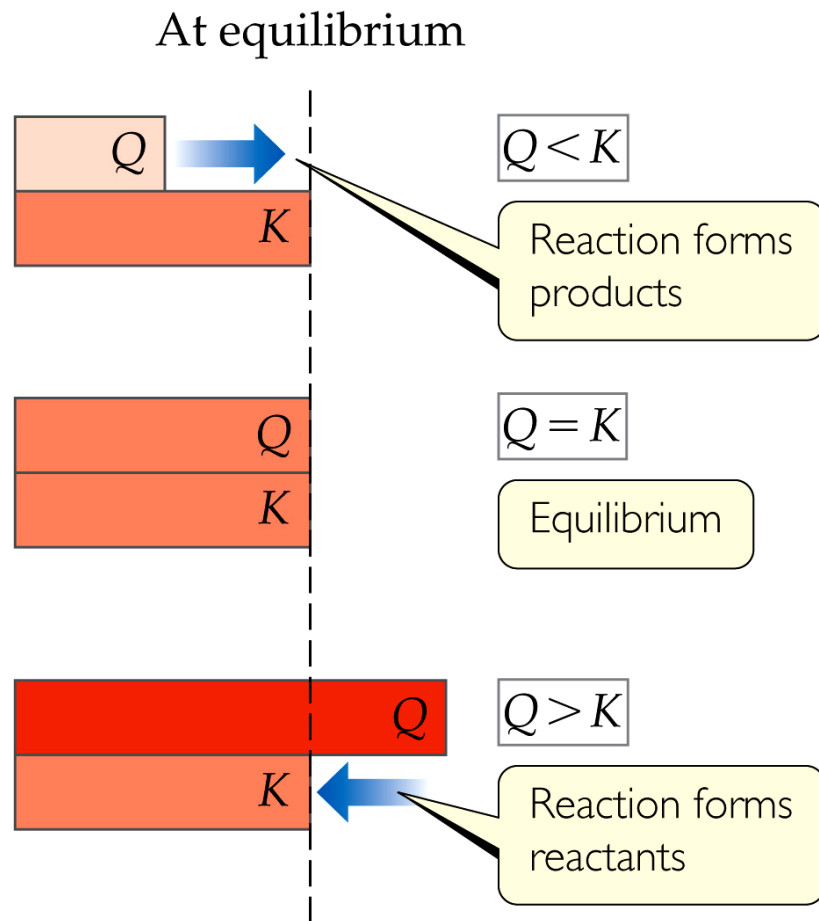


# ➤ Will a Precipitate Form?

□ In a solution,

- If  $Q < K_{sp}$ , more solid can dissolve until  $Q = K_{sp}$ .
- If  $Q = K_{sp}$ , the system is at equilibrium and the solution is saturated.

If  $Q > K_{sp}$ , the salt will precipitate until  $Q = K_{sp}$ .



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



$$Q_c = \frac{[\text{D}]^d[\text{E}]^e}{[\text{A}]^a[\text{B}]^b}$$

**Q: reaction quotient (反应商)**

**SAMPLE EXERCISE 17.16****Calculating Ion Concentrations for Precipitation**

A solution contains  $1.0 \times 10^{-2} M \text{Ag}^+$  and  $2.0 \times 10^{-2} M \text{Pb}^{2+}$ . When  $\text{Cl}^-$  is added, both  $\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ ) and  $\text{PbCl}_2$  ( $K_{sp} = 1.7 \times 10^{-5}$ ) can precipitate. What concentration of  $\text{Cl}^-$  is necessary to begin the precipitation of each salt? Which salt precipitates first?

**Solve** For  $\text{AgCl}$  we have  $K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$

Because  $[\text{Ag}^+] = 1.0 \times 10^{-2} M$ , the greatest concentration of  $\text{Cl}^-$  that can be present without causing precipitation of  $\text{AgCl}$  can be calculated from the  $K_{sp}$  expression:

$$K_{sp} = (1.0 \times 10^{-2})[\text{Cl}^-] = 1.8 \times 10^{-10}$$
$$[\text{Cl}^-] = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-2}} = 1.8 \times 10^{-8} M$$

Any  $\text{Cl}^-$  in excess of this very small concentration will cause  $\text{AgCl}$  to precipitate from solution.

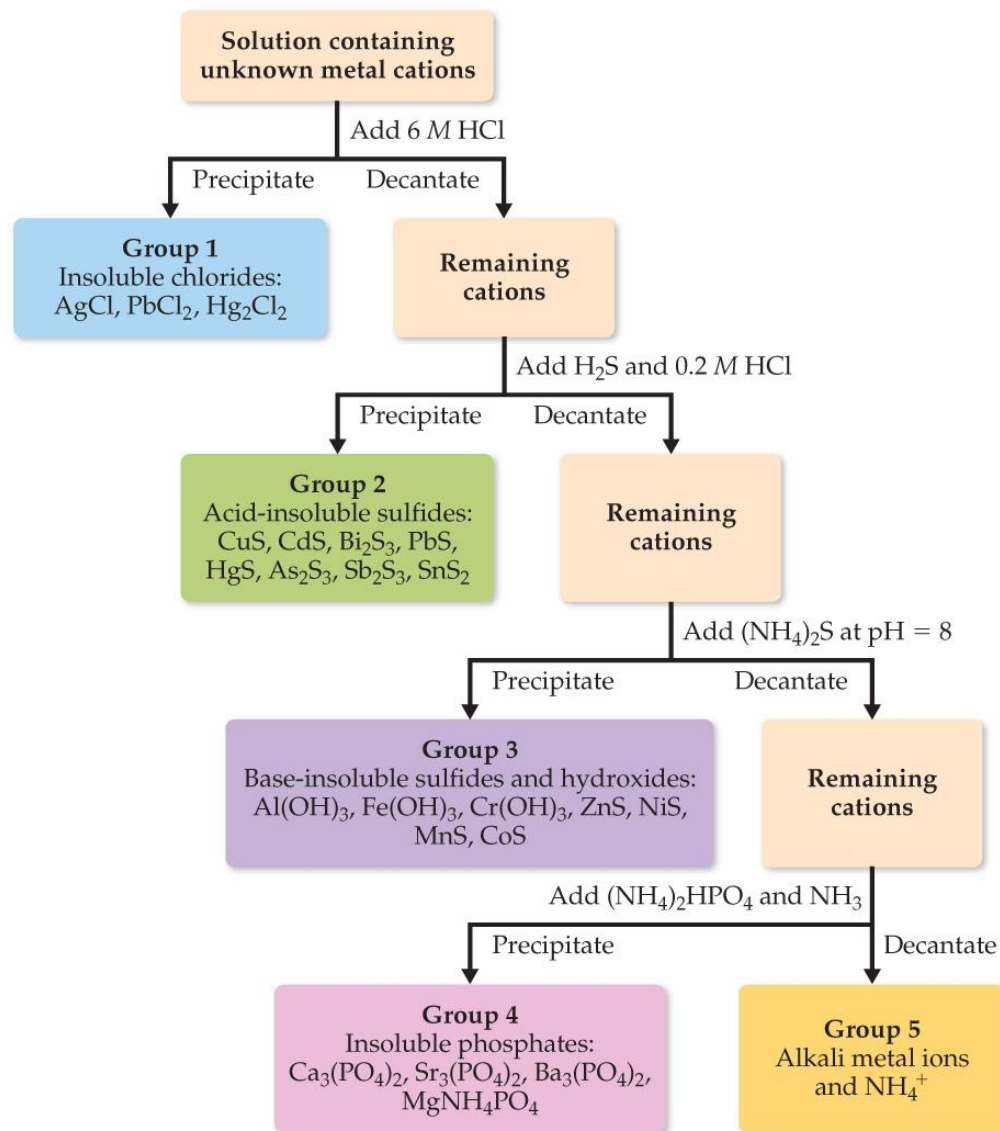
Proceeding similarly for  $\text{PbCl}_2$ , we have

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.7 \times 10^{-5}$$

$$[\text{Cl}^-] = \sqrt{8.5 \times 10^{-4}} = 2.9 \times 10^{-2} M$$

Comparing the  $\text{Cl}^-$  concentration required to precipitate each salt, we see that as  $\text{Cl}^-$  is added,  $\text{AgCl}$  precipitates first because it requires a much smaller concentration of  $\text{Cl}^-$ . Thus,  $\text{Ag}^+$  can be separated from  $\text{Pb}^{2+}$  by slowly adding  $\text{Cl}^-$  so that the chloride ion concentration remains between  $1.8 \times 10^{-8} M$  and  $2.9 \times 10^{-2} M$ .

# ➤ Selective Precipitation of Ions



❑ One can use differences in solubilities of salts to separate ions in a mixture.



# ➤ Selective Precipitation of Ions

## Group 1

Insoluble chlorides:  
 $\text{AgCl}$ ,  $\text{PbCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$

## Group 2

Acid-insoluble sulfides:  
 $\text{CuS}$ ,  $\text{CdS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{PbS}$ ,  
 $\text{HgS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}_2$

## Group 3

Base-insoluble sulfides and hydroxides:  
 $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{ZnS}$ ,  $\text{NiS}$ ,  
 $\text{MnS}$ ,  $\text{CoS}$

## Group 4

Insoluble phosphates:  
 $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Sr}_3(\text{PO}_4)_2$ ,  $\text{Ba}_3(\text{PO}_4)_2$ ,  
 $\text{MgNH}_4\text{PO}_4$

## Group 5

Alkali metal ions  
and  $\text{NH}_4^+$

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  $\text{Hg}_2^{2+}$ .

# **The End of Chapter 17**

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



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

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

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

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

Henderson–Hasselbalch equation

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

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

**Henderson–Hasselbalch equation**

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

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

**Henderson–Hasselbalch equation**

When titrating a weak base with a strong acid, 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



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- d. None of the above

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 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.  $\text{NH}_4^{1+}$