

# Chapter 18

## Acid – Base Equilibria & Solubility Equilibria



# Common-Ion Effect

The extent of ionization of a weak electrolyte is decreased by the addition of a strong electrolyte that has an ion in common with the weak electrolyte.

Equilibrium process – presence of product ions shifts process back to reactants – Le Chatelier!

Ex: A solution is made with 1.0M HF and 2.0M NaF



Add extra F<sup>-</sup> from NaF

Shift equilibrium

Will affect pH if solution is acidic or basic  
– in this case shift toward reactants  
decreases concentration of H<sub>3</sub>O<sup>+</sup> in solution.

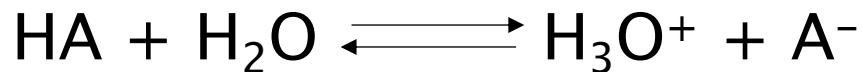
# Common-Ion pH Calculations

1. Calculate the pH of a solution containing 0.085M nitrous acid ( $\text{HNO}_2$ ;  $K_a = 4.5 \times 10^{-4}$ ) and 0.10M potassium nitrite ( $\text{KNO}_2$ ).

# Buffer Solutions (Buffers)

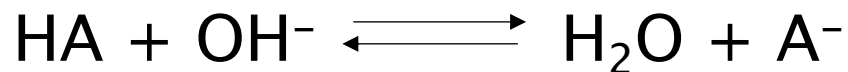
Solutions that resist changes in pH when small amounts of acid or base are added

- Must contain a weak acid or base **and**
- The conjugate (salt) of the weak acid or base
- i.e. Contain a weak conjugate acid/base pair
- pH is controlled by equilibrium [ $K_a$  (or  $K_b$ )]

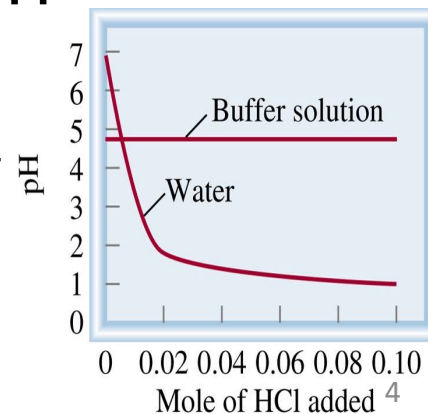
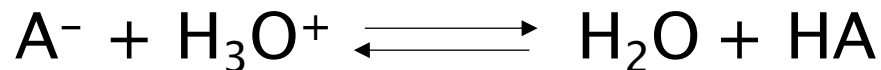


When small amounts of a strong acid or base are added:

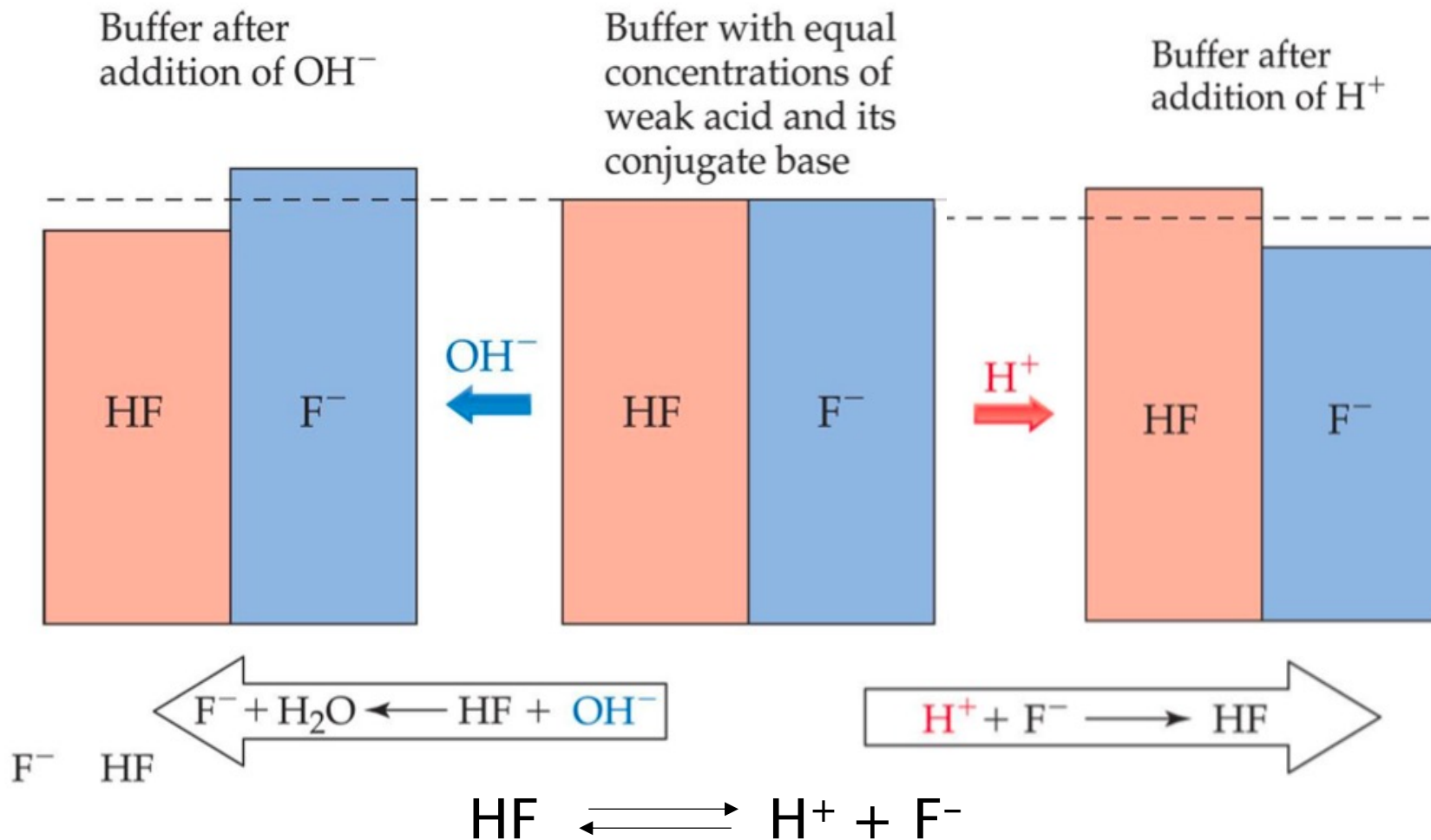
- Acidic species in buffer neutralizes added  $\text{OH}^-$



- Basic species in buffer neutralizes added  $\text{H}^+$



# How Buffers Work – Le Châtelier's Principle



- Add  $\text{OH}^-$ , reduce  $\text{H}^+$ , shift equilibrium toward conj. Base
  - $\text{OH}^-$  will react with  $\text{H}^+$  to form water
- Add  $\text{H}^+$ , shift equilibrium toward undissociated acid

# Henderson-Hasselbalch Equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Comes from the equilibrium expression for:  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

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

Take the  $-\log$  of both sides:

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

$\text{pK}_a$  points to  $-\log K_a$   
 $\text{pH}$  points to  $-\log [\text{H}^+]$   
Conj. base points to  $[\text{A}^-]$   
acid points to  $[\text{HA}]$

Therefore:

$$\text{pK}_a = \text{pH} + -\log \frac{[\text{A}^-]}{[\text{HA}]}$$

For bases:

$$\text{pOH} = \text{pK}_b + -\log \frac{[\text{BH}^+]}{[\text{B}]}$$

Rearrange to get Henderson-Hasselbalch

# Buffer Calculations

1. A 1.00L buffer solution is prepared that contains 0.150M nitrous acid and 0.200M sodium nitrite. What is its pH?

$$K_a = 4.5 \times 10^{-4}$$

Ice Table Method

# Buffer Calculations

1. A 1.00L buffer solution is prepared that contains 0.150M nitrous acid and 0.200M sodium nitrite. What is its pH?

$$K_a = 4.5 \times 10^{-4}$$

H-H equation method:



## Buffer Calculations

2. How many grams of sodium lactate ( $\text{CH}_3\text{CH}(\text{OH})\text{COONa}$ ) should be added to 1.0L of a 0.150M lactic acid ( $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ ) to form a buffer solution with  $\text{pH}=4.00$ ?  
 $K_a = 1.4 \times 10^{-4}$ ; molar mass of sodium lactate = 112.1g/mol

# Buffer Capacity

**Buffer Capacity: The amount of acid or base a buffer can neutralize before there is a significant change in pH.**

- Ratio of weak base to weak acid ( $[A^-]/[HA]$ ) should be between 0.1 & 10.
- Most effective when  $[A^-] = [HA]$  (i.e. ratio = 1)
  - Equal ability to neutralize acids & bases
- Buffer capacity depends on:
  - $K_a$  of the acid
  - Concentration of buffer components
    - More concentrated = higher capacity

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

# pH Range

**pH Range: The range of pH values over which a buffer system works effectively**

- Best to choose an acid with a  $pK_a$  close to the desired pH
- If  $[A^-] = [HA]$ , then  $pH = pK_a$

$$\text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]} \quad \log(1) = 0$$

- Buffer generally usable within  $\pm 1$  pH unit of the  $pK_a$

# Criteria for Making a Buffer

## 1. Choose a weak acid & conjugate base

- Must have the same anion!
  - ex.  $\text{HNO}_2$  &  $\text{NaNO}_2$ ;  $\text{HF}$  &  $\text{LiF}$

## 2. Select acid based on desired pH range

- $\text{pK}_a < 7$  buffer is acidic;  $\text{pK}_a > 7$  buffer is basic
- Buffers can usually be adjusted to  $\pm 1$  desired pH

## 3. Buffer salts (conjugate base) must be soluble & dissociate completely

- Most commonly sodium or potassium salts
- $\text{NH}_4^+$  salts are acidic because  $\text{NH}_4^+$  dissociates

## 4. Concentrations of $[\text{HA}]$ & $[\text{A}^-] > 0.01\text{M}$

- Must be able to neutralize sufficient acid/base
- Can use ICE table to get an idea of what concentration is needed.

# Buffer Calculations: Adding Acid or Base

1. A buffer is made by adding 0.600 mol  $\text{CH}_3\text{COOH}$  and 0.600 mol  $\text{CH}_3\text{COONa}$  to enough water to make 2.00L of solution.  $K_a = 1.8 \times 10^{-5}$ .

(a) What is the pH of the buffer? A: 4.74

(b) Calculate the pH after 0.040 mol HCl is added. A: 4.69

(c) Calculate the pH after 0.040 mol NaOH is added. A: 4.80

(d) Calculate the pH after 4.00mL of 3.00M  $\text{HNO}_3$  is added.

A:4.73

# Buffer Calculations: Adding Acid or Base

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# Buffer Calculations: Adding Acid or Base

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(a) What is the pH of the buffer? **A: 4.74**

(d) Calculate the pH after 4.00mL of 3.00M  $\text{HNO}_3$  is added.

**A:4.73**



# Buffer Calculations: Adding Acid or Base

## DIY Additional Practice

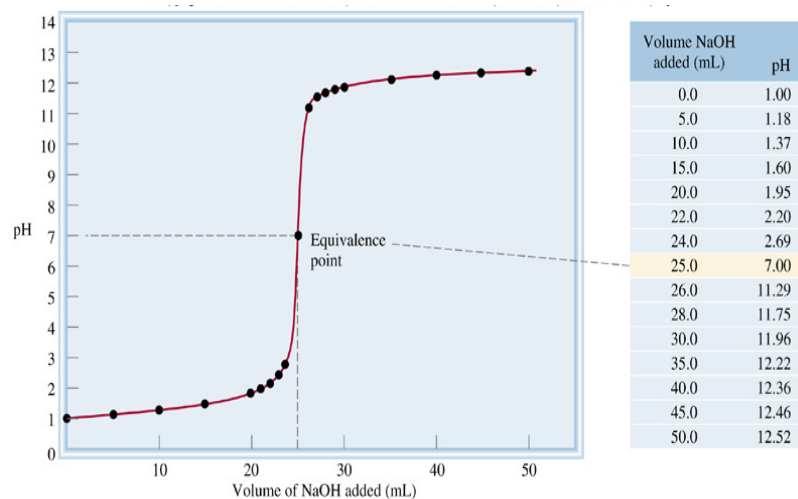
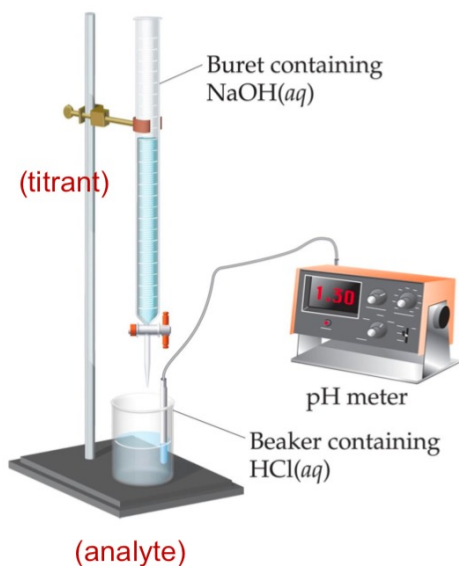
A 1.0 L buffer solution contains 0.150 M nitrous acid and 0.200 M sodium nitrite.  $K_a = 7.2 \times 10^{-4}$  (a) What is the pH of the buffer? (b) What is the pH after adding 1.00 g HBr?

A: (a) 3.27  
(b) 3.21

# Titration

A technique where a known concentration of acid (or base) is added to a solution of base (or acid).

- Used to determine the concentration of an unknown
- In CHM 101 we looked at strong acid/base systems
  - No equilibrium
  - Equivalence point is pH 7
- Indicators or pH meters are used to determine the equivalence point.

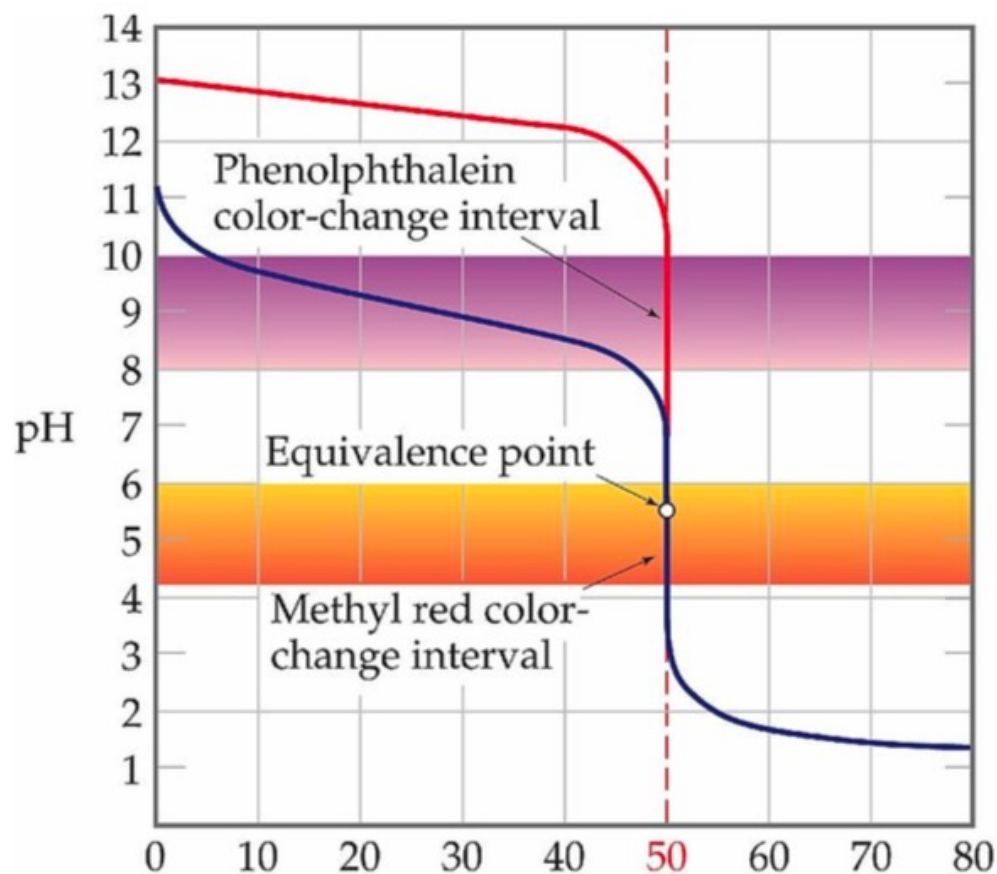


# Titration Terminology

## Equivalence Point:

Point at which the stoichiometric amount of acid and base are equal.

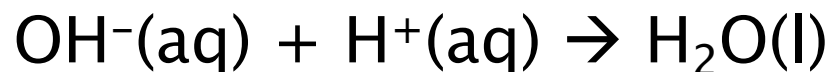
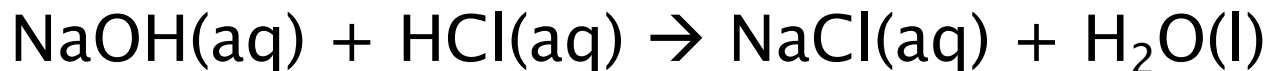
**End Point:** Point in the titration where the indicator changes color.



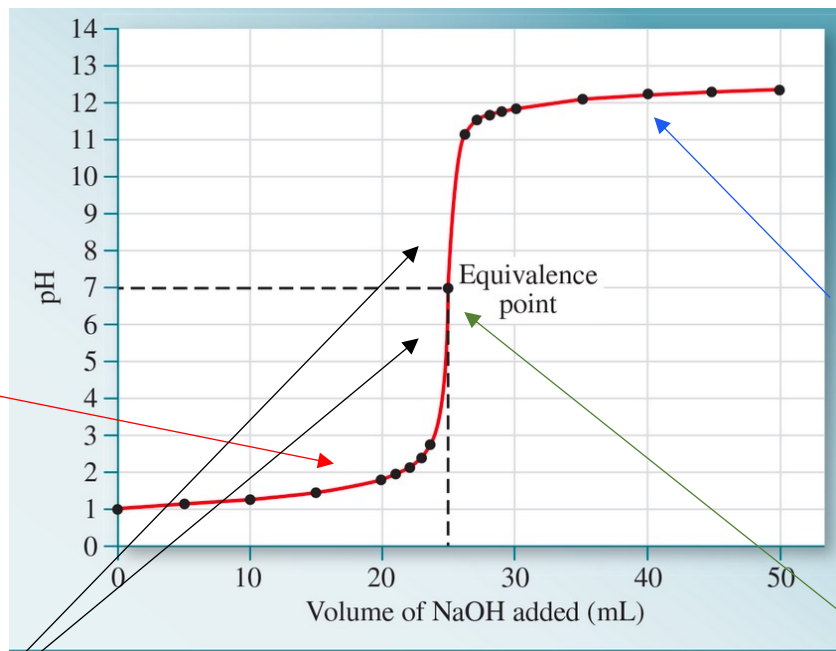
# Solving More Complex Titration Problems

- 1. Read the question carefully to see what it is asking**
  - pH or concentration at a particular point
  - Moles or molarity of original solution
  - pH or volume at equivalence point
- 2. Identify all reactants and products**
  - Write the balanced equation
  - Use stoichiometry to determine amounts of products
  - Identify whether the solution is acidic or basic
- 3. Determine whether it is an equilibrium process**
  - You will have at most one equilibrium
  - Strong acids/bases – just stoichiometry
  - Weak acids/bases – stoichiometry + equilibrium
- 4. Volume increases during titrations so be aware that there will likely be changes in concentration due to volume as well as due to the neutralization reaction.**

# Titration of a Strong Acid with a Strong Base



From the start of the titration to near the endpoint, the pH increases slowly



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

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

At the equivalence point, moles acid = moles base  
Solution contains only water and salt (neutral)

**Both strong = NO EQUILIBRIUM**

# Strong Acid/Strong Base Calculations

In the titration of 25.0mL of 0.100M KOH with 0.100M  $\text{HNO}_3$ , determine the pH:

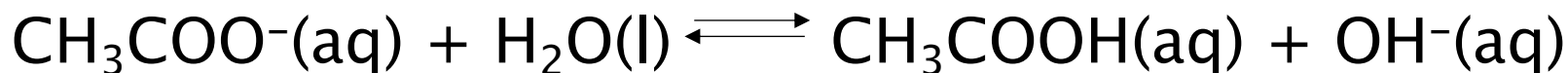
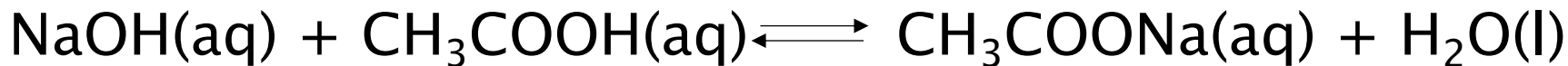
- (a) At the start of the titration (no acid added) A:13.000
- (b) When 24.9mL acid has been added A: 10.3
- (c) When 25.1mL acid has been added A: 3.7

# Strong Acid/Strong Base Calculations

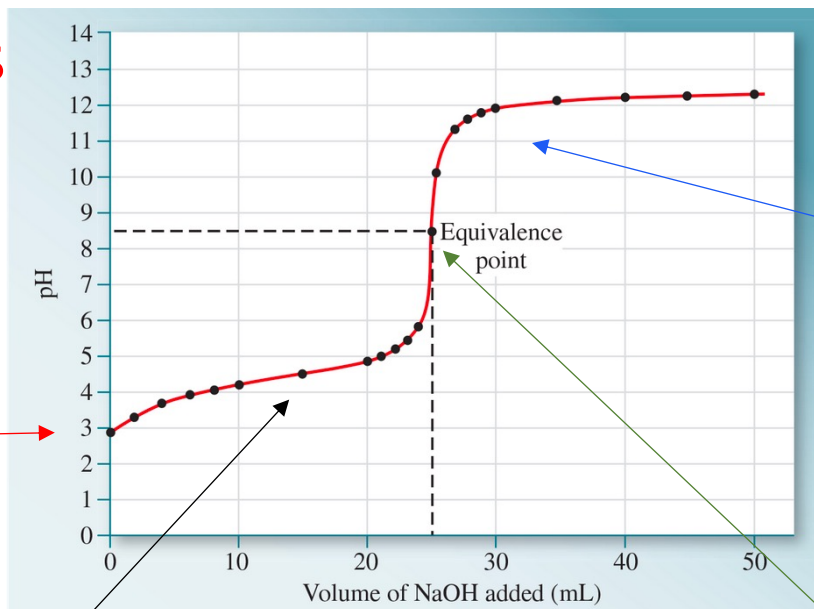
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# Titration of a Weak Acid with a Strong Base



Initially there is only the weak acid; pH depends on concentration &  $K_a$



After the equivalence pt., pH depends on concentration of excess strong base

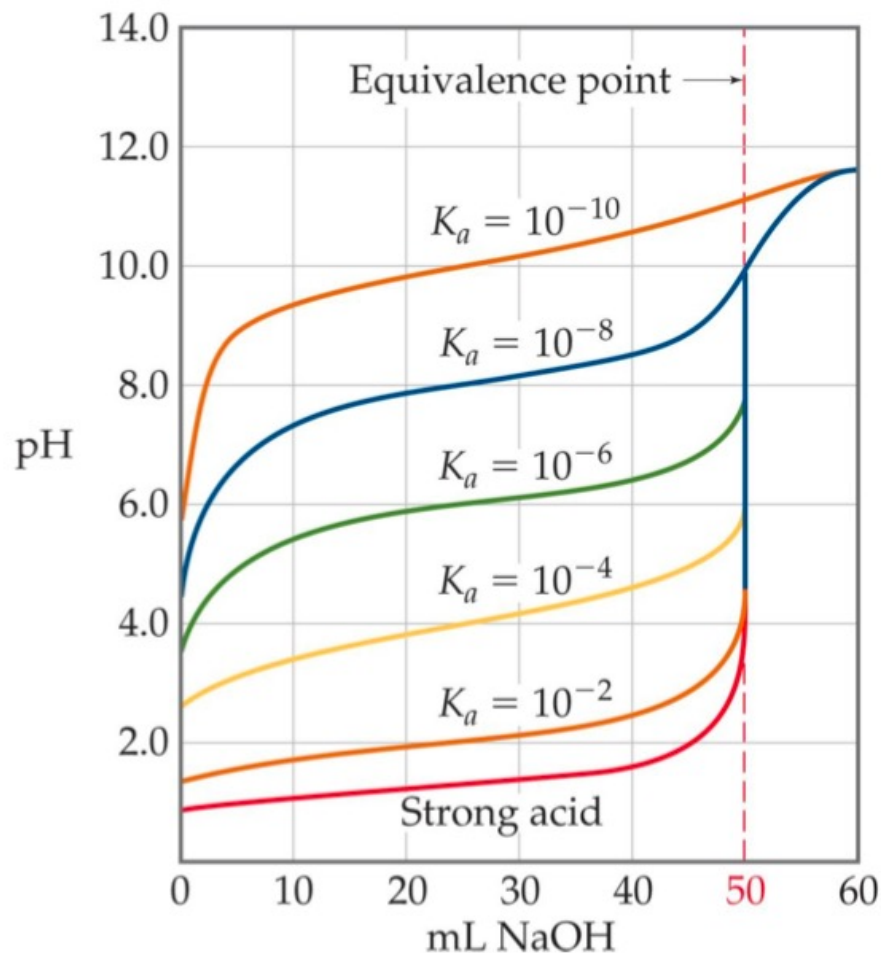
Before the equivalence pt., the solution contains both the weak acid & its conjugate base

At the equivalence pt. (moles acid = moles base) pH is  $>7$  because the conjugate base of the acid affects the pH

**pH depends on stoichiometry & Equilibrium!**



# Titration of a Weak Acid with a Strong Base



With weak acids:

- Initial pH is higher
- pH changes near the equivalence point are more subtle (smaller)
- pH > 7 at equivalence point due to the formation of a basic salt (conjugate base of weak acid; ex:  $\text{CH}_3\text{COONa}$ )

# Weak Acid/Strong Base Calculations

## Things to Keep in Mind

### 1. Acid/Base titration always gives a salt & water



### 2. Initial pH only depends on the weak acid

- $K_a$ /equilibrium & concentration

### 3. Addition of base up to just before equivalence point

- Added base is strong – not the conjugate of the weak acid
- Solution contains weak acid & its conjugate base (salt) – all of the strong base is used up in the neutralization
- **First use stoichiometry to determine how many moles of the acid have been neutralized**
- Determine the new concentration of acid based on moles remaining and new volume (if base is added as a solution)
- Use the equilibrium expression to determine  $[\text{H}_3\text{O}^+]$  (can also use H-H if want pH)

### 4. Whether or not volume increases depends on added base – if the base is in solution, volume increases<sup>26</sup>

# Weak Acid/Strong Base Calculations

## Things to Keep in Mind con't

### 4. At equivalence point: all initial acid & added base are neutralized – the solution only contains the salt

- The salt will be basic – it is the product of a weak acid & a strong base
- The basic salt will react with water to produce  $\text{OH}^-$
- $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$
- Since the solution is basic – need to use  $K_b$  & equilibrium to get the  $\text{OH}^-$  concentration
- Moles acid neutralized = initial moles acid = moles salt formed.
- Use total volume to get concentration.

### 5. After equivalence point: only excess strong base matters

- pH depends on moles of excess strong base & total volume. Strong so NO EQUILIBRIUM!

# Weak Acid/Strong Base Calculations

35.0mL of 0.150M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.8 \times 10^{-5}$ ) was titrated with 0.250M NaOH. Determine the pH:

- At the start of the titration **A: 2.78**
- When 15.0mL of 0.250M NaOH has been added
- At the equivalence point
- When 30.0mL of 0.250M NaOH has been added

# Weak Acid/Strong Base Calculations

35.0mL of 0.150M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.8 \times 10^{-5}$ ) was titrated with 0.250M NaOH. Determine the pH:

b.) When 15.0mL of 0.250M NaOH has been added **A: 5.14**

# Weak Acid/Strong Base Calculations

35.0mL of 0.150M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.8 \times 10^{-5}$ ) was titrated with 0.250M NaOH. Determine the pH:

c.) At the equivalence point **A: 8.86**

# Weak Acid/Strong Base Calculations

35.0mL of 0.150M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.8 \times 10^{-5}$ ) was titrated with 0.250M NaOH. Determine the pH:

d.) When 30.0mL of 0.250M NaOH has been added **A: 12.54**

# Weak Acid/Strong Base Calculations

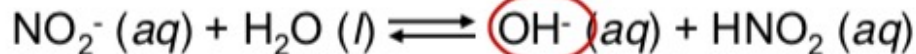
When 100.0 mL of 0.10 M HNO<sub>2</sub> are titrated with a 0.10 M NaOH solution, what is the pH at the equivalence point?  $K_a \text{ HNO}_2 = 4.5 \times 10^{-4}$

start (moles)	0.010	0.010	
	HNO <sub>2</sub> (aq)	+ OH <sup>-</sup> (aq)	→ NO <sub>2</sub> <sup>-</sup> (aq) + H <sub>2</sub> O (l)
end (moles)	0.0	0.0	0.010

Final volume = 200 mL  $\Rightarrow$   $[\text{NO}_2^-] = \frac{0.010}{0.200} = 0.050 \text{ M}$

Use  $K_b$   
 $K_b = 2.2 \times 10^{-11}$

Hydrolysis of basic salt



Initial (M)	0.050	0.00	0.00
Change (M)	-x	+x	+x
Equilibrium (M)	0.050 - x	x	x

$$K_b = \frac{[\text{OH}^-][\text{HNO}_2]}{[\text{NO}_2^-]} = \frac{x^2}{0.050} = 2.2 \times 10^{-11}$$

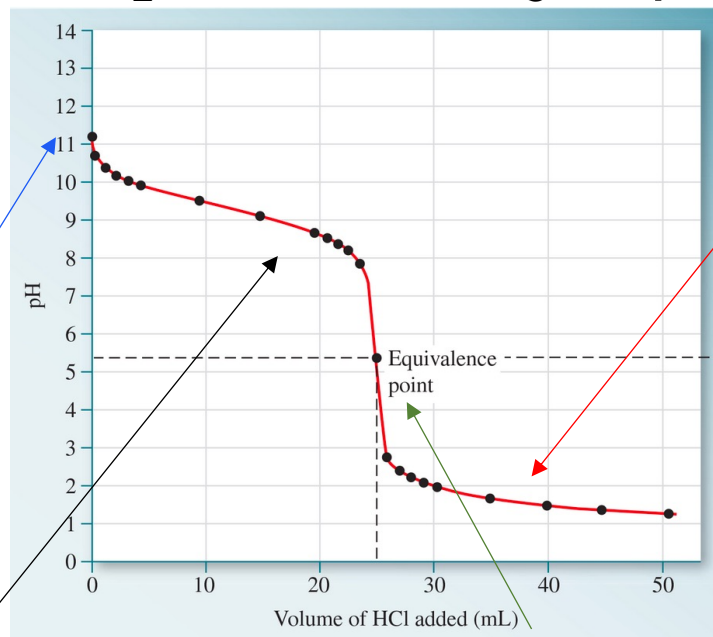
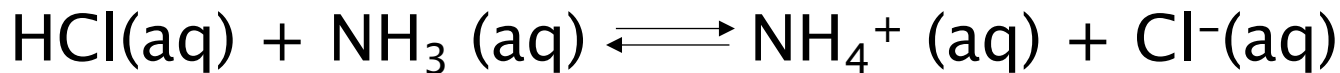
$$x = 1.05 \times 10^{-6} = [\text{OH}^-]$$

$$\text{pOH} = 5.98$$

$$\text{pH} = 14 - 5.98 = 8.02$$



# Titration of a Weak Base with a Strong Acid



Initially there is only the weak base; pH depends on concentration &  $K_b$

Before the equivalence pt., the solution contains the weak base & its conjugate acid

After the equivalence pt., pH depends on concentration of excess strong acid

At the equivalence pt. (moles acid = moles base) pH is  $< 7$  because the conjugate acid of the base affects the pH

**pH depends on stoichiometry & Equilibrium!**

# Weak Base/Strong Acid Calculations

30.0mL of 0.0300M  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ) was titrated with 0.0250M HCl. Determine the pH:

- a.) At the start of the titration A: 10.87
- b.) When 20.0mL of 0.0250M HCl has been added A: 9.16
- c.) At the equivalence point A: 5.56
- d.) When 37.0mL of 0.025M HCl has been added A: 3.43

a.) At the start of the titration (no acid added) – just a solution of a weak base – pH depends on concentration & equilibrium



I	0.03M	0	0	$K_b = \frac{x^2}{0.0300} = 1.8 \times 10^{-5}$
C	-x	+x	+x	
E	<del>0.03-x</del>	x	x	

$$x^2 = 5.4 \times 10^{-7}$$

$$\text{pOH} = -\log (7.35 \times 10^{-4}) = 3.13$$

$$x = 7.35 \times 10^{-4} = [\text{OH}^-]$$

$$\text{pH} = 14 - 3.13 = 10.87$$

# Weak Base/Strong Acid Calculations

30.0mL of 0.0300M  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ) was titrated with 0.0250M HCl. Determine the pH:

b.) When 20.0mL of 0.0250M HCl has been added **A: 9.16**

• All added HCl is used in the titration – need to determine how much  $\text{NH}_3$  remains & how much  $\text{NH}_4^+$  has been produced.



$$0.0300 \frac{\text{mol}}{\text{L}} \text{NH}_3 \times 0.0300\text{L} = 9.00 \times 10^{-4} \text{mol NH}_3 \text{ initial}$$

$$0.0250 \frac{\text{mol}}{\text{L}} \times 0.0200\text{L} = 5.00 \times 10^{-4} \text{mol HCl added}$$

$$5.00 \times 10^{-4} \text{mol HCl} \times \frac{1 \text{ mol NH}_3}{1 \text{ mol HCl}} = 5.00 \times 10^{-4} \text{mol NH}_3 \text{ neutralized}$$

$$9.00 \times 10^{-4} \text{mol init.} - 5.00 \times 10^{-4} \text{mol neut.} = 4.00 \times 10^{-4} \text{mole NH}_3 \text{ remaining}$$

$$5.00 \times 10^{-4} \text{mol HCl} \times \frac{1 \text{ mol NH}_4^+}{1 \text{ mol HCl}} = 5.00 \times 10^{-4} \text{mol NH}_4^+ \text{ produced}$$

$$\text{New volume: } 0.0300\text{L} + 0.0200\text{L} = 0.0500\text{L}$$

$$4.00 \times 10^{-4} \text{mol NH}_3 / 0.0500\text{L} = 8.00 \times 10^{-3} \text{M NH}_3$$

$$5.00 \times 10^{-4} \text{mol NH}_4^+ / 0.0500\text{L} = 1.00 \times 10^{-2} \text{M NH}_4^+$$

$$4.00 \times 10^{-4} \text{ mol NH}_3 / 0.0500 \text{ L} = 8.00 \times 10^{-3} \text{ M NH}_3$$

$$5.00 \times 10^{-4} \text{ mol NH}_4^+ / 0.0500 \text{ L} = 1.00 \times 10^{-2} \text{ M NH}_4^+$$

New equilibrium with NH<sub>3</sub> & NH<sub>4</sub><sup>+</sup> present:



I	0.008M	0.01M	0
C	-x	+x	+x
E	0.008- <del>x</del>	0.01 + <del>x</del>	x

$$K_b = \frac{(0.01)(x)}{0.008} = 1.8 \times 10^{-5}$$

$$0.01x = 1.44 \times 10^{-7}$$

$$x = 1.44 \times 10^{-7} / 0.01 = 1.44 \times 10^{-5} = [\text{OH}^-]$$

$$\text{pOH} = -\log(1.44 \times 10^{-5}) = 4.84164$$

$$\text{pH} = 14 - 4.84164 = 9.1594 \rightarrow \mathbf{9.16}$$

Could also use the NH<sub>3</sub> & NH<sub>4</sub><sup>+</sup> molarities listed above in the H-H eq - but for H-H would need to use pK<sub>a</sub> and make sure to have [A<sup>-</sup>] and [HA] in the correct locations

# Weak Base/Strong Acid Calculations

30.0mL of 0.0300M  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ) was titrated with 0.0250M HCl. Determine the pH:

c.) At the equivalence point **A: 5.56**

- At the equivalence point, moles added acid = initial moles base
- All added acid & initial base are neutralized (i.e. all  $\text{NH}_3$  became  $\text{NH}_4^+$ )
- pH depends on equilibrium of CONJUGATE acid

Conjugate acid of  $\text{NH}_3$  is  $\text{NH}_4^+$ .

Moles  $\text{NH}_4^+$  = moles  $\text{NH}_3$  neutralized:  $0.0300 \frac{\text{mol}}{\text{L}} \times 0.0300\text{L} = 9.00 \times 10^{-4} \text{mol}$

Volume acid needed for neutralization = volume containing  $9.00 \times 10^{-4}$  mol HCl:  $9.00 \times 10^{-4} \text{mol HCl} \times \frac{1\text{L HCl}}{0.0250 \text{mol HCl}} = 0.036\text{L HCl solution}$

Total volume = 0.0360L added + 0.0300L initial = 0.0660L

Concentration of  $\text{NH}_4^+$  =  $9.00 \times 10^{-4} \text{mol} / 0.0660\text{L} = 0.013636\text{M}$

Equilibrium is:





I	0.013536	0	0
C	-x	+x	+x
E	0.013636 - x	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$K_a = \frac{x^2}{0.013636} = 5.56 \times 10^{-10}$$

$$x^2 = 7.576 \times 10^{-12}$$

$$x = 2.752 \times 10^{-6} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(2.752 \times 10^{-6}) = 5.5603 \rightarrow 5.56$$

# Weak Base/Strong Acid Calculations

30.0mL of 0.0300M  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ) was titrated with 0.0250M HCl. Determine the pH:

d.) When 37.0mL of 0.025M HCl has been added **A: 3.43**

- Excess HCl has been added. HCl is strong. pH depends on amount of HCl left over after neutralization.
- Strong acid = no equilibrium

Reaction:  $\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$

Moles HCl added:  $\frac{0.0250 \text{ mol HCl}}{1 \text{ L}} \times 0.0370 \text{ L} = 9.25 \times 10^{-4} \text{ mol HCl}$

Moles HCl needed for neutralization:

$$9.00 \times 10^{-4} \text{ mol NH}_3 \times \frac{1 \text{ mol HCl}}{1 \text{ mol NH}_3} = 9.00 \times 10^{-4} \text{ mol HCl}$$

Moles HCl not used in neutralization:

$$9.25 \times 10^{-4} \text{ mol added} - 9.00 \times 10^{-4} \text{ mol used} = 2.5 \times 10^{-5} \text{ mol HCl left over}$$

Total volume =  $0.0300 \text{ L} + 0.0370 \text{ L} = 0.0670 \text{ L}$

Concentration of HCl =  $2.5 \times 10^{-5} \text{ mol} / 0.0670 \text{ L} = 3.73 \times 10^{-4} \text{ M}$

Strong acid so  $[\text{H}_3\text{O}^+] = 3.73 \times 10^{-4} \text{ M}$      $\text{pH} = -\log(3.73 \times 10^{-4}) = 3.43$

# Acid-Base Indicators

Chemical added during a titration to cause a color change at a particular pH allowing the user to detect the endpoint.

Things to consider when choosing an indicator:

Example: titration of  $\text{CH}_3\text{COOH}$  with  $\text{NaOH}$

- What kind of titration is it? Weak acid with strong base
- What kind of salt is formed? Basic salt
- What happens to pH due to hydrolysis? Salt is basic so  $\text{pH} > 7.0$

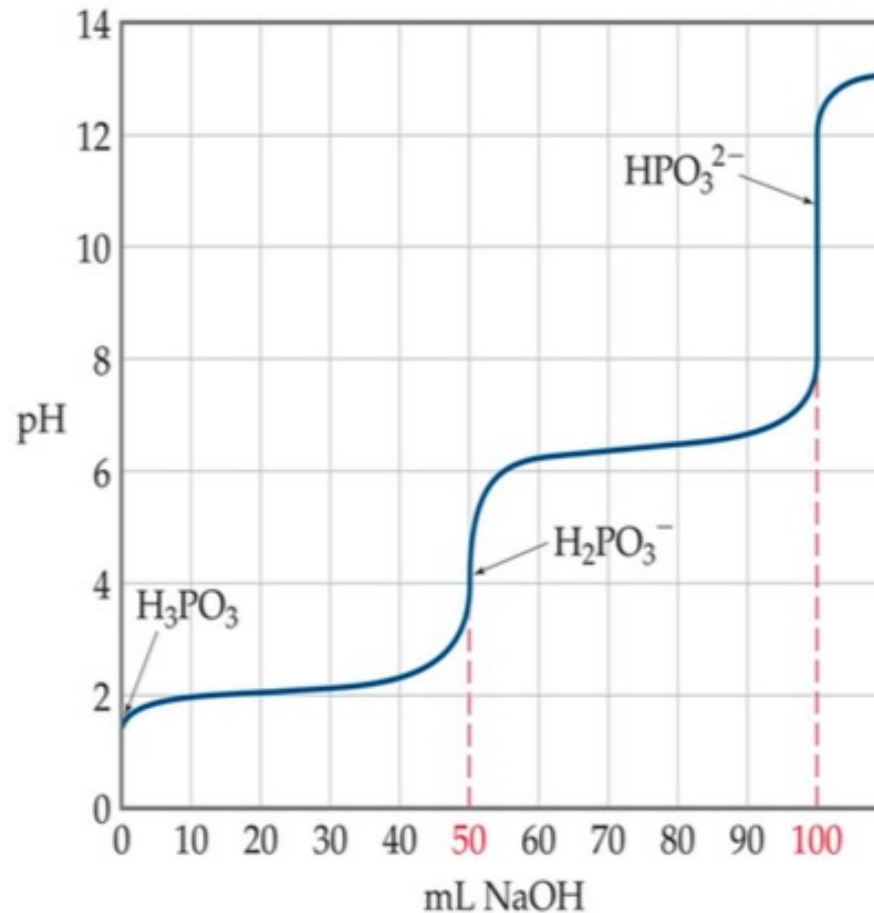
TABLE 17.1 Some Common Acid-Base Indicators

Indicator	Color		pH Range*
	In Acid	In Base	
Thymol blue	Red	Yellow	1.2–2.8
Bromophenol blue	Yellow	Bluish purple	3.0–4.6
Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8
Phenolphthalein	Colorless	Reddish pink	8.3–10.0

\*The pH range is defined as the range over which the indicator changes from the acid color to the base color.



# Titrations of Polyprotic Acids



The titration of a polyprotic acid with a base will give an equivalence point for each acidic proton.

# Solubility Equilibria

## Aqueous Salt Solutions & Solubility

### CHM 101

- Ionic compounds were considered soluble or insoluble
- Soluble compounds dissociated fully in water
- Basic stoichiometry rules were used

### CHM 112

- Most ionic compounds are “slightly” soluble – they do dissolve a little, but not very much
- A small amount of dissolved & dissociated material is present with the bulk undissolved
- Ions are constantly moving between the dissolved and undissolved states – **EQUILIBRIUM!**
- Solubility constant is  $K_{sp}$  (solubility product constant)
- Discussed in terms of Molar Solubility –
  - moles solute/ 1L saturated solution

# CHM 101 Solubility Rules for ions

**Soluble**

Ammonium ( $\text{NH}_4^+$ )  
Hydrogen ( $\text{H}^+$ )  
Alkali metals (group 1A)      Always soluble  
Nitrate ( $\text{NO}_3^-$ )  
Perchlorate ( $\text{ClO}_4^-$ )  
Acetate ( $\text{CH}_3\text{COO}^-$ )

**Usually Soluble**

Halides ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , &  $\text{I}^-$ )      **Exceptions (insoluble if with):**  
 **$\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Ag}^+$**

---

Sulfate ( $\text{SO}_4^{2-}$ )       **$\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$**

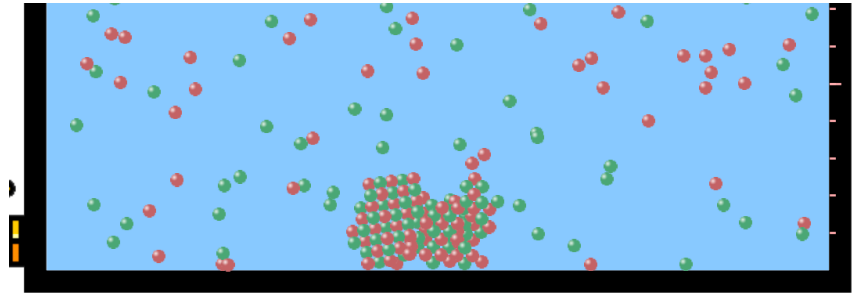
**Sparingly Soluble (Insoluble)**

**Sulfide ( $\text{S}^{2-}$ )**  
**Hydroxide ( $\text{OH}^-$ )**  
**Oxide ( $\text{O}^{2-}$ )**  
**Carbonate ( $\text{CO}_3^{2-}$ )**  
**Phosphate ( $\text{PO}_4^{3-}$ )**

**Exceptions:**  
**soluble if with any of the cations listed in the always soluble box**

# Solubility Product Constant ( $K_{sp}$ )

A slightly soluble ionic material is placed in water.



- The solubility is low so most will not dissolve
- What does dissolve will dissociate into ions



- The solid is in equilibrium with the dissolved ions
- The equilibrium expression is:

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

- Note that the  $\text{PbCl}_2(\text{s})$  is not included in the equilibrium expression. Why?

# Solubility Product Constant ( $K_{sp}$ )

- $K_{sp}$  is an approximation used to estimate solubility
- Measures the extent to which a substance will dissolve in water
- Larger  $K_{sp}$  = higher solubility
- Amount of solid material present does not alter  $K_{sp}$ 
  - Solids are not included in equilibrium expressions!

TABLE 17.2 Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

Compound	$K_{sp}$	Compound	$K_{sp}$
Aluminum hydroxide [Al(OH) <sub>3</sub> ]	$1.8 \times 10^{-33}$	Lead(II) chromate (PbCrO <sub>4</sub> )	$2.0 \times 10^{-14}$
Barium carbonate (BaCO <sub>3</sub> )	$8.1 \times 10^{-9}$	Lead(II) fluoride (PbF <sub>2</sub> )	$4.1 \times 10^{-8}$
Barium fluoride (BaF <sub>2</sub> )	$1.7 \times 10^{-6}$	Lead(II) iodide (PbI <sub>2</sub> )	$1.4 \times 10^{-8}$
Barium sulfate (BaSO <sub>4</sub> )	$1.1 \times 10^{-10}$	Lead(II) sulfide (PbS)	$3.4 \times 10^{-28}$
Bismuth sulfide (Bi <sub>2</sub> S <sub>3</sub> )	$1.6 \times 10^{-72}$	Magnesium carbonate (MgCO <sub>3</sub> )	$4.0 \times 10^{-5}$
Cadmium sulfide (CdS)	$8.0 \times 10^{-28}$	Magnesium hydroxide [Mg(OH) <sub>2</sub> ]	$1.2 \times 10^{-11}$
Calcium carbonate (CaCO <sub>3</sub> )	$8.7 \times 10^{-9}$	Manganese(II) sulfide (MnS)	$3.0 \times 10^{-14}$
Calcium fluoride (CaF <sub>2</sub> )	$4.0 \times 10^{-11}$	Mercury(I) chloride (Hg <sub>2</sub> Cl <sub>2</sub> )	$3.5 \times 10^{-18}$
Calcium hydroxide [Ca(OH) <sub>2</sub> ]	$8.0 \times 10^{-6}$	Mercury(II) sulfide (HgS)	$4.0 \times 10^{-54}$
Calcium phosphate [Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ]	$1.2 \times 10^{-26}$	Nickel(II) sulfide (NiS)	$1.4 \times 10^{-24}$
Chromium(III) hydroxide [Cr(OH) <sub>3</sub> ]	$3.0 \times 10^{-29}$	Silver bromide (AgBr)	$7.7 \times 10^{-13}$
Cobalt(II) sulfide (CoS)	$4.0 \times 10^{-21}$	Silver carbonate (Ag <sub>2</sub> CO <sub>3</sub> )	$8.1 \times 10^{-12}$
Copper(I) bromide (CuBr)	$4.2 \times 10^{-8}$	Silver chloride (AgCl)	$1.6 \times 10^{-10}$
Copper(I) iodide (CuI)	$5.1 \times 10^{-12}$	Silver iodide (AgI)	$8.3 \times 10^{-17}$
Copper(II) hydroxide [Cu(OH) <sub>2</sub> ]	$2.2 \times 10^{-20}$	Silver sulfate (Ag <sub>2</sub> SO <sub>4</sub> )	$1.4 \times 10^{-5}$
Copper(II) sulfide (CuS)	$6.0 \times 10^{-37}$	Silver sulfide (Ag <sub>2</sub> S)	$6.0 \times 10^{-51}$
Iron(II) hydroxide [Fe(OH) <sub>2</sub> ]	$1.6 \times 10^{-14}$	Strontium carbonate (SrCO <sub>3</sub> )	$1.6 \times 10^{-9}$
Iron(III) hydroxide [Fe(OH) <sub>3</sub> ]	$1.1 \times 10^{-36}$	Strontium sulfate (SrSO <sub>4</sub> )	$3.8 \times 10^{-7}$
Iron(II) sulfide (FeS)	$6.0 \times 10^{-19}$	Tin(II) sulfide (SnS)	$1.0 \times 10^{-26}$
Lead(II) carbonate (PbCO <sub>3</sub> )	$3.3 \times 10^{-14}$	Zinc hydroxide [Zn(OH) <sub>2</sub> ]	$1.8 \times 10^{-14}$
Lead(II) chloride (PbCl <sub>2</sub> )	$2.4 \times 10^{-4}$	Zinc sulfide (ZnS)	$3.0 \times 10^{-23}$

## Calculating $K_{sp}$ from Solubility

The molar solubility of  $\text{CaF}_2$  at  $35^\circ\text{C}$  is  $1.24 \times 10^{-3} \text{ M}$ .

(a) What is the solubility of  $\text{CaF}_2$  in g/L? A:  $0.0968 \text{ g/L}$

(b) What is  $K_{sp}$  at this temperature? A:  $7.63 \times 10^{-9}$

# Calculating Solubility from $K_{sp}$

The  $K_{sp}$  for  $\text{LaF}_3$  is  $2.0 \times 10^{-19}$ .

(a) What is the molar solubility of  $\text{LaF}_3$  in water? **A:  $9.3 \times 10^{-6} \text{M}$**

(b) What is the solubility in g/L? **A:  $1.8 \times 10^{-3} \text{g/L}$**

# Comparing Molar Solubilities vs. $K_{sp}$

Compound	$K_{sp}$	Molar Solubility
$BaSO_4$	$1.1 \times 10^{-10}$	$1.0 \times 10^{-5} M$
$Mg_3(AsO_4)_2$	$2.0 \times 10^{-20}$	$5.0 \times 10^{-5} M$

## Molar Solubility Comparison:

$Mg_3(AsO_4)_2$  molar solubility is 5X greater than  $BaSO_4$

## $K_{sp}$ Comparison

$BaSO_4$  has a  $K_{sp}$  that is  $10^9$  X greater than  $Mg_3(AsO_4)_2$

## Be careful using $K_{sp}$ directly to compare solubilities

- Number of ions present also matters
- Can only directly compare  $K_{sp}$  if # ions produced is identical



# Factors Affecting Solubility:

## Common-Ion Effect

- One of the ions in the compound is also part of another compound present in the solution

## pH

- Presence of hydroxide ( $\text{OH}^-$ ) or hydronium ions ( $\text{H}_3\text{O}^+$ )

## Complexation

- Formation of coordinate bonds with solvent or other molecules present in solution

# Common-Ion Effect

The extent of ionization of a weak electrolyte is decreased by the addition of a strong electrolyte that has an ion in common with the weak electrolyte.

Equilibrium process – presence of product ions shifts process back to reactants – Le Chatelier!

Ex: A solution is made with 1.0M CaCl<sub>2</sub> and 2.0M Ca(OH)<sub>2</sub>



Add extra Ca<sup>2+</sup>  
from CaCl<sub>2</sub>  
Shift equilibrium

For solubility equilibria, the presence of a common ion will decrease the solubility of the slightly soluble compound.

1. The  $K_{sp}$  of  $Mn(OH)_2$  is  $1.6 \times 10^{-13}$ . Calculate the molar solubility of  $Mn(OH)_2$  in:

a.) water A:  $3.4 \times 10^{-5} M$

b.) A solution that contains 0.020M NaOH A:  $4.0 \times 10^{-10} M$

c.) Compare the solubility of  $Mn(OH)_2$  in these solutions

A: 85,000 times more soluble in water

2.) How much is the solubility of lead (II) chloride changed in the presence of 0.85M NaCl?  $K_{sp} = 1.6 \times 10^{-5}$

More than 700X less  
soluble than in water

# Effect of pH

## If the Compound Contains a(n):

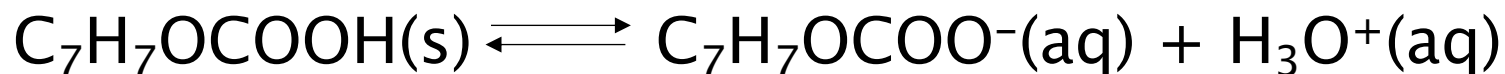
- **Basic Anion:** More soluble in acidic solution



In acidic solution:  $\text{OH}^{-}(\text{aq}) + \text{H}_3\text{O}^{+}(\text{aq}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$

$\text{OH}^{-}$  removed from solution, dissolution equilibrium shifts toward more dissolved product

- **Acidic Cation:** More soluble in basic solution



In basic solution:  $\text{OH}^{-}(\text{aq}) + \text{H}_3\text{O}^{+}(\text{aq}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$

$\text{H}_3\text{O}^{+}$  removed from solution, dissolution equilibrium shifts toward more dissolved product

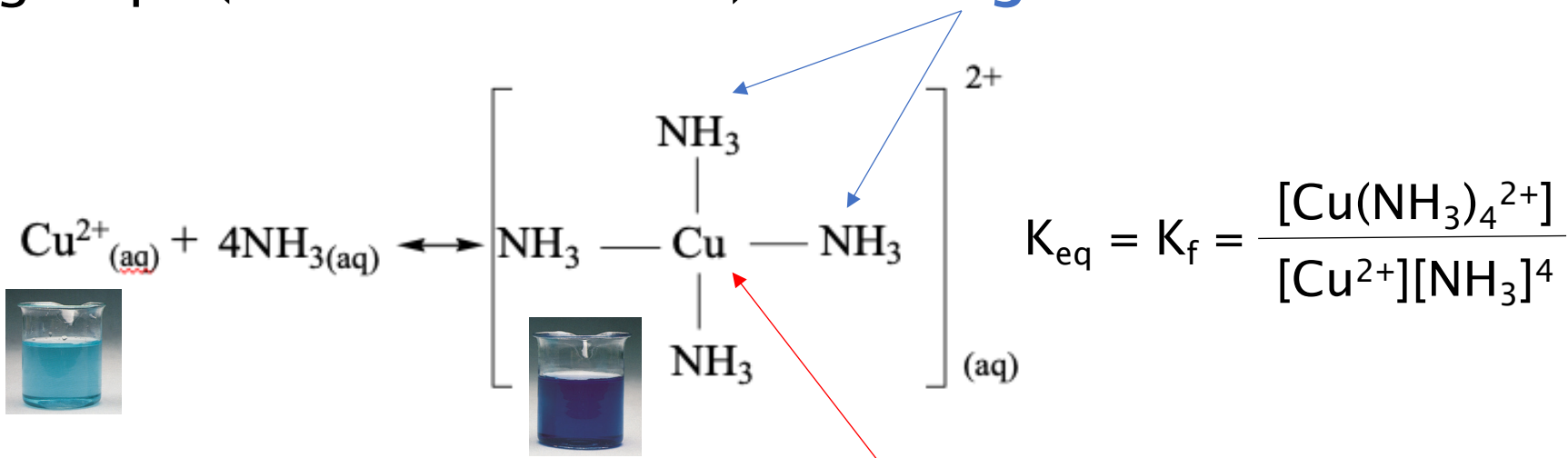
# Effect of pH Calculations

Calculate the solubility of  $\text{Mg}(\text{OH})_2$  (one of the ingredients in the antacid Maalox) in grams per liter when buffered at pH: (a) 12.50; (b) 7.00    A: a.)  $7.0 \times 10^{-7}$  g/L; b.)  $7.0 \times 10^4$  g/L

$K_{\text{sp}}$  of  $\text{Mg}(\text{OH})_2 = 1.2 \times 10^{-11}$ ; MM  $\text{Mg}(\text{OH})_2 = 58.32$  g/mol

# Complex Ion Formation

**Complex Ion:** A central metal ion surrounded by other groups (molecules or ions) called **ligands**.



The metal center (Cu) is a **Lewis Acid** that accepts electron pairs from the ligands ( $\text{NH}_3$ ), which act as **Lewis Bases** by donating electron pairs.

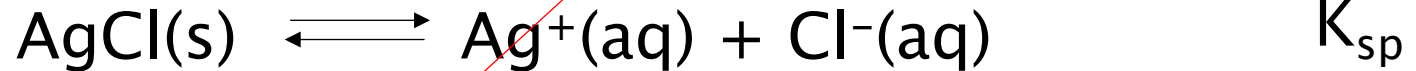
Formation of a complex ion is a reversible equilibrium reaction with its own equilibrium constant,  $K_{\text{f}}$ .

**$K_{\text{f}}$  = formation constant**

Common Complex Ion Ligands:  $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{OH}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$

# Complex Ion Formation & Solubility

## Formation of a Complex Ion can increase solubility



- $\text{Ag}^+$  is removed from solution, shifting solubility equilibrium to the dissociated products
- More  $\text{AgCl(s)}$  dissolves
- $K_{\text{sp}}$  governs first process
- $K_{\text{f}}$  governs second process
- Two processes are added together
- $K_{\text{c}}$  (overall equilibrium expression) =  $K_{\text{sp}} \times K_{\text{f}}$



# $K_f$ Values for Selected Complex Ions

**TABLE 18.5**
**Formation Constants of Selected Complex Ions in Water at 25°C**

Complex Ion	Equilibrium Expression	Formation Constant ( $K_f$ )
$\text{Ag}(\text{NH}_3)_2^+$	$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$	$1.5 \times 10^7$
$\text{Ag}(\text{CN})_2^-$	$\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_2^-$	$1.0 \times 10^{21}$
$\text{Cu}(\text{CN})_4^{2-}$	$\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}$	$1.0 \times 10^{25}$
$\text{Cu}(\text{NH}_3)_4^{2+}$	$\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$	$5.0 \times 10^{13}$
$\text{Cd}(\text{CN})_4^{2-}$	$\text{Cd}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Cd}(\text{CN})_4^{2-}$	$7.1 \times 10^{16}$
$\text{CdI}_4^{2-}$	$\text{Cd}^{2+} + 4\text{I}^- \rightleftharpoons \text{CdI}_4^{2-}$	$2.0 \times 10^6$
$\text{HgCl}_4^{2-}$	$\text{Hg}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{HgCl}_4^{2-}$	$1.7 \times 10^{16}$
$\text{HgI}_4^{2-}$	$\text{Hg}^{2+} + 4\text{I}^- \rightleftharpoons \text{HgI}_4^{2-}$	$2.0 \times 10^{30}$
$\text{Hg}(\text{CN})_4^{2-}$	$\text{Hg}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Hg}(\text{CN})_4^{2-}$	$2.5 \times 10^{41}$
$\text{Co}(\text{NH}_3)_6^{3+}$	$\text{Co}^{3+} + 6\text{NH}_3 \rightleftharpoons \text{Co}(\text{NH}_3)_6^{3+}$	$5.0 \times 10^{31}$
$\text{Zn}(\text{NH}_3)_4^{2+}$	$\text{Zn}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Zn}(\text{NH}_3)_4^{2+}$	$2.9 \times 10^9$
$\text{Cr}(\text{OH})_4^-$	$\text{Cr}^{3+} + 4\text{OH}^- \rightleftharpoons \text{Cr}(\text{OH})_4^-$	$8 \times 10^{29}$

# Complex Ion Formation & Solubility

1. Determine the equilibrium constant for the reaction:



$$K_{\text{sp}} \text{ AgI} = 8.3 \times 10^{-17}; K_{\text{f}} \text{ Ag(CN)}_2^{-} = 1 \times 10^{21}$$

# Complex Ion Formation & Solubility

2. Calculate the molar solubility of zinc carbonate at 25°C in (a) pure water and (b) 1.0M NH<sub>3</sub>

$K_{sp} = 1.4 \times 10^{-11}$ ;  $K_f = 4.1 \times 10^8$  for  $Zn(NH_3)_4^{2+}$

A: (a)  $3.7 \times 10^{-6} M$

(b)  $7.6 \times 10^{-2} M$

# Complex Ion Formation & Solubility

## A note about the homework:

- Complex ion formation is often highly favored, which means the K values are high. This makes it less likely that the approximation method can be used.
- To get around this issue, Connect tends to reverse the process so that the value of K will be very low.
- Options were limited, so one of these questions is included in your assignment.

The formation constant,  $K_f$ , for the complex ion  $\text{Co}(\text{NH}_3)_6^{3+}$  is  $5.00 \times 10^{31}$ .

The reverse process has an equilibrium constant of  $1 / K_f = 2.00 \times 10^{-32}$ .

$$2.00 \times 10^{-32} = \frac{[\text{Co}^{3+}][\text{NH}_3]^6}{[\text{Co}(\text{NH}_3)_6^{3+}]}$$

# Prediction of Precipitation

Whether or not a precipitate will form depends on concentration.

Can use  $Q_c$  values to predict precipitate formation

Calculate  $Q_c$  based on given concentrations & compare  $Q_c$  to  $K_{sp}$

- $Q_c > K_{sp}$  Concentration too high  $\rightarrow$  Precipitate will form
- $Q_c < K_{sp}$  Concentration low  $\rightarrow$  all ions remain in solution
- $Q_c = K_{sp}$  At Equilibrium  $\rightarrow$  saturated solution

## Prediction of Precipitation

1.) If 2.00mL of 0.200M NaOH are added to 1.00L of 0.100M CaCl<sub>2</sub>, will a precipitate form? **A: no precipitate will form**

## Prediction of Precipitation

2.) How many grams of solid  $\text{K}_2\text{SO}_4$  (174.3g/mol) would need to be added to 50.0mL of a 0.0010M  $\text{Ca}(\text{NO}_3)_2$  solution in order to (a) start precipitation and (b) precipitate 99% of the calcium?

A: 0.079g

## Prediction of Precipitation

2.) How many grams of solid  $\text{K}_2\text{SO}_4$  (174.3g/mol) would need to be added to 50.0mL of a 0.0010M  $\text{Ca}(\text{NO}_3)_2$  solution in order to (a) start precipitation and (b) precipitate 99% of the calcium?



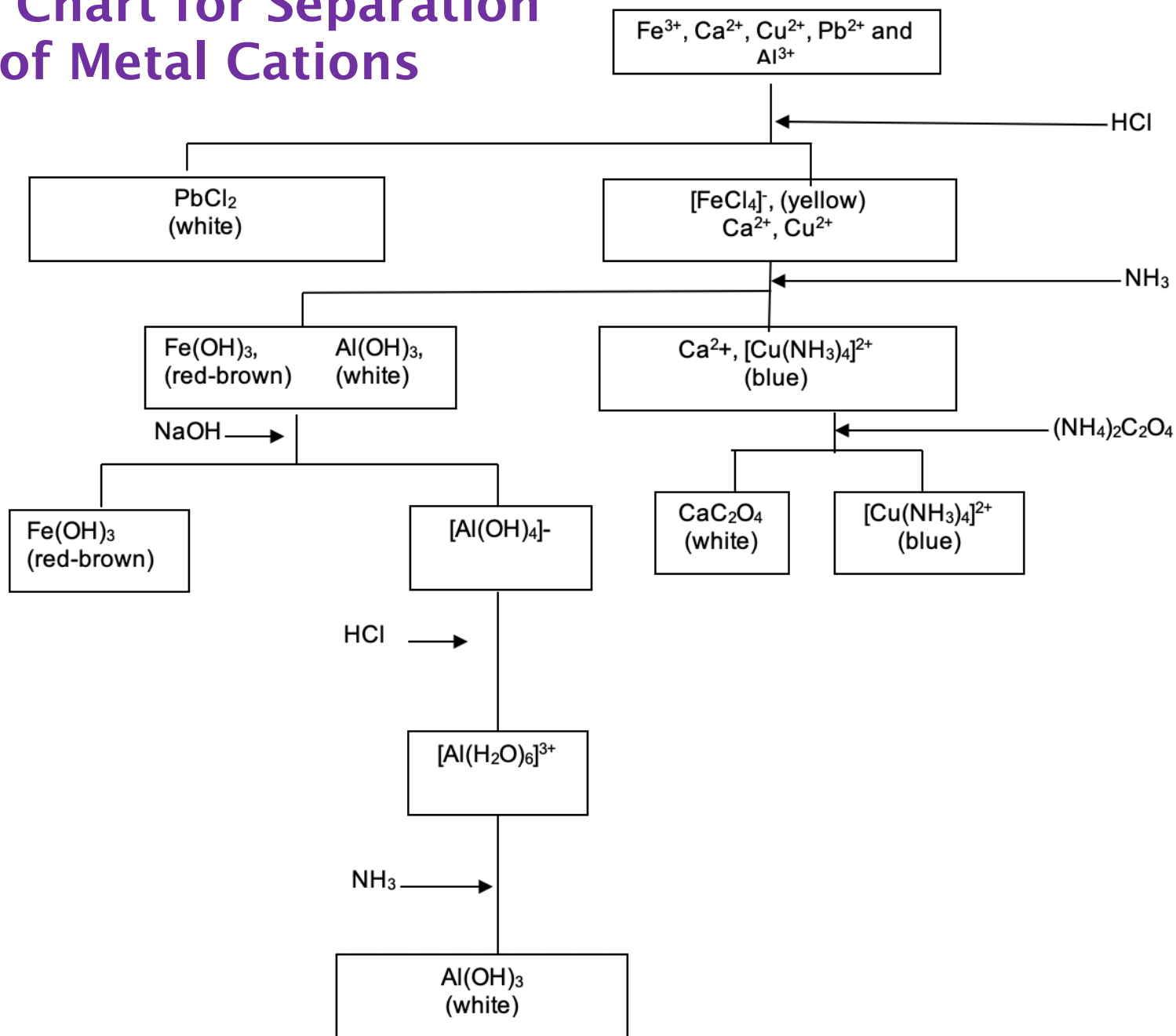
# Qualitative Analysis of Metal Ions

## Ways to determine which ions are present in solution

- **Selective (fractional) precipitation**
  - One compound has very low  $K_{sp}$  and will form a precipitate
  - Other compounds have very high (or no)  $K_{sp}$
- **Complex formation**
  - Ligands will only form complex with one ion present
  - May cause a precipitate to dissolve
- **Flame tests**
  - Color of flame can be used for ID
  - CHM 101 – energy levels!

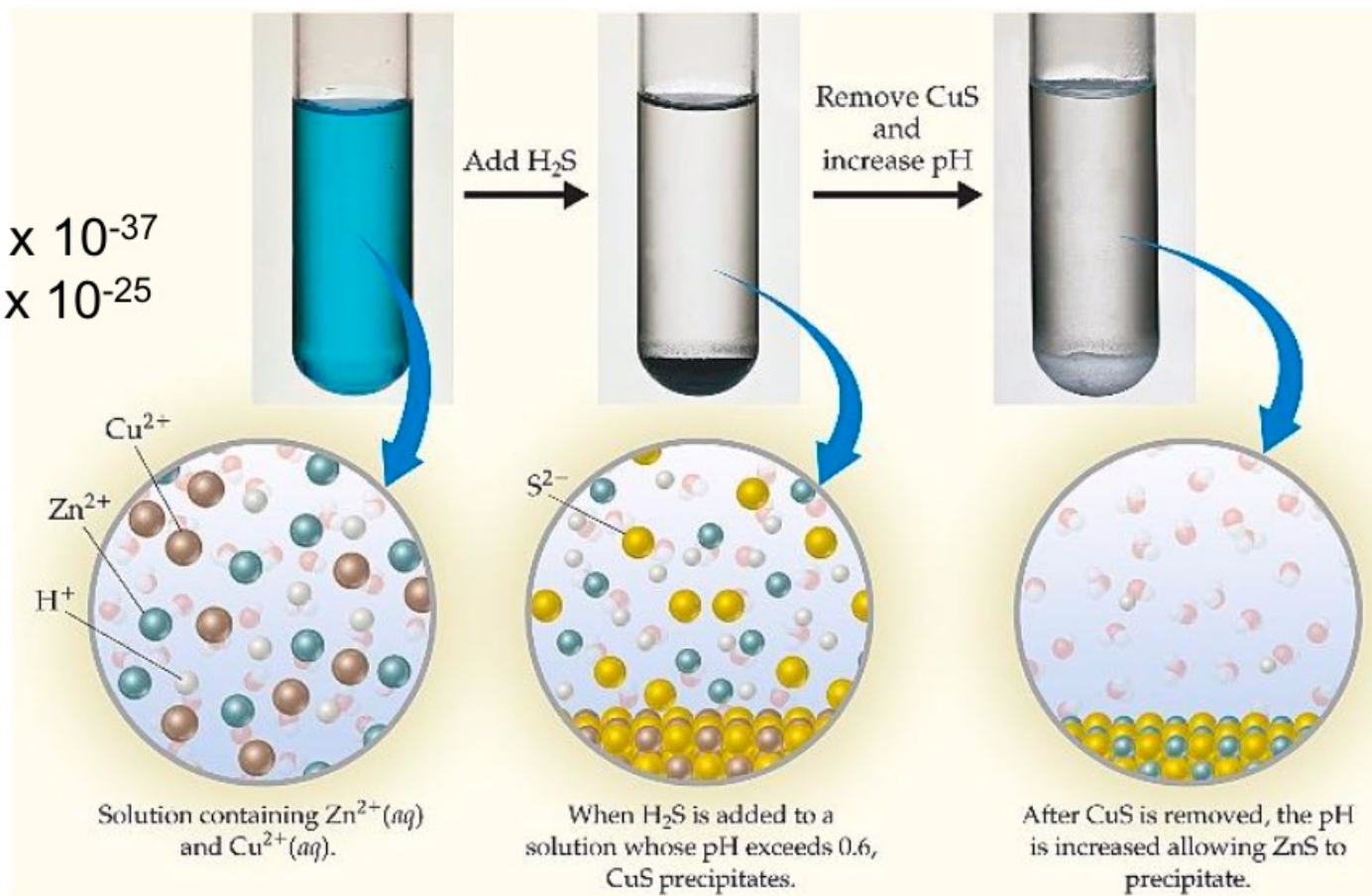


# Flow Chart for Separation of Metal Cations



# Selective Precipitation

$$K_{sp}:$$
$$\text{CuS} = 6 \times 10^{-37}$$
$$\text{ZnS} = 2 \times 10^{-25}$$



Solution contains  
 $\text{Zn}^{2+}(\text{aq})$  &  $\text{Cu}^{2+}(\text{aq})$

$\text{H}_2\text{S}$  is added  
At low pH (but  $> 0.6$ )  
 $\text{CuS}$  precipitates

$\text{CuS}$  is removed  
then pH is  
increased causing  
 $\text{ZnS}$  to precipitate

# Selective Precipitation

A solution contains 0.050M  $\text{Mg}^{2+}$  and 0.020M  $\text{Cu}^{2+}$ . Solid NaOH is added to the solution.  $K_{\text{sp}} \text{Mg}(\text{OH})_2 = 1.8 \times 10^{-11}$ ;  
 $K_{\text{sp}} \text{Cu}(\text{OH})_2 = 4.8 \times 10^{-20}$

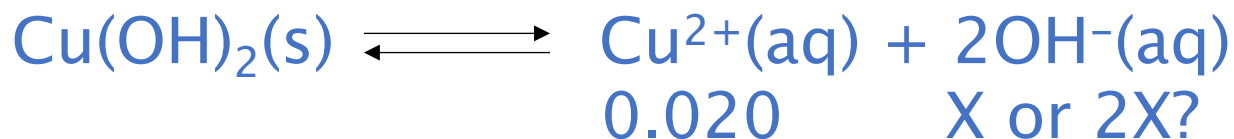
(a) Which ion will precipitate first? A:  $\text{Cu}^{2+}$

(b) What concentration of  $\text{OH}^-$  is necessary to begin precipitation of each cation. A:  $\text{Cu}^{2+}$  needs  $1.5 \times 10^{-9}\text{M}$   
 $\text{Mg}^{2+}$  needs  $1.9 \times 10^{-5}\text{M}$

# Selective Precipitation

A solution contains 0.050M  $\text{Mg}^{2+}$  and 0.020M  $\text{Cu}^{2+}$ . Solid NaOH is added to the solution.  $K_{\text{sp}} \text{Mg}(\text{OH})_2 = 1.8 \times 10^{-11}$ ;  
 $K_{\text{sp}} \text{Cu}(\text{OH})_2 = 4.8 \times 10^{-20}$  A:  $\text{Cu}^{2+}$  needs  $1.5 \times 10^{-9}\text{M}$

(a) What concentration of  $\text{OH}^-$  is necessary to begin precipitation of  $\text{Cu}^{2+}$ ?



$$K_{\text{sp}} = [0.020][X]^2 = 4.8 \times 10^{-20}$$

$$X^2 = 2.4 \times 10^{-18}$$

$$X = [\text{OH}] = 1.5 \times 10^{-9}\text{M}$$

$\text{OH}^-$  can be designated as  $X$  or as  $2X$ ; the answer will remain the same.

$$K_{\text{sp}} = [0.020][2X]^2 = 4.8 \times 10^{-20}$$

$$K_{\text{sp}} = 0.080X^2 = 4.8 \times 10^{-20}$$

$$X^2 = 6.0 \times 10^{-19}$$

$$X = 7.75 \times 10^{-10}\text{M}$$

$$[\text{OH}] = 2X = 2(7.75 \times 10^{-10}\text{M})$$

$$[\text{OH}] = 1.5 \times 10^{-9}\text{M}$$