Chapter 17

Acid – Base Equilibria
&
Solubility Equilibria

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Buffer Solutions (Buffers)

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

- Must contain a <u>weak</u> acid or base **<u>and</u>**
- The <u>conjugate</u> (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)]

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

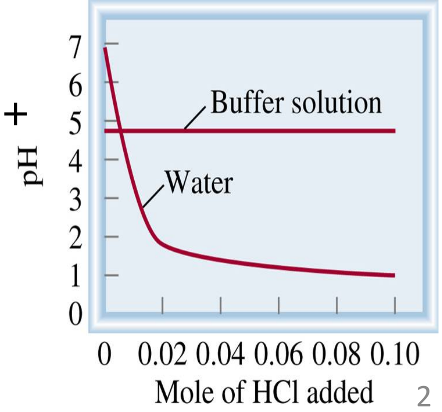
When small amounts of a strong acid or base are added:

- Acidic species in buffer neutralizes added OH^-

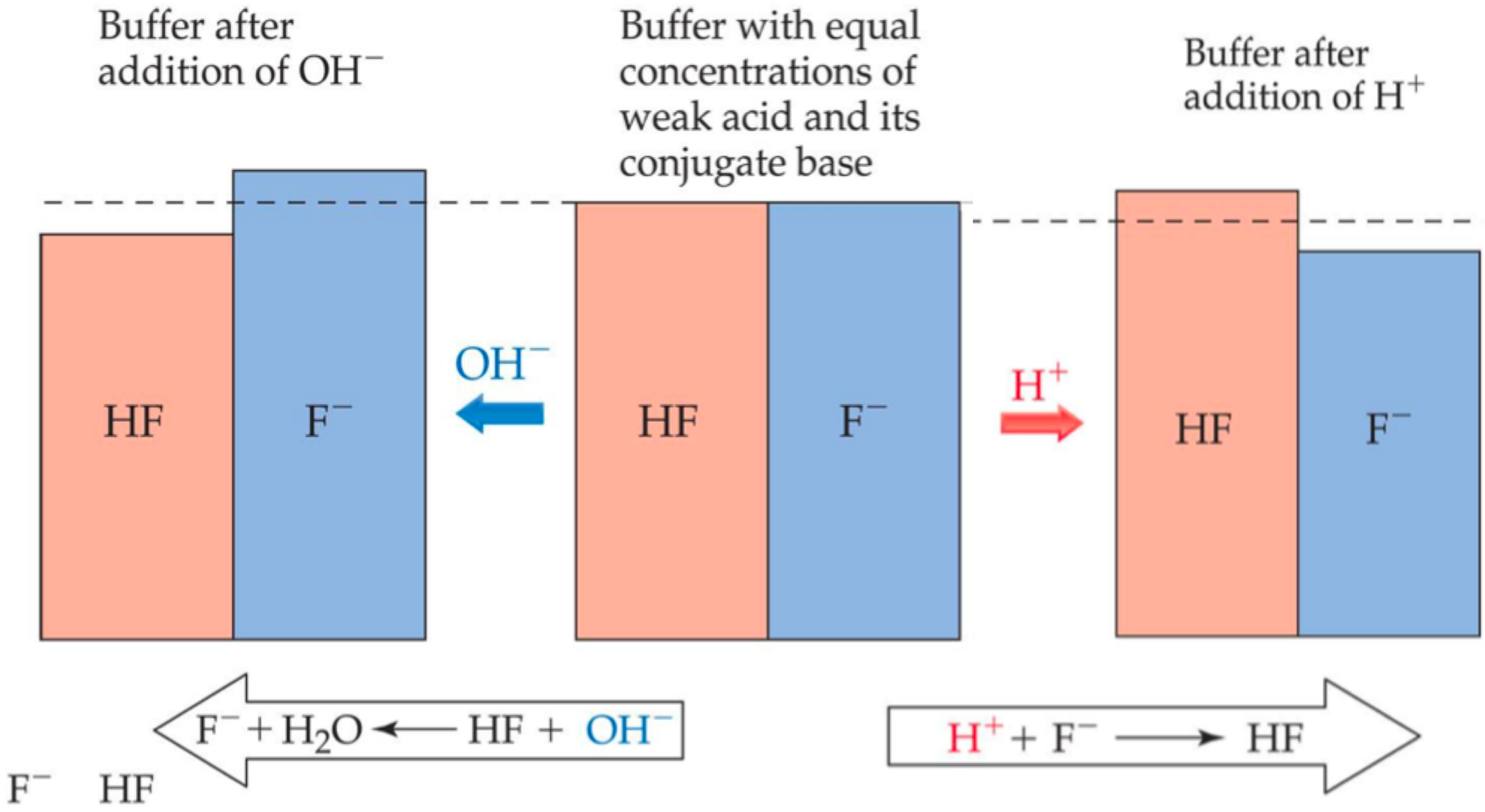
$$HA + OH^- \rightleftharpoons H_2O + A^-$$

- Basic species in buffer neutralizes added H^+

$$A^- + H_3O^+ \rightleftharpoons H_2O + HA$$



How Buffers Work – Le Châtelier’s Principle



$$HF \rightleftharpoons H^+ + F^-$$

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

Henderson–Hasselbalch Equation

$$\boxed{\mathbf{pH = pK_a + \log \frac{[A^-]}{[HA]}}}$$

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

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

Take the –log of both sides:

$$\underbrace{-\log K_a}_{pK_a} = \underbrace{-\log [H^+]}_{pH} + -\log \frac{\overbrace{[A^-]}^{\text{Conj. base}}}{\underbrace{[HA]}_{\text{acid}}}$$

Therefore:

$$pK_a = pH + -\log\frac{[A^-]}{[HA]}$$

For bases:

$$pOH = pK_b + -\log\frac{[BH^+]}{[B]}$$

Rearrange to get Henderson-Hasselbalch

Using the Henderson–Hasselbalch Equation

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

$K_a = 7.2x10^{-4}$

Ice Table Method

pH = 3.27

Using the Henderson–Hasselbalch Equation

1. A 1.00L buffer solution is prepared that contains 0.150M nitrous acid and 0.200M sodium nitrite. What is its pH? $K_a = 7.2 \times 10^{-4}$

H-H equation method:

pH = 3.27

Using the Henderson–Hasselbalch Equation

2. How many grams of sodium lactate ($CH_3CH(OH)COONa$) should be added to 1.0L of a 0.150M lactic acid ($CH_3CH(OH)COOH$) to form a buffer solution with pH=4.00? $K_a = 1.4x10^{-4}$; molar mass of sodium lactate = 112.1g/mol

A: 24g

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

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

pH Range

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

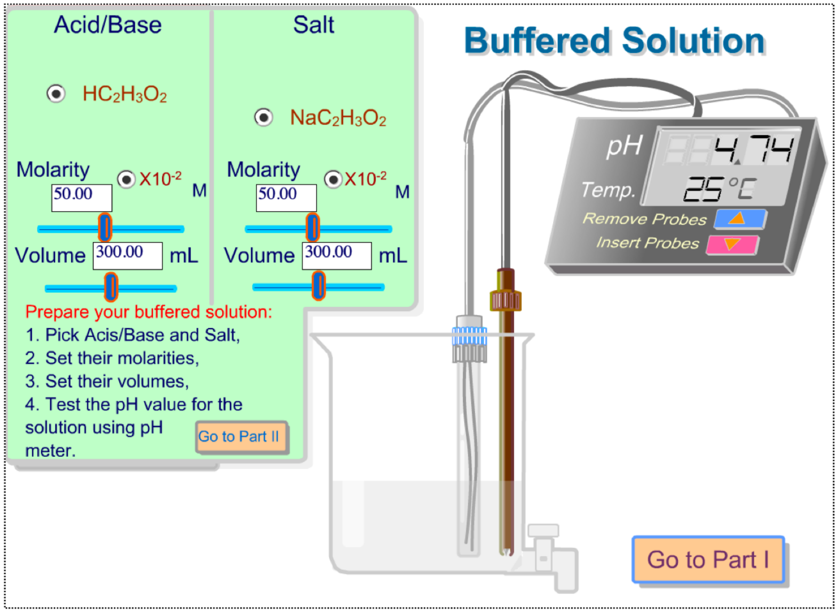
- Best to choose an acid with a pK_a close to the desired pH
- If $[A^-] = [HA]$, then $pH = pK_a$

$$\boxed{\mathbf{pH = pK_a + \cancel{\log \frac{[A^-]}{[HA]}}}} \qquad \log(1) = 0$$

- Buffer generally usable withing ± 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. HNO_2 & $NaNO_2$; HF & LiF
2. **Select acid based on desired pH range**
   - $pK_a < 7$ buffer is acidic; $pK_a > 7$ buffer is basic
   - Buffers can usually be adjusted to ±1 desired pH
3. **Buffer salts (conjugate base) must be soluble & dissociate completely**
   - Most commonly sodium or potassium salts
   - NH_4^+ salts are acidic because NH_4^+ dissociates
4. **Concentrations of [HA] & [A$^-$] > 0.01M**
   - Must be able to neutralize sufficient acid/base
   - Can use ICE table to get an idea of what concentration is needed.



Acid/Base: ● $HC_2H_3O_2$

Molarity 50.00 ● X10^{-2} M

Volume 300.00 mL

Salt: ● $NaC_2H_3O_2$

Molarity 50.00 ● X10^{-2} M

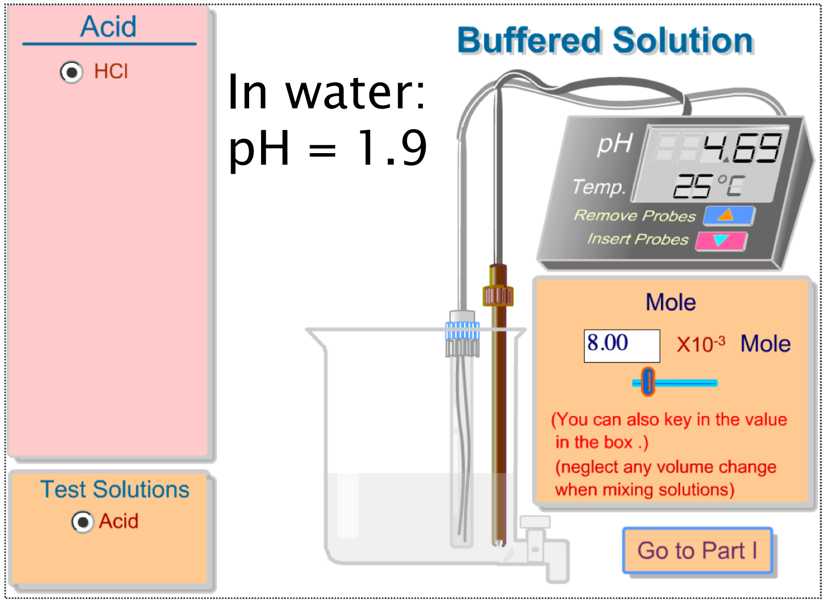
Volume 300.00 mL

Prepare your buffered solution:

1. Pick Acis/Base and Salt,
2. Set their molarities,
3. Set their volumes,
4. Test the pH value for the solution using pH meter.

pH 4.74

Temp. 25 °C



Acid: ● HCl

In water:
pH = 1.9

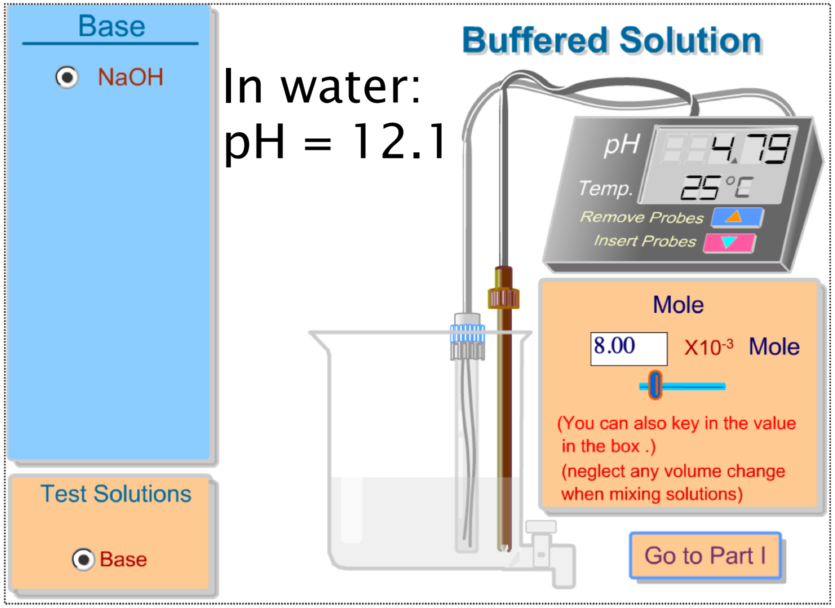
pH 4.69

Temp. 25 °C

Mole 8.00 X10^{-3} Mole

(You can also key in the value in the box .)
(neglect any volume change when mixing solutions)

Test Solutions: ● Acid



Base: ● NaOH

In water:
pH = 12.1

pH 4.79

Temp. 25 °C

Mole 8.00 X10^{-3} Mole

(You can also key in the value in the box .)
(neglect any volume change when mixing solutions)

Test Solutions: ● Base

https://pages.uoregon.edu/tgreenbo/pHbuffer20.html

Buffer calculations

1. A 1.0 L buffer solution contains 0.150 M nitrous acid and 0.200 M sodium nitrite. $K_a=7.2\times10^{-4}$ (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

Buffer calculations

2. A buffer is made by adding 0.600 mol CH_3COOH and 0.600 mol CH_3COONa to enough water to make 2.00L of solution. $K_a = 1.8x10^{-5}$.

(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

Buffer calculations

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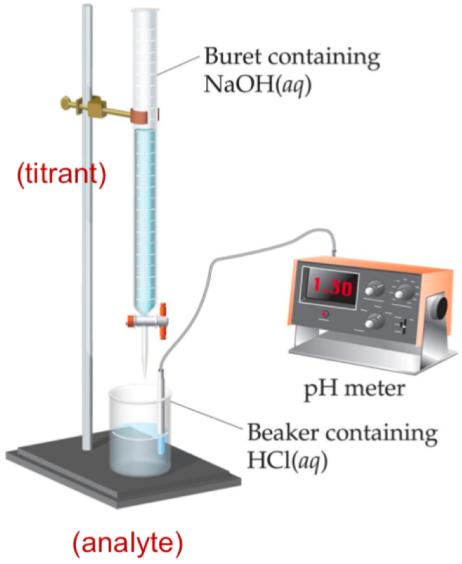
(a) What is the pH of the buffer? A: 4.74

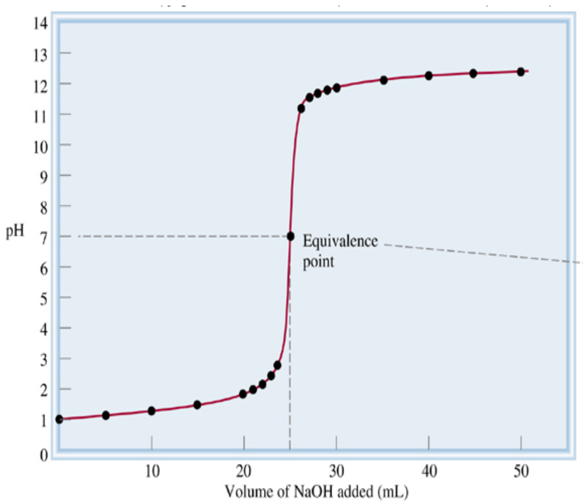
(c) Calculate the pH after 0.040 mol NaOH is added. A: 4.80

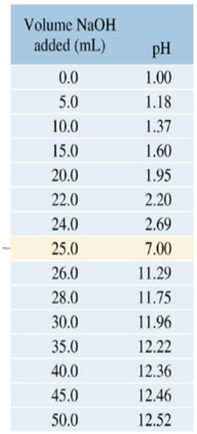
Titration

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 <u>strong</u> acid/base systems
  - No equilibrium
  - Equivalence point is pH 7
- Indicators or pH meters are used to determine the equivalence point.





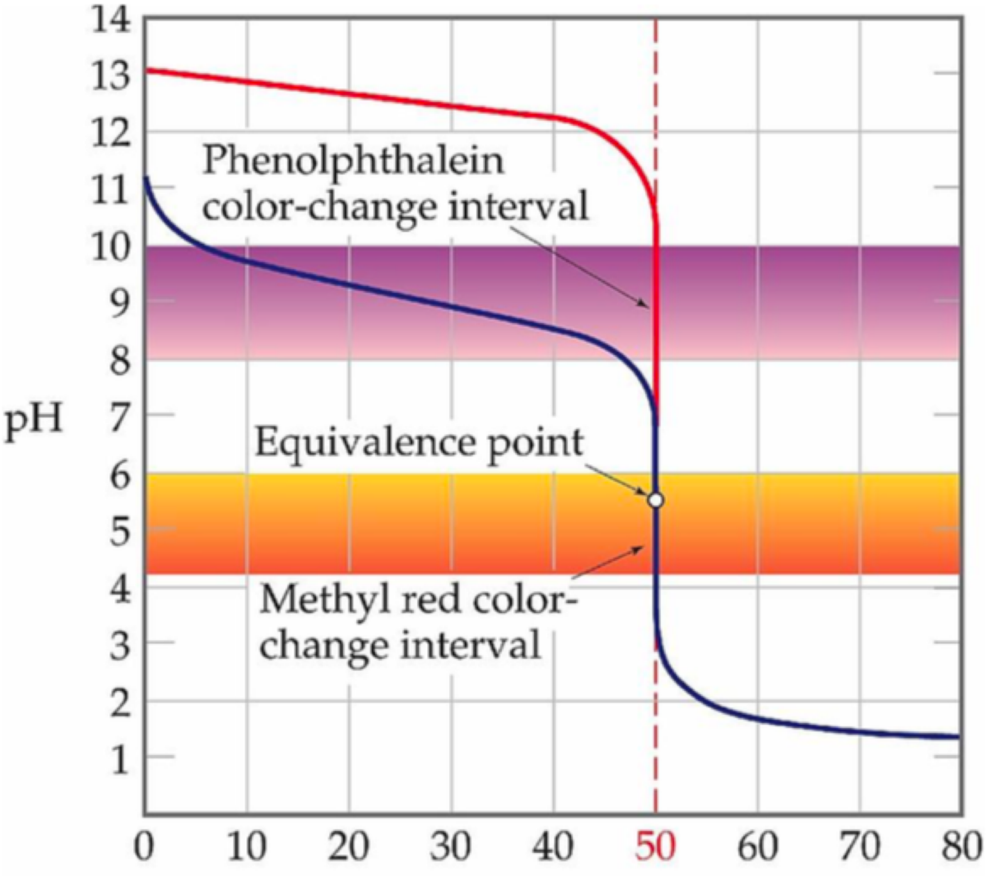


Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

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.



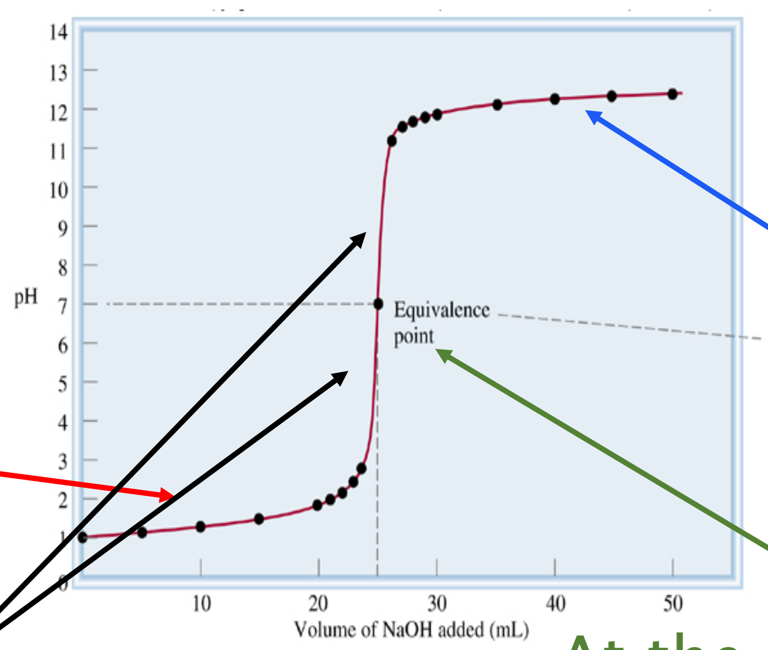
Solving More Complex Titration Problems

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

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$



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 HNO_3, determine the pH:

(a) At the start of the titration (no acid added) A:13.0

(b) When 24.9mL acid has been added A: 10.3

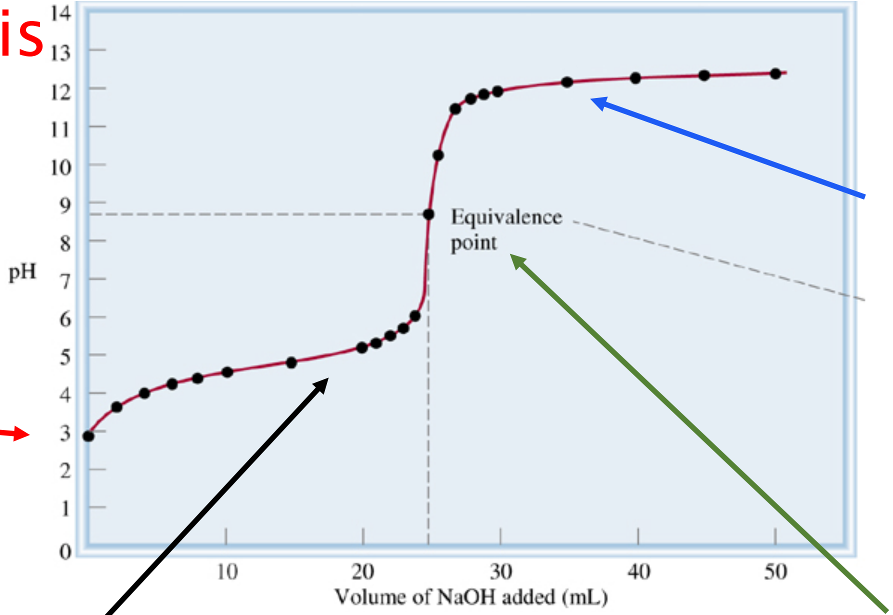
(c) When 25.1mL acid has been added A: 3.7

Titration of a Weak Acid with a Strong Base

$$NaOH(aq) + CH_3COOH(aq) \rightleftharpoons CH_3COONa(aq) + H_2O(l)$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

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



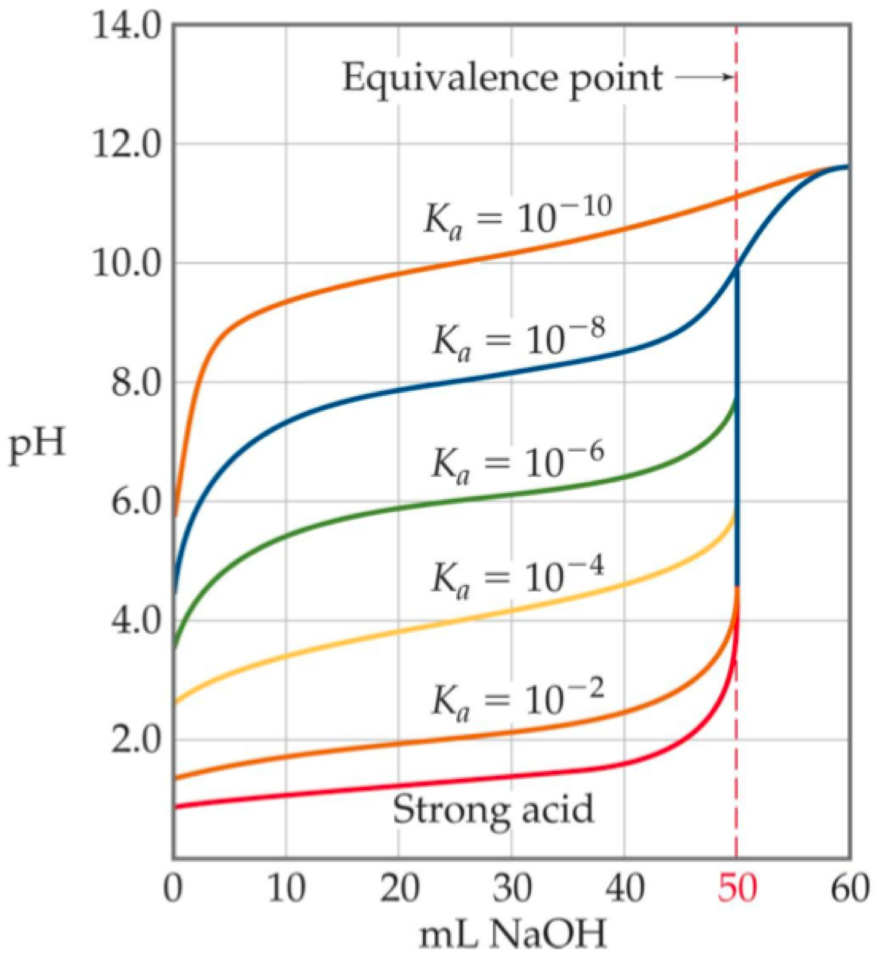
After the equivalence pt., pH depends on concentration of excess strong base

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: CH_3COONa

Weak Acid/Strong Base Calculations
Things to Keep in Mind

1. **Acid/Base titration always gives a salt & water**
   - $HA + OH \rightleftharpoons A^{-} + H_2O$
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 $[H_3O^+]$ (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**

Weak Acid/Strong Base Calculations
Things to Keep in Mind con’t

4. **At equivalence point: <u>all initial acid & added base are neutralized</u> - 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 OH^-
   - $A^- + H_2O \rightleftharpoons HA + OH^-$
   - Since the solution is basic – need to use $\mathbf{K_b}$ & equilibrium to get the OH^- concentration
   - Moles acid neutralized = initial moles acid = moles salt formed.
   - Use total volume to get concentration.
5. **After equivalence point: <u>only excess strong base matters</u>**
   - pH depends on moles of excess strong base & total volume. Strong so NO EQUILIBRIUM!

Weak Acid/Strong Base Calculations

35.0mL of 0.150M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) was titrated with 0.150M NaOH. Determine the pH:

a.) At the start of the titration A: 2.78

b.) When 20.0mL of 0.150M NaOH has been added A:4.87

c.) At the equivalence point A: 8.81

d.) When 50.0mL of 0.150M NaOH has been added A: 12.42

Weak Acid/Strong Base Calculations

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Weak Acid/Strong Base Calculations

35.0mL of 0.150M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) was titrated with 0.150M NaOH. Determine the pH:

d.) When 50.0mL of 0.150M NaOH has been added A: 12.42

Weak Acid/Strong Base Calculations

When 100.0 mL of 0.10 *M* HNO_2 are titrated with a 0.10 *M* NaOH solution, what is the pH at the equivalence point ? K_a $HNO_2 = 4.5 \times 10^{-4}$

	$HNO_2\,(aq)$	+	$OH^-\,(aq)$	$\longrightarrow$	$NO_2^-\,(aq)$	+	$H_2O\,(l)$
start (moles)	0.010		0.010				
end (moles)	0.0		0.0		0.010		

Use K_b

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

Final volume = 200 mL ⇨ $[NO_2^-] = \dfrac{0.010}{0.200} = 0.050\ M$

Hydrolysis of basic salt $NO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons \boxed{OH^-}\,(aq) + HNO_2\,(aq)$

	$NO_2^-\,(aq)$	$H_2O\,(l)$	$OH^-\,(aq)$	$HNO_2\,(aq)$
Initial (*M*)	0.050		0.00	0.00
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium (*M*)	$0.050 - \overset{0}{\cancel{x}}$		x	x

$$K_b = \frac{[OH^-][HNO_2]}{[NO_2^-]} = \frac{x^2}{0.050} = 2.2 \times 10^{-11}$$

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

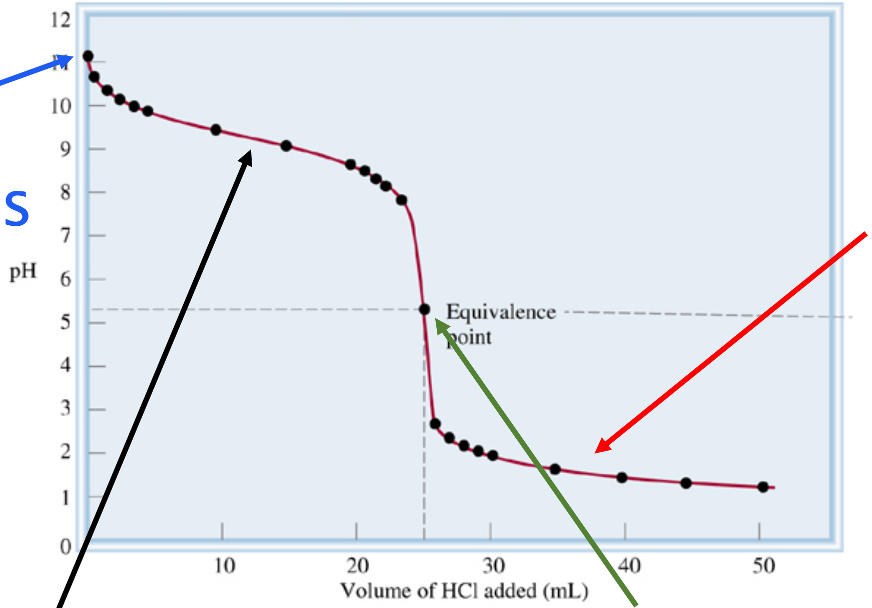
pOH = 5.98

pH = 14 – 5.98 = 8.02

Titration of a Weak Base with a Strong Acid

$$HCl(aq) + NH_3\ (aq) \rightleftharpoons NH_4^+\ (aq) + Cl^-(aq)$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3\ (aq) + H_3O^+(aq)$$



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

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

Before the equivalence pt., the solution contains the weak base & its conjugate 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 NH_3 ($K_b = 1.8x10^{-5}$) 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

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

I	0.03M	0	0
C	−x	+x	+x
E	$0.03\cancel{-x}$	x	x

$$K_b = \frac{x^2}{0.0300} = 1.8\text{x}10^{-5}$$

$x^2 = 5.4x10^{-7}$

$x = 7.35x10^{-4} = [OH^-]$

$pOH = -\log(7.35x10^{-4}) = 3.13$

$pH = 14 - 3.13 =$ 10.87

Weak Base/Strong Acid Calculations

30.0mL of 0.0300M NH_3 ($K_b = 1.8x10^{-5}$) 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 NH_3 remains & how much NH_4^+ has been produced.

$NH_3\ (aq) + HCl\ (aq) \rightarrow H_2O(l) + Cl^-(aq) + NH_4^+(aq)$

$$0.0300\frac{mol}{L}NH_3\ x\ 0.0300L = 9.00x10^{-4}mol\ NH_3\ initial$$

$$0.0250\frac{mol}{L}x\ 0.0200L = 5.00x10^{-4}mol\ HCl\ added$$

$$5.00x10^{-4}mol\ HCl\ x\ \frac{1\ mol\ NH_3}{1\ mol\ HCl} = 5.00x10^{-4}mol\ NH_3\ neutralized$$

$$9.00x10^{-4}mol\ init. - 5.00x10^{-4}mol\ neut. = 4.00x10^{-4}mole\ NH_3\ remaining$$

$$5.00x10^{-4}mol\ HCl\ x\ \frac{1\ mol\ NH_4^+}{1\ mol\ HCl} = 5.00x10^{-4}mol\ NH_4^+\ produced$$

New volume: 0.0300L + 0.0200L = 0.0500L

$4.00x10^{-4}mol\ NH_3\ /\ 0.0500L = 8.00x10^{-3}M\ NH_3$

$5.00x10^{-4}\ mol\ NH_4^+\ /\ 0.0500L = 1.00x10^{-2}M\ NH_4^+$

$4.00\text{x}10^{-4}\text{mol } NH_3 \ / \ 0.0500\text{L} = 8.00\text{x}10^{-3}\text{M } NH_3$

$5.00\text{x}10^{-4} \text{ mol } NH_4^+ \ / \ 0.0500\text{L} = 1.00\text{x}10^{-2}\text{M } NH_4^+$

New equilibrium with NH_3 & NH_4^+ present:

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

I	0.008M	0.01M	0
C	$-x$	$+x$	$+x$
E	$0.008\cancel{-x}$	$0.01\cancel{+x}$	x

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

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

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

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

$$pH = 14 - 4.84164 = 9.1594 \rightarrow 9.16$$

Could also use the NH_3 & NH_4^+ molarities listed above in the H–H eq – but for H–H would need to use pKa and make sure to have $[A^-]$ and $[HA]$ in the correct locations

Weak Base/Strong Acid Calculations

30.0mL of 0.0300M NH_3 (K_b = 1.8x10^{-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 NH_3 became NH_4^+)
- pH depends on equilibrium of CONJUGATE acid

Conjugate acid of NH_3 is NH_4^+.

Moles NH_4^+ = moles NH_3 neutralized: $0.0300\frac{mol}{L}x\ 0.0300L = 9.00x10^{-4}mol$

Volume acid needed for neutralization = volume containing 9.00x10^{-4} mol HCl: $9.00x10^{-4}mol\ HCl\ x\ \frac{1L\ HCl}{0.0250mol\ HCl} = 0.036L\ HCl\ solution$

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

Concentration of NH_4^+ = 9.00x10^{-4}mol/0.0660L = 0.013636M

Equilibrium is:

NH_4+(aq) + H_2O(l) $\rightleftharpoons$ NH_3(aq) + H_3O^+(aq)

$$NH_4+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

I	0.013536	0	0
C	$-x$	$+x$	$+x$
E	$0.013636\cancel{-x}$	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.00x10^{-14}}{1.8x10^{-5}} = 5.56x10^{-10}$$

$$K_a = \frac{x^2}{0.013636} = 5.56x10^{-10}$$

$$x^2 = 7.576x10^{-12}$$

$$x = 2.752x10^{-6} = [H_3O^+]$$

$$pH = -\log (2.752x10^{-6}) = 5.5603 \rightarrow 5.56$$

Weak Base/Strong Acid Calculations

30.0mL of 0.0300M NH_3 (K_b = 1.8x10^{-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: $NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

Moles HCl added: $\frac{0.0250\, mol\, HCl}{1\, L}\, x\, 0.0370L = 9.25x10^{-4} mol\, HCl$

Moles HCl needed for neutralization:

$$9.00x10^{-4} mol\, NH_3 x \frac{1 mol\, HCl}{1 mol\, NH_3} = 9.00x10^{-4} mol\, HCl$$

Moles HCl not used in neutralization:

9.25x10^{-4}mol added – 9.00x10^{-4}mol used = 2.5x10^{-5}mol HCl left over

Total volume = 0.0300L + 0.0370L = 0.0670L

Concentration of HCl = 2.5x10^{-5}mol/0.0670L = 3.73x10^{-4}M

Strong acid so [H_3O^+] = 3.73x10^{-4}M   pH = –log(3.73x10^{-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 CH_3COOH with 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 pH > 7.0

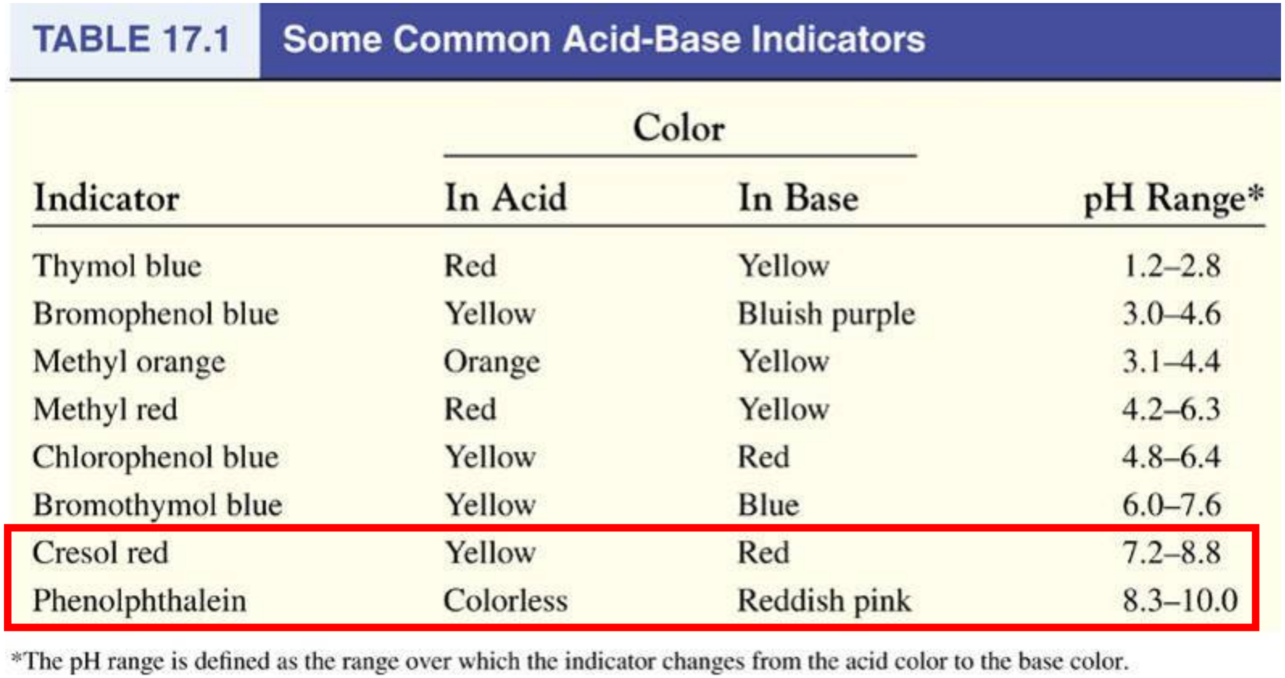
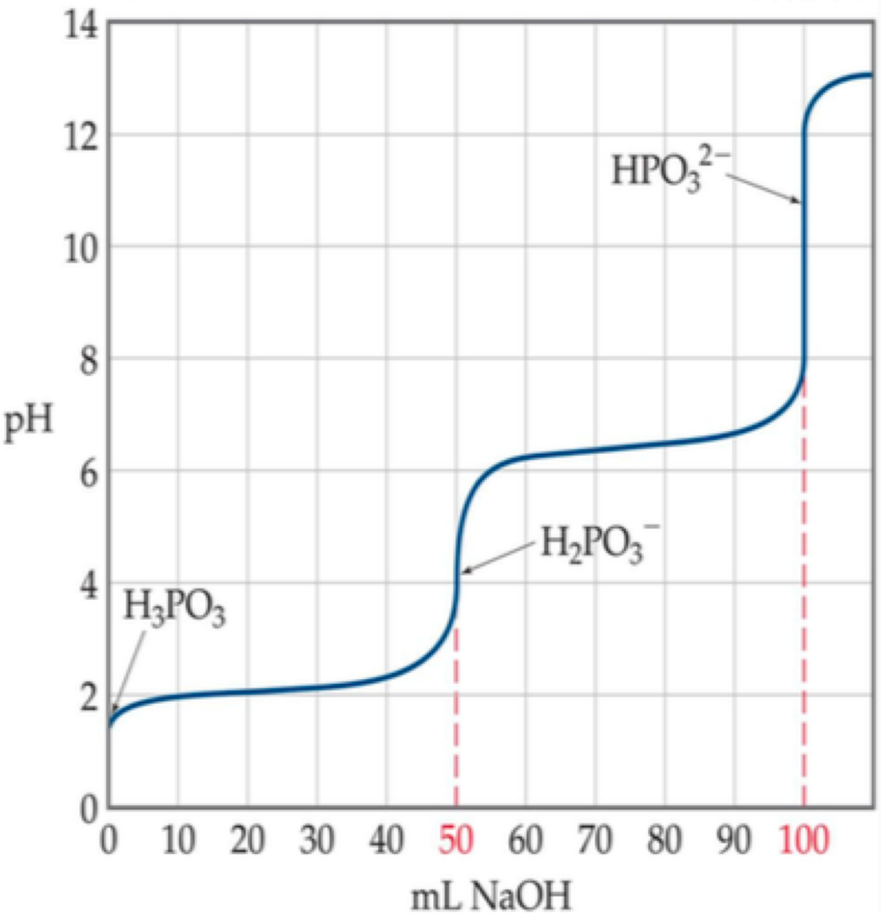


TABLE 17.1 Some Common Acid-Base Indicators

Indicator	Color In Acid	 In Base	pH Range*
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 (NH_4^+)
Hydrogen (H^+)
Alkali metals (group 1A)
Nitrate (NO_3^-)
Perchlorate (ClO_4^-)
Acetate (CH_3COO^-)

Always soluble

Usually Soluble

Exceptions (insoluble if with):

Halides (F^-,Cl^-,Br^-,& I^-)
Pb^{2+}, Hg_2^{2+}, Ag^+

Sulfate (SO_4^{2-})
Pb^{2+}, Hg_2^{2+}, Ag^+, Ba^{2+}, Ca^{2+}, Sr^{2+}

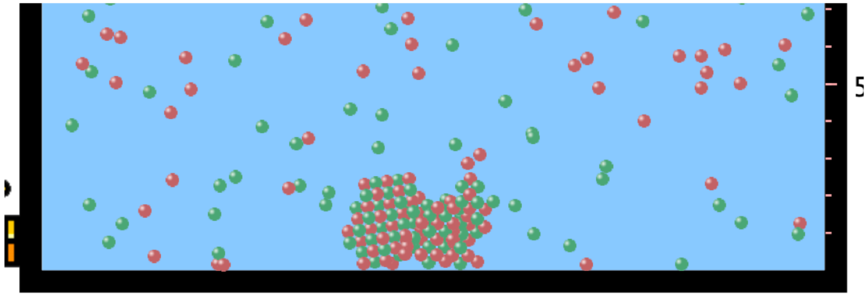
Sparingly Soluble (Insoluble)

Sulfide (S^{2-})
Hydroxide (OH^-)
Oxide (O^{2-})
Carbonate (CO_3^{2-})
Phosphate (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

$$PbCl_2\ (s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$$

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

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

- Note that the $PbCl_2(s)$ 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 [$Al(OH)_3$]	1.8×10^{-33}	Lead(II) chromate ($PbCrO_4$)	2.0×10^{-14}
Barium carbonate ($BaCO_3$)	8.1×10^{-9}	Lead(II) fluoride (PbF_2)	4.1×10^{-8}
Barium fluoride (BaF_2)	1.7×10^{-6}	Lead(II) iodide (PbI_2)	1.4×10^{-8}
Barium sulfate ($BaSO_4$)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi_2S_3)	1.6×10^{-72}	Magnesium carbonate ($MgCO_3$)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [$Mg(OH)_2$]	1.2×10^{-11}
Calcium carbonate ($CaCO_3$)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF_2)	4.0×10^{-11}	Mercury(I) chloride (Hg_2Cl_2)	3.5×10^{-18}
Calcium hydroxide [$Ca(OH)_2$]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [$Ca_3(PO_4)_2$]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [$Cr(OH)_3$]	3.0×10^{-29}	Silver bromide ($AgBr$)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate (Ag_2CO_3)	8.1×10^{-12}
Copper(I) bromide ($CuBr$)	4.2×10^{-8}	Silver chloride ($AgCl$)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [$Cu(OH)_2$]	2.2×10^{-20}	Silver sulfate (Ag_2SO_4)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag_2S)	6.0×10^{-51}
Iron(II) hydroxide [$Fe(OH)_2$]	1.6×10^{-14}	Strontium carbonate ($SrCO_3$)	1.6×10^{-9}
Iron(III) hydroxide [$Fe(OH)_3$]	1.1×10^{-36}	Strontium sulfate ($SrSO_4$)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate ($PbCO_3$)	3.3×10^{-14}	Zinc hydroxide [$Zn(OH)_2$]	1.8×10^{-14}
Lead(II) chloride ($PbCl_2$)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

Calculating K_{sp} from Solubility

The molar solubility of CaF_2 at 35˚C is $1.24\text{x}10^{-3}$ M.

(a) What is the solubility of CaF_2 in g/L? A: 0.968g/L

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

Calculating Solubility from K_{sp}

The K_{sp} for LaF_3 is 2.0×10^{-19}.

(a) What is the molar solubility of LaF_3 in water? A: 9.3×10^{-6}M

(b) What is the solubility in g/L? A: 1.8×10^{-3}g/L

Comparing Molar Solubilities vs. K_{sp}

Compound	**K_{sp}**	**Molar Solubility**
$BaSO_4$	$1.1x10^{-20}$	$1.0x10^{-5}M$
$Mg_3(AsO_4)_2$	$2.0x10^{-20}$	$5.0x10^{-5}M$

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 (OH^-) or hydronium ions (H_3O^+)

Complexation

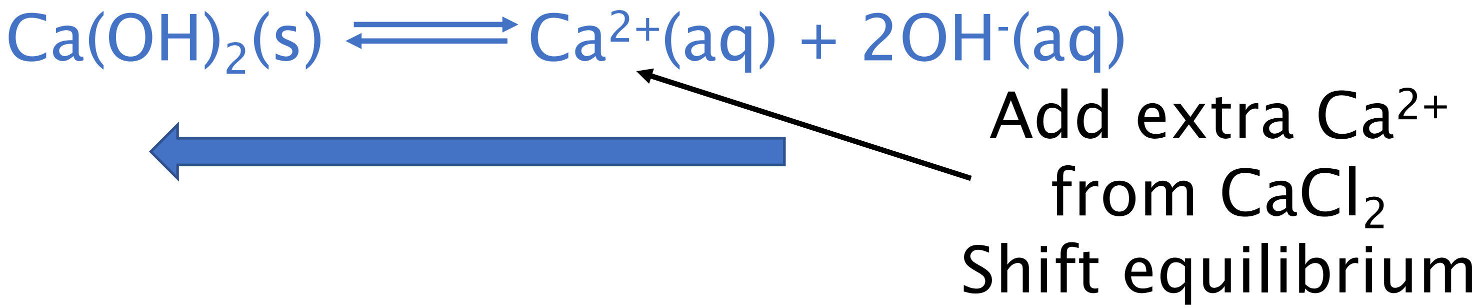
- Formation of coordinate bonds with solvent or other molecules present in solution

Common-Ion Effect

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

Equilibrium process – presence of ions shifts process back to reactants.

Ex: A solution is made with 1.0M $CaCl_2$ and 2.0M $Ca(OH)_2$



$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

Add extra Ca^{2+}
from $CaCl_2$
Shift equilibrium

Will affect pH if solution is acidic or basic - in this case shift toward reactants decreases concentration of OH^- in solution.

Common-Ion Calculations

1. Calculate the pH of a solution containing 0.085M nitrous acid (HNO_2; $K_a = 4.5 \times 10^{-4}$) and 0.10M potassium nitrite (KNO_2).

A: pH = 3.42

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

a.) water A: 3.4×10^{-5}M

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

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

A: 85,000 times more soluble in water

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

More than 700X less soluble than in water

Effect of pH

If the Compound Contains a(n):

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

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

In acidic solution: $OH^-(aq) + H_3O^+(aq) \rightleftharpoons 2H_2O(l)$

OH^- removed from solution, dissolution equilibrium shifts toward more dissolved product

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

$$C_7H_7OCOOH(s) \rightleftharpoons C_7H_7OCOO^-(aq) + H_3O^+(aq)$$

In basic solution: $OH^-(aq) + H_3O^+(aq) \rightleftharpoons 2H_2O(l)$

H_3O^+ removed from solution, dissolution equilibrium shifts toward more dissolved product

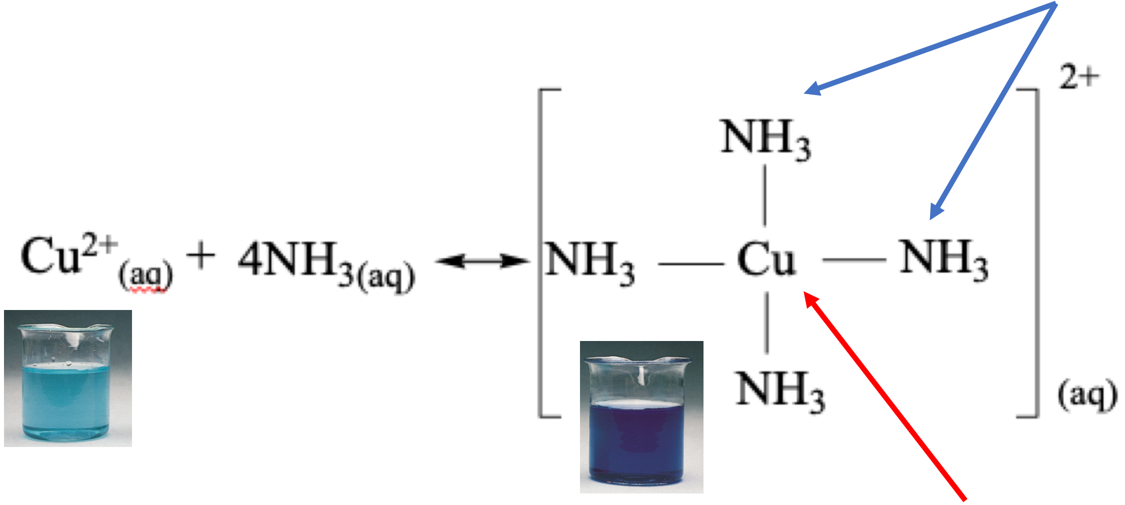
Effect of pH Calculations

Calculate the solubility of $Mg(OH)_2$ (one of the ingredients in the antacid Maalox) in grams per liter when buffered at pH: (a) 12.50; (b) 7.00 A: a.) 7.01×10^{-7} g/L; b.) 7.00×10^{4} g/L

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

Complex Ion Formation

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



$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \longleftrightarrow \left[Cu(NH_3)_4 \right]^{2+}_{(aq)}$$

$$K_{eq} = K_f = \frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4}$$

The metal center (Cu) is a Lewis Acid that accepts electron pairs from the ligands (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_f.

K_f = formation constant

Common Complex Ion Ligands: NH_3, CN^-, OH^-, Br^-, I^-

K_f Values for Selected Complex Ions

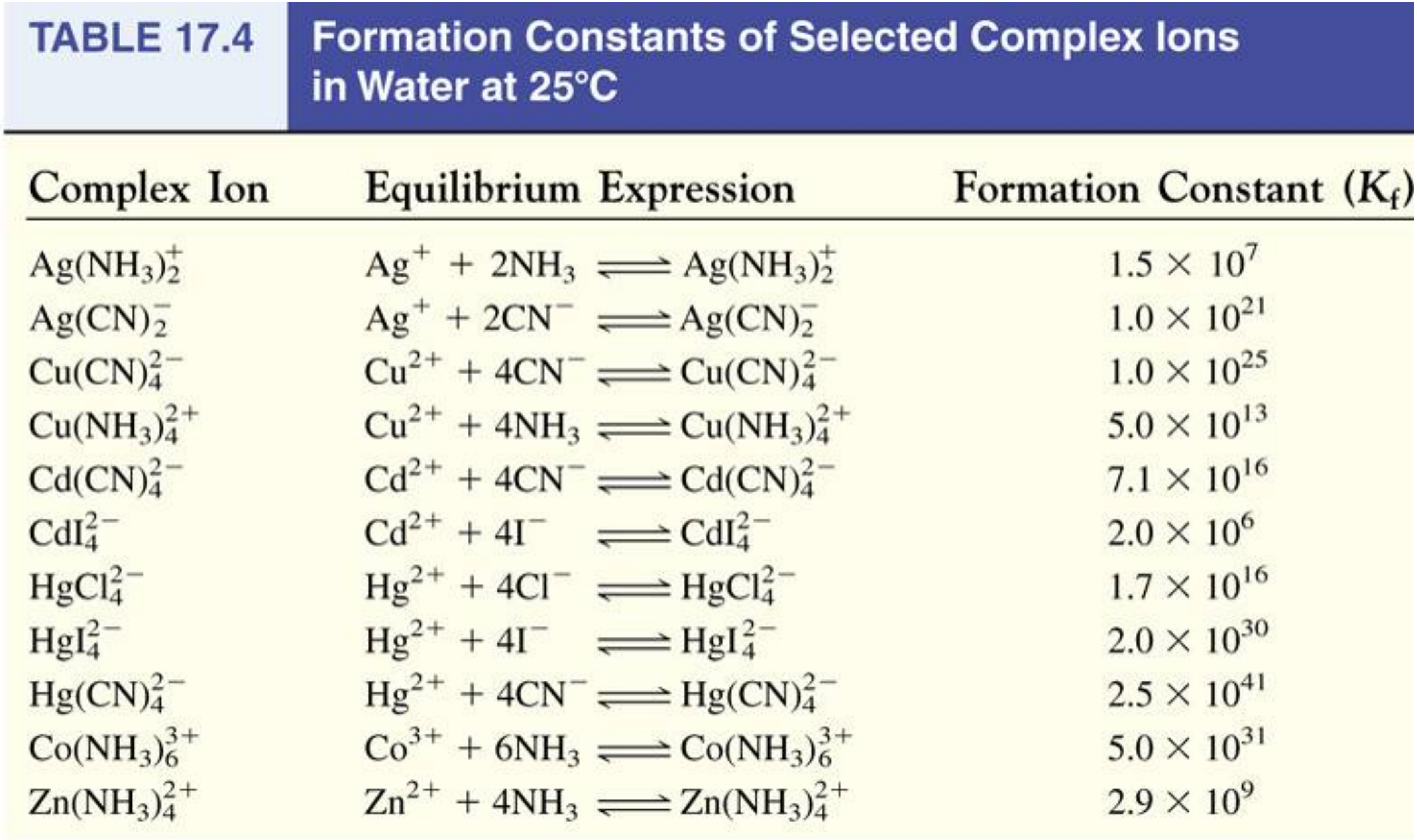


TABLE 17.4 Formation Constants of Selected Complex Ions in Water at 25°C

Complex Ion	Equilibrium Expression	Formation Constant (K_f)
$Ag(NH_3)_2^+$	$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$	1.5×10^7
$Ag(CN)_2^-$	$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$	1.0×10^{21}
$Cu(CN)_4^{2-}$	$Cu^{2+} + 4CN^- \rightleftharpoons Cu(CN)_4^{2-}$	1.0×10^{25}
$Cu(NH_3)_4^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$	5.0×10^{13}
$Cd(CN)_4^{2-}$	$Cd^{2+} + 4CN^- \rightleftharpoons Cd(CN)_4^{2-}$	7.1×10^{16}
CdI_4^{2-}	$Cd^{2+} + 4I^- \rightleftharpoons CdI_4^{2-}$	2.0×10^6
$HgCl_4^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons HgCl_4^{2-}$	1.7×10^{16}
HgI_4^{2-}	$Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$	2.0×10^{30}
$Hg(CN)_4^{2-}$	$Hg^{2+} + 4CN^- \rightleftharpoons Hg(CN)_4^{2-}$	2.5×10^{41}
$Co(NH_3)_6^{3+}$	$Co^{3+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{3+}$	5.0×10^{31}
$Zn(NH_3)_4^{2+}$	$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$	2.9×10^9

Complex Ion Formation & Solubility

Formation of a Complex Ion can increase solubility

$$\begin{array}{rcll}
\mathrm{AgCl}(s) & \rightleftharpoons & \cancel{\mathrm{Ag}^{+}}(aq) + \mathrm{Cl}^{-}(aq) & K_{sp} \\
\cancel{\mathrm{Ag}^{+}}(aq) + 2\mathrm{NH}_3(aq) & \rightleftharpoons & \mathrm{Ag(NH_3)_2}^{+}(aq) & K_f \\
\hline
\mathrm{AgCl}(s) + 2\mathrm{NH}_3(aq) & \rightleftharpoons & \mathrm{Ag(NH_3)_2}^{+}(aq) + \mathrm{Cl}^{-}(aq) & K_c
\end{array}$$

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

Complex Ion Formation & Solubility

1. Determine the equilibrium constant for the reaction:

$$AgI(s) + 2CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq) + I^-(aq)$$

K_{sp} AgI = 8.3×10^{-17}; K_f $Ag(CN)_2^-$ = 1×10^{21}

A: 8×10^4

Complex Ion Formation & Solubility

2. Calculate the molar solubility of zinc carbonate at 25˚C in (a) pure water and (b) 1.0M NH_3

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

A: (a) $3.7\text{x}10^{-6}$M
(b) $7.6\text{x}10^{-2}$M

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 → Precipitate will form
- $Q_c < K_{sp}$ Concentration low → all ions remain in solution
- $Q_c = K_{sp}$ At Equilibrium → saturated solution

Prediction of Precipitation

1.) If 2.00mL of 0.200M NaOH are added to 1.00L of 0.100M $CaCl_2$, will a precipitate form? A: no precipitate will form

Prediction of Precipitation

2.) How many grams of solid K_2SO_4 (174.3g/mol) would need to be added to 50.0mL of a 0.0010M $Ca(NO_3)_2$ 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 K_2SO_4 (174.3g/mol) would need to be added to 50.0mL of a 0.0010M $Ca(NO_3)_2$ solution in order to (a) start precipitation and (b) precipitate 99% of the calcium?

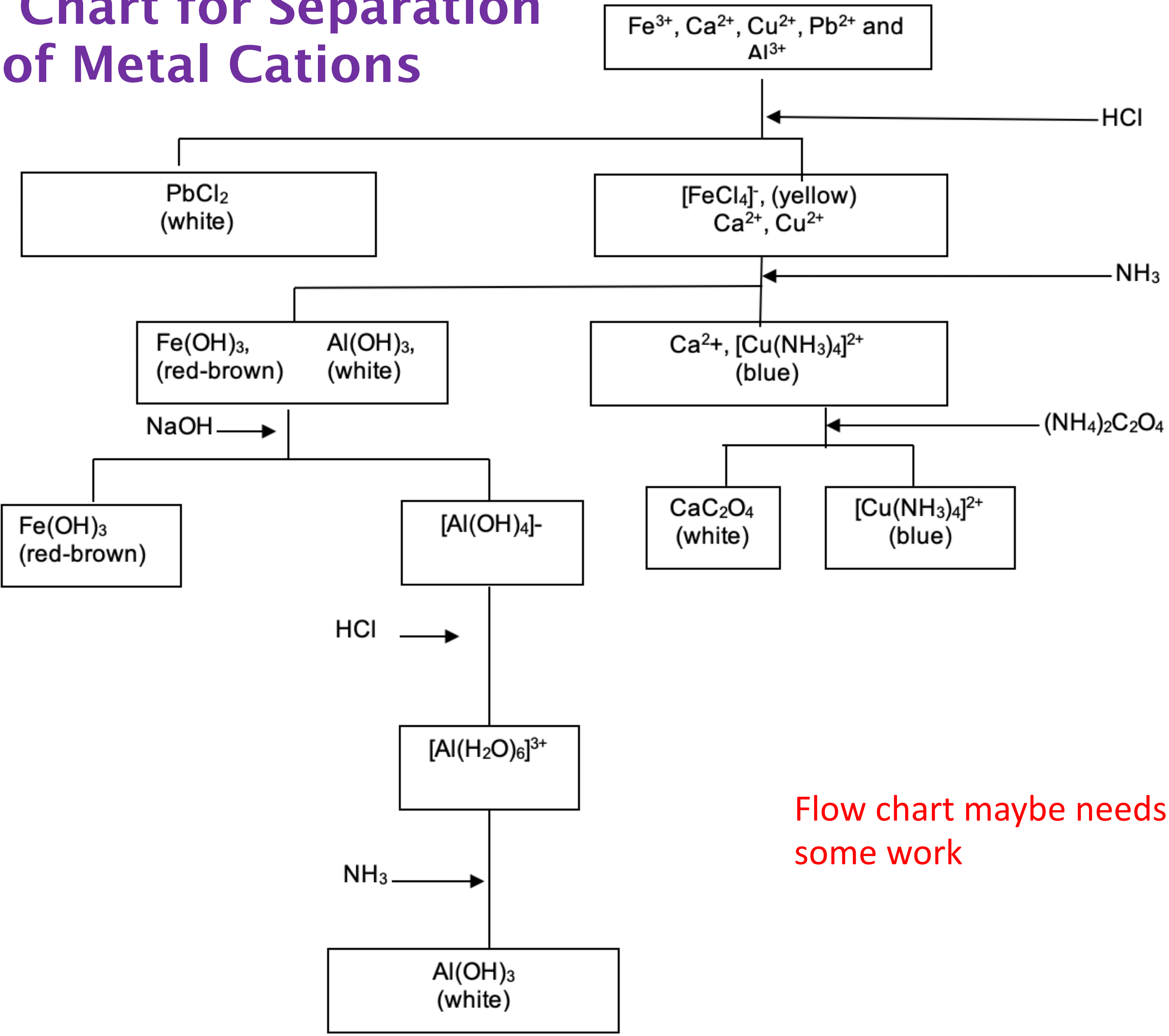
A: 7.9g

Qualitative Analysis of Metal Ions

Ways to determine which ions are present in solution

- **Selective 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



Fe^{3+}, Ca^{2+}, Cu^{2+}, Pb^{2+} and Al^{3+}

HCl

$PbCl_2$ (white)

$[FeCl_4]^-$, (yellow) Ca^{2+}, Cu^{2+}

NH_3

$Fe(OH)_3$, (red-brown) $Al(OH)_3$, (white)

Ca^{2+}, $[Cu(NH_3)_4]^{2+}$ (blue)

NaOH

$(NH_4)_2C_2O_4$

$Fe(OH)_3$ (red-brown)

$[Al(OH)_4]^-$

CaC_2O_4 (white)

$[Cu(NH_3)_4]^{2+}$ (blue)

HCl

$[Al(H_2O)_6]^{3+}$

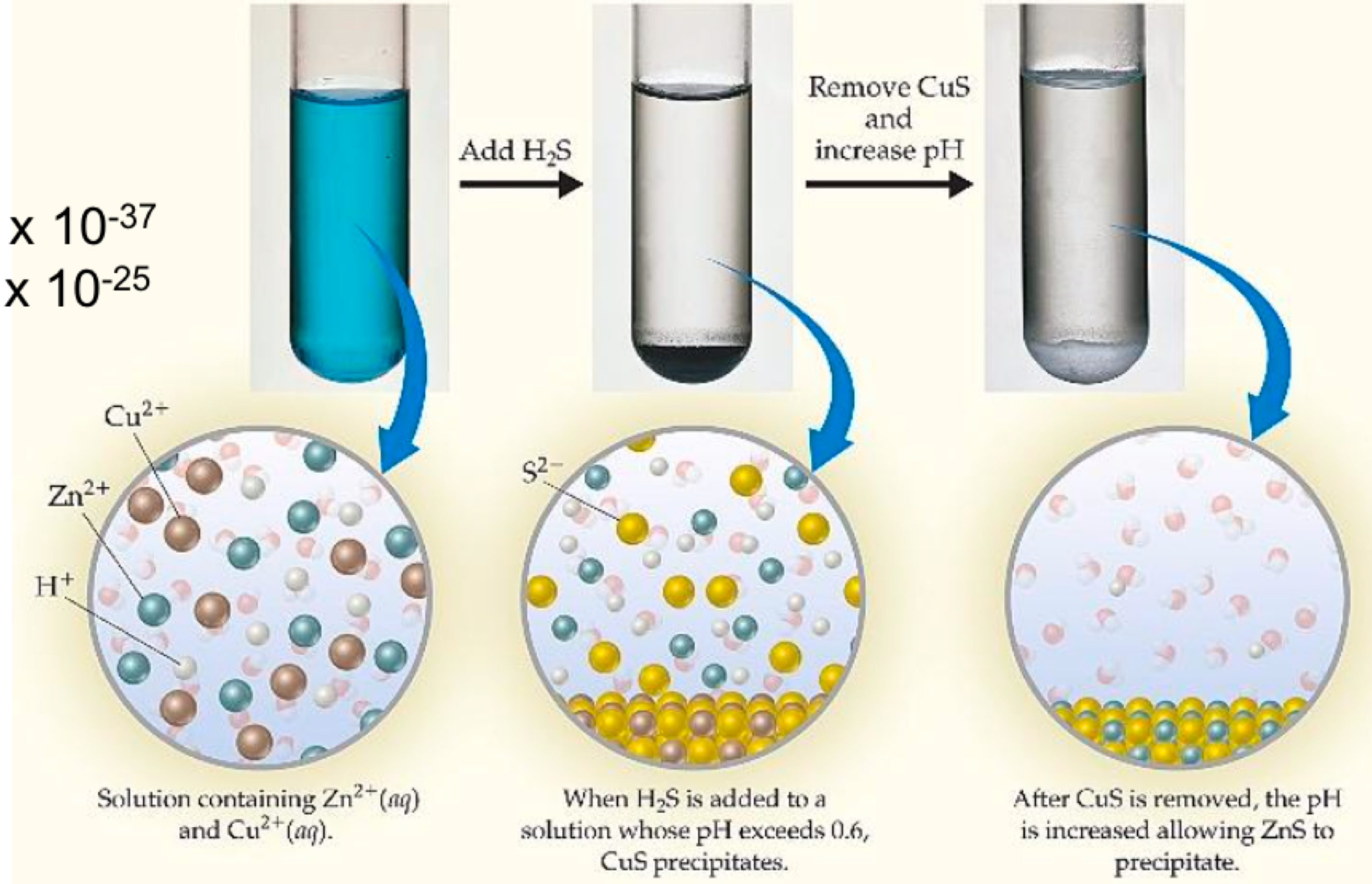
NH_3

$Al(OH)_3$ (white)

Flow chart maybe needs some work

Selective Precipitation

K_{sp}:
CuS = 6×10^{-37}
ZnS = 2×10^{-25}



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

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

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

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

H_2S is added
At low pH (but > 0.6)
CuS precipitates

CuS is removed then pH is increased causing ZnS to precipitate

Selective Precipitation

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

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

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

Selective Precipitation

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

A: Cu^{2+} needs 1.5×10^{-9}M
Mg^{2+} needs 1.9×10^{-5}M

(a) What concentration of OH^- is necessary to begin precipitation of each cation.

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$

0.020 X or 2X?

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

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

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

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

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

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

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

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

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