Chapter 15

Applications of Aqueous Equilibria

Contents

- Acid-base equilibria
  - Common ion effect
  - Buffered solutions
  - Titrations and pH curves
  - Acid base indicators
- Solubility equilibria
- Complex equilibria

15.1 Solutions of acids and bases containing a common ion

- What happens when a salt with the anion of a weak acid is added to that acid?
- Adding of NaF salt to a solution of HF ($K_a = 7.2 \times 10^{-4}$)
- $NaF(s) \longrightarrow Na^+(aq) + F^-(aq)$

  $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

  $\longleftarrow$

- It reverses the dissociation of the acid.
- It Lowers the percent dissociation of the acid.

- The same principle applies to salts with the cation of a weak base.
- Adding NH4Cl to a solution of NH_3
- $NH_4Cl(s) \longrightarrow NH_4^+(aq) + Cl^-(aq)$

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

$\longleftarrow$

- When NH_4^+ is added the equilibrium will shift to this direction

- $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

Adding NaCl(aq) shifts equilibrium position to left

- The common ion effect is also important in solutions of polyprotic acids
- The production of protons by the first step would inhibit the succeeding dissociation steps that are expected to produce protons

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$

$HCO3^- \rightleftharpoons CO_3^{2-} + H^+$

Calculations involving acidic solutions containing common ions

- Calculate $[H^+]$ and the percent dissociation of HF in a solution containing 1.0M HF ($K_a = 7.2 \times 10^{-4}$) and 1.0M NaF.

	HF	$\rightleftharpoons$	$H^+(aq)$	$+$	$F^-(aq)$
Initial	1.0M		0		1.0M
Change	-x		+x		+x
Equilib.	1.0-x		x		1.0 +x

$$1.0 - x \approx 1.0;\ 1.0 + x \approx 1.0$$

$X = [H^+] = 7.2 \times 10^{-4}$ M

% dissociation = $(7.2 \times 10^{-4} / 1.0)\ X100 = 0.072\%$

% dissociation of 1.0 M HF?

$HF \rightleftharpoons H^+(aq) + F^-(aq)$

$[H^+] = 2.7X10^{-3}$ M

% dissociation = $(2.7X10^{-2} /1.0)$ X100

= 2.7%

Thus, % dissociation has decreased significantly in the presence of a common ion (0.0072% with 1.0 M NaF)

15.2 Buffered solutions

- A solution that resists a change in pH when either OH^- or H^+ ions are added
- Either a weak acid and its salt or a weak base and its salt.
- Weak acid and its conjugate base or a weak base and its conjugate acid
- We can make a buffer of any pH by varying the concentrations of the acid and its salt.

What is the pH of a solution containing 0.30 *M* HCOOH and 0.52 *M* HCOONa?

Mixture of weak acid and conjugate base!

$$HCOOH\,(aq) \rightleftharpoons H^+\,(aq) + HCOO^-\,(aq)$$

Initial (*M*)	0.30	0.00	0.52
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.30 - x$	x	$0.52 + x$

K_a for HCOOH = 1.8×10^{-4}

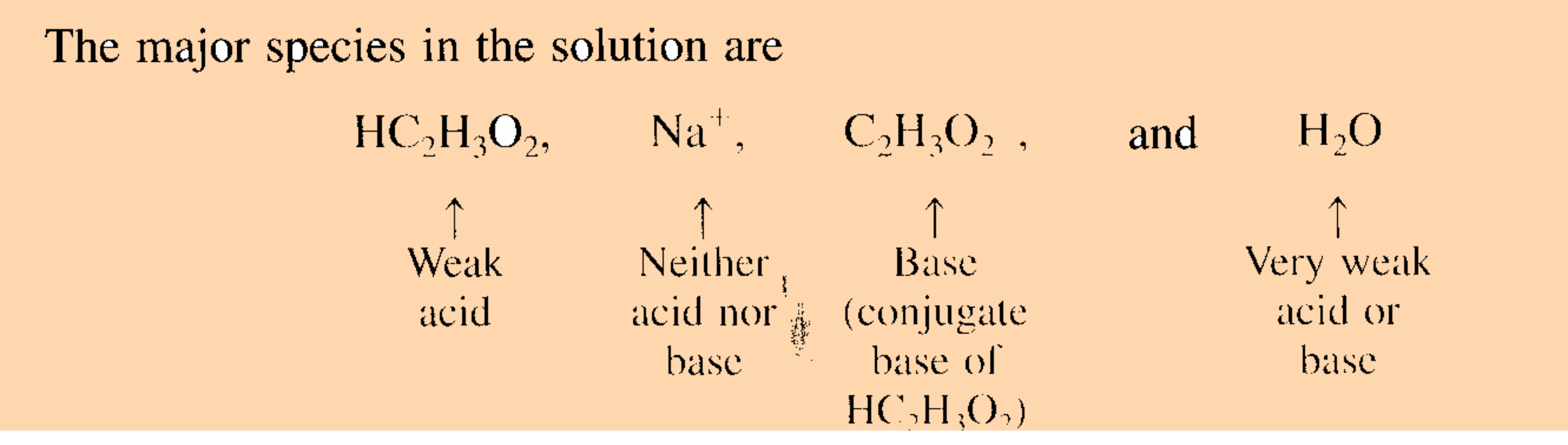
$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$x = 1.038 \times 10^{-4}$

pH = 3.98

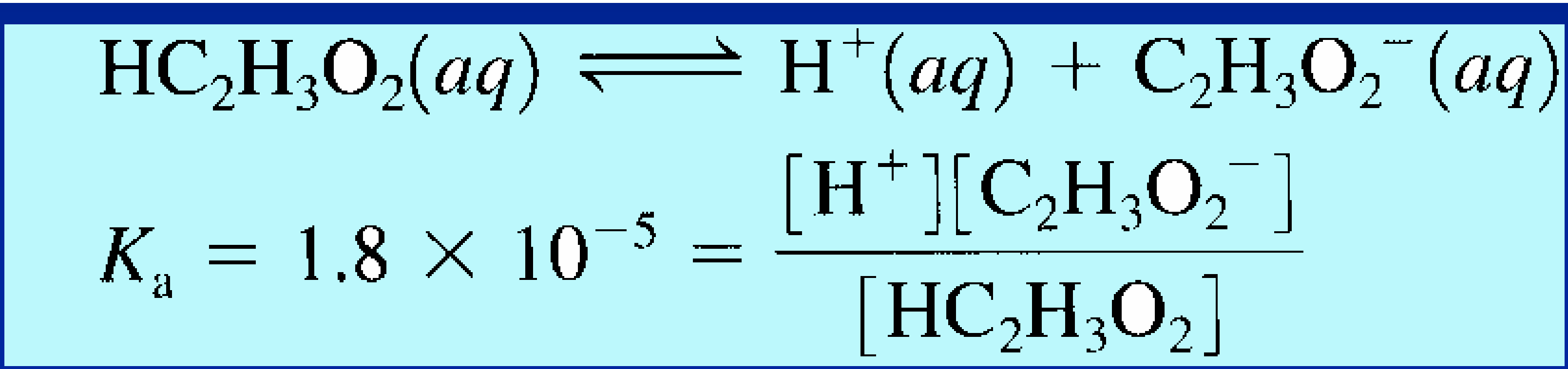
pH of a buffered solution

- **Calculate the pH of a solution that is 0.50 M HAc and 0.5 M NaAc (Ka = 1.8 x 10^{-5})**



The major species in the solution are

$HC_2H_3O_2$,	Na^+,	$C_2H_3O_2^-$,	and	H_2O
↑	↑	↑		↑
Weak acid	Neither acid nor base	Base (conjugate base of $HC_2H_3O_2$)		Very weak acid or base



$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Initial Concentration (mol/L)

$[HC_2H_3O_2]_0 = 0.50$
$[C_2H_3O_2^-]_0 = 0.50$
$[H^+]_0 \approx 0$

$$\xrightarrow[\text{dissociates to reach equilibrium}]{x \text{ mol/L of } HC_2H_3O_2}$$

Equilibrium Concentration (mol/L)

$[HC_2H_3O_2] = 0.50 - x$
$[C_2H_3O_2^-] = 0.50 + x$
$[H^+] = x$

The corresponding ICE table is:

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$C_2H_3O_2^-(aq)$
Initial:	0.50		≈ 0		0.50
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.50 - x$		x		$0.50 + x$

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(0.50 + x)}{0.50 - x} \approx \frac{(x)(0.50)}{0.50}$$

and

$$x \approx 1.8 \times 10^{-5}$$

The approximations are valid (by the 5% rule), so

$$[H^+] = x = 1.8 \times 10^{-5}\,M \qquad \text{and} \qquad \text{pH} = 4.74$$

Calculating pH after adding a strong acid or base

- Do the stoichiometry first.
- A strong base will take protons from the weak acid reducing $[HA]_0$
- A strong acid will add its proton to the anion of the salt reducing $[A^-]_0$
- Then do the equilibrium problem.

Calculating pH changes in buffered solutions

- Calculate the change in pH that occurs when 0.010 mole solid NaOH is added to 1.0 liter of a buffered solution of 0.50M HCH_3CO_2 and 0.50M $NaC_2H_3O_2$. Compare this pH change with that occurs when 0.010 mol solid NaOH is added to 1.0 L of water.
- The major species in the solution before any reaction takes place are:

$HC_2H_3O_2$, Na^+, $C_2H_3O_2$, OH, and H_2O.

- The best source of protons is HCH_3CO_2; these protons will react with OH^- from NaOH

$$OH^- + HC_2H_3O_2 \longrightarrow H_2O + C_2H_3O_2^-$$

1. *The stoichiometry problem.* The stoichiometry for the reaction is shown below.

$$HC_2H_3O_2 + OH^- \longrightarrow C_2H_3O_2^- + H_2O$$

	$HC_2H_3O_2$	OH^-	$C_2H_3O_2^-$	H_2O
Before reaction:	1.0 L × 0.50 *M* = 0.50 mol	0.010 mol	1.0 L × 0.50 *M* = 0.50 mol	
After reaction:	0.50 − 0.010 = 0.49 mol	0.010 − 0.010 = 0 mol	0.50 + 0.010 = 0.51 mol	

Note that 0.010 mol $HC_2H_3O_2$ has been converted to 0.010 mol $C_2H_3O_2^-$ by the added OH^-.

2. *The equilibrium problem.* After the reaction between OH^- and $HC_2H_3O_2$ is complete, the major species in solution are

$$HC_2H_3O_2,\quad Na^+,\quad C_2H_3O_2\ ,\quad \text{and}\quad H_2O$$

The dominant equilibrium involves the dissociation of acetic acid.

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$C_2H_3O_2^-(a$
Initial:	0.49		0		0.51
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.49 - x$		x		$0.51 + x$

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(0.51 + x)}{0.49 - x} \approx \frac{(x)(0.51)}{0.49}$$

$$x \approx 1.7 \times 10^{-5}$$

The approximations are valid (by the 5% rule), so

$$[H^+] = x = 1.7 \times 10^{-5} \quad \text{and} \quad pH = 4.76$$

The change in pH produced by the addition of 0.01 mol OH⁻ to this buffere
solution is then

$$\underset{\substack{\uparrow \\ \text{New solution}}}{4.76} - \underset{\substack{\uparrow \\ \text{Original solution}}}{4.74} = +0.02$$

ed by 0.02 pH units.

Now compare this with what happens when 0.01 mol solid NaOH is added t
1.0 L water to give 0.01 *M* NaOH. In this case $[OH^-] = 0.01\ M$ and

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}$$

$$pH = 12.00$$

Thus the change in pH is

$$\underset{\text{New solution}}{\underset{\uparrow}{12.00}} \quad - \quad \underset{\text{Pure water}}{\underset{\uparrow}{7.00}} \quad = +5.00$$

The increase is 5.00 pH units. Note how well the buffered solution resists a change in pH as compared with pure water.

Buffered Solution Characteristics

- Buffers contain relatively large amounts of weak acid and corresponding conjugate base.
- Added H^+ reacts to completion with the weak base.
- Added OH^- reacts to completion with the weak acid.
- The pH is determined by the ratio of the concentrations of the weak acid and its conjugate base.

Buffering: How does it work?

- Suppose a buffered solution contains relatively large quantities of an acid HA and its conjugate base A^-.
- When hydroxide ions are added to the solution, since the weak acid represents the best source of protons, the following, reaction occurs:

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

- The net result is that OH^- ions are not allowed to accumulate but are replaced by A^- ions.

How does pH of the buffered solution stay stable?

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

pH is determined
By this ratio

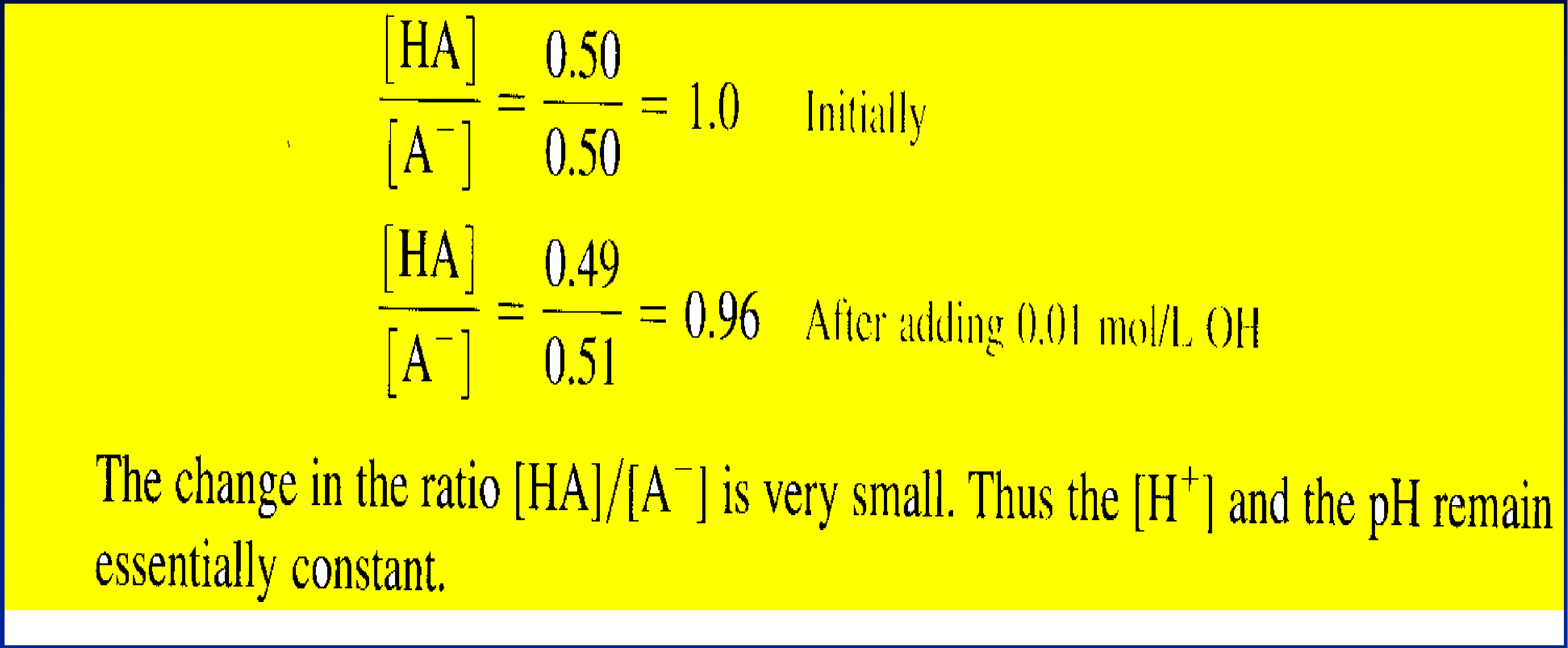
$$\text{So, } [\text{H}^+] = \text{ka}\,\frac{[\text{HA}]}{[\text{A}^-]}$$

pH is determined
By this ratio

$$\text{So, } [H^+] = ka \frac{[HA]}{[A^-]}$$

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

- **When OH^- ions are added, HA is converted to A^-, and the ratio $[HA]/[A^-]$ decreases.**
- **However, if *the amounts of HA and A^- originally present are very large compared with the amount of OH^- added,* the change in the [HA]/[A$^-$l ratio will be small.**



$$\frac{[\mathrm{HA}]}{[\mathrm{A}^-]} = \frac{0.50}{0.50} = 1.0 \quad \text{Initially}$$

$$\frac{[\mathrm{HA}]}{[\mathrm{A}^-]} = \frac{0.49}{0.51} = 0.96 \quad \text{After adding 0.01 mol/L OH}$$

The change in the ratio $[\mathrm{HA}]/[\mathrm{A}^-]$ is very small. Thus the $[\mathrm{H}^+]$ and the pH remain essentially constant.

General buffer equation: Henderson-Hasselbalch eq.

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

$$\text{So, } [\text{H}^+] = \text{ka}\,\frac{[\text{HA}]}{[\text{A}^-]}$$

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

$$pH = pKa - \log(\frac{[HA]}{[A^-]})$$

$$pH = pKa + \log(\frac{[A^-]}{[HA]})$$

$$pH = pKa + \log(\frac{[base]}{[acid]})$$

Using Henderson-Hasselbach equation to calculate pH of a buffered solution

Calculate the pH of the following mixtures:

- 0.75 M lactic acid ($HC_3H_5O_3$) and 0.25 M sodium lactate (Ka = 1.4 x 10^{-4})

$$\mathrm{pH} = \mathrm{pk_a} + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right)$$

$$\mathrm{pH} = \mathrm{pk_a} + \log\left(\frac{[\mathrm{base}]}{[\mathrm{acid}]}\right)$$

$$pH = -\log 1.4 \times 10^{-4} + \log\left(\frac{0.25}{0.75}\right)$$

pH = 3.38

Calculate the pH of the following mixture:

0.25 M NH_3 and 0.40 M NH_4Cl

($Kb = 1.8 \times 10^{-5}$)

$$\mathrm{pH} = \mathrm{pk_a} + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right)$$

$$\mathrm{pH} = \mathrm{pk_a} + \log\left(\frac{[\mathrm{base}]}{[\mathrm{acid}]}\right)$$

- NH_3 is the base; NH_4^+ is its conjugate acid

NH_3

- Ka (NH_4^+) = $\boxed{\frac{Kw}{Kb}}$

$$pH = -\log\frac{1X10^{-14}}{1.8X10^{-5}} + \log\left(\frac{0.25}{0.40}\right) = 9.05$$

Another solution

	NH_3	+	H_2O	$\rightleftharpoons$	NH_4^+	+	OH^-
Init	0.25				0.40		≈ 0
Δ	-x				+x		+x
Eq.	**0.25-x**				**0.40+x**		**x**

x<<0.25

$$k_b = 1.8X10^{-5} = \frac{[NH^{4^+}][OH^-]}{[NH_3]}$$

$$= \frac{(0.40 + x)(x)}{0.25 - x}$$

$$\approx \frac{(0.40)(x)}{0.25}$$

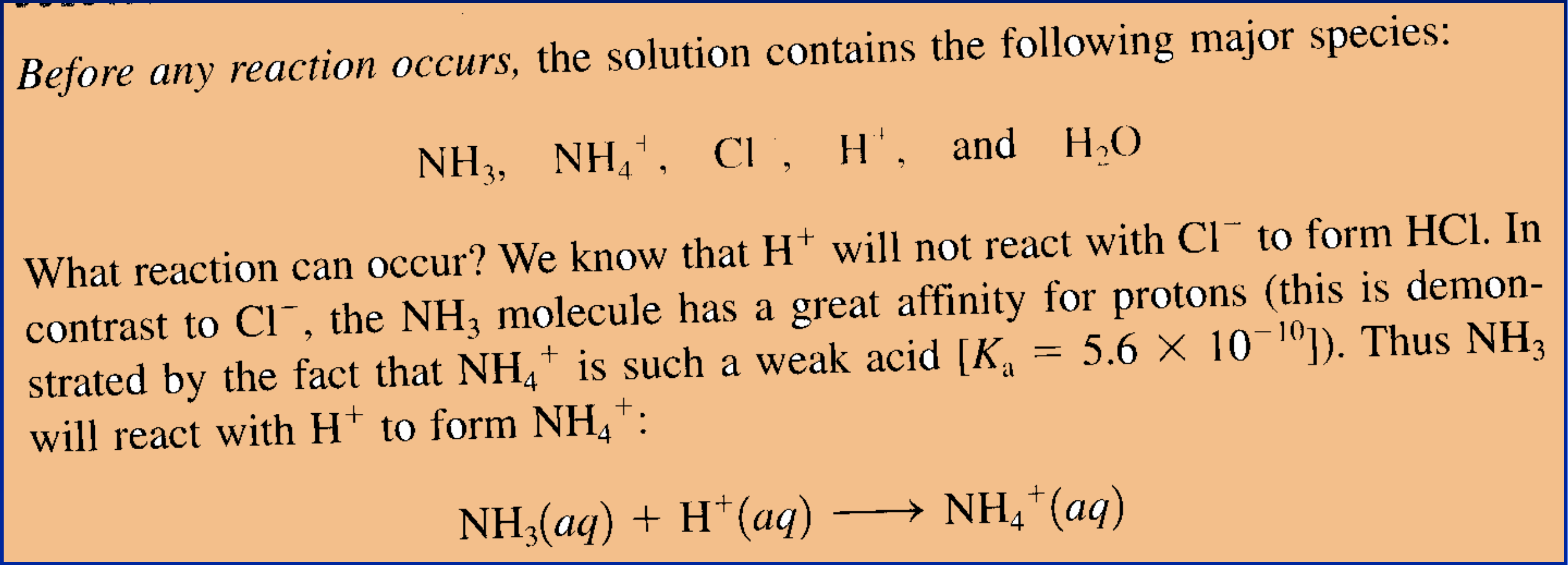
$X \approx 1.1X10^{-5}$

$OH- = x = 1.1X10^{-5}$

pOH = 4.95; pH = 9.05

Adding strong acid to a buffered solution

- Calculate the pH of the solution that results when 0.10 M gaseous HCl is added to 1.0 L of the 0.25 M NH_3 and 0.40 M NH_4Cl. (Kb = 1.8×10^{-5})

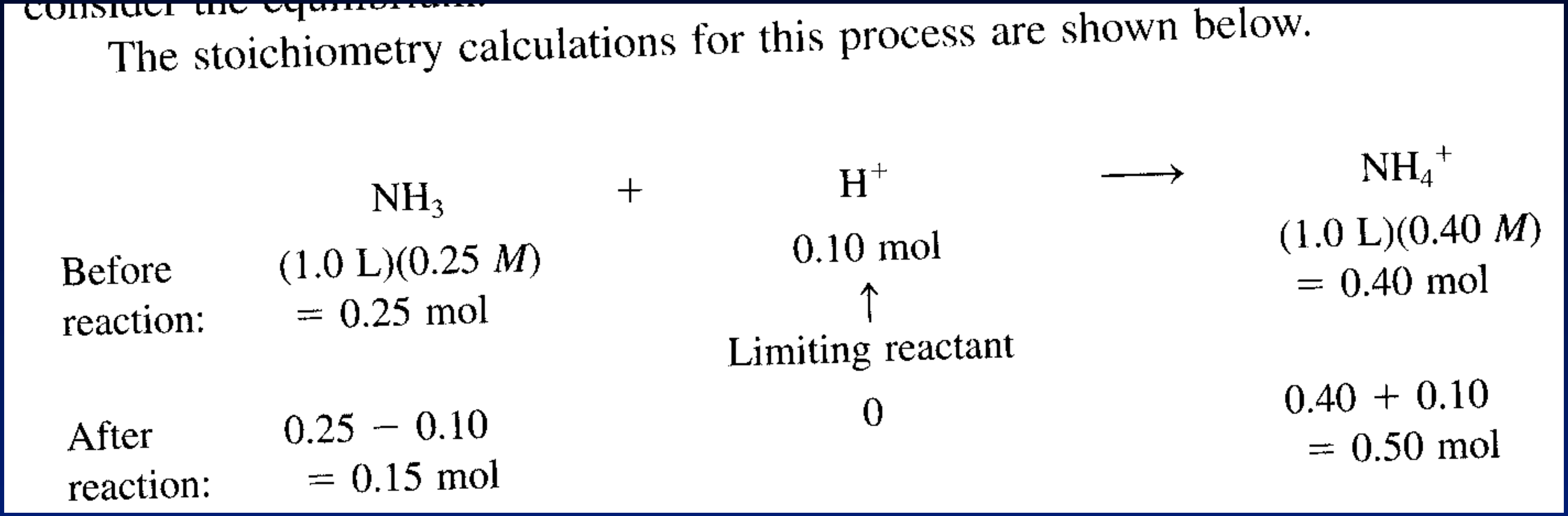


Before any reaction occurs, the solution contains the following major species:

$$NH_3,\quad NH_4^+,\quad Cl^-,\quad H^+,\quad \text{and}\quad H_2O$$

What reaction can occur? We know that H^+ will not react with Cl^- to form HCl. In contrast to Cl^-, the NH_3 molecule has a great affinity for protons (this is demonstrated by the fact that NH_4^+ is such a weak acid [$K_a = 5.6 \times 10^{-10}$]). Thus NH_3 will react with H^+ to form NH_4^+:

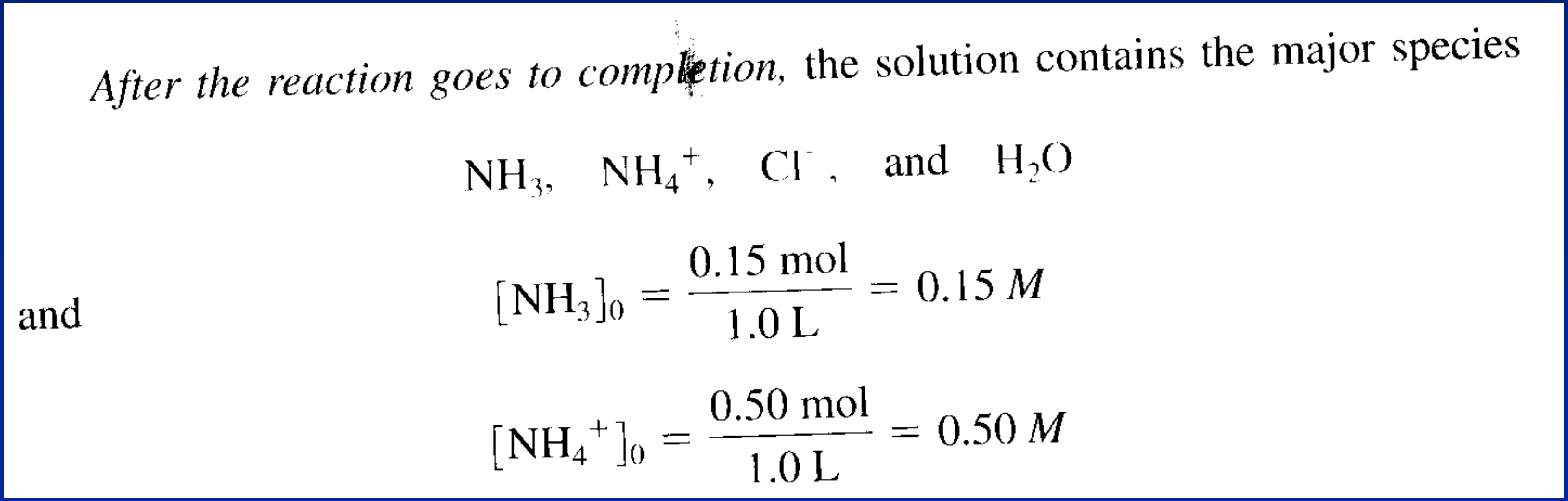
$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$$



consider the equilibrium.

The stoichiometry calculations for this process are shown below.

	NH_3	+	H^+	$\longrightarrow$	NH_4^+
Before reaction:	(1.0 L)(0.25 M) = 0.25 mol		0.10 mol ↑ Limiting reactant		(1.0 L)(0.40 M) = 0.40 mol
After reaction:	0.25 − 0.10 = 0.15 mol		0		0.40 + 0.10 = 0.50 mol



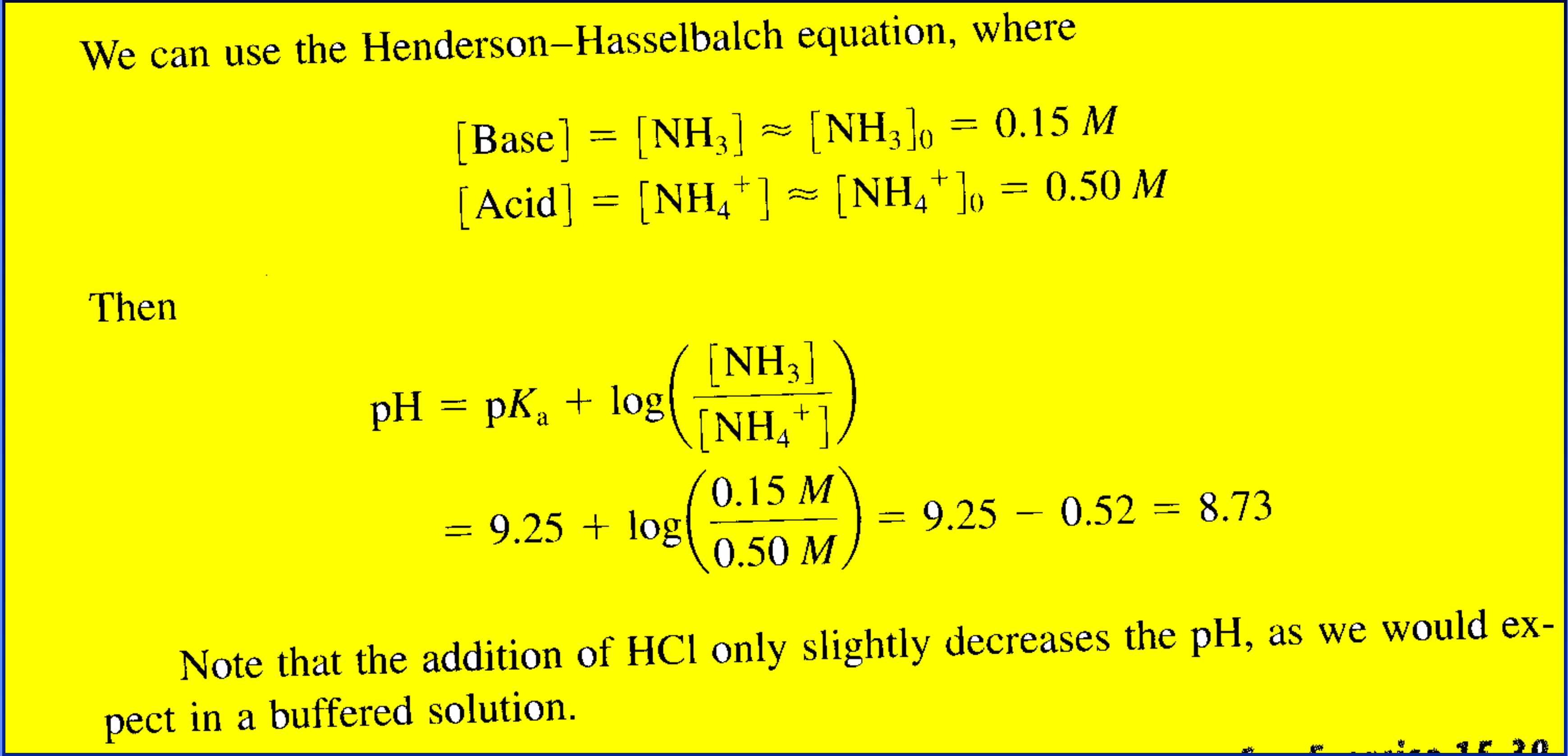
After the reaction goes to completion, the solution contains the major species

NH_3, NH_4^+, Cl^-, and H_2O

and

$$[NH_3]_0 = \frac{0.15\text{ mol}}{1.0\text{ L}} = 0.15\ M$$

$$[NH_4^+]_0 = \frac{0.50\text{ mol}}{1.0\text{ L}} = 0.50\ M$$



We can use the Henderson–Hasselbalch equation, where

$$[\text{Base}] = [\text{NH}_3] \approx [\text{NH}_3]_0 = 0.15\ M$$
$$[\text{Acid}] = [\text{NH}_4{}^+] \approx [\text{NH}_4{}^+]_0 = 0.50\ M$$

Then

$$\text{pH} = \text{p}K_\text{a} + \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4{}^+]}\right)$$
$$= 9.25 + \log\left(\frac{0.15\ M}{0.50\ M}\right) = 9.25 - 0.52 = 8.73$$

Note that the addition of HCl only slightly decreases the pH, as we would expect in a buffered solution.

15.3 Buffering Capacity

$$pH = pk_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

- The pH of a buffered solution is determined by the ratio

$$\frac{[A^-]}{[HA]}$$

- As long as this doesn’t change much the pH won’t change much.
- The more concentrated these two are the more H^+ and OH^- the solution will be able to absorb.
- Larger concentrations bigger buffer capacity.

Buffering Capacity

- Buffering capacity

  it represents the amount of protons or hydroxide ions the buffer can absorb without a significant change in pH

Buffering Capacity

- Calculate the change in pH that occurs when 0.010 mol of HCl(g) is added to 1.0L of each of the following:
- 5.00 M HAc and 5.00 M NaAc
- 0.050 M HAc and 0.050 M NaAc
- $K_a = 1.8 \times 10^{-5}$

Change in $\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$ for two solutions when 0.01 mol H^+ is added to 1.0 L of each

Solution	$(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]})\mathrm{orig}$	$(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]})\mathrm{new}$	Change	% Change
A	$\frac{5.00M}{5.00M}=1.00$	$\frac{4.99M}{5.01M}=0.996$	1.00→0.996	Neglig.
B	$\frac{0.050M}{0.050M}=1.0$	$\frac{0.04M}{0.06M}=0.67$	1.0→ 0.67	Signif.

Much higher buffer capacity

Buffering Capacity

- pH in both solutions is 4.74
- pH of solution A after addition of HCl is 4.74; NO CHANGE
- pH of solution B after addition of HCl is 4.56; THERE IS A REAL CHANGE
- A buffer with much larger quantities of buffering components has much higher buffering capacity

Change in $\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$ for two solutions when 0.01 mol H^+ is added to 1.0 L of each

Solution	$(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]})$orig	$(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]})$new	Change	% Change
A	$\frac{1.00M}{1.00M}=1.00$	$\frac{0.99M}{1.01M}=0.98$	1.00→ 0.98	2.00
B	$\frac{1.00M}{0.01M}=100$	$\frac{0.99M}{0.02M}=49.5$	100 → 49.5	50.5

Small changes in ratio

Large changes in ratio

Which solution has more buffering capacity?

- pH of Solution A

Before	After
4.74	4.74

- pH of Solution B

Before	After
6.74	6.44

- Large changes in the ratio [A-]/[HA] produce large changes in pH

- For most effective buffering large changes in the ratio should be avoided

Buffering Capacity

- The optimal buffering occurs when we have the ratio $[A^-]/[HA] = 1$
  - This buffer is most resistant to change when H^+ or OH^- ions are added
- This is true when $[A^-] = [HA]$
  - That is when pH = pKa (since log1=0)
- Thus pka of the weak acid to be used in the buffer should be as close as possible to the desired pH

15.4 Titrations and pH curves

- Millimole (mmol) = 1/1000 mol
- Molarity = mmol/mL = mol/L
- # mmoles = volume (in mL) X Molarity
  - This makes calculations easier because we will rarely add Liters of solution.
- Titration is adding a solution of known concentration until the substance being tested is consumed.
  - This point is called the equivalence point (or End-point)
- Graph of pH vs. mL is a titration curve.

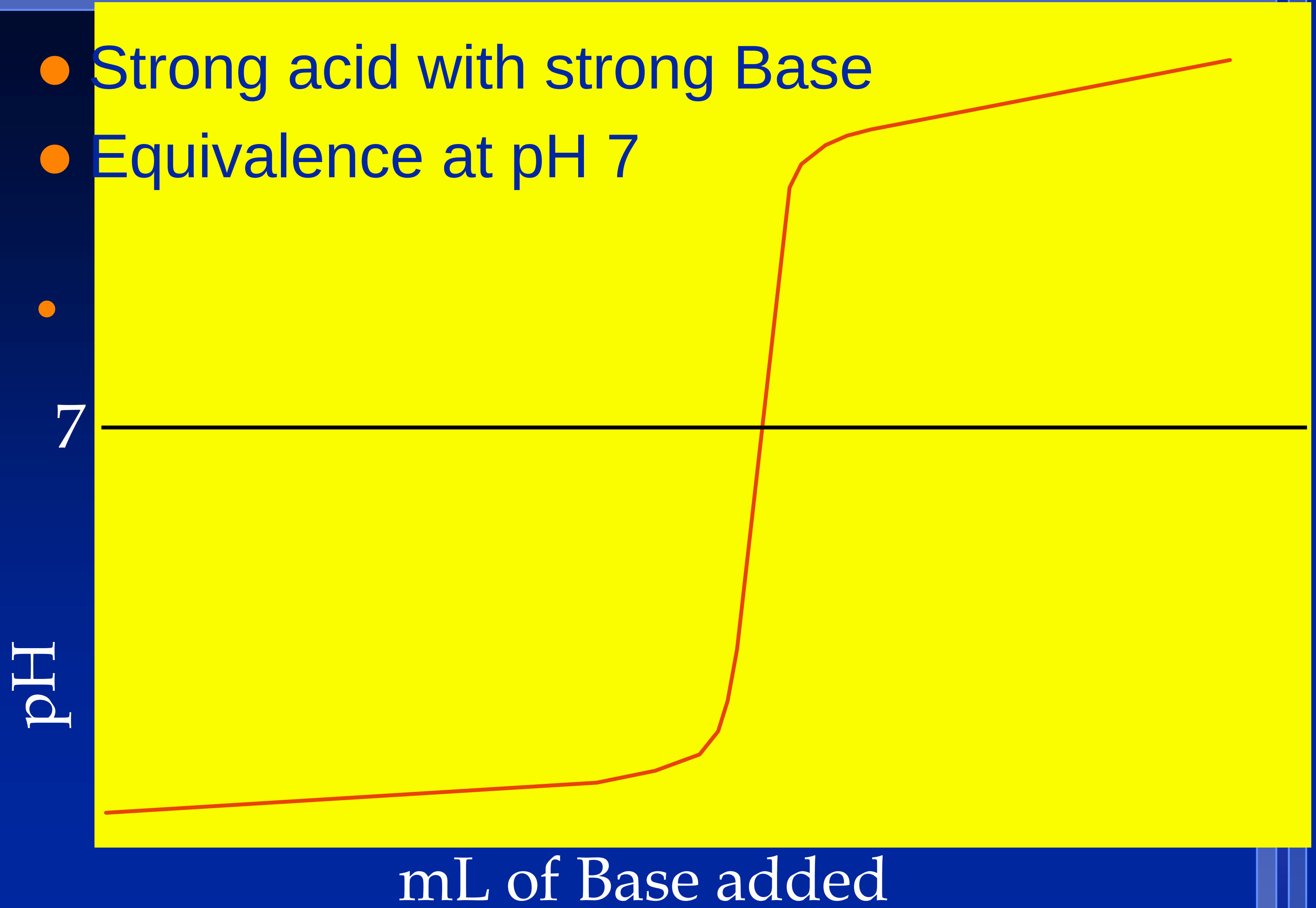
Strong acid - Strong Base Titrations

- Do the stoichiometry.
- There is no equilibrium .
- They both dissociate completely.

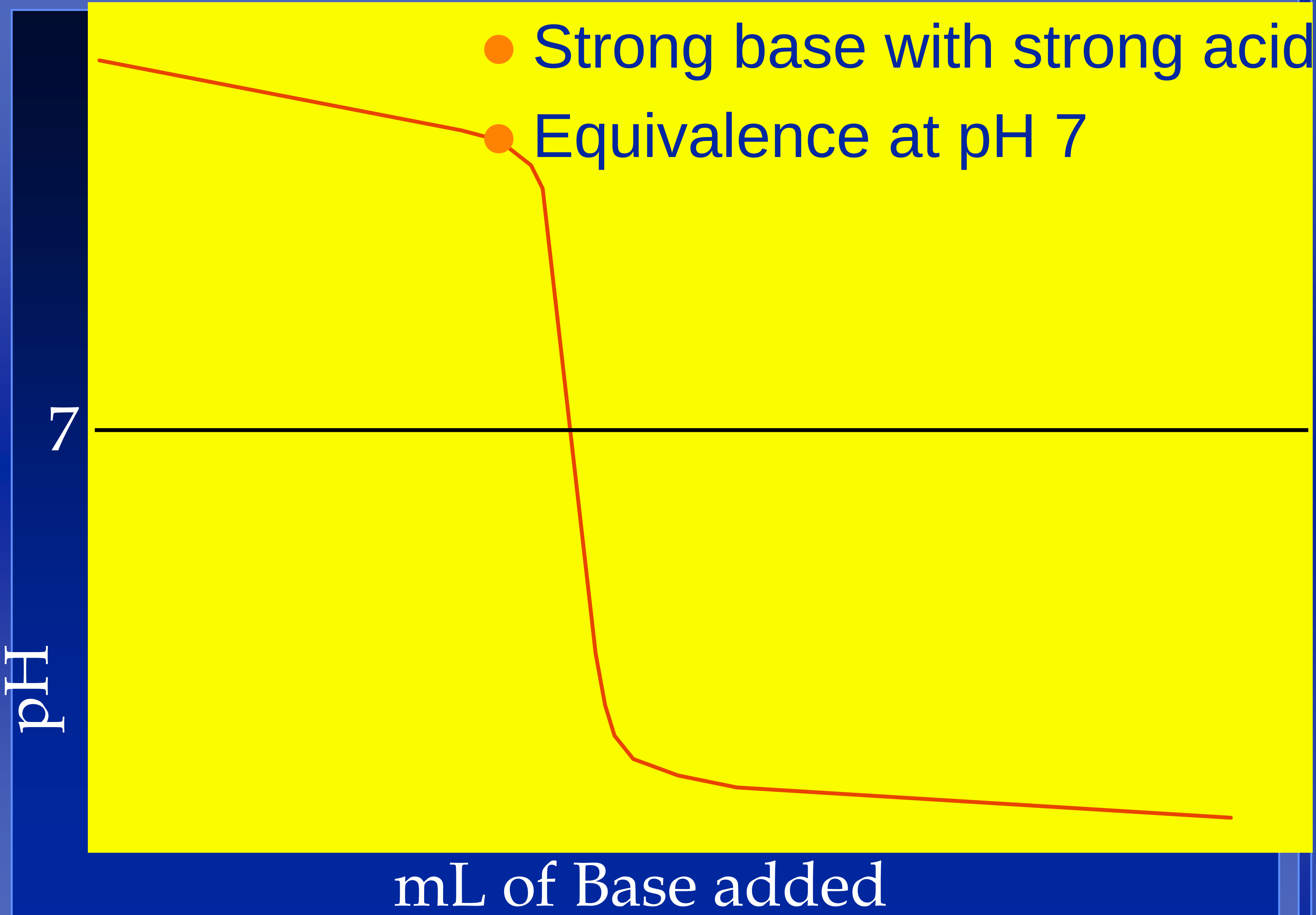
Case Study:

- The titration of 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH. Calculate the pH at the following stages:
  - Before any NaOH is added
  - When 10 mL of NaOH has been added
  - When 20.0 mL of NaOH has been added
  - When 50.0mL of NaOH has been added
  - When 100.0 mL of NaOH has been added
  - When 200.0 mL has been added

- Strong acid with strong Base
- Equivalence at pH 7



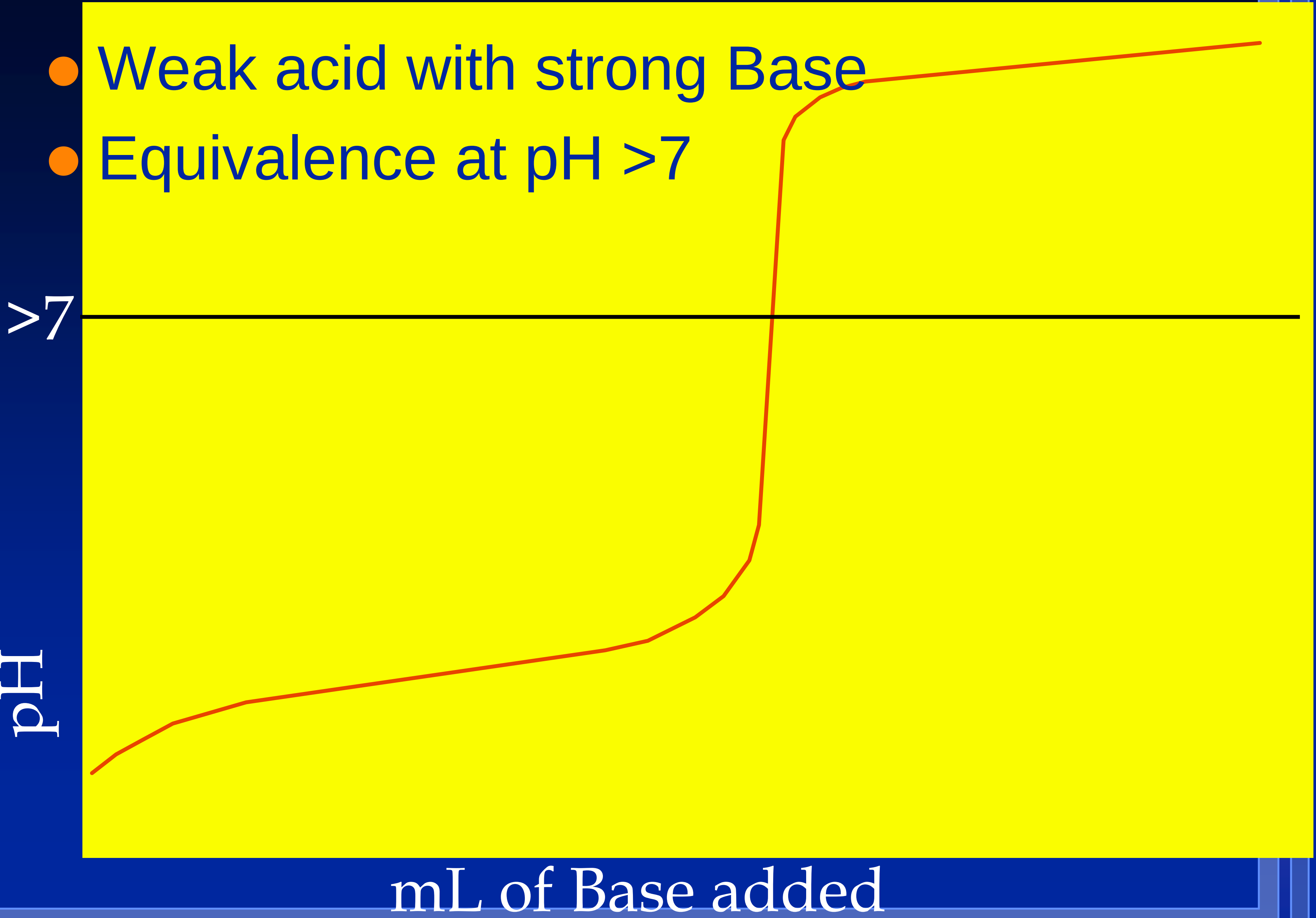
- Strong base with strong acid
- Equivalence at pH 7



Titration of weak acids with Strong bases

- There is an equilibrium.
- Do stoichiometry.
- Then do equilibrium.
- Titrate 50.0 mL of 0.10 M acetic acid
  (Ka = 1.8 x 10^{-5}) with 0.10 M NaOH
- Calculate the pH at the following stages:
  - Before any NaOH is added
  - When 10 mL of NaOH has been added
  - When 25.0 mL of NaOH has been added
  - When 40.0mL of NaOH has been added
  - When 50.0 mL of NaOH has been added
  - When 60.0 mL NaOH has been added
  - When 50.0 mL of NaOH has been added

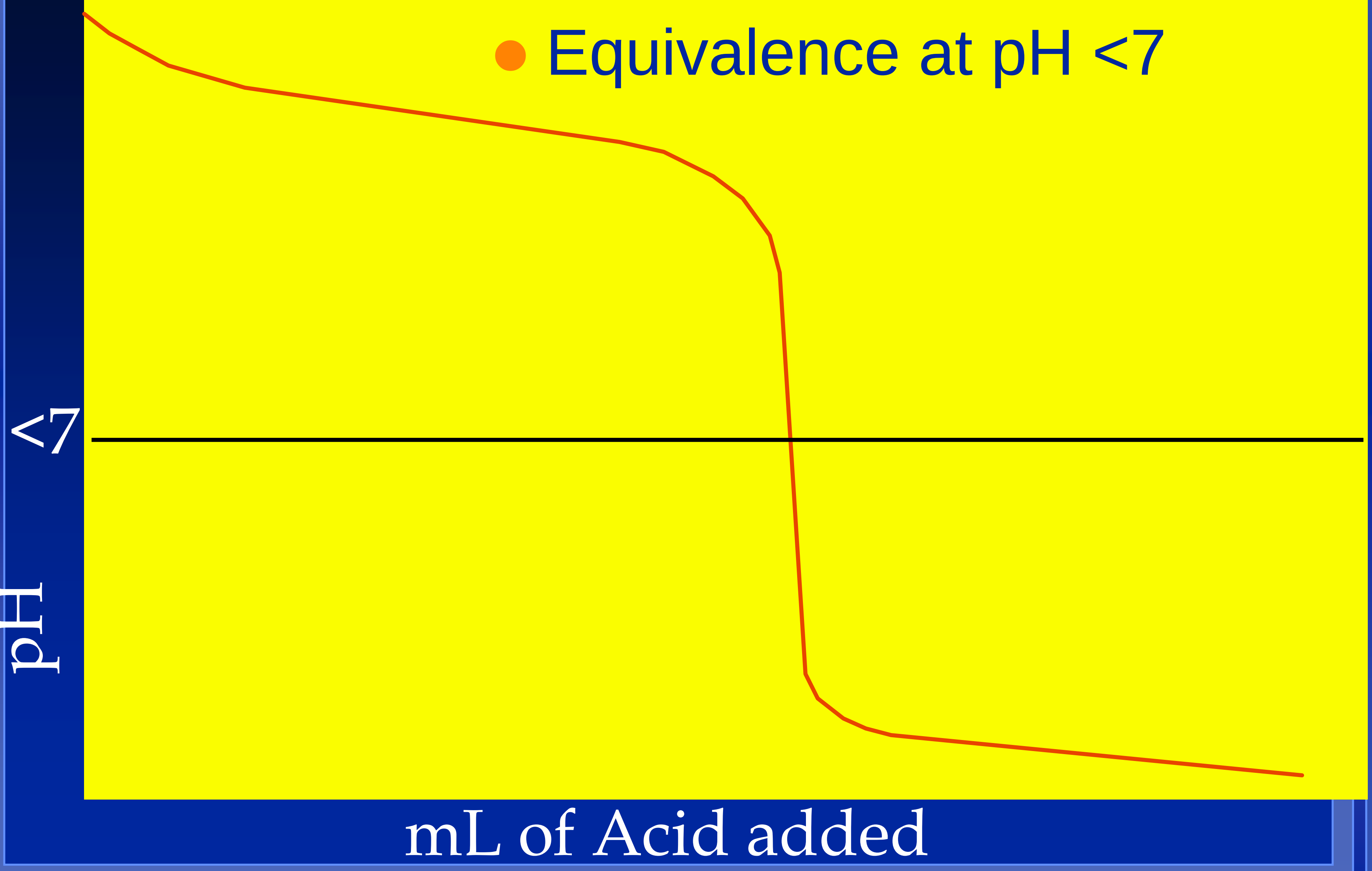
- Weak acid with strong Base
- Equivalence at pH >7



Titration of weak basis with Strong acid

- There is an equilibrium.
- Do stoichiometry.
- Then do equilibrium.
- Titrate 100.0 mL of 0.05 M NH3 (Kb = 1.8 x 10^{-5}) with 0.10 M HCl
- Calculate the pH at the following stages:
  - Before any HCl is added
  - Before the equivalence point
  - At the equivalence point
  - Beyond the equivalence point

- Weak base with strong acid
- Equivalence at pH <7



Titrations

In a ***titration*** a solution of accurately known concentration is added gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

Equivalence point – the point at which the reaction is complete

Indicator – substance that changes color at the **endpoint** (hopefully close to the equivalence point)

Slowly add base
to unknown acid
UNTIL

The indicator
changes color
(pink)

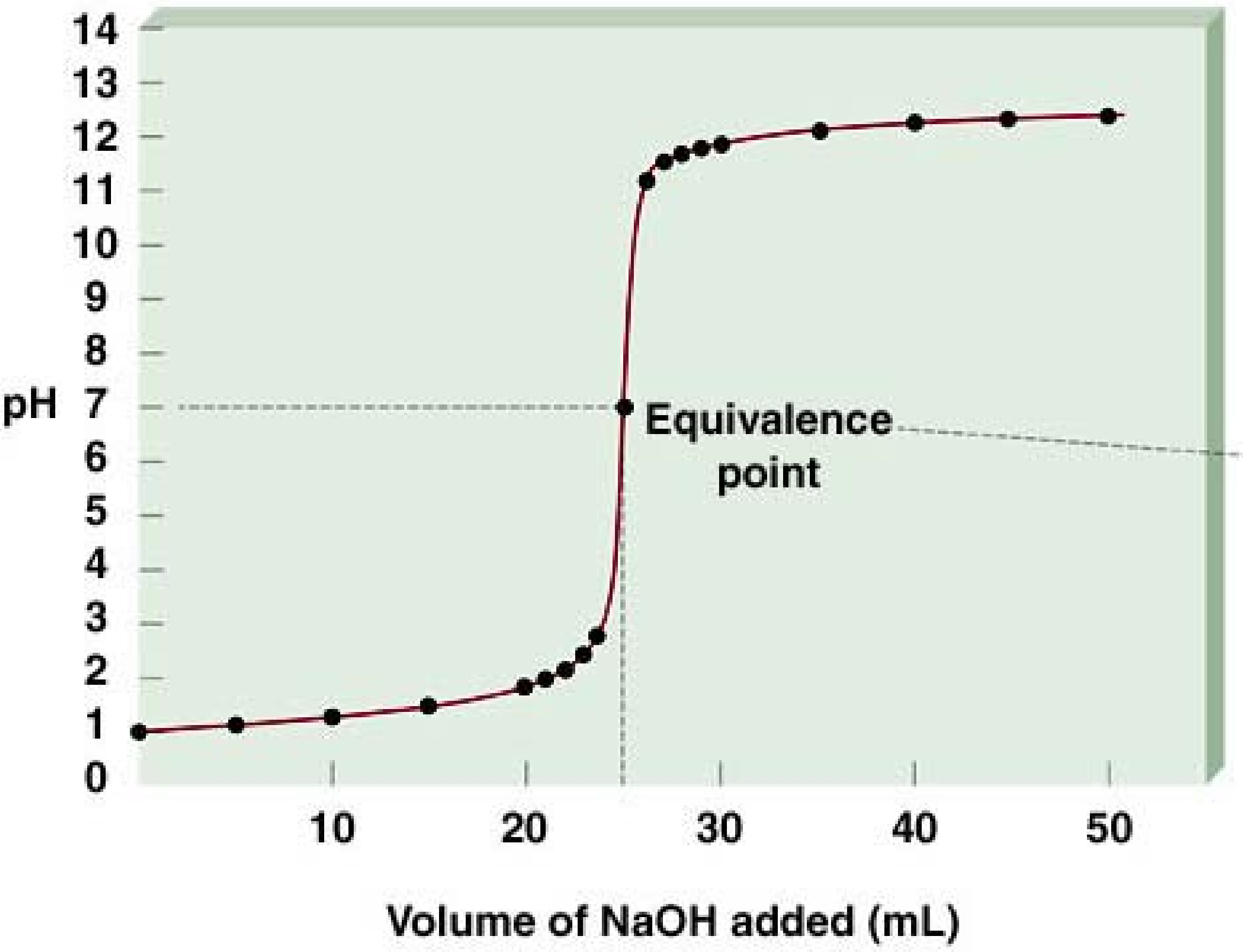
Strong Acid-Strong Base Titrations

NaOH (*aq*) + HCl (*aq*) $\longrightarrow$ H_2O (*l*) + NaCl (*aq*)

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

100% ionization!

No equilibrium



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

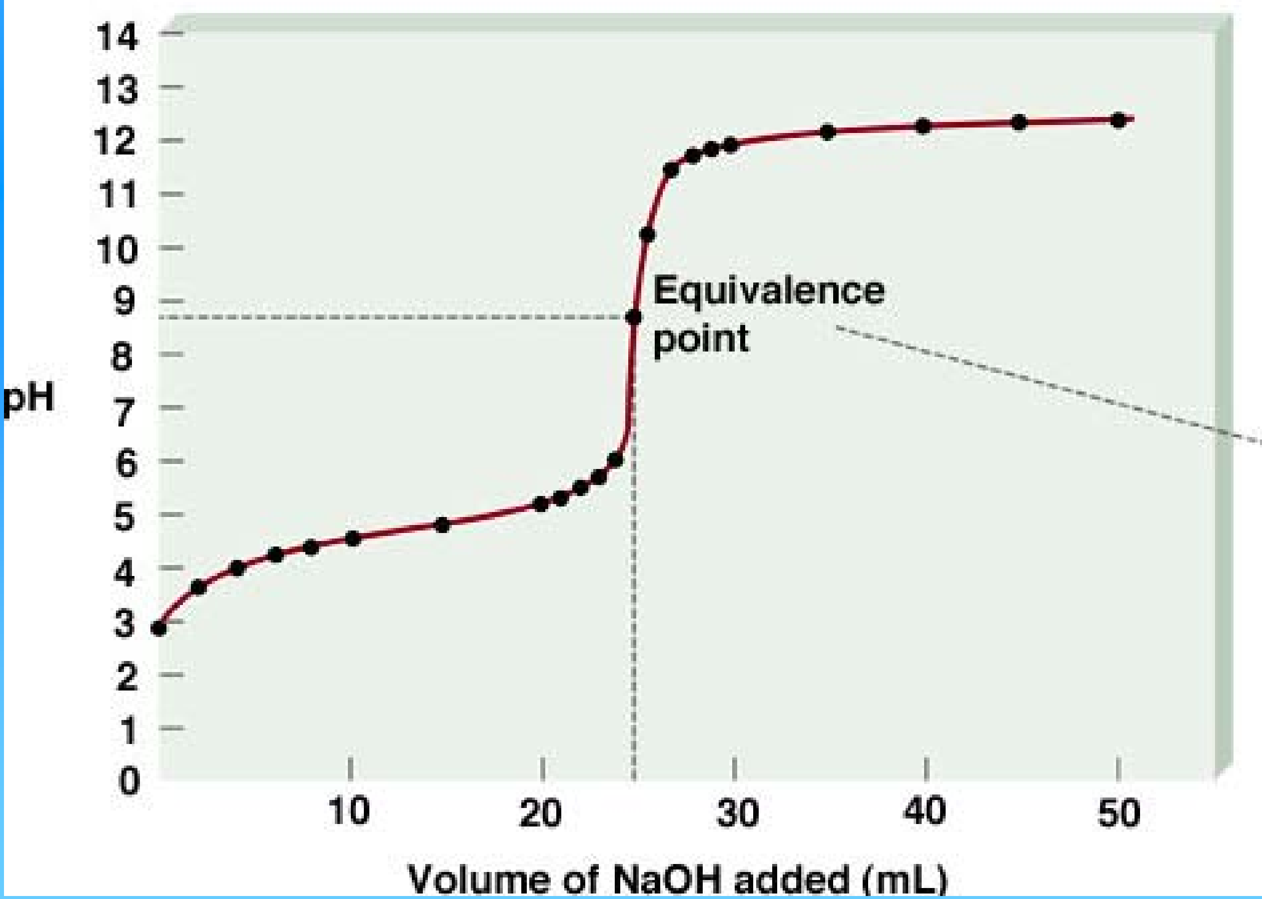
Weak Acid-Strong Base Titrations

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

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

At equivalence point (pH > 7):

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



Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

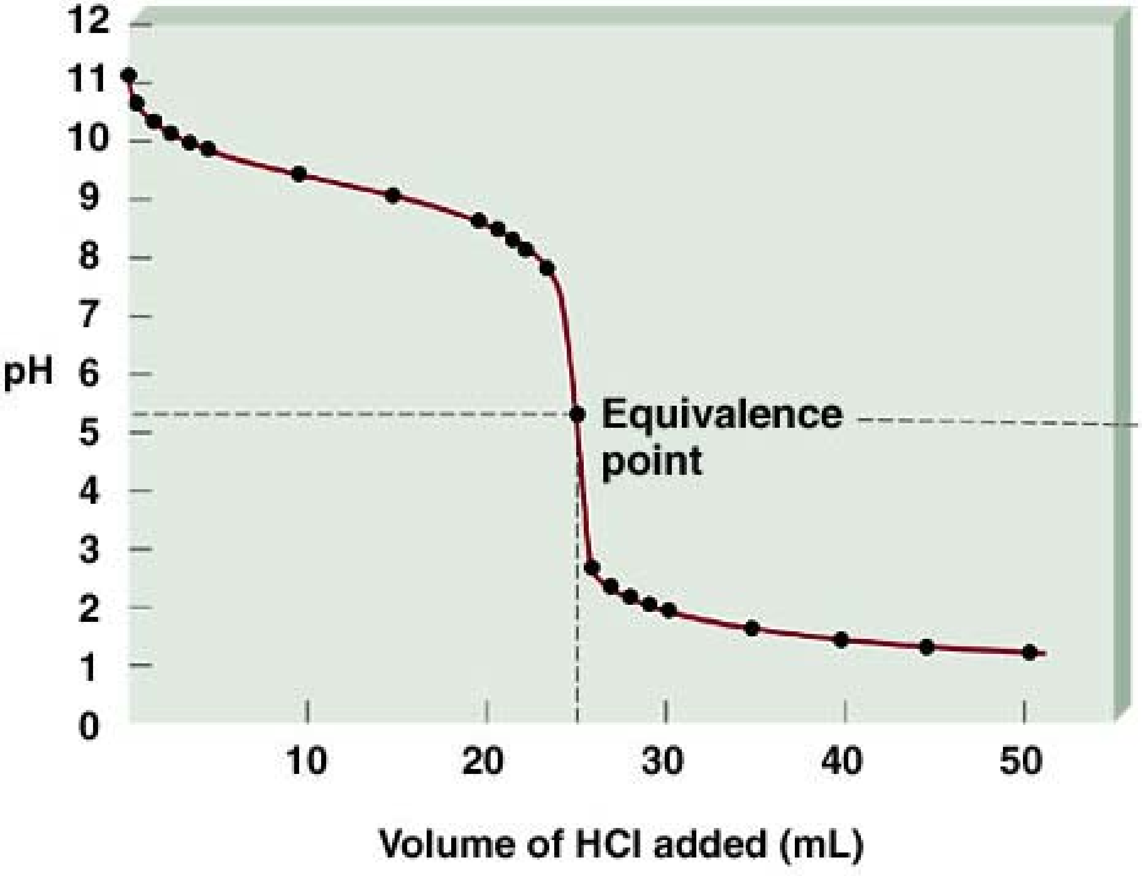
Strong Acid-Weak Base Titrations

$HCl\ (aq) + NH_3\ (aq) \longrightarrow NH_4Cl\ (aq)$

$H^+\ (aq) + NH_3\ (aq) \longrightarrow NH_4Cl\ (aq)$

At equivalence point (pH < 7):

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



Volume HCl added (mL)	pH
0.0	11.13
5.0	9.86
10.0	9.44
15.0	9.08
20.0	8.66
22.0	8.39
24.0	7.88
25.0	5.28
26.0	2.70
28.0	2.22
30.0	2.00
35.0	1.70
40.0	1.52
45.0	1.40
50.0	1.30

Summary

- Strong acid and base just stoichiometry.
- Determine Ka, use for 0 mL base
- Weak acid before equivalence point
  - Stoichiometry first
  - Then Henderson-Hasselbach
- Weak acid at equivalence point Kb
- Weak base after equivalence - leftover strong base.

Summary

- Determine Ka, use for 0 mL acid.
- Weak base before equivalence point.
    - Stoichiometry first
    - Then Henderson-Hasselbach
- Weak base at equivalence point Ka.
- Weak base after equivalence - leftover strong acid.

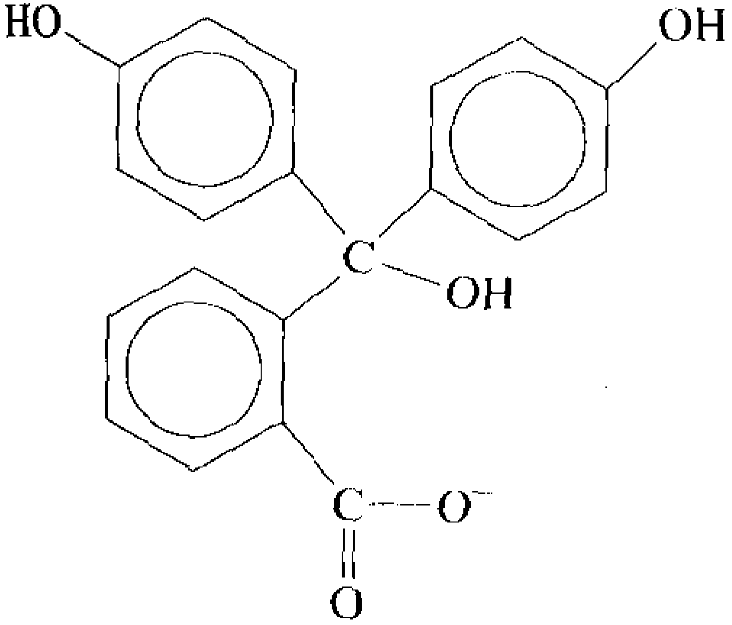
15.5 Acid-base Indicators

- Weak acids that change color at a certain pH
- weak acid written, HIn, has a certain color when the proton is attached to the molecule and a different color when the proton is dissociated, In^-.

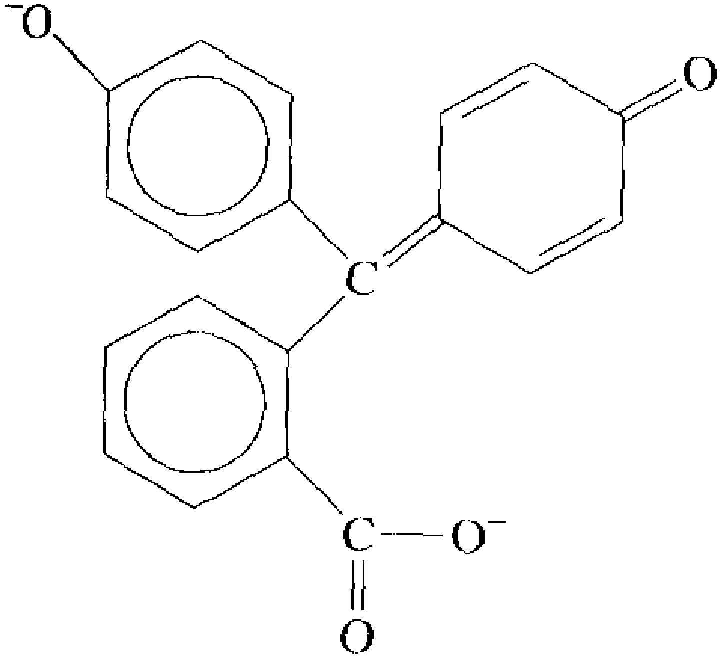
$$HIn \rightleftharpoons H^+ + In^-$$

colorless red

- Equilibrium is controlled by pH
- End point is reached when the indicator changes color.



(Colorless acid form, HIn)



(Pink base form, In^-)

Indicators

- Since it is an equilibrium the color change is gradual.
- It is noticeable when the ratio of $[In^-]/[HI]$ or $[HI]/[In^-]$ is 1/10
- Since the Indicator is a weak acid, it has a K_a.
- pH the indicator changes at is.
- $pH = pKa + \log([In^-]/[HI]) = pKa + \log(1/10)$
- $pH = pKa - 1$ ***on the way up***

Indicators

- $pH=pKa + \log([HI]/[In^-]) = pKa + \log(10)$
- $pH=pKa+1$ on the way down
- Choose the indicator with a pKa 1 less than the pH at equivalence point if you are titrating with base.
- Choose the indicator with a pKa 1 greater than the pH at equivalence point if you are titrating with acid.

15.6 Solubility equilibria and solubility product

- If there is not much solid it will all dissolve.
- As more solid is added the solution will become saturated.
- Solid $\rightleftharpoons$ dissolved
- The solid will precipitate as fast as it dissolves until Equilibrium is reached

Solubility Product/Solubility

- An example of dynamic equilibrium of slightly soluble compounds

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

The equilibrium expression for this reaction is:

$K_{eq} = K_{sp} = [Ca^{2+}][F^{-}]^2$

Ksp is called solubility product const $\frac{1}{2}$ t or simply Solubility product

- Solubility = s = $[Ca^{2+}] = [F^{-}]$

Solubility Product/Solubility

- For solids dissolving to form aqueous solutions.
- $Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$
- $K_{sp} = [Bi^{3+}]^2\,[S^{2-}]^3$
- Solubility = $s = \frac{1}{2}[Bi^{3+}] = \frac{1}{3}[S^{2-}]$

Solubility Product/Solubility

- Solubility is not the same as solubility product.
- Solubility product is an equilibrium constant.
- It doesn’t change except with temperature.
- Solubility is an equilibrium position for how much can dissolve.
- A common ion can change this.

Calculating K_{sp} from solubility

- The solubility of CuBr(s) = 2.0×10^{-4}M at 25^{o}C. Calculate Ksp

- Calculate Ksp for Bi_2S_3 $\frac{1mol}{}$ that has the solubility of 1.0×10^{-13} mol/L

- The solubility of Li_2CO_3 is 5.48 g/L. Molar mass of Li_2CO_3 is 73.88.
  (Molarity = $\frac{5.48g}{L} X \frac{1molLi_2CO_3}{73.88g}$ = 7.4×10^{-2}M)

Calculating Solubility from Ksp

- The solubility is determined by equilibrium.
- Its an equilibrium problem.
- Calculate the solubility of $SrSO_4$, with a Ksp of 3.2×10^{-7} in M and g/L.
- Calculate the solubility of Ag_2CrO_4, with a Ksp of 9.0×10^{-12} in M and g/L.

Relative solubilities

- Ksp will only allow us to compare the solubility of solids that fall apart into the same number of ions.
- The bigger the Ksp of those the more soluble. This is applicable only when salts being compared produce same number of ions.,, and

AgI = $1.5 X 10^{-16}$

CuI = $5.0 X 10^{-12}$

$CaSO_4$ = $6.1 X 10^{-5}$

Relative solubilities

- When salts produce different number of ions when dissolved in water, Ksp values cannot be compared directly to determine relative solubilities

CuS Ksp = $8.5X10^{-45}$

Ag2S Ksp = $1.6X10^{-49}$

Bi_2S_3 Ksp = $1.1X10^{-73}$

$Bi_2S_3 > Ag_2S > CuS$ (opposite to the order of Ksp values

Common Ion Effect

- If we try to dissolve the solid in a solution with either the cation or anion already present less will dissolve.
- Calculate the solubility of Ag_2CrO_4, with a Ksp of 9.0×10^{-12} in M and g/L in a solution of 0.10 M $AgNO_3$.
- Calculate the solubility of CaF_2, with a Ksp of 4.0×10^{-11} in M and g/L in a solution of 0.025 M NaF

pH and solubility

- $Mg(OH)_2\ (s) \rightleftharpoons Mg^{2+}(aq) + OH^-(aq)$
- OH^- can be a common ion. Thus, addition of OH^- will affect the solubility of $Mg(OH)_2$
- $Mg(OH)_2$ is more soluble in acid.
- For other anions if they come from a weak acid they are more soluble in a acidic solution than in water.
- $CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$
- $H^+ + C_2O_4^{2-} \rightleftharpoons HC_2O_4^-$
- Reduces $C_2O_4^{2-}$ in acidic solution.

pH and Solubility

- **AgCl(s)** has same solubility in acidic or basic solutions?
- Cl^- is coming from a strong acid and its solution is neutral.
- ***$CaCO_3$*** dissolves in water that has some CO_2 dissolved in it. CO_2 will make the water acidic.
  - While this solution is dripping in the caves CO_2 escapes leading to an increase in the pH and a consequent decrease in solubility; thus, stalactites and stalagmites will be formed.

15.7 Precipitation and qualitative analysis

- $M_aX_b(s) \rightleftharpoons aM^{b+} + bX^{a-}$
- Ion Product, $Q = [M^+]^a[X^-]^b$
- If $Q > K_{sp}$ a precipitate forms.
- If $Q < K_{sp}$ No precipitate.
- If $Q = K_{sp}$ equilibrium.
- A solution of 750.0 mL of 4.00×10^{-3}M $Ce(NO_3)_3$ is added to 300.0 mL of 2.00×10^{-2}M KIO_3. Will $Ce(IO_3)_3$ ($K_{sp} = 1.9 \times 10^{-10}$ M) precipitate and if so, what is the concentration of the ions?

- $[Ce^{3+}] = 2.86 \times 10^{-3}$ M
- $[IO_3^-] = 5.71 \times 10^{-3}$ M
- $Q = [Ce^{3+}]_0 [IO^{3-}]_0^3 = 5.32 \times 10^{-10}$
- Q>Ksp, then $Ce(IO_3)_3$ will precipitate

- (# mmoles of $Ce^{3+})_0 = 3.0$
- # mmoles of $IO_3^- = 6.0$
- $Ce^{3+} + 3IO_3^- \longrightarrow Ce(IO_3)_3$ (s)
- # mmoles of Ce^{3+} left = 3-2 =1
- $[Ce^{3+}]$left = 1/1050 = 9.5×10^{-4} M
- $[IO_3^-] = 1.2 \times 10^{-3}$ M

- $Ce(IO_3)_3\ (s) \rightleftharpoons Ce^{3+} + 3IO_3^-$

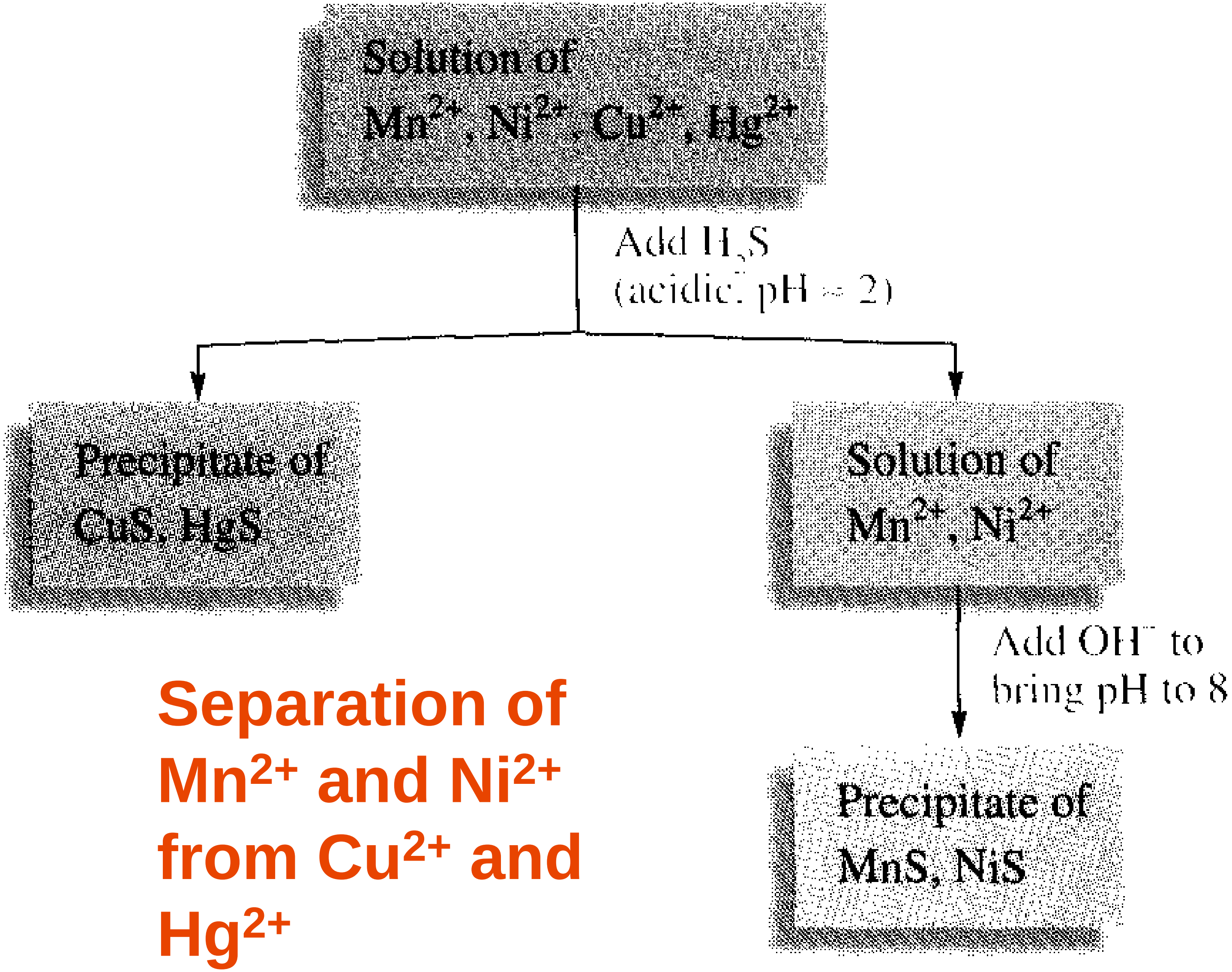
$S + 9.5X10^{-4}$ $3S$

$Ksp = (S+9.5X10^{-4})\ (3S)^3 \approx 2.85X10^{-3}\ S^3 = 1.9X10^{-10}$

Selective Precipitations

- This property is used to separate and purify mixtures of metal ions in solutions.
- Add anion that will only precipitate one or certain metals at a time.
- S^{2-} of H_2S is basic, thus precipitation can be made effective by adjusting the pH
- $H_2S \rightleftharpoons H^+ + HS^-$

  $HS \rightleftharpoons H^+ + S^{2-}$
- In acidic solution Hg^{2+}, Cd^{2+}, Bi^{3+}, Cu^{2+}, Sn^{4+} will precipitate.



Solution of
Mn^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}

Add H_2S
(acidic: pH ≈ 2)

Precipitate of
CuS, HgS

Solution of
Mn^{2+}, Ni^{2+}

Add OH^- to
bring pH to 8

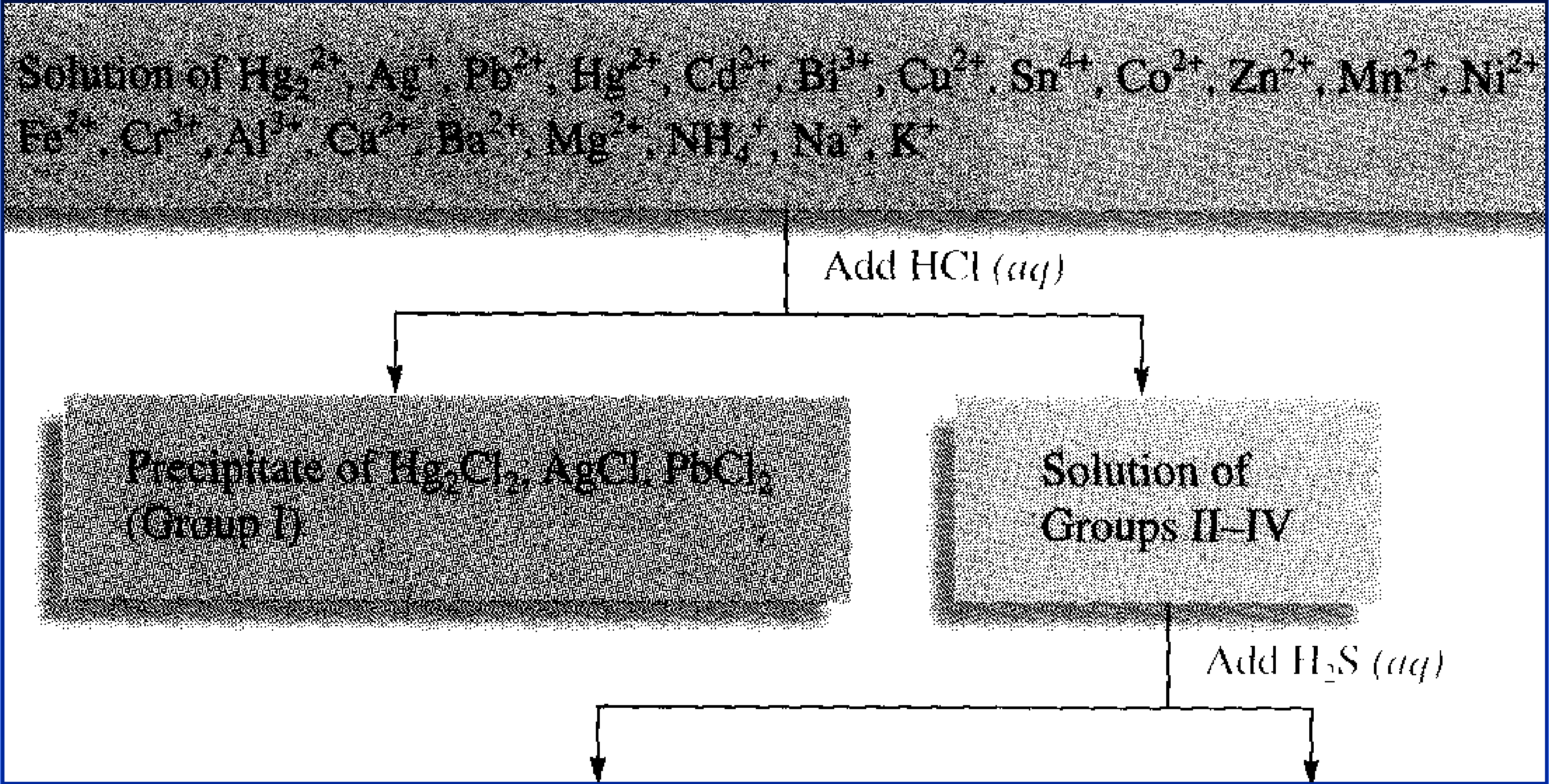
Precipitate of
MnS, NiS

Separation of Mn^{2+} and Ni^{2+} from Cu^{2+} and Hg^{2+}

Qualitative analysis

- Group I: insoluble chlorides
- GroupII: insoluble sulfides in acid solutions
- GroupIII: insoluble sulfides in basic solutions
- Group IV: insoluble carbonate
- Group V: Alkali metals and NH_4^+ ions

Qualitative Analysis



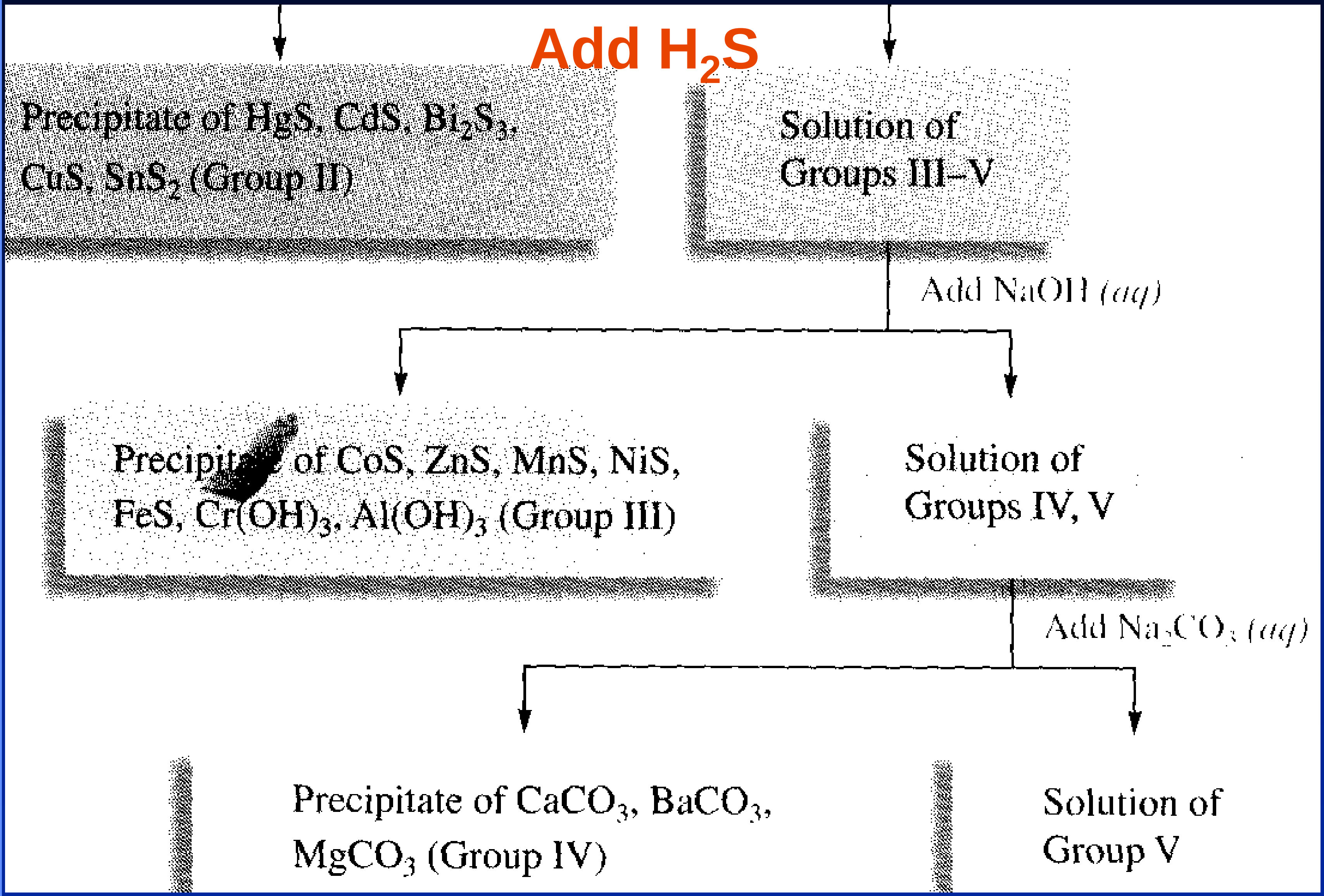
Solution of Hg_2^{2+}, Ag^+, Pb^{2+}, Hg^{2+}, Cd^{2+}, Bi^{3+}, Cu^{2+}, Sn^{4+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Fe^{2+}, Cr^{3+}, Al^{3+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, NH_4^+, Na^+, K^+

Add HCl (*aq*)

Precipitate of Hg_2Cl_2, $AgCl$, $PbCl_2$ (Group I)

Solution of Groups II–IV

Add H_2S (*aq*)



Add H_2S

Precipitate of HgS, CdS, Bi_2S_3, CuS, SnS_2 (Group II)

Solution of Groups III–V

Add $NaOH(aq)$

Precipitate of CoS, ZnS, MnS, NiS, FeS, $Cr(OH)_3$, $Al(OH)_3$ (Group III)

Solution of Groups IV, V

Add $Na_2CO_3(aq)$

Precipitate of $CaCO_3$, $BaCO_3$, $MgCO_3$ (Group IV)

Solution of Group V

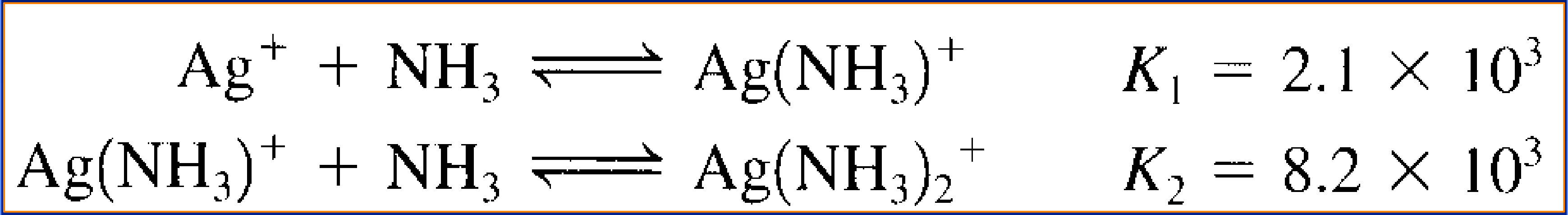
Complex ion Equilibria

15.8 Equilibria involving complex ions

- A complex ion is a charged ion surrounded by ligands.
- Ligands are Lewis bases (molecules or ions) using their lone pair to stabilize the charged metal ions.
- Common ligands are NH_3, H_2O, Cl^-,CN^-
- Coordination number is the number of attached ligands.
- $Cu(NH_3)_4^{+2}$ has a coordination # of 4
- Most common coordination numbers are 6 and 4. Others are known

Equilibria involving complex ions

- Metal ions add ligands one at a time in steps
- The steps are characterized by an equilibrium constant called Formation constant or Stability constant, K_1, K_2, …



$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+ \qquad K_1 = 2.1 \times 10^3$$

$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_2 = 8.2 \times 10^3$$

Example

- **Consider a solution prepared by mixing 100.0 mL of 2.0 *M* NH_3 with 100.0 mL of 1.0 X 10^{-3} *M* $AgN0_3$. Calculate the concnetration of Ag^+, $Ag(NH_3)^+$ and $Ag(NH_3)^{2+}$ in the solution**

- We are interested only in the following equilibria:

$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+ \qquad K_1 = 2.1 \times 10^3$$

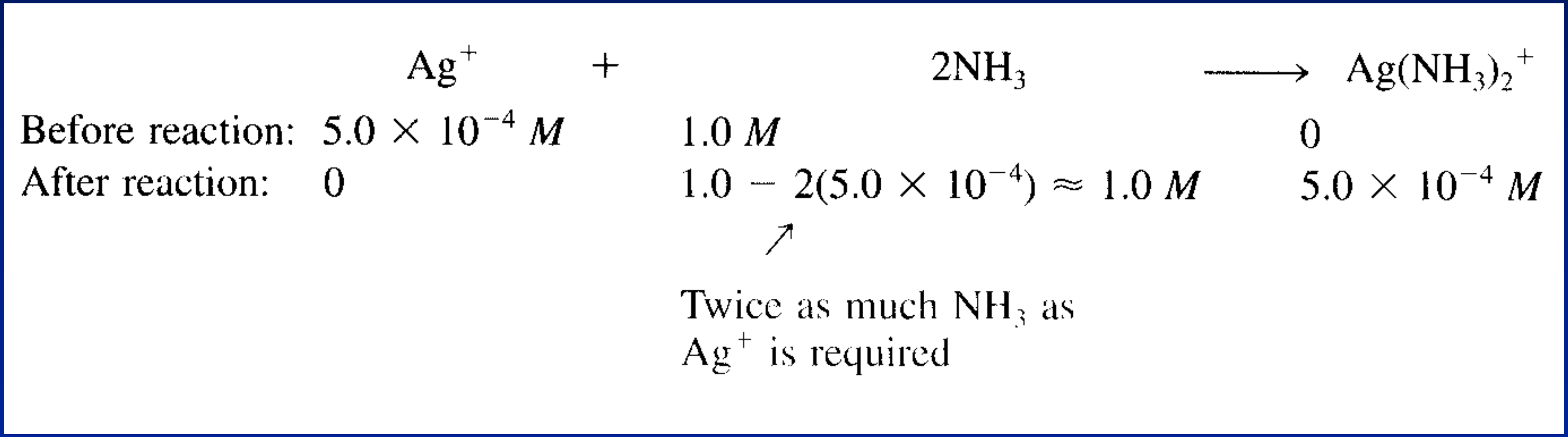
$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_2 = 8.2 \times 10^3$$

- Initial concentrations:

$$[Ag^+]_0 = \frac{(100.0\text{ mL})(1.0 \times 10^{-3}\,M)}{\underbrace{(200.0\text{ mL})}_{\text{Total volume}}} = 5.0 \times 10^{-4}\,M$$

$$[NH_3]_0 = \frac{(100.0\text{ mL})(2.0\,M)}{(200.0\text{ mL})} = 1.0\,M$$

- **Since both K_1 and K_2 are large, and since there is a large excess of NH_3, both reactions can be assumed to go essentially to completion.**
- **This is equivalent to writing the net reaction in the solution as follows:**



	Ag^+	+	$2NH_3$	$\longrightarrow$	$Ag(NH_3)_2^+$
Before reaction:	5.0×10^{-4} *M*		1.0 *M*		0
After reaction:	0		$1.0 - 2(5.0 \times 10^{-4}) \approx 1.0$ *M*		5.0×10^{-4} *M*

↗

Twice as much NH_3 as
Ag^+ is required

- **We can safely assume that $[Ag(NH_3)^{2+}]$ is $5.0X10^{-4}$ M since its dissociation is very small**
- **Also $[NH_3]$ is 1.0 M since the amount reacted is very small**

To calculate the equilibrium concentration of $Ag(NH_3)^+$, we use

$$K_2 = 8.2 \times 10^3 = \frac{[Ag(NH_3)_2{}^+]}{[Ag(NH_3)^+][NH_3]}$$

since $[Ag(NH_3)_2{}^+]$ and $[NH_3]$ are known. Rearranging and solving for [Ag(NH
give

$$[Ag(NH_3)^+] = \frac{[Ag(NH_3)_2{}^+]}{K_2[NH_3]} = \frac{5.0 \times 10^{-4}}{(8.2 \times 10^3)(1.0)} = 6.1 \times 10^{-8}\ M$$

Now the equilibrium concentration of Ag^+ can be calculated using K_1:

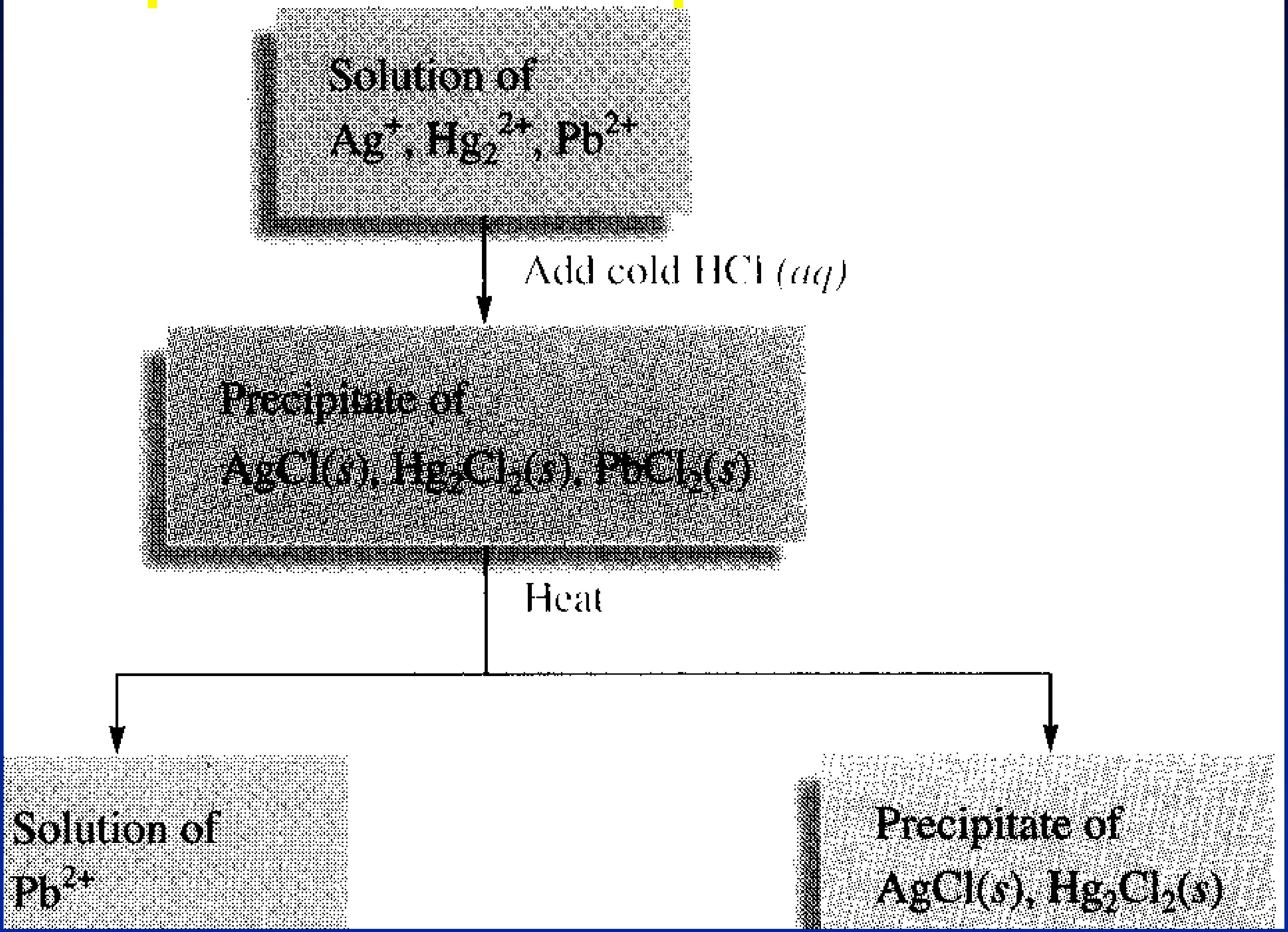
$$K_1 = 2.1 \times 10^3 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]} = \frac{6.1 \times 10^{-8}}{[Ag^+](1.0)}$$

$$[Ag^+] = \frac{6.1 \times 10^{-8}}{(2.1 \times 10^3)(1.0)} = 2.9 \times 10^{-11}\ M$$

These values clearly support the conclusion that

$$[Ag(NH_3)_2{}^+] \gg [Ag(NH_3)^+] \gg [Ag^+]$$

Complex ions and solubility
Separation of Group I ions



Solution of Ag^{+}, Hg_2^{2+}, Pb^{2+}

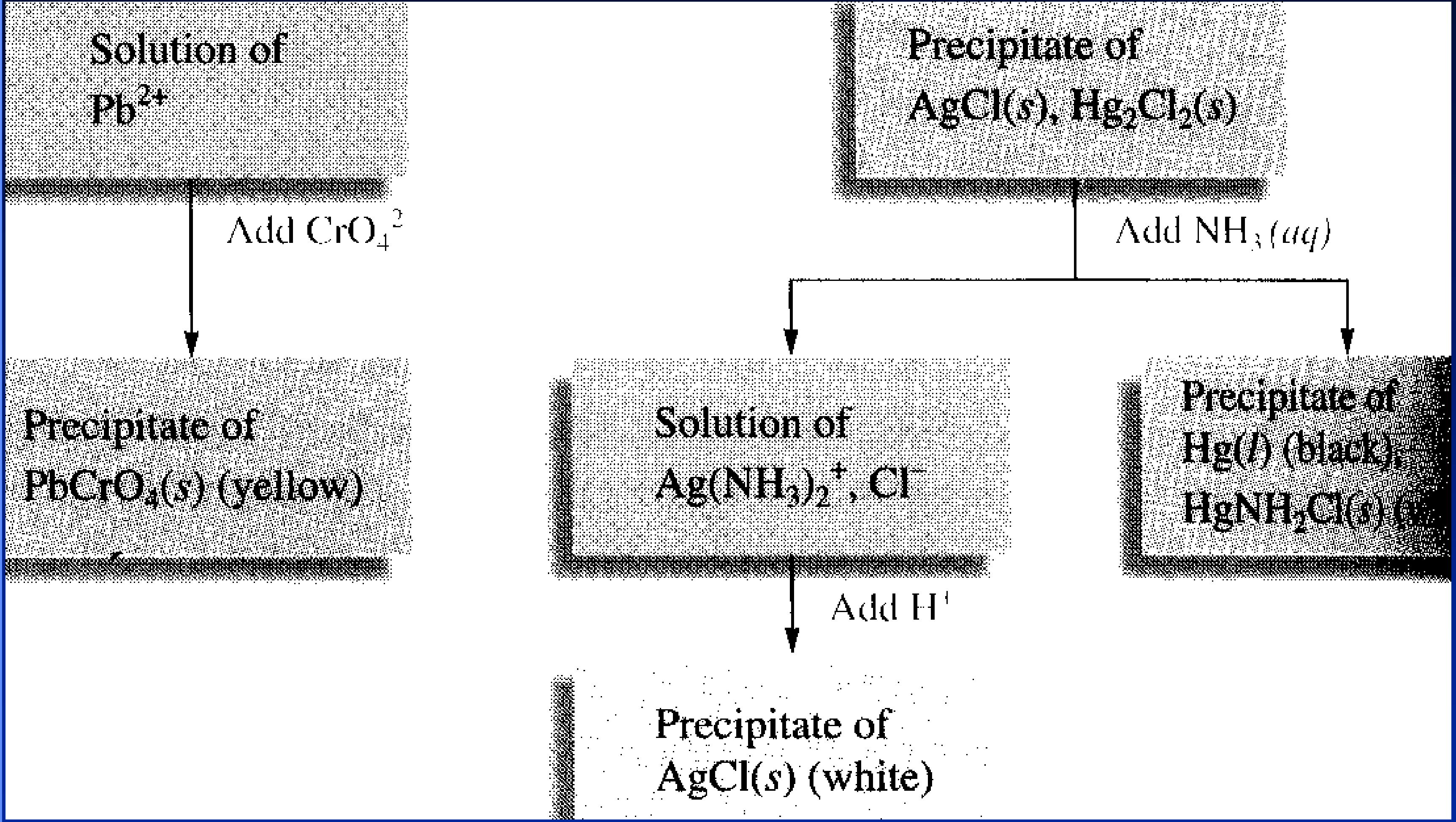
Add cold $HCl(aq)$

Precipitate of $AgCl(s)$, $Hg_2Cl_2(s)$, $PbCl_2(s)$

Heat

Solution of Pb^{2+}

Precipitate of $AgCl(s)$, $Hg_2Cl_2(s)$



Solution of Pb^{2+}

Add CrO_4^{2-}

Precipitate of $PbCrO_4(s)$ (yellow)

Precipitate of $AgCl(s)$, $Hg_2Cl_2(s)$

Add $NH_3(aq)$

Solution of $Ag(NH_3)_2^+$, Cl^-

Add H^+

Precipitate of $AgCl(s)$ (white)

Precipitate of $Hg(l)$ (black), $HgNH_2Cl(s)$ (