CHAPTER 7
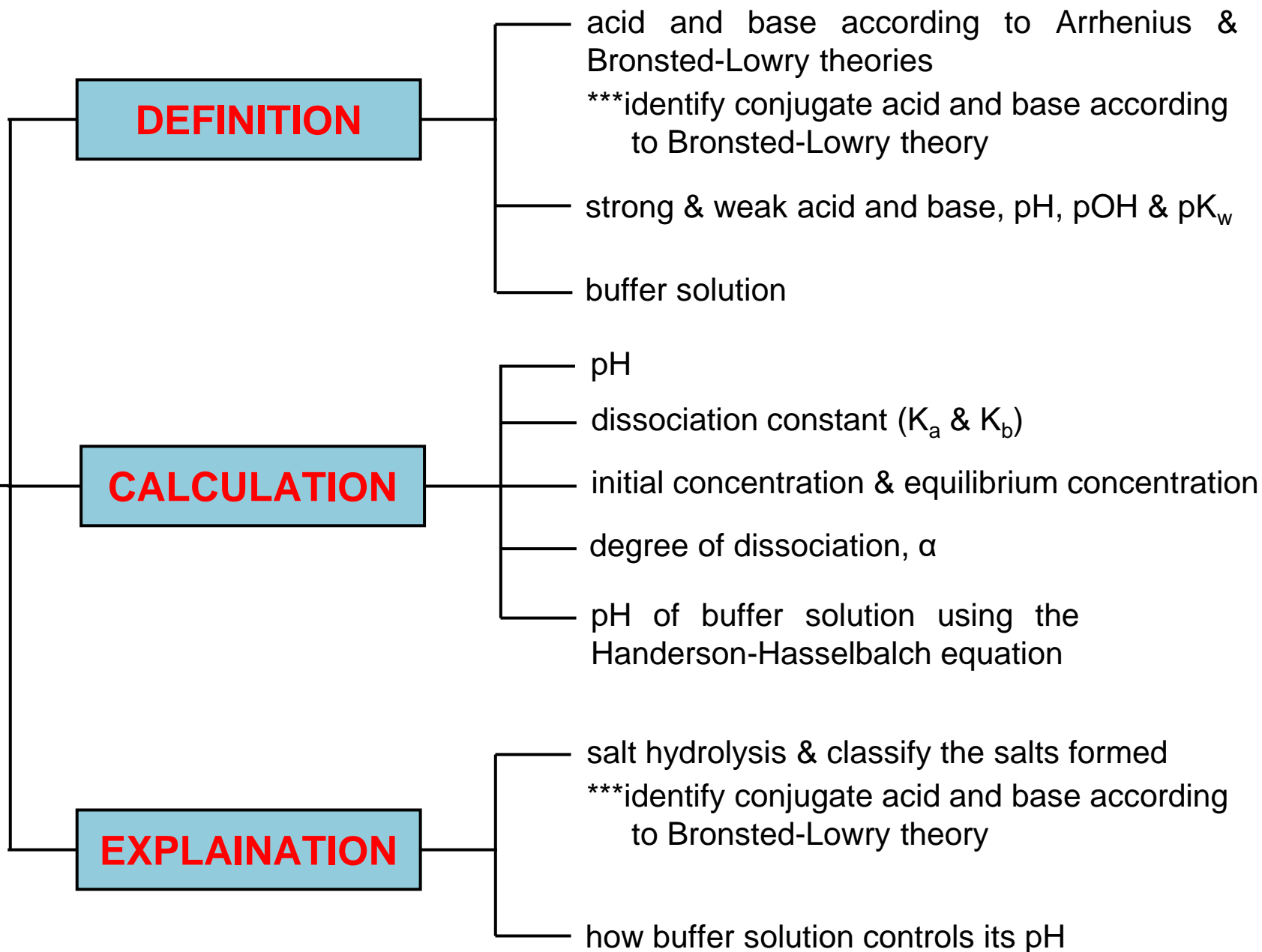# IONIC EQUILIBRIUM

7.1 Acids and Bases
7.2 Acid-base Titration
7.3 Solubility Equilibrium

7.1 ACIDS AND BASES

DEFINITION
- acid and base according to Arrhenius & Bronsted-Lowry theories
  ***identify conjugate acid and base according to Bronsted-Lowry theory
- strong & weak acid and base, pH, pOH & pK_w
- buffer solution

CALCULATION
- pH
- dissociation constant (K_a & K_b)
- initial concentration & equilibrium concentration
- degree of dissociation, α
- pH of buffer solution using the Handerson-Hasselbalch equation

EXPLAINATION
- salt hydrolysis & classify the salts formed
  ***identify conjugate acid and base according to Bronsted-Lowry theory
- how buffer solution controls its pH

7.1 a) Definition of Acids and Bases

There are 2 main definitions for acids and bases:

* **Arrhenius**
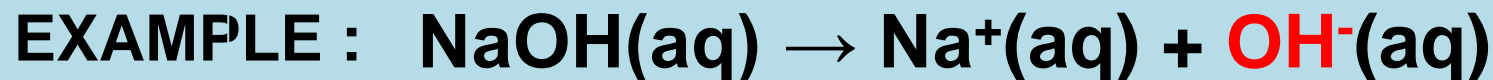
* **Brönsted-Lowry**

Arrhenius

Johannes Nicolaus Bronsted 1923

Thomas Martin Lowry 1923

Arrhenius Theory

Acid

Substance that dissociate in water to produce H_3O^+ ion.

EXAMPLE : $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

Base

Substance that dissociate in water to produce OH^- ion.

EXAMPLE : $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

Bronsted-Lowry Theory

Acid

Any substance that can donate a proton,(H^+) to other substance.

EXAMPLE:

$$HNO_3 \text{ (aq)} + H_2O \text{ (l)} \longrightarrow NO_3^- \text{ (aq)} + H_3O^+ \text{ (aq)}$$

acid

$$NH_4^+ \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons NH_3 \text{ (aq)} + H_3O^+ \text{ (aq)}$$
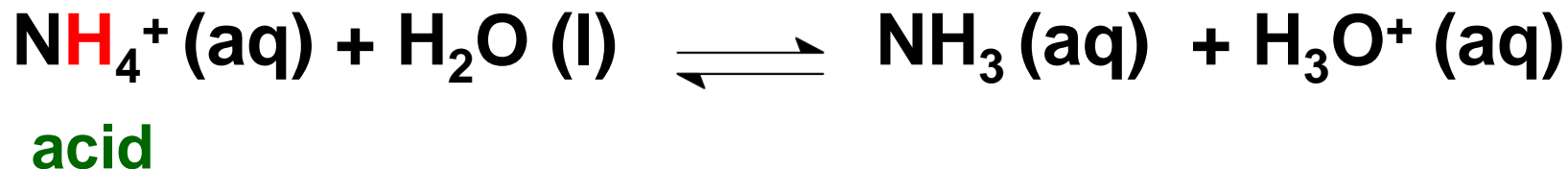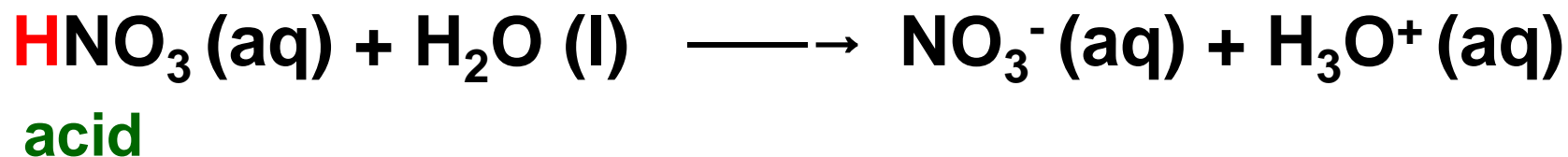
acid

Bronsted-Lowry Theory

Base

Any substance that can accept a proton, (H$^+$) from other substance.

EXAMPLE:

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

CO_3^{2-} (*aq*) + H_2O(*l*) $\rightleftharpoons$ HCO_3^- (*aq*) + OH^-(*aq*)
base
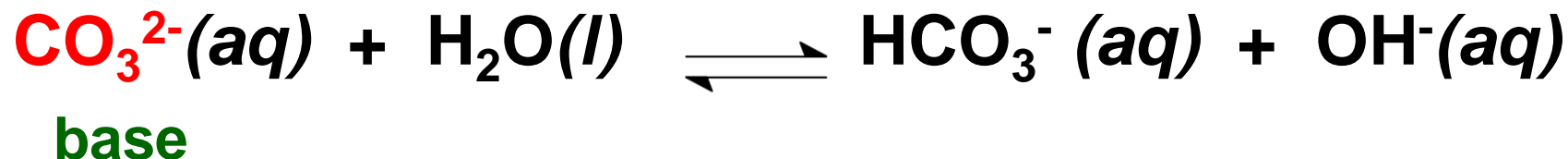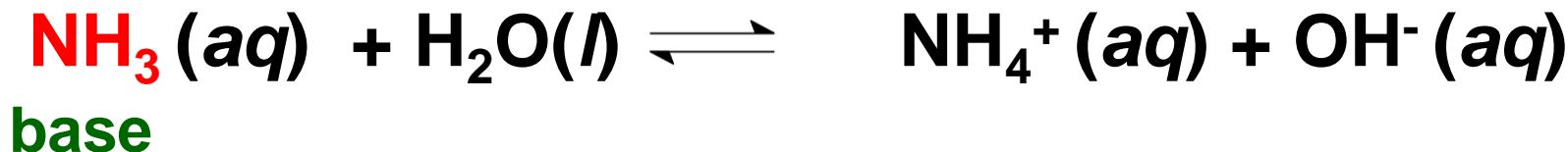
- **An acid can exist as "+" charge, "-" charge or neutral.**
  Example: H_3O^+, H_2SO_4, HCO_3^-, NH_4^+

- **A base can only exist as "-" charge or neutral.**
  Example: OH^-, CN^-, NH_3, NH_2^-

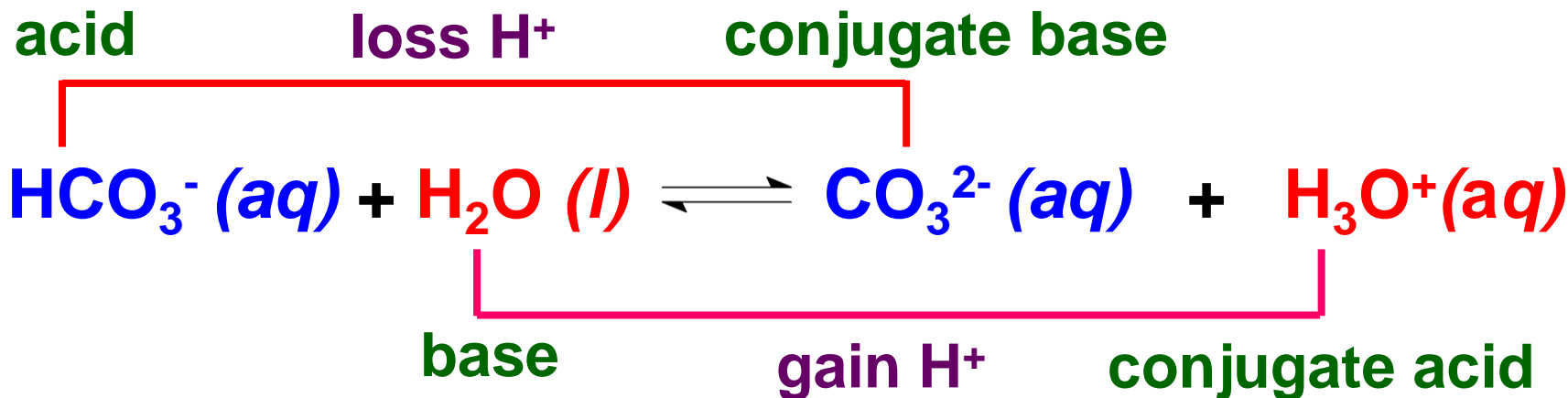- **H_2O is amphoteric : able to act as an acid or a base**

7.1 b) Conjugate Acid-Base Pairs

Conjugate Acid

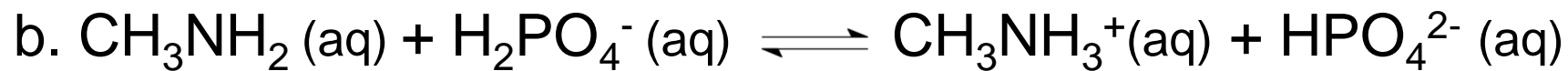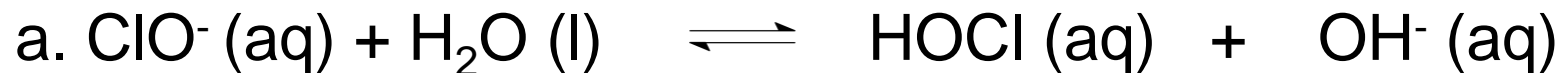A species that remains when **one proton,(H⁺)** has been **added** to the **base.**
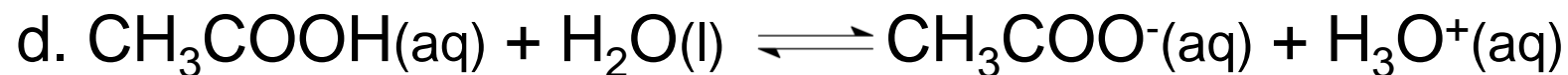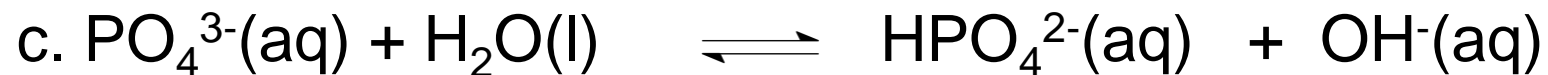
Conjugate Base

A species that remains when **one proton,(H⁺)** has been **removed** from the **acid.**

acid   loss H⁺   conjugate base

$$HCO_3^- \ (aq) + H_2O \ (l) \rightleftharpoons CO_3^{2-} \ (aq) + H_3O^+(aq)$$

base   gain H⁺   conjugate acid

EXERCISE 1

In the following reactions, identify the acid-base conjugate pairs.

a. $ClO^- (aq) + H_2O (l) \rightleftharpoons HOCl (aq) + OH^- (aq)$

b. $CH_3NH_2 (aq) + H_2PO_4^- (aq) \rightleftharpoons CH_3NH_3^+ (aq) + HPO_4^{2-} (aq)$

c. $PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$

d. $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

7.1 c) The water Ionization Constant, K_w

Water ionizes to a small degree to form very small amount of H_3O^+ and OH^-.

$$H_2O \ (l) + H_2O(l) \rightleftharpoons H_3O^+ \ (aq) \ OH^-(aq)$$
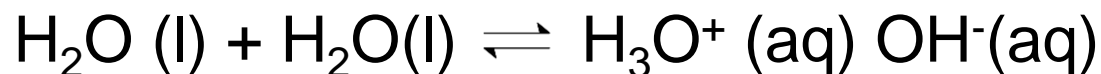
$$\boxed{Kw = [H_3O^+] \ [OH^-] \ = 1 \times 10^{-14}}$$ *ionic product of water at 25°C*

Negative log of both sides of the expression

$$-log \ (K_w) = - log \ (\ [H_3O^+] \ [OH^-] \ )$$

$$-log \ (1.0 \times 10^{-14}) = (-log \ [H_3O^+] \ ) + (-log \ [OH^-] \ )$$

$$14 = pH + pOH$$

The value of K_w increases with temperature because the dissociation of water is an endothermic process. For aqueous solution at 25°C,

| ACIDIC SOLUTION	NEUTRAL SOLUTION	BASIC SOLUTION
$[H_3O^+] > [OH^-]$ $[H_3O^+] > 1.0 \times 10^{-7} \text{ M}$ @ $[OH^-] < 1.0 \times 10^{-7} \text{ M}$	$[H_3O^+] = [OH^-]$ $= 1.0 \times 10^{-7} \text{ M}$	$[OH^-] > [H_3O^+]$ $[OH^-] > 1.0 \times 10^{-7} \text{ M}$ @ $[H_3O^+] < 1.0 \times 10^{-7} \text{ M}$

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7.1 d) Strong and Weak Acids

- When an acid **HA** dissolves in water, equilibrium is established

$$\text{HA}(aq) + H_2O\ (l) \rightleftharpoons A^-(aq) + H_3O^+\ (aq)$$
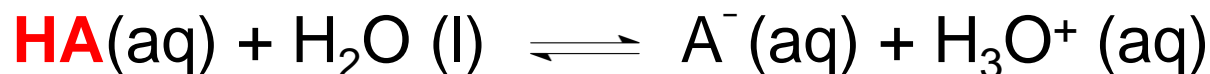
- The stronger the acid, the further the position of the equilibrium lies to right, the higher degree of dissociation.

$$\text{HCl}\ (aq) \rightarrow Cl^-(aq) + H^+\ (aq)$$

- **Strong acids** *completely* dissociated in aqueous solution

$$\text{HCN}(aq) + H_2O\ (l) \rightleftharpoons CN^-(aq) + H_3O^+\ (aq)$$
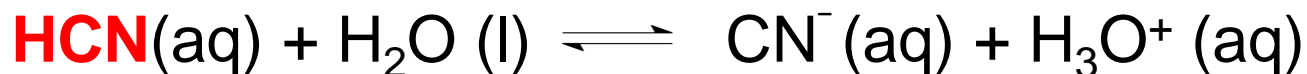
- **Weak acids** *partially* dissociate in aqueous solution.

Strong and Weak Bases

- When a base **X** dissolves in water, equilibrium is established

$$X(aq) + H_2O (l) \rightleftharpoons HX^+ (aq) + OH^-(aq)$$

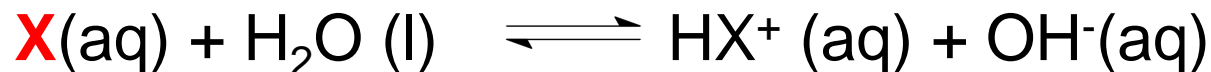- The stronger the base, the further the position of the equilibrium lies to right, the higher degree of dissociation.

$$NaOH (aq) \rightarrow Na^+(aq) + OH^- (aq)$$

- **Strong base** *completely* dissociated in aqueous solution

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

- **Weak base** *partially* dissociate in aqueous solution.

Example:

STRONG ACIDS	STRONG BASES
The hydrohalic acids e.g: **HCl, HBr and HI**	M_2O or **MOH**, where M is group 1 element : **Li, Na, K, Rb, Cs**
Oxoacids : the number of O atoms exceeds the number of ionizable protons by two or more. e.g: HNO_3 **and** $HClO_4$	**RO** or $R(OH)_2$, where R is **Ca, Sr, Ba**

Example:

WEAK ACIDS	WEAK BASES
Hydrohalic acids: HF	**Ammonia :** NH_3
Acids in which H not bonded to O or halogen: HCN **and** H_2S	**Amine :** $R\text{-}NH_2, R_2\text{-}NH$ **&** $R_3\text{-}N$ **such as** $CH_3CH_2\text{-}NH_2$ **& etc**
Oxoacids: $HClO$, HNO_2 **and** H_3PO_4	**Hydrazine :** N_2H_4
Organic acids (general formula = $R\text{–}COOH$**):** CH_3COOH **and** C_6H_5COOH	

pH	pOH	pKw
pH is a measure of the concentration of H^+/H_3O^+ ions in a solution	pOH is a measure of the concentration of OH^- ions a solution	pKw is a measure of negative logarithm (-log) of the dissociation or ionisation constant of water.
pH = -log [H^+]	pOH = -log [OH^-]	pKw = -log (K_w)

pH scale: Scale to express acidity/basicity
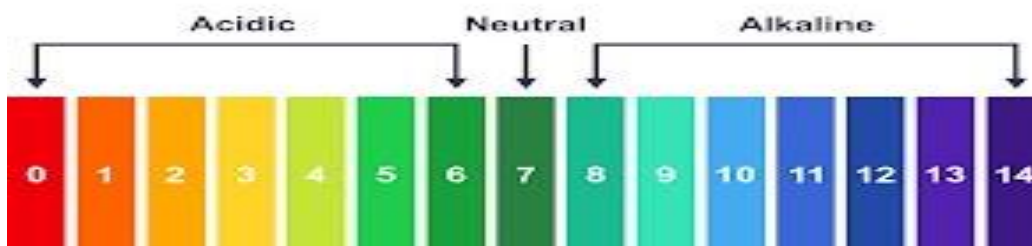
Neutral solution : pH =7   ;   [H_3O^+] = [OH^-]
Acidic solution: pH < 7   ;   [H_3O^+] > [OH^-]
Basic solution: pH> 7   ;   [H_3O^+] < [OH^-]

7.1 e) pH Calculation for Strong Acid & Strong Base

Example :

1. Calculate the pH of 0.15 mol dm^{-3} of HCl solution.

2. Calculate the pH of 0.20 M of NaOH solution.

Answer :

Question 1

	HCl(aq) $\longrightarrow$ H$^+$(aq)	+	Cl$^-$(aq)
Initial (M)	**0.15**	**0**	**0**
Final (M)	**0**	**0.15**	**0.15**

pH = - log [H$^+$]

= - log (0.15)

= 0.82

Answer :

Question 2

	NaOH(aq) $\longrightarrow$ OH⁻(aq) + Na⁺(aq)		
Initial (M)	**0.20**	**0**	**0**
Final (M)	**0**	**0.20**	**0.20**

pOH = - log [OH⁻]

= - log (0.20)

= 0.6989

pH = 14-pOH

= 14- 0.6989

= 13.30

HELPFUL TIPS

$$pH = -\log [H^+]$$

$$pOH = -\log [OH^-]$$

$$pH + pOH = 14$$

pH scale

0   7   14

acidic   neutral   basic

$[H^+] > [OH^-]$ $[H^+] = [OH^-]$ $[H^+] < [OH^-]$

Consider the acid-base conjugate pair of ammonium ion, NH_4^+ and ammonia, NH_3.

The dissociation of both species in water is given by,

$$NH_4^+(aq) \ + \ H_2O(l) \ \rightleftharpoons \ NH_3(aq) \ + \ \textcolor{red}{H_3O^+(aq)}$$

$$NH_3(aq) \ + \ H_2O(l) \ \rightleftharpoons \ NH_4^+(aq) \ + \ \textcolor{red}{OH^-(aq)}$$
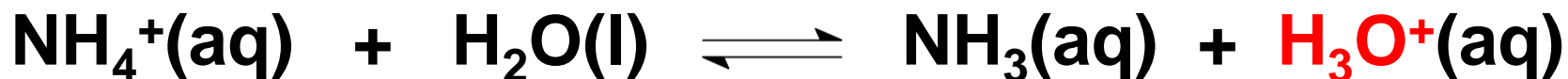
For ammonium ion, NH_4^+ the expression corresponding to K_a is :
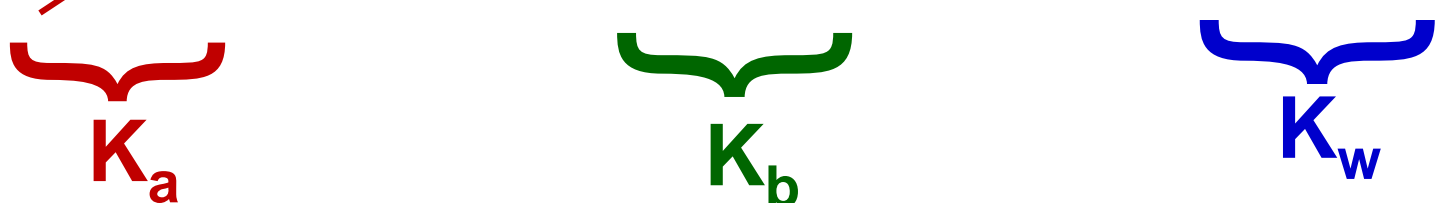
$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

For ammonia, NH_3 the expression corresponding to K_b is :

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Therefore, the product of K_a x K_b is:

$$\frac{[NH_3][H_3O^+]}{[NH_4^+]} \quad X \quad \frac{[NH_4^+][OH^-]}{[NH_3]} = [H_3O^+][OH^-]$$

$$\underbrace{}_{K_a} \qquad \underbrace{}_{K_b} \qquad \underbrace{}_{K_w}$$

$$K_a \ x \ K_b \ = \ K_w$$

$$- \log K_a \ + (- \log K_b) = - \log K_w$$

The equation above can be written as,

$$pK_a \ + \ pK_b = pK_w \ = \ 14$$

The Strengths of Acids And Bases

The strengths of acids and bases can be compared in terms of:

i. the degree of dissociation (α)

ii. the dissociation constant (*K*)

7.1 g) Degree of dissociation (α)

Ability of acids or bases to ionize or dissociate in aqueous solution

$$\alpha = \frac{\text{Concentration of acid or base dissociation}}{\text{Initial concentration}}$$

$$\alpha = \frac{x}{[\text{initial}]}$$

Example 1 :

Calculate the percent dissociation if amount of H^+ dissociated in a solution of 0.10 M acetic acid is 1.3×10^{-3} M.

ANSWER:

Percent dissociation $= \dfrac{1.3 \times 10^{-3}}{0.10} \times 100\%$

$= 1.3\%$

K_a or K_b value can be used to distinguish the relative acidity strength of weak acid and weak base.

☞ $K_a \uparrow$ (p$K_a \downarrow$) , $[H^+] \uparrow$, thus pH $\downarrow$ (more acidic)

☞ $K_b \uparrow$ (p$K_b \downarrow$) , $[OH^-] \uparrow$, thus pH $\uparrow$ (more basic)

Acid	pK_a		Base	pK_b
CH_3COOH	4.74		$C_6H_5NH_2$	9.37
HCOOH	3.76		NH_3	4.74

Conclusion :

➢ Relative acidity, HCOOH > CH_3COOH

➢ Relative basicity, NH_3 > $C_6H_5NH_2$

EXERCISE 1:

Find the values of [H$^+$] that correspond to each

of the following values of pH.

a) 2.90   (the approximate pH of lemon juice)

b) 11.61 (the pH of dilute, household ammonia)

Answer:
a.   1.26 x 10^{-3} *M*
b.   2.455 x 10^{-12} *M*

Solving Problems Involving Weak Acid & Weak Base Equilibria

Two general types of problems:

1. Equilibrium concentrations

☞ **find K_a (or K_b)**

2. K_a (or K_b) and some concentrations information are given.

☞ **find the other equilibrium concentrations.**

USE *ICE* TABLE

ASSUMPTIONS:

1. If the formation of H_3O^+ is very small,

   ☞ **therefore $[H_3O^+]$ is negligible**

2. A weak acid has a small K_a, ($K_a \leq 1.0 \times 10^{-5}$),

   ☞ x **is very small**

   ☞ $[\quad]_{initial} - x = [\quad]_{initial}$

apply 5% test to check the assumption is justified

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Degree of dissociation of 1.0 M solution of hydrazine, N_2H_4 at 25ºC is 3.5%. What is its base dissociation constant, K_b?

Answer :

$$\text{\% ionization of } N_2H_4 = \frac{\text{concentration dissociated } (x)}{\text{initial concentration } (c)} \times 100$$

$$3.5\ \% = \frac{x\ \text{M}}{1.0\ \text{M}} \times 100$$

$$x = 0.035\ \text{M}$$

	$N_2H_{4\ (aq)}$ + $H_2O_{(l)}$ $\rightleftharpoons$ $OH^-_{(aq)}$ + $N_2H_5^+_{(aq)}$			
Initial (M)	1.0	-	0	0
Change (M)	- 0.035	-	+ 0.035	+ 0.035
Equilibrium (M)	1.0 - 0.035 = 0.965	-	0.035	0.035

At equilibrium, K_b = $\dfrac{[N_2H_5^+]\,[OH^-]}{[N_2H_4]}$

$$= \frac{(0.035)\,(0.035)}{(0.965)} \quad = \quad 1.27 \times 10^{-3}$$

 Calculate the pH of a 0.20 M solution of HCN.
   [K_a for HCN is 4.90×10^{-10}.]

Answer :

	$HCN_{(aq)}$ + $H_2O_{(l)}$ $\rightleftharpoons$ $H_3O^+_{(aq)}$ + $CN^-_{(aq)}$			
Initial (M)	0.2	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	0.2 - x	-	x	x

K_a = $\dfrac{[H_3O^+]\,[CN^-]}{[HCN]}$ = 4.90×10^{-10}

 $K_a <<< 1$

∴ Assume x very small, therefore:

   $0.20 - x \approx 0.20$

$$4.90 \times 10^{-10} = \frac{(x)\,(x)}{(0.2)}$$

$$x^2 = (4.9 \times 10^{-10}\ M)\,(0.20\ M)$$

$$x = 9.9 \times 10^{-6}\ M$$

Therefore,

$$[H^+] = 9.9 \times 10^{-6}\ M$$

$$pH = -\log [H^+]$$

$$= \mathbf{\color{red}{5.00}}$$

Example 3:

The K_a for formic acid (HCOOH) is 1.8×10^{-4}. What is the pH of a 0.010 M solution of formic acid?

Answer :

	HCOOH$_{(aq)}$ + H$_2$O$_{(l)}$ $\rightleftharpoons$ H$_3$O$^+_{(aq)}$ + HCOO$^-_{(aq)}$			
Initial (M)	0.01	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	0.01 - x	-	x	x

At equilibrium,

$$K_a \quad = \quad \frac{[H_3O^+][HCOO^-]}{[HCOOH]} \quad = \quad 1.8 \times 10^{-4}$$

$K_a \ggg 1.0 \times 10^{-5}$

solve the calculation with quadratic equation. 39

$$1.8 \times 10^{-4} = \frac{(x)(x)}{(0.01 - x)}$$

$$x^2 = (1.8 \times 10^{-4})(0.01 - x)$$

$$x^2 + 1.8x \times 10^{-4}x - 1.8 \times 10^{-6} = 0$$

$$x_1 = 1.255 \times 10^{-3} \qquad x_2 = -1.435 \times 10^{-3} \text{ (neglected)}$$

$$[H^+] = 1.255 \times 10^{-3} \text{ M}$$

Therefore, $\text{pH} = -\log[H^+]$

$$= -\log(1.255 \times 10^{-3})$$

$$= \textbf{2.90}$$

Example 4:

The base-dissociation constant for ammonia, $NH_{3(aq)}$ is 1.8 x 10^{-5} M. Calculate the concentration of OH^- ion, pH and % dissociation at equilibrium if the initial concentration of NH_3 is 0.15 M.

Answer :

	$NH_{3\ (aq)}$ + $H_2O_{(l)}$ $\rightleftharpoons$ $OH^-_{(aq)}$ + $NH_4^+_{(aq)}$			
Initial (M)	0.15	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	0.15 - x	-	x	x

At equilibrium,

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$= \frac{(x)(x)}{(0.15 - x)} = 1.80 \times 10^{-5}$$

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$K_b <<< 1$

$\therefore$ Assume x very small, therefore:

0.15 − x ≈ 0.15

$$1.80 \times 10^{-5} = \frac{(x)\,(x)}{(0.15)}$$

x^2 = (1.8 x 10⁻⁵ M) (0.15 M)

x = 1.64 x 10⁻³ M

Therefore,

[OH⁻] = 1.64 x 10⁻³ M

pOH = -log [OH⁻]

= **2.79**

pH + pOH = 14

pH = 14 – 2.79
= 11. 21

% dissociation = $\dfrac{1.64 \times 10^{-3}}{0.15} \times 100\%$

= 1.09 %

≈ 1.1 %

Degree of dissociation, α **= 0.011**

7.1 h) Salt Hydrolysis

Salt is an ionic compound that is formed by the reaction of an acid with a base.

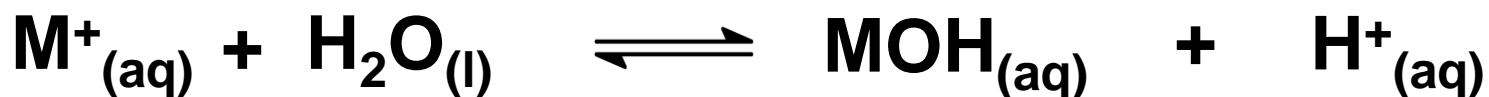General equation of neutralization:

$$\textbf{HX} \quad + \quad \textbf{MOH} \quad \longrightarrow \quad \textbf{MX} \quad + \quad \textbf{H}_2\textbf{O}$$

acid $\qquad$ base $\qquad\qquad$ salt $\qquad$ water
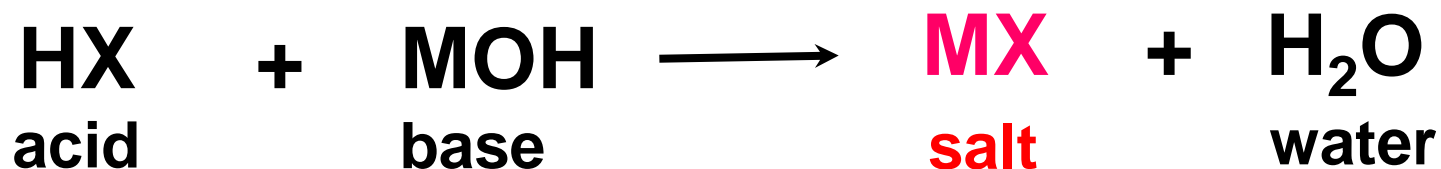
Hydrolysis is the reaction of cations/anions (or both) from salts with water molecules to produce H^+ or OH^-
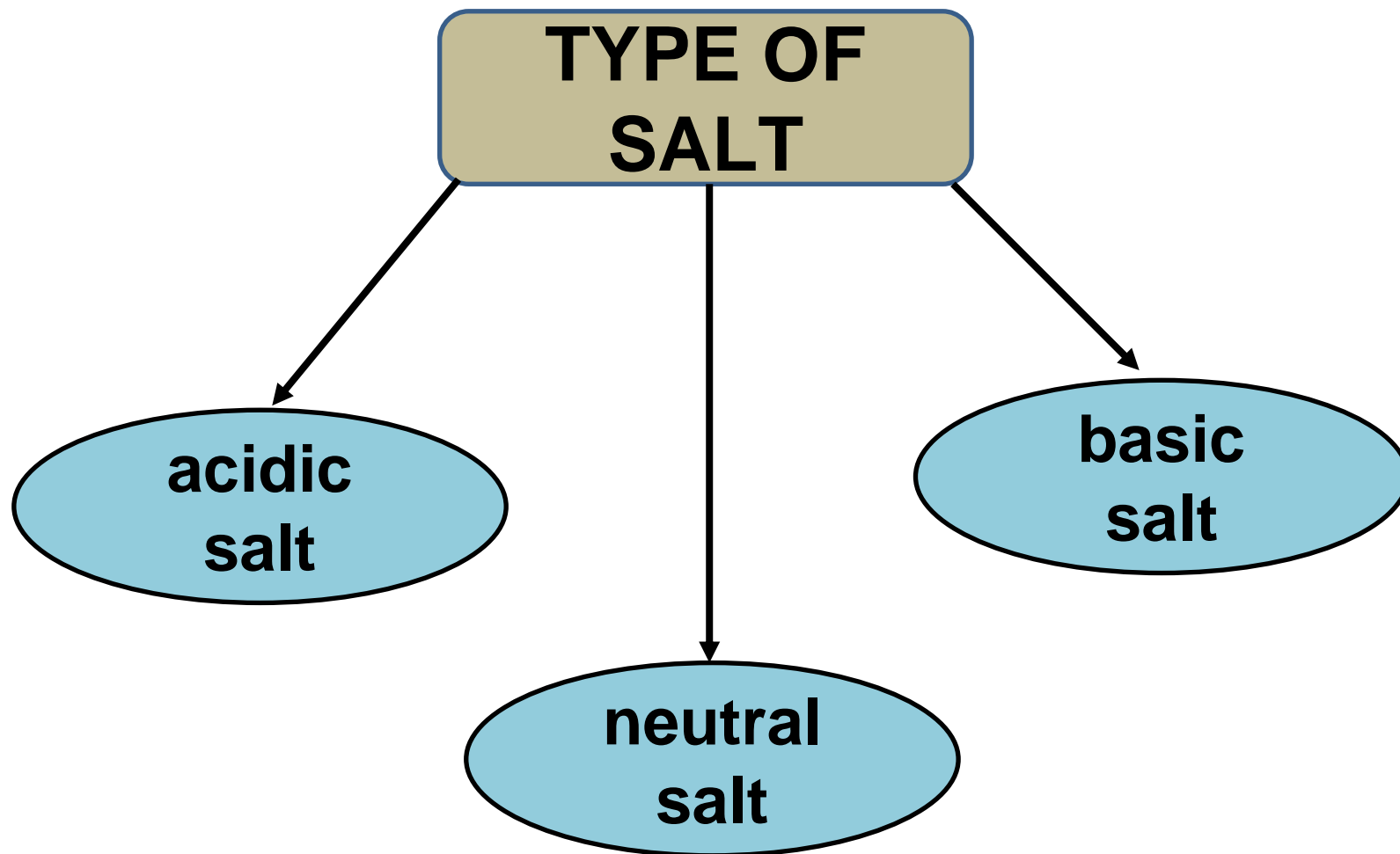
MX salt dissociation equation:

$$MX \longrightarrow M^+ + X^-$$

cation   anion

Cation Hydrolysis :

$$M^+_{(aq)} + H_2O_{(l)} \rightleftharpoons MOH_{(aq)} + H^+_{(aq)}$$

Anion Hydrolysis :

$$X^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HX_{(aq)} + OH^-_{(aq)}$$

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TYPE OF SALT

acidic salt

neutral salt

basic salt

Neutral Salt

* **Produced when a strong acid reacts with a strong base.**

* **Example: Sodium chloride, NaCl**

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

strong acid   **strong base**   **salt**
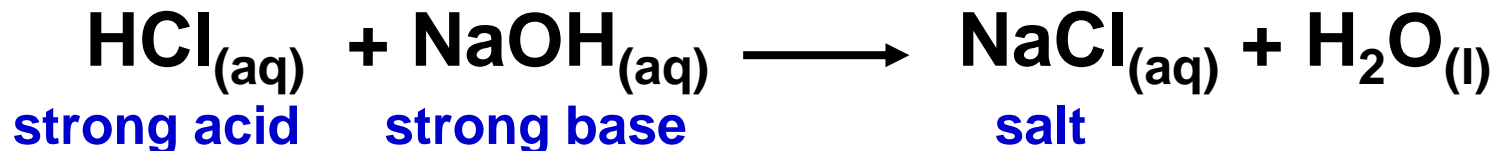
* **Dissociation of salt :**

$$NaCl_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

Neutral Salt

* Na^+ is **cation** of **strong base**, NaOH

☞ Na^+ **does not hydrolyzed** in water

* Cl^- is **anion** comes from **strong acid, HCl**

☞ Cl^- **does not hydrolyzed** in water

Neutral Salt

So, **pH** of a **solution** depends on the **autoionization of water**

$$H_2O_{(l)} \; + \; H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} \; + \; OH^-_{(aq)}$$

$$K_w \; = [H_3O^+] \; [OH^-]$$
$$= 1 \times 10^{-14}$$

$$[H^+] \; = \; [OH^-] \; = 1.0 \times 10^{-7} \, M$$

☞ pH = 7

Basic Salt

* Produced from the reaction of weak acid and strong base.
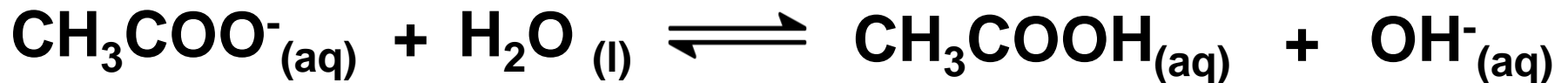
* Example : Sodium ethanoat, CH_3COONa

$$CH_3COONa_{(aq)} \longrightarrow Na^+_{(aq)} + CH_3COO^-_{(aq)}$$

Basic Salt

* **Na$^+$ is cation of strong base, NaOH**

   ☞ **Na$^+$ does not hydrolyzed in water**

* **CH$_3$COO$^-$ is conjugate base of weak acid, CH$_3$COOH**

   ☞ **CH$_3$COO$^-$ is hydrolyzed in water to produce OH$^-$**

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

☞ **The solution is basic because OH$^-$ formed**

☞ **pH > 7.0**

Acidic Salt

* **Produced from the reaction of strong acid and weak base.**

* **Example : Ammonium chloride, NH_4Cl**

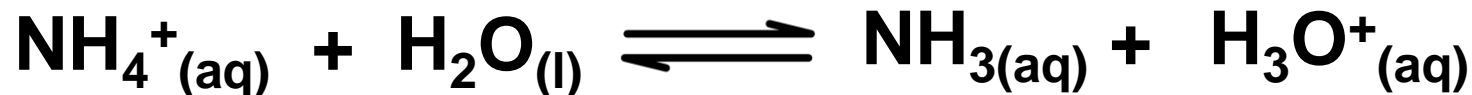$$NH_4Cl_{(s)} \xrightarrow{H_2O} NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

Acidic Salt

* Cl^- is anion of strong acid, HCl

☞ Cl^- does not hydrolyzed in water

* NH_4^+ is conjugate acid of weak base, NH_3

☞ NH_4^+ is hydrolyzed in water to produce H_3O^+

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)}$$

☞ The solution is acidic because H_3O^+ formed

☞ pH < 7.0

Example 1:

Sodium cyanide, NaCN is a salt formed when a strong base, NaOH is reacted with a weak acid, HCN.

Write a balanced equation to show the reaction between NaOH and HCN. Classify the salt formed.

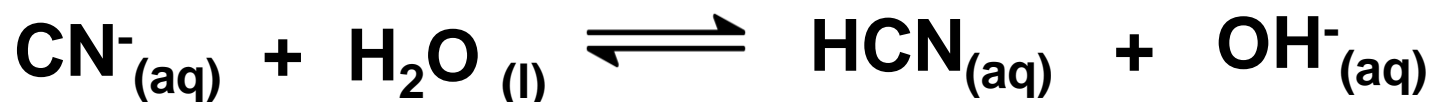**What would be expected pH of the NaCN solution? Explain the answer using equation(s).**

Answer :

* **Na⁺ is cation of strong base, NaOH**

☞ **Na⁺ does not hydrolyzed in water**

* **CN⁻ is conjugate base of weak acid, HCN**

☞ **CN⁻ is hydrolyzed in water to produce OH⁻**

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$$
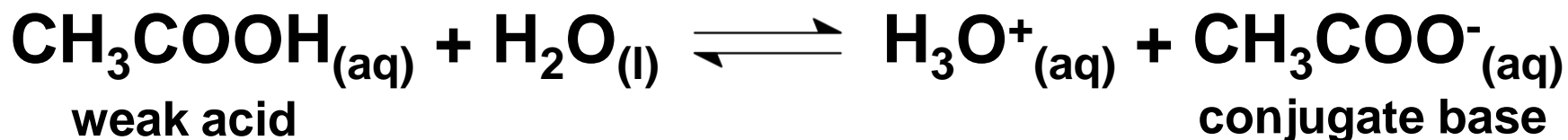
☞ **The solution is basic because OH⁻ formed**

☞ **pH > 7.0**

7.1 j) Buffer Solutions

- A solution which has the **ability to maintain its pH** when a small amount of **strong acid or strong base** is added to the solution.

- Two types of buffer solutions :

  i.   acidic buffer solution (pH < 7)

  ☞ a solution that contains a weak acid and its salt (or its conjugate base)

  ii.   basic buffer solution (pH > 7)

  ☞ a solution that contains a weak base and its salt (or its conjugate acid)
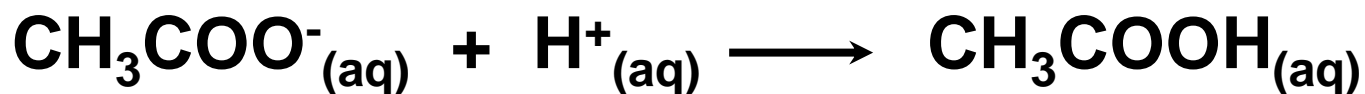
Acidic Buffer Solution

☞ **A solution that contains a mixing of weak acid and its salt (or its conjugate base).**

☞ **Example : CH_3COOH and CH_3COONa.**

$$CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$
  weak acid   **conjugate base**

7.1 k) How the Acidic Buffer Solution Works?

When a small amount of strong acid is added,

☞ **The H^+ ions will be react with ethanoate ion, CH_3COO^- to form CH_3COOH.**

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \longrightarrow CH_3COOH_{(aq)}$$

☞ **As a result, [CH_3COOH] increases and [CH_3COO^-] decreases.**

☞ **[H^+] & [OH^-] remains constant.**

☞ **Therefore, pH not much affected.**

How the Acidic Buffer Solution Works?

When a small amount of strong base is added,

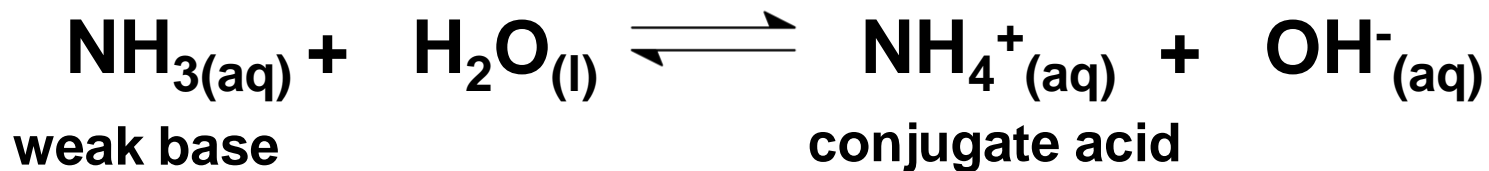☞ The OH$^-$ ions will be neutralized by the acid, CH_3COOH to form CH_3COO^- and H_2O.

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$$
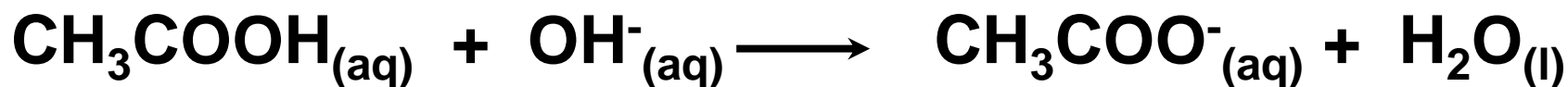
☞ As a result, $[CH_3COO^-]$ increases and $[CH_3COOH]$ decreases.

☞ $[H^+]$ & $[OH^-]$ remains constant.

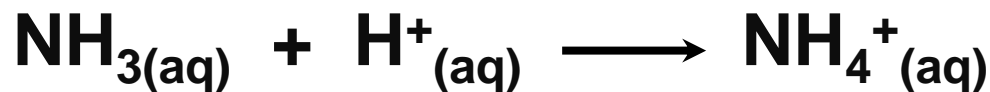☞ Therefore, pH not much affected.

Basic Buffer Solution

☞ **A solution that contains a mixing of weak base and its salt (or its conjugate acid).**

☞ **Example : NH_3 and NH_4Cl**

$$NH_4Cl_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

weak base   conjugate acid

How the Basic Buffer Solution Works?

When a small amount of strong acid is added,

☞ **The H$^+$ ions will be consumed by the ammonia, NH$_3$ to form NH$_4^+$ ion.**

$$NH_{3(aq)} + H^+_{(aq)} \longrightarrow NH_4^+_{(aq)}$$

☞ **As a result, [NH$_4^+$] increases and [NH$_3$] decreases.**

☞ **[H$^+$] & [OH$^-$] remains constant.**

☞ **Therefore, pH not much affected.**

How the Basic Buffer Solution Works?

When a small amount of strong base is added,

☞ The OH$^-$ ions will be neutralised by the ammonium ions, NH$_4$$^+$ to form NH$_3$ and H$_2$O.

$$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \longrightarrow NH_{3(aq)} + H_2O_{(l)}$$

☞ As a result, [NH$_3$] increases and [NH$_4$$^+$] decreases.

☞ [H$^+$] & [OH$^-$] remains constant.

☞ Therefore, pH not much affected.

7.1 I) Henderson-Hasselbalch Equation & Its Application

Acidic Buffer Solution

☞ **Example : CH_3COOH and CH_3COONa.**

☞ **Equations :**

$$CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

weak acid   **conjugate base**
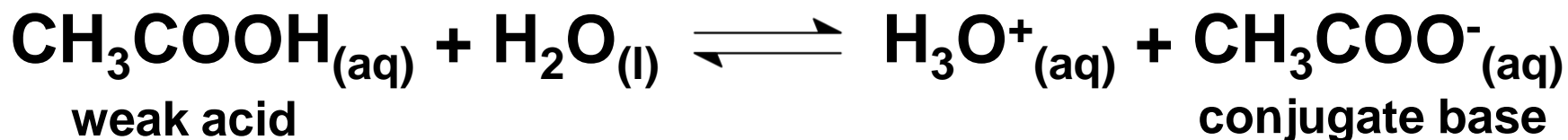
☞ **Henderson-Hasselbalch equation :**   **salt**

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

Acidic Buffer Solution

☞ **From the equations :** $K_a = \dfrac{[CH_3COO^-]\,[H_3O^+]}{[CH_3COOH]}$

∴ **Henderson-Hasselbalch equation for acidic buffer solution:**

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pK_a = -\log K_a$$

A buffer solution is prepared by adding 2.00 g of benzoic acid, C_6H_5COOH & 2.00 g sodium benzoate, C_6H_5COONa in enough water to make 1.00 L solution.
(K_a (C_6H_5COOH) = 6.3 x 10^{-5} M)

(i) Write its Henderson-Hasselbalch equation.

(ii) Calculate the pH of a solution.

$$C_6H_5COONa_{(aq)} \longrightarrow C_6H_5COO^-_{(aq)} + Na^+_{(aq)}$$

$$C_6H_5COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons C_6H_5COO^-_{(aq)} + H_3O^+_{(aq)}$$

weak acid   **conjugate base**
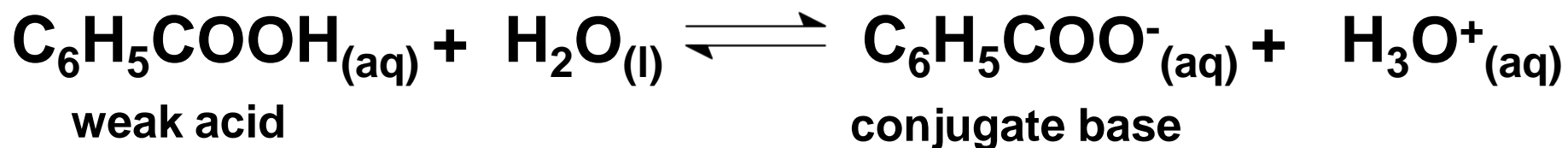
∴ **Henderson-Hasselbalch equation :**

$$pH = pK_a + \log \frac{[\, C_6H_5COO^- \,]}{[\, C_6H_5COOH \,]}$$

Mol C_6H_5COOH = $\dfrac{\text{2.00 g}}{\text{122.1 g mol}^{-1}}$ **= 1.64 x 10^{-2} mol**

$[C_6H_5COOH]$ = $\dfrac{\text{1.64 x }10^{-2}\text{ mol}}{\text{1.00 L}}$ **= 1.64 x 10^{-2} M**

Mol $C_6H_5COO^-$ = $\dfrac{\text{2.00 g}}{\text{144 g mol}^{-1}}$ **= 1.39 x 10^{-2} mol**

$[C_6H_5COO^-]$ = $\dfrac{\text{1.39 x }10^{-2}\text{ mol}}{\text{1.00 L}}$ **= 1.39 x 10^{-2} M**

$$pH = pK_a + \log \frac{[\, C_6H_5COO^- \,]}{[\, C_6H_5COOH \,]}$$

$$pH = -\log 6.3 \times 10^{-5} + \log \frac{1.39 \times 10^{-2}}{1.64 \times 10^{-2}}$$

$$= \mathbf{4.13}$$
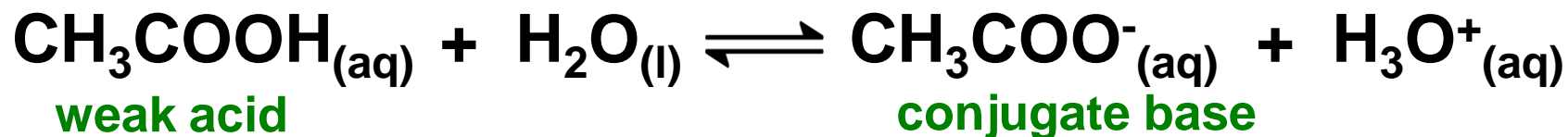
A buffer solution is prepared by dissolving 0.025 mol CH_3COONa in 250 cm³ aqueous solution of CH_3COOH (0.10 mol dm⁻³). Calculate the pH of the buffer solution.

K_a (CH_3COOH) = 1.74 x 10⁻⁵ moldm⁻³

(Assume addition of CH_3COONa does not change the volume of solution)

Answer :

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

weak acid   **conjugate base**

$$CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

$$[CH_3COO^-] = \frac{0.025 \text{ mol}}{0.250 \text{ dm}^3} = 0.10 \text{ mol dm}^{-3}$$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= -\log(1.74 \times 10^{-5}) + \log \frac{0.10}{0.10}$$

$$= 4.76$$

Basic Buffer Solution

☞ **Example : NH_3 and NH_4Cl**

☞ **Equations :**

$$NH_4Cl_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

weak base   **conjugate acid**
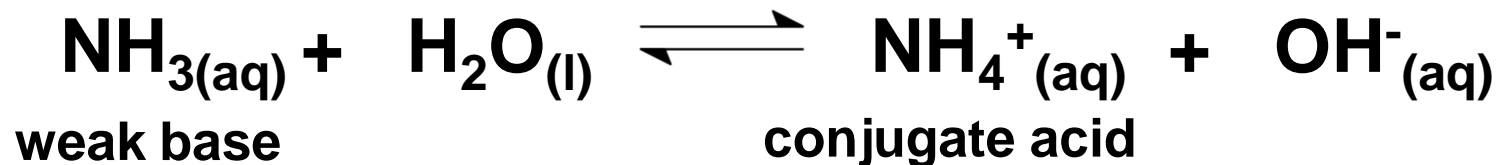
☞ **Henderson-Hasselbalch equation :**   **salt**

$$pOH = pK_b + \log \frac{[conjugate\ acid]}{[weak\ base]}$$

Basic Buffer Solution

☞ **From the equations :** $K_b = \dfrac{[NH_4^+]\,[OH^-]}{[NH_3]}$

∴ **Henderson-Hasselbalch equation for basic buffer solution:**

$$pOH = pK_b + \log\dfrac{[\,NH_4^+\,]}{[\,NH_3\,]}$$

$$pK_b = -\log K_b$$
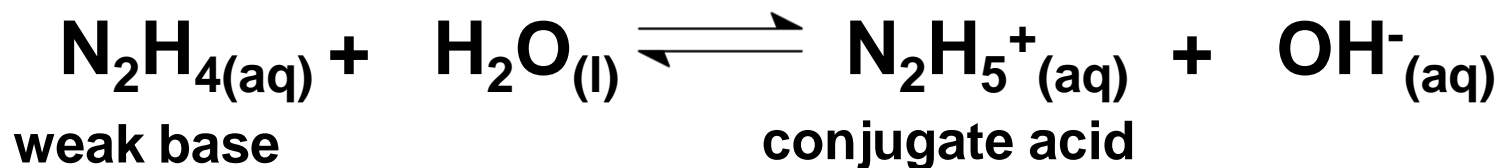
A buffer solution is prepared by mixing 500 mL 0.1 M hydrazinium chloride, N_2H_5Cl with 500 mL 0.2 M hydrazine, N_2H_4 .
(K_b = 1.7 x 10^{-7})

(i) Write its Henderson-Hasselbalch equation.

(ii) Calculate the pH of a solution.

Equations :

$$N_2H_5Cl_{(aq)} \longrightarrow N_2H_5^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$$N_2H_{4(aq)} + H_2O_{(l)} \rightleftharpoons N_2H_5^+{}_{(aq)} + OH^-{}_{(aq)}$$

weak base   **conjugate acid**

∴ **Henderson-Hasselbalch equation :**

$$pOH = pK_b + \log \frac{[N_2H_5^+]}{[N_2H_4]}$$

Answer :

salt

No. of moles of $N_2H_5^+$ = $\dfrac{500 \text{ mL} \quad \text{x} \quad 0.1 \text{ M}}{1000}$

= 0.05 moles

$\dfrac{\text{No. of mole}}{\text{Volume of solution (L)}}$

$500 \text{mL } N_2H_5Cl + 500 \text{mL } N_2H_4$

$[N_2H_5^+] = \dfrac{0.05}{(0.50 + 0.50)}$

= 0.05 M

No. of moles of N_2H_4 = $\dfrac{500 \text{ mL} \times 0.2 \text{ M}}{1000}$ **= 0.1 mol**

$$[N_2H_4] = \dfrac{0.1}{(0.50 + 0.50)} = 0.1 \text{ M}$$

pOH = pK_b + log $\dfrac{[\,N_2H_5^+\,]}{[\,N_2H_4\,]}$

pOH = -log (1.7 x 10^{-7}) + log $\dfrac{0.05}{0.1}$

= 6.47

pH = 14 - pOH
= 14 - 6.47
= 7.53

7.1 m) Calculation pH of buffer solution before and after the addition of strong acid or base

Calculate the change in pH when 1.00 cm³ of 1.00 M NaOH is added to a 1.00 dm³ buffer solution which contains a mixture of 0.10 M, CH₃COOH and 0.10 M CH₃COONa (pKₐ CH₃COOH = 4.750)

(NaOH), 1.0 cm³, (strong base)

CH₃COOH, 0.1M (weak acid)

CH₃COONa, 0.1 M (salt)

$V_{buffer} = 1.0\ dm^3$

pH before addition of NaOH

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= 4.750 + \log \frac{0.10}{0.10}$$

$$= \textcolor{red}{4.75}$$

pH after addition of NaOH

No. of moles of OH$^-$ ions in   = $\dfrac{1.0 \times 1.0}{1000}$
1.0 cm^3 of 1.0 mol dm^{-3} NaOH

$$= 1 \times 10^{-3} \text{ mol}$$

No. of moles of CH$_3$COOH = 0.1 x1.0 = 0.1 mol

No. of moles of CH$_3$COO$^-$ = 0.1 x 1.0 = 0.1 mol

Final volume of buffer = 1.001 dm^3

Buffer action :

	$CH_3COOH_{(aq)}$ +	$OH^-_{(aq)}$ $\longrightarrow$	$CH_3COO^-_{(aq)}$ +	$H_2O_{(l)}$
$(mol)_{initial}$	0.100	1×10^{-3}	0.100	-
$(mol)_{change}$	-1×10^{-3}	-1×10^{-3}	$+1 \times 10^{-3}$	-
$(mol)_{equilibrium}$	0.099	0	0.101	-

$$[CH_3COOH]_{new} = \frac{0.099}{1.001} \qquad\qquad [CH_3COO^-]_{new} = \frac{0.101}{1.001}$$

$$= 0.0989 \text{ M} \qquad\qquad\qquad\qquad = 0.1009 \text{ M}$$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= 4.750 + \log \frac{0.1009}{0.0989} \qquad = 4.75$$

Change in pH = 4.76 - 4.75 = 0.01 (small increase in pH)

Example 5:

A solution is made by mixing 500.00 cm^3 of 2.00 M butanoic acid with 500.00 cm^3 of 0.50 M sodium butanoate. Calculate the change in pH when 1.00 cm^3 of 0.50 M HCl is added to 1.00 dm^3 of the buffer solution. K_a for butanoic acid is 1.5 x 10^{-5}.

1.00 cm^3, 0.5 M HCl
(strong acid)

500 cm^3, 2.0 M
CH$_3$CH$_2$CH$_2$COOH
(weak acid)

500 cm^3, 0.5M
CH$_3$CH$_2$CH$_2$COONa
(salt)

V$_{buffer}$ = (500 + 500 cm^3)
= 1000 cm^3
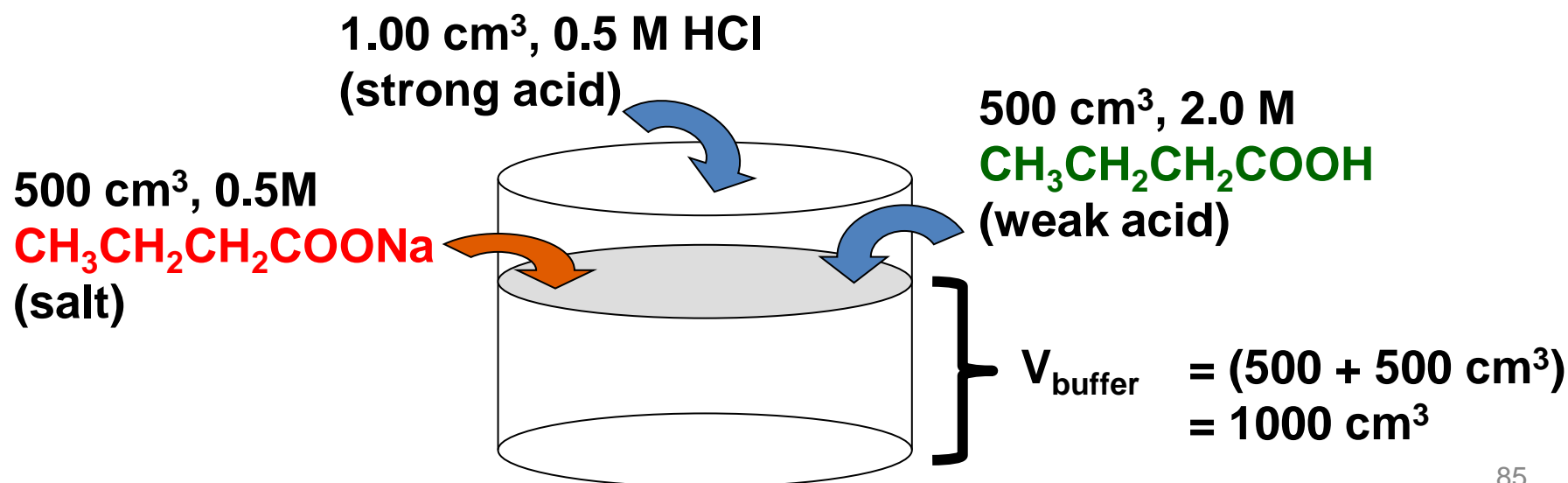
Answer :

pH before addition of HCl

Mol $CH_3CH_2CH_2COOH$ **=** **$\dfrac{2.0 \times 500}{1000}$** **= 1.00 mol**

Mol $CH_3CH_2CH_2COO^-$ **=** **$\dfrac{0.5 \times 500}{1000}$** **= 0.25 mol**

volume of buffer solution = 500+500 = 1000 cm^3 = 1 L

$[CH_3CH_2CH_2COOH]$ **=** **$\dfrac{1.00}{1.00}$** **= 1.00 M**

$[CH_3CH_2CH_2COO^-]$ **=** **$\dfrac{0.25}{1.00}$** **= 0.25 M**

pH before the addition of HCl

$$pH = pK_a + \log \frac{[CH_3CH_2CH_2COO^-]}{[CH_3CH_2CH_2COOH]}$$

$$= -\log(1.50 \times 10^{-5}) + \log \frac{0.25}{1.00}$$

$$= 4.2218$$

pH after the addition of HCl

No. of moles of HCl added $= \dfrac{0.5 \times 1.00}{1000}$

$= 5.0 \times 10^{-4}$ mol

Final volume of buffer $= 1000 + 1.00 = 1001$ cm^3

$= 1.001$ L

Buffer action :

	$CH_3CH_2CH_2COO^-_{(aq)}$ +	$H^+_{(aq)} \longrightarrow$	$CH_3CH_2CH_2COOH_{(aq)}$
(mol)$_{initial}$	0.250	5×10^{-4}	1.000
(mol)$_{change}$	$- 5 \times 10^{-4}$	$- 5 \times 10^{-4}$	$+ 5 \times 10^{-4}$
(mol)$_{final}$	0.2495	0	1.0005

$$[CH_3CH_2CH_2COO^-]_{new} = \frac{0.2495}{1.001} = 0.2493 \text{ M}$$

$$[CH_3CH_2CH_2COOH]_{new} = \frac{1.0005}{1.001} = 0.9995 \text{ M}$$

$$pH = pK_a + \log \frac{[CH_3CH_2CH_2COO^-]}{[CH_3CH_2CH_2COOH]}$$

$$= 4.824 + \log \frac{0.2493}{0.9995} = 4.2209$$

Change in pH = 4.2218 - 4.2209 = 0.0009 (small decrease in pH)

A buffer solution is prepared by mixing 400 mL of

1.50 M NH_4Cl solution with 600 mL of 0.10 M NH_3.

(a) Calculate the pH of the buffer solution.

(b) Calculate the pH of the buffer solution after the addition of

(i) 0.015 mol NaOH

(ii) 0.011 mol HCl

(Assume that the volume of the solution does not

change when HCl and NaOH is added)

[K_b for NH_3 = 1.8 x 10^{-5}]

Answer :

(a) pH of the buffer solution

$$\text{Mol NH}_3 \ = \ \frac{0.1 \times 600}{1000} \ = 0.06 \text{ mol}$$

$$\text{Mol NH}_4^+ \ = \ \frac{1.5 \times 400}{1000} \ = 0.6 \text{ mol}$$

volume of buffer solution = 600+400 = 1000 cm^3 = 1.00 L

$$[\text{NH}_3] \ = \ \frac{0.06}{1.00} \ = 0.06 \text{ M}$$

$$[\text{NH}_4^+] \ = \ \frac{0.6}{1.00} \ = 0.6 \text{ M}$$

$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]}$$

$$= -\log (1.8 \times 10^{-5}) + \log \frac{0.6}{0.06}$$

$$= \textcolor{red}{5.74}$$

$$pH + pOH = 14$$

$$pH = 14 - 5.74$$

$$= \textcolor{red}{8.26}$$

b) (i) pH of the buffer solution after the addition of 0.015 mol NaOH

	$NH_4^+{}_{(aq)}$ +	$OH^-{}_{(aq)}$ $\longrightarrow$	$NH_{3(aq)}$ +	$H_2O_{(l)}$
(mol)$_{initial}$	0.60	0.015	0.06	-
(mol)$_{change}$	- 0.015	- 0.015	+ 0.015	-
(mol)$_{equilibrium}$	0.585	0	0.075	-

$$[\ NH_3\ ]_{new} \ = \ \frac{0.075}{1\ L} \qquad [\ NH_4^+\ ]_{new} \ = \ \frac{0.585}{1\ L}$$

$$= \ 0.075\ M \qquad\qquad = \ 0.585\ M$$

$$pOH \ = \ pK_b + \log\ \frac{[NH_4^+]}{[NH_3]}$$

$$= - \log (1.8 \times 10^{-5})\ + \log\ \frac{0.585}{0.075} = \ \textcolor{red}{5.64}$$

$$pH \ + \ pOH \ = \ 14$$

$$pH \ = \ 14 - 5.64 \ \textcolor{red}{= \ 8.36}$$

b) (ii) pH of the buffer solution after the addition of 0.011 mol HCl

	$NH_{3(aq)}$ +	$H^+_{(aq)}$ $\longrightarrow$	$NH_4^+{}_{(aq)}$
(mol)$_{initial}$	0.06	0.011	0.60
(mol)$_{change}$	- 0.011	- 0.011	+ 0.011
(mol)$_{final}$	0.049	0	0.611

$$[\text{NH}_3]_{new} = \frac{0.049}{1L}$$
$$= 0.049 \text{ M}$$

$$[\text{NH}_4^+]_{new} = \frac{0.611}{1L}$$
$$= 0.611 \text{ M}$$

$$= -\log(1.8 \times 10^{-5}) + \log\frac{0.611}{0.049} = \textcolor{red}{5.84}$$

$$pH + pOH = 14$$

$$pH = 14 - 5.84 = \textcolor{red}{8.16}$$

Exercise:

A solution is prepared by mixing 100 cm³ aqueous NH_3 (0.1M) with 100 cm³ NH_4Cl (1.0 M). Calculate the pH of the solution before and after the addition of 1 cm³ HCl (0.1 M). Comment on the result.

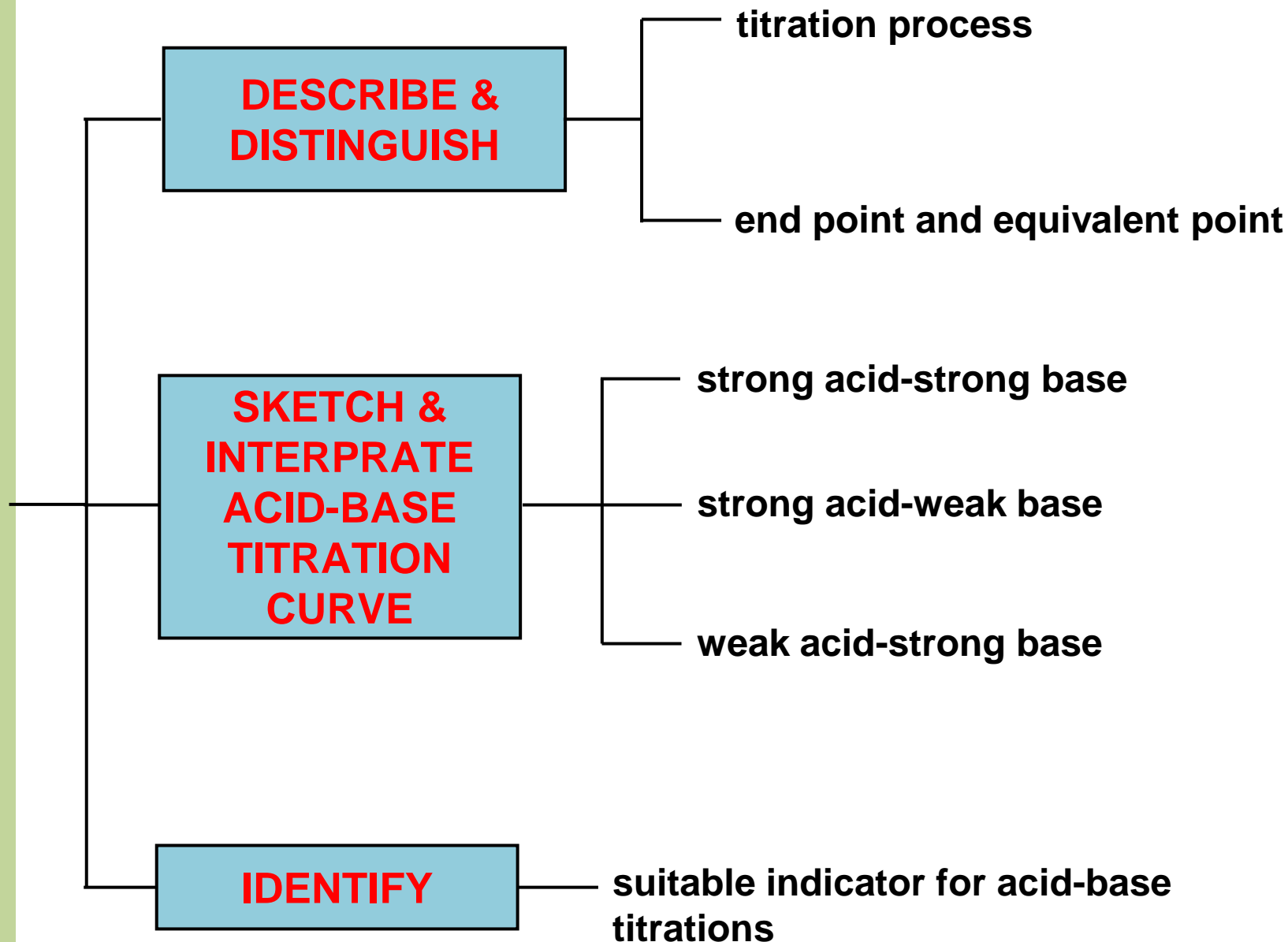$(K_b \text{ } NH_3 = 1.74 \times 10^{-5} \text{ M})$

Answer:
Before pH = 8.24
After pH = 8.24

7.2 ACID-BASE TITRATION

7.2 ACIDS – BASES TITRATION

DESCRIBE & DISTINGUISH
— titration process
— end point and equivalent point

SKETCH & INTERPRATE ACID-BASE TITRATION CURVE
— strong acid-strong base
— strong acid-weak base
— weak acid-strong base

IDENTIFY
— suitable indicator for acid-base titrations

TITRATION

Method for determining the concentration of an unknown solution by using another solution of known concentration (standard solution)

TITRANT

Standard solution is a solution of accurately known concentration

ANALYTE

The solution with unknown concentration

INDICATOR

A **weak organic acid** that has different color than it conjugate base and **color changes** occurring over a specific and relatively **narrow pH range**.
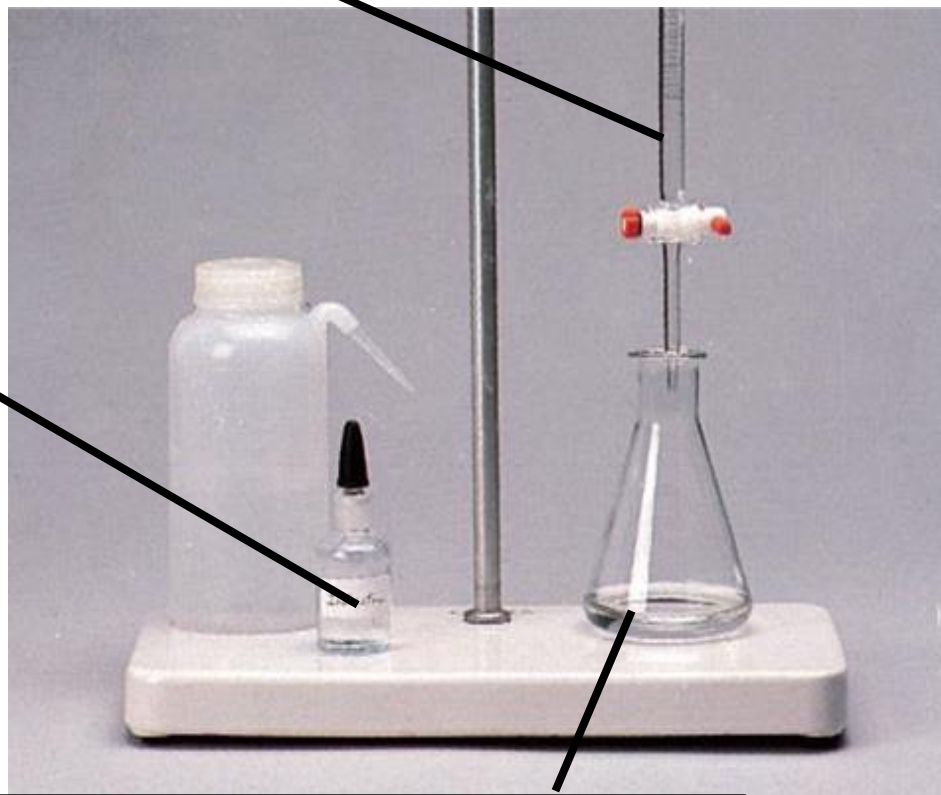
EQUIVALENT POINT

The point where the mole of acid and base is stoichiometrically equivalent @

mole of H$^+$ equals to mole of OH$^-$
(no more acid or base left in the solution)

END POINT

The point where an indicator **changes color**

Burette: (contains titrant) Concentration of solution inside: known Example: NaOH(*aq*)

Indicator: (Example: phenolphthalein)

Conical flask: (contains analyte) **Concentration** of solution inside: **unknown** Example: CH$_3$COOH(*aq*)

Acid-Base Titration Curve

A plot of the pH of a solution of acid (or base) versus the volume of base (or acid) added to the solution

TYPES OF TITRATION CURVE

✓ **Strong Acid-Strong Base**

✓ **Weak Acid-Strong Base**

✓ **Strong Acid-Weak Base**

weak acid-weak base titration not normally done because the equivalence point cannot be accurately observed.

How to Sketch a Titration Curve

1. Calculate the initial pH of an analyte (solution in the conical flask).

2. Determine the equivalence point : the volume and its pH.

3. Identify type of pH jump (steep portion)

4. Identify the final pH.
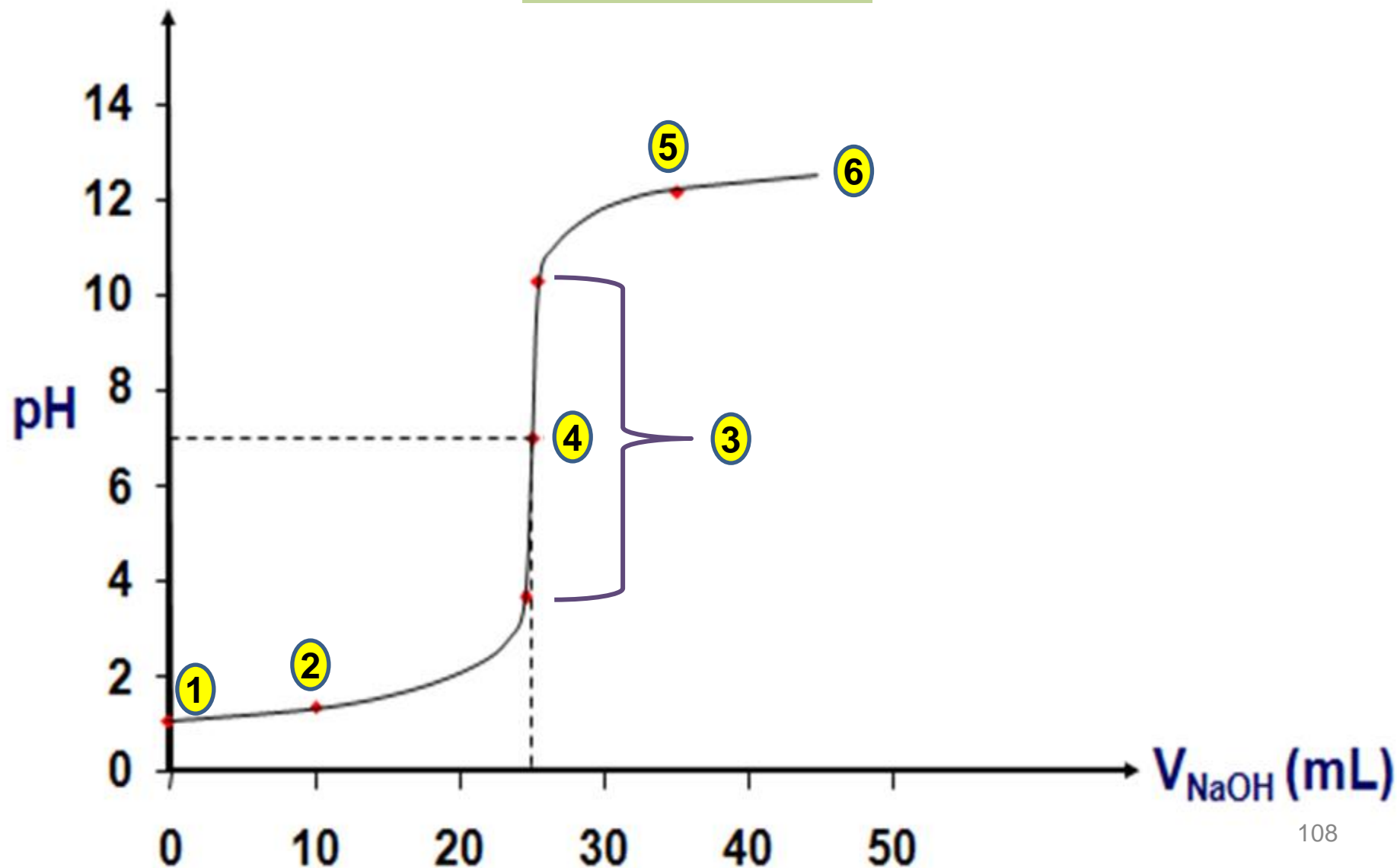   * depends on the [titrant] (solution in the burette).

pH Jump (Steep Portion / Sharp Portion)

* depends on the type of the titration

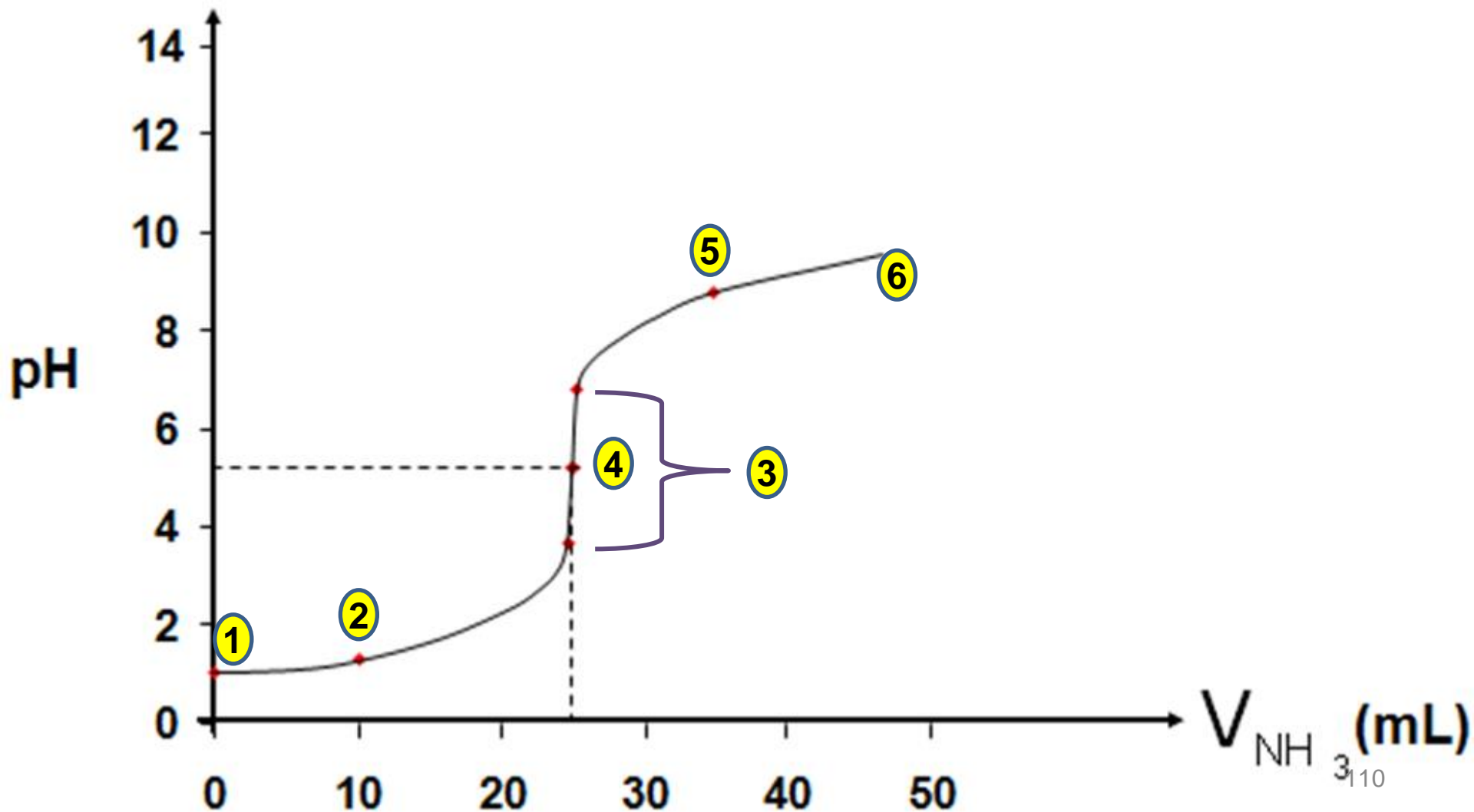| Type	pH jump
strong acid – strong base	3 – 11
strong acid – weak base	3 – 7
weak acid – strong base	7 – 11

Strong Acid-Strong Base Titration Curve

Example :

Description :

1. HCl as a strong acid. $pH = -\log [H_3O^+]$

2. NaOH is added. It makes $[H_3O^+]$ decreases. pH increases.

3. pH jump is 3-11

4. Equivalent point. Mole of H^+ equals to mole of OH^-. Neutral salt formed. pH = 7

5. Beyond equivalent point. pH increases slowly as excess OH^- added.

6. pH approaching 13.

Strong Acid-Weak Base Titration Curve

Example :

① **HCl as a strong acid. pH = - log [H$_3$O$^+$]**

② **NH$_3$ is added. It makes [H$_3$O$^+$] decreases. pH increases.**

③ **pH jump is 3-7**

④ **Equivalent point. Mole of H$^+$ equals to mole of OH$^-$. Acidic salt formed. pH < 7**

⑤ **Beyond equivalent point. pH increases slowly as excess OH$^-$ added.**

⑥ **pH approaching 11.**
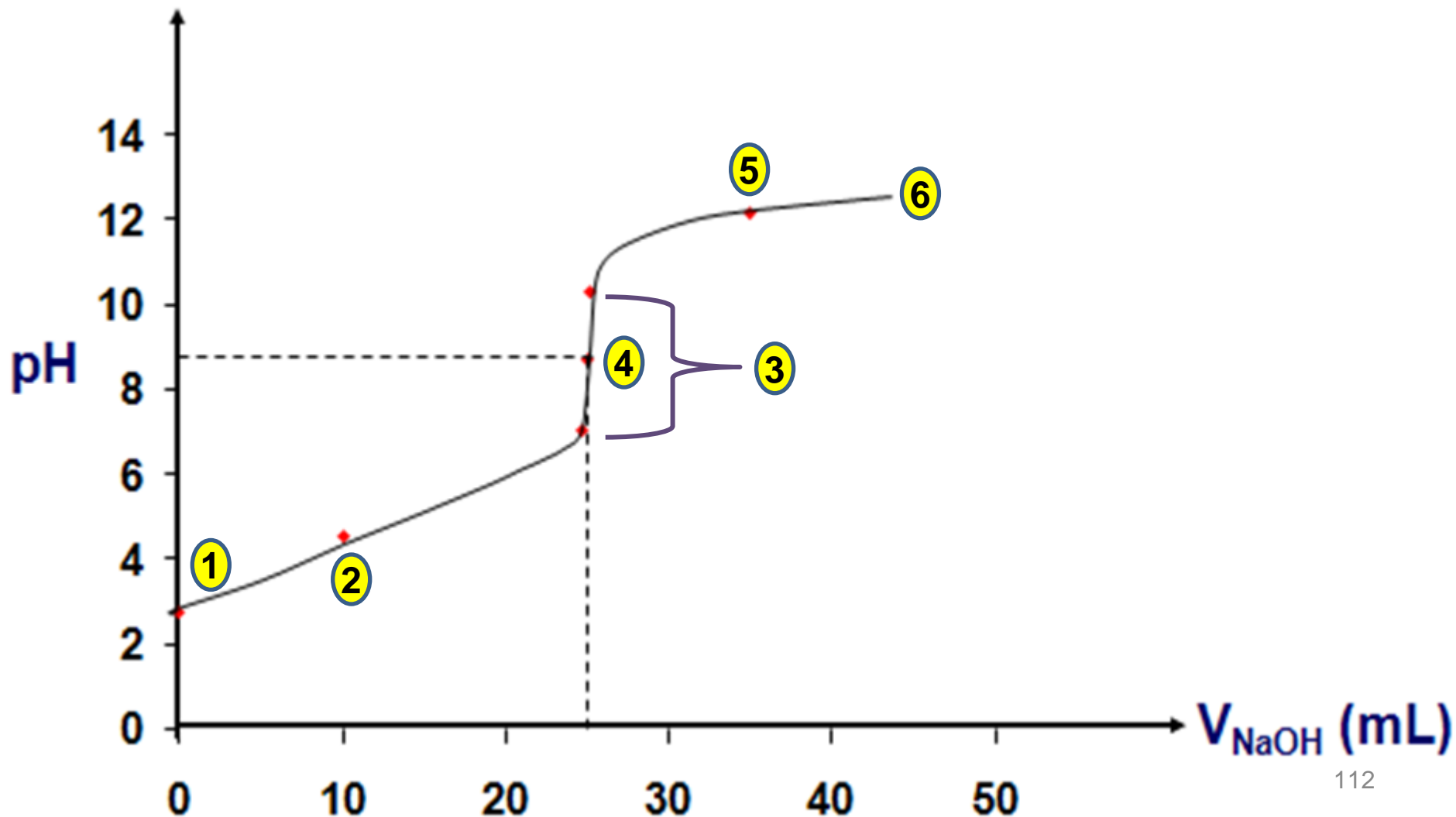
Strong Base-Weak Acid Titration Curve

Example :

Description :

1. CH_3COOH as a weak acid partially dissociate. The pH is about 2.8.

2. NaOH is added. It makes $[H_3O^+]$ decreases. pH increases.

3. pH jump is 7-11

4. Equivalent point. Mole of H^+ equals to mole of OH^-. Basic salt formed. pH > 7

5. Beyond equivalent point. pH increases slowly as excess OH^- added.

6. pH approaching 13.

Keep in mind!

- At the **midpoint** of the buffer region, **[base] = [acid]**, so the pH equals the pK_a

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

$$pH = pK_a + \log 1 = pK_a + 0$$

$$= pK_a$$

In fact, observing the **pH** at the **midpoint** of the buffer region is a common experimental method for **estimating the pK_a** of an unknown acid

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pH Calculation for Acid Base Titrations

Example 1 :

Sketch the titration curve of 25.0 mL 0.10 M HCl with 0.10 M NaOH.

Step 1 :

Analyte is a strong acid,

HCl – dissociates completely

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$[H^+] = [HCl] = 0.10 \text{ M}$$

$$pH = -\log[H^+]$$

$$= \textcolor{red}{1.0}$$

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

pH at equivalence:

- **the solution is NaCl (aq)**

- **both Na$^+$ and Cl$^-$ do not hydrolyse**

- **therefore pH = 7.0**

Volume equivalence:

$$n_{HCl} = n_{NaOH}$$

$$M_{HCl} \, V_{HCl} = M_{NaOH} \, V_{naOH}$$

$$V_{NaOH} = \frac{0.10 \times 25}{0.10} = 25 \text{ mL}$$

pH jump : 3 – 11 (strong acid-strong base)

Step 4 :

Titrant is a strong base, NaOH.

$$NaOH \ (aq) \longrightarrow Na^+ \ (aq) + OH^- \ (aq)$$

[OH-] = [NaOH] = 0.10 M

pOH = - log 0.10 = 1

pH = 14 – 1

        = 13

Final point approaching pH < 13.

Sketch a titration curve

pH

13

11

7

3

1

Equivalence point

25

Volume of NaOH added (mL)
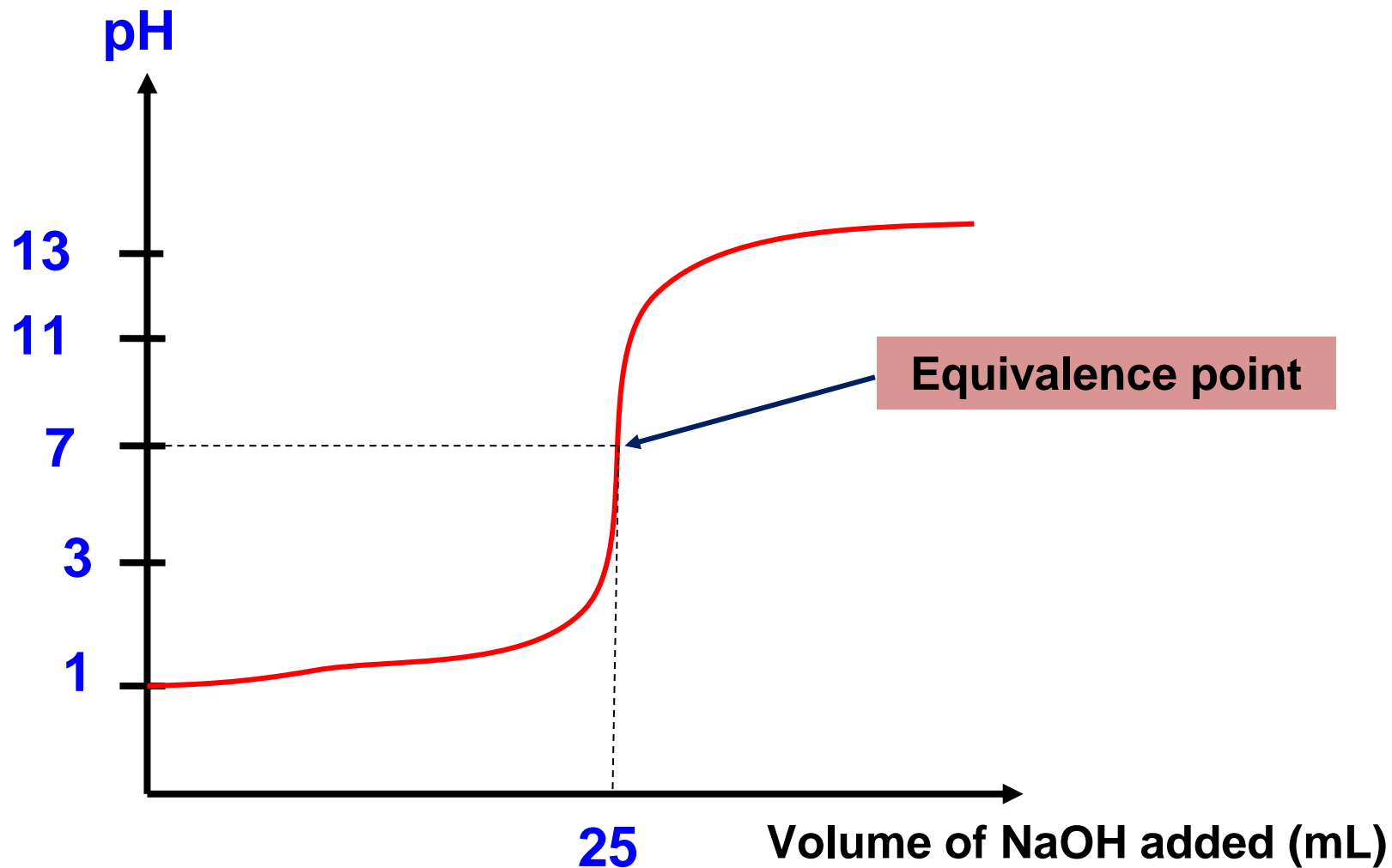
Example 2 :

Sketch the titration curve of 25.0 mL 0.10 M NH_3 and 0.10 M HCl.

Step 1 : Analyte is a weak base, NH_3

$$NH_3 \ (aq) \ + \ H_2O(l) \ \rightleftharpoons \ NH_4^+ \ (aq) + OH^- \ (aq)$$
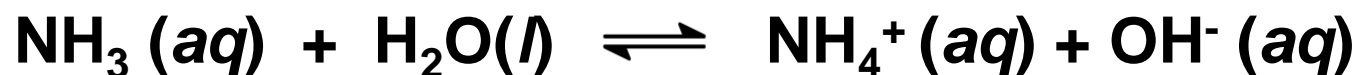
$$[OH^-] \ = \ [x] \ = \ ?$$

$$1.8 \times 10^{-5} \ = \ \frac{x^2}{0.10-x}$$

[x] = [OH⁻] = 1.3 × 10⁻³ M

$$pOH = -\log(1.3 \times 10^{-3})$$
$$= 2.90$$

$$pH = 14 - 2.90$$
$$= 11.10$$

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Step 2 : At equivalence point

$$HCl_{(aq)} + NH_{3\,(aq)} \longrightarrow NH_4Cl_{\,(aq)}$$
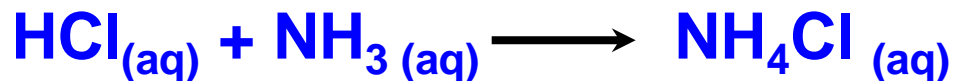
pH at equivalence

- the solution is NH_4Cl (aq)

- only NH_4^+ hydrolyses to form H_3O^+

- therefore pH < 7.0

Volume at equivalence

$$n\,NH_3 = n\,HCl \qquad M_{NH3}\,V_{NH3} = M_{HCl}\,V_{HCl}$$

$$\frac{M_{NH3}\,V_{NH3}}{M_{HCl}\,V_{HCl}} = \frac{1}{1}$$

$$V_{HCl} = \frac{0.10 \times 25.0}{0.10} = 25\ mL$$

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Step 3 :

Type of titration : strong acid-weak base

pH jump : 3 – 7

Step 4 :

Titrant is a strong acid, HCl.

Final point approaching pH < 2

Sketch a titration curve

pH

11

7   Equivalence point

3

1

25   Volume of HCl added (mL)
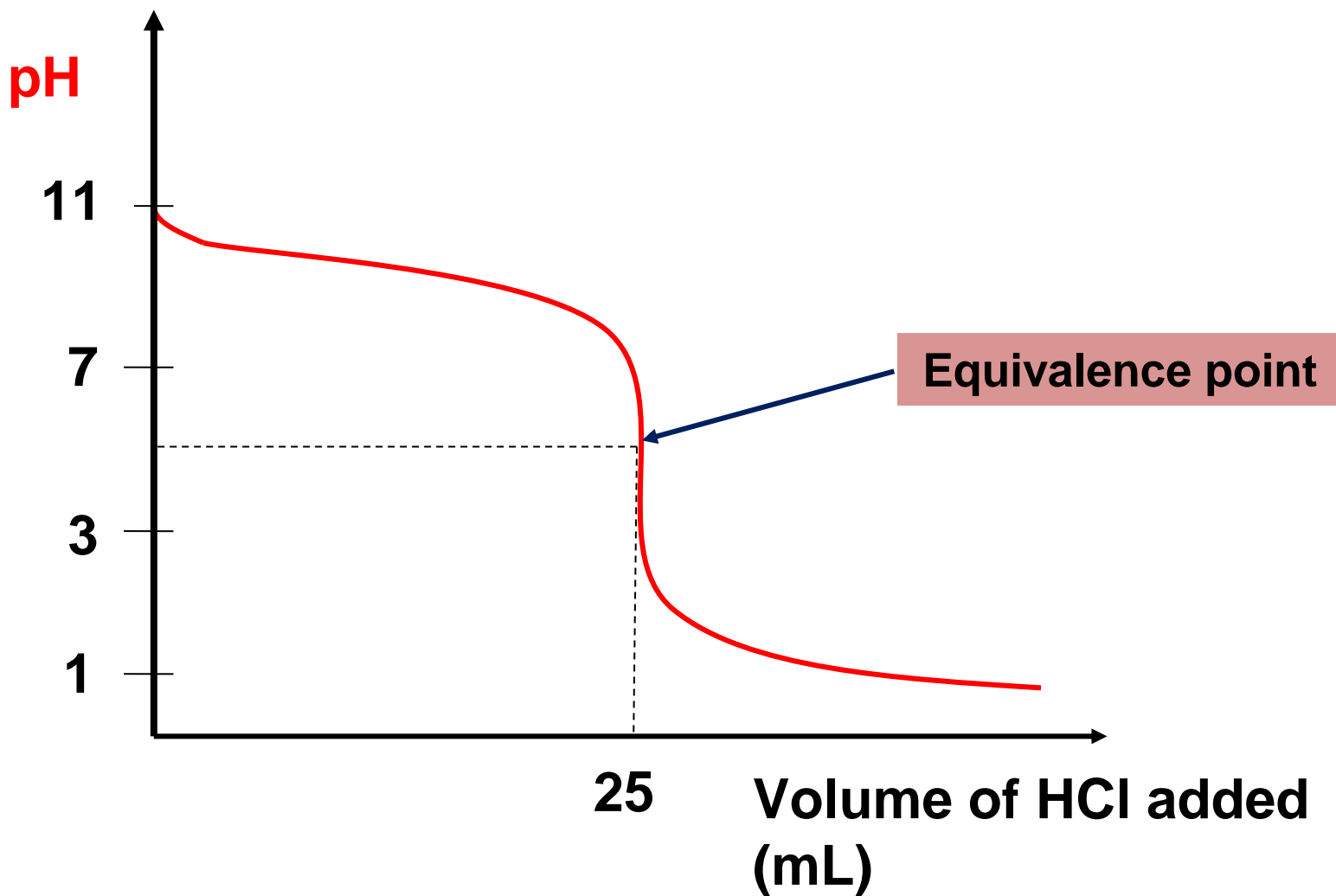
Example 3 :

Sketch the titration curve of 25.0 mL 0.10 M CH_3COOH and 0.10 M NaOH.

Step 1 : Analyte is a weak acid, CH_3COOH

$$CH_3COOH \text{ (aq)} + H_2O\text{(l)} \rightleftharpoons CH_3COO^- \text{ (aq)} + H_3O^+ \text{ (aq)}$$
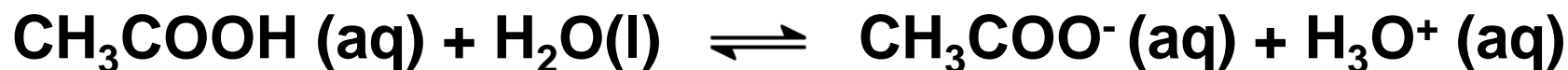
$$[H_3O^+] = [x] = \quad ?$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.10-x}$$

$$[x] = [H_3O^+] = 1.3 \times 10^{-3} \text{ M}$$

$$pH = -\log(1.3 \times 10^{-3}) = \textcolor{blue}{2.90}$$

Step 2 : At equivalence point

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

- pH equivalence

- the solution is CH_3COONa (aq)
- CH_3COO^- hydrolyses to form OH^-
- therefore pH >7.0

- Volume equivalence

n CH_3COOH =   n NaOH

$M_{CH3COOH}$ $V_{CH3COOH}$ = M_{NaOH} V_{NaOH}

$$V_{NaOH} = \frac{0.10 \times 25.0}{0.10} = 25 \text{ mL}$$

Step 3 :

Type of titration : **weak acid-strong base**

pH jump : 7 - 11

Step 4 :

Titrant is a strong base, NaOH.

Final point approaching pH < 13

Sketch a titration curve

pH

13

11 — Equivalence point

7

3

25   Volume of NaOH added (mL)

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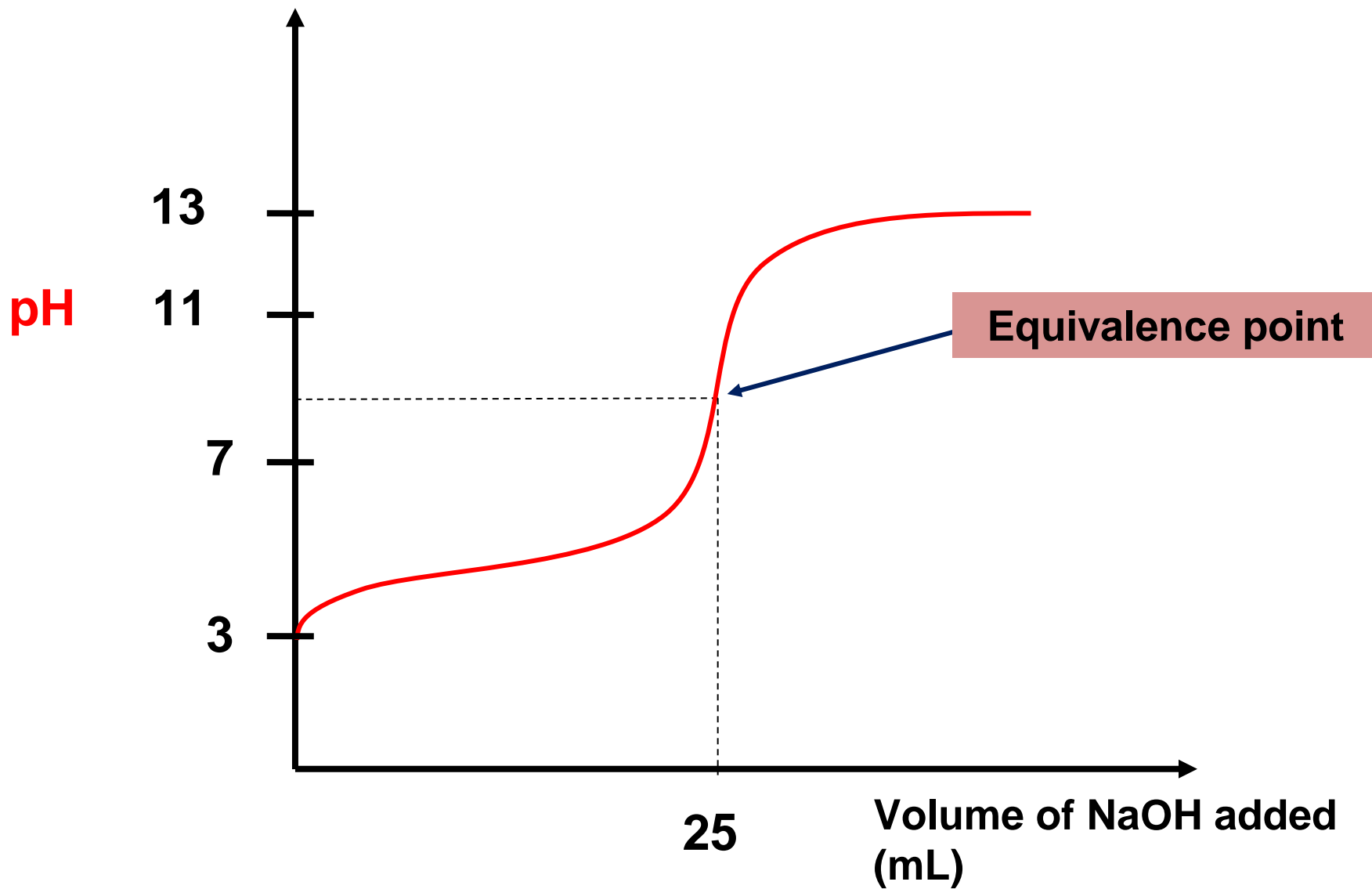
7.2 e) Acid-base Titration Indicator

- **Acid–base indicator is a weak organic acid that changes colour according to the concentration of hydrogen ions in the solution to which the indicator is added.**

- **The indicators can change colour because their ions have colours that are different from the undissociated molecule.**

Some Common Acid–Base Indicators

| | C o l o r | | |
Indicator	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.

pH Ranges for Different Type of Titrations

Type of titrations	End point of pH Range	Suitable Indicators
strong acid-strong base	3 -11	any indicator (except thymol blue)
weak acid-strong base	7 - 11	phenolpthalein, cresol red
strong acid-weak base	3 - 7	methyl orange, methyl red, bromophenol blue, chlorophenol blue

What indicator would be suitable for the titration of each of these:

(a)   NaOH with $HClO_4$
(b) CH_3COOH with KOH
(c) NH_3 solution with HBr

   Explain your choices.

(a)   NaOH (strong base) with HClO$_4$ (strong acid)

   Suitable indicator : bromothymol blue

(b)   CH$_3$COOH (weak acid) with KOH (strong base)

   Suitable indicator : phenolphthalein

(c)   NH$_3$ (weak base) solution with HBr (strong acid)

   Suitable indicator : methyl red

Reason:
All indicators are chosen because the equivalence points are within the range of the pH color changes.

7.3 SOLUBILITY EQUILIBRIA
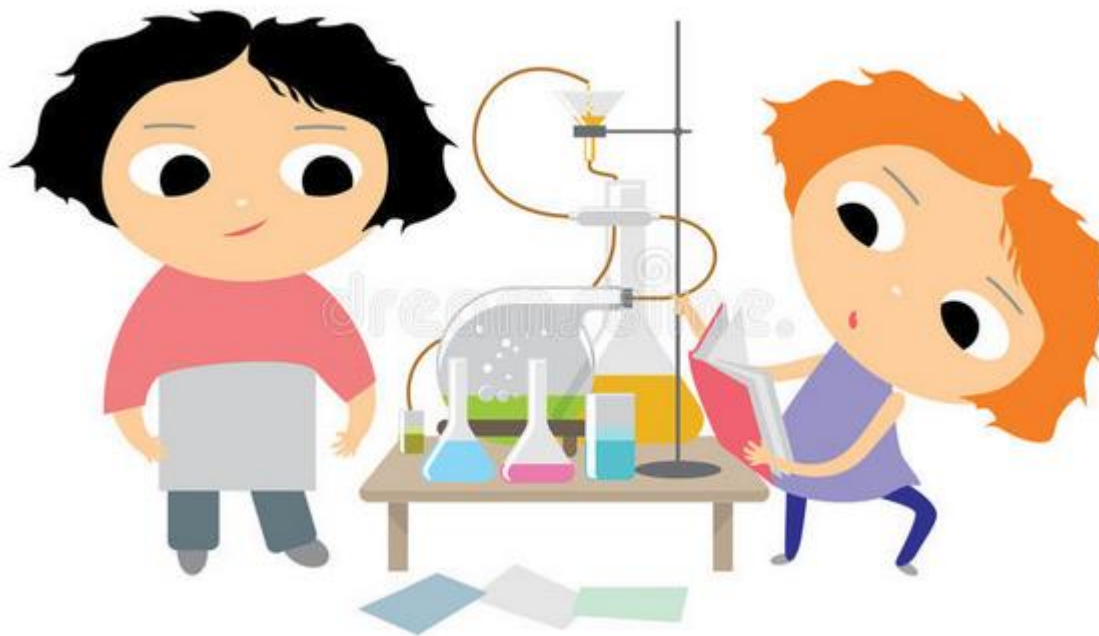
7.3 a) SALT SOLUBILITY

- Some salts are soluble but many are insoluble or slightly soluble in water.

  * The solubility of a salt is the **amount of solid that dissolved** in a **known value of saturated solution.**

  * The unit of solubility used may be **gL^{-1} or $molL^{-1}$**

Solubility (s)

- Mass of solute (g) dissolved in 1 L of a saturated solution.

- Unit : *g/L*

Molar solubility (s)

- Moles of solute dissolved in L of a saturated solution.

- Unit : *mol/L*

Solubility product (K_{sp})

- Is the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.

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EXAMPLE 1 :

Write the ion–product (K_{sp}) expression for each of the following:

(a) Silver carbonate

(a) Barium fluoride

(a) Copper(II) sulfide

(d) Iron(III) hydroxide

(a)   Silver carbonate

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

$$K_{sp} = [Ag^+]^2\,[CO_3^{2-}]$$

(b)   Barium fluoride

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$$
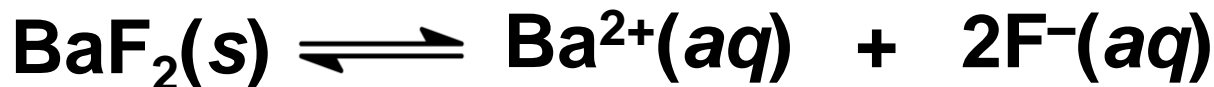
$$K_{sp} = [Ba^{2+}]\,[F^-]^2$$

(c) Copper(II) sulfide

$$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$$
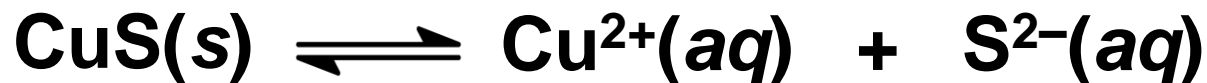
$$K_{sp} = [Cu^{2+}][S^{2-}]$$

(d) Iron(III) hydroxide

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$$
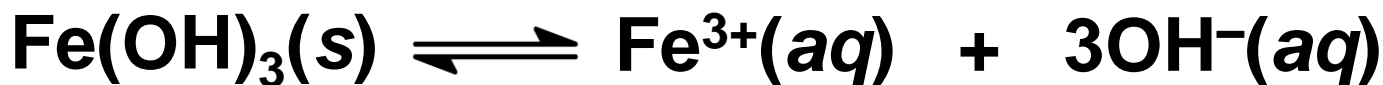
$$K_{sp} = [Fe^{3+}][OH^-]^3$$

EXAMPLE 2 :

Write solubility equilibrium equations that are described by the following K_{sp} expressions.

For example, $K_{sp} = [Ag^+][Cl^-]$ represent as

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

(a) $K_{sp} = [Ag^+]^2[SO_4^{2-}]$

(a) $K_{sp} = [Ni^{2+}]^3[PO_4^{3-}]^2$

(a) $K_{sp} = [Ag^+]^2 [SO_4^{2-}]$

$$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$

(b) $K_{sp} = [Ni^{2+}]^3 [PO_4^{3-}]^2$

$$Ni_3(PO_4)_2(s) \rightleftharpoons 3Ni^{2+}(aq) + 2PO_4^{3-}(aq)$$

K_{sp} AND SOLUBILITY

- The **higher** the K_{sp}, the **greater** the solubility.

- The **higher** the temperature, the **greater** the K_{sp}

EXAMPLE:

$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = 3.5 \times 10^{-8}$

$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$ $K_{sp} = 1.6 \times 10^{-8}$
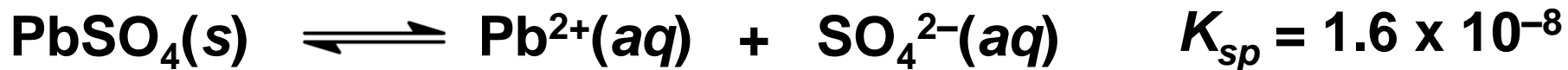
$MgCO_3$ is more soluble than $PbSO_4$

7.3 b) SOLVING PROBLEMS INVOLVING K_{sp}

Two general types of problems:

- **Determining K_{sp} from solubility (g/L) or molar solubility (mol/L)**

- **Determining solubility or molar solubility from K_{sp}**

USE *ICE* TABLE

EXAMPLE 3 :

A particular saturated solution of PbI_2 has $[Pb^{2+}] = 5.0 \times 10^{-3}$ M and $[I^-] = 1.3 \times 10^{-3}$ M.

(a)   What is the value of K_{sp} for PbI_2?

(b)   What is $[I^-]$ in a saturated solution of PbI_2 that has $[Pb^{2+}] = 2.5 \times 10^{-4}$ M?

(c)   What is $[Pb^{2+}]$ in a saturated solution has $[I^-] = 2.5 \times 10^{-4}$ M?

(a) $[Pb^{2+}] = 5.0 \times 10^{-3}$ M $\qquad$ $[I^-] = 1.3 \times 10^{-3}$ M

K_{sp} of PbI_2 = **?**

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

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

$$= (5.0 \times 10^{-3}) \times (1.3 \times 10^{-3})^2$$

$$= \boxed{8.5 \times 10^{-9}}$$

(b) $[Pb^{2+}] = 2.5 \times 10^{-4}\ M$ $[I^-]\ =\ $ **?**

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq)\ +\ 2I^-(aq)$$
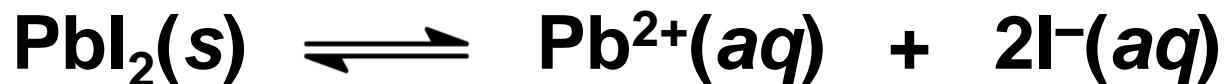
$$K_{sp} = [Pb^{2+}]\,[I^-]^2$$

$$[I^-]^2\ =\ \frac{K_{sp}}{[Pb^{2+}]}\ =\ \frac{8.5 \times 10^{-9}}{(\,2.5 \times 10^{-4}\,)}$$

$$[I^-]\ =\ \boxed{5.8 \times 10^{-3}\ M}$$

(c) $[I^-] = 2.5 \times 10^{-4} \ M$ $[Pb^{2+}] = $ **?**

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

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

$$[Pb^{2+}] = \frac{K_{sp}}{[I^-]^2} = \frac{8.5 \times 10^{-9}}{(2.5 \times 10^{-4})^2}$$

$$[Pb^{2+}] = \boxed{0.136 \ M}$$

The molar solubility of AgBr is 7.1×10^{-7} M at 25°C. Calculate K_{sp} for AgBr at this temperature.

	AgBr(s) $\rightleftharpoons$	Ag$^+$(aq)	+	Br$^-$(aq)
[ ]$_i$ (M)	–	0		0
$\triangle$(M)	–	+ s		+ s
[ ]$_{eq}$ (M)	–	s		s

$$K_{sp} = [Ag^+][Br^-]$$

$$= (s) \times (s)$$

$$= s^2 = (7.1 \times 10^{-7})^2$$

$$= \boxed{5.0 \times 10^{-13}}$$

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The solubility of calcium sulphate is found experimentally to be 0.67 g/L.

Calculate the value of K_{sp} for calcium sulphate.

(Molar mass of $CaSO_4$ = 136.2 g/mol)

Convert solubility (g/L) to molar solubility (mol/L (M)):

$$\frac{0.67 \text{ g CaSO}_4}{1 \text{ L solution}} \text{ X } \frac{1 \text{ mol CaSO}_4}{136.2 \text{ g CaSO}_4}$$

= 4.9 x 10^{-3} mol/L

= 4.9 x 10^{-3} M

	$CaSO_4(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	$+$	$SO_4^{2-}(aq)$
$[\ ]_i\ (M)$	–		0		0
$\triangle(M)$	–		$+s$		$+s$
$[\ ]_{eq}\ (M)$	–		s		s

$$K_{sp} = [Ca^{2+}]\,[SO_4^{2-}]$$

$$= (s) \times (s)$$

$$= s^2 = (4.9 \times 10^{-3})^2$$

$$= \boxed{2.4 \times 10^{-5}}$$

Calculate the molar solubility of $PbCl_2$.

$K_{sp} = 1.6 \times 10^{-5}$

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

	PbCl$_2$(s)	Pb^{2+}(aq)	2Cl$^-$(aq)
[ ]$_i$ (*M*)	–	0	0
Δ(*M*)	–	+ s	+ 2s
[ ]$_{eq}$ (*M*)	–	s	2s

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$
$$= (s) \times (2s)^2$$
$$= 4s^3 = 1.6 \times 10^{-5}$$

$$s = 1.6 \times 10^{-2}\ M$$

So, the molar solubility of PbCl$_2$ = 1.6 x 10^{-2} *M*

7.3 c) PREDICTING PRECIPITATION OF THE IONIC COMPOUNDS

☞ **Precipitate** is an insoluble solid formed in and separates from the solution

☞ **K_{sp} values** can be used to make general **prediction concerning precipitation reactions.**

☞ To predict whether a precipitate will form, **the ion- product, Q is compared with K_{sp}.**

☞ **Q has the same expression as K_{sp}** but the concentrations values are taken at any given time.

$$Q \ = \ K_{sp}$$

☞ **Saturated solution formed**

☞ **System is in equilibrium**

$$Q \ > \ K_{sp}$$

☞ **Solution is supersaturated**

☞ **Reaction proceeds from right to left**

☞ **Precipitate will formed until the ionic concentration product of the system equals the K_{sp} ($Q = K_{sp}$)**
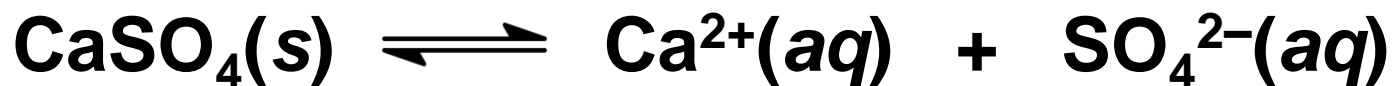
$$Q \ < \ K_{sp}$$

☞ **Reaction proceeds from left to right**
☞ **Solution is unsaturated and no precipitate formed**

Will a precipitate of $CaSO_4$ form in a solution if the Ca^{2+} concentration is 0.0025 M and the SO_4^{2-} concentration is 0.030 M ?

(K_{sp} of $CaSO_4$ = 2.4 x 10^{-5})

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = 2.4 \times 10^{-5}$$

$$[Ca^{2+}] = 0.0025 \ M$$

$$[SO_4^{2-}] = 0.030 \ M$$

$$Q = [Ca^{2+}][SO_4^{2-}]$$

$$= (0.0025) \times (0.030) = 7.5 \times 10^{-5}$$

$$Q > K_{sp}$$

So, $CaSO_4$ will precipitate until $Q = K_{sp}$

Does a precipitate form when 0.100 L of 0.30 *M* Ca(NO$_3$)$_2$ is mixed with 0.200 L of 0.060 *M* NaF?

K_{sp} of CaF$_2$ = 3.2 x 10^{-11}

$Ca(NO_3)_2(aq) + 2NaF(aq) \rightleftharpoons 2\ NaNO_3(aq) + CaF_2(s)$

Ions present: Ca^{2+}, NO_3^-, Na^+, F^-

Possible precipitate = CaF_2

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$
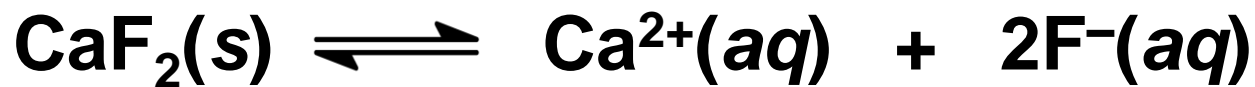
$K_{sp} = [Ca^{2+}][F^-]^2$

$= 3.2 \times 10^{-11}$

Mol of $Ca(NO_3)_2$

$$= \text{Molarity } \times \text{ volume of solution}$$

$$= 0.30 \text{ mol/L} \times 0.100 \text{ L}$$

$$= 0.030 \text{ mol } Ca(NO_3)_2$$

Total volume when $Ca(NO_3)_2$ mix with NaF

$$= 0.100 \text{ L} + 0.200 \text{ L}$$

$$= 0.300 \text{ L}$$

Molarity of Ca(NO$_3$)$_2$ solution $= \dfrac{\text{0.030 mol Ca(NO}_3)_2}{\text{0.300 L}}$

$$= \text{0.100 } M$$

$$\text{Ca(NO}_3)_2(aq) \quad \rightarrow \quad \text{Ca}^{2+}(aq) \quad + \quad 2\text{NO}_3^{-}(aq)$$
$$\quad \text{0.100 } M \qquad\qquad\quad \text{0.100 } M$$
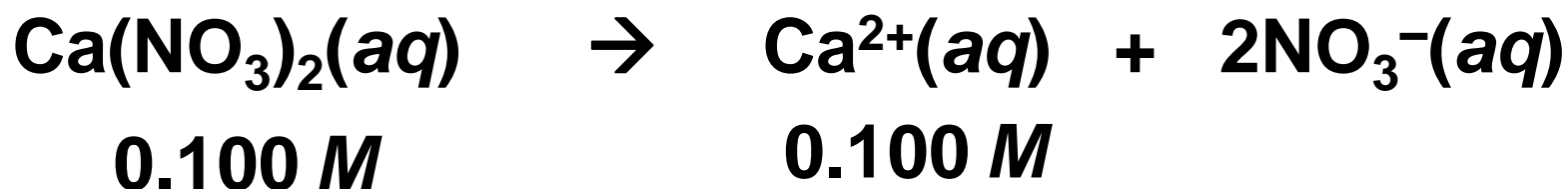
$$[\text{Ca}^{2+}] \;=\; \text{0.100 } M$$

Mol of NaF =   Molarity x Volume of solution

$$= \text{0.060 mol/L x 0.200 L}$$

$$= \text{0.012 mol NaF}$$

Total volume when $Ca(NO_3)_2$ mix with NaF

$$= \text{0.100 L + 0.200 L}$$

$$= \text{0.300 L}$$

Molarity of NaF solution $= \dfrac{\text{0.012 mol NaF}}{\text{0.300 L}}$

$$= \text{0.040 } M$$

$$\text{NaF}(aq) \quad \rightarrow \quad \text{Na}^{2+}(aq) \quad + \quad \text{F}^-(aq)$$

0.040 *M*   0.040 *M*
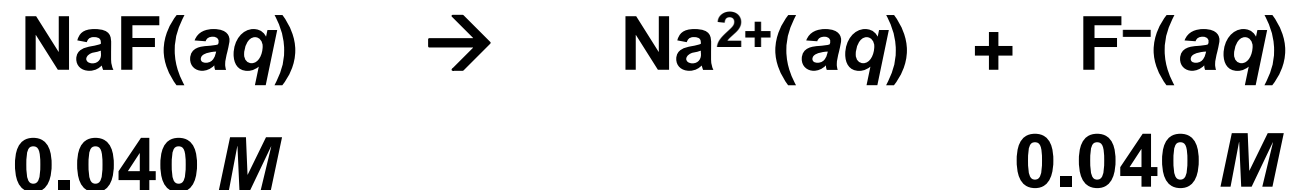
$$[\text{F}^-] = \text{0.040 } M$$

$$[Ca^{2+}] = 0.100 \ M$$

$$[F^-] = 0.040 \ M$$

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

$$= (0.100) \times (0.040)^2$$

$$= 1.6 \times 10^{-4}$$

$$Q > K_{sp}$$

So, CaF_2 **will precipitate until $Q = K_{sp}$**

7.3 d) COMMON ION EFFECT

Shift of equilibrium caused by addition or the presence of a compound having an ion in common with the dissolved substance

EXAMPLE:

Add CrO_4^{2-}

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) \ + \ CrO_4^{2-}(aq)$$
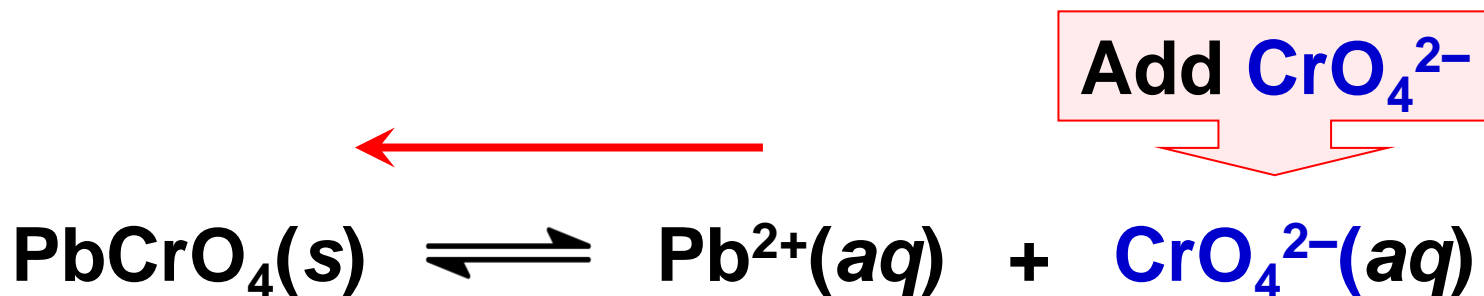
Common ion: CrO_4^{2-}

☞ **Presence of a common ion decreases solubility of slightly soluble ionic compound**

EXAMPLE: Addition of Na_2CrO_4 (soluble salt) to saturated solution of $PbCrO_4$

Add CrO_4^{2-}

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$$
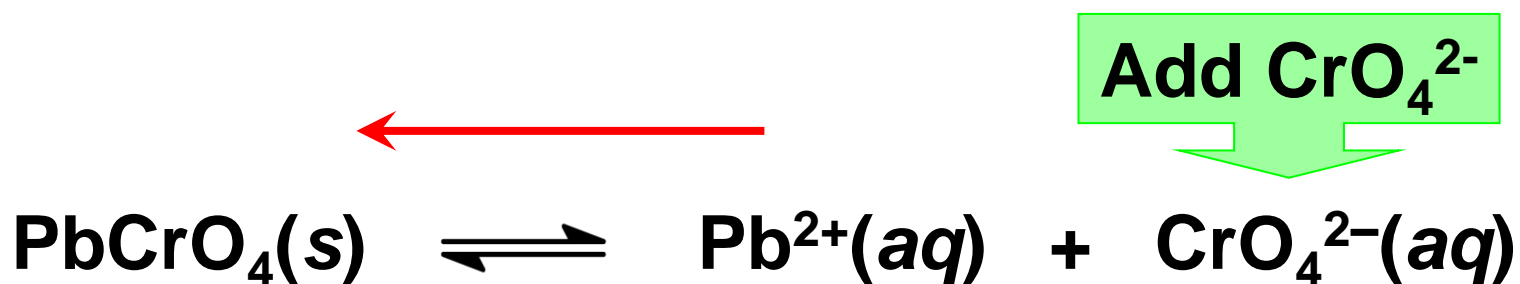
$$K_{sp} = [Pb^{2+}][CrO_4^{2-}]$$

$$= 2.3 \times 10^{-13}$$

EXAMPLE:

Add CrO_4^{2-}

$$PbCrO_4(s) \; \rightleftharpoons \; Pb^{2+}(aq) \; + \; CrO_4^{2-}(aq)$$

☞ **Effect of the addition of common ion CrO_4^{2-} :**

☞ **$[CrO_4^{2-}]$ increase**

☞ **Position of equilibrium will shift to the left. Some CrO_4^{2-} combine with Pb^{2+} to form solid $PbCrO_4$**

☞ **Solubility of $PbCrO_4$ decrease**

What is the solubility (in M) of $Ca(OH)_2$ in

0.10 M $Ca(NO_3)_2$?

K_{sp} of $Ca(OH)_2$ = 6.5 x 10^{-6}

	$Ca(OH)_2(s)$ $\rightleftharpoons$	$Ca^{2+}(aq)$	$+$	$2OH^-(aq)$
[ ]$_i$ (*M*)	–	0.10		0
$\triangle$(*M*)	–	$+ s$		$+ 2s$
[ ]$_{eq}$ (*M*)	–	$0.1 + s$		$2s$

Assume s is very small ☞ $0.1 + s \approx 0.1$

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

$$= (0.1) \times (2s)^2$$

$$= 0.4s^2 = 6.5 \times 10^{-6}$$

$$s = 4.0 \times 10^{-3} \, M$$

So, the molar solubility of $Ca(OH)_2$ = **4.0 x 10^{-3} *M***

EXAMPLE 10:

What is the molar solubility of AgBr in

(a) pure water

(b) 0.0010 M NaBr

(c) compare the solubility of AgBr in water and NaBr

$$K_{sp} \text{ of AgBr} = 7.7 \text{ x } 10^{-13}$$

(a)

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

	AgBr(s)	Ag$^+$(aq)	Br$^-$(aq)
[ ]$_i$ (M)	–	0	0
Δ (M)	–	+ s	+ s
[ ]$_{eq}$ (M)	–	s	s

$$K_{sp} = [Ag^+][Br^-]$$
$$= (s) \times (s)$$
$$= s^2 = 7.7 \times 10^{-13}$$
$$s = 8.8 \times 10^{-7} \ M$$

So, the molar solubility of AgBr in pure water = $8.8 \times 10^{-7} \ M$

(b)

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

	AgBr(s)	Ag⁺(aq)	Br⁻(aq)
$[\ ]_i$ (*M*)	–	0	0.0010
$\triangle$ (*M*)	–	+ *s*	+ *s*
$[\ ]_{eq}$ (*M*)	–	*s*	0.0010 + *s*

s is very small ☞ $0.0010 + s \approx 0.0010$

$$K_{sp} = [Ag^+][Br^-]$$

$$= (s) \times (0.0010)$$

$$= 0.0010s = 7.7 \times 10^{-13}$$

$$s = 7.7 \times 10^{-10} \ M$$

So, the molar solubility of AgBr in NaBr = $7.7 \times 10^{-10} \ M$

molar solubility of AgBr in NaBr = 7.7×10^{-10} *M*

molar solubility of AgBr in water = 8.8×10^{-7} *M*

☞ **The solubility of AgBr in NaBr is lower than in water.**

☞ **The presence of the common ion Br^- increases the concentration of Br^- ion and thus shifts the equilibrium position to the left. Hence increase the formation of AgBr and decrease/reduce the solubility**

K_{sp} for AgCl is 1.7×10^{-10}. Calculate the molar solubility of AgCl in:

i. Water   [1.30 x 10⁻⁵ M]

ii. In a solution of 0.1 mol dm⁻³ KCl.   [1.70 x 10⁻⁹ M]

EXERCISE 2

1. It was found experimentally that the solubility of calcium sulphate is 0.67 g L^{-1}. Calculate the K_{sp} for calcium sulphate.   (2.4 x 10^{-5})

2. The solubility of silver sulphate is 1.5 x 10^{-2} mol L^{-1}. Calculate the solubility product of the salt.

   (1.35 x 10^{-5})

3. Will precipitate form if 200 mL of 0.0040 M $BaCl_2$ are added to 600 mL of 0.0080 M K_2SO_4 ? K_{sp} $BaSO_4$ = 1.1 x 10^{-10})

   (Q> Ksp   therefore $BaSO_4$ will precipitate)

GLOSSARY

NO	TERM	SYMBOL/ FORMULA	DEFINE
1.	Arrhenius acid	-	Substance that dissociate in water to produce H_3O^+ ion.
2.	Arrhenius base	-	Substance that dissociate in water to produce OH^- ion.
3.	Bronsted-Lowry acid	-	Any substance that can donate a proton,(H^+) to other substance.
4.	Bronsted-Lowry base	-	Any substance that can accept a proton, (H^+) from other substance.
5.	Conjugate Acid	-	A species that remains when one proton,(H^+) has been added to the base.
6.	Conjugate Base	-	A species that remains when one proton,(H^+) has been removed from the acid.
7.	Strong acids	-	completely dissociated in aqueous solution

NO	TERM	SYMBOL/ FORMULA	DEFINE
8.	Weak acids	-	partially dissociate in aqueous solution.
9.	Strong base	-	completely dissociated in aqueous solution
10.	Weak base	-	partially dissociate in aqueous solution
11.	<u>pH</u>	$pH = -\log [H^+]$	pH is a measure of the concentration of H^+/H_3O^+ ions in a solution
12.	<u>pOH</u>	$pOH = -\log [OH^-]$	pOH is a measure of the concentration of OH^-ions a solution
13.	<u>pKw</u>	$pKw = -\log (K_w)$	pKw is a measure of negative logarithm (- log) of the dissociation or ionisation constant of water.
14.	Degree of dissociation (α)	α=Concentration of acid <u>or base dissociation</u> Initial concentration	Ability of acids or bases to ionize or dissociate in aqueous solution

NO	TERM	SYMBOL/ FORMULA	DEFINE
15.	Salt	-	an ionic compound that is formed by the reaction of an acid with a base.
16.	Hydrolysis	-	The reaction of cations/anions (or both) from salts with water molecules to produce H^+ or OH^-
17.	buffer	-	A solution which has the ability to maintain its pH when a small amount of strong acid or strong base is added to the solution.
18.	Acidic buffer	$pH = pK_a + log \dfrac{[conjugate\ base]}{[weak\ acid]}$	a solution that contains a weak acid and its salt (or its conjugate base)
19.	Basic buffer	$pOH = pK_b + log \dfrac{[conjugate\ acid]}{[weak\ base]}$	a solution that contains a weak base and its salt (or its conjugate acid)

NO	TERM	SYMBOL/ FORMULA	DEFINE
20.	Titration	-	Method for determining the concentration of an unknown solution by using another solution of known concentration
21.	Standard Solution	-	Solution of known concentration
22.	Titrant	-	The solution in a titration that is added from a burette to a measured quantity of another solution @ A solution of known concentration that is added (titrated) to another solution
23.	Analyte	-	A substance or sample being analyzed @ The solution with unknown concentration
24.	Acid-Base Titrations	-	A method of quantitative analysis for determining the concentration of an acid or base by exactly neutralizing it with a standard solution of base or acid having known concentration.

NO	TERM	SYMBOL/ FORMULA	DEFINE
25.	End Point	-	The point where an indicator changes color
26.	Equivalence Point	-	The point where the mole of acid and base is stoichiometrically equivalent @ mole of H^+ equals to mole of OH^- (no more acid or base left in the solution)
27.	Titration Curves	-	A plot of the pH of a solution of acid (or base) versus the volume of base (or acid) added to the solution
28.	pH Jump	-	Steep portion or sharp portion in titration curves.
29.	Indicators	-	A weak organic acid that has different color than it conjugate base and color changes occurring over a specific and relatively narrow pH range. @ A weak organic acid that changes colour according to the concentration of hydrogen ions in the solution to which the indicator is added

NO	TERM	SYMBOL/ FORMULA	DEFINE
30.	Solubility	s	Mass of solute (g) dissolved in 1 L of a saturated solution. Unit: g/L
31.	Molar Solubility	s	Moles of solute dissolved in L of a saturated solution. Unit: mol/L
32.	Solubility Product	Ksp	The product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.
33.	Common Ion Effect	-	Shift of equilibrium caused by addition or the presence of a compound having an ion in common with the dissolved substance
34.	Common Ion	-	An ion that is already contained in the solution
35.	Precipitation	-	The action or process of precipitating a substance from a solution.
36.	Precipitate	-	An insoluble solid formed in and separates from the solution