CHAPTER 7.0

IONIC EQUILIBRIA

CHEMISTRY 1
SK015

SESSION 2025/2026

STUDENT LEARNING TIME (SLT): LECTURE	
NON FACE-TO-FACE (PREPARATION)	FACE-TO-FACE (DURING CLASS)
3 HOURS	3 HOURS

CHEMISTRY UNIT, KMJ

7.0
IONIC EQUILIBRIA

7.1
ACIDS AND BASES

7.2
ACID-BASE TITRATION

7.3
SOLUBILITY EQUILIBRIA

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
  - 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 ACIDS AND BASES

Teaching and learning outcomes

At the end of the lesson, student should be able to

7.1	**Acids and Bases**
a)	Define acid and base according to Arrhenius and Bronsted- Lowry theories.
b)	Identify conjugate acid and conjugate base according to Bronsted- Lowry theory.
c)	Relate pH and pOH to the ionic product of water, K_w at 25^0C

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 DEFINITION

Acid:

Substance that has H in its formula and dissociates in water to yield H^+

EXAMPLE: HCl, HCN, HNO_3, H_2SO_4, CH_3COOH

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

$$HCl\,(aq) + H_2O\,(l) \longrightarrow H_3O^+(aq) + Cl^-\,(aq)$$

ARRHENIUS DEFINITION

Base:

Substance that has OH in its formula and dissociates in water to yield OH^-

EXAMPLE: $NaOH$, KOH, $Ba(OH)_2$

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

EXAMPLE – 01

Write the equation for the dissociation of the following substances in water:

(a) HCl
(b) $HClO_4$
(c) KOH

ANSWER– 01

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

(b) $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$

(c) $KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$

BRØNSTED–LOWRY DEFINITION

Acid:

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

Example:

$$HCOOH\,(aq) + H_2O\,(l) \rightleftharpoons HCOO^-\,(aq) + H_3O^+\,(aq)$$

acid

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

acid

BRØNSTED–LOWRY DEFINITION

Base:

Any substance that can accept a proton 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

H_2O is able to act as an acid or a base : AMPHOTERIC

- 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

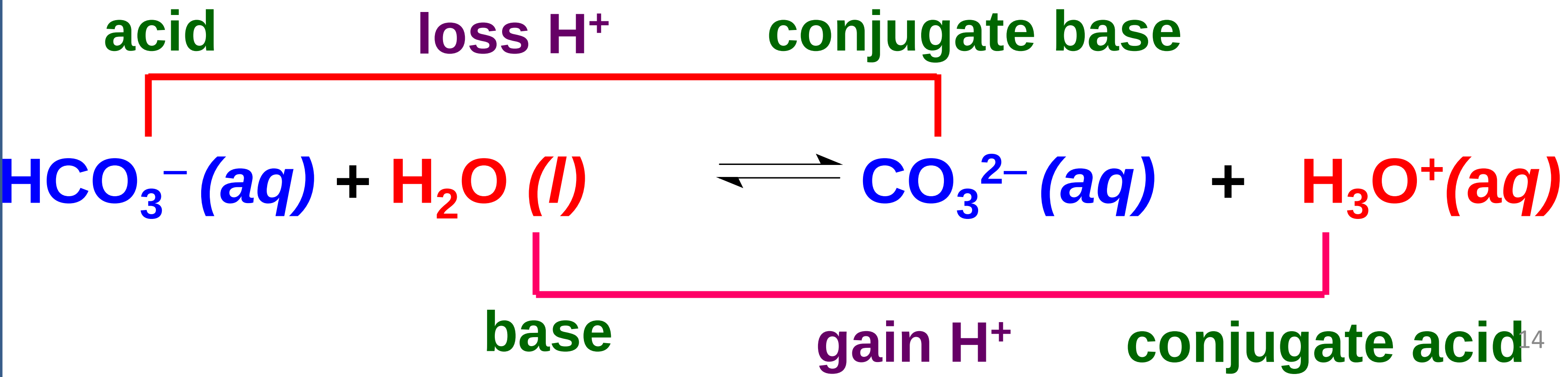
Conjugate Acid-Base Pairs

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

Example :

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

acid

base

conjugate base

conjugate acid

The weaker the acid, the stronger is its conjugate base.

The weaker the base, the stronger is its conjugate acid.

Since very little of CH_3COOH dissociates to produce H_3O^+, the equilibrium position lies very far to the left.

The tendency of $CH_3COO^–$ to gain a proton is much greater than the CH_3COOH to loose a proton.

Therefore, CH_3COOH is a weak acid, the $CH_3COO^–$ strong conjugate base

EXAMPLE – 02

Identify the conjugate acid–base pairs:

(a) $HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^{-}(aq) + H_3O^{+}(aq)$

(b) $H_2O(l) + F^{-}(aq) \rightleftharpoons OH^{-}(aq) + HF(aq)$

(c) $H_2PO_4^{-}(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^{-}(aq) + HPO_4^{2-}(aq)$

(d) $H_2O(l) + SO_3^{2-}(aq) \rightleftharpoons OH^{-}(aq) + HSO_3^{-}(aq)$

ANSWER– 02

A = acid **B = base**

cA = conjugate acid **cB = conjugate base**

$$\text{(a)}\quad \underset{\boxed{\text{A}}}{\mathrm{HCOOH}(aq)} + \underset{\boxed{\text{B}}}{\mathrm{H_2O}(l)} \rightleftharpoons \underset{\boxed{\text{cB}}}{\mathrm{HCOO^{-}}(aq)} + \underset{\boxed{\text{cA}}}{\mathrm{H_3O^{+}}(aq)}$$

$$\text{(b)}\quad \underset{\boxed{\text{A}}}{\mathrm{H_2O}(l)} + \underset{\boxed{\text{B}}}{\mathrm{F^{-}}(aq)} \rightleftharpoons \underset{\boxed{\text{cB}}}{\mathrm{OH^{-}}(aq)} + \underset{\boxed{\text{cA}}}{\mathrm{HF}(aq)}$$

(c) $H_2PO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + HPO_4^{2-}(aq)$

A **B** **cA** **cB**

(d) $H_2O(l) + SO_3^{2-}(aq) \rightleftharpoons OH^-(aq) + HSO_3^-(aq)$

A **B** **cB** **cA**

EXERCISE– 01

1. What is the conjugate base of each of the following acids:

   (a) $HClO_4$
   (b) H_2S

2. What is the conjugate acid of each of the following bases:

   (a) CN^-
   (b) SO_4^{2-}

ANSWER

i) (a) $HClO_4$

acid conjugate base ☞ ClO_4^-

(b) H_2S

acid conjugate base ☞ HS^-

ii) (a) CN^-

base conjugate acid ☞ HCN

(b) SO_4^{2-}

base conjugate acid ☞ HSO_4^-

7.1 ACIDS AND BASES

Teaching and learning outcomes

At the end of the lesson, student should be able to

7.1	Acids and Bases
d)	Define strong acid and base, weak acid and base, pH and pOH.
e)	Calculate the pH values of a strong acid and base.
f)	Relate the strength of weak acid and weak base to the respective dissociation constants, K_a and $_{Kb}$
g)	Perform calculation involving: i) pH ii) dissociation constant iii) initial concentration iv)equilibrium concentration v) degree of dissociation

STRONG ACID

- **Dissociate completely (100 %) into ions in water**

$$\mathrm{HA}(g \text{ or } l) + \mathrm{H_2O}(l) \rightarrow \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

- **K_c extremely large**

EXAMPLE:

	$HNO_3(aq)$	+ $H_2O(l)$	→ $H_3O^+(aq)$	+ $NO_3^-(aq)$
[Initial]	0.5 *M*	–	0	0
[Final]	0	–	0.5 *M*	0.5 *M*

3 ways to write the equation for dissociation of strong acid :

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

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

iii) $HCl\,(g) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)$

WEAK ACID

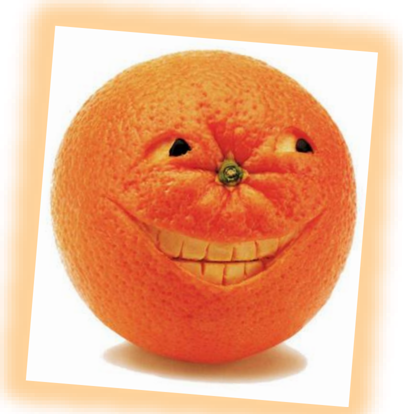
- **Dissociate very slightly into ions in water**

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

- **Great majority of HA molecules undissociated**
- **K_c very small**

EXAMPLE:

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$



Example:

STRONG ACIDS	WEAK ACIDS
The hydrohalic acids e.g: HCl, HBr and HI	Hydrohalic acids: HF
Oxoacids : the number of O atoms exceeds the number of ionizable protons by two or more. e.g: HNO_3 and $HClO_4$	Acids in which **H not bonded to O** or **halogen**: HCN and H_2S
	Oxoacids: HClO, HNO_2 and H_3PO_4
	Organic acids (general formula = R–COOH): CH_3COOH and C_6H_5COOH

STRONG BASE

- Dissociate completely (100 %) into ions in **water**
- K_c extremely **large**

EXAMPLE:

	$\text{NaOH}(aq)$	$\rightarrow$	$\text{Na}^+(aq)$	+	$\text{OH}^-(aq)$
[Initial]	0.5 M		0		0
[Final]	0		0.5 M		0.5 M

WEAK BASE

- **Dissociate very slightly into ions in water**
- K_c **very small**

EXAMPLE:

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

Example:

STRONG BASES	WEAK BASES
M_2O or MOH, where M is group 1 element : Li, Na, K, Rb, Cs	Ammonia : NH_3
RO or $R(OH)_2$, where R is Ca, Sr, Ba	Amine : $R\text{-}NH_2$, $R_2\text{-}NH$ & $R_3\text{-}N$ such as $CH_3CH_2\text{-}NH_2$ and $(CH_3)_2NH$
	Hydrazine : N_2H_4

EXAMPLE – 04

Classify each of the following compounds as a strong acid, weak acid, strong base, or weak base.

(a) $(CH_3)_2CHCOOH$
(b) KOH
(c) $(CH_3)_2CHNH_2$
(d) HNO_2

ANSWER-04

(a) $(CH_3)_2CHCOOH$ ☞ weak acid

(b) KOH ☞ strong base

(c) $(CH_3)_2CHNH_2$ ☞ weak base

(d) HNO_2 ☞ weak acid

ACID–DISSOCIATION CONSTANT (K_a)

- ❑ Dissociation of weak acid in water:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$\boxed{K_a = \frac{[H_3O^+][A^-]}{[HA]}}$$

EXAMPLE:

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

Keep in mind!

- $H^+(aq) = H_3O^+(aq)$

EXAMPLE:

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

$$K_a = \frac{\boxed{[H_3O^+]}\,[CN^-]}{[HCN]}$$

or

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

$$K_a = \frac{\boxed{[H^+]}\,[CN^-]}{[HCN]}$$

Keep in mind!

stronger acid

100% acid dissociated

higher $[H_3O^+]$

larger K_a

weaker acid

lower % acid dissociated

less $[H_3O^+]$

smaller K_a

Strong acids and bases (dissociate 100%): K_a or K_b values have not been measured

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

- ☞ **K_a ↑ (pK_a ↓) , [H^+] ↑ , thus pH ↓ (more acidic)**
- ☞ **K_b ↑ (pK_b ↓) , [OH^-] ↑ , thus pH ↑ (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 > $C_6H_5NH_2$**

AUTOIONIZATION OF WATER

Water dissociates into ions very slightly in an equilibrium (or self-ionization)

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$K_W = [H_3O^+][OH^-]$$

$$= 1.0 \times 10^{-14} \text{ (at } 25^oC)$$

K_W : ion product constant for water

In pure water;

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}\ M$$

$[H_3O^+]$ AND $[OH^-]$

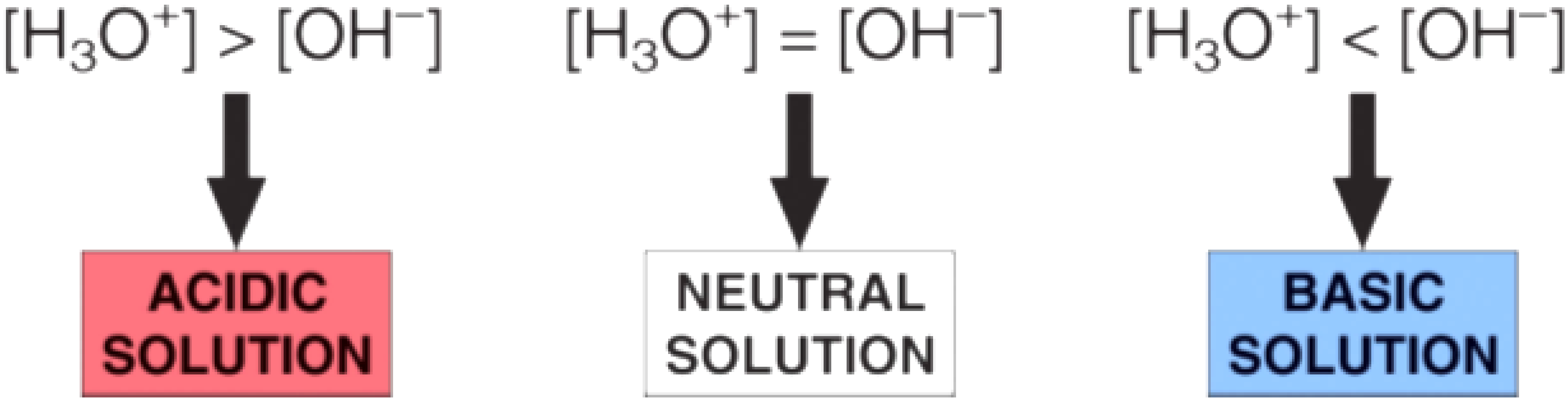
- A change in $[H_3O]^+$ causes an inverse change in $[OH^-]$

Higher $[H_3O^+]$ ☞ lower $[OH^-]$

Higher $[OH^-]$ ☞ lower $[H_3O^+]$

- Both ions are present in all aqueous systems
  - In acidic solution, $[H_3O^+] > [OH^-]$
  - In basic solution, $[H_3O^+] < [OH^-]$
  - In neutral solution, $[H_3O^+] = [OH^-]$

CALCULATING $[H_3O^+]$ AND $[OH^-]$ IN AQUEOUS SOLUTION



$[H_3O^+] > [OH^-]$ → **ACIDIC SOLUTION**

$[H_3O^+] = [OH^-]$ → **NEUTRAL SOLUTION**

$[H_3O^+] < [OH^-]$ → **BASIC SOLUTION**

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at 25°C)}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} \qquad [OH^-] = \frac{K_w}{[H_3O^+]}$$

EXAMPLE – 05

A research chemist adds a measured amount of HCl gas to pure water at 25°C and obtains a solution with $[H_3O^+] = 3.0 \times 10^{-4}$ *M*.

Calculate $[OH^-]$.

Is the solution neutral, acidic, or basic?

ANSWER-05

$$K_W = [\,H_3O^+\,][\,OH^-\,] = 1.0 \times 10^{-14} \text{ (at 25}^oC\text{)}$$

$$[\,OH^-\,] = \frac{K_W}{[H_3O^+\,]}$$

$$= \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-4}}$$

$$= \boxed{3.3 \times 10^{-11}\ M}$$

☞ $[H_3O^+] > [OH^-]$

So, the solution is **acidic**

pH and pOH STRONG ACIDS AND BASES

Strong acids and strong bases dissociate 100% in an aqueous solution

EXAMPLE

	$HCl(aq)$	+	$H_2O(l)$	→	$H_3O^+(aq)$	+	$Cl^-(aq)$
$[\ ]_i$:	0.020 *M*		–		0		0
$[\ ]_f$:	0		–		0.020 *M*		0.020 *M*

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log[0.020] \\ &= 1.70 \end{aligned}$$

pH SCALE

$pH = -\log [H_3O^+]$

$[H_3O]^+ = 10^{-pH}$

Or $[H_3O]^+ = \text{antilog}(-pH)$

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

☐ **The higher $[H_3O^+]$, the lower pH**

☐ **The higher the $[OH^-]$, the lower pOH**

K_W , pK_W , pH AND pOH

$$K_W = [\,H_3O^+\,][\,OH^-]$$

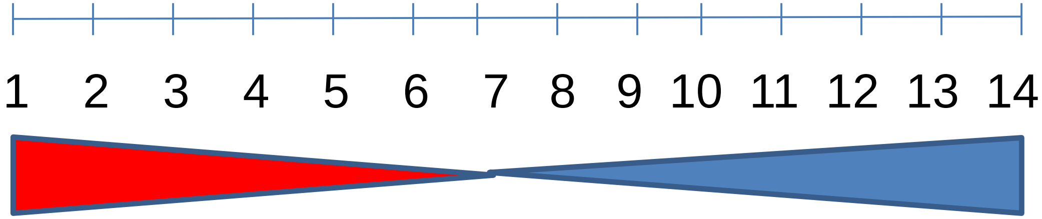
$$= 1.0 \times 10^{-14} \text{ (at } 25^oC)$$

↓ **negative logarithm**

$$pK_w = pH + pOH = 14.00 \text{ (at } 25^oC)$$

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

pH scale: Scale to express acidity/basicity



Neutral solution : $pH = 7$; $[H_3O^+] = [OH^-]$

Acidic solution: $pH < 7$; $[H_3O^+] > [OH^-]$

Basic solution: $pH > 7$; $[H_3O^+] < [OH^-]$

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

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

$$pH + pOH = 14$$

pH scale

0	7	14
acidic	neutral	basic
$[H^+] > [OH^-]$	$[H^+] = [OH^-]$	$[H^+] < [OH^-]$

EXAMPLE – 06

Calculate [H_3O^+], [Cl^-], and [OH^-] and pH in 0.015 *M* HCl(*aq*).

ANSWER – 06

	$HCl(aq)$	+	$H_2O(l)$	→	$H_3O^+(aq)$	+	$Cl^-(aq)$
$[\ ]_i$:	0.015 *M*		–		0		0
$[\ ]_f$:	0		–		0.015 *M*		0.015 *M*

$[H_3O^+] = \boxed{0.015\ M}$

$[Cl^-] = \boxed{0.015\ M}$

$$[\,OH^-\,] = \frac{K_W}{[H_3O^+\,]}$$

$$= \frac{1.0 \times 10^{-14}}{0.015}$$

$$= \boxed{6.7 \times 10^{-13}\ M}$$

$$[H_3O^+] = 0.015\ M$$

$$\mathrm{pH} = -\log [H_3O^+]$$

$$= -\log [0.015]$$

$$= 1.82$$

EXAMPLE – 07

What is the pH of 0.00035 *M* solution of $Ba(OH)_2$

ANSWER – 07

	$Ba(OH)_2(aq)$	$\rightarrow$	$Ba^{2+}(aq)$	+	$2OH^{-}(aq)$
$[\ ]_i$	0.00035 *M*		0		0
$[\ ]_f$	0		0.00035 *M*		0.00070 *M*

$$\begin{aligned} pOH &= -\log [OH^-] \\ &= -\log (0.00070) \\ &= 3.15 \end{aligned}$$

$$\begin{aligned} pH + pOH &= 14.00 \\ pH &= 14.00 - 3.15 \\ pH &= \boxed{10.85} \end{aligned}$$

EXAMPLE – 08

In art restoration project, a conservator prepares copper–plate etching solutions by diluting **concentrated HNO_3 to 0.0063 *M*.**

Calculate $[H_3O^+]$, pH, $[OH^-]$ and pOH of the solution at 25^oC.

ANSWER – 08

HNO_3 is a strong acid ☞ 100 % dissociates in water

	$HNO_3(aq)$	+	$H_2O(l)$	$\rightarrow$	$H_3O^+(aq)$	+	$NO_3^-(aq)$
$[\ ]_i$	$0.0063\ M$		—		0		0
$[\ ]_f$	0		—		$0.0063\ M$		$0.0063\ M$

$$[H_3O^+] = \boxed{0.0063\ M}$$

$$\begin{aligned} pH &= -\log\,[H_3O^+] \\ &= -\log\,[0.0063] \\ &= \boxed{2.20} \end{aligned}$$

$$\mathrm{p}K_w = \mathrm{pH} + \mathrm{pOH} = 14.00$$

$$\mathrm{pOH} = 14.00 - \mathrm{pH}$$

$$= 14.00 - 2.20$$

$$= \boxed{11.80}$$

$$[\,\mathrm{OH}^-\,] = \mathrm{Antilog}(-11.80)$$

$$= \boxed{1.6 \times 10^{-12}\ M}$$

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*)

Degree of dissociation (α)

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

$$\alpha = \frac{\text{concentration of acid or base dissociated}}{\text{initial concentration of acid or base}}$$

$$\%\text{ of }\alpha = \frac{[\text{ acid or base }]\text{ dissociated}}{\text{initial}[\text{ acid or base }]} \times 100\%$$

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:

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

$$= 1.3\ \%$$

K_a - Acid Dissociation Constant

- ☐ Dissociation of weak acid in water:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

EXAMPLE:

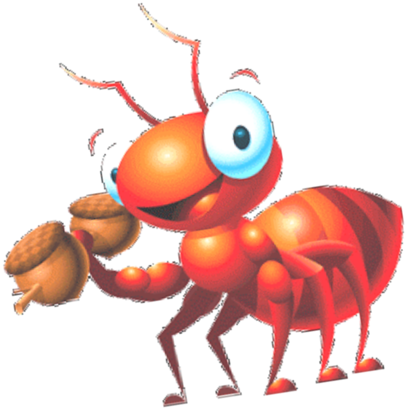
$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

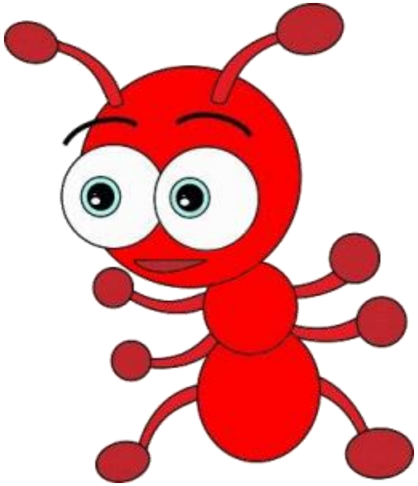
MAGNITUDE OF K_a (for weak acids)

- ☐ Higher $[H_3O^+]$ ☞ stronger acid (higher acidity)
  ☞ has larger K_a value

$$pK_a = -\log K_a$$



- ☐ Higher K_a ☞ lower pK_a
  ☞ stronger acid



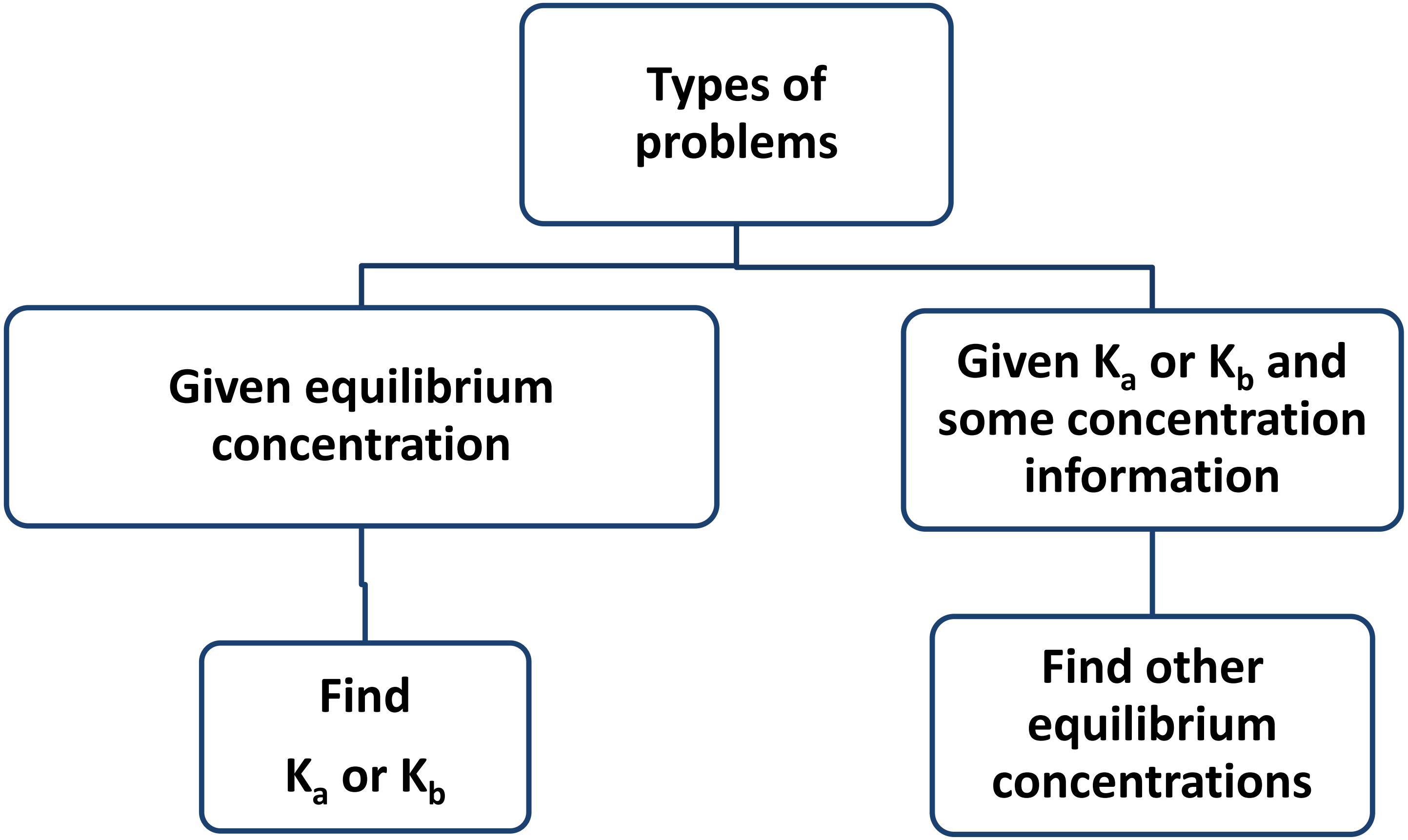
A weak acid has a small K_a, so:

$$[HA]_{initial} - [HA]_{dissoc} \approx [HA]_{initial}$$

$$\Downarrow$$

$$[HA]_{initial} - x = [HA]_{initial} \text{ (because } x \text{ very small)}$$

Solving Problems Involving Weak Acid & Weak Base Equilibria



Types of problems

Given equilibrium concentration

Find K_a or K_b

Given K_a or K_b and some concentration information

Find other equilibrium concentrations

USE *ICE* TABLE

EXAMPLE – 09

What is the pH of a 0.5 *M* HF solution (at 25°C)?

K_a of HF = 7.1×10^{-4}

ANSWER– 09

	$H_2O(l)$	$+$	$HF(aq)$	$\rightleftharpoons$	$H_3O^+(aq)$	$+$	$F^-(aq)$
$[\ ]_i$	–		0.50		0		0
$[\ ]_\Delta$	–		$-x$		$+x$		$+x$
$[\ ]_{eq}$	–		$0.50 - x$		x		x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{x^2}{0.50 - x} = 7.1 \times 10^{-4}$$

$$K_a = \frac{x^2}{0.50 - x}$$

$K_a << 1$ ☞ **assume x very small**

Assumption: $0.50 - x \approx 0.50$ **(x negligible)**

$$K_a = \frac{x^2}{0.50} = 7.1 \times 10^{-4}$$

$$x = 0.019$$

$x = 0.019$

Checking the assumption: $0.50 - x \approx 0.50$

$$\frac{x}{0.50} \times 100 = \frac{0.019}{0.50} \times 100$$

$$= 3.8\ \%$$

(< 5 % ☞ assumption justified)

$$[H_3O^+] \quad = \quad x \quad = \quad 0.019\ M$$

$$\text{pH} = -\log [H_3O^+]$$

$$= -\log 0.019$$

$$= \boxed{1.72}$$

EXAMPLE – 10

Butyric acid, C_3H_7COOH, is used to make compounds employed in artificial flavorings and syrups.

A 0.250 *M* aqueous solution of C_3H_7COOH is found to have pH of 2.72.

Determine K_a for butyric acid.

ANSWER – 10

$$H_2O(\mathit{l}) + C_3H_7COOH(\mathit{aq}) \rightleftharpoons H_3O^+(\mathit{aq}) + C_3H_7COO^-(\mathit{aq})$$

$[\ ]_i$	–	0.250	0	0
$[\ ]_\Delta$	–	$-x$	$+x$	$+x$
$[\ ]_{eq}$	–	$0.250 - x$	x	x

$$K_a = \frac{[H_3O^+][C_3H_7COO^-]}{[C_3H_7COOH]} = \frac{x^2}{0.250 - x}$$

$$\text{pH} = -\log [H_3O^+] = 2.72$$

$$\log [H_3O^+] = -2.72$$

$$[H_3O^+] = \text{antilog}(-2.72)$$

$$= 10^{-2.72}$$

$$= 1.91 \times 10^{-3}\ M$$

$$[H_3O^+] = x = 1.91 \times 10^{-3}\ M$$

$$x = 1.91 \times 10^{-3}$$

Checking the assumption: $0.250 - x \approx 0.250$

$$\frac{x}{0.250} \times 100 = \frac{1.91 \times 10^{-3}}{0.250} \times 100$$

$$= 0.8\ \%$$

($< 5\ \%$ ☞ assumption justified)

$$K_a = \frac{x^2}{0.250 - x}$$

$$x = 1.91 \times 10^{-3}\ M$$

$$K_a = \frac{x^2}{0.250 - x}$$

$$= \frac{(1.91 \times 10^{-3})^2}{0.250 - (1.91 \times 10^{-3})}$$

$$= \boxed{1.47 \times 10^{-5}}$$

Degree of dissociation (α)

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

$$\alpha = \frac{\text{concentration of acid or base dissociated}}{\text{initial concentration of acid or base}}$$

$$\%\ \text{of}\ \alpha = \frac{[\text{ acid or base }]\ \text{dissociated}}{\text{initial}\ [\text{ acid or base }]} \times 100\%$$

EXAMPLE – 11

Calculate the percent dissociation of 0.25 *M* benzoic acid, C_6H_5COOH.
(K_a of $C_6H_5COOH = 6.3 \times 10^{-5}$)

ANSWER – 11

	$H_2O(l)$ +	$C_6H_5COOH(aq)$ $\rightleftharpoons$	$H_3O^+(aq)$ +	$C_6H_5COO^-(aq)$
$[\ ]_i$	–	0.25	0	0
$[\ ]\Delta$	–	$-x$	$+x$	$+x$
$[\ ]_{eq}$	–	$0.25 - x$	x	x

$$K_a = \frac{[H_3O^+][C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{x^2}{0.25 - x}$$

$$K_a = \frac{x^2}{0.25 - x}$$

$K_a << 1$ ☞ assume x very small

Assumption: $0.25 - x \approx 0.25$

$$K_a = \frac{x^2}{0.25} = 6.3 \times 10^{-5}$$

$$x = 4.0 \times 10^{-3}$$

$x = 4.0 \times 10^{-3}$

Checking the assumption: $0.25 - x \approx 0.25$

$$\frac{x}{0.25} \times 100 = \frac{4.0 \times 10^{-3}}{0.25} \times 100$$

$$= 1.6\ \%$$

($< 5\ \%$ ☞ assumption justified)

$$[H_3O^+] = x = 4.0 \times 10^{-3}\ M$$

$$\text{Percent ionization} = \frac{x}{[C_6H_5COOH]_o} \times 100$$

$$= \frac{4.0 \times 10^{-3}\ M}{0.25\ M} \times 100$$

$$= \boxed{1.6\ \%}$$

K_b - Base Dissociation Constant

☐ Dissociation of weak base in water:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

EXAMPLE:

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

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

MAGNITUDE OF K_b (for weak bases)

❑ Higher $[OH^-]$ ☞ stronger base (higher basicity)
☞ has larger K_b

$$pK_b = -\log K_b$$

❑ Larger K_b ☞ lower pK_b
☞ stronger base

EXAMPLE – 12

Dimethylamine, $(CH_3)_2NH$, a key intermediate in detergent manufacture, has K_b of 5.9×10^{-4}. What is the pH of 1.5 M $(CH_3)_2NH$?

ANSWER – 12

$$H_2O(l) \; + \; (CH_3)_2NH(aq) \rightleftharpoons (CH_3)_2NH_2^+(aq) \; + \; OH^-(aq)$$

$[\;]_i$	–	1.5	0	0
$[\;]_\Delta$	–	$-x$	$+x$	$+x$
$[\;]_{eq}$	–	$1.5 - x$	x	x

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]} = \frac{x^2}{1.5 - x}$$

$$K_b = \frac{x^2}{1.5 - x}$$

$K_b << 1$ ☞ **assume x very small**

Assumption: $1.5 - x \approx 1.5$

$$K_b = \frac{x^2}{1.5} = 5.9 \times 10^{-4}$$

$$x = 0.0297$$

$$x = 0.0297$$

Checking the assumption: $1.5 - x \approx 1.5$

$$\frac{x}{1.5} \text{ x } 100 = \frac{0.0297}{1.5} \text{ x } 100$$

$$= 2\ \%$$

(< 5 % ☞ assumption justified)

$[OH^-] \;=\; x \;=\; 0.0297$

$$\begin{aligned} pOH &= -\log [OH^-] \\ &= -\log (0.0297) \\ &= 1.53 \end{aligned}$$

$pH + pOH = pK_w = 14.00$

$$\begin{aligned} pH &= 14.00 - 1.53 \\ &= \boxed{12.47} \end{aligned}$$

EXAMPLE – 13

Trimethylamine , $(CH_3)_3N$ is a weak base. Calculate the concentration of OH^- at equilibrium if 0.100 M $(CH_3)_3N$ is dissociate. ($K_b = 6.5 \times 10^{-5}$)

ANSWER– 13

$$H_2O(\mathit{l}) + (CH_3)_3N(\mathit{aq}) \rightleftharpoons (CH_3)_3NH^+(\mathit{aq}) + OH^-(\mathit{aq})$$

$[\ ]_i$	–	0.100	0	0
$[\ ]_\Delta$	–	$-x$	$+x$	$+x$
$[\ ]_{eq}$	–	$0.100 - x$	x	x

$$K_b = \frac{[(CH_3)_3NH^+]\ [OH^-]}{[(CH_3)_3N]} = \frac{x^2}{0.100 - x}$$

$$K_b = \frac{x^2}{0.100 - x}$$

$K_b << 1$ ☞ **assume x very small**

Assumption: $0.100 - x \approx 0.100$

$$K_b = \frac{x^2}{0.100} = 6.5 \times 10^{-5}$$

$$x = 2.55 \times 10^{-3}$$

❖ $x = [OH^-] \boxed{= 2.55 \times 10^{-3}\ M}$

$$x = 2.55 \times 10^{-3}$$

Checking the assumption: $0.100 - x \approx 0.100$

$$\frac{x}{0.100} \times 100 = \frac{2.55 \times 10^{-3}}{0.100} \times 100$$

$$= 2.6\%$$

(< 5 % ☞ assumption justified)

❖ $x = [OH^{-}]$ $\boxed{= 2.55 \times 10^{-3}\ M}$

7.1 ACIDS AND BASES

Teaching and learning outcomes

At the end of the lesson, student should be able to

7.1	**Acids and Bases**
h)	Explain qualitatively salt hydrolysis using hydrolysis equations of: i. Strong acid and strong base ii. Strong acid and weak base iii. Weak acid and strong base
i)	Classify the salts formed in (h) **Classify the salts as neutral, acidic or basic in (h)*

Salt Hydrolysis

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

General equation of neutralization:

$$\underset{\text{acid}}{HX} + \underset{\text{base}}{MOH} \longrightarrow \underset{\text{salt}}{MX} + \underset{\text{water}}{H_2O}$$

- **Salt hydrolysis is a chemical reaction between anion or cation of a salt with water molecules to form H_3O^+ or OH^-.**

MX salt dissociation equation:

$$MX \longrightarrow \underset{\text{cation}}{M^{+}} + \underset{\text{anion}}{X^{-}}$$

Cation Hydrolysis :

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

Anion Hydrolysis :

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

- The **pH** value of a solution **depends** on whether OH^{-} or H_3O^{+} is produced during **hydrolysis.**

SALTS

3 types of salts are :

1) **neutral salts**
2) **basic salts**
3) **acidic salts**

97

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

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

$$K_w = [H_3O^+]\ [OH^-]$$

$$= 1 \times 10^{-14}$$

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

☞ $pH = 7$

100

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_3COO^- is conjugate base of weak acid, CH_3COOH

☞ CH_3COO^- 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**

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

103

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 – 14

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

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

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

105

ANSWER – 14

a) $NaOH(aq) + HCN(aq) \longrightarrow NaCN + H_2O$

$NaCN(aq) \longrightarrow Na^+(aq) + CN^-(aq)$

- **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^-**

Hydrolysis of CN^- :

$$\text{CN-(aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{HCN(aq)} + \text{OH-(aq)}$$

- The solution is basic because the hydrolysis of CN^- produces OH^-

  So, the NaCN is basic salt

- pH of the basic salt solution is > 7.0

EXAMPLE – 15

CH_3NH_3Cl is a salt formed when a weak base,CH_3NH_2 is reacted with a strong acid, HCl.

a) **Write a balanced equation to show the reaction between CH_3NH_2 and HCl. Classify the salt formed.**

b) **What would be expected pH of the CH_3NH_3Cl solution ? Explain the answer using equation(s).**

108

ANSWER – 15

a) $CH_3NH_2(aq) + HCl\ (aq) \longrightarrow CH_3NH_3Cl\ (aq)$

- **Cl^- is anion of strong acid, HCl**
  - ☞ **Cl^- does not hydrolyzed in water**

- **$CH_3NH_3{}^+$ is conjugate acid of weak base, CH_3NH_2**
  - ☞ **$CH_3NH_3{}^+$ is hydrolyzed in water to produce H_3O^+**

Hydrolysis of $CH_3NH_3^+$:

$$CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$$

- The solution is acidic because hydrolysis of $CH_3NH_3^+$ produces H_3O^+

  So, the CH_3NH_3Cl is acidic salt

- pH of the acidic salt solution is < 7.0

7.1 ACIDS AND BASES

Teaching and learning outcomes

At the end of the lesson, student should be able to

7.1	**Acids and Bases**
j)	Define buffer solution.
k)	Explain how a buffer solution controls its pH
l)	Write the Henderson-Hasselbalch equation for a given buffer solution.
m)	Calculate the pH of buffer solutions using the Henderson-Hasselbalch equation before and after the addition of strong acid or base

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.**

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

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

113

How the Acidic Buffer Solution Works?

When a small amount of strong acid is added,

- ☞ **The H_3O^+dissociated from HCl will neutralize with CH_3COO^- ion (conjugate base)**

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

- ☞ **As a result, [CH_3COOH] increases and [CH_3COO^-] decreases.**
- ☞ **However, CH_3COOH is a weak acid and thus result in very small degree dissociation**
- ☞ **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 in buffer solution 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.**
- ☞ **When concentration of CH_3COO^- increase , the equilibrium position shift to the left and replace the amount of acid use**
- ☞ **Therefore, pH not much affected.**

Henderson-Hasselbalch Equation Acidic Buffer Solution

For any weak acid, HA, the dissociation equation and K_a expression are :

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearrange the expression,

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

By applying –log on both sides gives

$$-\log[H_3O^+] = -\log K_a + \left[-\log\frac{[HA]}{[A^-]}\right]$$

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

Concentration of the salt (conjugate base)

Concentration of weak acid

Henderson-Hasselbalch Equation

Generally,

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

Example : CH_3COOH and CH_3COONa.

☞ **Equations :**

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

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

☞ **Henderson-Hasselbalch equation :**

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

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

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

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

$$\boxed{pK_a = -\log K_a}$$

EXAMPLE -16

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

(K_a of HCOOH = 1.7×10^{-4})

ANSWER -16

Initial concentration of acidic component $= [\mathrm{HCOOH}] = 0.30\ M$

Initial concentration of basic component $= [\mathrm{HCOO^-}] = 0.52\ M$

By using Henderson–Hasselbalch equation:

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

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\,\text{HCOO}^-]}{[\,\text{HCOOH}]}$$

$$= -\log\,(1.7 \text{ x } 10\text{–}4) + \log \left(\frac{0.52}{0.30}\right)$$

$$= \boxed{4.01}$$

EXAMPLE -17

(a) Calculate the pH of a buffer system containing 1.0 *M* CH_3COOH and 1.0 *M* CH_3COONa.

(b) What is the pH after addition of 0.10 mole gaseous HCl to 1 L of the solution? Assume that the volume of the solution does not change when the HCl is added. (K_a for $CH_3COOH = 1.8 \times 10^{-5}$)

ANSWER-17

(a)

Initial concentration of acidic component = $[CH_3COOH]$ = $1.0\ M$

Initial concentration of basic component = $[CH_3COO^-]$ = $1.0\ M$

By using Henderson–Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\text{ conj. base}]}{[\text{acid}]}\right)$$

(a)

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

$$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{1.0}{1.0}\right)$$

$$= \boxed{4.74}$$

(b) **Before addition of HCl:**

No. of mole = MV

Moles of CH_3COOH = 1.0 mol/L x 1 L

= 1 mol CH_3COOH

Moles of CH_3COO^- = 1.0 mol/L x 1 L

= 1 mol CH_3COO^-

(b) **After addition of HCl:**

HCl dissociates completely in water.

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

0.10 mol 0.10 mol 0.10 mol

The added H_3O^+ from acid neutralized by CH_3COO^-:

$H_3O^+(aq) + CH_3COO^-(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$

(b)

$$H_3O^+(aq) + CH_3COO^-(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$$

n_i	0.1	1.00	1.00	-
Δn	- 0.1	-0.1	+0.1	-
n_f	0.0	0.9	1.10	-

$$pH = pKa + \log\left(\frac{[CH_3COO^-]_f}{[CH_3COOH]_f}\right)$$

$$= -\log(1.8 \times 10^{-5}) + \log\frac{[0.9 \text{ mol} / 1L]}{[1.10 \text{ mol} / 1L]}$$

$$= \boxed{4.66}$$

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

129

How the Basic Buffer Solution Works?

When a small amount of strong acid is added,

- ☞ **The H_3O^+ ions will be consumed by the ammonia, NH_3 to form NH_4^+ ion.**

$$NH_{3(aq)} + H_3O^+_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

- ☞ **As a result, $[NH_4^+]$ increases and $[NH_3]$ decreases.**
- ☞ **this will cause the position of equilibrium to shift to the left and replace the NH_3 used**
- ☞ **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_2O.**

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

- ☞ **As a result, $[NH_3]$ increases and $[NH_4^+]$ decreases.**
- ☞ **However, NH_3 is a weak base and thus result in very small degree dissociation**
- ☞ **Therefore, pH not much affected.**

Henderson-Hasselbalch Equation (Basic Buffer Solution)

For any weak base, B , the dissociation equation and K_b expression are :

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Rearrange the expression,

$$[OH^-] = K_b \times \frac{[B]}{[BH^+]}$$

By applying –log on both sides gives

$$-\log [OH^-] = -\log K_b + \left[-\log \frac{[B]}{[BH^+]} \right]$$

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

Concentration of the salt (conjugate acid)

Concentration of base

Henderson-Hasselbalch Equation

Generally,

$$pOH = pK_a + \log \frac{[salt]}{[base]}$$

$$pH + pOH = 14.00$$

Example : NH_3 and NH_4Cl

☞ **Equations :**

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

$$\underset{\text{weak base}}{NH_{3(aq)}} + H_2O_{(l)} \rightleftharpoons \underset{\text{conjugate acid}}{NH_4^+{}_{(aq)}} + OH^-{}_{(aq)}$$

☞ **Henderson-Hasselbalch equation :**

salt

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

134

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

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

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

$$\boxed{pK_b = -\log K_b}$$

EXAMPLE -18

Calculate the pH of the solution containing 0.30 *M* NH_3 and 0.36 *M* NH_4Cl.

K_b for ammonia = 1.8×10^{-5}

ANSWER-18

Initial concentration of acidic component $= [NH_4^+] = 0.36\ M$

Initial concentration of basic component $= [NH_3] = 0.30\ M$

By using Henderson–Hasselbalch equation:

$$\mathrm{pOH} = \mathrm{p}K_b + \log\left(\frac{[\text{conj. acid}]}{[\text{ base}]}\right)$$

$$\mathrm{pOH} = \mathrm{p}K_b + \log\left(\frac{[NH_4^+]}{[NH_3]}\right)$$

$$\mathrm{pOH} = \mathrm{p}K_b + \log\left(\frac{[\mathrm{NH_4^+}]}{[\mathrm{NH_3}]}\right)$$

$$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.36}{0.30}\right)$$

$$= 4.82$$

$$\mathrm{pH} = 14 - 4.82$$

$$\boxed{= 9.18}$$

EXAMPLE - 19

(a) Calculate the pH of the solution prepared by mixing 500 mL 0.1 M hydrazinium chloride, N_2H_5Cl with 500 mL 0.2 M hydrazine, N_2H_4.

(b) Calculate the new pH of the buffer after the addition of 2.0 mL of 0.2 M NaOH

[K_b N_2H_4 = 1.7×10^{-6}]

ANSWER - 19

(a) **Initial mole of acidic component, N_2H_5+** $= \dfrac{0.1 \times 500}{1000} = 0.05\ \text{mol}$

Initial mole of basic component, N_2H_4 $= \dfrac{0.2 \times 500}{1000} = 0.10\ \text{mol}$

By using Henderson–Hasselbalch equation:

$$\text{pOH} = \text{p}K_b + \log\left(\frac{[\text{conj. acid}]}{[\text{base}]}\right)$$

$$\text{pOH} = \text{p}K_b + \log\left(\frac{[\,N_2H_5^+]}{[\,N_2H_4]}\right)$$

(a)

$$\mathrm{pOH} = -\log(1.7 \times 10–6) + \log\left(\frac{0.05\ \mathrm{mol/1L}}{0.10\ \mathrm{mol/1L}}\right)$$

$$= 5.47$$

$$\mathrm{pH} = 14 - 5.47$$

$$\boxed{= 8.53}$$

(b) **After addition 2.0 mL of 0.2 M NaOH :**

NaOH dissociates completely in water.

$$\text{NaOH}\,(aq) \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq)$$
$$4 \times 10^{-4}\ \text{mol} \qquad 4 \times 10^{-4}\ \text{mol} \qquad 4 \times 10^{-4}\ \text{mol}$$

The added of OH^- from base neutralized by $N_2H_5^+$

$$\text{OH}^-(aq) + \text{N}_2\text{H}_5^+(aq) \rightarrow \text{N}_2\text{H}_4\,(aq) + \text{H}_2\text{O}(l)$$

(b) $$OH^-(aq) \; + \; N_2H_5^+(aq) \; \rightarrow \; N_2H_4(aq) \; + \; H_2O(l)$$

N_i	4.0×10^{-4}	0.05	0.1	-
Δn	$- 4.0 \times 10^{-4}$	$- 4.0 \times 10^{-4}$	4.0×10^{-4}	-
n_f	0.0	0.0496	0.1004	-

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

$$= \; -\log (1.7 \times 10^{-6}) \; + \; \log \frac{[0.0496 \text{ mol } /1.002 \text{ L}]_f}{[0.1004 \text{ mol } / \text{ } 1.002 \text{ L}]_f}$$

$$= \; 5.46$$

$$pH \; = \; 14 - 5.46$$

$$= \boxed{8.54}$$

Summary: Acidic & Basic Buffer Solution Action

ACIDIC BUFFER SOLUTION	BASIC BUFFER SOLUTION
$CH_3COONa(aq) \longrightarrow Na^+(aq) + CH_3COO^-(aq)$ Salt = Completely dissociate $CH_3COOH(aq) + H_2O(l) \boxed{\rightleftharpoons} H_3O^+ (aq) + CH_3COO^-(aq)$ Weak acid= partially dissociate	$NH_4Cl\ (aq) \longrightarrow NH_4^+\ (aq) + Cl^-(aq)$ Salt =Completely dissociate $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+\ (aq)$ Weak Base= partially dissociate
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3COOH(aq)$	$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$
i) Adding a small amount of acid(H_3O^+) to the solution: $CH_3COO^-(aq) + H_3O^+ (aq) \longrightarrow CH_3COOH(aq) + H_2O(l)$ ➢ CH_3COO^-(conjugate base) will neutralize it ➢ $[CH_3COO^{-+}]$ decreased , $[CH_3COOH]$ increase ➢ The pH of the solution is not much affected	i) Adding a small amount of acid(H_3O^+) to the solution: $NH_3(aq) + H_3O^+(aq) \longrightarrow NH_4^+(aq) + H_2O(l)$ ➢ NH_3 (weak base) will neutralize it ➢ $[NH_3]$ decreased, $[NH_4^+]$ increased ➢ The pH of the solution is not much affected
ii) Adding a small amount of base (OH^-) to the solution: $CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$ ➢ CH_3COOH (weak acid) will neutralize it ➢ $[CH_3COOH]$ decreased, $[CH_3COO^-]$ increased ➢ The pH of the solution is not much affected	ii) Adding a small amount of base(OH^-) to the solution: $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$ ➢ NH_4^+(conjugate acid) will neutralize it ➢ $[NH_4^+]$decreased,$[NH_3]$ increased ➢ The pH of the solution is not much affected

Thanks!

For Attention

See You The Next Subtopic

End Slide

CHEMISTRY UNIT, KMJ

7.2 ACID-BASES TITRATIONS

Teaching and learning outcomes

At the end of the lesson, student should be able to

7.2	**Acid-Bases Titrations**
a)	Describe the titration process.
b)	Distinguish between the end point and equivalence point
c)	Sketch and interpret the variation of pH against titre value for titrations between: i. strong acid-strong base ii. Strong acid- weak base iii. Weak acid-strong base.
d)	Interpret the variation of pH against titre values* in (c) **titre value is the amount of acid neutralized per mL titrant solution*
e)	Identify suitable indicators for acid-base titration.

TITRATION

A method for determining the concentration of a solution using another solution (known concentration), called standard solution.

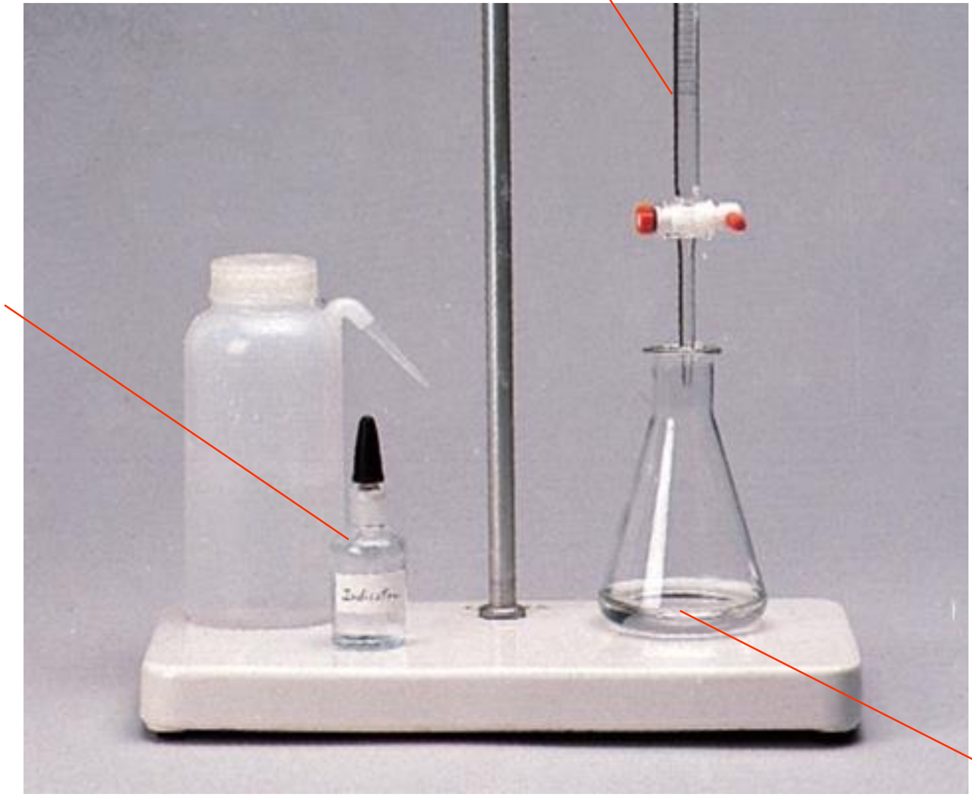
Burette:

EXAMPLE: NaOH(*aq*) - titrant

Indicator:

EXAMPLE:

phenolphthalein



Conical flask:

EXAMPLE: CH_3COOH(*aq*) - analyte

EQUIVALENCE POINT

- The point at which the reaction is complete

- The number of moles of base is stoichiometrically to the number of moles of acid have reacted

EXAMPLE:

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

0.1 mol 0.1 mol

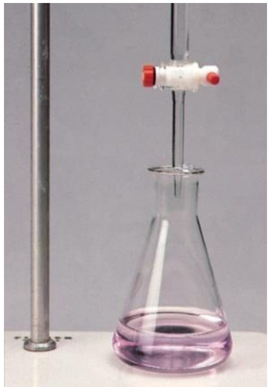
$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$

0.1 mol 0.2 mol

- No more acid or base left in the solution

END POINT

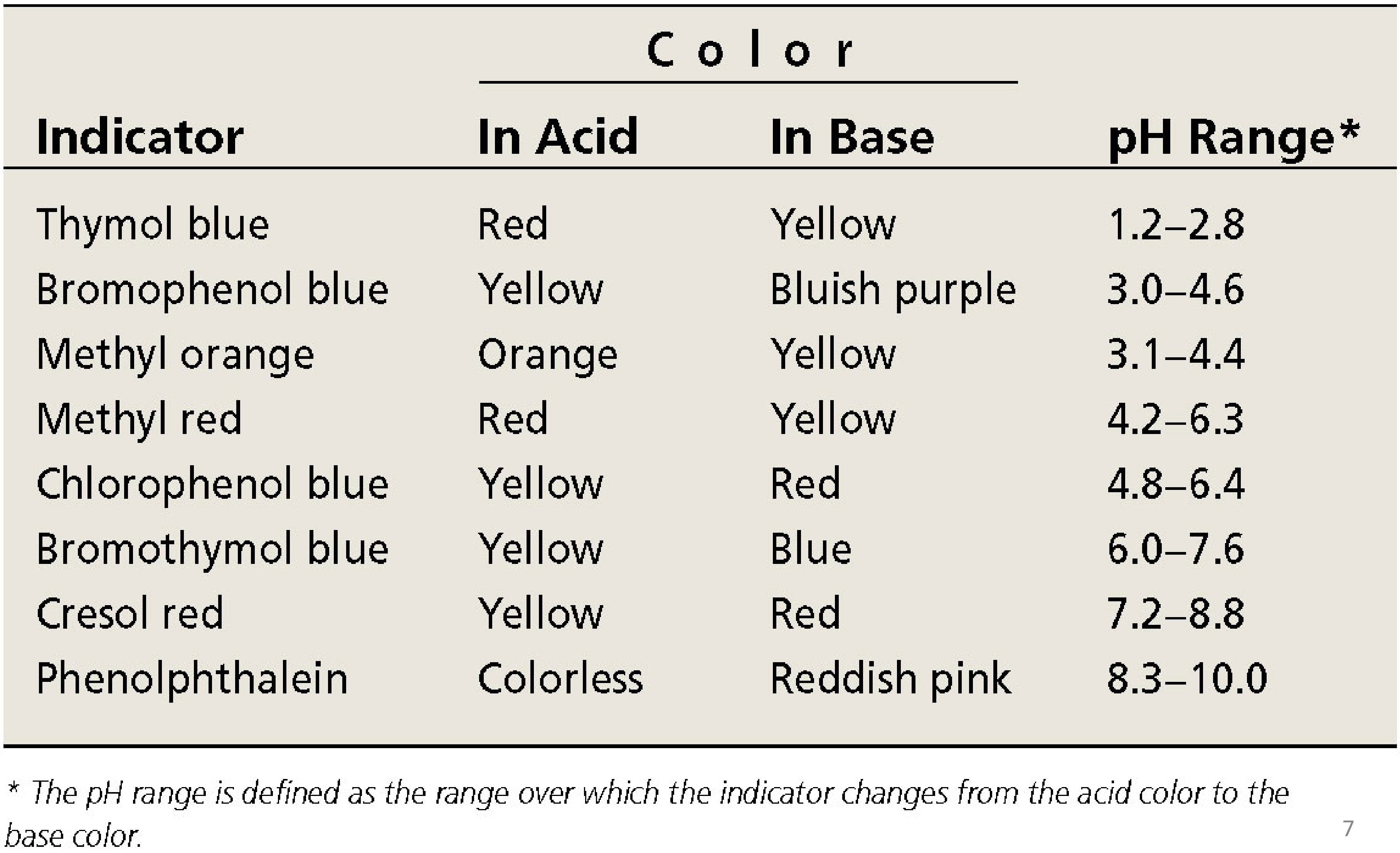
- The point at which the indicator change color
- The titration is stopped at the end point
- The end point should occur at the equivalence point. Therefore, selecting suitable indicator with an end point close to equivalence point is essential to obtain the ideal result in titration



INDICATOR

- Weak organic acid that has different colour than its conjugate base
- Commonly used to indicate the equivalence point of an acid-base titration by its colour change.
- Acid-base indicators has its own pH range in which the colour change occurs

Some Common Acid–Base Indicators



	Color		
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 RANGE

- Range over which the indicator changes from the acid color to the base color

EXAMPLE:

	pH range
Phenolphthalein	8.3 ~ 10.0
Methyl orange	3.1 ~ 4.4
Methyl red	4.2 ~ 6.3

☐ The pH range at the equivalence point is determined from the steep vertical portion in the titration curve

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

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).

The Titration of a Strong Acid with a Strong Base

Titration of 25.0 mL of 0.100 M HCl with 0.100 M NaOH

a) Initial pH (before adding any base)

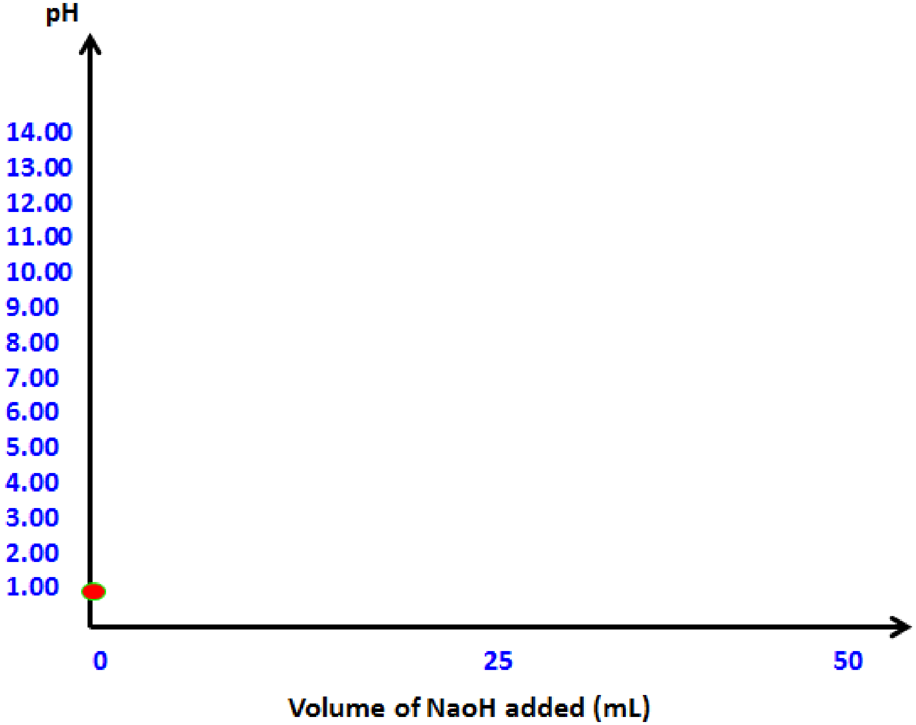
The initial pH of the solution is simply the pH of a 0.100 M HCl solution.

Since HCl is a strong acid, the concentration of H_3O^+ is also 0.100 M and the pH is 1.00

$$pH = -\log [\,H_3O^+]$$

$$pH = -\log (0.100)$$

pH = 1.00



b) pH after adding 5.00 mL NaOH

As NaOH is added to the solution, it neutralizes H_3O^+ :

$$\mathbf{HCl(\mathit{aq}) + NaOH(\mathit{aq}) \rightarrow NaCl(\mathit{aq}) + H_2O(\mathit{l})}$$

☞ **find moles of H_3O^+ remaining**

	HCl	NaOH
Initial mol	= 0.10 mol / L x 0.025 L = 0.0025	= 0.10 mol / L x 0.005 L = 0.0005
Change (mol)	– 0.0005	– 0.0005
Remaining (mol)	0.002	0

Total volume = 25 mL + 5 mL

= 30 mL

= 0.030 L

$$[\mathrm{HCl}] = \frac{\text{Mole of remaining HCl}}{\text{Total volume of solution (in L)}}$$

$$= \frac{0.002\ \text{mol}}{0.030\ \text{L}}$$

= 0.0667 *M*

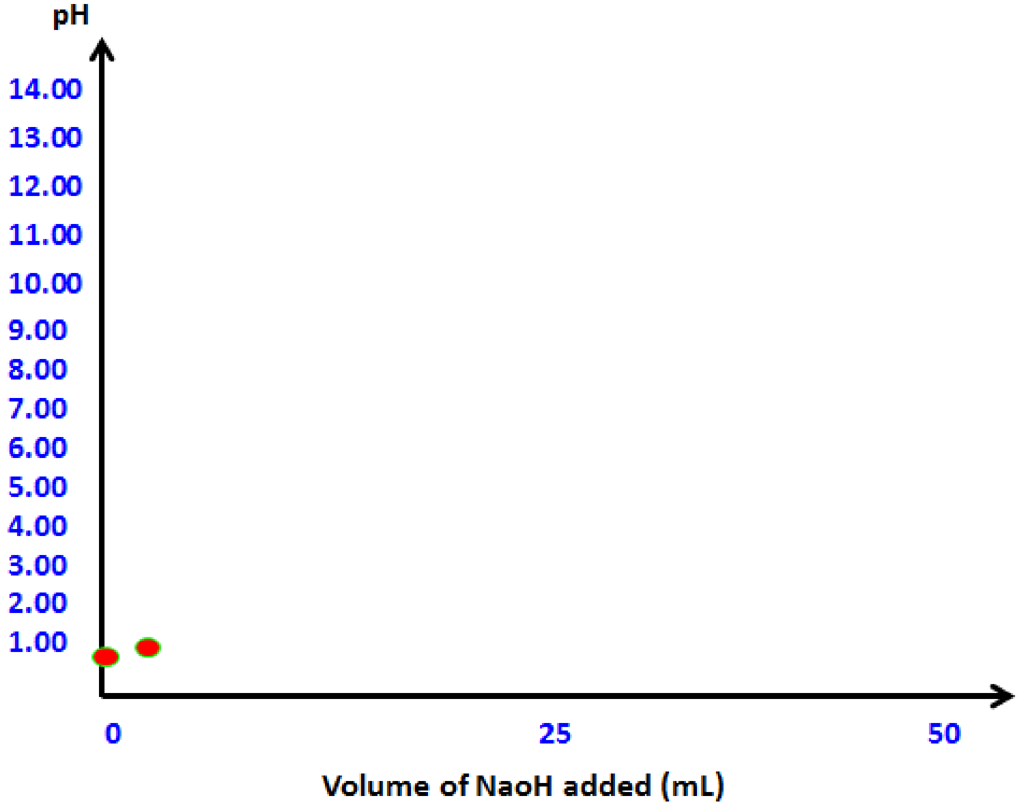
$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

0.0667 *M* 0.0667 *M*

$pH = -\log [H_3O^+]$

$= -\log (0.0667)$

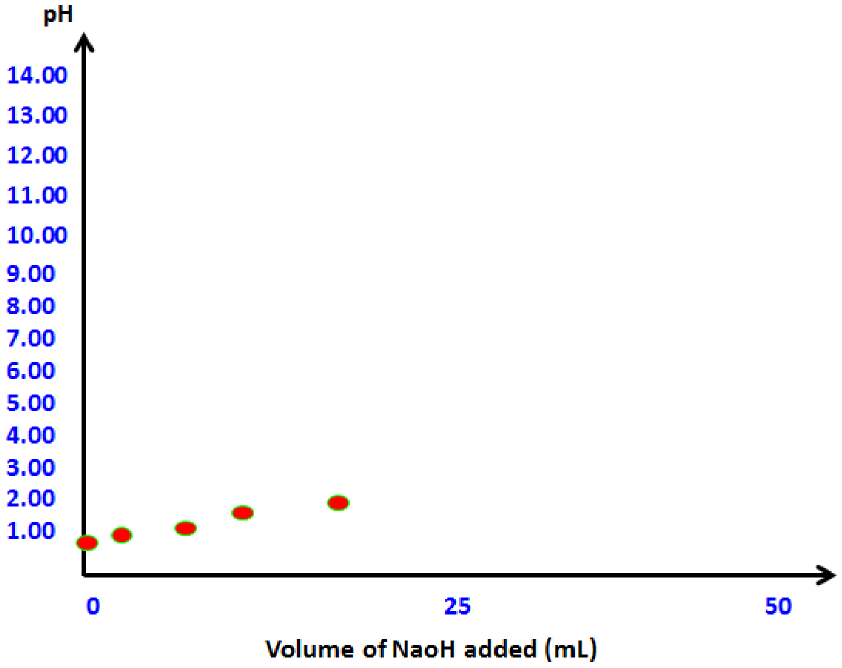
$= 1.18$



c) pH’s after adding 10.0, 15.0 and 20.0 mL NaOH

As more NaOH is added, it further neutralizes the H_3O^+ in the solution. The pH at each point is calculated in the same way that we calculated the pH at the 5.00 mL point.

Volume of NaOH added (mL)	pH
10.0	1.37
15.0	1.60
20.0	1.95



c) pH after adding 25.0 mL NaOH (Equivalence point)

At the equivalence point, the strong base has completely neutralized the strong acid. The solution contain salt and water

☞ **find pH of the salt solution**

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

	HCl	NaOH
Mole	= 0.10 mol / L x 0.025 L = 0.0025	= 0.10 mol / L x 0.025 L = 0.0025
Change (mol)	– 0.0025	– 0.0025
Remaining (mol)	0	0

$$\mathrm{HCl}(aq) \quad + \quad \mathrm{NaOH}(aq) \quad \rightarrow \quad \mathrm{NaCl}(aq) \quad + \quad \mathrm{H_2O}(l)$$

0.0025 mol 0.0025 mol

0.0025 mol of NaOH reacted with 0.0025 mol of HCl

☞ **no more HCl and NaOH**

Solution contains Na^+ and Cl^-

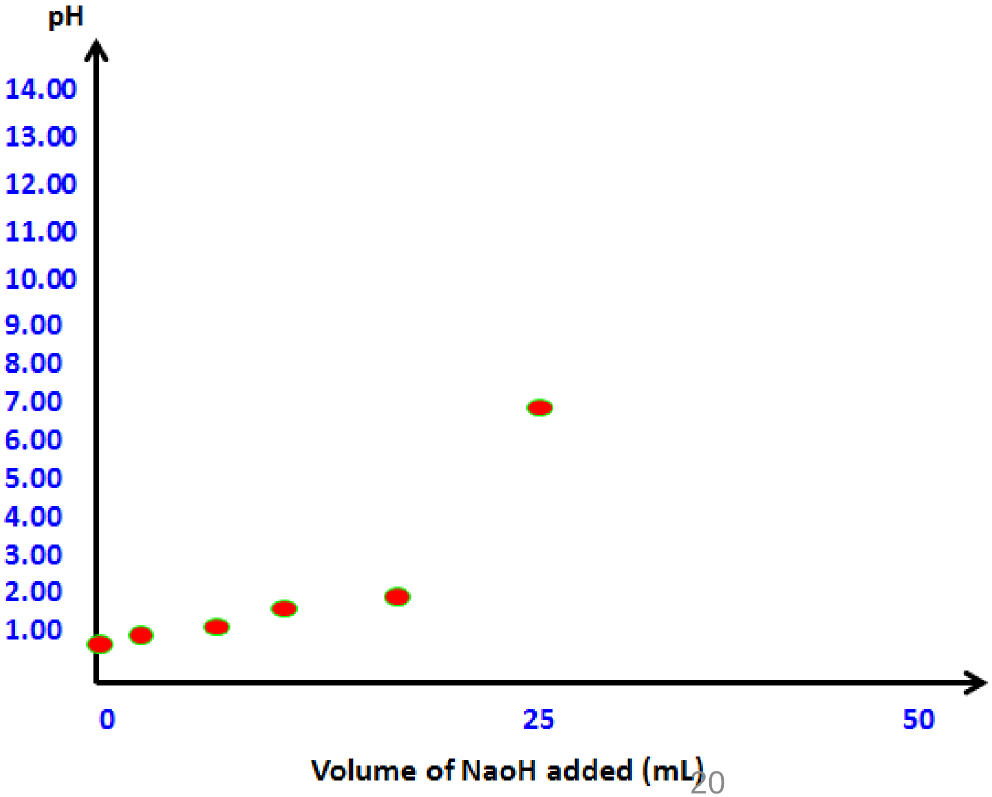
☞ **Na^+ and Cl^- do not hydrolysed**

The pH at equivalence point is calculated based on $[H_3O^+]$ from the autoionization of water.

The $[H_3O^+]$ from the autoionization of water is 1.00×10^{-7} M

$[H_3O^+] = 1.0 \times 10^{-7}$

pH = 7.00 (neutral)



d) pH after adding 30.0 mL NaOH

- After equivalence point:
  - ☞ Find moles of OH^- remaining

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

	HCl	NaOH
Mole	= 0.10 mol / L x 0.025 L = 0.0025	= 0.10 mol / L x 0.030 L = 0.0030
Change (mol)	– 0.0025	– 0.0025
Remaining (mol)	0	= 0.0005

Total Volume = 25 mL + 30 mL = 0.055 L

$$[\mathrm{NaOH}] = \frac{\text{Mole of NaOH remaining}}{\text{Total volume (in L)}}$$

$$= \frac{0.0005\ \text{mol}}{0.055\ \text{L}}$$

$$= 0.00909\ M$$

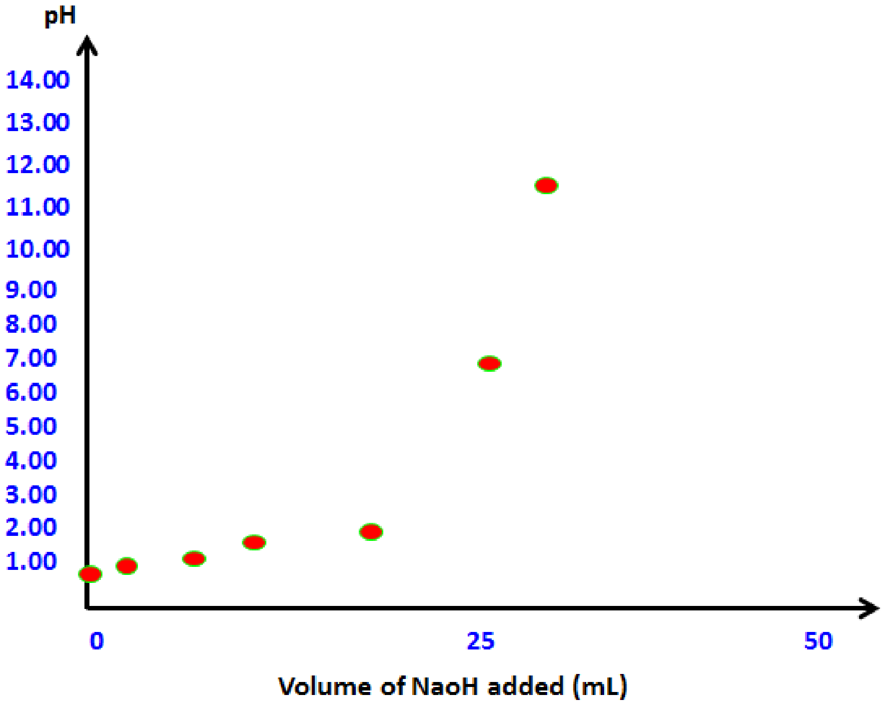
$$\mathrm{NaOH}(aq) \rightarrow \mathrm{Na}^{+}(aq) + \mathrm{OH}^{-}(aq)$$

$0.00909\ M$ $\qquad\qquad$ $0.00909\ M$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$= -\log(0.00909)$$

$$= 2.04$$



$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00$$

$$\text{pH} = \text{p}K_w - \text{pOH}$$

$$= 14.00 - 2.04$$

$$= 11.96$$

e) After adding 40.00 mL NaOH

- **After equivalence point:**
  - ☞ **Find moles of OH^- remaining**

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

	HCl	NaOH
Mole	= 0.10 mol / L x 0.025 L = 0.0025	= 0.10 mol / L x 0.040 L = 0.0040
Change (mol)	– 0.0025	– 0.0025
Remaining (mol)	0	= 0.0015

Total Volume = 25 mL + 40 mL = 0.065 L

$$[\mathrm{NaOH}] = \frac{\text{Mole of NaOH remaining}}{\text{Total volume (in L)}}$$

$$= \frac{0.0015\ \text{mol}}{0.065\ \text{L}}$$

$$= 0.02308\ M$$

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

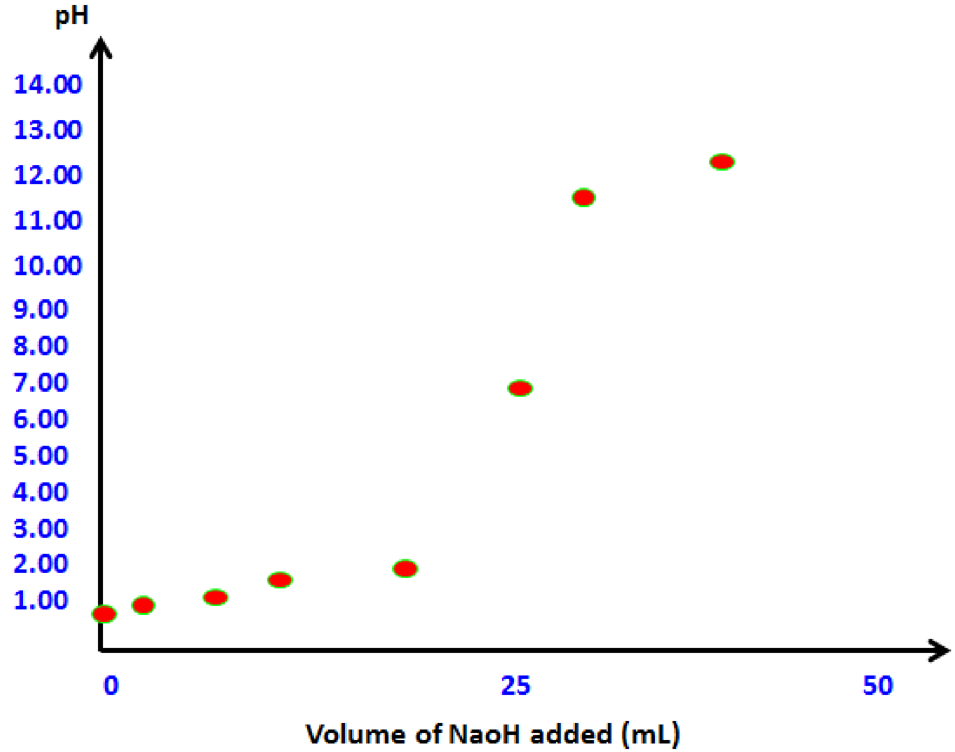
$\mathrm{NaOH}(aq)$	$\mathrm{Na^+}(aq)$	$\mathrm{OH^-}(aq)$
0.02308 M		0.02308 M

$$\text{pOH} = -\log[\text{OH}^-]$$

$$= -\log(0.02308)$$

$$= 1.64$$

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00$$



$$\text{pH} = \text{p}K_w - \text{pOH}$$

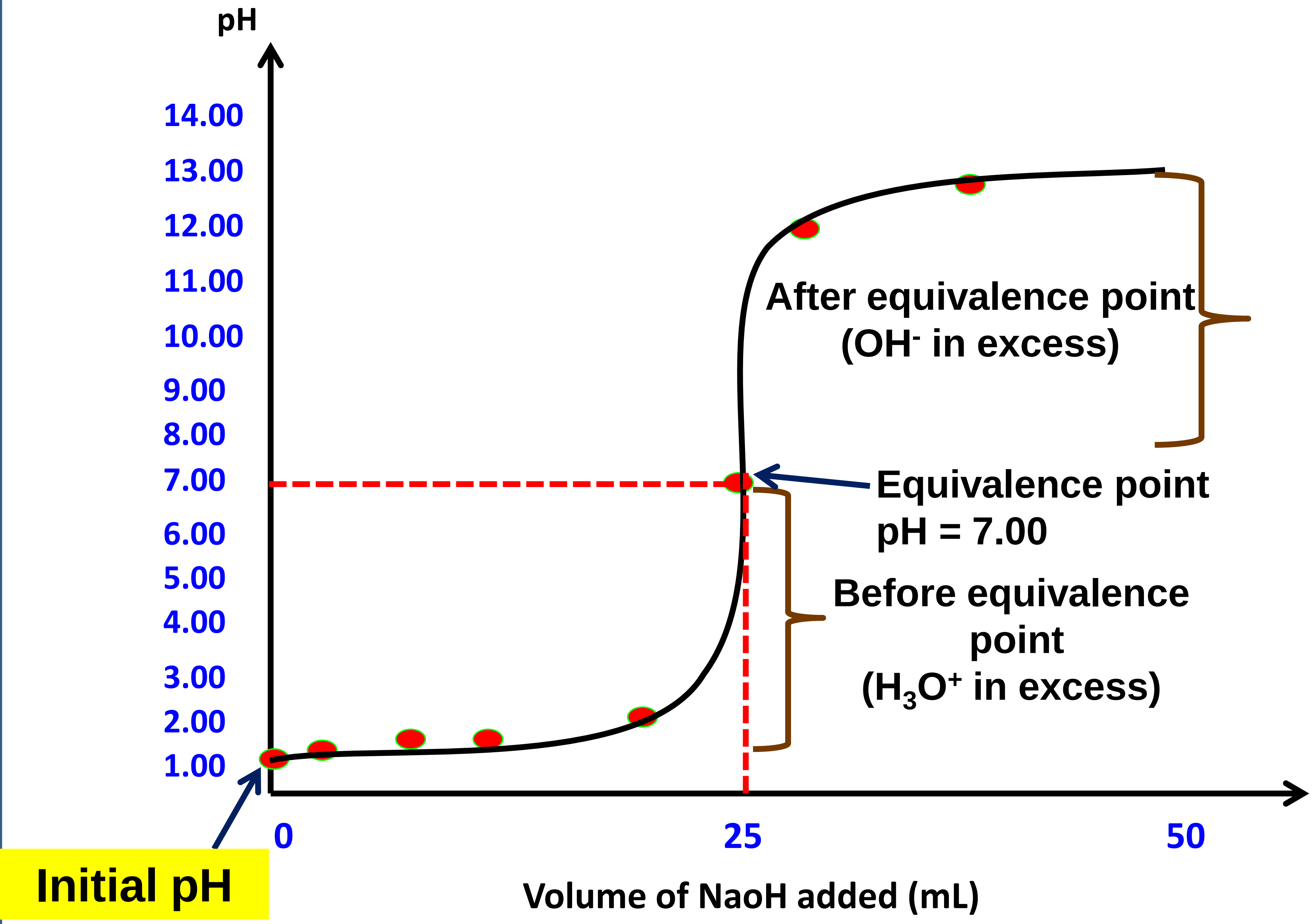
$$= 14.00 - 1.64$$

$$= 12.36$$

As NaOH is added beyond the equivalence point, it becomes the excess reagent. The [OH$^-$] remaining after neutralization is calculated.

STRONG ACID & STRONG BASE TITRATION CURVE

Titration curve: pH versus volume NaOH

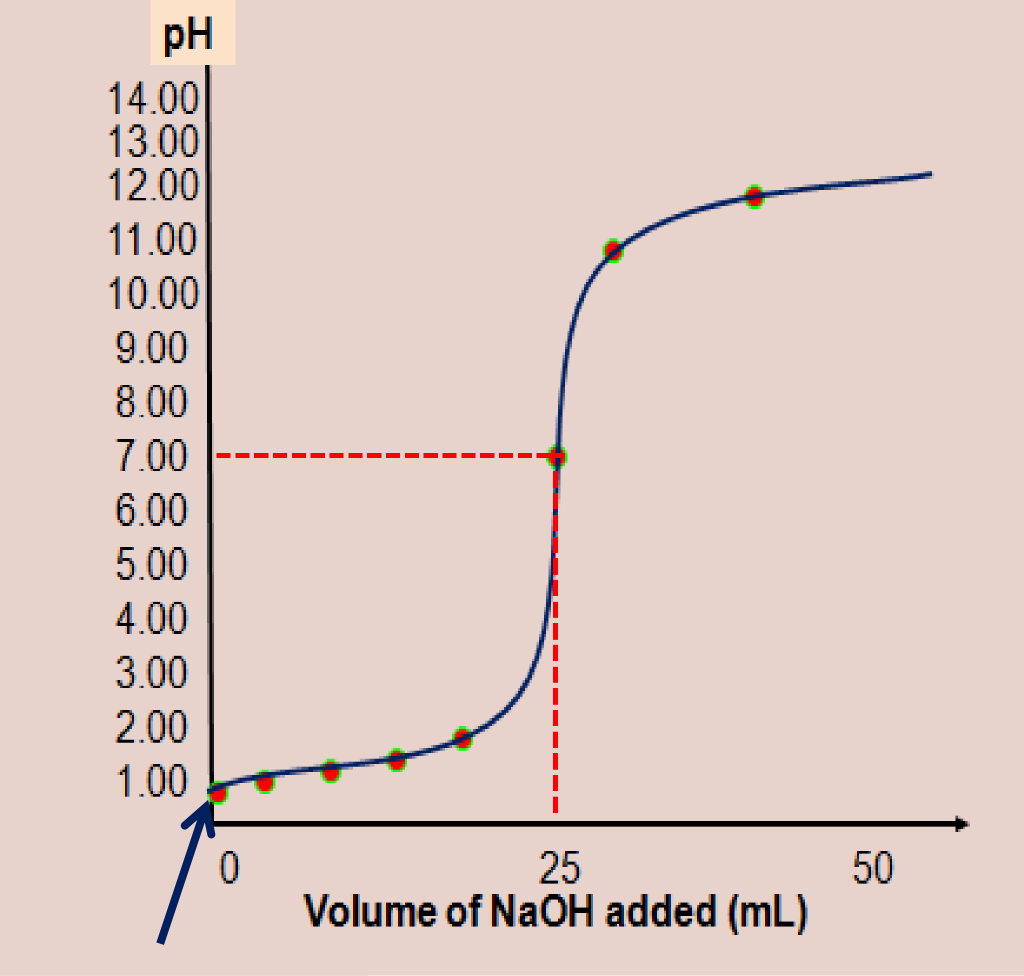


After equivalence point
(OH$^-$ in excess)

Equivalence point
pH = 7.00

Before equivalence point
(H_3O^+ in excess)

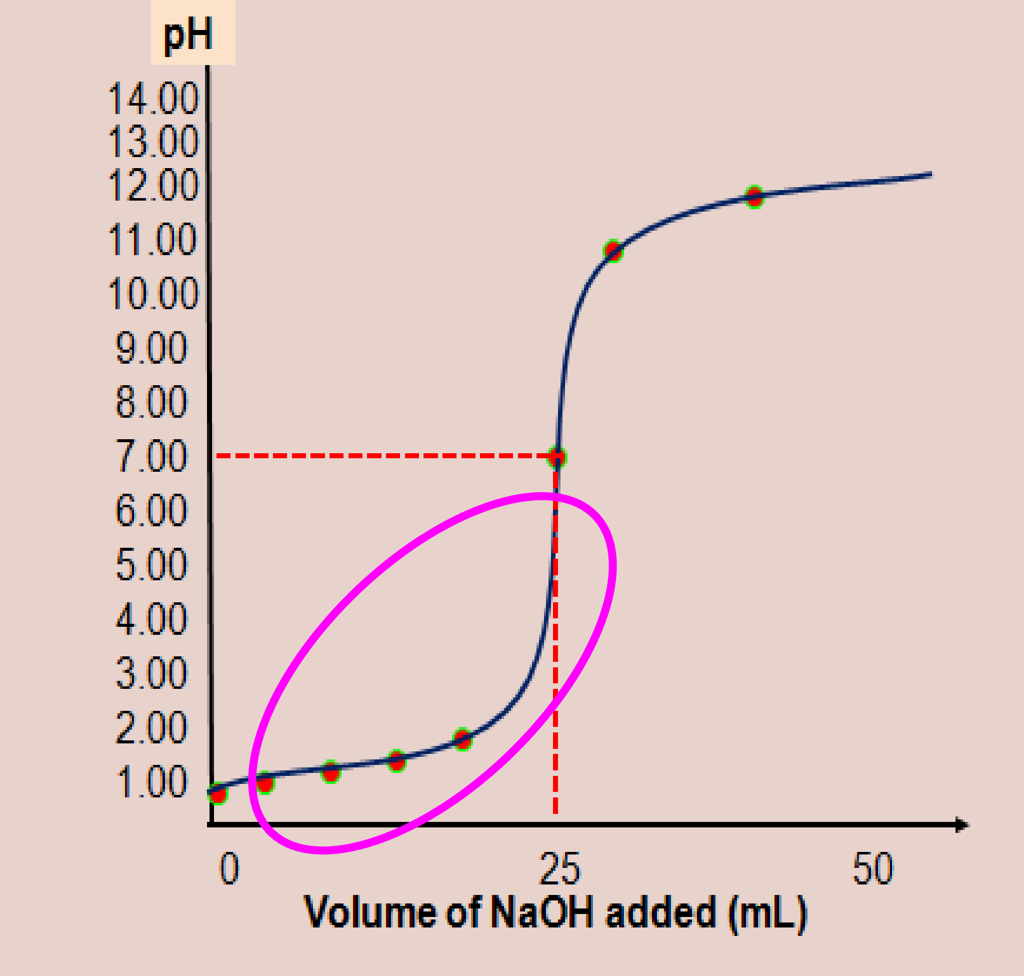
Initial pH



Initial pH

- **The pH of the solution before the addition of any base is determined by the initial concentration of the strong acid.**

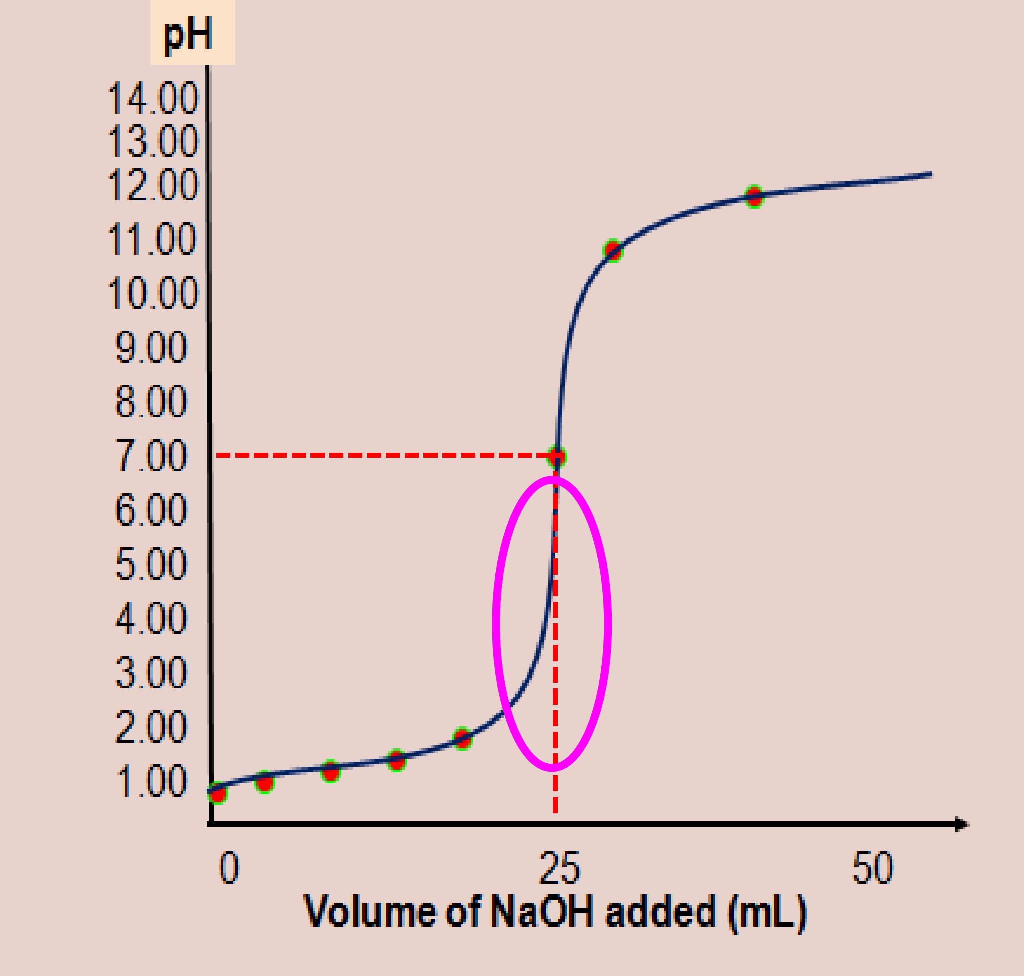
- **The pH starts out low, reflecting the high $[H_3O^+]$ of the strong acid**



Between initial pH and equivalence point

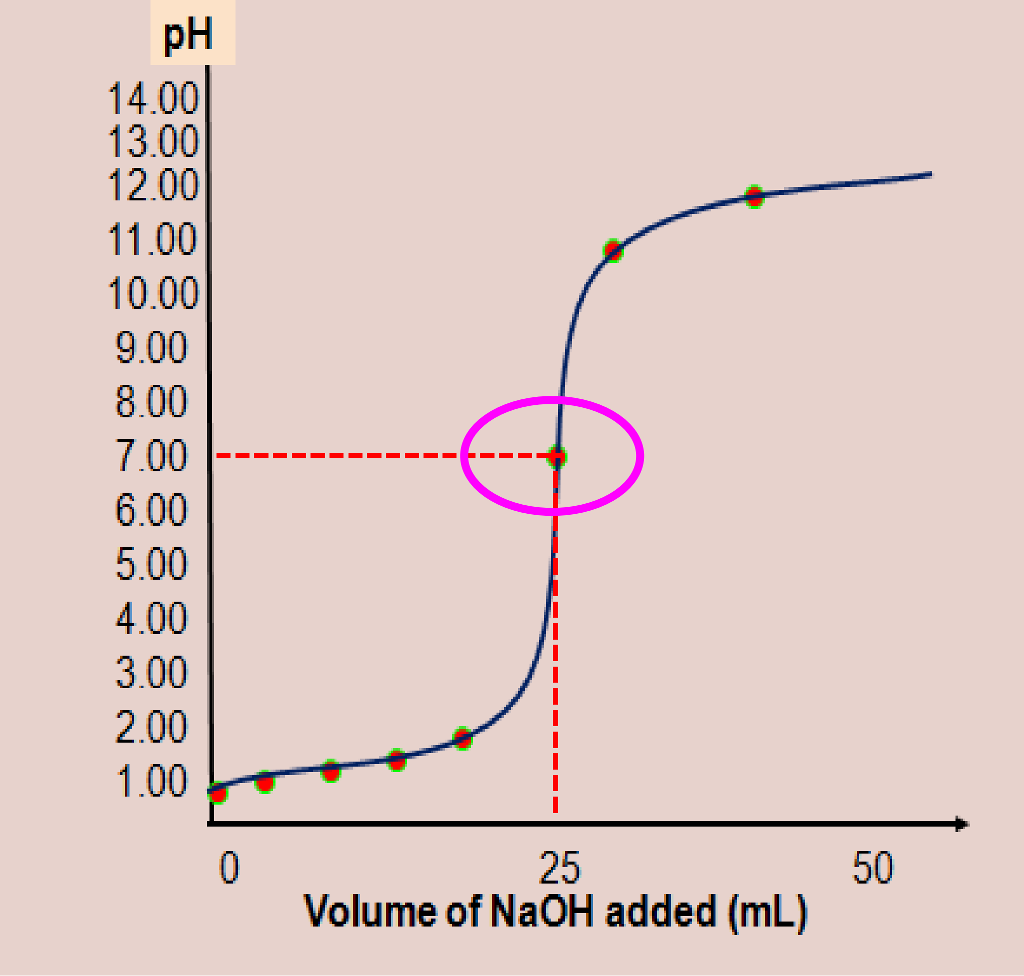
- As NaOH is added, the pH increases gradually as acid is being neutralised by the added base.

- The pH before equivalence point is determined by the $[H_3O^+]$ not yet neutralised.



- The pH rises **sharply** when the **mole of OH^- added nearly equal to the mole of H_3O^+**

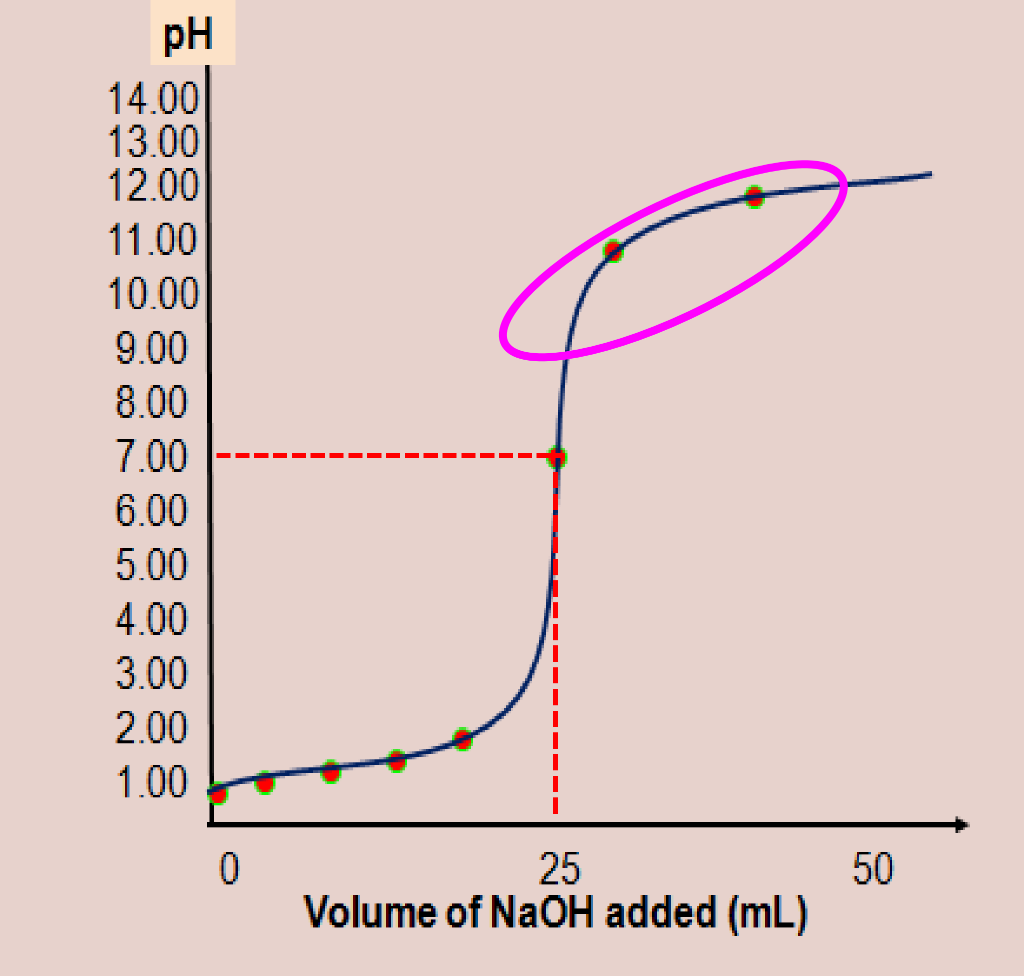
pH at equivalence point



- At the equivalencene point, the number of moles of base added is stoichiometrically to the number of moles acid have reacted

- The solution consists of salt and water

- Neither reactant is in excess and the pH = 7.00



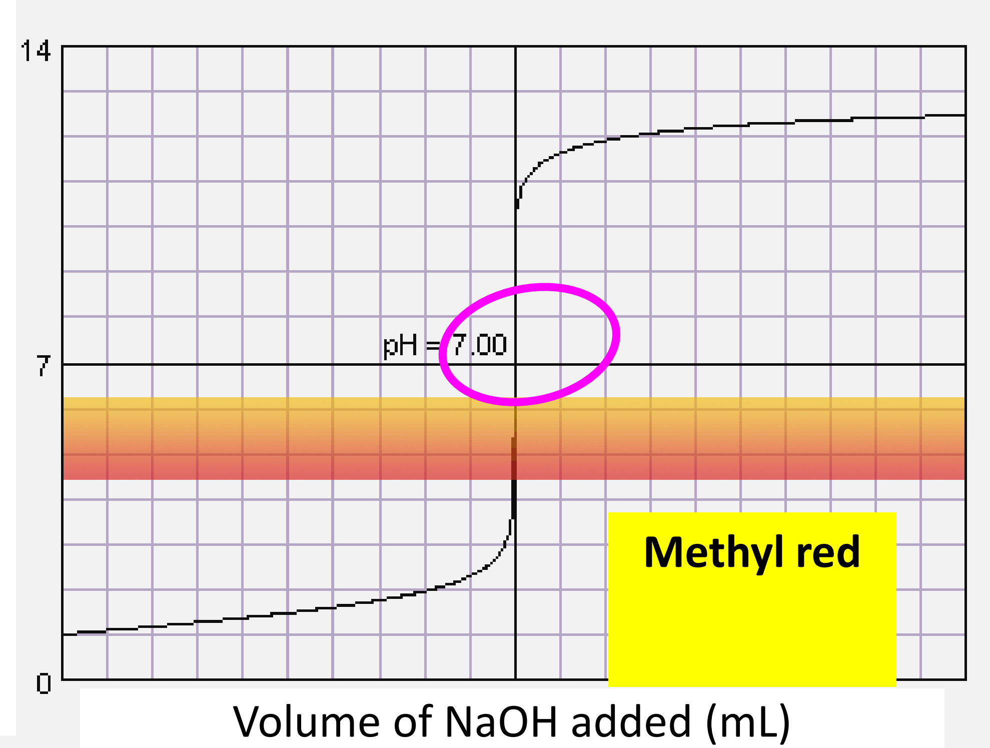
After equivalence point

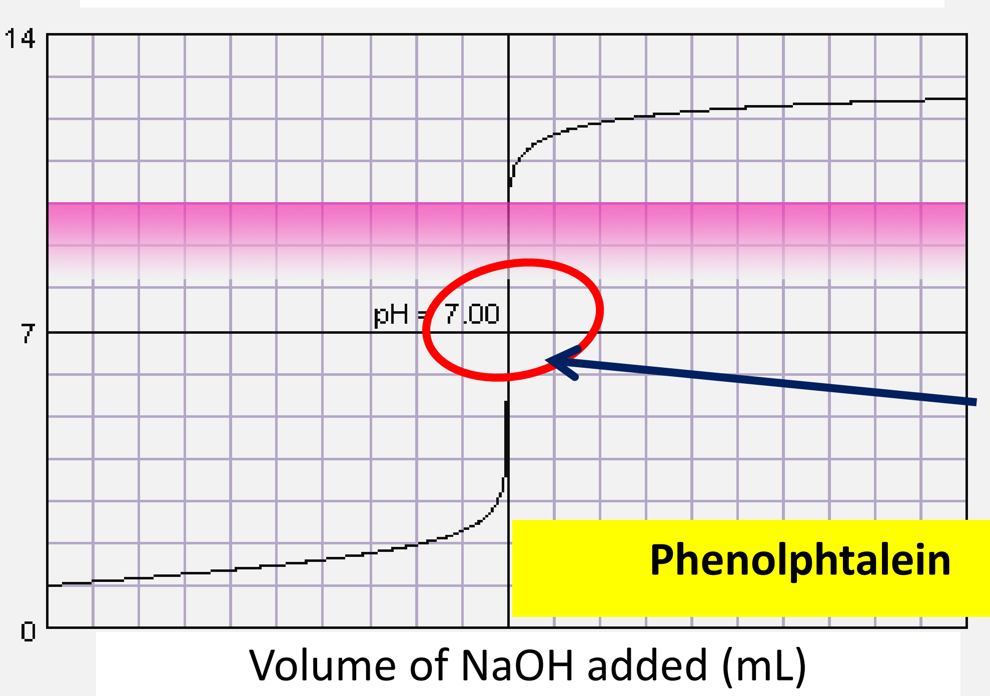
- After the equivalence point, OH^- is in excess. The pH of the solution is determined by the concentration of excess base in the solution.

- The pH increases slowly again as more base is added

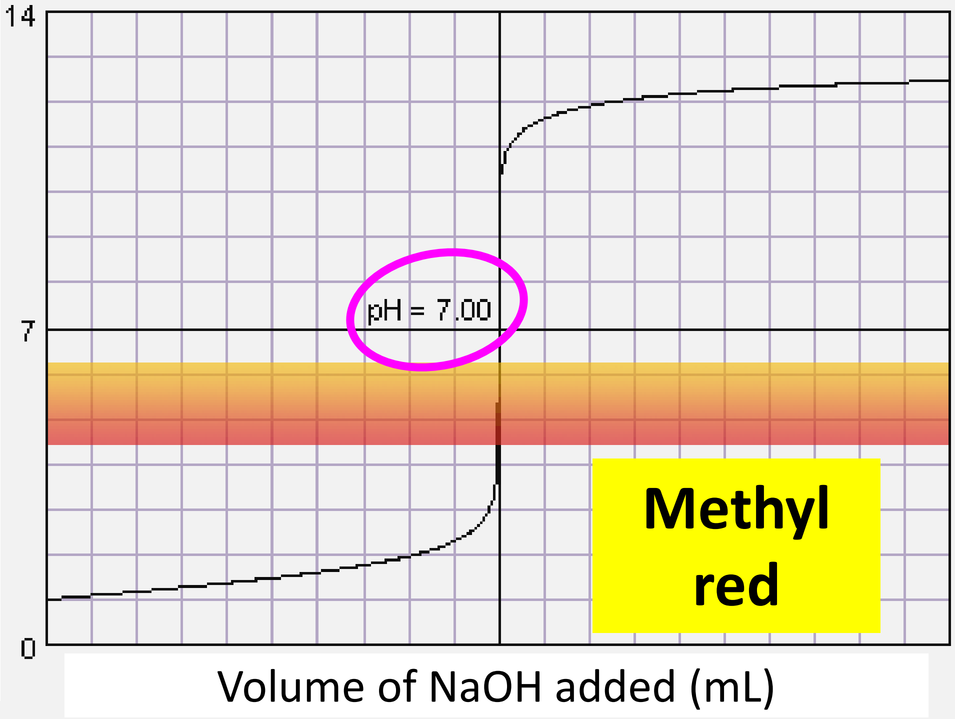
	pH range
Phenolphthalein	**8.3 ~ 10.0**
Methyl red	**4.2 ~ 6.3**

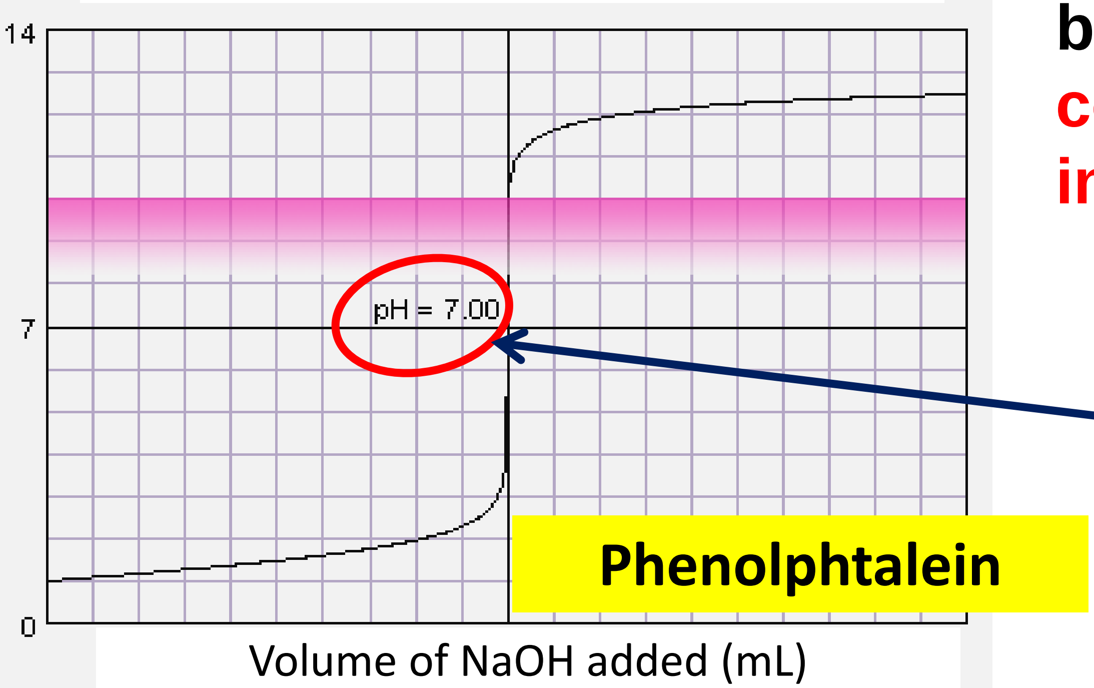
Either methyl red or phenolphthalein is a suitable indicator because each changes color on the sharp increased of the curve





Equivalence point
pH = 7.00



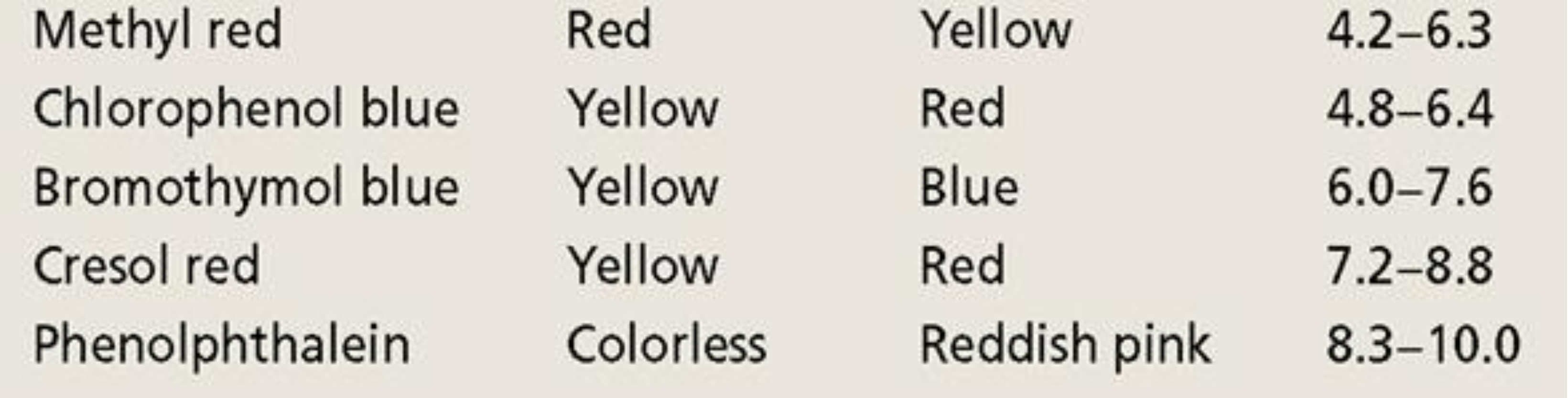


	pH range
Phenolphthalein	**8.3 ~ 10.0**
Methyl red	**4.2 ~ 6.3**

Either methyl red or phenolphthalein is a suitable indicator because each changes color on the sharp increased of the curve

Equivalence point
pH = 7.00

Suitable indicators for strong acid-strong base titration are :



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

Reason :

The indicators above are suitable because the pH range of indicators (the colour change) fall within the pH at the equivalent point of the titration.

pH = 10

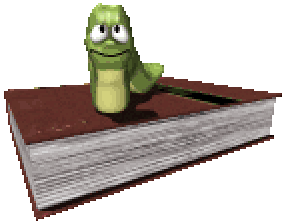
pH = 5

pH = 2

METHYL RED

Equivalence point detected using phenophtalein

EXERCISE 1 :



Sketch the titration curve when :

- a) 5.00 mL
- b) 10.00 mL
- c) 15.00 mL
- d) 24.90 mL
- e) 25.00 mL
- f) 25.10 mL
- g) 30.00 mL
- h) 45.00 ml

0.100 M HNO_3 is added to 25 mL 0.100 M NaOH

pH before addition of acid.

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

0.100 M 0.100 M

$$\mathrm{pOH} = -\log[\mathrm{OH}^{-}]$$

$$= -\log(0.100)$$

$$= 1.00$$

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_w = 14.00$$

$$\mathrm{pH} = \mathrm{p}K_w - \mathrm{pOH}$$

$$= 14.00 - 1.00$$

$$= 13.00$$

a) pH after addition of 5.00 mL HNO_3

	HNO_3	NaOH
Initial mol	$0.100\ mol\ L^{-1} \times 0.005\ L$ $= 5 \times 10^{-4}$	$0.100\ mol\ L^{-1} \times 0.025\ L$ $= 2.5 \times 10^{-3}$
Change (mol)	-5×10^{-4}	-5×10^{-4}
Remaining (mol)	0	2×10^{-3}

$$[NaOH] = \frac{\text{Mole of remaining NaOH}}{\text{Total volume of solution (in L)}}$$

$$= \frac{0.002\ mol}{0.030\ L}$$

$$= 0.0667\ M$$

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

0.0667 M 0.0667 M

$$\mathrm{pOH} = -\log[\mathrm{OH}^{-}]$$

$$= -\log(0.0667)$$

$$= 1.18$$

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_{w} = 14.00$$

$$\mathrm{pH} = \mathrm{p}K_{w} - \mathrm{pOH}$$

$$= 14.00 - 1.18$$

$$= 12.82$$

b) pH after addition of 10.00 mL HNO_3

	HNO_3	NaOH
Initial mol	0.100 mol L^{-1} x 0.010 L = 1 x 10^{-3}	0.100 mol L^{-1} x 0.025 L = 2.5 x 10^{-3}
Change (mol)	– 1 x 10^{-3}	– 1 x 10^{-3}
Remaining (mol)	0	1.5 x 10^{-3}

$$[NaOH] = \frac{\text{Mole of remaining NaOH}}{\text{Total volume of solution (in L)}}$$

$$= \frac{0.0015\ \text{mol}}{0.035\ \text{L}}$$

= 0.0429 *M*

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

0.0429 M 0.0429 M

$$\mathrm{pOH} = -\log[\mathrm{OH^-}]$$

$$= -\log(0.0429)$$

$$= 1.37$$

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_w = 14.00$$

$$\mathrm{pH} = \mathrm{p}K_w - \mathrm{pOH}$$

$$= 14.00 - 1.37$$

$$= 12.63$$

c) pH after addition of 15.00 mL HNO_3

	HNO_3	NaOH
Initial mol	$0.100 \text{ mol L}^{-1} \times 0.015 \text{ L}$ $= 1.5 \times 10^{-3}$	$0.100 \text{ mol L}^{-1} \times 0.025 \text{ L}$ $= 2.5 \times 10^{-3}$
Change (mol)	-1.5×10^{-3}	-1.5×10^{-3}
Remaining (mol)	0	1.0×10^{-3}

$$[\text{NaOH}] = \frac{\text{Mole of remaining NaOH}}{\text{Total volume of solution (in L)}}$$

$$= \frac{0.0010 \text{ mol}}{0.040 \text{ L}}$$

$$= 0.025\ M$$

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

0.025 M 0.025 M

$$\mathrm{pOH} = -\log[\mathrm{OH^-}]$$

$$= -\log(0.025)$$

$$= 1.60$$

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_w = 14.00$$

$$\mathrm{pH} = \mathrm{p}K_w - \mathrm{pOH}$$

$$= 14.00 - 1.60$$

$$= 12.40$$

c) pH after addition of 24.90 mL HNO_3

	HNO_3	NaOH
Initial mol	$0.100\ \text{mol L}^{-1} \times 0.0249\ \text{L}$ $= 2.49 \times 10^{-3}$	$0.100\ \text{mol L}^{-1} \times 0.025\ \text{L}$ $= 2.5 \times 10^{-3}$
Change (mol)	$-\ 2.49 \times 10^{-3}$	$-\ 2.49 \times 10^{-3}$
Remaining (mol)	0	1.0×10^{-5}

$$[\text{NaOH}] = \frac{\text{Mole of remaining NaOH}}{\text{Total volume of solution (in L)}}$$

$$= \frac{0.0010\ \text{mol}}{0.0499\ \text{L}}$$

$$= 0.0002\ M$$

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

0.0002 M 0.0002 M

$$\mathrm{pOH} = -\log[\mathrm{OH}^-]$$

$$= -\log(0.0002)$$

$$= 3.70$$

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_w = 14.00$$

$$\mathrm{pH} = \mathrm{p}K_w - \mathrm{pOH}$$

$$= 14.00 - 3.70$$

$$= 10.30$$

e) pH after adding 25.0 mL NaOH (Equivalence point)

At the equivalence point, the strong base has completely neutralized the strong acid. The solution contain salt and water

☞ **find pH of the salt solution**

$$HNO_3(aq) + NaOH(aq) \rightarrow NaNO_3(aq) + H_2O(l)$$

	HNO_3	NaOH
Mole	= 0.10 mol / L x 0.025 L = 0.0025	= 0.10 mol / L x 0.025 L = 0.0025
Change (mol)	– 0.0025	– 0.0025
Remaining (mol)	0	0

$HNO_3(aq)$ + $NaOH(aq)$ → $NaNO_3(aq)$ + $H_2O(l)$

0.0025 mol 0.0025 mol

0.0025 mol of NaOH reacted with 0.0025 mol of HNO_3

☞ **no more HNO_3 and NaOH**

Solution contains Na^+ and $Cl^–$

☞ **Na^+ and $NO_3^–$ do not hydrolysed**

The pH at equivalence point is calculated based on $[H_3O^+]$ from the autoionization of water.

The $[H_3O^+]$ from the autoionization of water is 1.00×10^{-7} M

$[H_3O^+] = 1.0 \times 10^{-7}$

pH = 7.00 (neutral)

f) pH after addition of 25.10 mL HNO_3

	HNO_3	NaOH
Initial mol	$0.100\ mol\ L^{-1} \times 0.0251\ L$ $= 2.51 \times 10^{-3}$	$0.100\ mol\ L^{-1} \times 0.025\ L$ $= 2.5 \times 10^{-3}$
Change (mol)	-2.5×10^{-5}	-1.0×10^{-5}
Remaining (mol)	1.0×10^{-5}	0

$$[NaOH] = \frac{\text{Mole of remaining NaOH}}{\text{Total volume of solution (in L)}}$$

$$= \frac{1.0 \times 10^{-5}\ mol}{0.0501\ L}$$

$$= 2 \times 10^{-4}\ M$$

$$\mathrm{HNO_3}(aq) \quad + \quad \mathrm{H_2O}(l) \quad \rightarrow \quad \mathrm{H_3O^+}(aq) \quad + \quad \mathrm{NO_3^-}(aq)$$

$2 \times 10^{-4} M$ $\qquad\qquad$ $2 \times 10^{-4} M$

$$\mathrm{pH} = -\log\,[\mathrm{H_3O^+}]$$

$$= -\log\,(2 \times 10^{-4})$$

$$= 3.70$$

g) pH after addition of 30.00 mL HNO_3

	HNO_3	NaOH
Initial mol	$0.100 \text{ mol L}^{-1} \times 0.030 \text{ L}$ $= 3 \times 10^{-3}$	$0.100 \text{ mol L}^{-1} \times 0.025 \text{ L}$ $= 2.5 \times 10^{-3}$
Change (mol)	-2.5×10^{-3}	-2.5×10^{-3}
Remaining (mol)	5×10^{-4}	0

$$[\text{NaOH}] = \frac{\text{Mole of remaining NaOH}}{\text{Total volume of solution (in L)}}$$

$$= \frac{5 \times 10^{-4} \text{ mol}}{0.055 \text{ L}}$$

$$= 9.09 \times 10^{-3}\ M$$

$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

$9.09 \times 10^{-3} M$ $9.09 \times 10^{-3} M$

$pH = -\log [H_3O^+]$

$= -\log (9.09 \times 10^{-3})$

$= 2.04$

h) pH after addition of 45.00 mL HNO_3

	HNO_3	NaOH
Initial mol	0.100 mol L^{-1} x 0.045 L = 4.5 x 10^{-3}	0.100 mol L^{-1} x 0.025 L = 2.5 x 10^{-3}
Change (mol)	– 2.5 x 10^{-3}	– 2.5 x 10^{-3}
Remaining (mol)	2 x 10^{-3}	0

$$[NaOH] = \frac{\text{Mole of remaining NaOH}}{\text{Total volume of solution (in L)}}$$

$$= \frac{2 \times 10^{-3}\ \text{mol}}{0.070\ \text{L}}$$

$$= 0.029\ M$$

$$\mathrm{HNO_3}(aq) \quad + \quad \mathrm{H_2O}(l) \quad \rightarrow \quad \mathrm{H_3O^+}(aq) \quad + \quad \mathrm{NO_3^-}(aq)$$

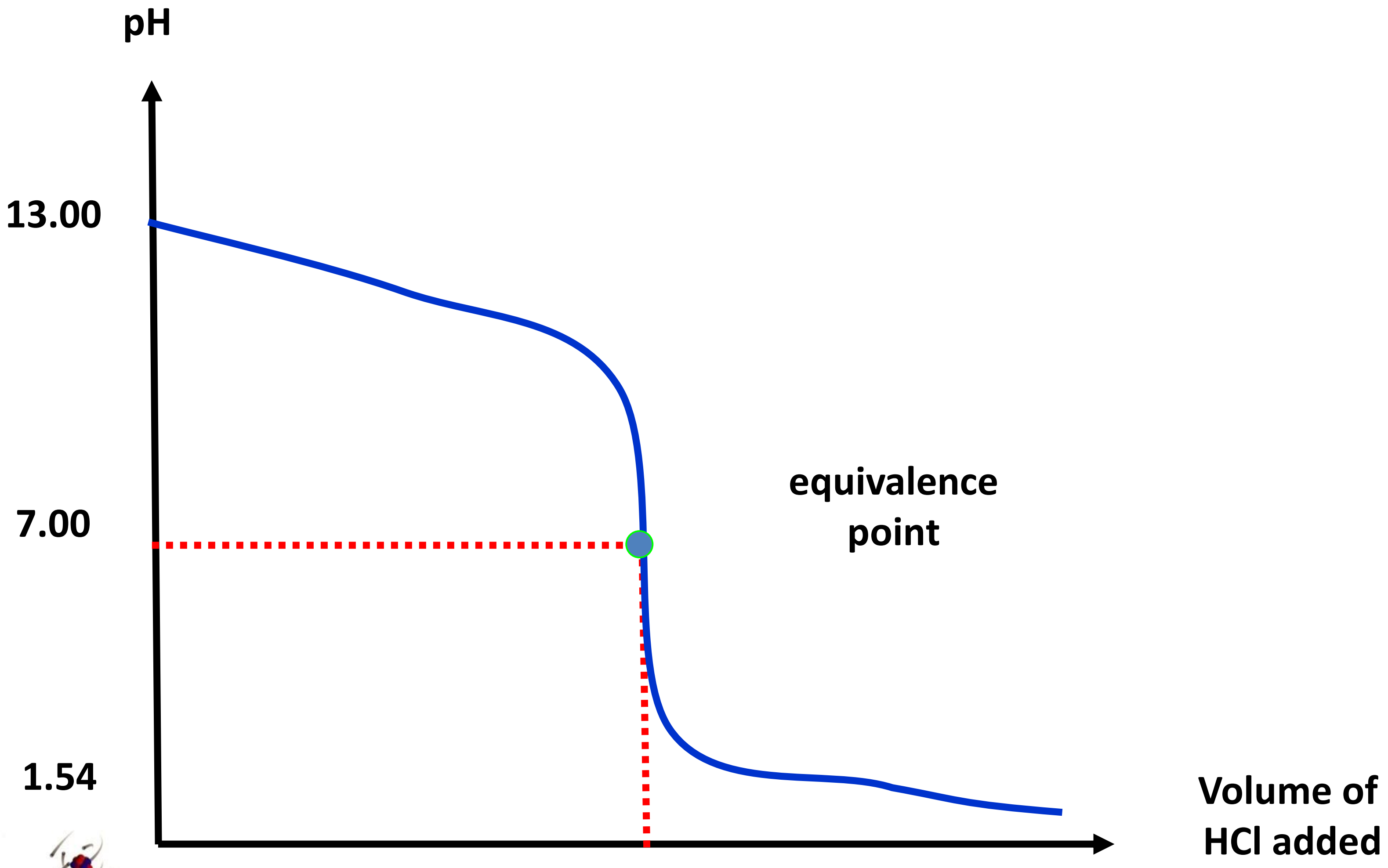
$0.029\ M$ $\qquad\qquad$ $0.029\ M$

$$\mathrm{pH} = -\log\,[\mathrm{H_3O^+}]$$

$$= -\log\,(0.029)$$

$$= 1.54$$

Titration curve: pH versus volume HCl



The Titration of weak acid and strong base

Titration of 25.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH.

a) Initial pH (before adding any base)

The initial pH of the solution is the pH of a 0.100 M CH_3COOH solution.

Since CH_3COOH is a weak acid, the concentration of H_3O^+ and the pH are calculated from the incomplete dissociation in aqueous solution

K_a $CH_3COOH = 1.8 \times 10^{-5}$

59

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

$[\ ]_i$	–	0.100	0	0
$[\ ]_\Delta$	–	$-x$	$+x$	$+x$
$[\ ]_{eq}$	–	$0.100 - x$	x	x

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{x^2}{0.100 - x} = 1.8 \times 10^{-5}$$

$$K_a = \frac{x^2}{0.100 - x}$$

$K_a << 1$ ☞ assume x very small

Assumption: $0.100 - x \approx 0.100$

$$K_a = \frac{x^2}{0.100} = 1.8 \times 10^{-5}$$

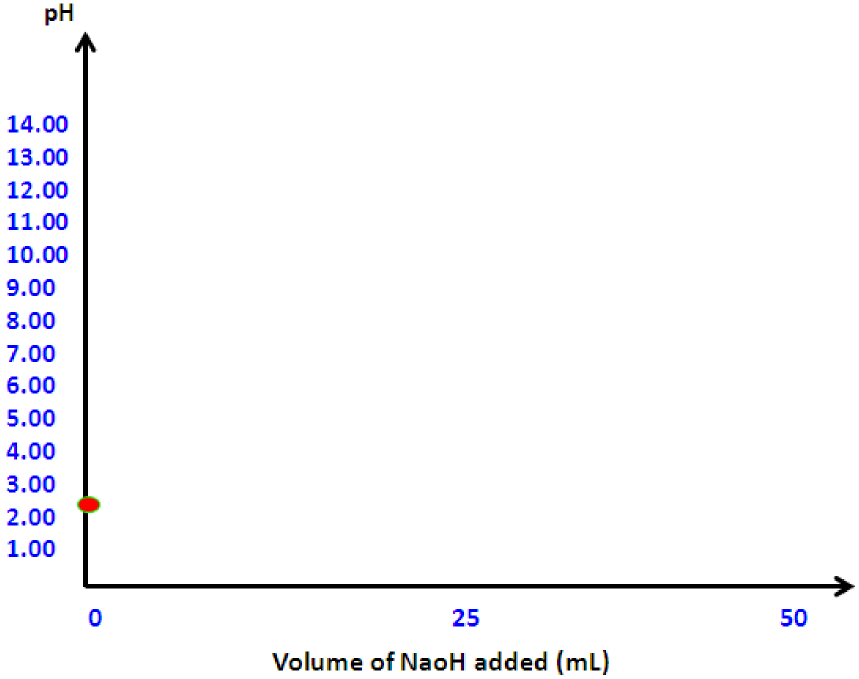
$x = 1.34 \times 10^{-3}$ M

$$[H_3O^+] \quad = \quad x \quad = \quad 1.34 \times 10^{-3}\ M$$

$$pH = -\log [H_3O^+]$$

$$= -\log (1.34 \times 10^{-3})$$

$$= \boxed{2.82}$$



The pH is initially at a higher values (less acidic) than it is for a strong acid of the same concentration

b) pH after adding 5.00 mL NaOH

The solution contains excess weak acid and its salt. Thus, the solution contains a mixture of CH_3COOH and $CH_3COO^–$ **(buffer solution)**.

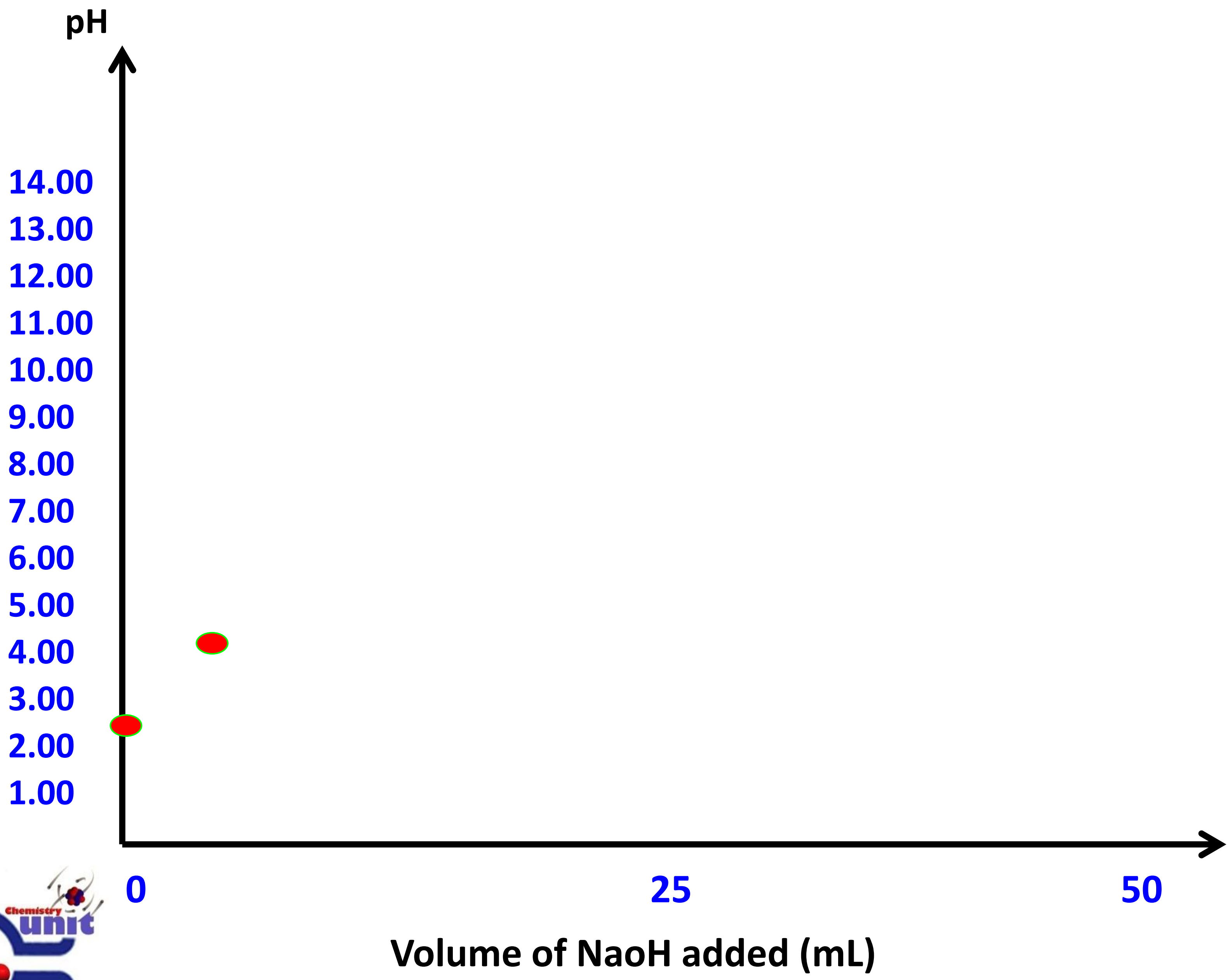
Determination of the pH involves two steps :

- consider the neutralisation reaction between CH_3COOH and OH^- to determine $[CH_3COOH]$ and $[CH_3COO^–]$.
- calculate the pH of this buffer pair

$$CH_3COOH(aq) \quad + \quad NaOH(aq) \quad \rightarrow CH_3COONa(aq) \quad + \quad H_2O(l)$$

	$CH_3COOH(aq)$ +	$OH^-(aq)$ →	$CH_3COO^-(aq)$	+ $H_2O(l)$
n_i	0.0025	0.0005	0	-
n_Δ	– 0.0005	– 0.0005	+ 0.0005	-
n_f	0.0020	0	0.0005	-

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


pH
14.00
13.00
12.00
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
25
50
Volume of NaoH added (mL)

Total Volume = 25 mL + 5 mL = 30 mL = 0.030 L

$$[CH_3COO^-] = \frac{0.0005\ \text{mol}}{0.030\ \text{L}} = 0.0167\ \text{M}$$

$$[CH_3COOH] = \frac{0.0020\ \text{mol}}{0.030\ \text{L}} = 0.00667\ \text{M}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log\frac{0.0167}{0.00667}$$

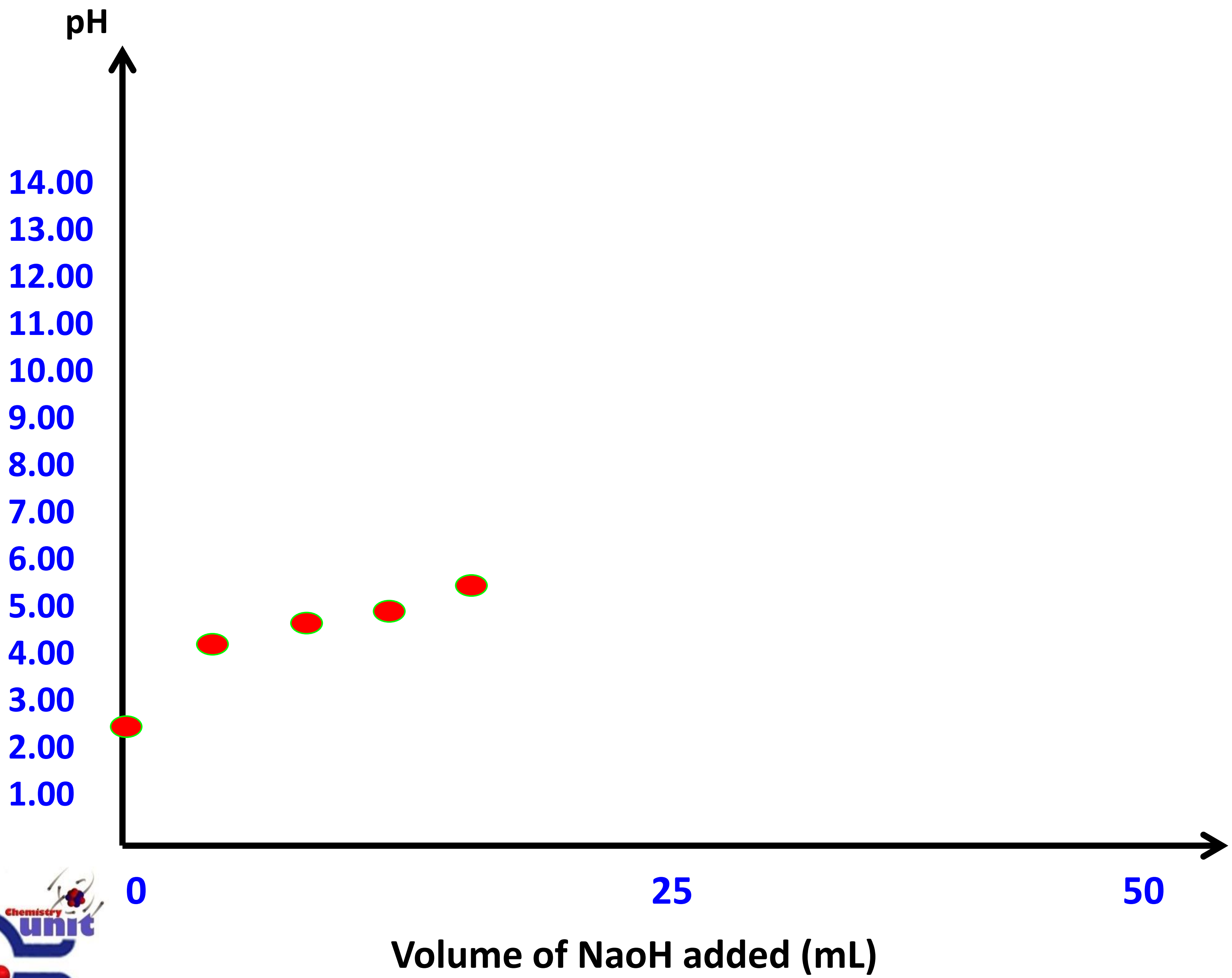
$$= \boxed{4.15}$$

d) pH after adding 10.0, 15.0 and 20.0 mL NaOH

As more NaOH is added, it converts more CH_3COOH into CH_3COO^-.

The pH of buffer solution is calculated by using Handerson-Hasselbalch equation

Volume of NaOH added (mL)	**Mol of CH_3COO^-**	**Mol of CH_3COOH**	**pH**
10.0	0.001	0.0015	4.58
15.0	0.0015	0.001	4.93
20.0	0.0020	0.0005	5.35


pH
14.00
13.00
12.00
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
25
50
Volume of NaoH added (mL)

c) pH after adding 25.0 mL NaOH (Equivalence point)

At the equivalence point, 0.0025 mol of NaOH have been added and therefore all of the CH_3COOH has been converted into its conjugate base, CH_3COO^- .

No more CH_3COOH and NaOH left. Thus, the solution contains CH_3COONa (salt) and water.

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

0.0025 mol	0.0025 mol	0.0025 mol

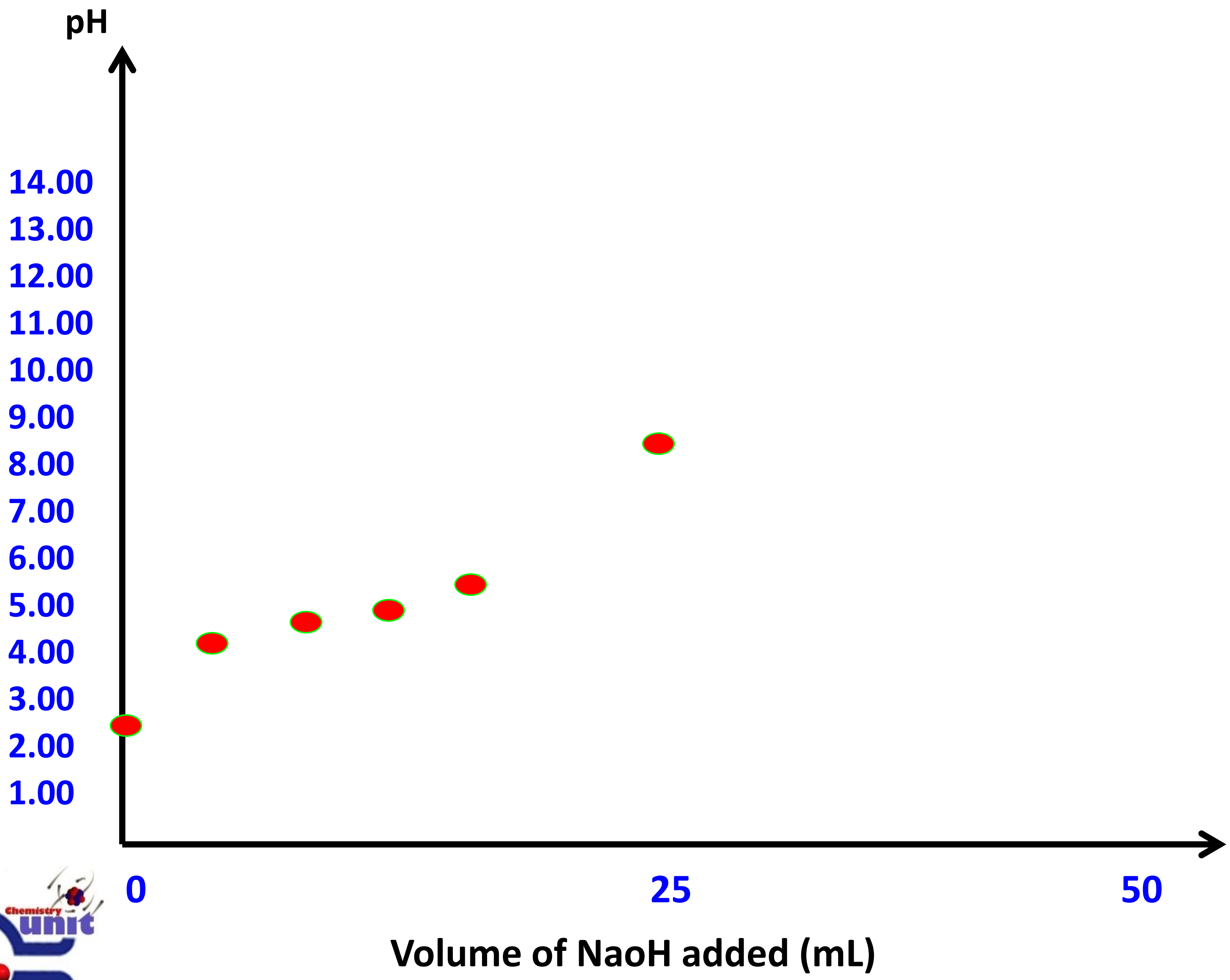
The salt will dissociate :

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

The conjugate base undergoes hydrolysis :

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

Since the OH^- formed in the hydrolysis process, the salt formed is a **basic salt at equivalence point (pH > 7.00)**.


pH
14.00
13.00
12.00
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
25
50
Volume of NaoH added (mL)

d) pH after adding 30.0 mL NaOH

At this point in the titration, 0.0030 mol of OH^- have been added. NaOH has thus become the excess reagent.

	$CH_3COOH(aq)$	$+ OH^-(aq) \rightarrow$	$CH_3COO^-(aq)$	$+ H_2O(l)$
n_i	**0.0025**	**0.003**	**0**	**-**
n_Δ	**– 0.0025**	**– 0.0025**	**+ 0.0025**	**-**
n_f	**0**	**0.0005**	**0.0025**	**-**

The solution is now a mixture of a strong base (NaOH) and a weak base (CH_3COO^-)

In this region, $[OH^-]$ from the reaction of CH_3COO^- with water is negligible relative to $[OH^-]$ from the excess NaOH. Thus, the pH is determined by the concentration of OH^- from the excess NaOH.

Total Volume = 25 mL + 30 mL = 55 mL = 0.055 L

$$[OH^-] = \frac{0.0005\ \text{mol}}{0.055\ \text{L}} = 0.0091\ \text{M}$$

$\text{pOH} = -\log[\text{OH}^-]$

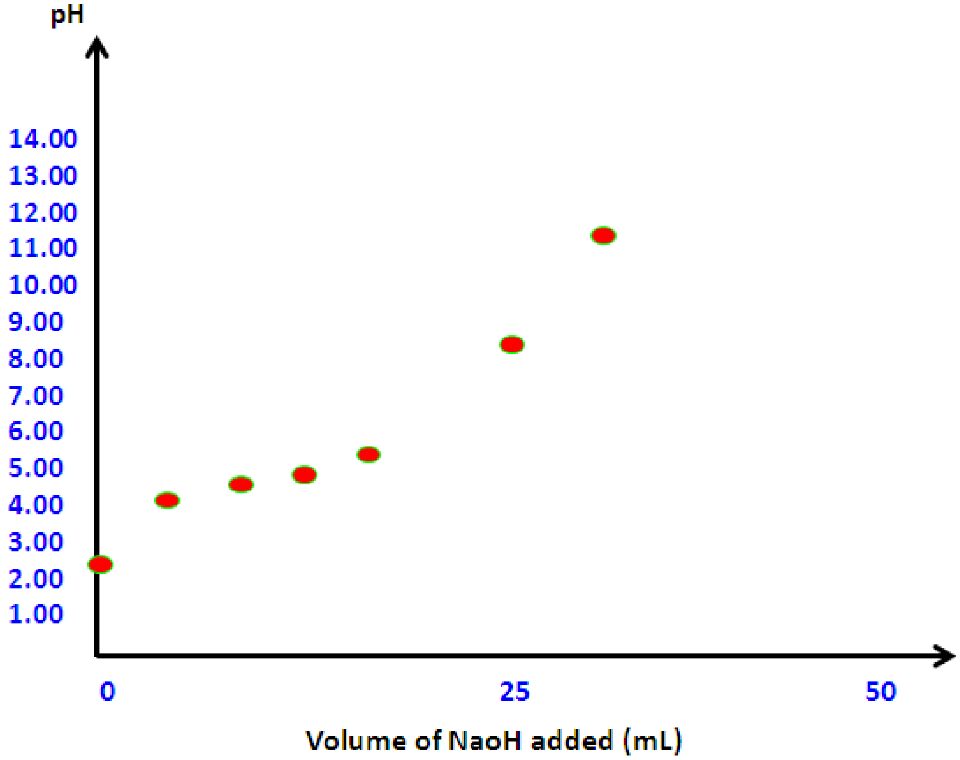
$= -\log(0.0091)$

$= 2.04$

$\text{pH} = \text{p}K_w - \text{pOH}$

$= 14.00 - 2.04$

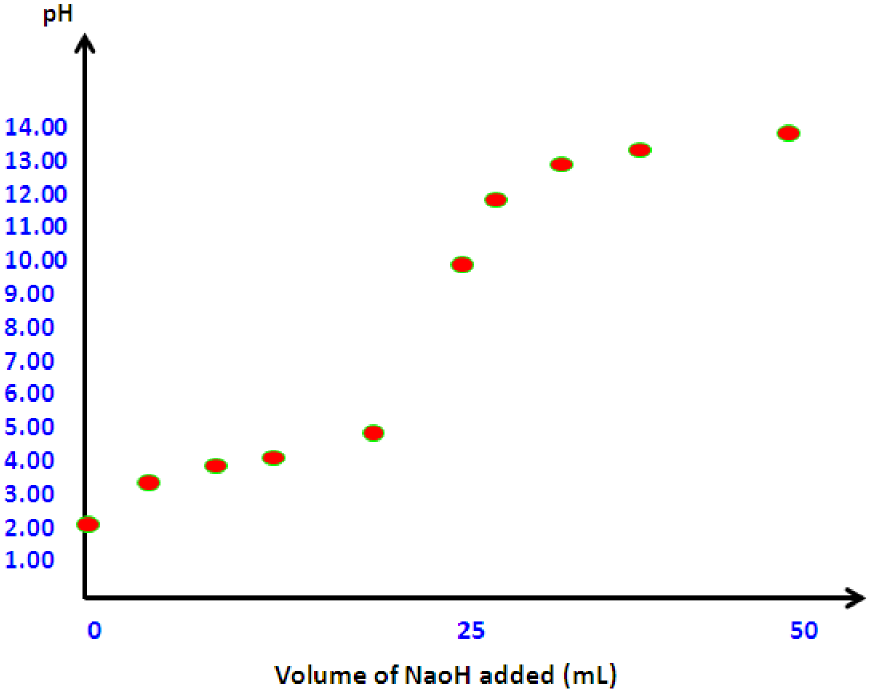
$= 11.96$



e) After adding 35.0, 40.0 and 50.0 mL NaOH

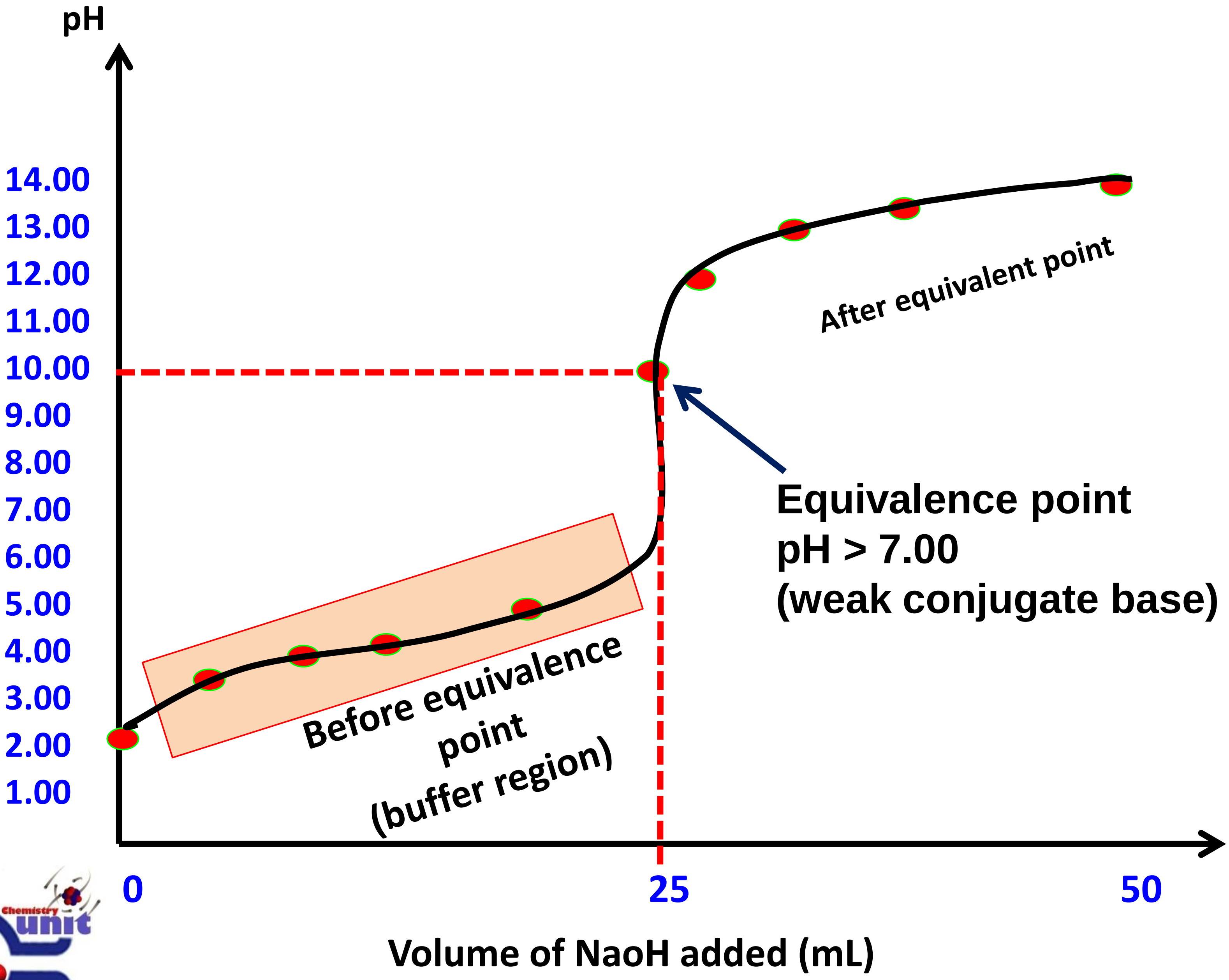
As more NaOH is added, the basicity of the solution increases further. The OH^- in the solution is in excess. The pH is determined by the concentration of OH^-

Volume of NaOH added (mL)	pH
35.0	12.22
40.0	12.37
50.0	12.52



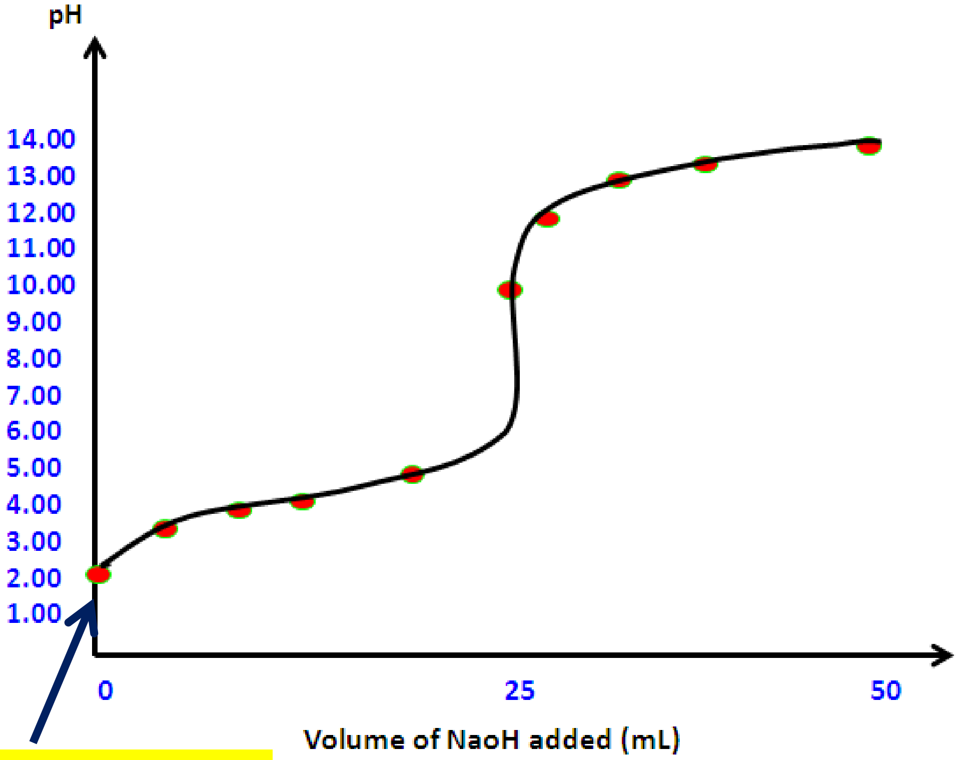
WEAK ACID & STRONG BASE TITRATION CURVE

Titration curve: pH versus volume of NaOH



Equivalence point
pH > 7.00
(weak conjugate base)

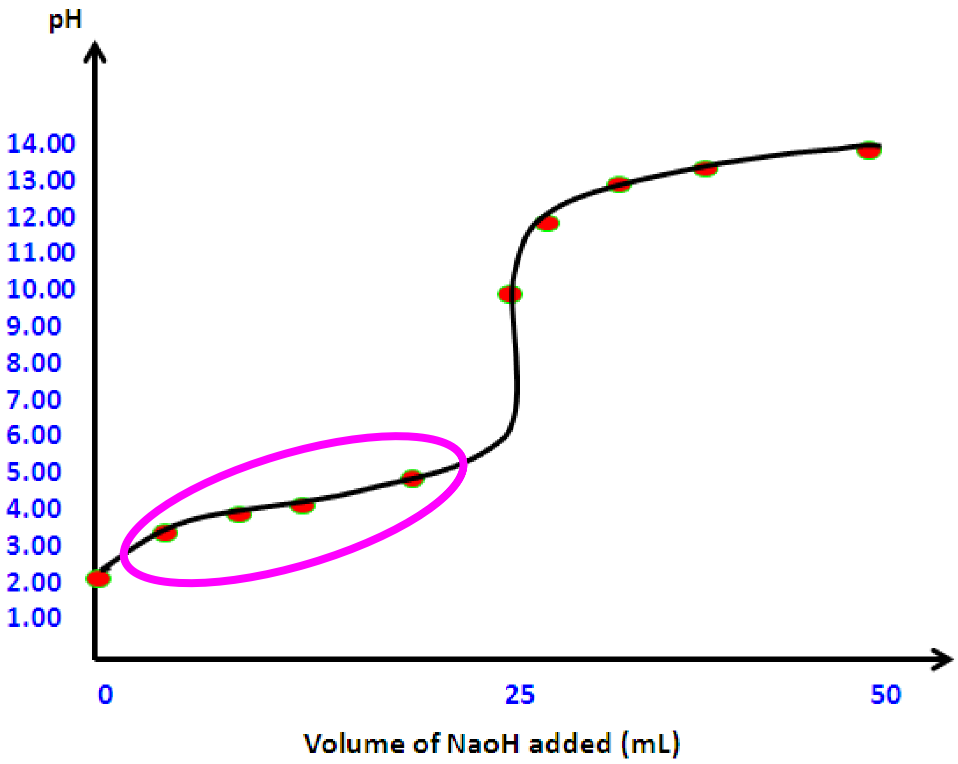
Initial pH



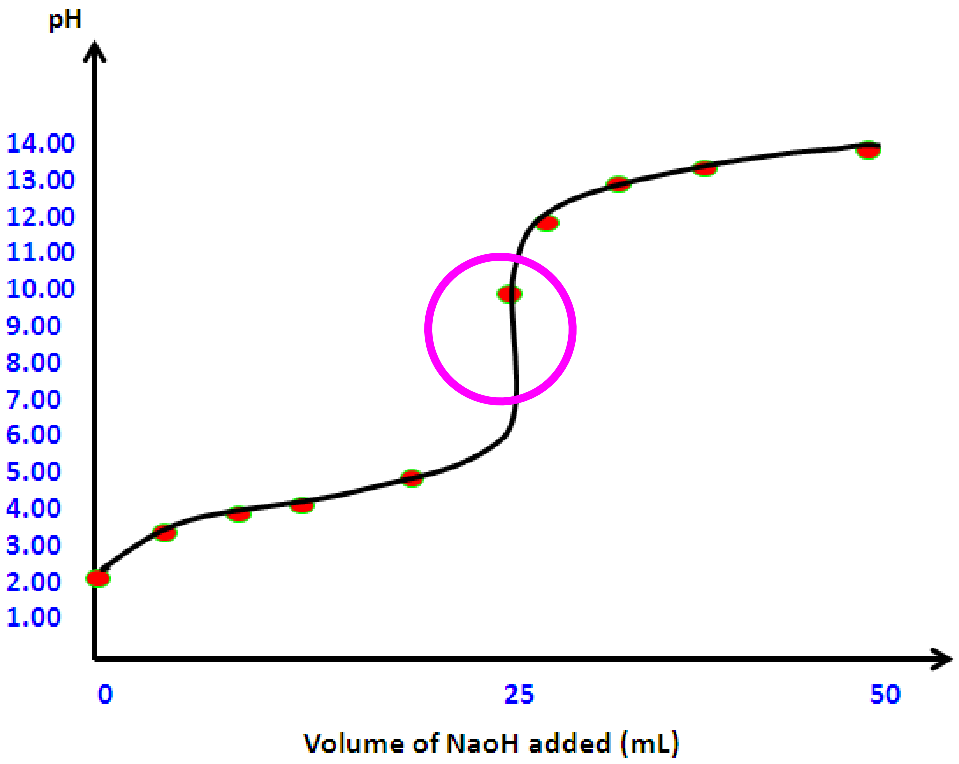
Initial pH

The initial pH is higher than strong acid-strong base titration curve because the weak acid dissociates only slightly, less H_3O^+ is present.

Between initial pH and equivalence point



A gradually rising portion of the curve, called the **buffer region**, appears before the sharp rise to the equivalence point.

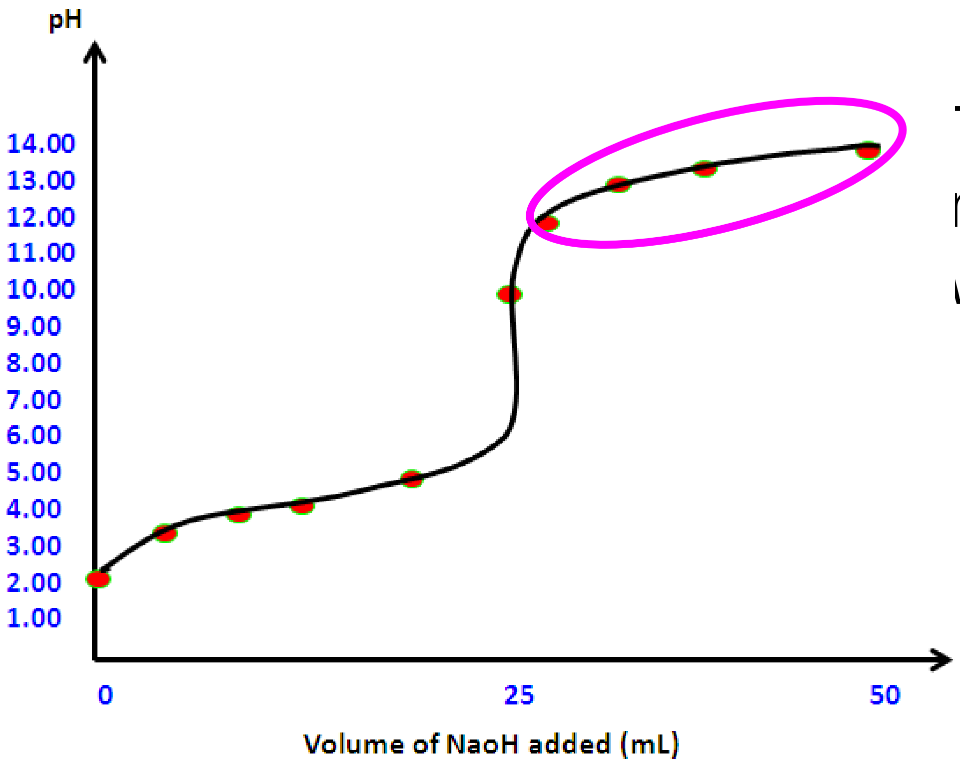


pH at equivalence point

The **pH at the equivalence point > 7.00**

The solution contains the **basic salt.**

pH after equivalence point

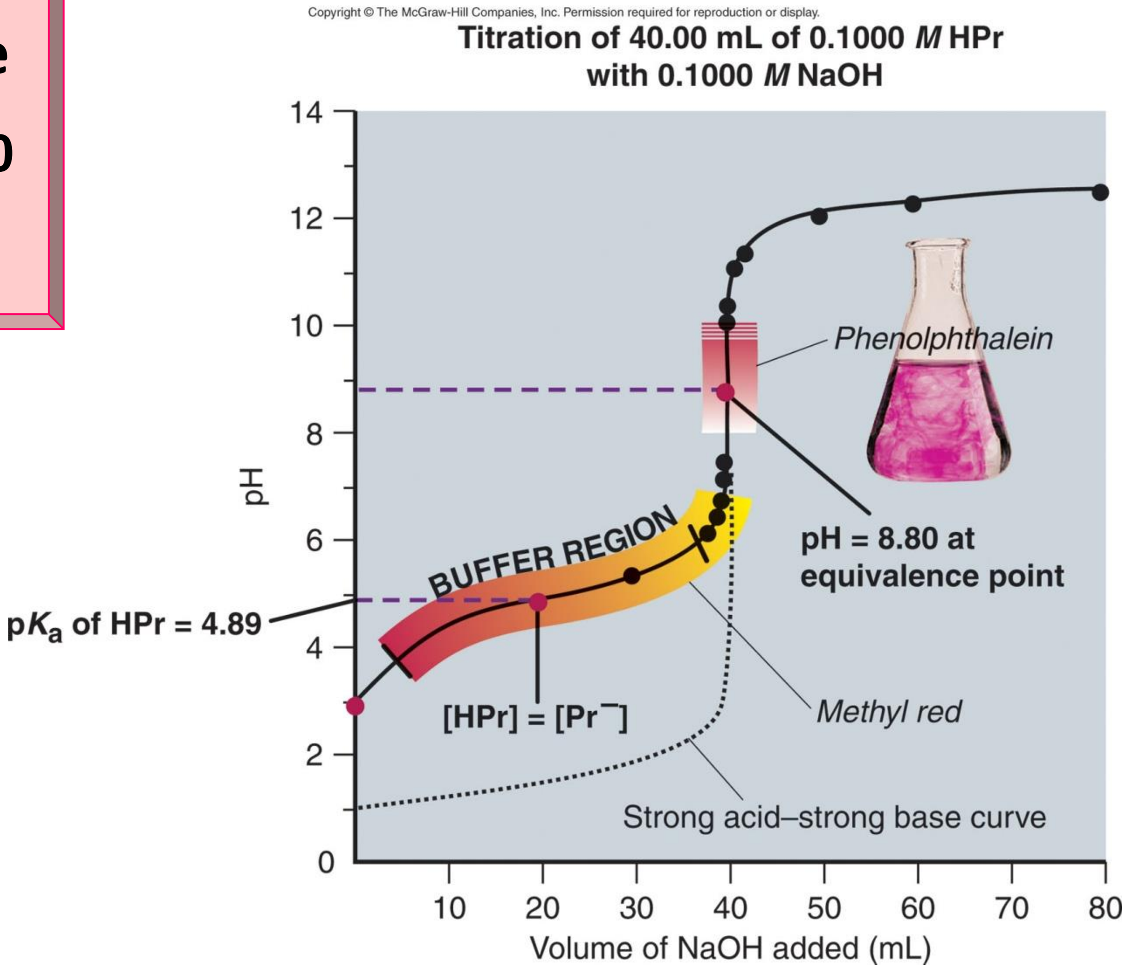


The solution is now contains mixture of strong base and weak base.

The strong base completely overwhelms the weak base

The pH is determined by the concentration of OH^- from excess strong base

	pH range
Phenolphthalein	**8.3 ~ 10.0**
Methyl red	**4.2 ~ 6.3**



Titration of 40.00 mL of 0.1000 *M* HPr with 0.1000 *M* NaOH

Phenolphthalein is a suitable indicator because it changes color on the steep portion of the curve, but methyl red is not its color changes over a large volume range

The Titration of weak base and strong acid

EXAMPLE: 25 mL 0.100 M NH_3(*aq*) in conical flask
0.100 M HCl(*aq*) in burette

a) Initial pH (before adding any acid)

The initial pH of the solution is the pH 0.100 M of NH_3 .

Since NH_3 is a weak base, the concentration of H_3O^+ and the pH are calculated from the incomplete dissociation in aqueous solution

K_b NH_3 = 1.8×10^{-5}

	$H_2O(l)$ +	$NH_3(aq)$ $\rightleftharpoons$	$OH^-(aq)$ +	$NH_4^+(aq)$
$[\ ]_i$	–	0.100	0	0
$[\ ]_\Delta$	–	$-x$	$+x$	$+x$
$[\ ]_{eq}$	–	$0.100 - x$	x	x

$$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} = \frac{x^2}{0.100 - x} = 1.8 \times 10^{-5}$$

$$K_b = \frac{x^2}{0.100 - x}$$

$K_b << 1$ ☞ assume x very small

Assumption: $0.100 - x \approx 0.100$ (x negligible)

$$K_a = \frac{x^2}{0.100} = 1.8 \times 10^{-5}$$

$$x = 1.34 \times 10^{-3}\ \text{M}$$

$[OH^-] \;=\; x \;=\; 1.34 \times 10^{-3}$ M

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

$= -\log (1.34 \times 10^{-3})$

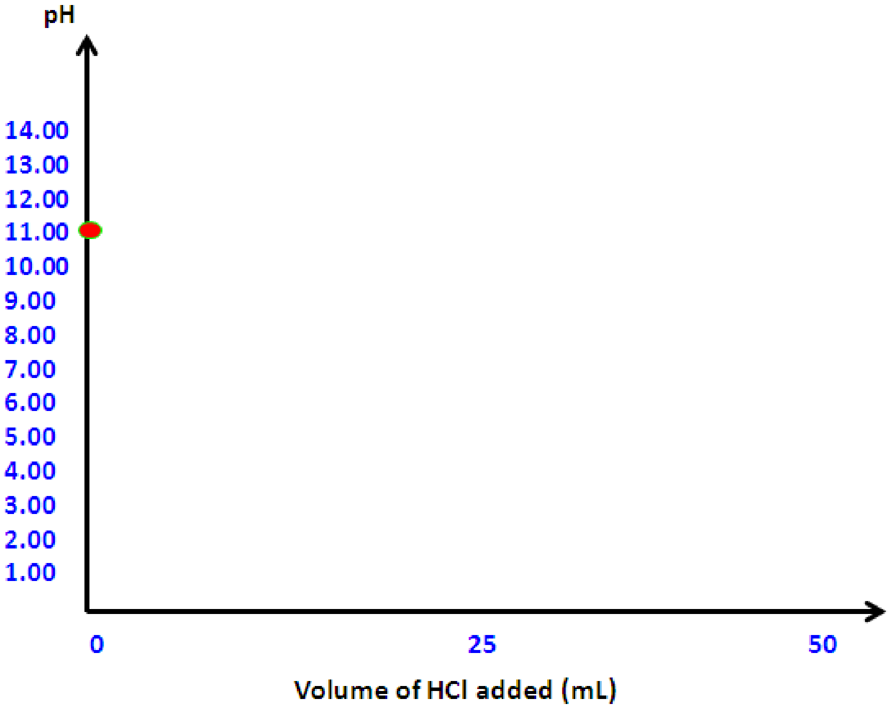
$= 2.82$

$pH + pOH = pK_w = 14.00$

$pH = pK_w - pOH$

$= 14.00 - 2.82$

$= 11.18$



b) pH after adding 5.00 mL HCl

The added HCl converts a stoichiometric amount of the base into its conjugate acid. Thus, the solution contains a mixture of NH_3 and NH_4^+ **(buffer solution)**.

Determination of the pH involves two steps :

- consider the neutralisation reaction between NH_3 and HCl to determine $[NH_3]$ and $[NH_4^+]$.
- calculate the pH of this buffer pair

$NH_3(aq)$ + $HCl(aq)$ → $NH_4Cl(aq)$ + $H_2O(l)$

	$NH_3(aq)$ +	$H_3O^+(aq)$ →	$NH_4^+(aq)$ +	$H_2O(l)$
n_i	0.0025	0.0005	0	-
n_Δ	– 0.0005	– 0.0005	+ 0.0005	-
n_f	0.0020	0	0.0005	-

$$pOH = pK_b + \log\left(\frac{[NH_4^+]}{[NH_3]}\right)$$

Total Volume = 25 mL + 5 mL = 30 mL = 0.030 L

$$[NH_4^+] = \frac{0.0005\ \text{mol}}{0.030\ \text{L}} = 0.0167\ \text{M}$$

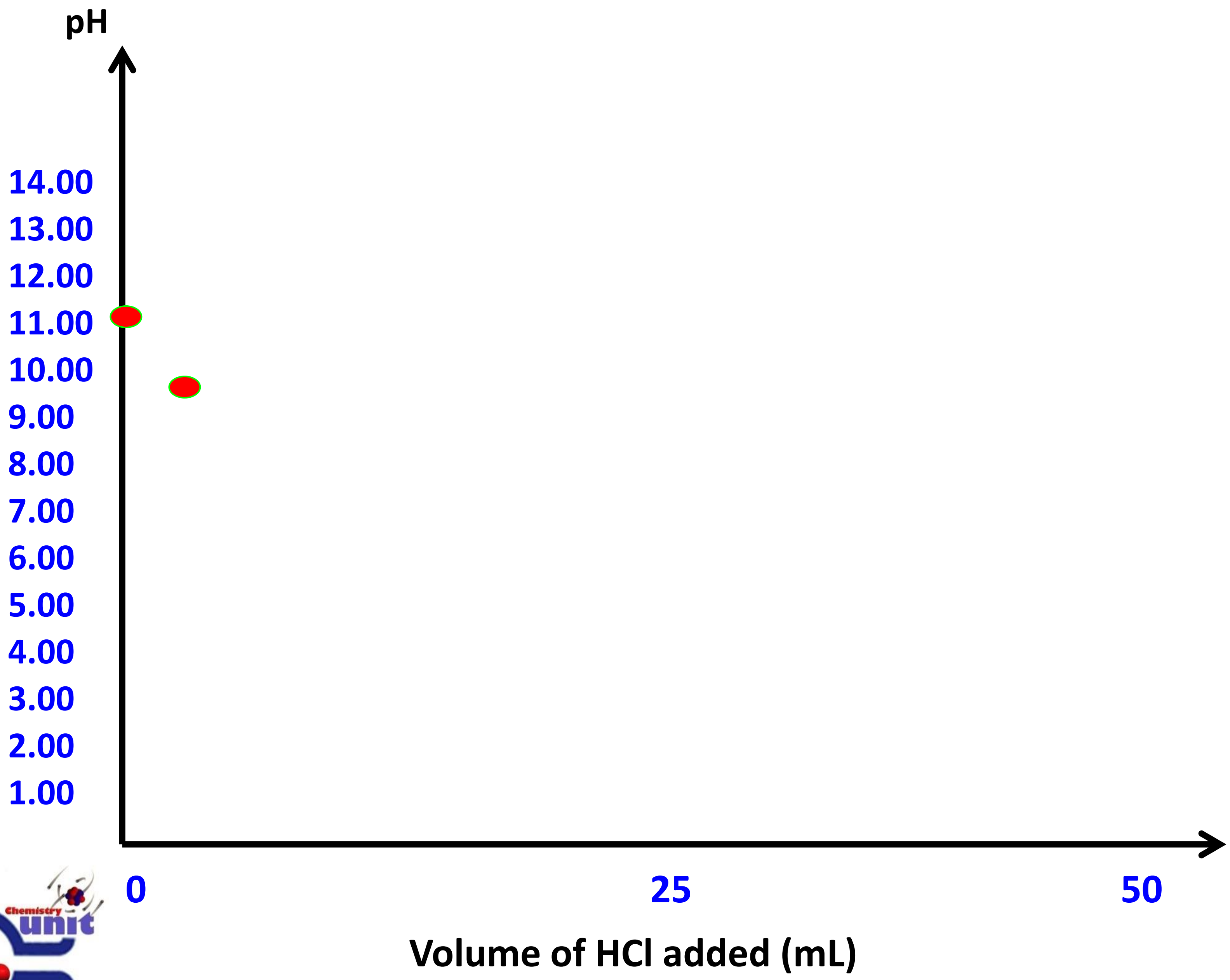
$$[NH_3] = \frac{0.0020\ \text{mol}}{0.030\ \text{L}} = 0.00667\ \text{M}$$

$$\text{pOH} = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.0167}{0.00667}\right)$$

$$= 4.35$$

$$\text{pH} = 14.00 - 4.35$$

$$= 9.65$$

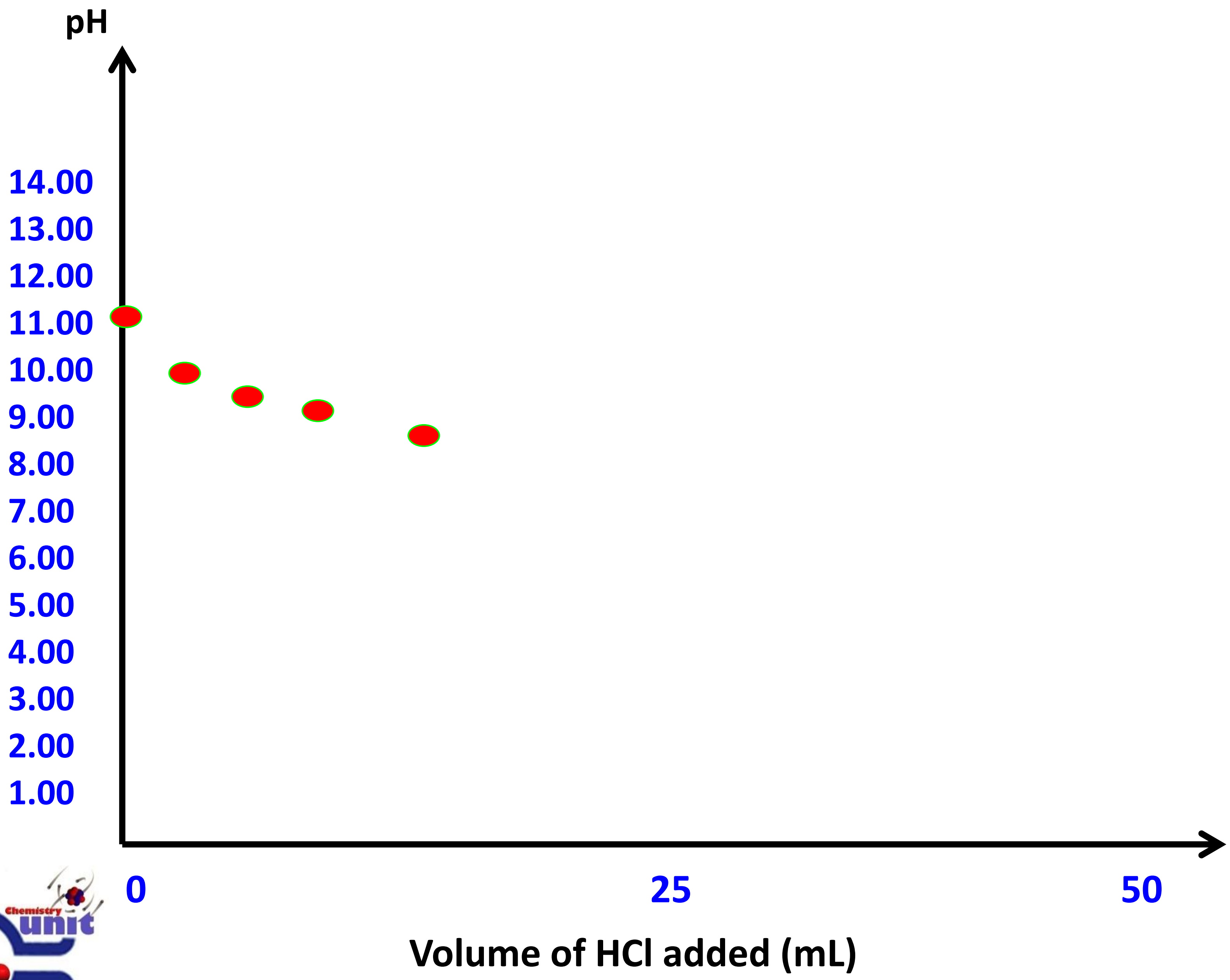

pH
14.00
13.00
12.00
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
25
50
Volume of HCl added (mL)

d) pH after adding 10.0, 15.0 and 20.0 mL HCl

As more HCl is added, it converts more NH_3 into NH_4^+The solution is now a buffer.

The pH of buffer solution is calculated by using Henderson-Hasselbalch equation

Volume of HCl added (mL)	Mol of NH_4^+	Mol of NH_3	pH
10.0	0.001	0.005	9.43
15.0	0.005	0.001	9.07
20.0	0.002	0.0005	8.65


pH
14.00
13.00
12.00
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
25
50
Volume of HCl added (mL)

c) pH after adding 25.0 mL HCl (Equivalence point)

At the equivalence point, 0.0025 mol of HCl have been added and therefore all of the NH_3 has been converted into its conjugate acid, NH_4^+.

No more NH_3 and HCl left. Thus, the solution contains NH_4Cl (salt) and water.

$$\mathbf{NH_3(\mathit{aq}) \quad + \quad HCl(\mathit{aq}) \quad \rightarrow NH_4Cl(\mathit{aq}) \quad + \quad H_2O(\mathit{l})}$$

0.0025 mol	0.0025 mol	0.0025 mol

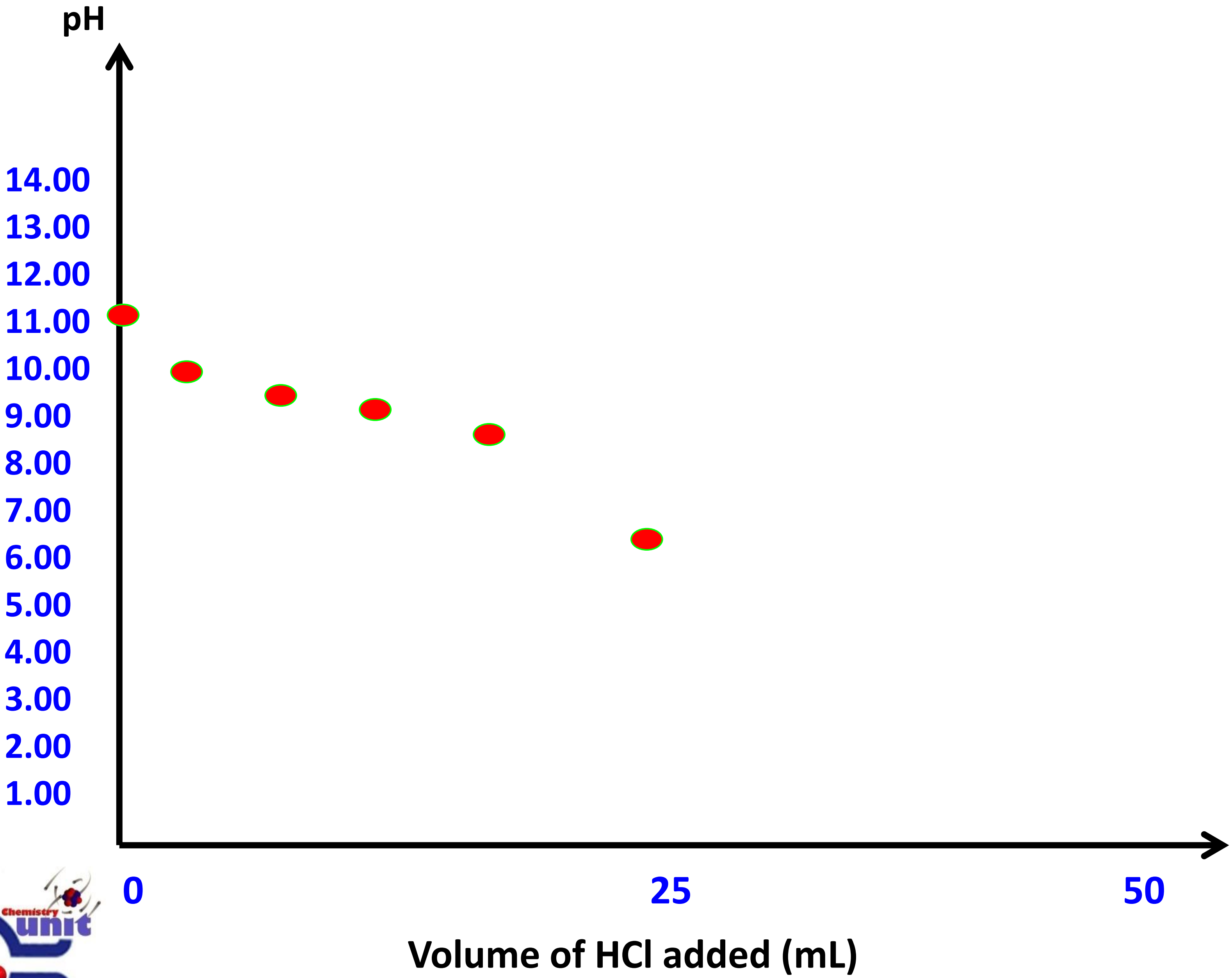
The salt will dissociate :

$$NH_4Cl(\textit{aq}) \rightarrow NH_4^+(\textit{aq}) \quad + \quad Cl^- (\textit{aq})$$

The conjugate base undergoes hydrolysis :

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

Since the H_3O^+ is formed in the hydrolysis process, the salt formed is an **acidic salt at equivalence point** **(pH < 7.00)**.


pH
14.00
13.00
12.00
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
25
50
Volume of HCl added (mL)

d) pH after adding 30.0 mL HCl

At this point in the titration, 0.0030 mol of H_3O^+ have been added. HCl has thus become the excess reagent.

	$NH_3(aq)$ +	$H_3O^+(aq) \rightarrow$	$NH_4^+aq)$ +	$H_2O(l)$
n_i	0.0025	0.003	0	-
n_Δ	– 0.0025	– 0.0025	+ 0.0025	-
n_f	0	0.0005	0.0025	-

The solution is now a mixture of a strong acid (HCl) and a weak acid (NH_4^+)

In this region, $[H_3O^+]$ from the reaction of NH_4^+ with water is negligible relative to $[H_3O^+]$ from the excess HCl. Thus, the pH is determined by the concentration of H_3O^+ from the excess HCl.

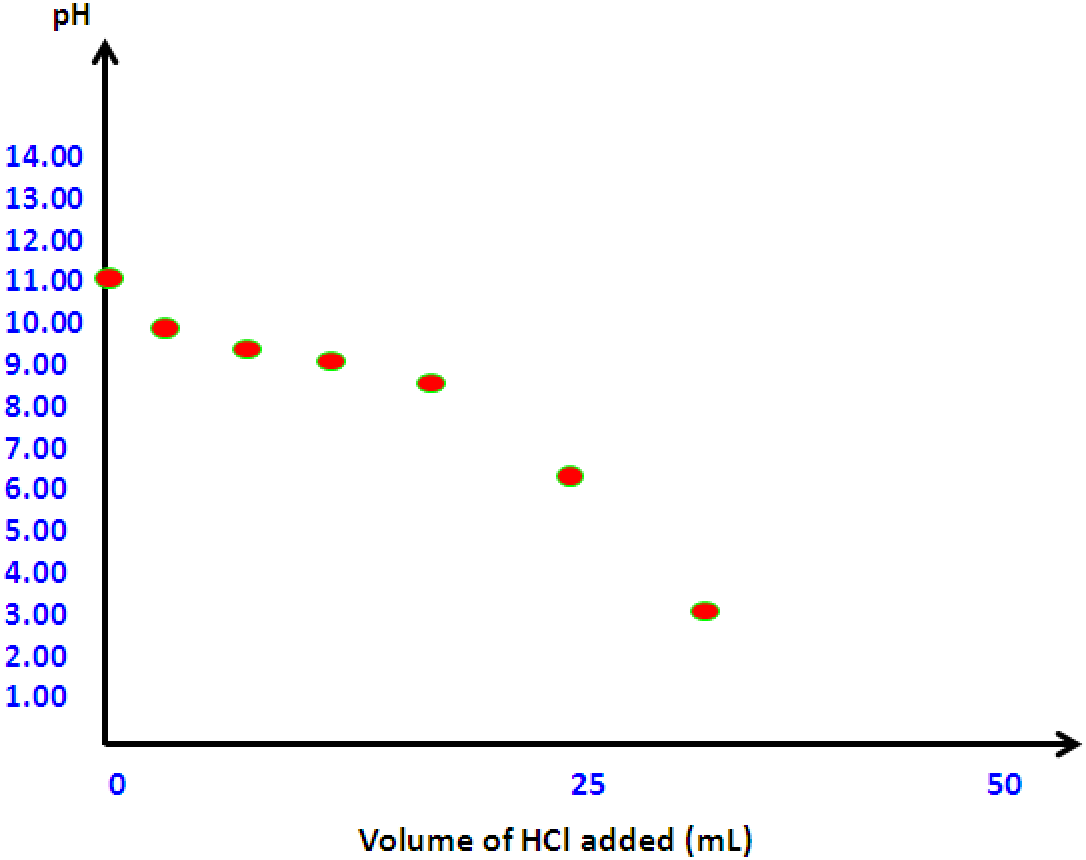
Total Volume = 25 mL + 30 mL = 55 mL = 0.055 L

$$[H_3O^+] = \frac{0.0005 \text{ mol}}{0.055 \text{ L}} = 0.0091 \text{ M}$$

$$pH = -\log [H_3O^+]$$

$$= -\log (0.0091)$$

$$= 2.04$$



$$[OH^-] = \frac{1 \times 10^{-14}}{0.0091\ M}$$

$[OH^-] = 1.1 \times 10^{-12}$ M

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

$= -\log (1.1 \times 10^{-12})$

$= 11.96$

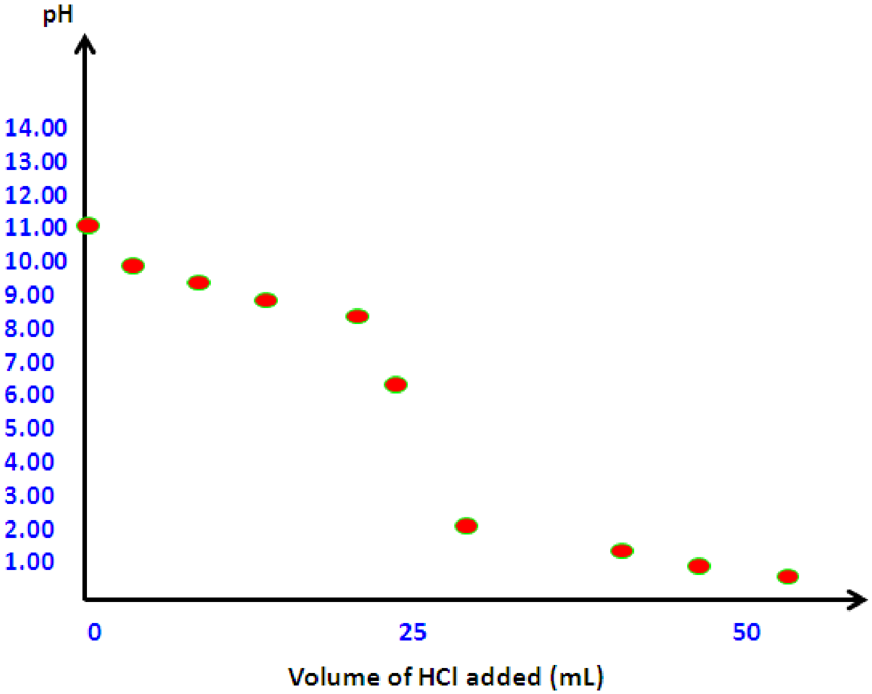
$pH = 14.00 - 11.96$

$= 2.04$

e) After adding 35.0, 40.0 and 50.0 mL HCl

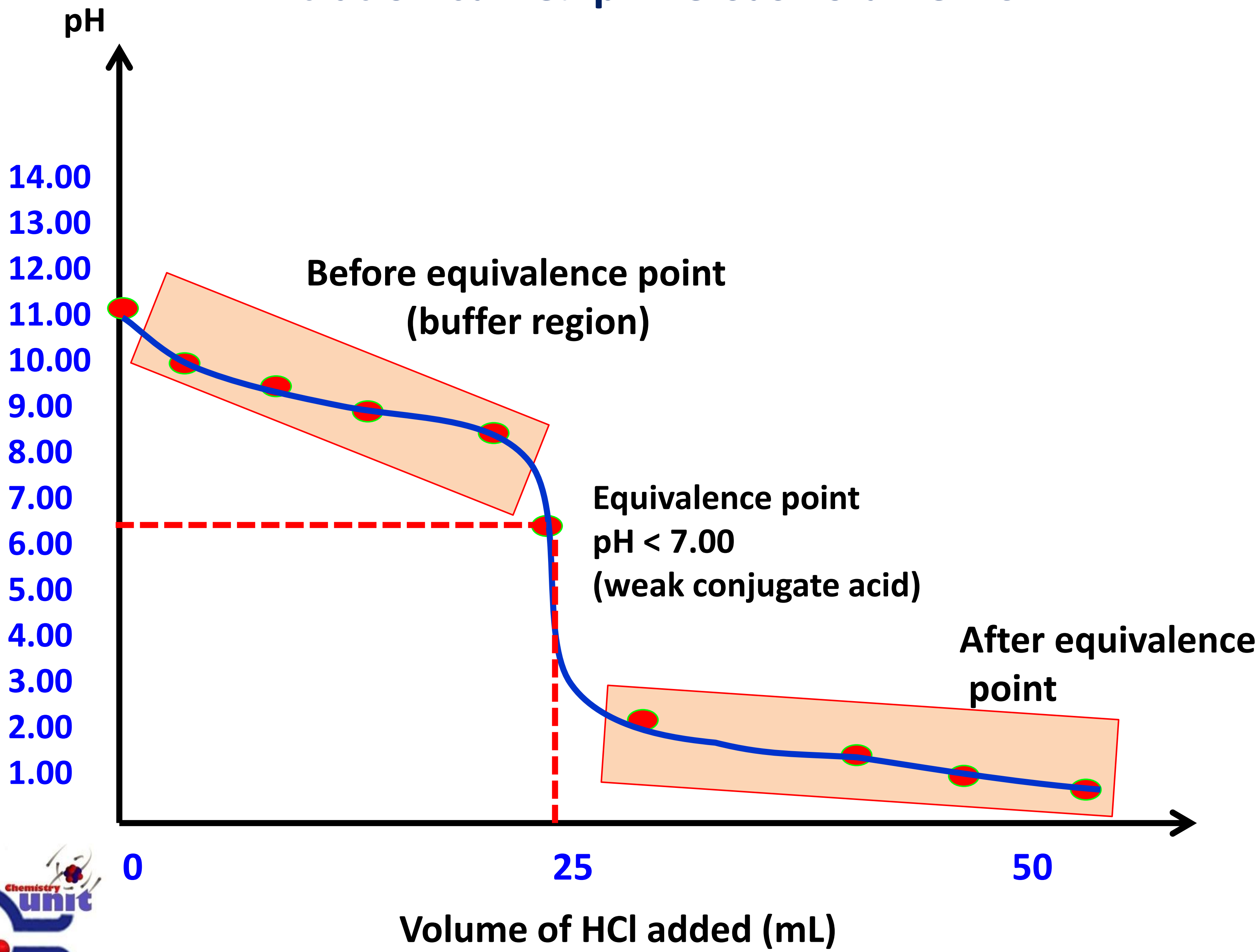
As more HCl is added, the acidity of the solution increases further. H_3O^+ in the solution is in excess. The pH is determined by the concentration of H_3O^+ from HCl

Volume of HCl added (mL)	pH
35.0	0.0167
40.0	0.023
50.0	0.033



WEAK BASE & STRONG ACID TITRATION CURVE

Titration curve: pH versus volume HCl

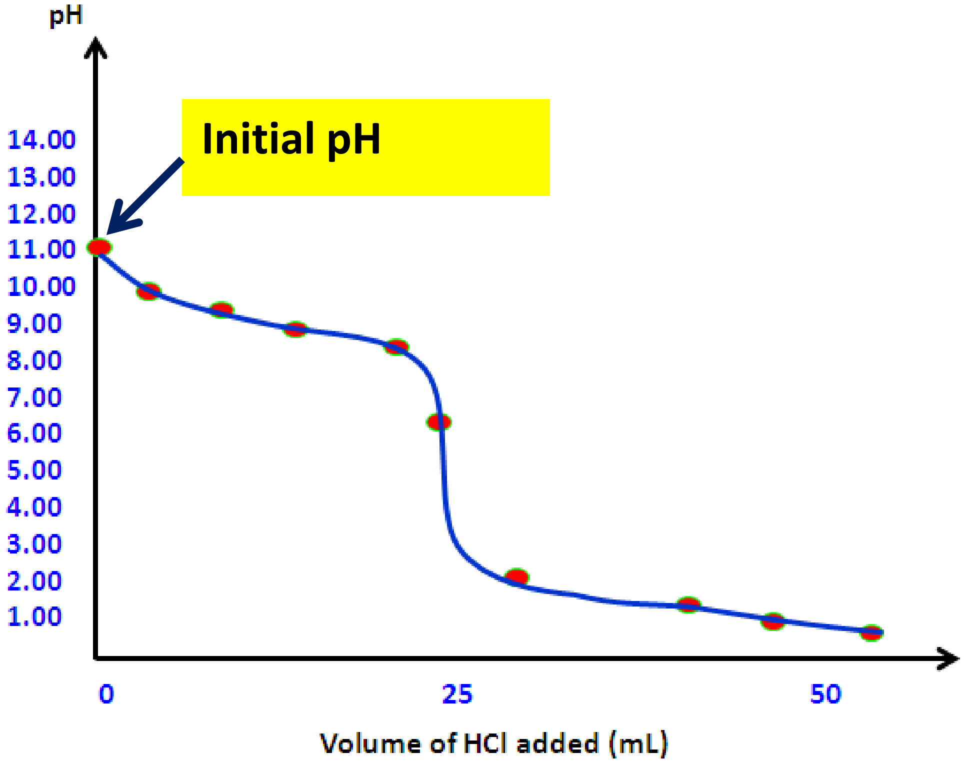


Before equivalence point
(buffer region)

Equivalence point
pH < 7.00
(weak conjugate acid)

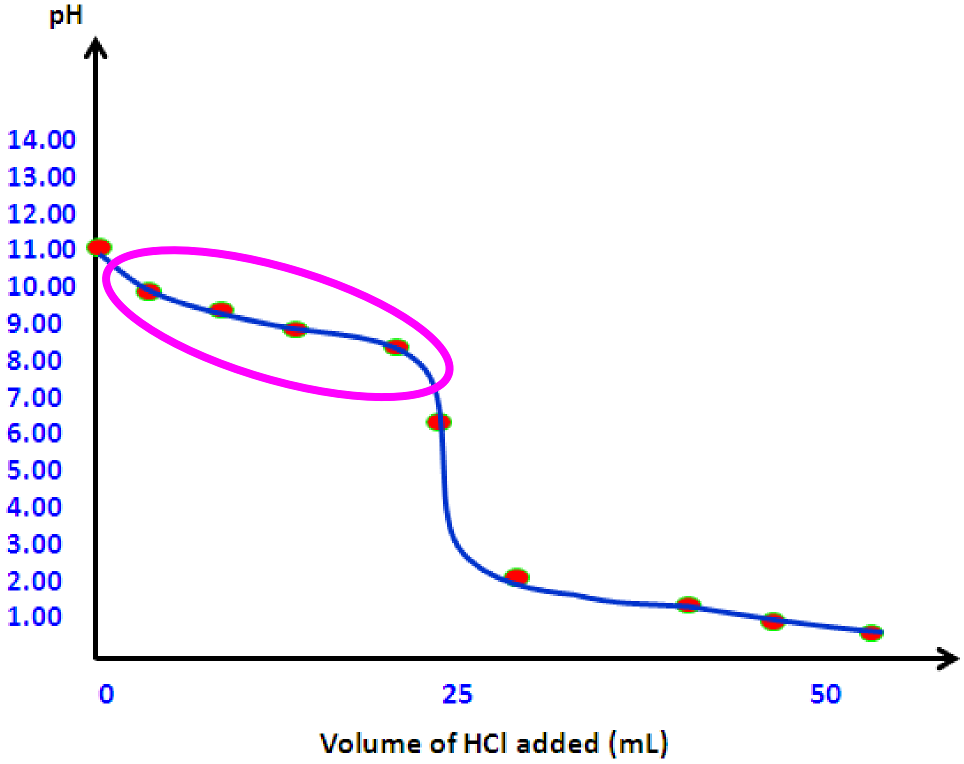
After equivalence
point

Initial pH



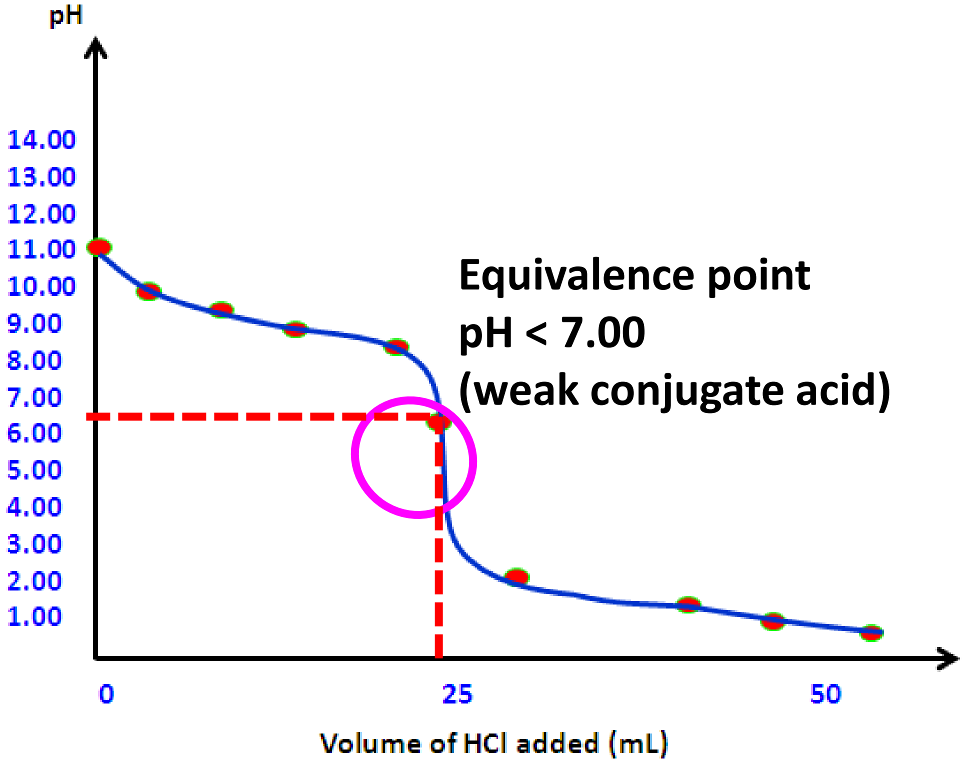
The pH starts above 7.0 (~11) because the weak base dissociates only slightly.

pH between initial and equivalence point



The pH decreases gradually in the buffer region.

pH at equivalence point



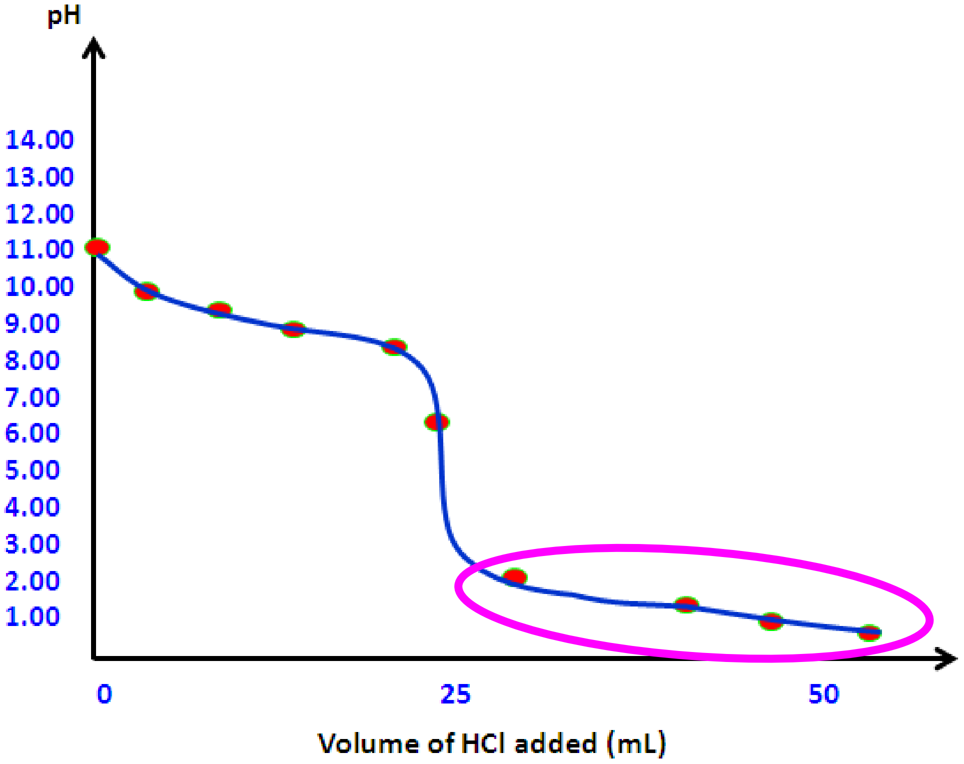
Equivalence point
pH < 7.00
(weak conjugate acid)

After the buffer region, the **curve drops vertically** to the equivalence point.

The **pH at equivalence point is < 7.00**

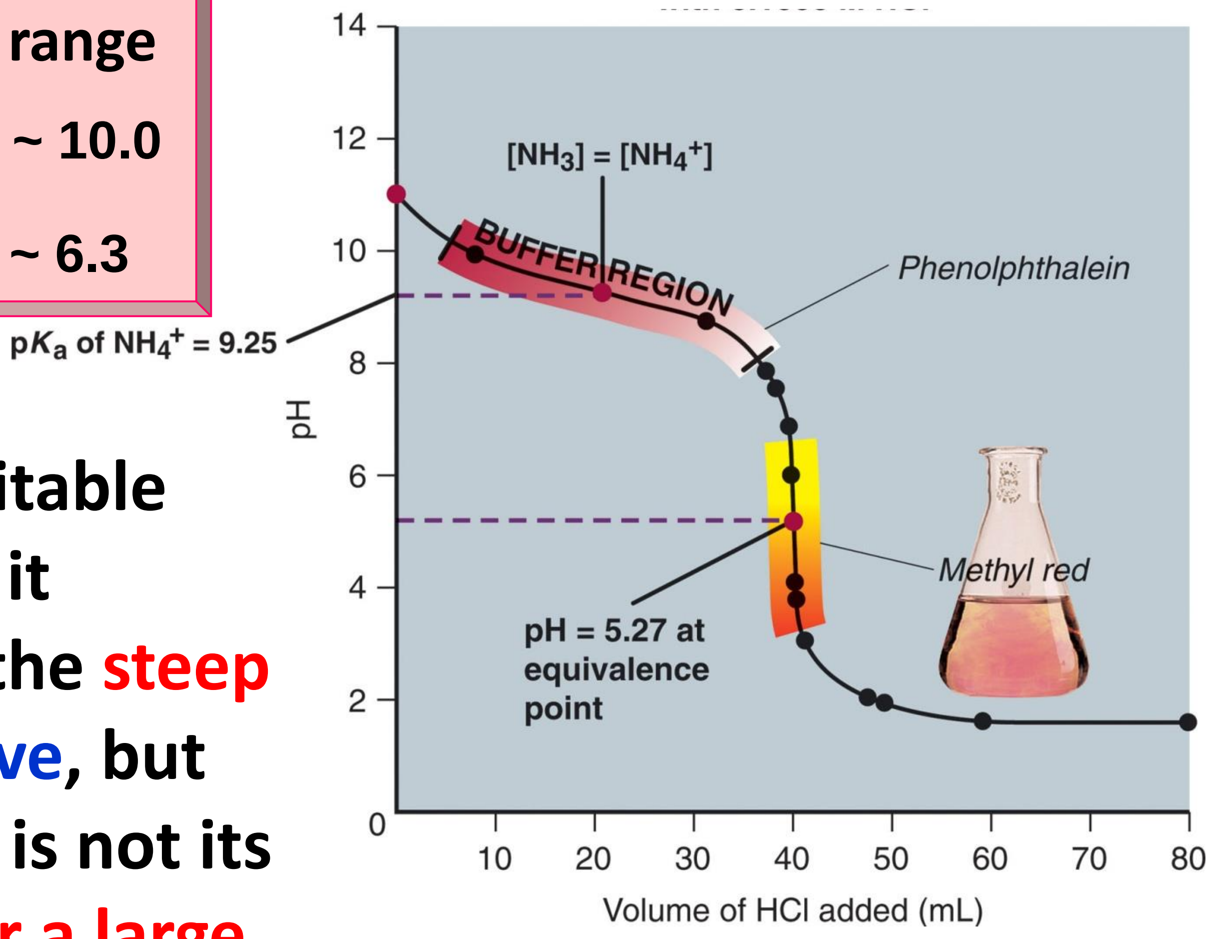
.

pH after equivalence point



Beyond the equivalence point, the pH decreases slowly as excess H_3O^+ is added.

	pH range
Phenolphthalein	**8.3 ~ 10.0**
Methyl red	**4.2 ~ 6.3**



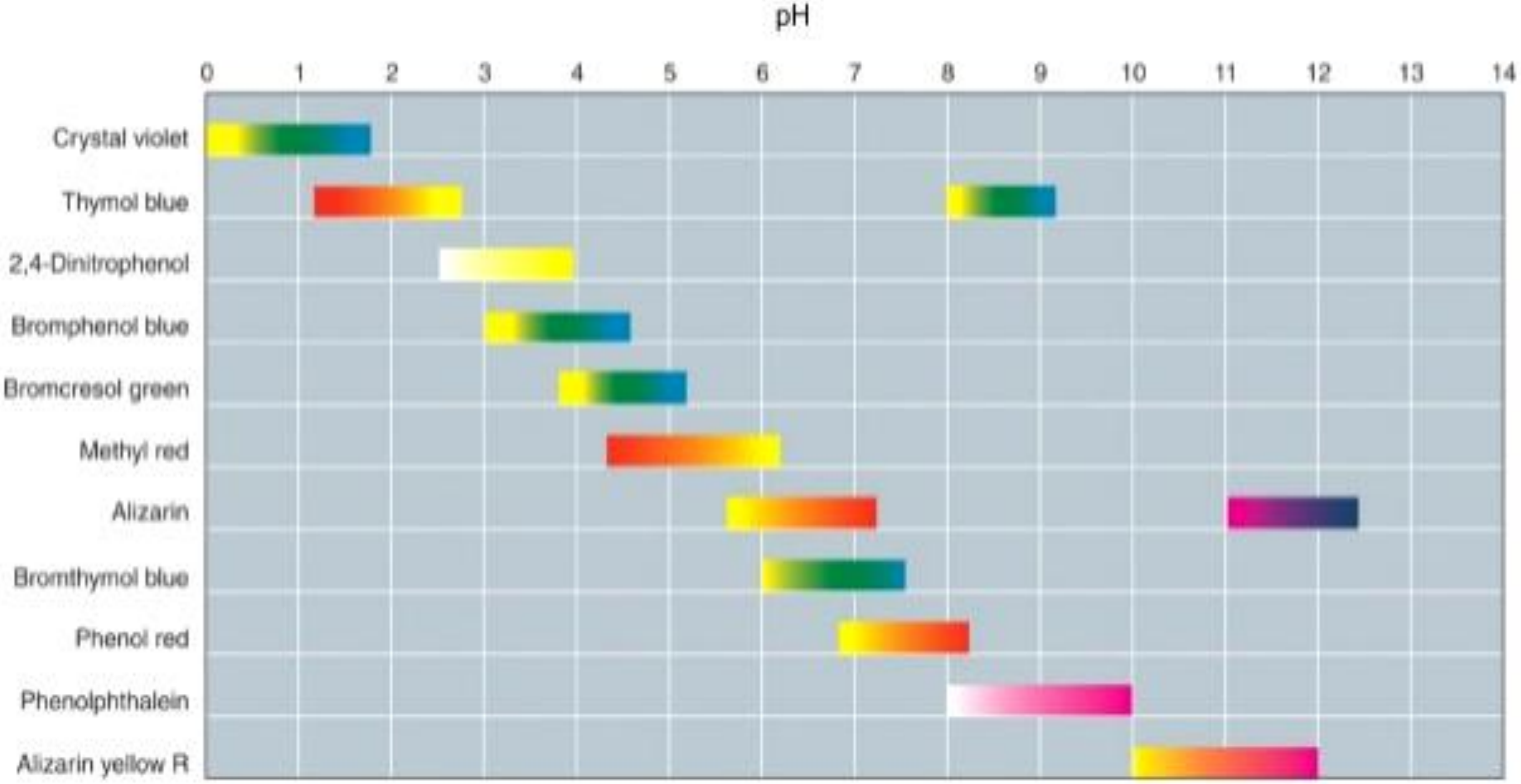
Methyl red is a suitable indicator because it changes color on the steep portion of the curve, but phenolphathalein is not its color changes over a large volume range

How to determine the suitable indicator for titrations

- **Choose an indicator which the endpoint pH range lies on the steep portion of the titration curve.**
- **This choice ensures that the pH at the equivalent point will fall within the range over which indicator changes color.**

Types of Titrations	pH jump	Suitable Indicators
Strong Acid-Strong Base	3 – 11	Any Indicator except thymol blue
Weak Acid-Strong Base	7 – 11	Phenolphthalein, cresol red
Strong Acid-weak Base	3 – 7	Methyl orange, methyl red, chlorophenol blue, bromophenol blue

Figure 19.5 Colors and approximate pH range of some common acid-base indicators.



Keep in mind!

How to sketch a titration curve

Steps :

1. **Calculate the initial pH of the solution**

   - identify the analyte (solution in the conical flask).

   Whether strong acid, weak acid, strong base or weak base.

2. **Determine the equivalence point :**

   - Volume and pH

110

3. **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**

4. **Identify the final pH**

- depends on the concentration of the titrant (solution in the burette).

EXERCISE 2 :

Sketch the titration curve of 25 mL 0.2 M HCl and 0.1 M NH_3.

Step 1 : Analyte is a strong acid, HCl

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

$$[H_3O^+] = [HCl] = 0.2\ M$$

$$pH = -\log [H_3O^+]$$

$$= \mathbf{0.70}$$

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

$$M_{NH3}\ V_{NH3} = M_{HCl}\ V_{HCl}$$

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

$$V_{HCl} = \frac{0.2 \times 25.0}{0.1} = 50 \text{ mL}$$

Step 3 :

Type of titration : strong acid-weak base

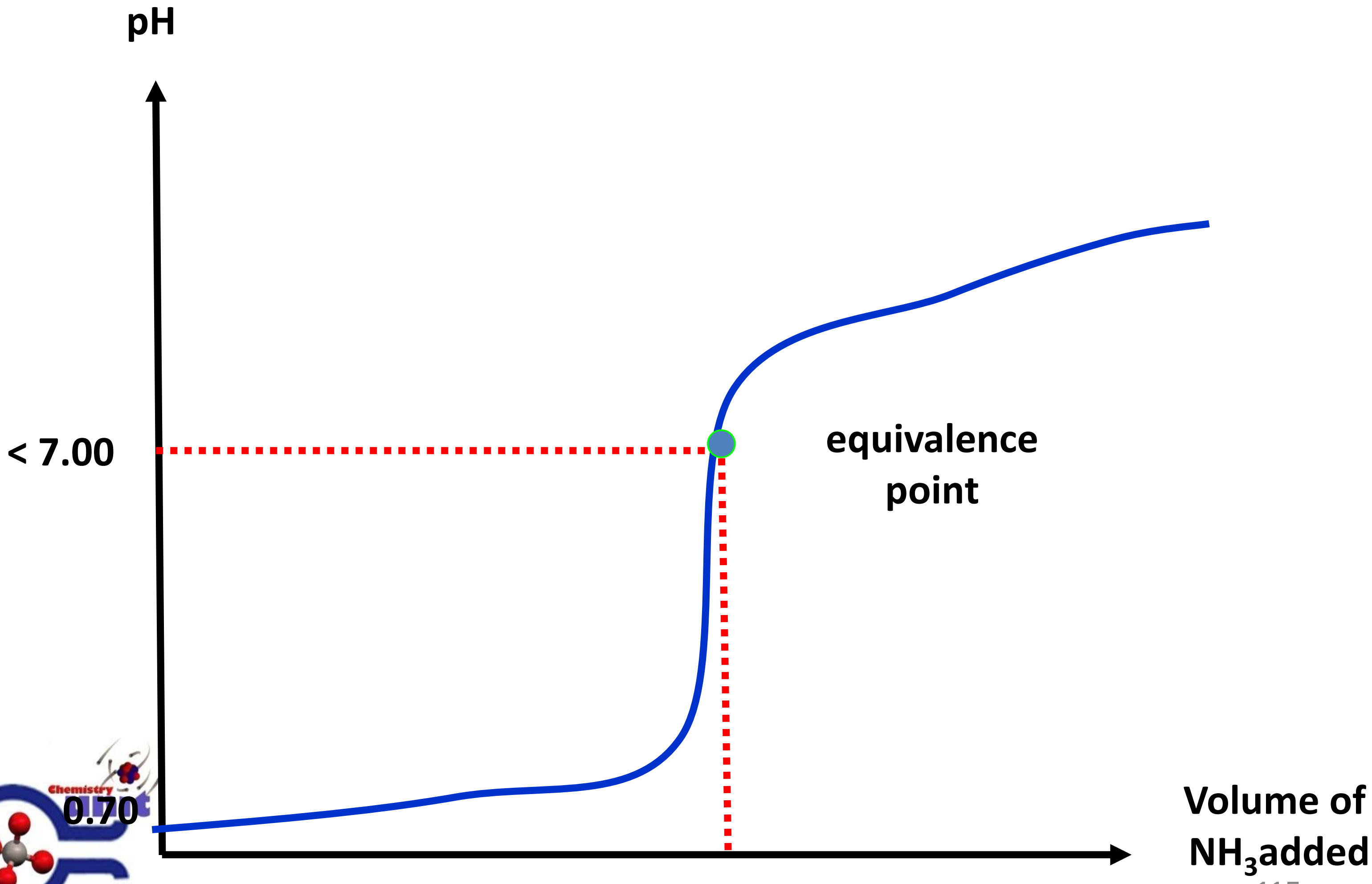
pH jump : 3 – 7

Step 4 :

Titrant is a weak base, NH_3.

Final point approaching pH < 11

Titration curve: pH versus volume NH_3



Thanks!

For Attention

See You The Next Subtopic

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