15

Chemistry of Aqueous Solutions: Acid-Base Equilibria

GUIDING QUESTIONS:

- What is a strong or weak acid/base?
- How can the strength of acids and bases be represented and determined?
- What is the relationship between concentration of acid (base), pH (pOH) and strength of acid (base)?
- What are buffers? How do buffers work? How can the pH of buffers be determined?
- What are the changes in pH during acid-base titrations? How can these pH changes be explained?

LEARNING OUTCOMES

Students should be able to:

4(b) show understanding of, and apply the Bronsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases

(Refer to Topic 4 Reactions and Stoichiometry for **4(b)**)

5(e)(v) describe and explain the reactions of the chlorides with water (for $NaCl$; $MgCl_2$; $AlCl_3$; $SiCl_4$; PCl_5)

10.1(a) explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation

10.1(b) explain the terms pH; K_a; pK_a; K_b; pK_b; K_w and apply them in calculations, including the relationship $K_w = K_aK_b$

10.1(c) calculate [H^+(aq)] and pH values for strong acids, weak monobasic (monoprotic) acids, strong bases, and weak monoacidic bases [Calculations involving weak acids/bases will **not** require solving of quadratic equations]

10.1(d) describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases

10.1(e) explain the choice of suitable indicators for acid-base titrations, given appropriate data

10.1(f) **(i)** explain how buffer solutions control pH

(ii) describe and explain their uses, including the role of H_2CO_3/HCO_3^- in controlling pH in blood

10.1(g) calculate the pH of buffer solutions, given appropriate data

REFERENCES

1. Peter Cann & Peter Hughes, *Cambridge International AS and A Level Chemistry*, Hodder Education, Chapters 6 & 22
2. Martin S. Silberberg, *Chemistry – The Molecular Nature of Matter & Change*, McGraw Hill, Chapter 18 & 19

LOOKING BACK

In Topic 4 Reactions and Stoichiometry, we learnt to define acids and bases according to three models: Arrhenius Theory, Bronsted-Lowry Theory and Lewis Theory of acids and bases. In this topic, we shall use the Bronsted-Lowry Theory in our understanding of acids and bases and apply the concept of equilibrium learnt from Topic 7 Chemical Equilibria specifically to acid–base systems.

1 Introduction

Acids and bases are important in many chemical processes that occur around us, from industrial processes to biological ones and from reactions in the laboratory to those in our environment. In this topic, we will examine equilibria involving acids and bases and study the pH of solutions containing strong acids and bases, weak acids and bases, salts and buffers.

Recall from Topic 4 Reactions and Stoichiometry that, according to the **Bronsted-Lowry Theory of acids and bases**:

- An acid is a proton-donor and a base is a proton-acceptor.
- An acid-base reaction therefore involves a transfer of a proton from an acid to a base.

1.1 Conjugate Acid-Base pair

LO 4(b): show understanding of, and apply the Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases

Consider the following acid-base reaction:

$$\underset{\text{acid}}{CH_3CO_2H} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conjugate base}}{CH_3CO_2^-} + \underset{\text{conjugate acid}}{H_3O^+}$$

In the forward reaction:
CH_3CO_2H acts as a Bronsted acid, donating a proton to the Bronsted base, H_2O.

In the reverse reaction:
$CH_3CO_2^-$ acts as a Bronsted base, accepting a proton from the Bronsted acid, H_3O^+, to re-form the Bronsted acid, CH_3CO_2H.

- CH_3CO_2H and $CH_3CO_2^-$ form a conjugate acid-base pair;
- H_2O and H_3O^+ form another conjugate acid-base pair.

In general,

conjugate acid-base pair

$$\text{acid 1} + \text{base 2} \rightleftharpoons \text{base 1} + \text{acid 2}$$

conjugate acid-base pair

- **A conjugate acid-base pair constitutes two species which differ from each other by a proton.**
- An acid after donating a proton forms its conjugate base.
- A base after accepting a proton forms its conjugate acid.
- In any acid-base reaction, there are two conjugate acid-base pairs.

Lecture Exercise 1.1

Identify the conjugate acid-base pairs in each of the following reactions:

1. $HNO_3 + NH_3 \rightarrow NO_3^- + NH_4^+$

2. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

1.2 Strong and Weak Acids and Bases

LO 10.1(a): explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation

A **strong Bronsted acid** is a **proton-donor** that **dissociates or ionises <u>completely</u>** in water to give H_3O^+. It donates a proton more readily compared to the H_3O^+ ion.

e.g. $\underset{\text{strong acid}}{HCl} + H_2O \rightarrow \underset{\text{conjugate base}}{Cl^-} + H_3O^+$

- The conjugate base of a strong acid has a very low tendency to accept a proton.
- So the reverse reaction is negligible ∴ single–headed arrow (→).
- Other examples of strong acids: HNO_3, HBr, HI, $HClO_3$, $HClO_4$, H_2SO_4

A **weak Bronsted acid** is a **proton-donor** that **dissociates <u>partially</u>** in water to give H_3O^+. It donates a proton less readily compared to the H_3O^+ ion.

e.g. $\underset{\text{weak acid}}{CH_3CO_2H} + H_2O \rightleftharpoons \underset{\text{conjugate base}}{CH_3CO_2^-} + H_3O^+$

- The conjugate base of a weak acid ($CH_3CO_2^-$) has a tendency to accept a proton.
- CH_3CO_2H and $CH_3CO_2^-$ is a conjugate acid-base pair that differ by a proton
- So the reverse reaction occurs to some extent ∴ double–headed arrow (⇌).
- A mixture of mainly undissociated CH_3CO_2H molecules and the ions exists in solution.
- Other examples of weak acids: H_2SO_3, HNO_2, H_2CO_3, H_2S, HF, HCN, most organic acids

A **strong Bronsted base** is a **proton-acceptor** that **dissociates / ionises <u>completely</u>** in water to give OH^-.

e.g. $NaOH \rightarrow Na^+ + OH^-$

- Other examples of strong bases: KOH, $Ba(OH)_2$

A **weak Bronsted base** is a **proton-acceptor** that **dissociates / ionises <u>partially</u>** in water to give OH^-.

e.g. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

- Other examples of weak bases: hydrazine N_2H_4, amines such as CH_3NH_2, $C_6H_5NH_2$

The <u>strength</u> of an acid (or base) is *different* from the <u>concentration</u> of the acid (or base).
Strength of an acid (or base) refers to the extent of its dissociation at equilibrium.
Concentration of an acid (or base) refers to the no. of moles of acid (or base) dissolved in 1 dm^3 of solution.

Lecture Exercise 1.2

Match each acid on the left with the correct description on the right.

0.001 mol dm^{-3} HNO_3	•	•	concentrated but weak acid
4.0 mol dm^{-3} CH_3CO_2H	•	•	dilute but strong acid
0.001 mol dm^{-3} $CH_3CH_2CO_2H$	•	•	dilute and weak acid

2 CALCULATIONS INVOLVING ACIDS AND BASES

LO 10.1(b)part: explain the terms pH; K_w and apply them in calculations

2.1 Definition of pH and pOH

The concentration of H^+ and OH^- in an aqueous solution is usually quite small. Hence it is more convenient to express the concentration of $H^+(aq)$ in terms of its negative logarithm to base 10.

$$\boxed{\mathbf{pH = -lg\,[H^+(aq)]}}$$

where symbol 'p' means '$-\log_{10}$'

Hence, $\boxed{\mathbf{[H^+(aq)] = 10^{-pH}}}$

E.g. for 0.01 mol dm^{-3} HCl, $[H^+(aq)] = 10^{-2}$ mol dm^{-3} and pH = 2.

<u>Note</u>:
pH is a measure of the (total) concentration of H^+ in a solution. It is <u>not</u> a measure of the strength of the acid unless the two acids being compared have the same initial concentration (see Section 2.8).

Similarly, the concentration of $OH^-(aq)$ is commonly expressed in terms of its negative logarithm to base 10.

$$\boxed{\mathbf{pOH = -lg\,[OH^-(aq)]}}$$

and $\boxed{\mathbf{[OH^-(aq)] = 10^{-pOH}}}$

E.g. for 0.01 mol dm^{-3} NaOH, $[OH^-(aq)] = 10^{-2}$ mol dm^{-3} and pOH = 2.

2.2 Ionic product of water, K_w

Pure water conducts electricity slightly, due to the very slight self-ionisation or autoionisation of water which produces trace concentrations of ions.

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

A simpler way of representing the equilibrium is:

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

The equilibrium constant, K_c, for the reaction is given by:

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

$[H_2O]$ = 55.6 mol dm^{-3} (water has density 1.00 g cm^{-3}, so 1 dm^3 of water has mass of 1000 g. Since molar mass of water is 18.0 g mol^{-1}, therefore 1000 g (1 dm^3) of water contains 1000/18.0 = 55.6 mol of water.)

The extent of self-ionisation of water is very small compared to the concentration of water (55.6 mol dm^{-3}), hence $[H_2O]$ is almost constant.

Therefore, $K_c \times [H_2O] = [H^+][OH^-]$

or $$\boxed{\mathbf{K_w = [H^+][OH^-]}}$$

where K_w is known as the **ionic product of water**. The value of K_w depends only on temperature. It is always a constant at constant temperature.

Taking –lg on both sides of equation:

$$-\lg K_w = (-\lg [H^+]) + (-\lg [OH^-])$$

$$\boxed{\mathbf{pK_w = pH + pOH}}$$

* remember the symbol 'p' means '$-\log_{10}$'

Hence, we can determine the value of pH, given K_w value at the specified temperature and the pOH value, and vice versa.

2.3 Relationship between $[H^+(aq)]$, $[OH^-(aq)]$ and pH

In pure water as well as *any* aqueous solution, the following equilibrium exists:

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

where K_w always = $[H^+][OH^-]$ and pK_w = pH + pOH.

When $[H^+(aq)] = [OH^-(aq)]$ ➔ *neutral* solution
$[H^+(aq)] > [OH^-(aq)]$ ➔ *acidic* solution
$[H^+(aq)] < [OH^-(aq)]$ ➔ *alkaline* solution

At **25°C,** **K_w = 1.00 × 10^{-14} mol² dm^{-6}** (value is given in the *Data Booklet*)

And so **pK_w = pH + pOH = 14**

Hence at 25° C, the pH of acidic, basic and neutral solutions can be calculated as follows:

Table 1. Summary of [H⁺], [OH⁻], pH and pOH of acidic, basic and neutral solution at 25 °C

Type of solution	**$[H^+]$ / mol dm^{-3}**	**$[OH^-]$ / mol dm^{-3}**	**pH**	**pOH**
Neutral	= 1.0×10^{-7}	= 1.0×10^{-7}	= 7.00	= 7.00
Acidic	> 1.0×10^{-7}	< 1.0×10^{-7}	< 7.00	> 7.00
Basic	< 1.0×10^{-7}	> 1.0×10^{-7}	> 7.00	< 7.00

Like other equilibrium constants, the **value of K_w depends *only* on temperature**:

Table 2. K_w values and [H⁺] of water at different temperatures

Temperature / °C	**K_w / mol² dm^{-6}**	**$[H^+] = [OH^-] = \sqrt{K_w}$ / mol dm^{-3}**
0	1.5×10^{-15}	3.9×10^{-8}
10	3.0×10^{-15}	5.5×10^{-8}
25	1.0×10^{-14}	1.0×10^{-7}
40	3.0×10^{-14}	1.7×10^{-7}
60	9.5×10^{-14}	3.1×10^{-7}

Lecture Exercise 2.1

With reference to the above data on K_w, state whether the following statements are true or false.

(i) The ionic dissociation of water, $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$, is an endothermic process.

(ii) When water is heated, the concentration of H^+(aq) increases.

(iii) When water is heated, the concentration of OH^-(aq) increases.

(iv) In pure water, the concentration of H^+(aq) is higher than that of OH^-(aq) at 60 °C.

(v) Water remains a neutral liquid at 60 °C.

(vi) The pH of pure water at temperatures greater than 25 °C is greater than 7.

2.4 pH of Strong Acid / Strong base solutions

LO 10.1(c)part: calculate [H⁺(aq)] and pH values for strong acids, strong bases

Strong acids and strong bases are fully dissociated, hence

$[H^+]$ = [strong monobasic acid] and $[H^+]$ = 2 × [strong dibasic acid]

Similarly, $[OH^-]$ = [strong monoacidic base] and $[OH^-]$ = 2 × [strong diacidic base]

Note: If the concentration of the acid or base is 10^{-7} mol dm^{-3} or lower, the contribution of H^+ or OH^- from auto-ionisation of H_2O becomes significant. We should then take into consideration the contribution of H^+ or OH^- from auto-ionisation of H_2O in the calculation (See Lecture Exercise 2.2 (3))

Lecture Exercise 2.2

1. An aqueous solution contains 1.0 × 10^{-5} mol dm^{-3} of hydrogen iodide (a strong acid). Calculate the concentration of H^+ in mol dm^{-3}, and hence the pH of this solution at 25 °C.

Ans: $[H^+]$ = 1.00 × 10^{-5} mol dm^{-3}, pH = 5.00

2. An aqueous solution contains 0.010 mol dm^{-3} of $Ba(OH)_2$ (a strong base) and 0.050 mol dm^{-3} of KOH. Calculate the pH of this solution at 25 °C.

Ans: pH = 12.8

3. An aqueous solution contains 1 × 10^{-8} mol dm^{-3} of HNO_3. Calculate the pH of this solution.

Ans: 6.96

Self-Practice 2.1

1. An aqueous solution contains 0.10 mol dm^{-3} of calcium hydroxide (a strong base). Calculate the concentration of OH^- in mol dm^{-3}, and hence the pH of this solution at 25 °C.

Ans: $[OH^-]$ = 0.20 mol dm^{-3}, pH = 13.3

2. Solution *X* contains HC*l*, it has pH 2.2. Solution *Y* has the same volume as solution *X*. Solution Y contains HNO_3 and has pH 1.6. The two solutions are mixed. Calculate the pH of the resulting solution.

Ans: 1.80

2.5 Acid Dissociation Constant (K_a) and Base Dissociation constant (K_b)

LO 10.1(b)part: explain the terms K_a; pK_a; K_b; pK_b and apply them in calculations, including the relationship $K_w = K_aK_b$

2.5.1 Acid Dissociation Constant (K_a)

A weak acid HA dissociates **partially** in water to give H_3O^+.

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

In dilute aqueous solution, $[H_2O]$ is almost constant (at 55.6 mol dm^{-3}). The equilibrium constant may be written as:

$$\boxed{K_a = \frac{[H^+]_{eqm}[A^-]_{eqm}}{[HA]_{eqm}} \text{ mol dm}^{-3}}$$

and $\boxed{pK_a = -\lg K_a}$

- For strong acids, e.g. HC*l*, K_a is very large and not used.
- The value of K_a indicates the **extent** to which the weak acid dissociates in water at the specified temperature.
- To compare the strength of two weak acids, compare their K_a values.
- At the same temperature, **larger K_a (smaller pK_a) ⇒ stronger acid**.
- Like other equilibrium constants, the value of K_a depends <u>only</u> on temperature.

Table 3. Some weak acids and their K_a values at 25 °C

Acid Dissociation equilibrium reaction	**K_a /mol dm^{-3}**
$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$	1.8×10^{-5}
$HCO_2H + H_2O \rightleftharpoons HCO_2^- + H_3O^+$	1.8×10^{-4}
$C_6H_5CO_2H + H_2O \rightleftharpoons C_6H_5CO_2^- + H_3O^+$	6.5×10^{-5}
$HCN + H_2O \rightleftharpoons CN^- + H_3O^+$	4.9×10^{-10}

2.5.2 Base Dissociation Constant (K_b)

A weak base dissociates **partially** in water to give OH^-.

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

In dilute aqueous solution, $[H_2O]$ is almost constant (at 55.6 mol dm^{-3}). The equilibrium constant may be written as:

$$\boxed{K_b = \frac{[BH^+]_{eqm}[OH^-]_{eqm}}{[B]_{eqm}} \text{ mol dm}^{-3}}$$

and $\boxed{pK_b = -\lg K_b}$

- For strong bases, e.g. NaOH, K_b is very large and not used.
- The value of K_b indicates the **extent** to which the weak base dissociates in water at the specified temperature.
- To compare the strength of two weak bases, compare their K_b values.
- At the same temperature, **larger K_b (smaller pK_b) ⇒ stronger base**.
- The value of K_b depends only on temperature.

Table 4. Some weak bases and their K_b values at 25 °C

Base Dissociation equilibrium reaction	**K_b /mol dm^{-3}**
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$	5.6×10^{-10}

- In aqueous solution, the two large classes of weak bases are nitrogen-containing molecules such as NH_3 and amines (e.g. $CH_3CH_2NH_2$), and the anions or conjugate bases of weak acids (e.g. ethanoate ion, $CH_3CO_2^-$).

2.5.3 Relationship between K_a, K_b and K_w for conjugate acid-base pairs

Consider the weak acid, CH_3CO_2H, and its conjugate base, $CH_3CO_2^-$.

$$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$$

$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]} \quad \text{———————— (1)}$$

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$$

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]} \quad \text{———————— (2)}$$

(1) × (2), $K_a \times K_b = [H^+][OH^-] = K_w$

Therefore, **for any conjugate acid–base pair,**

$$\boxed{\boldsymbol{K_a \times K_b = K_w}}$$

Taking –lg on both sides of equation:

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

$$\boxed{\mathbf{p}\boldsymbol{K_a} + \mathbf{p}\boldsymbol{K_b} = \mathbf{p}\boldsymbol{K_w}}$$

* remember the symbol 'p' means '$-\log_{10}$'

Hence, we can determine the value of K_a of an acid, given the K_b value of its conjugate base and vice versa.

From $K_a \times K_b = K_w$, we see that for a conjugate acid-base pair,
as the strength of the acid decreases (smaller K_a), the strength of its conjugate base increases (larger K_b) and vice versa.

2.6 Degree of dissociation

The **fraction** of molecules which is **ionised** into ions in water is called the degree of dissociation, α.

For an acid,

$$\boxed{\alpha = \frac{\textbf{amount ionised}}{\textbf{initial amount}} = \frac{\textbf{[acid]}_{\textbf{dissociated}}}{\textbf{[acid]}_{\textbf{initial}}}}$$

In general, for a strong acid or strong base, α is close to 1
for a weak acid or weak base, $\alpha \ll 1$

2.7 pH of Weak Acid / Weak Base Solutions

*LO 10.1(c)part: calculate [H⁺(aq)] and pH values for weak monobasic (monoprotic) acids, and weak monoacidic bases [Calculations involving weak acids/bases will **not** require solving of quadratic equations]*

Since weak acids and weak bases dissociate **partially** in water, $[H^+]$ or $[OH^-]$ in the solution will be **lower than** the initial concentration of the weak acid or weak base.

We use K_a or K_b to calculate the $[H^+]$ or $[OH^-]$ in the solution at equilibrium.

Lecture Exercise 2.3

1. Find **(a)** the pH and **(b)** the degree of dissociation of a solution of ethanoic acid, CH_3CO_2H, of concentration 0.1 mol dm^{-3}. [Given: K_a of CH_3CO_2H = 1.8×10^{-5} mol dm^{-3}]

Ans: 2.87; 1.34×10^{-2} or 1.34 %

Important note:
$[H^+]_{eqm} = [A^-]_{eqm}$ is true only if the solution contains *only* weak acid HA (i.e. all H^+ ions and A^- ions present in the solution come only from the dissociation of HA and there are no added H^+ ions or A^- ions). This equation cannot be used for calculations involving buffer solutions (see Section 4.4).

Note:
Solving quadratic equations is not required for Chemistry 'A' Levels. The assumption (x << 0.1) is valid since a weak acid only dissociates partially. Without the approximation, the answer would have been 1.33×10^{-3} mol dm^{-3}. The difference is insignificant because it is within the limits of the accuracy to which the data is given.

Self-Practice 2.2
Calculate (a) the pH and (b) the degree of dissociation of a solution of 0.125 mol dm^{-3} aqueous ammonia at 298 K. [Given K_b for ammonia = 1.78×10^{-5} mol dm^{-3} at 298 K]

Ans: (a) 11.2 ; (b) 1.19×10^{-2} or 1.19%

Lecture Exercise 2.4

Caffeine, $C_8H_{10}N_4O_2$, a stimulant found in coffee and tea, is a weak base.

$$C_8H_{10}N_4O_2 + H_2O \rightleftharpoons (C_8H_{11}N_4O_2)^+ + OH^-$$

At 25 °C, a 0.020 mol dm^{-3} caffeine solution has a pH of 11.5.

(a) Write the K_b expression of caffeine and calculate its value at 25 °C.

(b) Calculate the degree of dissociation, α for caffeine at 25 °C.

Ans: 5.94×10^{-4} mol dm^{-3}; 0.158 or 15.8 %

Note: If $[H^+]$ at equilibrium is known, the assumption $[H^+] << [HA]$ should not be made in the calculations.

Self-Practice 2.3

The pH of a weak acid, HA, of concentration 0.100 mol dm^{-3} was found to be 3.0.
Calculate the K_a and pK_a of the acid.

Ans: $K_a = 1.01 \times 10^{-5}$ mol dm^{-3}, $pK_a = 5.00$

2.8 Strength of Acids and Bases

LO 10.1(a): explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation

The strength of an acid (or base):

- is a measure of **how readily** the acid (or base) donates its proton (or accepts a proton).
- depends on its **structure** (refer to Organic Chemistry Topic 16 Hydroxy Compounds, Topic 18 Carboxylic Acids for acid strengths of different phenols and carboxylic acids, as well as Topic 19 Nitrogen compounds to compare the basic strength of amines)
- is indicated by its **K_a (or K_b)** value [see Section 2.5.1 and 2.5.2]
- is *different* from the concentration of the acid (or base) [see Lecture Exercise 2.3]

Are pH or degree of dissociation, α, reliable indicators of the strength of an acid (or base)?

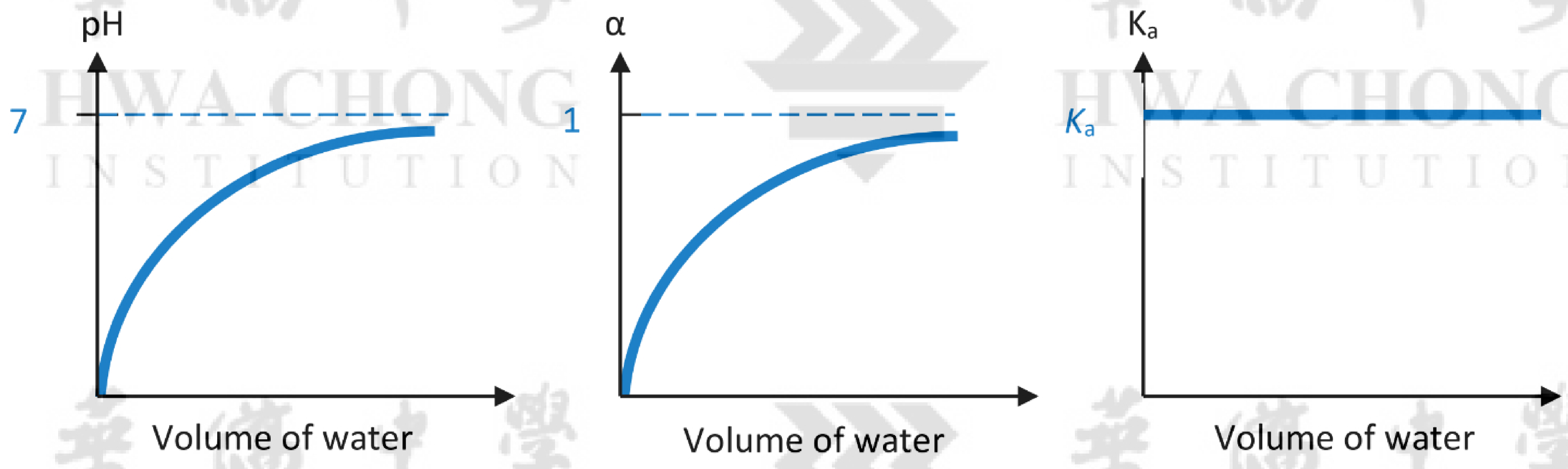
Lecture Exercise 2.5

In Exercise 2.3, the pH and the degree of dissociation of a solution of ethanoic acid of concentration 0.1 mol dm^{-3} were found to be:

pH: ………………………… degree of dissociation, α: …………………………

Now, find **(a)** the pH and **(b)** the degree of dissociation of ethanoic acid of concentration 0.001 mol dm^{-3}. How have the pH and α been affected by the dilution?

The diagrams below show how the values of pH, α and K_a for a weak acid vary with dilution (i.e. volume of water increases) at a constant temperature:



(pH → 7 as dilution → ∞) (α → 1 as dilution → ∞)

K_a does not vary with concentration. It is a constant at constant temperature. Therefore K_a is the best indicator of the strength of a weak acid.

Lecture Exercise 2.6

Each of the following reactions contains two Bronsted acids and two Bronsted bases. Suggest with brief reasoning which is the stronger acid and which is the stronger base.

(a) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_c = 3.2 \times 10^{-7}$

(b) $C_6H_5O^- + CH_3CO_2H \rightleftharpoons C_6H_5OH + CH_3CO_2^- \qquad K_c = 1.3 \times 10^{5}$

Note:
From part **(b)**, we see that the stronger acid is able to protonate the conjugate base of the weaker acid.
Strong acids (e.g. HC*l*) are often used to liberate the weak acids (e.g. CH_3CO_2H) from their salt (e.g. $CH_3CO_2^-Na^+$).

$$\underset{\text{stronger acid}}{HCl\,(aq)} + \underset{\text{conjugate base}}{CH_3CO_2^-(aq)} \rightarrow Cl^-(aq) + \underset{\text{weaker acid}}{CH_3CO_2H(aq)}$$

3 SALT HYDROLYSIS

LO 4(b): show understanding of, and apply the Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases
LO 10.1(b): explain the terms pH; K_a; pK_a; K_b; pK_b; K_w and apply them in calculations, including the relationship $K_w = K_aK_b$
*LO 10.1(c)part: calculate [H^+(aq)] and pH values for weak monobasic (monoprotic) acids, and weak monoacidic bases [Calculations involving weak acids/bases will **not** require solving of quadratic equations]*

An ionic salt may be prepared from a reaction between an aqueous acid and an aqueous base.
E.g. KC*l* may be prepared from KOH(aq) and HC*l* (aq).

Salt hydrolysis is a reaction in which ions of a salt react with water to produce OH^- or H_3O^+ ions.

Ions in salts derived from a strong acid and a strong base (e.g. NaC*l*, KNO_3) **do not** undergo salt hydrolysis. Hence the resulting solution is neutral ⇒ pH = 7 at 25 °C.

However, ions in salts derived from weak acids/bases, as well as metal cations with high charge density, could undergo hydrolysis to result in acidic or alkaline solutions (pH greater/less than 7 at 25 °C).

3.1.1 Salt derived from a weak acid and a strong base

- Consider $CH_3CO_2^-Na^+$ which is derived from the salt of CH_3CO_2H and NaOH.

- CH_3CO_2H is a weak acid so its conjugate base **$CH_3CO_2^-$ is a stronger base than water**. $CH_3CO_2^-$ undergoes **hydrolysis** forming OH^- ions.

$$CH_3CO_2^-(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad CH_3CO_2H(aq) \quad + \quad \mathbf{OH^-(aq)}$$

- Hence $[OH^-] > [H_3O^+]$ and the salt solution of $CH_3CO_2^-Na^+$ is alkaline.
- **At 25 °C, pH of a solution of $CH_3CO_2^-Na^+$ is > 7**.

Note:
  - $CH_3CO_2^-$ (aq) is a stronger base than water so is able to accept a proton from water.
  - However, it is still a weak base (K_b of $CH_3CO_2^- = 5.6 \times 10^{-10}$ mol dm^{-3}). Hence a reversible arrow ⇌ is used in the salt hydrolysis equation.
  - The cation Na^+ does not undergo hydrolysis due to its low charge density.

3.1.2 Salt derived from a strong acid and a weak base

- Consider $NH_4^+Cl^-$ which is derived from the salt of HC*l* and NH_3.

- NH_3 is a weak base so its conjugate acid **NH_4^+ is a stronger acid than water**. NH_4^+ undergoes **hydrolysis** forming H_3O^+ ions.

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

- Hence $[H_3O^+] > [OH^-]$ and the salt solution of NH_4Cl is acidic.
- **At 25 °C, pH of a solution of NH_4Cl is < 7**.

Note:
  - NH_4^+ is a stronger acid than water so is able to donate a proton to water. (see Lecture Exercise 2.6)
  - However, it is still a weak acid (K_a of $NH_4^+ = 5.56 \times 10^{-10}$ mol dm^{-3}). Hence a reversible arrow ⇌ is used in the salt hydrolysis equation.
  - The anion Cl^- (derived from strong acid HC*l*) is a weaker base than water and so does not hydrolyse.

3.1.3 Salt derived from a weak acid and a weak base

E.g. $CH_3CO_2^-NH_4^+$

- Both cation and anion hydrolyse.
- pH of the salt solution depends on K_a of the acid (cation) and K_b of the base (anion)

If K_a(cation) > K_b(anion) → salt solution is acidic

K_a(cation) = K_b(anion) → salt solution is neutral

K_a(cation) < K_b(anion) → salt solution is basic

3.1.4 Salt containing an aqueous metal cation with high charge density

LO 5(e)(iv)part: describe and explain the reactions of the chlorides with water (for $AlCl_3$)

Consider the ionic compound, aluminium nitrate $Al(NO_3)_3$. When it dissolves in water, the Al^{3+} and NO_3^- ions are separated and surrounded by water molecules.

$$Al(NO_3)_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3NO_3^-(aq)$$

The Al^{3+} cations are coordinated to water molecules through dative (co–ordinate) bonds to form the complex ion, $[Al(H_2O)_6]^{3+}$.

The Al^{3+} ion is **small and highly charged**, so it has **high charge density**. It **withdraws sufficient electron density from the O–H bonds of the coordinated H_2O molecules, weakening the O–H bonds**. When one O–H bond breaks, a proton is released:

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + \mathbf{H_3O^+(aq)}$$

We call this a **hydrolysis** reaction. Observe that $[Al(H_2O)_6]^{3+}$ is acting as a weak Bronsted acid. Since $[H_3O^+] > [OH^-]$, Al^{3+}(aq) is **acidic and pH < 7 at 25 °C**.

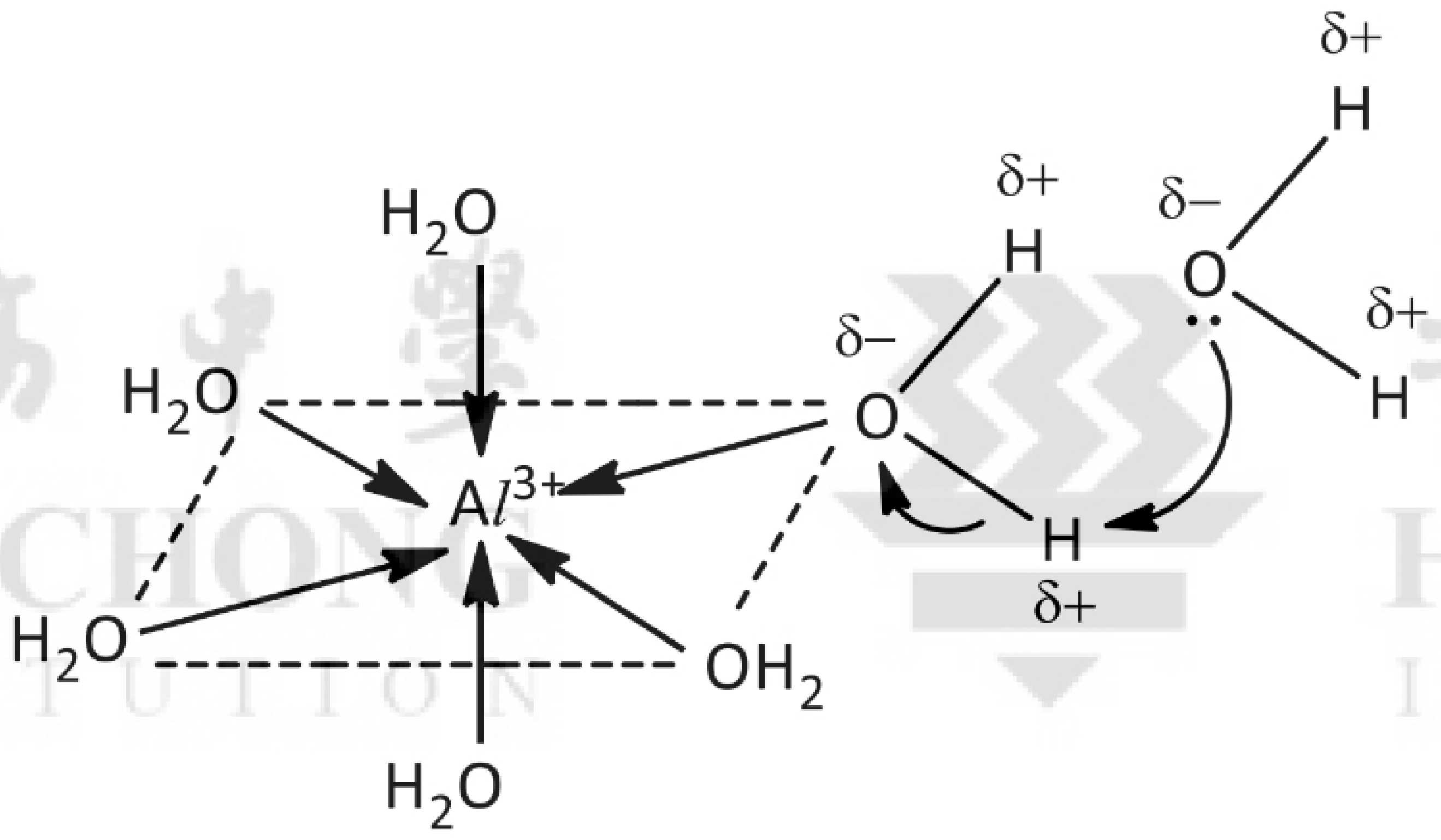


Figure 1. $[Al(H_2O)_6]^{3+}$ acting as an acid, donating a proton to another H_2O molecule

Other metal cations like Fe^{3+} and Cr^{3+} also form complex ions with water which undergo the hydrolysis reaction to produce an acidic solution.

Table 5. Formula of the complex ions of Fe^{3+}, Cr^{3+} and Al^{3+} with water and their K_a values

Metal ion	Complex ion formed with water	K_a / mol dm^{-3} (at 25 °C)
Fe^{3+}	$[Fe(H_2O)_6]^{3+}(aq)$	6×10^{-3}
Cr^{3+}	$[Cr(H_2O)_6]^{3+}(aq)$	1×10^{-4}
Al^{3+}	$[Al(H_2O)_6]^{3+}(aq)$	1×10^{-5}

Lecture Exercise 3.1

State whether the following solutions are acidic, alkaline or neutral. Write an equation, including state symbols, for any hydrolysis reaction.

(a) KBr(aq)

(b) $Na_2CO_3(aq)$, given: K_a of HCO_3^- = 4.7×10^{-11} mol dm^{-3}

(c) $CH_3NH_3^+Cl^-(aq)$

(d) $NH_4HS(aq)$, given: K_b of NH_3 = 1.8×10^{-5} mol dm^{-3}
K_{a1} of H_2S = 9×10^{-8} mol dm^{-3}

(e) $FeCl_3(aq)$

3.2 pH of salt solutions

The pH of salt solutions can be calculated using the following general strategy:

1. Determine whether the ions in the salt undergoes hydrolysis in water by considering the strength of acid and base from which the salt is derived
2. Write an equation for any hydrolysis that takes place in water to produce H_3O^+ or OH^- ions.
3. Calculate $[H_3O^+]$ or $[OH^-]$ using the K_a or K_b of the ion that undergoes hydrolysis in water.

Lecture Exercise 3.2

Calculate the pH of a 0.10 mol dm^{-3} $CH_3CO_2^-$ $Na^+(aq)$ at 25°C.

K_a value for ethanoic acid is 1.8×10^{-5} mol dm^{-3}.

Ans: 8.87

Self Practice 3.1

Calculate the pH of 0.450 mol dm^{-3} ammonium chloride at 298 K

(Given K_b for ammonia = 1.78×10^{-5} mol dm^{-3})

Ans : 4.80

4 BUFFER SOLUTIONS

4.1 Definition of Buffer solutions

LO 10.1(f)(i): explain how buffer solutions control pH

A *buffer solution* is one that is able to **resist pH changes** upon addition of a **small amount** of **acid or base**.

A buffer (usually) consists of two species which make up a **conjugate acid-base pair of a weak acid or base** – one species acts as weak Bronsted acid and the other species acts a weak Bronsted base. An example is a mixture of ethanoic acid (CH_3CO_2H) and ethanoate ion ($CH_3CO_2^-$).

Lecture Exercise 4.1

State whether the following mixture can act as a buffer solution.

1. $NaHCO_3$ and Na_2CO_3
2. CH_3CO_2H and $NaCl$
3. HNO_3 and $NaNO_3$

4.2 Preparing a Buffer (Background info)

4.2.1 Mixing a weak acid and its conjugate base

Consider a buffer consisting of **a weak acid**, CH_3CO_2H, **and its conjugate base**, $CH_3CO_2^-$ ions

Ethanoic acid is a weak acid and dissociates partially.

$$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq) \quad \text{———————} (1)$$

Adding sodium ethanoate (completely soluble in water) to this solution adds a lot of extra ethanoate ions.

$$CH_3CO_2^-Na^+(aq) \rightarrow CH_3CO_2^-(aq) + Na^+(aq)$$

According to Le Chatelier's Principle, the position of equilibrium (1) shifts further to the left (i.e. the dissociation of ethanoic acid is suppressed). Similarly, hydrolysis of the ethanoate ion in water is suppressed by the presence of the ethanoic acid.

The solution now contains the following:

- large reservoir of un-ionised **ethanoic acid**;
- large reservoir of **ethanoate ions** from the sodium ethanoate;

and can act as a **buffer** solution.

4.2.2 Mixing a weak base and its conjugate acid

Consider a buffer consisting of **a weak base**, aqueous NH_3 and **its conjugate acid**, NH_4^+ ions

Ammonia is a weak base and dissociates partially.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad \text{———————————}(2)$$

Adding ammonium chloride (completely soluble) to this solution adds a lot of extra ammonium ions.

$$NH_4^+Cl^-(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

In a similar explanation to Section 4.2.1, the solution now contains a large reservoir of un-ionised **ammonia** and a large reservoir of **ammonium ions** from the ammonium chloride, and can act as a **buffer** solution.

Note: Buffer solutions with pH < 7 (at 25 °C) may be referred to as 'acidic' buffers while buffer solutions with pH > 7 (at 25 °C) may be referred to as 'alkaline' buffers.

4.2.3 Partial neutralisation of a weak acid (or weak base)

Another way to prepare a buffer is to form one of the species by *partial neutralisation* of the other species. For example, the ethanoic acid/ethanoate buffer can be prepared by mixing suitable amounts of ethanoic acid and NaOH. The key is to add less NaOH than is required for complete neutralisation, such that the OH^- ions will react with part of the total ethanoic acid present to produce the ethanoate ions needed, at the same time leaving some ethanoic acid behind, to give a mixture consisting of *both* ethanoic acid and ethanoate ions.

This method is based on the same chemical process that occurs when a weak acid is titrated with a strong base (see Section 5.1.2) or when a weak base is titrated with a strong acid (see Section 5.1.3).

Self-practice 4.1

Which combination of substance, when mixed, would **not** give a buffer solution?

A 25 cm^3 of 0.1 mol dm^{-3} HCl and 50 cm^3 of 0.1 mol dm^{-3} NH_3
B 25 cm^3 of 0.1 mol dm^{-3} NaOH and 25 cm^3 of 0.2 mol dm^{-3} NH_4^+
C 25 cm^3 of 0.2 mol dm^{-3} HCl and 25 cm^3 of 0.1 mol dm^{-3} $CH_3CO_2^-$
B 25 cm^3 of 0.1 mol dm^{-3} NaOH and 25 cm^3 of 0.2 mol dm^{-3} CH_3CO_2H

4.3 Explaining Buffer Action

LO 10.1(f)(i): explain how buffer solutions control pH

How does the buffer consisting of large reservoirs of CH_3CO_2H *and its conjugate base* $CH_3CO_2^-$ *resist pH changes on addition of small amount of acid or base?*

(i) When a small amount of **H^+** is added to this buffer, the H^+ ions **react with** the large reservoir of the **$CH_3CO_2^-$ (conjugate base)**:

$$CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$$

The added H^+ ions are removed and $[CH_3CO_2H]$ increases slightly and $[CH_3CO_2^-]$ decreases slightly.
As the original amounts of CH_3CO_2H and $CH_3CO_2^-$ are large compared to the amount of H^+ ions added, the ratio $[CH_3CO_2^-] / [CH_3CO_2H]$ remains almost constant.
Since $K_a = [H^+][CH_3CO_2^-] / [CH_3CO_2H]$, and K_a is a constant, so $[H^+]$ and pH remains almost constant.

(ii) When a small amount of **OH^-** is added to this buffer, the OH^- ions **react with** the large reservoir of the un–ionised **CH_3CO_2H molecules**:

$$CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$$

The added OH^- ions are removed and $[CH_3CO_2H]$ decreases slightly and $[CH_3CO_2^-]$ increases slightly.
As the original amounts of CH_3CO_2H and $CH_3CO_2^-$ are large compared to the amount of OH^- ions added, the ratio $[CH_3CO_2^-] / [CH_3CO_2H]$ remains almost constant.
Since $K_a = [H^+][CH_3CO_2^-] / [CH_3CO_2H]$, and K_a is a constant, so $[H^+]$ and pH remains almost constant.

Note: Buffer action equations are written with single (non-reversible) arrows.

Self-practice 4.2
How does a buffer solution containing NH_3(aq) and NH_4Cl(aq) resist changes in pH when small amounts of acid or alkali are added?

4.4 Calculating pH of Buffer solutions

LO 10.1(g): calculate the pH of buffer solutions, given appropriate data

4.4.1 pH of buffer consisting of weak acid HA and its conjugate base A^-

In a buffer consisting of HA and its conjugate base A^-, the following equilibrium exists:

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

and $$K_a = \frac{[H^+]_{eqm}[A^-]_{eqm}}{[HA]_{eqm}}$$

As the presence of excess A^-(aq) suppresses the dissociation of HA,

$[HA]_{eqm} \approx [HA]_{initial}$ (since α is very small)

$[A^-]_{eqm} \approx [A^-]_{initial}$ (since $[A^-]_{\text{from HA}}$ is very small)

therefore $$K_a \approx \frac{[H^+]_{eqm}[A^-]_{initial}}{[HA]_{initial}} = \frac{\mathbf{[H^+]_{eqm}[conjugate\ base]}}{\mathbf{[acid]}}$$

and $$\boxed{[H^+] = K_a \frac{[acid]}{[conjugate\ base]}}$$

Hence pH of the buffer can be found easily.

Important note:

In this case of the buffer, **$[H^+] \neq [A^-]$** since the solution consists of *significant* amounts of HA and A^- and the A^- ions do not just come from the weak acid dissociation of HA alone, unlike in a solution of pure weak acid HA (see Lecture Exercise 2.3).

Alternatively, to find pH of a buffer, take –lg on both sides of boxed equation,

$$-\lg[H^+] = -\lg K_a - \lg\frac{[acid]}{[conjugate\ base]}$$

$$\boxed{pH = pK_a + \lg\frac{[conjugate\ base]}{[acid]}}$$ **Henderson–Hasselbalch Equation**

4.4.2 pH of buffer consisting of weak base and its conjugate acid

In a similar manner as above, the pOH and pH of this buffer can be found using:

$$\boxed{[OH^-] = K_b\frac{[base]}{[conjugate\ acid]}} \quad \text{or} \quad \boxed{pOH = pK_b + \lg\frac{[conjugate\ acid]}{[base]}}$$

Lecture Exercise 4.2

Calculate the pH of a solution consisting of **0.010** mol of ethanoic acid and **0.010** mol of sodium ethanoate dissolved in 1 dm^3 of water. (K_a of ethanoic acid = 1.8×10^{-5} mol dm^{-3})

Ans: 4.74

Application Example

Calculate the change in pH when 1 cm^3 of a 1.00 mol dm^{-3} NaOH is added to 1 dm^3 of

(a) water; **(b)** the buffer solution in Exercise 4.2 above.

(a) No. of moles of NaOH added = 1 ÷ 1000 × 1.00 = 0.001

$[OH^-] = (0.001 \div 1001 \times 1000)$

$= 9.99 \times 10^{-4}$ mol dm^{-3}

Note: Remember to divide by the new total volume as volume of solution has changed upon adding aq. NaOH.

pOH = 3.00 ∴ pH = 11.0

Change in pH = 11.0 – 7 = <u>+4 units</u>

(b) $CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$

Strategy: Decide which buffer component removes the added NaOH, then work out the new concentration of each buffer component.

No. of moles of NaOH added = 0.001

After the reaction,

$[CH_3CO_2^-] = (0.010 + 0.001) / V$

$[CH_3CO_2H] = (0.010 - 0.001) / V$

Tip: The new total volume of the solution can just be denoted as V, as this would cancel in the K_a expression.

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+]\,(0.010 + 0.001) / V}{(0.010 - 0.001) / V}$$

$[H^+] = 1.47 \times 10^{-5}$ mol dm^{-3}

∴ pH $= -\lg [H^+] = 4.83$

Change in pH = 4.83 – 4.74= <u>+0.09 units</u>

From the above calculation, we can see that a buffer solution resists pH changes much better when a small amount of strong base is added.

4.5 Buffer Capacity (Background info)

The capacity of a buffer is the quantity of H_3O^+ or OH^- it can remove before its pH changes drastically. A buffer should have high [weak acid] and [conjugate base], or high [weak base] and [conjugate acid], to provide a large reservoir of the relevant components. The more concentrated the components of a buffer, the greater the buffer capacity.

Buffer capacity also depends on the ratio of [weak acid] and [conjugate base], or ratio of [weak base] and [conjugate acid]. For example, if a buffer contains a much higher proportion of the weak acid compared to its conjugate base, then it is more effective in resisting changes in pH on addition of OH^- as compared to the addition of H_3O^+. It can be shown that the most effective buffer has

$$\frac{[\text{conjugate base}]}{[\text{acid}]} = 1 \qquad \text{or} \qquad \frac{[\text{conjugate acid}]}{[\text{base}]} = 1$$

LO 10.1(d): describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases

Using the boxed equations in Section 4.4.1 and 4.4.2, it follows that, for this most effective buffer,

$pH = pK_a$ (for acidic buffer) or $pOH = pK_b$ (for alkaline buffer)

This buffer is said to have the ***maximum buffer capacity*** and it can most effectively resist a change in pH in either direction (i.e. when either acid or base is added).

4.6 Effective Buffer Range (Background info)

The further the buffer-component concentration ratio is from 1, the less effective the buffering action (i.e., lower buffer capacity).

In practice, a buffer is no longer effective when
[acid]/[conjugate base] or [base]/[conjugate acid] > 10/1 or < 1/10.

Since $\log_{10}(10/1) = +1$ and $\log_{10}(1/10) = -1$,

for an acidic buffer, $[H^+] = K_a \times \frac{[\text{acid}]}{[\text{conjugate base}]}$ $\Rightarrow$ **effective buffer pH range = $pK_a \pm 1$**

for an alkaline buffer, $[OH^-] = K_b \times \frac{[\text{base}]}{[\text{conjugate acid}]}$ $\Rightarrow$ **effective buffer pOH range = $pK_b \pm 1$**

Lecture Exercise 4.3

Which of the following acids would be the best choice to combine with its sodium salt to make a solution buffered at pH 4.25?
For your choice, calculate the ratio of the conjugate base to the acid concentrations required to attain the desired pH.

Acid	**pK_a**
chlorous acid ($HClO_2$)	1.95
nitrous acid (HNO_2)	3.34
methanoic acid (HCO_2H)	3.74
hypochlorous acid ($HClO$)	7.54

4.7 Buffer System in Human Blood

LO 10.1(f)(ii): describe and explain uses of buffer solutions, including the role of H_2CO_3/HCO_3^- in controlling pH in blood

The pH of our blood must be kept constant at about 7.4 since enzymes operate only within a narrow pH range. Blood contains large amounts of the weak acid carbonic acid, **H_2CO_3** (an aqueous solution of CO_2), and its conjugate base, **HCO_3^-** ions (bicarbonate). Together they help maintain the pH of blood at 7.4. If blood pH falls below 6.8 or rises above 7.8, one can become sick or die. The bicarbonate neutralises excess acids in the blood while the carbonic acid neutralises excess bases.

The following equilibria operate in the H_2CO_3/HCO_3^- buffer system:

$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$$

When H^+ is added to the blood as a result of metabolic processes, the following reaction occurs

$$H^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq)$$

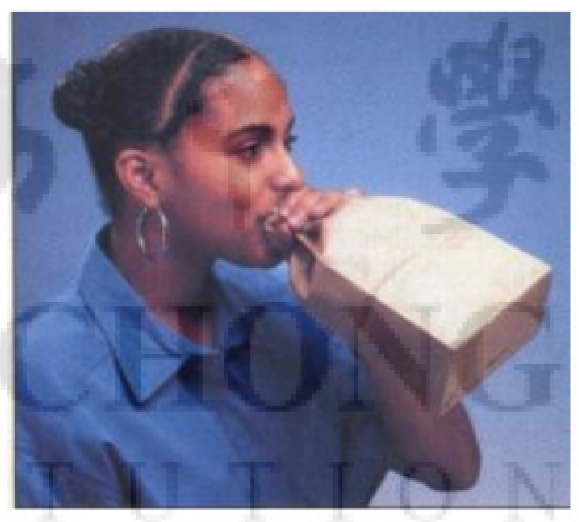
The amount of HCO_3^- (relative to the amount of CO_2) decreases; however, the amount of the change is tiny compared to the large amount of HCO_3^- present in the blood.

When OH- is added, it is removed by the carbonic acid.

$$H_2CO_3(aq) + OH^- \rightarrow HCO_3^-(aq) + H_2O(l)$$

$$\text{Or} \quad CO_2(aq) + OH^-(aq) \rightarrow HCO_3^-(aq)$$

If blood pH rises above about 7.45, you can suffer from a condition called *alkalosis*. This can arise from hyperventilation or oxygen deficiency at high altitude. It can lead to over excitability of the central nervous system, muscle spasms and death. One way to treat alkalosis is to breathe into a paper bag. The CO_2 exhaled is recycled into the body. *Can you explain how that helps?*



pH Regulation During Exercise : a tutorial on buffer in the body

http://www.chemistry.wustl.edu/~edudev/LabTutorials/CourseTutorials/bb/Buffer/Buffers.pdf

Self-Practice 4.3

The main buffering agent in blood plasma is the carbon dioxide/hydrogen carbonate system.

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \qquad K_a = 7.90 \times 10^{-7}\ \text{mol dm}^{-3}$$

(a) Explain how the system above acts as a buffer when
(i) H^+ ions, **(ii)** OH^- ions
are added to the blood plasma

(b) The pH of normal blood plasma is 7.40. Use the data above to calculate the ratio $[HCO_3^-]/[CO_2]$ and hence deduce whether blood has a greater capacity for absorbing H^+ or OH^- ions.

(c) Using the above buffer system, briefly explain why strenuous exercise leads to an increase rate of breathing.

5 ACID-BASE TITRATIONS

LO 10.1(d): describe the changes in pH during acid–base titrations and explain these changes in terms of the strengths of the acids and bases

5.1 Acid-Base Titration Curves

During an acid-base titration, for example when a base is added from the burette into an acid placed in a conical flask, the pH of the solution in the conical flask changes. Before the point of complete neutralisation, the acid is in excess while after the point of complete neutralisation, the base is in excess. A salt is also formed in the process. The pH of the solution depends on the species present in the conical flask after neutralisation of the acid by the base. These changes in pH can be monitored by measuring the pH of the solution using a pH meter as the base is added to the acid.

A ***titration curve*** is a graph of pH against the volume of the titrant added and it shows how the pH changes during a titration.

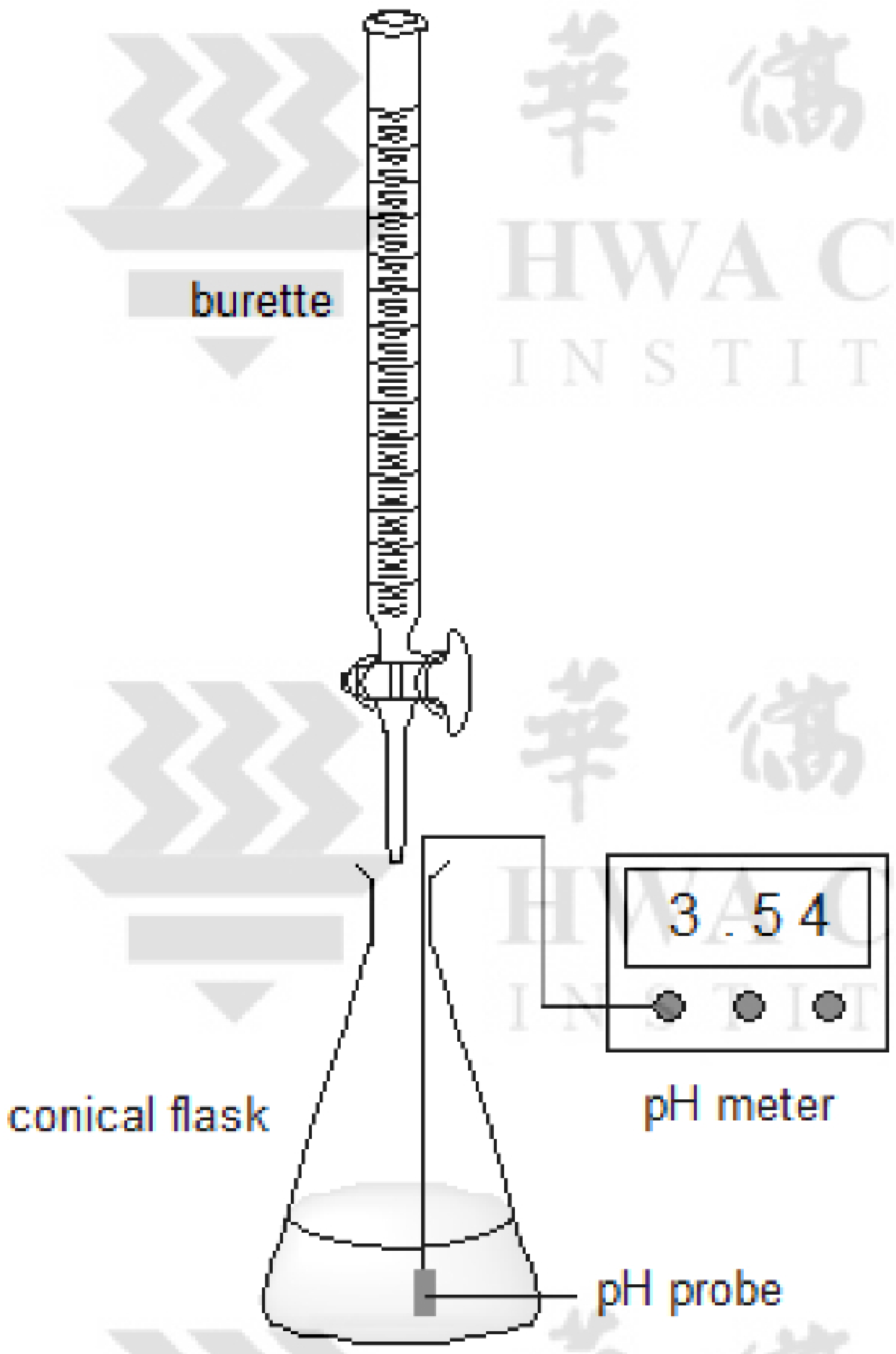
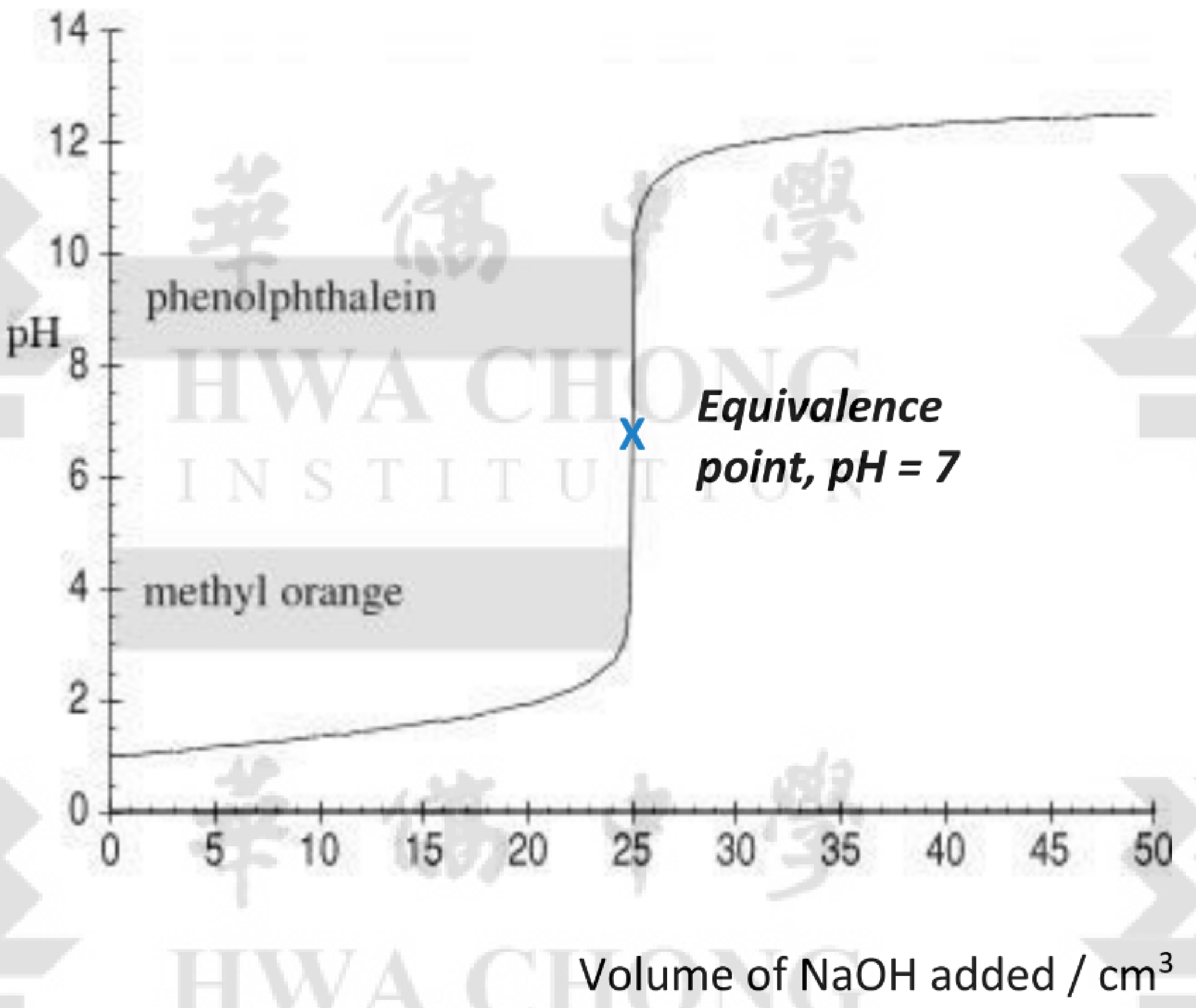


Figure 2. Monitoring pH changes during a titration with a pH meter

Four types of acid-base titration curves are shown on the following pages. Note that in all of them, the acid is in the conical flask while the base is added from the burette. We will look at how we calculate the pH of the solution at various points of the curve. You will need to apply the concepts you have learnt earlier on calculation of pH involving strong acid / base, weak acid / base, salt solutions and buffer solutions.

5.1.1 Strong Acid – Strong Base Titration

Consider addition of 0.10 mol dm^{-3} NaOH to 25.0 cm^3 of 0.10 mol dm^{-3} HC*l*.



Features of the curve:

- **At V_{NaOH} = 0 cm^3**
  Initial pH = pH of 0.10 mol dm^{-3} HC*l* = –lg 0.10 = 1
  HC*l* is a strong acid (fully dissociated in water), so [H$^+$] = [HC*l*].

- **At 0 < V_{NaOH} < 25 cm^3**
  pH gradually rises as an increasing amount of H$^+$ is neutralised by the NaOH added.

- **At V_{NaOH} = 25 cm^3**
  Equivalence point is reached. This is the point where the acid is completely neutralised by the base.
  pH = 7 as the salt formed does not undergo hydrolysis.

  Suitable indicator:
  methyl orange, screened methyl orange, phenolphthalein, thymol blue, thymolphathalein

  Note the sharp pH change near equivalence point (see Homework 1, parts **(c)** and **(e)**).

- **At V_{NaOH} > 25 cm^3**
  There is excess NaOH present in the solution. As NaOH is a strong base, [OH$^-$] is high, hence pH is high (exact value depends on [NaOH] that is in excess).

Homework 1
Determine the pH of the solution in the conical flask at the point when each of the following volumes of NaOH is added.

(a) 0.00 cm^3 Ans: 1.00

(b) 12.50 cm^3 (This is called the **half–neutralisation** or **half–equivalence point**.) Ans: 1.48

(c) 24.90 cm^3 Ans: 3.70

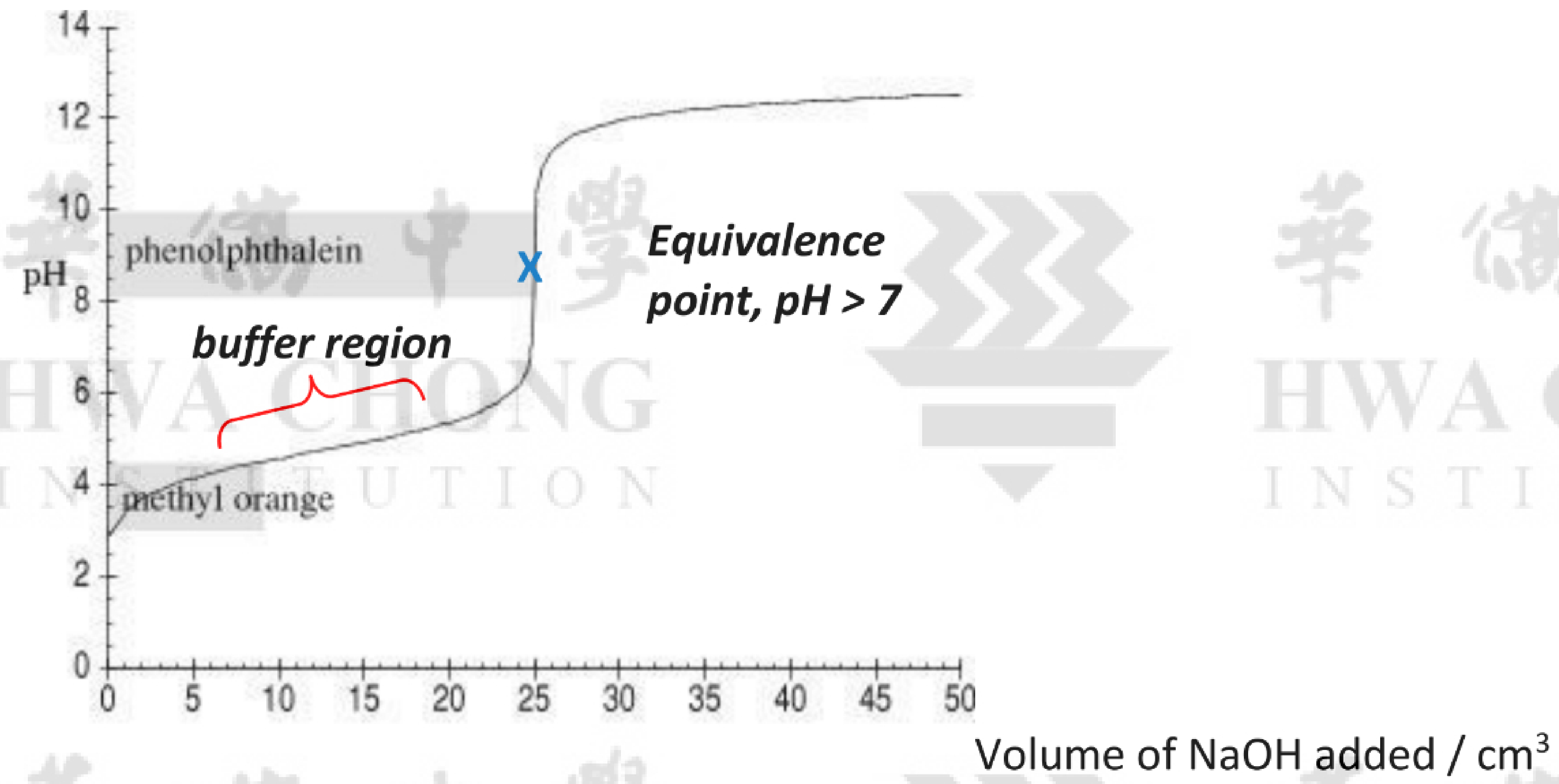
(d) 25.00 cm^3 (This is called the **equivalence point**.) Ans: 7.00

(e) 25.10 cm^3 Ans: 10.3

(f) 50.00 cm^3 Ans: 12.5

5.1.2 Weak Acid – Strong Base Titration

Consider addition of 0.10 mol dm^{-3} NaOH to 25.0 cm^3 of 0.10 mol dm^{-3} CH_3CO_2H



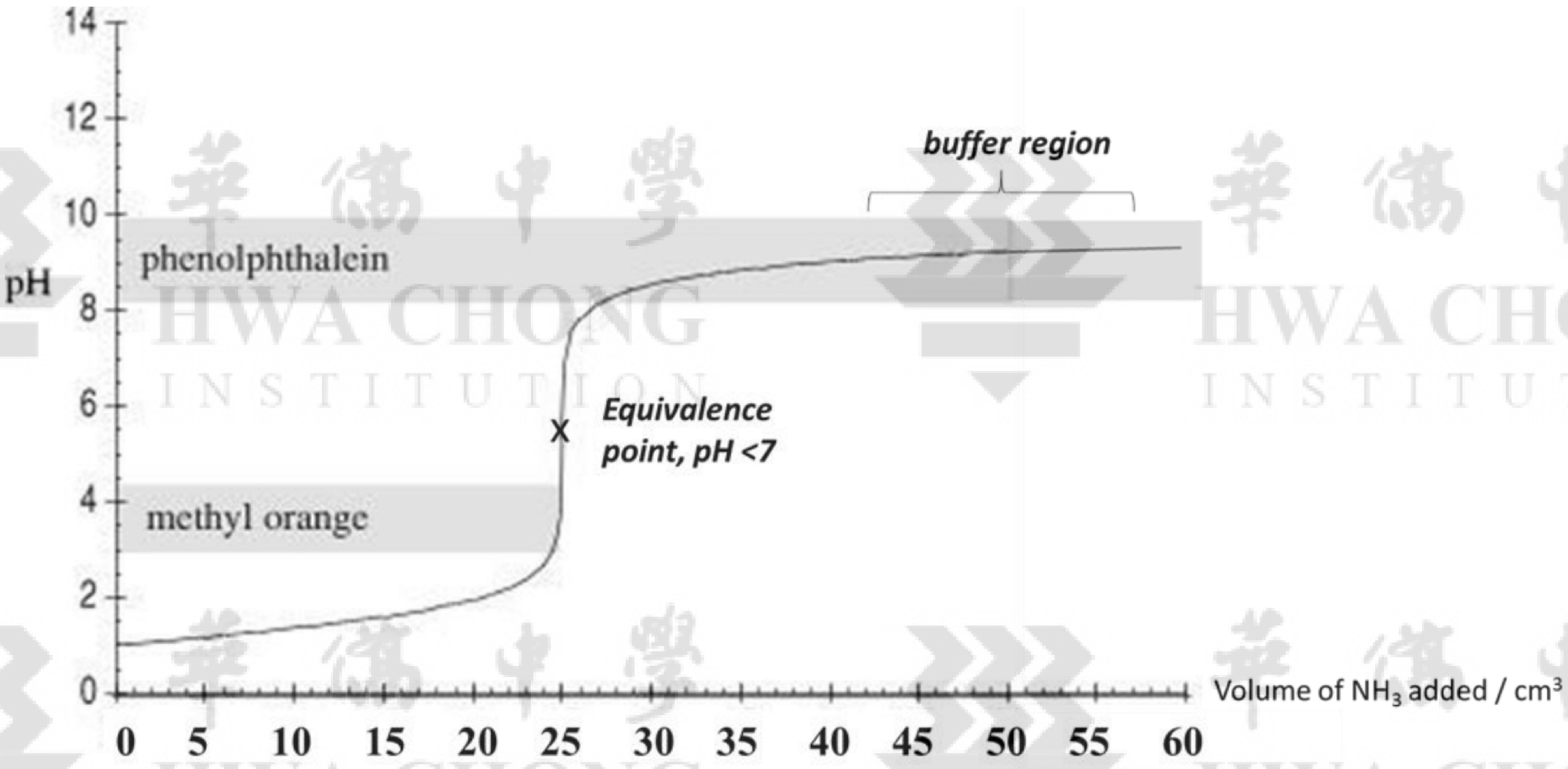
Features of the curve:

• **At V_{NaOH} = 0 cm^3** Initial pH = pH of 0.10 mol dm^{-3} CH_3CO_2H pH is not equal to 1.0 as CH_3CO_2H is a weak acid (only ionises partially in water).	*Calculation of pH of the solution in the conical flask when V_{NaOH} = 0 cm^3.* K_a of CH_3CO_2H = 1.8 × 10^{-5} mol dm^{-3}
• **At 0 <V_{NaOH} < 25 cm^3** 1. Once the NaOH is added and some acid is neutralised, the solution contains a mixture of weak acid and its conjugate base ⇒ a **buffer solution** forms. 2. The pH at the initial part of the titration curve and the part immediately before complete neutralisation changes more sharply as these lie outside the effective buffer range of the buffer. 3. The **maximum buffer capacity** occurs when half of the number of moles of acid is neutralised at V_{NaOH} = 12.50 cm^3 (where [acid] = [conjugate base]). At this point, **pH = pK_a** of the weak acid.	*Calculation of pH of the solution in the conical flask when V_{NaOH} = 12.50 cm^3*

• **At V_{NaOH} = 25 cm^3** **Suitable indicator: phenolphthalein or thymol blue or thymolphthalein** The sharp change in pH in the curve near equivalence point occurs over a smaller pH range compared to the previous strong acid–strong base titration.	Equivalence point is reached. pH > 7 as the anion undergoes **hydrolysis** to produce OH^-: $CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$
• **At V_{NaOH} > 25 cm^3** There is excess NaOH present in the solution. As NaOH is a strong base, $[OH^-]$ is high and hence pH is high (exact value depends on [NaOH] in excess).	*Calculation of pH of the solution in the conical flask when V_{NaOH} = 30.00 cm^3*

5.1.3 Strong Acid – Weak base Titration

Consider addition of 0.10 mol dm^{-3} NH_3 to 25.0 cm^3 of 0.10 mol dm^{-3} HC*l*.



Features of the curve:

- **At V$_{\text{weak base}}$ = 0 cm^3**
  Initial pH = pH of 0.10 mol dm^{-3} HC*l* = –lg 0.10 = 1
  HC*l* is a strong acid (fully dissociated in water).

- **At 0 < V$_{\text{weak base}}$ < 25 cm^3**
  pH gradually rises as increasing amount of H^+ is neutralised by added weak base. However, no buffer is formed as there is no weak base present in excess in the conical flask.

- **At V$_{\text{weak base}}$ = 25 cm^3**
  Equivalence point is reached. pH < 7 as the cation undergoes **hydrolysis** to produce H_3O^+:

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

  Suitable indicator: methyl orange or screened methyl orange

- **At V$_{\text{weak base}}$ > 25 cm^3**
  There is excess weak base present. The solution contains a mixture of weak base and its conjugate acid ⟹ a **buffer solution** forms.

Self-Practice 5.1

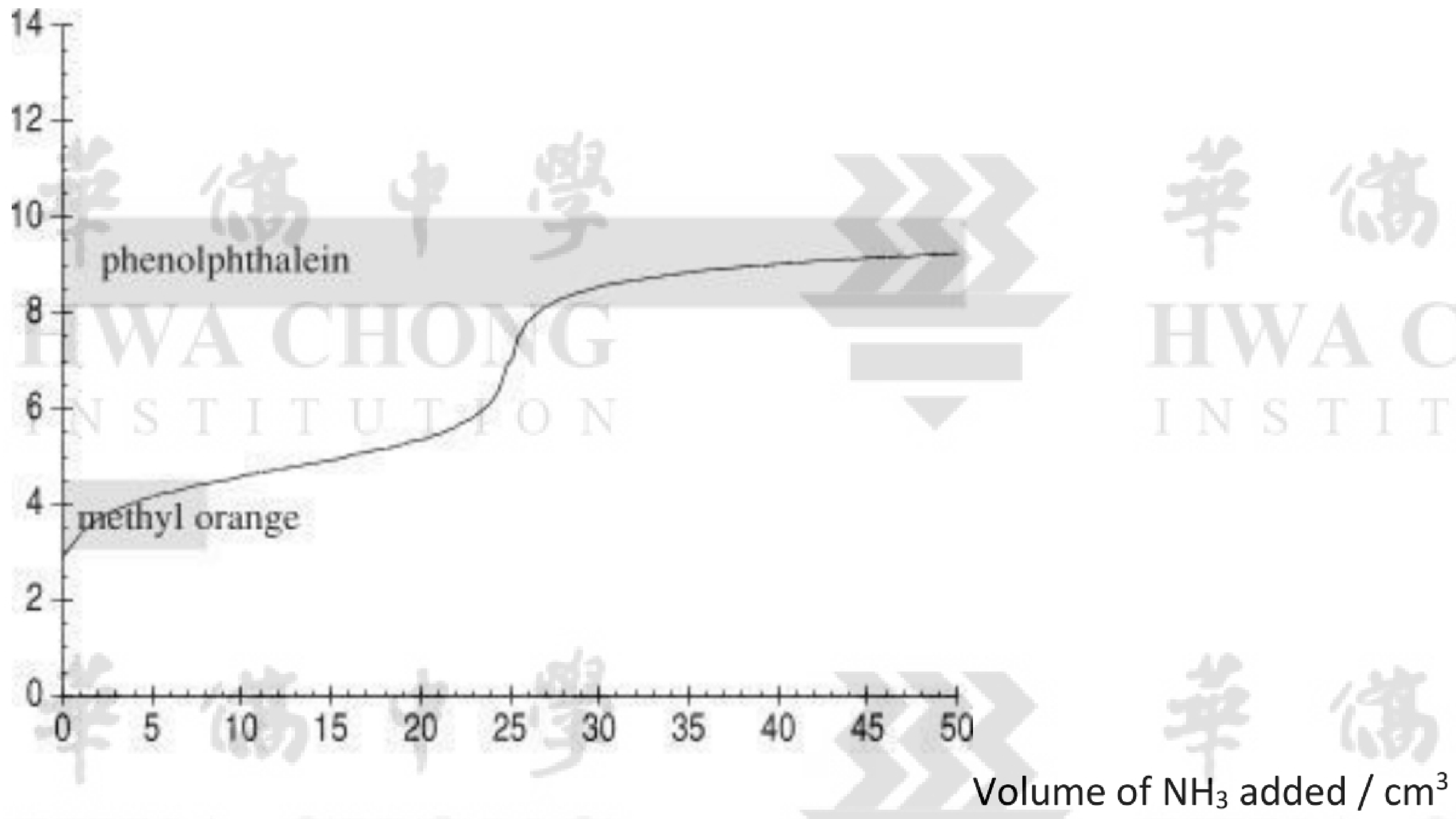
With reference to the above example, determine the pH of the solution in the conical flask at the point when 12.50 cm^3 of NH_3 is added. (K_b of NH_3 = 1.8 × 10^{-5} mol dm^{-3})

What is volume of NH_3 added when maximum buffer capacity occurs? What is the pH at this point?

Ans: 1.48, Volume of NH_3 at maximum buffer capacity = 50.00 cm^3, pH = 9.26

5.1.4 Weak Acid – Weak Base titration

Consider addition of 0.10 mol dm^{-3} NH_3 to 25.0 cm^3 of 0.10 mol dm^{-3} CH_3CO_2H



Features of the curve:

- **At $V_{weak\ base}$ = 0 cm^3**
  Initial pH = pH of 0.10 mol dm^{-3} CH_3CO_2H
  pH is not equal to 1.0 as CH_3CO_2H is a weak acid (only ionises partially in water).

- **At 0 < $V_{weak\ base}$ < 25 cm^3**
  Once the weak base is added and some acid is neutralised, the solution contains a mixture of weak acid and its conjugate base ⇒ a buffer solution forms.

- **At $V_{weak\ base}$ = 25 cm^3**
  Equivalence point is reached. **There is no sharp change in pH, hence no suitable indicator can be used, a pH meter may be used to help detect the equivalence point**.
  Both the cation and anion undergo hydrolysis (see Section 3.1.3).

- **At $V_{weak\ base}$ > 25 cm^3**
  There is excess weak base present in the solution together with its conjugate acid ⇒ another buffer region is formed.

5.1.5 Titration Curves involving polyprotic acids or bases

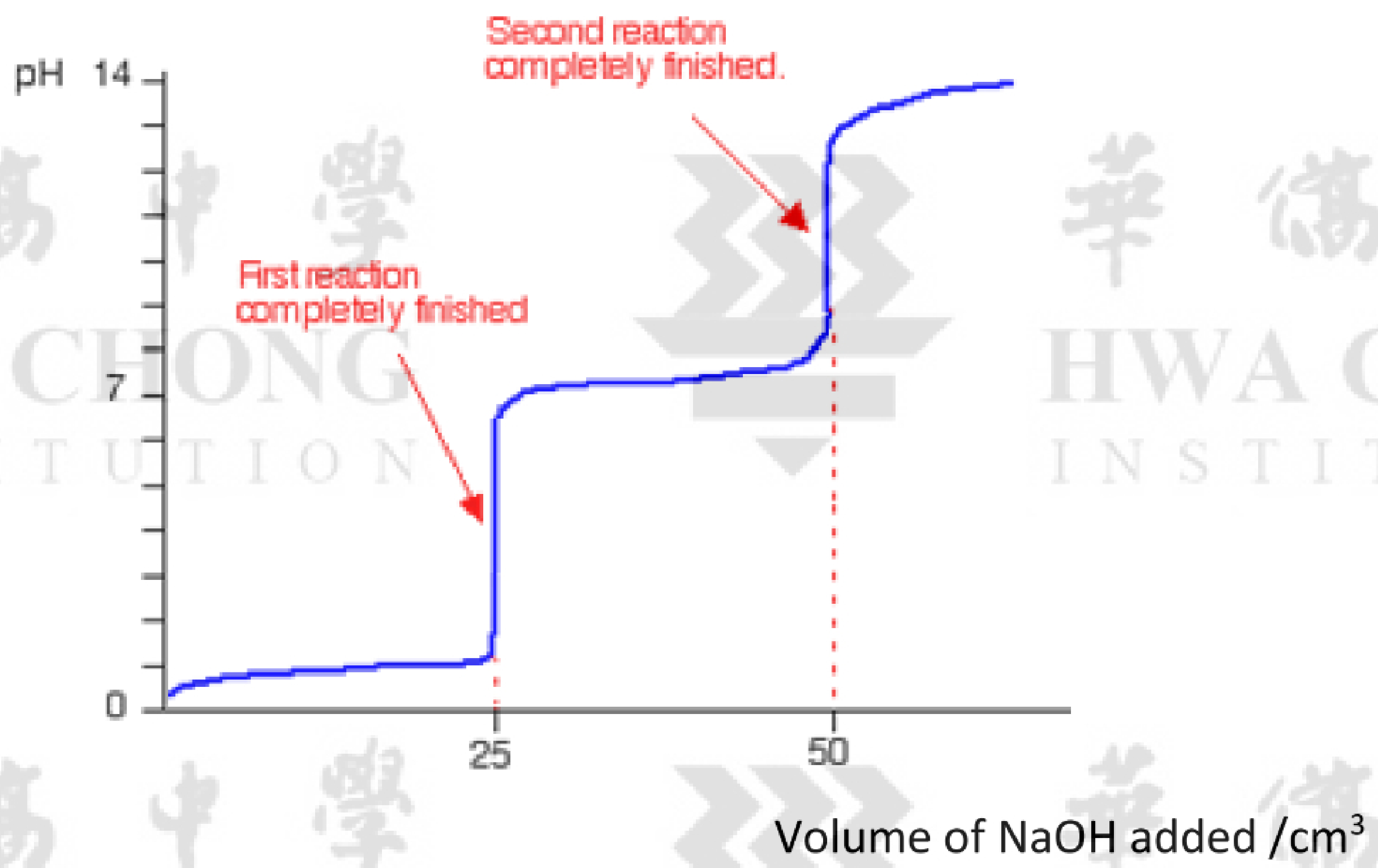
Polyprotic acids have more than one ionisable proton. The successive K_a values may differ by several orders of magnitude. This means the first H^+ is lost more easily than subsequent ones. (Why?)

E.g. $H_2SO_3(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H_3O^+(aq)$ $K_{a1} = 1.4 \times 10^{-2}$ mol dm^{-3}

$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq)$ $K_{a2} = 6.5 \times 10^{-8}$ mol dm^{-3}

In a titration of H_2SO_3, we can assume that all the H_2SO_3 molecules will lose one H^+ ion before any of the HSO_3^- ions loses its H^+.

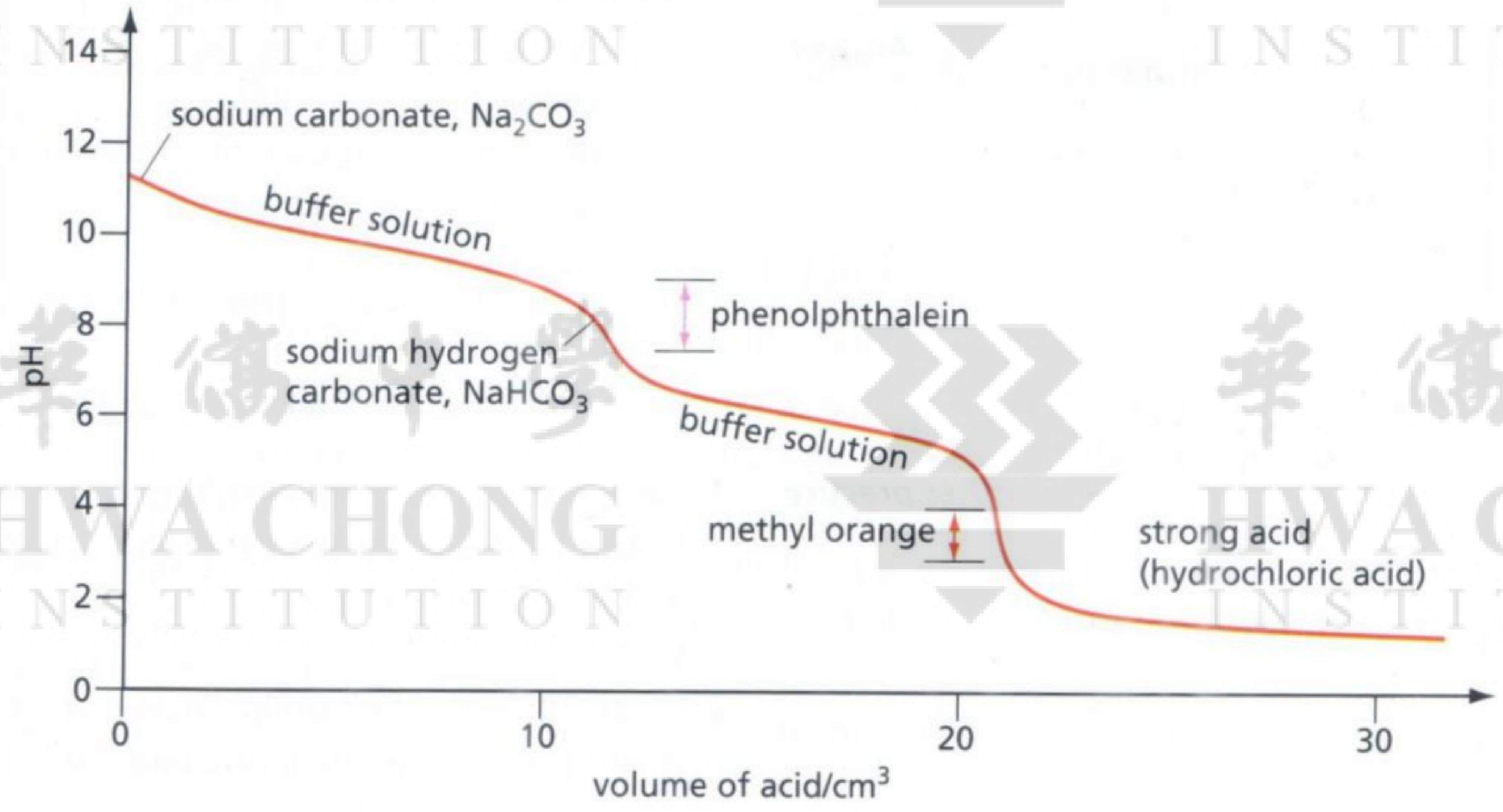
$$H_2SO_3 \xrightarrow{OH^-} HSO_3^- \xrightarrow{OH^-} SO_3^{2-}$$



Note that the titration curve usually has **two steep portions**, which corresponds to **two equivalence points**.

A similar curve is also obtained for a titration involving a mixture of two acids with an appreciable difference in K_a values (or a mixture of 2 bases with an appreciable difference in K_b values). In practice, we can observe the two separate end–points with the proper choice and use of two different indicators.

Consider the titration of sodium carbonate with dilute HC*l*.



There are 2 stages in the titration:

$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$ ————————————(1)

$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$ ————————————(2)

The first rapid change in pH for reaction (1) occurs at pH = 8.5. Therefore a suitable indicator for the first equivalence point is phenolphthalein.

The second rapid change in pH for reaction (2) occurs at pH = 3.5. Therefore a suitable indicator for the second equivalence point is methyl orange.

To observe the two end–points separately, phenolphthalein is first added. Methyl orange is added only after the first equivalence point is reached.

If methyl orange is used at the start of the experiment, only one end–point is observed and the titre obtained is twice that obtained with phenolphthalein.

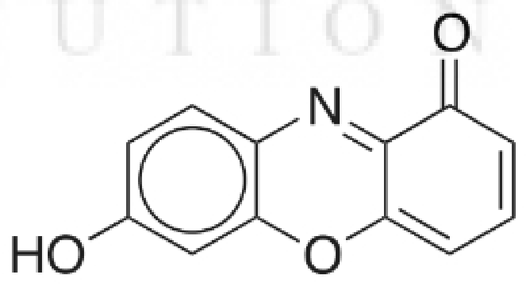
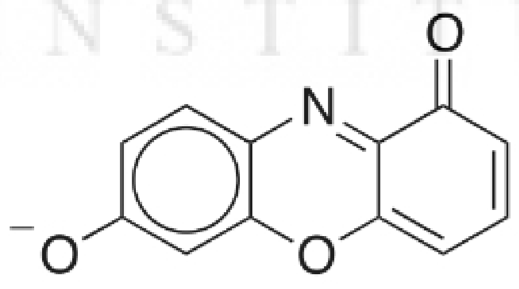
Lecture Exercise 5.1

A 25.0 cm^3 portion of a solution containing sodium carbonate and sodium hydrogencarbonate needed 22.50 cm^3 of a solution of hydrochloric acid of concentration 0.100 mol dm^{-3} to decolourise phenolphthalein. On addition of methyl orange, a further 28.50 cm^3 of the acid was needed to turn this indicator orange. Calculate the concentration of sodium carbonate and sodium hydrogencarbonate in the solution.

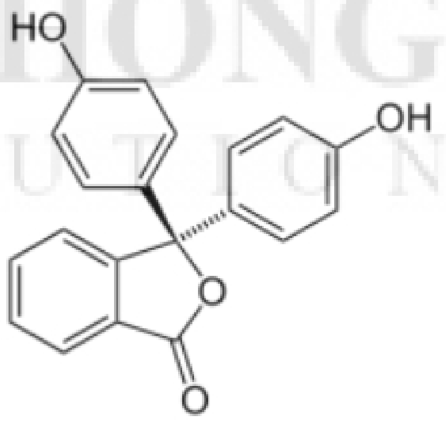
Ans: 0.0900 mol dm^{-3}; 0.0240 mol dm^{-3}

5.2 Acid-Base Indicators (Background Info)

An acid-base indicator is a weak aqueous acid whose acid form, HIn, is a different colour from its ionised form (or conjugate base form), In^-. As such, it shows different colours in solutions of different pH.

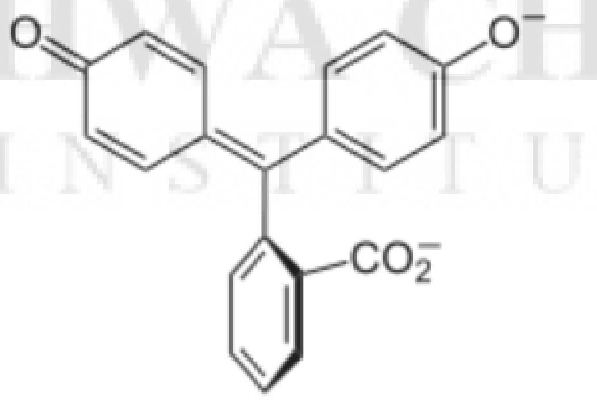
General equation	$HIn(aq)$ acid form (colour 1)	⇌	$H^+(aq)$ +	$In^-(aq)$ ionised form (colour 2)
litmus	 red	⇌	$H^+(aq)$ +	 blue

Phenolphthalein



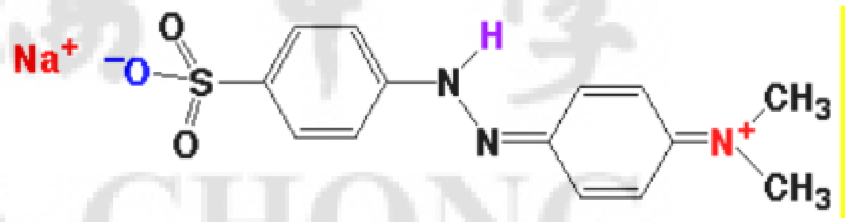
colourless

⇌ $H^+(aq)$ +



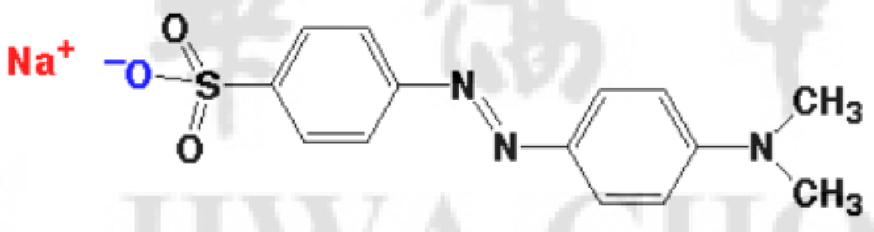
pink

Methyl orange



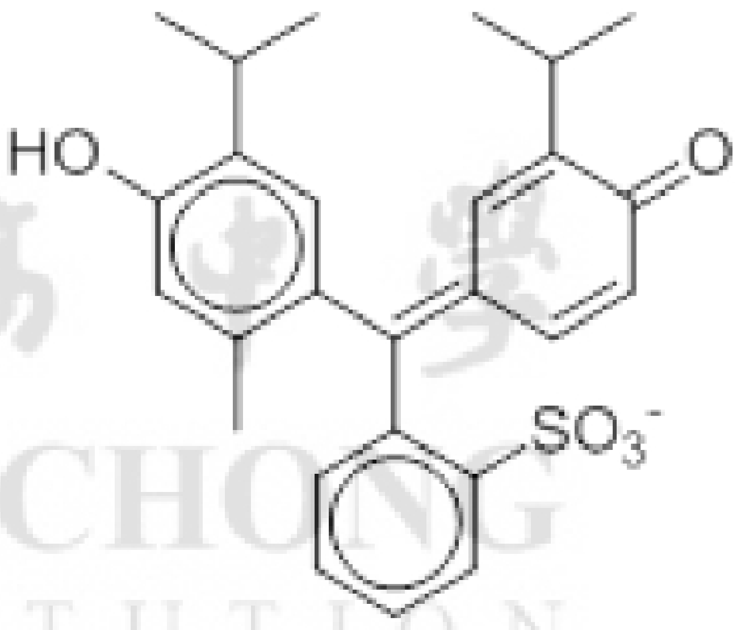
red

⇌ $H^+(aq)$ +



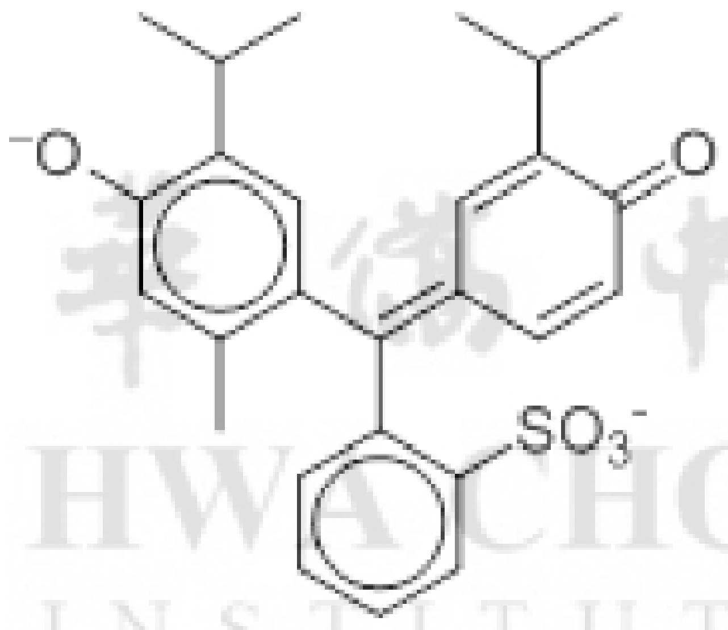
yellow

Thymol blue



yellow

⇌ $H^+(aq)$ +



blue

At different pH values, the proportion of HIn to In^- is different, giving rise to different colours.

For litmus:

- In acidic solutions, $[H^+]$ is high. The position of equilibrium lies on the left. Predominant form of litmus is HIn, so the solution will appear red.
- In alkaline solutions, $[OH^-]$ is high so $[H^+]$ is low. The position of equilibrium lies on the right. Predominant form of litmus is In^-. Hence the solution will appear blue.

5.3 Working pH Range of Indicators (Background info)

For most indicators, the predominant form must be at least **10 times** more concentrated than the other form for its colour to be distinguished from the other coloured form.

Since for an indicator, $HIn\ (aq) \rightleftharpoons H^+\ (aq) + In^-\ (aq)$

The dissociation constant of an indicator, K_{In}, will be:

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

Taking –lg on both sides and rearranging,

$$pH = pK_{In} + \lg\frac{[In^-]}{[HIn]}$$

For litmus:

If the ratio of $[In^-]/[HIn] \geq 10/1$, i.e. **$pH \geq pK_{In} + 1$**, the solution appears blue.

If the ratio of $[In^-]/[HIn] \leq 1/10$, i.e. **$pH \leq pK_{In} - 1$**, the solution appears red.

Therefore, the litmus changes from red to blue over a pH range of

$$pH = pK_{In} - 1 \quad \text{to} \quad pH = pK_{In} + 1$$

That is, the **working range** of an indicator (i.e. pH range where a marked colour change occurs) is approximately $\boxed{\mathbf{pK_{In} \pm 1}}$.

Colours of common indicators for acid-base titrations

Table 6 Some common indicators and their working pH range

Indicators	pH working range	Colour in acidic region	Colour in basic region
methyl orange	3.1 – 4.4	red	yellow
screened methyl orange	3.0 – 4.6	violet	green
bromothymol blue	6.0 – 7.6	yellow	blue
phenolphthalein (not used in lab)	8.0 – 9.6	colourless	pink
thymol blue*	8.0 – 9.6	yellow	blue
thymolphthalein*	9.3 – 10.5	colorless	blue

*can be used as an alternative indicator in place of phenolphthalein to indicate end point of weak acid-strong base titration

Self-practice 5.2

At low pH, the colour of bromocresol green is yellow, and at high pH, the colour is blue. Calculate the pH range at which the colour of bromocresol green ($K_{In} = 1.58 \times 10^{-5}$) is green.

$$\underset{\text{yellow}}{HIn(aq)} \rightleftharpoons H^+(aq) + \underset{\text{blue}}{In^-(aq)}$$

Ans: 3.80 – 5.80

5.4 Choice of Indicators

LO 10.1(e): explain the choice of suitable indicators for acid–base titrations, given appropriate data

During an acid-base titration, one solution is run into the other in the presence of an indicator.

- **End-point**: the point in a titration at which the indicator changes colour when 1 drop of excess titrant is added.

- **Equivalence point**: the point in a titration at which the exact number of moles of acid and base react completely.

The end-point tells us the equivalence point **only when a suitable indicator is used**.

- The indicator must have a **distinct colour change**.
- The **working pH range** of the indicator must **coincide with the rapid pH change at the equivalence point** for the titration.

The rapid pH change for the titration depends on the strengths of acid and alkali used. Either the acid or the alkali, or both, may be strong or weak, so that there are four possible combinations.

Table 7. Suitable indicators for different types of titration

Type	suitable indicator
strong acid – strong alkali	methyl orange or phenolphthalein or thymol blue
strong acid – weak alkali	methyl orange
weak acid – strong alkali	Phenolphthalein or thymol blue
weak acid – weak alkali	no suitable indicator

Self-practice 5.3

A 25.0 cm^3 solution containing 0.120 mol dm^{-3} of lactic acid is titrated with aqueous NaOH of concentration 0.100 mol dm^{-3}. The pH at the equivalence point was found to be 8.29.

The table below lists the working ranges of some acid-base indicators. Comment on the whether each of the following indicators can be used for this titration.

Indicator	Working range	Low pH color	High pH color
Bromophenol blue	3.0–4.6	yellow	purple
Methyl red	4.4–6.2	red	yellow
Neutral red	6.8–8.0	red	yellow
Thymol blue	8.0–9.6	yellow	blue
Naphtholphthalein	7.3–8.7	colorless	green-blue
Thymolphthalein	9.3–10.5	colorless	blue

Planning Questions involving Acid-Base Equilibria

Using the concepts in this chapter, you may be asked to plan experiments involving acid-base equilibria. Some examples are as follows.

1. Determination of pKa of a weak acid or pK_b of a weak base. (See 2013 HCI JC2 BT2 Paper 2 Q1 in "Examples of Acid-Base Equilibria Planning Qns" in Moodle)
2. Preparation of a specific buffer for a particular purpose. (See 2011 HCI JC2 BT2 Paper 2 Q1 in "Examples of Acid-Base Equilibria Planning Qns" in Moodle)

LOOKING AHEAD

Acidity of organic acids and phenols as well as basicity of amines will be covered under organic carboxylic acids, phenols and amines. The charges in an amino acid is also related to pH of solution.

Salt hydrolysis due to high charge density of cations will be covered in the chapters on Transition Elements and Periodicity.

Acid-Base Equilibria – Summary

Concept	Application
A Bronsted acid is a proton donor. A Bronsted base is a proton acceptor.	To identify if a molecule or ion is behaving as an acid or base given an equation or vice versa
p*X* = –log₁₀*X* $\Rightarrow$ $X = 10^{-pX}$	To define quantities such as pH, pOH, pK_w, pK_a and pK_b
K_w = [H⁺][OH⁻] $= 1 \times 10^{-14}$ (at 25°C) K_w shows the relationship between $[H^+]$ and $[OH^-]$ in **any** aqueous solutions.	To calculate $[H^+]$ or $[OH^-]$ given the value of the other. In pure water, $[H^+] = [OH^-] = 1 \times 10^{-7}$ (at 25°C)
pK_w = pH + pOH = 14 (at 25°C)	To calculate pH from pOH, or vice versa
For any <u>conjugate</u> acid–base pair, **$K_a \times K_b = K_w$** pK_a + pK_b = pK_w = 14 (at 25 °C)	To calculate K_a from K_b, or vice versa. You use this equation when you need one of these *K* values but have the other.
$HA \rightleftharpoons H^+ + A^-$ $K_a = \dfrac{[H^+]_{eqm}[A^-]_{eqm}}{[HA]_{eqm}}$	To calculate the pH of a • weak acid, $K_a \approx \dfrac{[H^+]^2_{eqm}}{[HA]_{initial}}$ • buffer, $K_a \approx \dfrac{[H^+]_{eqm}[salt]_{initial}}{[acid]_{initial}}$ To compare the *strength* of weak acids. The larger the K_a value, the stronger the acid.
$B + H_2O \rightleftharpoons BH^+ + OH^-$ $K_b = \dfrac{[BH^+]_{eqm}[OH^-]_{eqm}}{[B]_{eqm}}$	To calculate the pH of a • weak base, $K_b \approx \dfrac{[OH^-]^2_{eqm}}{[B]_{initial}}$ • buffer, $K_b \approx \dfrac{[OH^-]_{eqm}[salt]_{initial}}{[base]_{initial}}$ To compare the *strength* of weak bases. The larger the K_b value, the stronger the base.
Salt hydrolysis – a reaction in which ions react with water to form acidic or alkaline solutions e.g. $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ $CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$	To explain why the pH of a salt derived from • strong acid and weak base (e.g. NH_4Cl) is < 7 • weak acid and strong base (e.g. CH_3CO_2Na) is > 7

<u>**Checklist for pH calculations**</u>

Do you know how to calculate the pH of a solution containing each of the following?

✓ a strong acid or strong base
✓ a weak acid or weak base
✓ a salt such as CH_3CO_2Na or NH_4Cl
✓ a buffer

Using the above, can you sketch a titration curve, and mark the various key points on the curve (initial pH, equivalence point, buffer with maximum capacity)