St. Andrew's Junior College

H1 Chemistry 2022

Lecture Notes

Theories of Acids and Bases

Assessment Objectives

Candidates should be able to:

(a) show understanding of, and apply the Arrhenius theory of acids and bases

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

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

(d) explain the terms pH; K_a; K_b; K_w [The relationship $K_w = K_aK_b$ is not required];

(e) calculate $[H^+(aq)]$ and pH values for strong acids, and strong bases;

(f) explain the choice of suitable indicators for acid-base titrations, given appropriate data, in terms of the strengths of the acids and bases;

(g) (i) explain how buffer solutions control pH;

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

Lecture Outline:

1. Theories of acids and bases
2. Autoionisation of water
3. Dissociation of weak acid and bases
4. Acid-Base Properties of Salt Solutions
5. Indicators for acid-base titrations
6. Monoprotic Acid-Base Titration Curves
7. Buffer solutions

References:

1. Chemistry by Silberberg
2. Chemistry by Raymond Chang
3. Chemistry for Advanced level by Peter Cann
4. Chemistry in context by Hill and Holman
5. A – level Chemistry by Ramsden

1. THEORIES OF ACIDS AND BASES

Candidates should be able to:
• show understanding of, and apply the Arrhenius theory of acids and bases • show understanding of, and apply the Brønsted–Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases

1.1 Arrhenius theory of acids and bases

An Arrhenius acid is a substance that produces H^+ in aqueous solution.

An Arrhenius base is a substance that produces OH^- in aqueous solution.

E.g.: $HNO_3(l) + H_2O(l) \longrightarrow NO_3^-(aq) + H_3O^+(aq)$

Note: H_3O^+ is hydronium ion, which is the same as H^+ (aq)

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

- An acid-base reaction involves the formation of salt and water

1.2 Brønsted–Lowry theory of acids and bases

A Brønsted–Lowry acid is a proton (H^+) donor.

A Brønsted–Lowry base is a proton (H^+) acceptor.

base → conjugate acid

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

Acid → conjugate base

base → conjugate acid

E.g.: $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$

acid → conjugate base

- An acid–base reaction involves the transfer of a proton from the acid to the base.
- When a Brønsted–Lowry acid (HA) loses a proton, the resulting product (A^-) is called the conjugate base of HA.

- When a Brønsted–Lowry base (B) accepts a proton, the resulting product (BH^+) is called the conjugate acid of B.
- A conjugate acid-base pair differs by a H^+.

Examples of conjugate pairs:

HCl / Cl^-	NH_3 / NH_4^+
H_2O / OH^-	H_2O / H_3O^+
CH_3COOH / CH_3COO^-	CH_3NH_2 / $CH_3NH_3^+$

Exercise 1

Identify the acid, base, conjugate acid and conjugate base in the following reactions :

a) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

acid **base** **conjugate base** **conjugate acid**

b) $CH_3COOH + HCl \longrightarrow CH_3COOH_2^+ + Cl^-$

base **acid** **conjugate acid** **conjugate base**

c) $HNO_3 + H_2O \longrightarrow NO_3^- + H_3O^+$

acid **base** **conjugate base** **conjugate acid**

d) $HNO_3 + H_2SO_4 \longrightarrow HSO_4^- + H_2NO_3^+$

base **acid** **conjugate base** **conjugate acid**

👉 **Self–Check: Q1**

💪 In Summary 💪

	Arrhenius	**Brønsted-Lowry**
Acids	produces H^+ in water	donates H^+
Bases	produces OH^- in water	accepts H^+

Candidates should be able to:

- Explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation.

Acid

Strong acid completely dissociates in water.

E.g.: HCl (g) + aq ⟶ H^+(aq) + Cl^-(aq)

Most mineral acids are strong acids. E.g.: HI, HBr, H_2SO_4, HNO_3 etc.

⟶ represents complete dissociation

Weak acid partially dissociates in water.

E.g.: CH_3COOH (*l*) + aq ⇌ CH_3COO^-(aq) + H^+(aq)

Most organic acids are weak acids. E.g.: CH_3COOH, H_2CO_3, HCN etc.

⇌ means an equilibrium is established between the undissociated molecules and the dissociated ions.

Base

Strong base completely dissociates in water.

E.g.: NaOH(s) + aq ⟶ Na^+(aq) + OH^-(aq)

Examples of strong bases are NaOH, KOH, $Ba(OH)_2$ etc.

Weak base partially dissociates in water.

E.g.: NH_3 + H_2O ⇌ NH_4^+(aq) + OH^-(aq)

Examples of weak bases are NH_3, CH_3NH_2, Na_2CO_3 etc.

Which is a stronger acid, 0.0001 mol dm^{-3} HCl or 1 mol dm^{-3} CH_3COOH?

HCl is a strong acid, regardless of its concentration.

CH_3COOH is a weak acid, regardless of its concentration. It only partially dissociates in water

Strength of acid $\neq$ Concentration of acid

Candidates should be able to:

- explain pH and apply them in calculations

1.4 The pH scale

Concentration of H^+ can be used as a measure of acidity and alkalinity of a solution.

However, $[H^+]$ can be very small values. Hence, we can express these values as pH.

pH = – *log₁₀* [H⁺]	or	$[H^+] = 10^{-pH}$	$[H^+]$ in mol dm^{-3}

A solution with <u>low</u> pH has a <u>high</u> $[H^+]$, and is more acidic than a solution with higher pH.

Similarly,

$$\mathbf{pOH = -\log_{10}[OH^-]}$$

Note: The logarithm used are to the base 10 (not to the base e), so make sure when doing calculations, you press the log or lg button on your calculator (not the ln button)

1.5 Basicity of acid

- HCl and CH_3COOH are **<u>monoprotic</u>** (monobasic) **acids** as each acid can only lose **one H^+**.
- H_2SO_4 is a **<u>diprotic</u>** (dibasic) acid as it can lose **two H^+**.

$$H_2SO_4 + H_2O \longrightarrow H_3O^+ + \underset{\text{conjugate base}}{HSO_4^-}$$

$$HSO_4^- + H_2O \longrightarrow H_3O^+ + \underset{\text{conjugate base}}{SO_4^{2-}}$$

- Conversely for bases, NaOH is a monoacidic base and $Ca(OH)_2$ is a diacidic base.

Candidates should be able to:
- explain K_w and apply them in calculations
- calculate $[H^+(aq)]$ and pH values for strong acids and strong bases

2. AUTOIONISATION OF WATER

Water dissociates very slightly to give ions.

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

When $[H^+] = [OH^-]$, the solution is neutral.

When $[H^+] > [OH^-]$, the solution is acidic.

When $[H^+] < [OH^-]$, the solution is alkaline.

We name the equilibrium constant for the autoionisation of water as <u>ionic product of water</u>, $\boldsymbol{K_w}$.

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

Note: $[H_2O]$ is not reflected in K_w

$pK_w = -\log_{10} K_w = -\log_{10}([H^+][OH^-])$

$= -\log_{10}[H^+] - \log_{10}[OH^-]$

$pK_w = pH + pOH$

$pH = pK_w - pOH$

Note: Derivation of pK_w is not required

At **25 °C**

$K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}

in Data Booklet

$pK_w = 14$

$pK_w = pH + pOH$

$14 = pH + pOH$

$pH = 14 - pOH$

Note: Derivation of pK_w is not required

In pure water at 25°C,

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

$[H^+] = [OH^-] = 1.00 \times 10^{-7}$ mol dm^{-3}

$pH = pOH = -\lg(1.00 \times 10^{-7}) = 7.0$

The autoionisation of water molecules is an endothermic process.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad \Delta H > 0$$

$K_w = \frac{kf}{kb}\frac{kf}{kb}$. When temperature increases, both k_f and k_b increases. Since the forward reaction is endothermic and is favoured, k_f increases more than k_b. Hence, K_w increases when temperature increases.

Table 1: Variation of ionic product of water, K_w, with temperature

Temperature / °C	K_w / mol^2 dm^{-6}
20	0.68×10^{-14}
30	1.47×10^{-14}
40	2.92×10^{-14}

💪 **In summary** 💪

$K_w = [H^+][OH^-]$

$pH = pK_w - pOH$

$K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 25°C

Exercise 2

[2018 P1 Q14]

The ionic product of water, K_w, is affected by temperature.

Temperature / °C	K_w x 10^{-14} / mol^2 dm^{-6}
10	0.293
40	2.92

Which statement describes what happens as the temperature of water is increased from 10 °C to 40 °C?

A pH of water decreases and $[H^+] = [OH^-]$

B pH of water decreases and $[H^+]$ is greater than $[OH^-]$

C pH of water increases and $[H^+] = [OH^-]$

D pH of water increases and $[H^+]$ is less than $[OH^-]$

Ans: A

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

At 40°C

$K_w = [H^+][OH^-] = 2.92 \times 10^{-14}$

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

$[H^+]^2 = 2.92 \times 10^{-14}$

$[H^+] = 1.709 \times 10^{-7}$ mol dm^{-3}

pH = 6.77

pH of pure water at 40°C is less than pH 7, but it DOES NOT mean that the water is not neutral! A **neutral solution has pH 7 only at 25 °C**. As **K_w changes with temperature**, **pH of a neutral solution can change with temperature**. Hence, as long as **$[H^+] = [OH^-]$**, a **solution is neutral**.

Steps in Calculating pH of Strong Acid/Base

1. Write equation to illustrate complete dissociation (if necessary).
2. Determine $[H^+]$ for acids (or $[OH^-]$ for bases)
3. Determine pH or pOH using

Acids	**Bases**
$pH = -\log_{10}[H^+]$	**$pOH = -\log_{10}[OH^-]$** **$pH = 14 - pOH$ at 25°C**

Exercise 3

Calculate the pH of a) 0.0100 mol dm^{-3} sulfuric acid

b) 0.00250 mol dm^{-3} aqueous sodium hydroxide

a) **$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$**

0.0100 mol dm^{-3} 0.0200 mol dm^{-3}

pH = **– *lg* (0.0200)**

= 1.70

b) **$NaOH \longrightarrow Na^+ + OH^-$**

0.00250 mol dm^{-3} 0.00250 mol dm^{-3}

pOH = – *lg* (0.00250)

= 2.602

pH = **$pK_w - pOH$**

= **14 – 2.602**

= 11.4

Exercise 4

The concentration of OH^- ions in a certain household ammonia cleaning solution is 0.0025 mol dm^{-3}. Calculate the pH of the solution.

$[OH^-]$ = 0.0025 mol dm^{3}

Since $[H^+][OH^-] = 10^{-14}$

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

$$= \frac{10^{-14}}{0.0025}$$

= 4 x 10^{-12} mol dm^{-3}

pH = – *lg* (4 x 10^{-12})

= 11.4

OR

- calculate pOH,
- Hence, find pH by taking 14 – pOH

👉 **Self–Check: Q2 – 5**

Candidates should be able to:
- explain the terms K_a; K_b

3 DISSOCIATION OF WEAK ACIDS AND BASES

3.1 Dissociation constants of acids/bases, K_a / K_b

I. Acid dissociation constant, K_a for a weak acid

For a weak monobasic (monoprotic) acid, the dissociation can be represented as follows:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

We name the equilibrium constant for the dissociation of an acid its **acid dissociation constant**, K_a.

$$K_a = \frac{[H_3O^+]_{eqm}[A^-]_{eqm}}{[HA]_{eqm}}$$ Units: mol dm^{-3}

$$pK_a = -\log_{10} K_a$$

Note: $[H_2O]$ is ignored in K_a as it is present in large amount and its concentration remains almost constant

- K_a is temperature dependent.

Table 2: Dissociation constants of acids in water at 25 °C

Acids	Formula	K_a / mol dm^{-3}	pK_a	
Ethanoic acid	CH_3COOH	1.74×10^{-5}	4.75	stronger acid
Phenol	C_6H_5OH	1.28×10^{-10}	9.89	weaker acid

- K_a and pK_a gives a good measurement of the strength of an acid, as it indicates the extent to which the acid is dissociated. The higher the K_a or the lower the pK_a, the stronger the acid.

Which of the following best indicates the strength of an acid?

(1) K_a (2) pH

K_a best indicates the strength of an acid. It does not vary with concentration of acids. At the same temperature, a stronger acid would have a higher K_a, indicating that it has a larger extent of dissociation of H^+.

pH only indicates the concentration of H^+(aq) in solution. It varies with concentration of the acid. A weak acid of high concentration can give a lower pH than a stronger acid of lower concentration.

Eg: pH of 0.1 mol dm^{-3} aqueous CH_3COOH (weak acid) 2.9

pH of 10^{-5} mol dm^{-3} aqueous HC*l* (strong acid) = 5.0

pH can only be used to compare the acid strength of two acids when they have the same concentration.

Eg: pH of 0.1 mol dm^{-3} aqueous CH_3COOH (weak acid) 2.9

pH of 0.1 mol dm^{-3} aqueous HC*l* (strong acid) = 1.0

Polybasic (polyprotic) acids, such as H_3PO_4, have more than one dissociation constant.

Table 3: Dissociation constants of phosphoric acid, H_3PO_4 (triprotic)

Dissociation	Equilibrium	K_a / mol dm^{-3}	pK_a
K_{a1}	$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$	7.52×10^{-3}	2.12
K_{a2}	$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$	6.23×10^{-8}	7.21

K_{a3}	$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$	2.20×10^{-13}	12.7

Why is $K_{a3} < K_{a2} < K_{a1}$ in a polyprotic acid?

It becomes more difficult to lose a proton from a negatively charged ion due to the stronger electrostatic forces of attraction between the anion and proton.

II. Base dissociation constant, K_b

Consider a weak base B in water:

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

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

$$pK_b = -\log_{10} K_b$$

- K_b is temperature dependent.

Table 4: Dissociation constants of bases in water at 25 °C

Bases	**Formula**	**K_b / mol dm^{-3}**	**pK_b**
Methylamine	CH_3NH_2	4.54×10^{-4}	3.34 stronger base
Ammonia	NH_3	1.74×10^{-5}	4.76 weaker base

- K_b and pK_b gives a good measurement of the strength of a base. The higher the K_b or the lower the pK_b, the stronger the base.

💪 **In Summary** 💪

weak acid	**weak base**
$K_a \approx \frac{[H^+]^2}{[HA]_{initial}}$	$K_b \approx \frac{[OH^-]^2}{[B]_{initial}}$

👉 **Self–Check: Q6**

3.2 Degree of dissociation, α

The degree of dissociation, **α**, of a substance is defined as the fraction of substance that has undergone dissociation at equilibrium.

$$\alpha = \frac{\text{amount dissociated}}{\text{total initial amount}}$$

For (monoprotic) strong acids / bases which dissociate completely, α = 1

For (monoprotic) weak acids / bases which dissociate partially, α << 1

Exercise 5

HA is a weak monobasic acid of concentration 0.100 mol dm^{-3}. The concentration of the H^+(aq) at equilibrium was found to be 0.001 mol dm^{-3}. What is the degree of dissociation for HA?

$$HA \rightleftharpoons H^+ + A^-$$

0.100 mol dm^{-3} 0.001 mol dm^{-3}

$$\alpha = \frac{\text{amount dissociated}}{\text{total initial amount}} = \frac{0.001}{0.100} = 0.01$$

Self–Check: Q7 and Q8

Differences between strong / weak vs concentrated / diluted acids

https://www.youtube.com/watch?v=RE3CKkkMljo

4. ACID–BASE PROPERTIES OF SALT SOLUTIONS

- Salts can from solutions that are neutral, acidic or basic.

  If the ions in the salt undergo <u>hydrolysis</u>, they will form acidic or alkaline solutions. The salt is termed acidic salt or basic salt.

  If the ions in the salt do not undergo hydrolysis, the solution remains neutral. The salt is termed neutral salt.

- ***Neutral Salt of a Strong Base and Strong Acid***

  $NaOH + HCl \longrightarrow NaCl + H_2O$

  $NaCl$ in water form hydrated ions:

  $NaCl \longrightarrow Na^+(aq) + Cl^-(aq)$

Na^+ and Cl^- do not undergo hydrolysis in water. Thus, the resultant solution is neutral.

- ***Basic Salt of a Strong Base & Weak Acid***

  $NaOH + CH_3COOH \longrightarrow CH_3COO^-Na^+ + H_2O$

  CH_3COONa in water form hydrated ions:

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

  Na^+ does not hydrolyse

  CH_3COO^- is a conjugate base of weak acid CH_3COOH. CH_3COO^- partially hydrolyses in water to give OH^-. Thus, the resultant solution is alkaline.

  $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \mathbf{OH^-}$

  A K_b expression can be written for this hydrolysis.

  $$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

- ***Acidic Salt of a Strong Acid and Weak Base***

  $HCl + NH_3 \longrightarrow NH_4Cl$

  NH_4Cl in water form hydrated ions:

  $NH_4Cl \longrightarrow NH_4^+(aq) + Cl^-(aq)$

  Cl^- does not hydrolyse

  NH_4^+ is a conjugate acid of weak base NH_3. NH_4^+ partially hydrolyses in water to give H_3O^+. Thus, the resultant solution is acidic.

  $NH_4^+ + H_2O \rightleftharpoons NH_3 + \mathbf{H_3O^+}$

  A K_a expression can be written for this hydrolysis.

  $$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

💪 In Summary 💪

Type of acids and bases mixed	Type of salt formed	Example	Solution formed
Strong base + strong acid	Neutral salt	$NaCl$	Neutral
Strong base + weak acid	Basic salt	$CH_3COO^-Na^+$	Alkaline
Strong acid + weak base	Acidic salt	$NH_4^+Cl^-$	Acidic

👉 **Self–Check: Q9**

Candidates should be able to: • explain the choice of suitable indicators for acid–base titrations, given appropriate data in terms of the strengths of the acids & bases

5. INDICATORS

5.1 Indicators for acid–base titrations

Most indicators for acid–base titrations are themselves weak acids or bases that exhibit different colours in their dissociated and undissociated forms.

For example, let the formula of methyl orange be HIn

At equilibrium,

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

(undissociated form) (dissociated form)

Red Yellow

At low pH, $[H^+]$ is high, the equilibrium position lies to the <u>left</u>.

$[HIn] >> [In^-]$,

colour observed: <u>red</u>

At high pH, $[H^+]$ is low, the equilibrium position lies to the <u>right</u>.

$[In^-] >> [HIn]$

colour observed: <u>yellow</u>

<u>End point of titration</u>

The end point of a titration occurs when the indicator changes colour.

In the case of methyl orange, the end point occurs when it changes colour from red to orange, or yellow to orange, when the initial solution is acidic or basic respectively.

<u>Choice of indicator</u>

The choice of an indicator for a particular titration is based on its <u>pH range for colour change</u> (working range), which must <u>coincide with the region of rapid pH change in the titration curve</u> (vertical section of the titration curve). (See titration curve in next section)

Table 5: Some common Acid–base Indicators

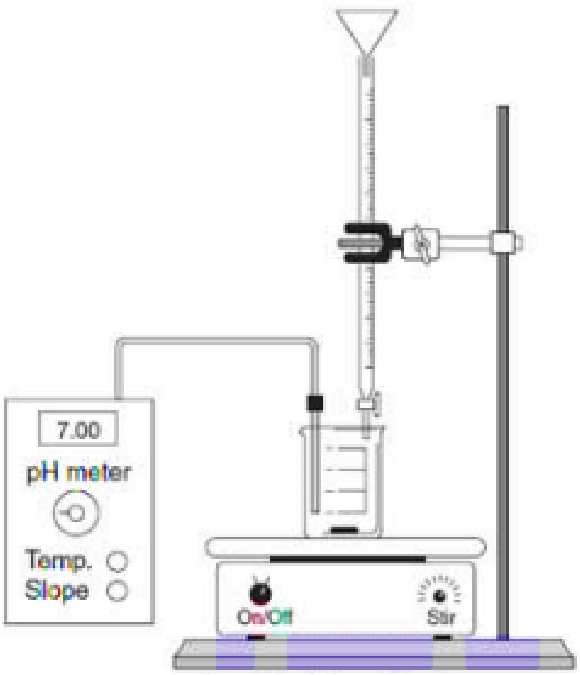
Indicator	Colour		pH range for colour change / working range
	Acid	Base	
Methyl orange	Red	Yellow	3.2 – 4.4
Screened methyl orange	Violet	Green	3.2 – 4.4
Bromothymol blue	Yellow	Blue	6.0 – 7.6
Phenolphthalein	Colourless	Pink	8.2 – 10.0
Thymolphthalein	Colourless	Blue	9.3 – 10.5

Titration	Type of salt formed	Indicator
strong acid – strong base	Neutral salt	Any indicator
weak acid – strong base	Basic salt	Phenolphthalein Thymolthalein
strong acid – weak base	Acidic salt	methyl orange screened methyl orange

6. MONOPROTIC ACID–BASE TITRATION CURVES

Consider a titration carried out by adding a base/acid from a burette to an acid/base in a conical flask.

The change in pH throughout the titration can be recorded using a pH meter as shown below.



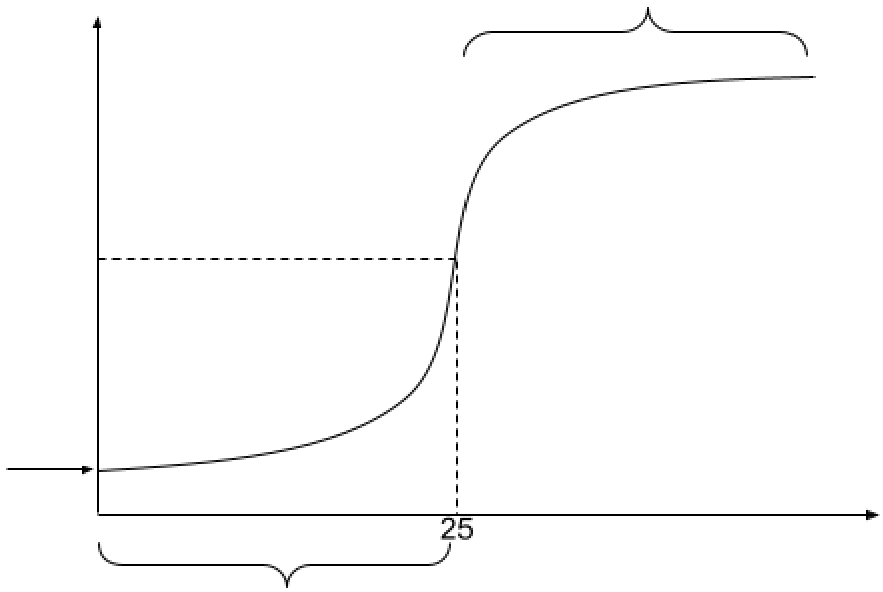
If the pH is plotted against volume of base added, a titration curve will be obtained. Several possible types of titration curve are obtained.

- o **Titration of strong acid against strong base / strong base against strong acid**
- o **Titration of weak acid against strong base / strong base against weak acid**
- o **Titration of strong acid against weak base / weak base against strong acid**

6.1 Strong Acid – Strong Base titration

Consider a titration of 25.0 cm^3 of 1.00 mol dm^{-3} HC*l* with 1.00 mol dm^{-3} NaOH.

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



Note: NaOH (aq) is in the burette.
HCl (aq) is in the conical flask.

Initial pH (before titration)

The conical flask contains only strong acid.

Eg:

$[H^+]$ = **[HC*l*] = 1.00 mol dm^{-3}**

pH = 0

When some strong acid is neutralised (before equivalence point)

- ❖ pH increases as the acid in the conical flask is gradually neutralised by the added base.
- ❖ The solution in the conical flask contains remaining strong acid and salt formed. The

remaining strong acid determines the pH.

Eg: When 24.90 cm³ of 1.00 mol dm⁻³ NaOH is added to 25.0 cm³ of 1.00 mol dm⁻³ HCl

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

	NaOH(aq)	HCl(aq)
Initial amt / mol	0.0249	0.025
Amt after neutralisation/ mol	0	0.025 – 0.0249 = 0.0001

$[H^+]$ = **[HCl]** = $\frac{0.0001}{49.9/1000}$ = **2.004×10^{-3} mol dm⁻³**

pH = 2.70

At equivalence point

- The number of moles of base added just neutralise the number of moles of acid present.
- The solution in the conical flask contains only the neutral salt and water formed. Hence, **pH = 7** at 25°C (from the dissociation of water at 25°C).

When excess strong base is added (after equivalence point)

All the strong acid in the conical flask has been completely neutralised at equivalence point. As excess strong base is still added, the solution in the conical flask contains excess strong base and the salt previously formed. The excess strong base determines the pH of the solution.

Eg: When 25.10 cm³ of 1.00 mol dm⁻³ NaOH is added to 25.0 cm³ of 1.00 mol dm⁻³ HCl,

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

	NaOH(aq)	HCl(aq)
Initial amt / mol	0.0251	0.025
Amt after neutralisation/ mol	0.0251 – 0.025 = 0.0001	0

$[OH^-]$ = **[NaOH]** = $\frac{0.0001}{0.0251+0.025}$ $\frac{0.0001}{0.0251+0.025}$ = **1.996×10^{-3} mol dm⁻³**

pOH = – *lg* (1.996×10^{-3})

= 2.699

pH = **14 – 2.699**

= 11.3

The pH changes rapidly near the equivalence point from pH = 2.70 when 24.90 cm³ of NaOH was added, to pH = 11.3 when 25.10 cm³ of NaOH was added.

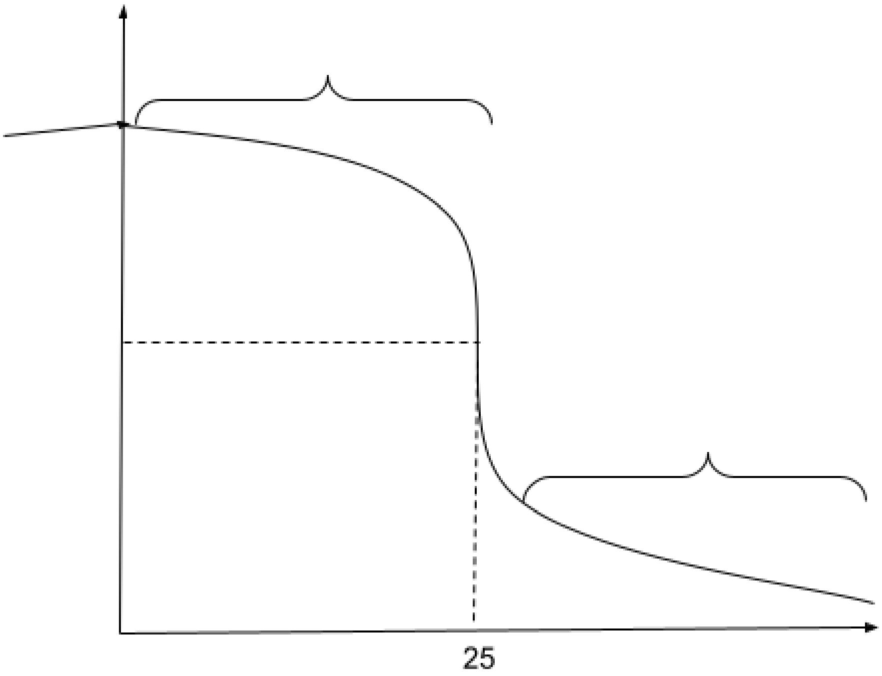
Suitable Indicator:

- Any indicator which changes colour within the region of rapid pH change in the titration curve is suitable: methyl orange / screened methyl orange / phenolphthalein /

thymolphthalein.

Consider a titration of 25.0 cm^3 of 1.00 mol dm^{-3} NaOH with 1.00 mol dm^{-3} HC*l*.

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

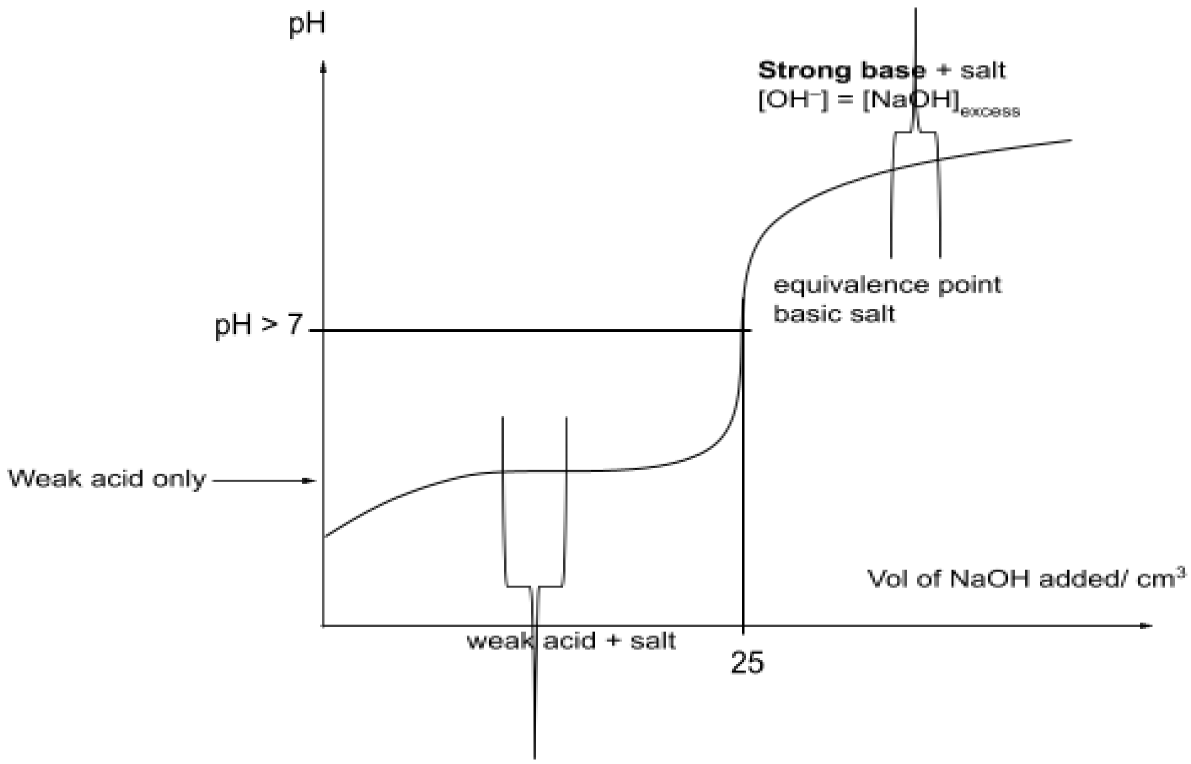


Note: HCl (aq) is in the burette.
NaOH (aq) is in the conical flask.

6.2 Weak Acid – Strong Base titration

Consider a titration of 25.0 cm^3 of 1.00 mol dm^{-3} CH_3COOH with 1.00 mol dm^{-3} NaOH.

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



Initial pH

The conical flask contains only weak acid.

Before equivalence point

The solution in the conical flask contains remaining weak acid and its conjugate base from the salt formed.

At equivalence point

- ❖ The number of moles of base added just neutralise the number of moles of acid present.
- ❖ The solution in the conical flask contains the basic salt and water formed.

After equivalence point

All the weak acid in the conical flask has been completely neutralised at equivalence point. As excess strong base is still added, the solution in the conical flask contains excess strong base and the salt previously formed. The excess strong base determines the pH of the solution.

Eg: When 25.10 cm^3 of 1.00 mol dm^{-3} NaOH is added to 25.0 cm^3 of 1.00 mol dm^{-3} CH_3COOH

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

	CH_3COOH	NaOH	CH_3COONa
Initial amt / mol	0.025	0.0251	0
Amt after neutralisation/ mol	0	0.0251 – 0.025 = 0.0001	0.025

$[OH^-]$ = **[NaOH]** = $\frac{0.0001}{0.0251+0.025}$ $\frac{0.0001}{0.0251+0.025}$ = **1.996 x 10^{-3} mol dm^{-3}**

pOH = 2.699

pH = **14 – 2.699**

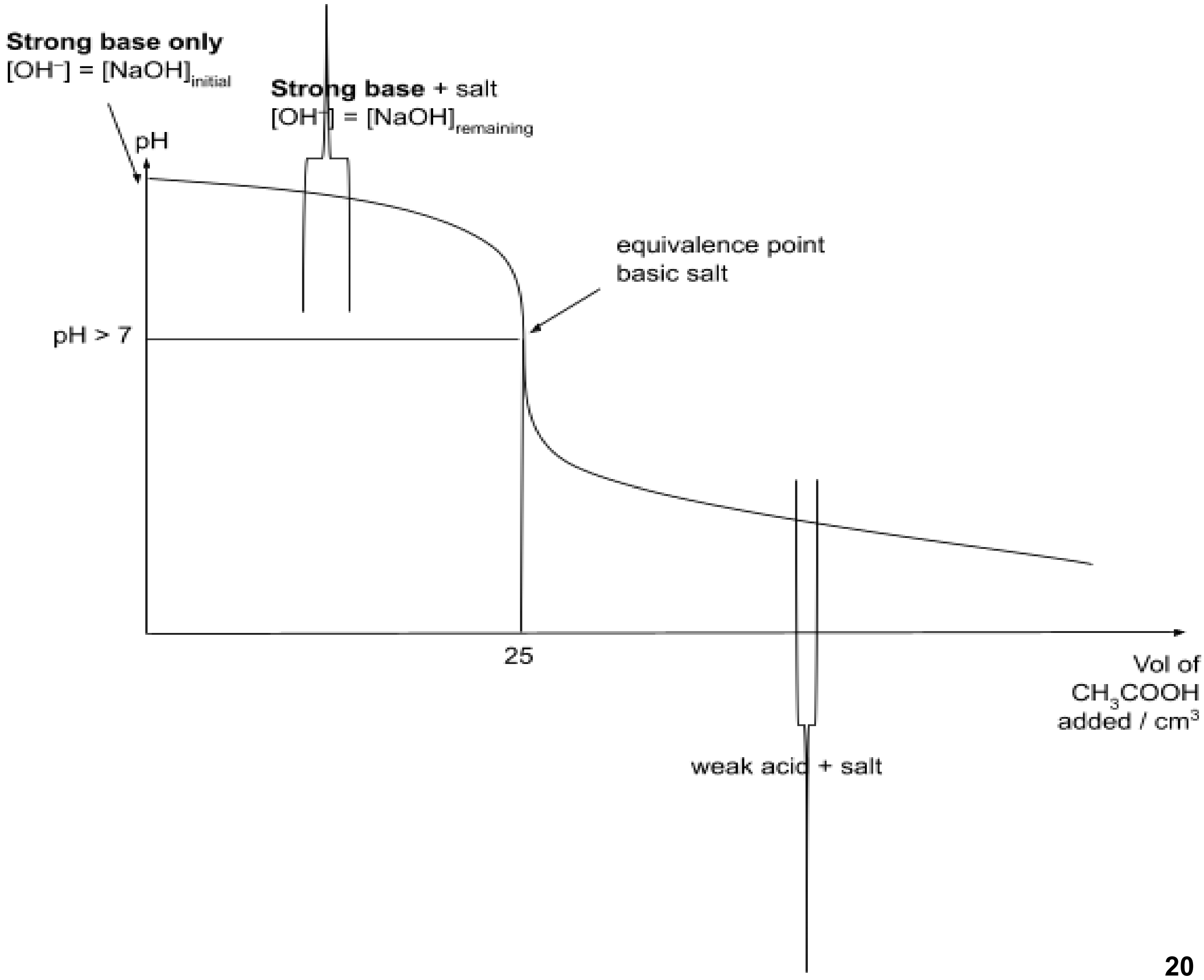
= 11.3

Suitable Indicator

Phenolphthalein / thymolphthalein

Consider a titration of 25.0 cm^3 of 1.00 mol dm^{-3} NaOH with 1.00 mol dm^{-3} CH_3COOH.

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



6.3 Strong Acid – Weak Base titration

Consider a titration of 25.0 cm^3 of 1.00 mol dm^{-3} HC*l* with 1.00 mol dm^{-3} NH_3.

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

Initial pH

The conical flask contains only strong acid.

Before equivalence point

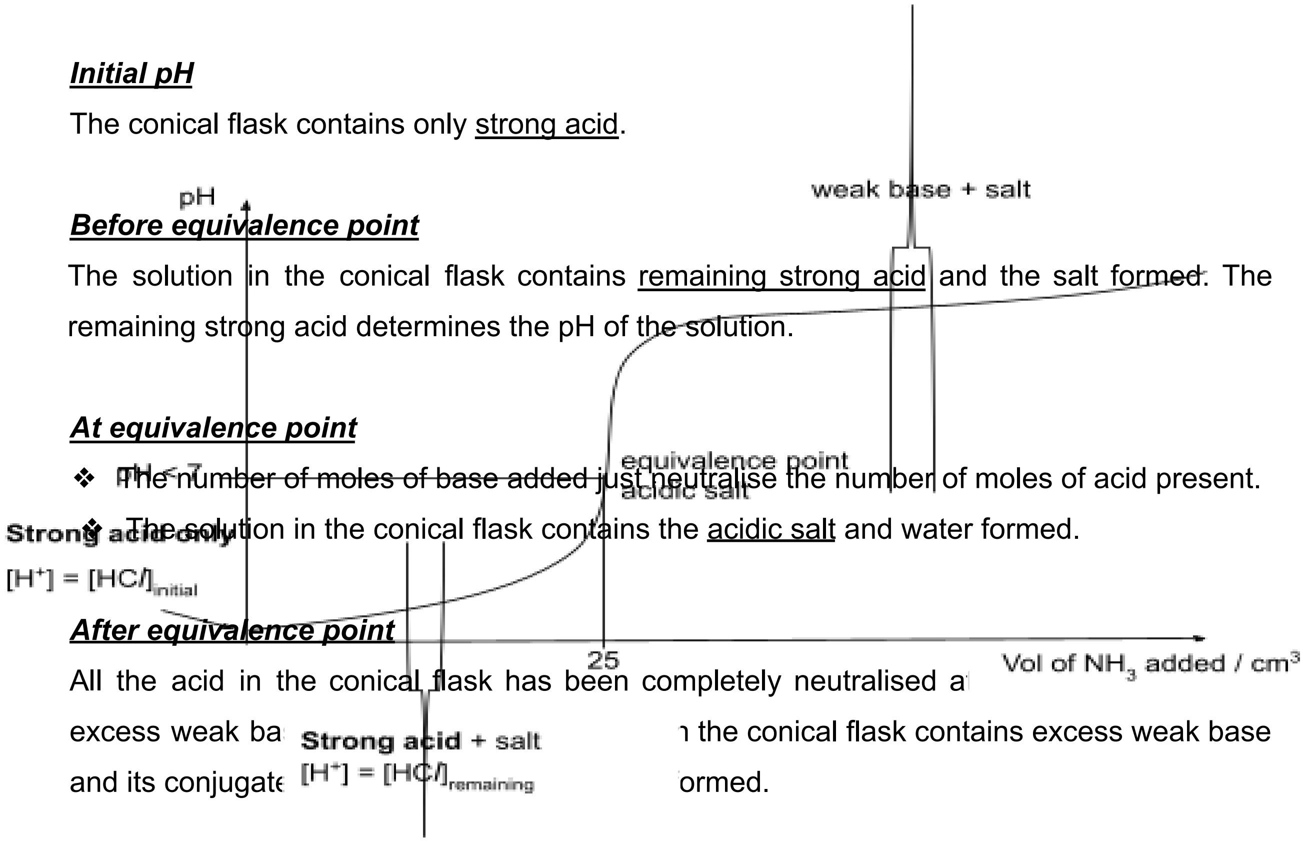
The solution in the conical flask contains remaining strong acid and the salt formed. The remaining strong acid determines the pH of the solution.

At equivalence point

- ❖ The number of moles of base added just neutralise the number of moles of acid present.
- ❖ The solution in the conical flask contains the acidic salt and water formed.

After equivalence point

All the acid in the conical flask has been completely neutralised a excess weak ba n the conical flask contains excess weak base and its conjugate ormed.

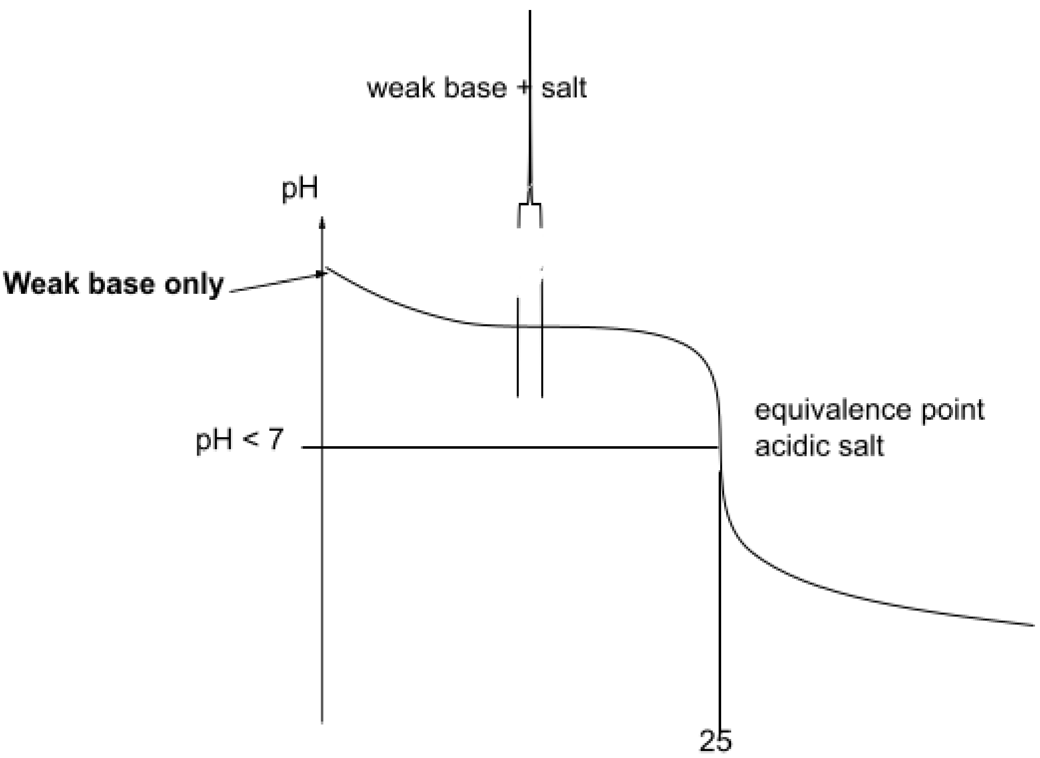


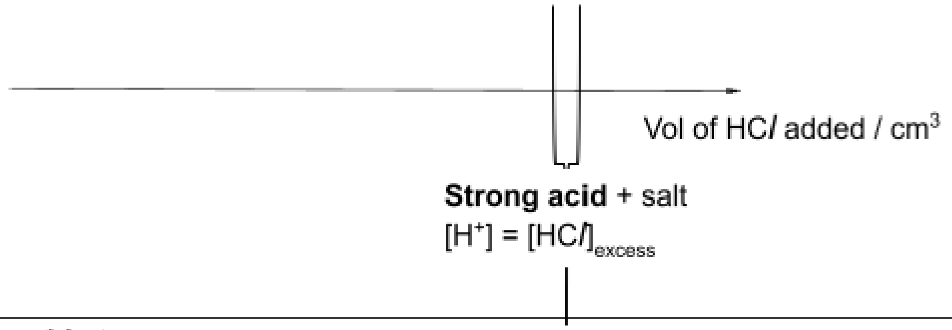
Suitable Indicator

Methyl orange/screened methyl orange

Consider a titration of 25.0 cm^3 of 1 mol dm^{-3} NH_3 with 1.00 mol dm^{-3} HC*l*.

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





> **Candidates should be able to:**
> - explain how buffer solutions control pH
> - describe & explain their uses, including the role of H_2CO_3 / HCO_3^- in controlling the pH in blood

7. BUFFER SOLUTIONS

7.1 Definition of buffer

A buffer solution is a solution whose pH remains almost unchanged when a small amount of H^+ or OH^- is added to it. It maintains the pH by removing the added H^+ or OH^-.

In general there are two types of buffer:

a) Acidic buffer – A solution of a weak acid and its conjugate base

E.g. CH_3COOH and CH_3COONa

b) Basic buffer– A solution of a weak base and its conjugate acid

E.g NH_3 and NH_4Cl

7.2 Action of a buffer

a) ***Acidic buffer***

Consider a mixture of

CH_3COOH – weak acid

CH_3COONa – contains its conjugate base, CH_3COO^-

On adding a small amount of H^+

$$H^+ + CH_3COO^- \longrightarrow CH_3COOH$$

The small amount of added H^+ is removed by the large amount of CH_3COO^- in the buffer.

On adding small amount of OH^-

$$OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O$$

The small amount of added OH^- is removed by the large amount of CH_3COOH in the buffer.

Therefore pH remains almost unchanged.

b) ***Basic buffer***

Consider a mixture of

NH_3 – weak base

NH_4Cl – contains its conjugate acid NH_4^+

On adding a small amount of OH^-

$$OH^- + NH_4^+ \longrightarrow NH_3 + H_2O$$

The small amount of added OH^- is removed by the large amount of NH_4^+ in the buffer.

On adding a small amount of H^+

$$H^+ + NH_3 \longrightarrow NH_4^+$$

The small amount of added H^+ is removed by the large amount of NH_3 in the buffer.

Therefore, pH remains almost unchanged.

7.3 Uses of Buffer Solutions

Buffer solutions are used in situations where it is necessary to maintain pH.

In many biological systems, a change in pH can have a great effect on the functioning of a cell. Therefore, they are usually buffered.

Blood buffer system of H_2CO_3 and HCO_3^-

The pH of human blood must be maintained within a narrow range of 7.35 – 7.45. The buffer in blood consists of a mixture carbonates (HCO_3^-/H_2CO_3).

The cells in our body produce CO_2 as a product of aerobic respiration. CO_2 dissolves with water in the blood to form carbonic acid, which dissociates partially to give hydrogen carbonate.

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

H_2CO_3/HCO_3^- forms a buffer system in blood.

When $[H^+]$ in the blood increases (e.g. from the lactic acid which is produced during exercise), HCO_3^- reacts with H^+, decreasing the $[H^+]$ and helps keep the pH almost constant.

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

When $[H^+]$ in the blood decreases (e.g: from hyperventilation), the position of equilibrium shifts right, increasing the $[H^+]$ and helps keep the pH almost constant.

$$H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$$

When $[OH^-]$ in the blood increases, H_2CO_3 reacts with OH^-, decreasing the $[OH^-]$ and helps keep the pH almost constant.

The blood buffer system https://www.youtube.com/watch?v=r6UAEbhRXNI

👉 **Self–Check: Q10**