Raffles Institution
Year 6 H2 Chemistry 2018
Lecture Notes 14a
Ionic Equilibria 1 – Acid-Base Equilibria

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Content

1 Arrhenius, Brønsted-Lowry and Lewis theories of acids and bases
2 Acid dissociation constants, K_a and the use of pK_a
3 Base dissociation constants, K_b and the use of pK_b
4 The ionic product of water, K_w
5 pH; choice of pH indicators
6 Buffer solutions

Learning Outcomes

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 Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases.
(c) Show understanding of, and apply the Lewis theory of acids and bases (including non-aqueous system, e.g. reaction between BF_3 and NH_3).
(d) Explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation.
(e) Explain the terms pH; K_a; pK_a; K_b; pK_b; K_w and apply them in calculations, including the relationship $K_w = K_aK_b$.
(f) 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 involve the solving of quadratic equations.]
(g) **(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.
(h) Calculate the pH of buffer solutions, given appropriate data.
(i) Explain the choice of suitable indicators for acid-base titrations, given appropriate data.
(j) Describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases.

Lecture Outline

1 Introduction
2 Theories of acids and bases
3 pH Calculations for strong acids and bases
4 The ionic product of water
5 pH Calculations for weak acids
6 pH Calculations for weak bases
7 Relationship between K_a and K_b
8 Degree of ionisation
9 Salt hydrolysis
10 Buffer solutions
11 pH Calculations involving buffer solutions
12 More on buffer solutions
13 Acid-base titration and indicators
14 Acid-base titration curves
15 Summary
16 Appendix

References

- Chemistry. The Molecular Nature of Matter and Change (by Silberberg)
- Chemistry in Context (by Hill & Holman)
- A-level Chemistry (by Ramsden)

Website

- www.chemguide.co.uk

1 Introduction

1.1 Acids

(a) Strong acids and weak acids

An acid can be classified as strong or weak, based on its extent of dissociation in aqueous solution.

	Strong acid	Weak acid
Definition	A strong acid is one which undergoes complete dissociation in aqueous solution.	A weak acid is one which undergoes partial dissociation in aqueous solution.
Examples	$HCl(aq)$, $HNO_3(aq)$	$CH_3COOH(aq)$, $HCN(aq)$
Equations	$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$ or $HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$	$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$ or $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
Note	$[H^+]$ = initial $[HCl]$	At equilibrium, $[H^+]$ < initial $[CH_3COOH]$

(b) Concentrated and dilute acids

The concentration of an acid in aqueous solution is the amount of the acid per unit volume of the solution.

- A concentrated acid is one in which the proportion of acid to water is high.
- A dilute acid is one in which the proportion of acid to water is low.

- dilute strong acid
- concentrated weak acid.

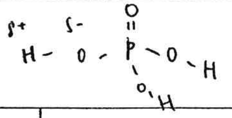
Note:

strong acid / weak acid — strength of acid ≠ concentration of acid — concentrated acid / dilute acid

refers to **extent of dissociation** of acid

refers to **amount of acid per dm^3** of solution

(c) Basicity of an acid



tribasic acid.

	Number of H atoms ionisable (as H^+ ion) per molecule	Examples
monobasic (or monoprotic) acid	$HCl \rightarrow H^+ + Cl^-$ 1	HCl, HNO_3 and CH_3COOH
dibasic (or diprotic) acid	$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$ 2	H_2SO_4, HOOC–COOH
tribasic (or triprotic) acid	3	H_3PO_4

1.2 Bases

- Bases are compounds which neutralise acids. Not all bases are soluble in water.
- A strong base is one which undergoes complete ionisation in aqueous solution.

  Examples of strong base: $NaOH(aq)$, $KOH(aq)$, $Ba(OH)_2(aq)$

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

- A weak base is one which undergoes partial ionisation in aqueous solution.

  Examples of weak base: $NH_3(aq)$, $Na_2CO_3(aq)$, $CH_3CH_2NH_2(aq)$

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

  monoacidic base : NaOH
  diacidic bases : Na_2CO_3 , $Ba(OH)_2$

2 Theories of Acids and Bases

2.1 The Arrhenius theory of acids and bases

(a) Definitions

In 1884, the Swedish chemist Svante Arrhenius suggested the following definitions:

Acid -	Base
• An acid is a hydrogen-containing substance that ionises and releases hydrogen ions (i.e. H^+ ions) in aqueous solution. • Example: $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$	• A base is a hydroxide-containing substance that ionises and releases hydroxide ions (i.e. OH^- ions) in aqueous solution. • Example: $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

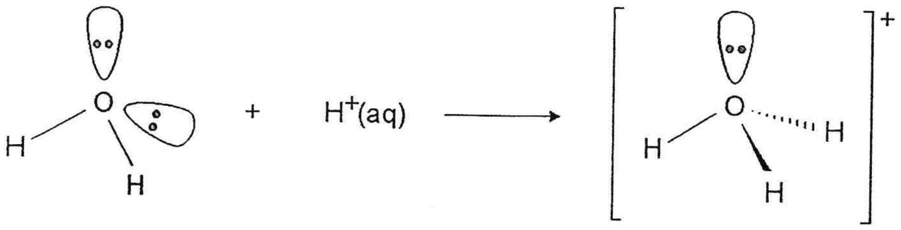
(b) Limitations of Arrhenius theory:

- It restricted acid-base reactions to those which occur in aqueous solutions. RNH_2
- It did not account for the basic properties of ammonia and some organic substances (such as the amines) that do not contain the hydroxide group.
- It focused on the existence of the hydrogen ion, H^+, in aqueous solution but no such ion can exist in aqueous solutions.

(c) The hydrated proton $HCl(aq) + H_2O \longrightarrow H_3O^+ + Cl^-(aq)$.

- The hydrogen ion is a bare proton, a fundamental particle. It is very small (10^{-15} m diameter) and has a relatively high charge density such that it attracts any molecule with unshared electrons such as H_2O. $\downarrow \frac{\text{charge}}{\text{volume}}$
- Therefore, in aqueous solution, a water molecule forms a dative covalent bond to the H^+ ion to produce the hydronium ion (also known as 'hydroxonium ion'), H_3O^+.

$$H_2O(l) \quad + \quad H^+(aq) \longrightarrow H_3O^+(aq)$$



Note:

- When talking about acidic solutions, the term 'hydrogen ion' is often used. Strictly speaking, we should always remember that protons do not exist in solution and should talk about the hydronium ion, writing $H_3O^+(aq)$ instead of $H^+(aq)$.
- In practice, $H^+(aq)$ is commonly used for simplicity sake. We will use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably. This means that any equation you see written with '$H^+(aq)$' has an equivalent form with '$H_3O^+(aq)$' and vice versa.

2.2 The Brønsted-Lowry theory of acids and bases

- In 1923, J.N. Brønsted and T.M. Lowry proposed the proton transfer theory of acids and bases.
- Definitions

Brønsted-Lowry Acid	Brønsted-Lowry Base
A Brønsted-Lowry acid is a **proton donor**.	A Brønsted-Lowry base is a **proton acceptor**.

- In this case, an acid-base reaction involves the transfer of a proton (i.e. H^+ ion) from the acid to the base. An acid is only an acid in the presence of a base, and a base is only a base in the presence of an acid.

H_2O is amphiprotic – can either donate or accept a proton, thus acting as an acid or a base.

- Examples:

$$\underset{\text{acid}}{HCl(g)} + \underset{\text{base}}{NH_3(g)} \longrightarrow NH_4Cl(s)$$

$$\underset{\text{acid}}{HCl(aq)} + \underset{\text{base}}{H_2O(l)} \longrightarrow Cl^-(aq) + H_3O^+(aq)$$

$$\underset{\text{acid}}{CH_3COOH(aq)} + \underset{\text{base}}{OH^-(aq)} \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

$$\underset{\text{base}}{CO_3^{2-}(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

2.3 Lewis acids and bases

- In 1938, the American chemist G.N. Lewis produced a theory which extends the concept of acids and bases even further than that of Brønsted and Lowry.
- Definitions

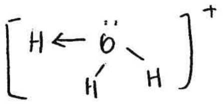
Lewis Acid	Lewis Base
A Lewis acid is any species that can accept a pair of electrons from a base to form a dative covalent bond, i.e. **a Lewis acid is an electron-pair acceptor**.	A Lewis base is any species that can donate a pair of electrons to an acid to form a dative covalent bond, i.e. **a Lewis base is an electron-pair donor**.

- Examples:

e^- deficient

$$\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow H_3N{\rightarrow}BF_3$$

$$\underset{\text{Lewis acid}}{H^+} + \underset{\text{Lewis base}}{H_2O:} \longrightarrow H_3O^+$$



$$\underset{\text{Lewis acid}}{AlCl_3} + \underset{\text{Lewis base}}{:Cl^-} \longrightarrow AlCl_4^-$$

- The Lewis theory of acids and bases is much broader than the Arrhenius and Brønsted-Lowry definitions. It extends the range of acid-base reactions to include those which do not involve protons.

2.4 Conjugate acid-base pairs

- We are primarily concerned with aqueous solutions in which acid-base phenomena involve proton transfer, and so the **Brønsted-Lowry theory of acids and bases** is of most use to us.

- Consider the following reaction between an acid HA and a base B.

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{B} \rightleftharpoons \underset{\text{conjugate base of HA}}{A^-} + \underset{\text{conjugate acid of base B}}{HB^+}$$

- Note:-

In the forward reaction	• HA is an acid as it donates a proton to B. • B is a base as it accepts a proton from HA.
In the backward reaction	• HB^+ is an acid since it donates a proton to A^-. • A^- is a base since it accepts a proton from HB^+.
Conjugate acid-base pairs	• HA and A^- • HB^+ and B

- Notice that in each conjugate pair, **<u>the acid and base differ from each other by a proton, H^+</u>**.

- Examples

loses H^+

gains H^+

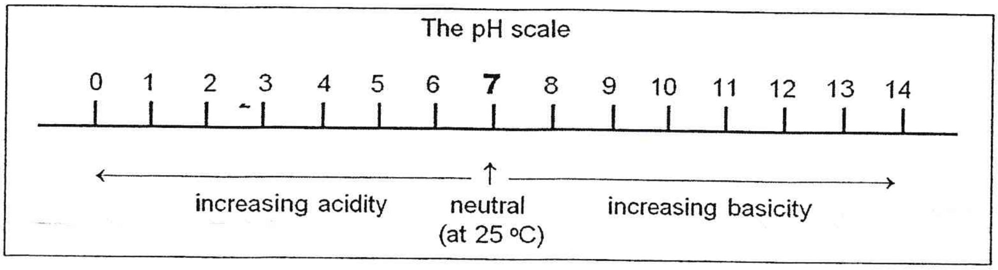
	Reaction (forward reaction)	acid	conjugate base	base	conjugate acid
1	$HCl(aq) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$	HCl	Cl^-	H_2O	H_3O^+
2	$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$	H_2O	OH^-	CH_3NH_2	$CH_3NH_3^+$
3	$NH_3(aq) + CH_3COOH(aq) \rightarrow CH_3COO^-NH_4^+(aq)$	CH_3COOH	CH_3COO^-	NH_3	NH_4^+

3 pH Calculations for Strong Acids and Bases

3.1 The pH scale

- The concentration of hydrogen ions in a solution is a measure of acidity or alkalinity of the solution. Most hydrogen ion concentrations fall between values of 10^0 and 10^{-14} mol dm^{-3}.

- The Danish biochemist S.P.L. Sørensen (1909) realised that this wide range of hydrogen ion concentrations could conveniently be expressed by the numbers 0 to 14 using **the pH scale**.



3.2 Definition of pH

- The pH of a solution is defined as **the negative logarithm to base ten of the hydrogen ion concentration in mol dm^{-3}**.

$$\boxed{pH = -\lg [H^+]}$$

- If the pH of a solution is known, the concentration of hydrogen ion (in mol dm^{-3}) in the solution can be calculated.

$$\boxed{[H^+] = 10^{-pH}}$$

Note:

- The **higher** the **[H$^+$]** in a solution, the **lower** is the **pH** of the solution.
  ⇒ A solution with a lower pH is more acidic than a solution with a higher pH.
- An aqueous solution with pH = 7 at 298 K is considered to be **neutral** because **[H$^+$] = [OH$^-$]**. *(refer to Section 4.4)*

pH is dependent on [ ] of acid/base ⇒ ∴ not a good indicator of acid/base strength.

3.3 Calculating the pH of a solution of a strong acid

■● Worked Example 1 ●■

(a) Calculate the pH of 0.200 mol dm^{-3} HC*l*(aq).	**(b)** Calculate the pH of 1.00 mol dm^{-3} H_2SO_4(aq).
$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$ $[H^+] = [HCl(aq)] = 0.200$ mol dm^{-3} $pH = -\lg [H^+] = -\lg (0.200) = \underline{0.699}$	$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$ $[H^+] = 2 \times 1.00 = 2.00$ mol dm^{-3} $pH = -\lg [H^+] = -\lg (2.00) = -0.301.$

3.4 Calculating [H$^+$] from pH

■● Worked Example 2 ●■

(a) Calculate the [H$^+$] in urine of pH 4.1	**(b)** Calculate the [H$^+$] in pancreatic juice of pH 8.1.
$[H^+] = 10^{-pH} = 10^{-4.1}$ $= \underline{7.94 \times 10^{-5} \text{ mol dm}^{-3}}$	$[H^+] = 10^{-8.1} = 7.94 \times 10^{-9}$ mol dm^{-3}

■● Exercise 1 ●■ [N2014/I/12]

10 cm^3 of a 0.01 mol dm^{-3} solution of nitric acid is diluted with 90 cm^3 of water.

What is the pH of the resulting solution?

A 1 B 2 [✓ C 3] D 4

$n(H^+) = n(HNO_3) = \frac{10}{1000} \times 0.01 = 0.0001$ mol.

$[H^+] = \frac{0.0001}{100} \times 1000 = 0.001$ mol dm^{-3}

$pH = -\lg [H^+] = -\lg (0.001) = 3$

3.5 Definition of pOH

- The pOH of a solution is the **negative logarithm to base ten of the hydroxide ion concentration of the solution in mol dm^{-3}**

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

- If the pOH of a solution is known, the concentration of hydroxide ions (in mol dm^{-3}) in the solution can be calculated.

$[OH^-] = 10^{-pOH}$

3.6 Relationship between pH and pOH at 25 °C

- Experimentally, it has been determined that at 25 °C, pH + pOH = 14
- Hence **pH = 14 – pOH** and **pOH = 14 – pH** at 25 °C.
- Refer to **Section 4** for more details.

At 25 °C,

pH + pOH = 14

3.7 Calculating the pH of a solution of a strong base

■● Worked Example 3 ●■

(a) Calculate the pH of 0.100 mol dm^{-3} KOH(aq).	**(b)** Calculate the pH of 1.00 mol dm^{-3} $Ba(OH)_2$(aq).
$KOH (aq) \longrightarrow K^+(aq) + OH^-(aq)$ $[OH^-]$ = 0.100 mol dm^{-3} pOH = –lg (0.100) = 1 pH = 14 – 1 = <u>13.0</u>	$Ba(OH)_2 (aq) \longrightarrow Ba^{2+}(aq) + 2OH^-(aq)$ $[OH^-]$ = 2 × 1.00 = 2.00 mol dm^{-3} pOH = –lg (2.00) = –0.30 pH = 14 – (–0.30) = 14.3

3.8 Calculating $[OH^-]$ from pH or pOH

■● Worked Example 4 ●■

(a) Calculate the $[OH^-]$ in KOH(aq) of pOH 3.0.	**(b)** Calculate the $[OH^-]$ in baking soda of pH 8.4.
pOH = 3.0 $[OH^-] = 10^{-pOH} = 10^{-3}$ = <u>1.00 x 10^{-3} mol dm^{-3}</u>	pH = 8.4 ⇒ pOH = 14 – 8.4 = 5.6 $[OH^-] = 10^{-5.6}$ = 2.51 x 10^{-6} mol dm^{-3}

3.9 Measuring the pH of a solution

- Main methods available to determine the pH (and hydrogen ion concentration) of a solution:
  ① using <u>universal indicator paper or solution</u> for an approximate pH value.
  ② using a <u>pH meter</u> for an accurate pH determination.

- The pH values of some familiar aqueous solutions are shown in the diagram below.

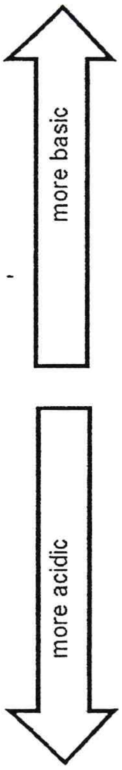
pH values of some familiar substances

Note:

The diagram gives the pH values of a number of familiar items.

Keep in mind that because pH is on a logarithmic scale, every unit change in pH represents a tenfold change in $[H^+]$.

Thus lemon juice is approximately 100 times more acidic than tomato juice.



	pH	$[H^+]$ /mol dm^{-3}	$[OH^-]$ /mol dm^{-3}	pOH
1.0 mol dm^{-3} NaOH	14	1×10^{-14}	1×10^{0}	0
0.1 mol dm^{-3} NaOH household bleach	13	1×10^{-13}	1×10^{-1}	1
	12	1×10^{-12}	1×10^{-2}	2
	11	1×10^{-11}	1×10^{-3}	3
limewater				
milk of magnesia	10	1×10^{-10}	1×10^{-4}	4
	9	1×10^{-9}	1×10^{-5}	5
baking soda				
	8	1×10^{-8}	1×10^{-6}	6
human blood, tears **pure water at 298 K** saliva, fresh milk	**7**	**1×10^{-7}**	**1×10^{-7}**	**7**
	6	1×10^{-6}	1×10^{-8}	8
rainwater (normal)				
black coffee	5	1×10^{-5}	1×10^{-9}	9
tomatoes wine	4	1×10^{-4}	1×10^{-10}	10
vinegar	3	1×10^{-3}	1×10^{-11}	11
lemon juice	2	1×10^{-2}	1×10^{-12}	12
stomach 'juices' (contains $HCl(aq)$)	1	1×10^{-1}	1×10^{-13}	13
1.0 mol dm^{-3} $HCl(aq)$	0	1×10^{0}	1×10^{-14}	14

■● **Exercise 2** ●■ [N2005/I/9]

The pH of normal human blood is 7.4. Strenuous exercise can cause the condition called acidosis in which the pH falls. If the pH drops to 6.8, death may occur.

How many times greater is the hydrogen ion concentration in blood at pH 6.8 compared with that at pH 7.4?

A 1.1 B 2.0 [✓ C 4.0] D 60.0

$$\frac{[H^+]_{6.8}}{[H^+]_{7.4}} = \frac{10^{-6.8}}{10^{-7.4}} = 3.98.$$

4 The Ionic Product of Water, K_w

4.1 Deriving the expression for K_w

- The electrical conductivity of even the purest water never falls to exactly zero. This is due to the presence of ions produced from the self-ionisation of water as represented by the equation below.

$$\underset{\text{base}}{H_2O(l)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

or for simplicity: $$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

- At equilibrium, the equilibrium constant, $K_c = \dfrac{[H^+][OH^-]}{[H_2O]}$

  Rearranging gives: $K_c[H_2O] = [H^+][OH^-]$

  Since water is a weak electrolyte, the amount of water ionised is very small such that $[H_2O]$ is effectively constant. Hence $K_c\,[H_2O]$ is another constant.

  Let $K_w = K_c\,[H_2O]$.

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

- K_w is termed the **ionic product of water**. It has **units of mol² dm⁻⁶**.

- The exact value of K_w depends on temperature.

$$\boxed{\text{At } 25\ ^\circ C,\ K_w = [H^+][OH^-] = 1.0 \times 10^{-14}\ mol^2\ dm^{-6}}$$

- The following expression for K_w is also commonly used.

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$	$K_w = [H_3O^+][OH^-]$

Note:

- For all aqueous solutions at the same temperature,

  $[H^+][OH^-]$ = **constant** = K_w at that temperature

- If $[H^+]$ becomes larger, $[OH^-]$ becomes smaller and vice versa.

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

4.2 Calculations involving K_w

■● Worked Example 5 ●■

(a) Calculate the $[OH^-]$ in 0.10 mol dm^{-3} $HCl(aq)$.

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

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

$$= \frac{1.00 \times 10^{-14}}{0.10} = \underline{1.00 \times 10^{-13} \text{ mol dm}^{-3}}$$

(b) Calculate the $[H^+]$ in 0.020 mol dm^{-3} $Ba(OH)_2(aq)$.

$$[OH^-] = 2 \times 0.020 = 0.040 \text{ mol dm}^{-3}$$

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

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.040} = 2.50 \times 10^{-13} \text{ mol dm}^{-3}$$

4.3 Relationship between pK_w, pH and pOH

- By definition,
  pK_w is the negative logarithm to base ten of K_w.

$$\boxed{pK_w = -\lg K_w}$$

- pK_w can be expressed in terms of pH and pOH.

$$K_w = [H^+][OH^-]$$
$$-\lg K_w = -\lg [H^+] - \lg [OH^-]$$
$$\Rightarrow pK_w = pH + pOH$$

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

- At 25 °C,

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$
$$\Rightarrow pK_w = pH + pOH = -\lg (1.0 \times 10^{-14}) = 14$$

At 25 °C,

pK_w = pH + pOH = 14

4.4 pH and pOH of a neutral aqueous solution at 25 °C

- For an aqueous solution, $K_w = [H^+][OH^-]$.
- For a <u>neutral</u> aqueous solution, **$[H^+] = [OH^-]$**.
- Consider a <u>neutral</u> aqueous solution at 25 °C.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$
$$\Rightarrow [H^+]^2 = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$
$$\Rightarrow [H^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$
$$\textbf{pH} = -\lg [H^+] = -\lg (1.0 \times 10^{-7}) = \mathbf{7}$$
$$[OH^-] = [H^+] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$
$$\textbf{pOH} = -\lg [OH^-] = -\lg (1.0 \times 10^{-7}) = \mathbf{7}$$

For a <u>neutral</u> aqueous solution at 25 °C,

$[H^+] = [OH^-]$
$= 1.0 \times 10^{-7}$ mol dm^{-3}

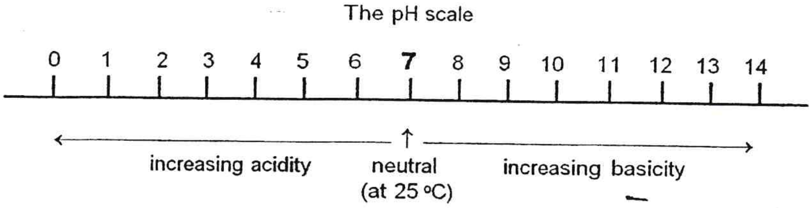
pH = pOH = 7

- For <u>pure water</u> (at 25 °C) which is **neutral**,

$[H^+] = [OH^-] = 1.0 \times 10^{-7}$ mol dm^{-3}

$\Rightarrow$ pH = pOH = 7 (at 25 °C)

Note:



A neutral solution has pH 7 only at a temperature of 25 °C.

neutral solution	$[H^+] = [OH^-]$	pH = 7 at 25 °C
acidic solution	$[H^+] > [OH^-]$	pH < 7 at 25 °C
basic solution	$[H^+] < [OH^-]$	pH > 7 at 25 °C

4.5 The effect of temperature on K_w

- The table below shows the variation of the ionic product of water, K_w, with temperature.

Temperature / °C	K_w / mol² dm⁻⁶	pH of water $= -\lg\sqrt{K_w}$
10	0.29×10^{-14}	7.27
20	0.68×10^{-14}	7.08
25	$\mathbf{1.00 \times 10^{-14}}$	**7.00**
30	1.47×10^{-14}	6.92
40	2.92×10^{-14}	6.77
50	5.48×10^{-14}	6.63
100	51.3×10^{-14}	6.14

- The value of K_w increases with temperature as shown in the table. This is because the self-ionisation of water is an endothermic process.

temp ↑ pH ↓

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \Delta H > 0$$

or

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

As T↑, $[H^+]\uparrow \rightarrow$ pH ↓

- As temperature is increased, the equilibrium position of the above reaction shifts to the right to absorb the heat added. This is in accordance with Le Chatelier's principle.

- With the forward endothermic reaction favoured as temperature is increased, there will be higher concentrations of H^+ and OH^- ions.

- Since $K_w = [H^+][OH^-]$, the value of K_w increases as temperature increases.

■● Exercise 3 ●■ [N2013/I/11]

The dissociation constant, K_w, for the ionisation of water, $H_2O \rightleftharpoons H^+ + OH^-$, at different temperatures is given below.

temperature/°C	K_w / mol² dm⁻⁶
0	1.15×10^{-15}
25	1.00×10^{-14}
50	5.50×10^{-14}

What can be deduced from this information?

A Only at 25 °C are $[H^+]$ and $[OH^-]$ equal. Neutral → $[H^+] = [OH^-]$

B The equilibrium lies furthest to the right at 0°C.

C The forward reaction is exothermic.

D The pH of water decreases as temperature increases.

5 pH Calculations for Weak Acids

- Although the pH of a solution provides some measure of the strength of a constituent acid, the use of pH is very limited in this context since its value will change as the concentration changes.
- Consequently, chemists looked for a more useful, yet quantitative, means of representing the strength of an acid. They found this by considering the dissociation equilibria of acids in aqueous solution.

5.1 Acid dissociation constant, K_a

- Consider the dissociation of a <u>weak monobasic acid HA</u> (e.g. CH_3COOH) in an aqueous solution.

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

Or for simplicity: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

- For the above reaction at equilibrium,

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

- K_a is termed the **<u>acid dissociation constant</u>** of the acid HA.

Note:

- K_a is a **measure of the strength** of the acid HA.
- K_a provides a quantitative indication of the extent to which the acid is dissociated.
- K_a has units of **mol dm^{-3}**.
- The value of K_a is **dependent on temperature.**

- The following expression for K_a is also commonly used.

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$	$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$

- The K_a and pK_a values of different acids can be used to compare the strength of the acids.
- The pK_a of an acid is the **negative logarithm to base ten of the K_a** of the acid.

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

■● Worked Example 6 ●■

Ethanoic acid is an organic acid with K_a value of 1.8×10^{-5} mol dm^{-3}.
Write down the K_a expression for ethanoic acid.

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ $K_a = \frac{[H^+]\,[A^-]}{[HA]}$

<u>Solution</u>

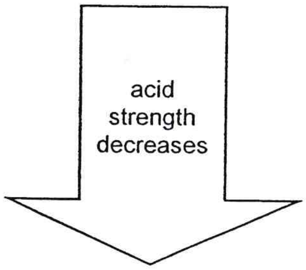
$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

5.2 Interpreting K_a values

- The K_a values of some acids at 298 K are shown in the table below.

Acid	K_a / mol dm^{-3}	pK_a
$HCl(aq)$	1×10^{7}	–7
$HF(aq)$	5.6×10^{-4}	3.25
$HNO_2(aq)$	4.5×10^{-4}	3.35
$C_6H_5COOH(aq)$	6.3×10^{-5}	4.20
$CH_3COOH(aq)$	1.8×10^{-5}	4.74
$NH_4^+(aq)$	5.7×10^{-10}	9.24
$HCN(aq)$	4.9×10^{-10}	9.31
$C_6H_5OH(aq)$	1.3×10^{-10}	9.89



Note:

- The **larger** the K_a value, the **stronger** the acid.
- The **larger** (i.e. **more positive**) the **pK_a** value, the **weaker** the acid.

- Consider HF(aq) and HCN(aq).

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \quad \ldots\ldots\ldots\ldots\ldots(1)$$

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \quad \ldots\ldots\ldots\ldots\ldots(2)$$

Since K_a of HF > K_a of HCN,

- HF is a stronger acid than HCN
- For HF(aq) and HCN(aq) of the same concentration,
  - the equilibrium position of reaction (1) lies more to the right.
  - HF dissociates to a greater extent than HCN.
  - HF dissociates to yield a higher $[H^+]$ at equilibrium.
  - pH of HF(aq) is lower than pH of HCN(aq).

5.3 Acid dissociation constants of weak polyprotic acids

- Polyprotic acids such as H_2S, H_2CO_3 and H_3PO_4 have more than one K_a values.

- For example H_3PO_4, which is a triprotic acid, has three K_a values. These are called first (K_{a1}), second (K_{a2}) and third (K_{a3}) acid dissociation constants respectively.

Dissociation	Equilibrium in aqueous solution	K_a / mol dm^{-3}	pK_a
First	$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$	7.5×10^{-3}	2.1
Second	$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$	6.2×10^{-8}	7.2
Third	$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$	4.2×10^{-13}	12.4

neutral molecule > singly charged ion > doubly charged ion.

- It can be seen that $K_{a1} > K_{a2} > K_{a3}$.

- Successive K_a values become smaller because successive dissociations involve acidic species that are increasingly more negatively charged, making the donation of positively charged H^+ ion increasingly more difficult.

5.4 Calculating the pH of a weak acid

- Problem:

Consider a C_o mol dm^{-3} HA(aq). Calculate its pH given the K_a of HA.

- Solution:

Let $[H^+]$ = x mol dm^{-3} at equilibrium.

Concentration / mol dm^{-3}	$HA(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$A^-(aq)$
Initial	C_o		–		–
Change	– x		+x		+x
Equilibrium	$(C_o - x)$		x		x

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{(C_o - x)} = \frac{x^2}{(C_o - x)}$$

Since HA is a weak acid with a relatively small K_a, assume $x \ll C_o$.
Then $(C_o - x) \approx C_o$.

$$K_a = \frac{x^2}{C_o}$$

$$x = \sqrt{K_a C_o}$$

concentration of H+ at equilibrium.

$$\boxed{[H^+] = \sqrt{K_a C_o}}$$

$$pH = -\lg [H^+] = -\lg\sqrt{K_a C_o}$$

1 Define x as unknown $[H^+]$ at equilibrium.

2 Construct the 'ICE' table.

3 Write the K_a expression.

4 Substitute values into the K_a expression.

5 Make assumption to simplify the calculation.

6 Solve for x and determine $[H^+]$.

7 Calculate pH.

- There are <u>two key assumptions</u> made to simplify the arithmetic.

1) The $[H^+]$ from the self-ionisation of water is negligible and ignored.
    - This is usually justified since the presence of H^+ from HA will suppress the self-ionisation of water.
    - This assumption is not valid if HA(aq) is very dilute.

2) The degree of dissociation is negligible, i.e. $x \ll C_o$ such that $(C_o - x) \approx C_o$ where C_o = initial [HA] and $x = [H^+] = [HA]_{dissociated}$

Degree of dissociation, $(\frac{x}{C_o})(100\%)$	Validity of assumption
$(\frac{x}{C_o})(100\%) \leq 5\%$	The assumption is valid and approximation can be used.
$(\frac{x}{C_o})(100\%) > 5\%$	The assumption is not valid and x has to be found by solving the quadratic equation.

- **Note:**

$x = [H^+] = \sqrt{K_a C_o}$	• This formula is useful for solving multiple-choice questions. • This formula is useful for checking if $(C_o - x) \approx C_o$.

■● Worked Example 7 ●■

Calculate the pH of a 0.200 mol dm^{-3} ethanoic acid solution (K_a = 1.8 x 10^{-5} mol dm^{-3}).

Solution 1

Let [H$^+$] = x mol dm^{-3} at equilibrium.

Concentration / mol dm^{-3}	$CH_3COOH(aq)$	$\rightleftharpoons$	$CH_3COO^-(aq)$	+	$H^+(aq)$
Initial	0.200		–		–
Change	–x		+x		+x
Equilibrium	0.200 – x		x		x

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(x)(x)}{(0.200 - x)} = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

Since CH_3COOH is a weak acid with a relatively small K_a, assume x << 0.200.
Then (0.200–x) $\approx$ 0.200.

$$\frac{x^2}{0.200} = 1.8 \times 10^{-5}$$

$$x = \sqrt{(1.8 \times 10^{-5})(0.200)} = 1.897 \times 10^{-3}$$

$$[H^+] = 1.897 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\lg (1.897 \times 10^{-3}) = \underline{2.72}$$

Check

$$\left(\frac{[H^+]}{0.200}\right)(100\%) = \left(\frac{1.897 \times 10^{-3}}{0.200}\right)(100\%)$$

$$= 0.949\% < 5\%$$

$\Rightarrow$ Assumption is valid.

Solution 2

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

At equilibrium, [H$^+$] = [CH_3COO^-].

Since CH_3COOH is a weak acid with a small K_a,
assume that at equilibrium, [CH_3COOH] = 0.200 mol dm^{-3}

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

$$\frac{[H^+][H^+]}{0.200} = 1.8 \times 10^{-5}$$

$$[H^+] = \sqrt{(1.8 \times 10^{-5})(0.200)} = 1.897 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\lg (1.897 \times 10^{-3}) = 2.72.$$

Alternative way to present the working for the calculation of pH of a weak acid.

- Write the relevant reaction equation.
- State clearly the [HA], [H$^+$] and [A$^-$] at equilibrium including any assumption made.
- Apply [H$^+$] = $\sqrt{K_a C_o}$
- Calculate [H$^+$] and then pH.

Solution 3 $[H^+] = \sqrt{K_a c_o}$

[H$^+$] = $\sqrt{K_a \times [CH_3COOH]}$ = $\sqrt{(1.8 \times 10^{-5})(0.200)}$ = 1.897 x 10^{-3} mol dm^{-3}
pH = –lg (1.897 x 10^{-3}) = $\underline{2.72}$

- Use this method for MCQ.

- Compare the above answer with that of Worked Example 1(a) on page 6.
- **Note:** The pH of a weak acid is <u>higher</u> than that of a strong acid of the <u>same concentration</u>.

5.5 Calculating the K_a of a weak acid

■● Worked Example 8 ●■

The pH of a solution containing 0.35 mol dm^{-3} hydrofluoric acid is 1.82.
Calculate the K_a of hydrofluoric acid.

Solution 1

pH = 1.82 $\Rightarrow$ $[H^+] = 10^{-1.82}$ = 0.01514 mol dm^{-3}

Concentration / mol dm^{-3}	$HF(aq) \rightleftharpoons$	$H^+(aq)$ +	$F^-(aq)$
Initial	0.35	–	–
Change	−0.01514	+0.01514	+0.01514
Equilibrium	0.35 − 0.01514	0.01514	0.01514

$$K_a \text{ of HF} = \frac{[H^+][F^-]}{[HF]} = \frac{(0.01514)^2}{0.35 - 0.01514} = 6.85 \times 10^{-4} \text{ mol dm}^{-3}$$

Solution 2 *(Alternative way to present the working)*

$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$
pH = 1.82 $\Rightarrow$ $[H^+] = 10^{-1.82}$ = 0.01514 mol dm^{-3}

At equilibrium, $[F^-] = [H^+]$ = 0.01514 mol dm^{-3} and [HF] = (0.35 – 0.01514) = 0.3349 mol dm^{-3}

$$K_a \text{ of HF} = \frac{[H^+][F^-]}{[HF]} = \frac{(0.01514)^2}{0.3349} = \underline{6.85 \times 10^{-4} \text{ mol dm}^{-3}}$$

Note: For this question, there is no need to assume $(C_o - x) \approx C_o$ since $x = [H^+]$ can be calculated from the given pH of the solution.

5.6 Calculating the pH of an extremely dilute strong acid

■● Worked Example 9 ●■

Calculate the pH of 1.0×10^{-8} mol dm^{-3} $HNO_3(aq)$ at 298 K.

Solution

- The given nitric acid solution is very dilute. Hence the contribution of H^+ ions from the self-ionisation of water is not negligible and has to be taken into consideration in calculating the pH of the solution.
- There are therefore two sources of H^+ ions:
  1 from the complete dissociation of HNO_3: $HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$
  2 from the self-ionisation of water: $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

The presence of H^+ ions from the complete dissociation of HNO_3 will suppress the ionisation of H_2O.
Let $[H^+]$ from the self-ionisation of water = y mol dm^{-3}
Then $[OH^-]$ due to the self-ionisation of water = y mol dm^{-3}.

Hence $[H^+]_{total} = [H^+]_{nitric\ acid} + [H^+]_{water} = (1.0 \times 10^{-8} + y)$ mol dm^{-3}

At 298 K, $K_w = [H^+]_{total}[OH^-] = 1.0 \times 10^{-14}$ mol² dm^{-6}
$(1.0 \times 10^{-8} + y)(y) = 1.0 \times 10^{-14}$
$y^2 + 1.0\times10^{-8}y - 1.0 \times 10^{-14} = 0$

Solving using GC,
$y = 9.51 \times 10^{-8}$ or $y = -1.05 \times 10^{-7}$ (rejected since y > 0)
$[H^+]_{total} = (1.0 \times 10^{-8} + 9.51 \times 10^{-8}) = 1.051 \times 10^{-7}$ mol dm^{-3}
$\therefore$ pH = $-\lg [H^+] = -\lg (1.051 \times 10^{-7})$ = $\underline{6.98}$

A Simplified Approach

Assume $[H^+]$ from the self-ionisation of $H_2O = 1.0 \times 10^{-7}$ mol dm^{-3}.

$[H^+]_{total} = [H^+]_{nitric\ acid} + [H^+]_{water}$
$= (1.0 \times 10^{-8} + 1.0 \times 10^{-7})$
$\approx 1.1 \times 10^{-7}$ mol dm^{-3}

pH = $-\lg [H^+] = -\lg (1.1 \times 10^{-7})$ = $\underline{6.96}$

6 pH Calculations for Weak Bases

6.1 Base dissociation constant of a weak base B

- Consider an aqueous solution of a weak monoacidic base B (e.g. NH_3) in which the following equilibrium is established:

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

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

- Deriving the expression for K_b:

At equilibrium, $K_c = \dfrac{[BH^+][OH^-]}{[B][H_2O]}$

$$K_c\,[H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

Since $[H_2O]$ in aqueous medium is effectively constant, $K_c\,[H_2O]$ is another constant.

Let $K_b = K_c\,[H_2O]$.

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

- For the above reaction at equilibrium,

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

- K_b is termed the **base dissociation constant** of the base B.

Note:

- K_b is a **measure of the basic strength** of the weak base B.
- K_b is a measure of the ability of the Brønsted-Lowry base B to accept a proton.
- K_b has units of **mol dm^{-3}**.
- The value of K_b is **dependent on temperature.**

- The K_b and pK_b values of different bases can be used to compare the strengths of the bases.

- The pK_b of a base is the **negative logarithm to base ten of the K_b** of the base.

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

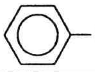
■● Worked Example 10 ●■

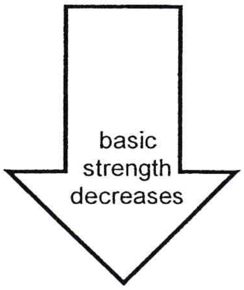
Write the K_b expression for the following reaction: $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$.

Solution: $K_b = \dfrac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$

6.2 Interpreting K_b values

- The table below shows the base dissociation constants of some bases in water at 298 K.

Base	K_b / mol dm^{-3}	pK_b
$CH_3CH_2NH_2(aq)$	5.1×10^{-4}	3.29
$CO_3^{2-}(aq)$	2.1×10^{-4}	3.68
$NH_3(aq)$	1.8×10^{-5}	4.74
$HS^-(aq)$	1.8×10^{-7}	6.74
$CH_3COO^-(aq)$	5.7×10^{-10}	9.24
 $-NH_2$ (aq)	4.2×10^{-10}	9.38



Note:
- The **larger** the K_b value, the **stronger** is the **base**.
- The **larger** the **pK_b** value, the **weaker** is the **base**.

- Consider NH_3 and $CH_3CO_2^-$.

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ ……………….(1)

$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$ ………..(2)

Since K_b of NH_3 > K_b of $CH_3CO_2^-$,
- NH_3 is a stronger base than $CH_3CO_2^-$.
- For $NH_3(aq)$ and $CH_3CO_2^-(aq)$ of the <u>same concentration</u>,
  - the equilibrium position of reaction (1) lies more to the right.
  - NH_3 ionises to a greater extent than $CH_3CO_2^-$.
  - NH_3 ionises to yield a higher $[OH^-]$ at equilibrium.

$pOH = -lg [OH^-]$

$pH = 14 - pOH$

pOH of NH_3 < pOH of $CH_3CO_2^-$

pH of NH_3 > pH of $CH_3CO_2^-$.

6.3 Calculating the pH of a weak base

- Problem: Consider a C_o mol dm^{-3} B(aq). Calculate its pH given the K_b of B.
- Solution:

Let $[OH^-]$ = y mol dm^{-3} at equilibrium.

Concentration/mol dm^{-3}	$B(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$BH^+(aq)$ +	$OH^-(aq)$
Initial	C_o	–	–
Change	$-y$	$+y$	$+y$
Equilibrium	$(C_o - y)$	y	y

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(y)\,(y)}{(C_o - y)} = \frac{y^2}{(C_o - y)}$$

Since B is a weak base with a relatively small K_b, assume y << C_o.
Then $(C_o - y) \approx C_o$.

$$K_b = \frac{y^2}{C_o}$$

$$y = \sqrt{K_bC_o}$$

and. $$\boxed{[OH^-] = \sqrt{K_bC_o}}$$

$$pOH = -lg\,[OH^-] = -lg\sqrt{K_bC_o}$$

$$pH = pK_w - pOH$$

Note:
The approach is similar to that of finding the pH of a weak acid.

■● Worked Example 11 ●■

Calculate the pH of 0.100 mol dm^{-3} $NH_3(aq)$ at 25 °C. K_b of NH_3 is 1.74×10^{-5} mol dm^{-3}.

Solution 1

Let $[OH^-]$ = y mol dm^{-3} at equilibrium.

Concentration/mol dm^{-3}	$NH_3(aq)$	+ $H_2O(l)$ ⇌	$NH_4^+(aq)$ +	$OH^-(aq)$
initial	0.100		–	–
change	– y		+y	+y
equilibrium	(0.100 – y)		y	y

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{y^2}{(0.100 - y)} = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$$

Since NH_3 is a weak base with a relatively small K_b, assume y << 0.100.
Then (0.100 – y) ≈ 0.100.

$$\frac{y^2}{0.100} = 1.74 \times 10^{-5}$$

$$y = \sqrt{(1.74 \times 10^{-5})(0.100)} = 1.319 \times 10^{-3}$$

$$\Rightarrow [OH^-] = 1.319 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pOH = -\lg(1.319 \times 10^{-3}) = 2.88$$

$$pH = pK_w - pOH = 14 - 2.88 = 11.1$$

Check

$$\left(\frac{[OH^-]}{0.100}\right)(100\%) = \left(\frac{1.319 \times 10^{-3}}{0.100}\right)(100\%)$$

$$= 1.32\% < 5\%$$

⇒ Assumption is valid.

Solution 2

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

At equilibrium, $[OH^-] = [NH_4^+]$
Since NH_3 is a weak base with a very small K_b,
assume that at equilibrium, $[NH_3]$ = 0.100 mol dm^{-3}.

$$K_b \text{ for } NH_3 = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[OH^-][OH^-]}{0.100} = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[OH^-] = \sqrt{(1.74 \times 10^{-5})(0.100)} = 1.319 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pOH = -\lg(1.319 \times 10^{-3}) = 2.88$$

$$pH = pK_w - pOH = 14 - 2.88 = 11.1$$

Alternative way to present the working for the calculation of pH of a weak base.

- Write the relevant reaction equation.
- State clearly the [B], $[BH^+]$ and $[OH^-]$ at equilibrium including any assumption made.
- Apply $[OH^-] = \sqrt{K_b C_o}$
- Calculate $[OH^-]$, pOH and then pH.

Solution 3

$$[OH^-] = \sqrt{K_b \times [NH_3]} = \sqrt{(1.74 \times 10^{-5})(0.100)} = 1.319 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pOH = -\lg(1.319 \times 10^{-3}) = 2.88$$

$$pH = pK_w - pOH = 14 - 2.88 = 11.12$$

- Remember the formula and use it when answering MCQ.

- Compare the above answer with that of Worked Example 3(a), page 7.
- **Note:** The pH of a weak base is lower than that of a strong base of the same concentration.

6.4 Calculating the K_b of a weak base

■● Worked Example 12 ●■

The pH of a 0.200 mol dm^{-3} sodium ethanoate solution is 9.02. Calculate the K_b of ethanoate ion.

<u>Solution 1</u>

At 298 K, pOH = 14 – pH = 14 – 9.02 = 4.98

$[OH^-] = 10^{-4.98} = 1.047 \times 10^{-5}$ mol dm^{-3}

Concentration/mol dm^{-3}	$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons$	$CH_3COOH(aq)$ +	$OH^-(aq)$
initial	0.200	–	–
change	-1.047×10^{-5}	$+1.047 \times 10^{-5}$	$+1.047 \times 10^{-5}$
equilibrium	$0.200 - (1.047 \times 10^{-5})$ $= 0.200$	1.047×10^{-5}	1.047×10^{-5}

$$K_b = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} = \frac{(1.047 \times 10^{-5})^2}{0.200} = \underline{5.48 \times 10^{-10} \text{ mol dm}^{-3}}$$

<u>Solution 2</u> *(Alternative way to present the working)*

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

pOH = 14 – 9.02 = 4.98
$[OH^-] = 10^{-4.98} = 1.047 \times 10^{-5}$ mol dm^{-3}

At equilibrium, $[CH_3COOH] = [OH^-] = 1.047 \times 10^{-5}$ mol dm^{-3}

$[CH_3COO^-] = 0.200 - 1.047 \times 10^{-5} = 0.200$ mol dm^{-3}

$$K_b = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} = \frac{(1.047 \times 10^{-5})^2}{0.200} = 5.48 \times 10^{-10} \text{ mol dm}^{-3}$$

Note: For this question, there is no need to assume $(C_o - y) \approx C_o$ since y = $[OH^-]$ can be calculated from the given pH of the solution.

7 Relationship between K_a and K_b for a Conjugate Acid-Base Pair

7.1 K_a, K_b and K_w

- There is a simple relationship between the ionic product of water and the dissociation constants of an acid and its conjugate base. This relationship can be derived by considering the dissociation of ethanoic acid and ionisation of ethanoate ion in water.

- For ethanoic acid, we have

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

$$K_a \text{ of } CH_3COOH = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

- For ethanoate ion, which is the conjugate base of ethanoic acid, we have

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

$$\boxed{K_b \text{ of } CH_3COO^- = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]}}$$

- By multiplying the above two expressions together, we have

$$\begin{aligned}(K_a \text{ of } CH_3COOH)\,(K_b \text{ of } CH_3COO^-) &= \left(\frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}\right)\left(\frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]}\right)\\ &= [H^+]\,[OH^-]\\ &= K_w\end{aligned}$$

- Hence, in general for a **conjugate acid–base pair**, we have

For an acid and its conjugate base	K_a of acid HA x K_b of conjugate base A^- = K_w $\Rightarrow K_b \text{ of } A^- = \dfrac{K_w}{K_a \text{ of HA}}$
For a base and its conjugate acid	K_b of base B x K_a of conjugate acid BH^+ = K_w $\Rightarrow K_a \text{ of } BH^+ = \dfrac{K_w}{K_b \text{ of B}}$

- Note that a relationship also exists between pK_a and pK_b for a conjugate acid-base pair.

$K_w = K_a \times K_b$ and $pK_w = pK_a + pK_b$	At 25 °C, $K_a \times K_b = K_w = 1.0 \times 10^{-14}$ $mol^2\ dm^{-6}$ and $pK_a + pK_b = pK_w = 14$

■● Worked Example 13 ●■

(a) The K_a of CH_3COOH is 1.80×10^{-5} mol dm^{-3}. Calculate the K_b of CH_3COO^-.

Solution

$$K_b \text{ of } CH_3COO^- = \frac{K_w}{K_a \text{ of } CH_3COOH} = \frac{1.0 \times 10^{-14}}{1.80 \times 10^{-5}} = \underline{5.56 \times 10^{-10}\ \text{mol dm}^{-3}}$$

(b) The K_b of NH_3 is 1.74×10^{-5} mol dm^{-3}. Calculate the K_a of NH_4^+.

Solution

$$K_a \text{ of } NH_4^+ = \frac{K_w}{K_b \text{ of } NH_3} = \frac{1.0 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.75 \times 10^{-10}\ \text{mol dm}^{-3}$$

7.2 Relative strengths of acid and base in a conjugate acid-base pair

- Consider a conjugate acid-base pair at 298 K.

$K_a \times K_b = K_w = 1.0 \times 10^{-14}$ mol² dm⁻⁶	$K_b = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{K_a}$
From either one of the equations, • the **larger** the K_a of an **acid**, the **smaller** is the K_b of its **conjugate base**. • the **stronger** the acidity of the **acid**, the **weaker** is the basicity of its **conjugate base**.	

- Consider two weak acids, HA and HB.

• If HA is a stronger acid than HB, then A^- is a weaker base than B^-.
• Reasoning: HA is a stronger acid than HB $\Rightarrow$ K_a of HA $>$ K_a of HB $\Rightarrow \dfrac{K_w}{K_b \text{ of } A^-} > \dfrac{K_w}{K_b \text{ of } B^-}$ $\Rightarrow$ K_b of A^- $<$ K_b of B^- $\Rightarrow$ A^- is a weaker base than B^-
• If HA is a stronger acid than HB, the reaction between HA and B^- will occur to a greater extent than that between HB and A^-. $$\underset{\text{stronger acid}}{HA} + \underset{\text{stronger base}}{B^-} \rightleftharpoons \underset{\text{weaker acid}}{HB} + \underset{\text{weaker base}}{A^-}$$

- The table below shows the strengths of different conjugate acid-base pairs.

		ACID	BASE		
strong acids	complete dissociation	HNO_3	NO_3^-	weak conjugate bases	extremely weak bases
		HCl	Cl^-		
		H_3O^+	H_2O		
weak acids	acid strength decreases ↓	H_2SO_3	HSO_3^-	basic strength increases ↓	weak bases
		$ClCH_2COOH$	$ClCH_2COO^-$		
		H_3PO_4	$H_2PO_4^-$		
		HF	F^-		
		HNO_2	NO_2^-		
		CH_3COOH	CH_3COO^-		
		$[Al(H_2O)_6]^{3+}$	$[Al(OH)(H_2O)_5]^{2+}$		
		H_2CO_3	HCO_3^-		
		H_2S	HS^-		
		NH_4^+	NH_3		
		H_2O	OH^-		
are essentially not acids	weak conjugate acids	NH_3	NH_2^-	complete protonation	strong bases

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{NH_2^-} \rightleftharpoons \underset{\text{base}}{OH^-} + \underset{\text{acid}}{NH_3}$$

- In general,

strong Brønsted-Lowry acids have weak conjugate bases	• HC*l* is a strong acid. • C*l*⁻ is said to be a weak conjugate base.	K_a of HC*l* = 1×10^7 mol dm⁻³ K_b of C*l*⁻ = $\dfrac{1.0 \times 10^{-14}}{1 \times 10^7} = 1.00 \times 10^{-21}$ mol dm⁻³
weak Brønsted-Lowry acids have strong conjugate bases	• CH_3COOH is a weak acid. • CH_3COO^- is said to be a strong conjugate base.	K_a of CH_2COOH = 1.80×10^{-5} mol dm⁻³ K_b of CH_3COO^- = $\dfrac{1.0 \times 10^{-14}}{1.80 \times 10^{-5}} = 5.56 \times 10^{-10}$ mol dm⁻³

8 Degree of Ionisation, α

8.1 Defining degree of ionisation

- The degree of ionisation (or degree of dissociation), α, of an electrolyte can be defined as the fraction of molecules which is ionised at equilibrium.

$$\alpha = \frac{\text{number of moles of molecules which are ionised at equilibrium}}{\text{number of moles of molecules present initially}}$$

  - For strong acids/bases which ionise completely $\Rightarrow \alpha = 1$
  - For weak acids/bases which ionise partially $\Rightarrow 0 < \alpha < 1$

- The degree of ionisation may also be expressed in percentage.

8.2 Variation of α with concentration

- Consider a weak monobasic acid HA of concentration C_o mol dm^{-3} and degree of ionisation α.

Concentration / mol dm^{-3}	HA(aq) $\rightleftharpoons$	H$^+$(aq) +	A$^-$(aq)
Initial	C_o	–	–
Change	$-\alpha C_o$	$+\alpha C_o$	$+\alpha C_o$
Equilibrium	$C_o(1-\alpha)$	αC_o	αC_o

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(\alpha C_o)(\alpha C_o)}{C_o(1-\alpha)} = \frac{\alpha^2 C_o}{(1-\alpha)}$$

$$\Rightarrow K_a = \frac{\alpha^2 C_o}{(1-\alpha)}$$

- Consider a weak acid in which α is very small such that $\alpha << 1$.
  Then $(1-\alpha) \approx 1$. In this case, the K_a expression is simplified as shown below.

$K_a = \alpha^2 C_o$	$\alpha = \sqrt{\frac{K_a}{C_o}}$

- Since K_a is constant at a given temperature, it can be seen from the last expression that for a weak acid, α **increases with increasing dilution (i.e. decreasing concentration of acid)** and is therefore **not constant at a given temperature**.

- For a weak base B of concentration C_o mol dm^{-3} and degree of ionisation α, the above equations apply with K_b of B replacing K_a of HA.

Note:

Which is the best indicator of the strength of an acid: pH, α or K_a?

- **K_a is the best indicator** as it is **constant at constant temperature** and **does not vary with the concentration** of the acid. The K_a of a stronger acid is always larger than that of a weaker acid.
- The pH of an acid varies with the concentration of the acid. The pH of a stronger acid can be larger or smaller than that of a weaker acid depending on the concentrations of the two acids.
- Like pH, the degree of ionisation, α, varies with the concentration of the acid. It increases with decreasing concentration (or increasing dilution) of the acid. Like pH, it can be used to compare the strength of acids only provided if the concentrations of the acids are the same.

8.3 Calculations involving α

■● Worked Example 14 ●■

The pH of 0.20 mol dm^{-3} NH_3(aq) solution is 11.30 at 298 K. Calculate K_b of NH_3 and the degree of ionisation of NH_3 in this solution.

Solution

pH = 11.30

pOH = 14 – 11.30 = 2.70 ⇒ $[OH^-] = 10^{-2.70} = 1.995 \times 10^{-3}$ mol dm^{-3}

Concentration/mol dm^{-3}	NH_3(aq) + H_2O(l) $\rightleftharpoons$	NH_4^+(aq) +	OH^-(aq)
initial	0.20	–	–
change	-1.995×10^{-3}	$+1.995 \times 10^{-3}$	$+1.995 \times 10^{-3}$
equilibrium	0.198	1.995×10^{-3}	1.995×10^{-3}

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(1.995 \times 10^{-3})(1.995 \times 10^{-3})}{0.198} = \underline{2.01 \times 10^{-5}\text{ mol dm}^{-3}}$$

$$\text{Hence degree of ionisation} = \frac{1.995 \times 10^{-3}}{0.20} = \underline{9.98 \times 10^{-3}}$$

$$\text{Alternatively, degree of ionisation, } \alpha = \sqrt{\frac{K_b}{C_0}} = \sqrt{\frac{2.01 \times 10^{-5}}{0.20}} = 0.0100$$

■● Worked Example 15 ●■

Calculate the pH of 0.010 mol dm^{-3} CH_3COOH solution if the degree of ionisation of CH_3COOH is 0.041. Hence determine the K_a of CH_3COOH.

Solution

Concentration / mol dm^{-3}	CH_3COOH(aq) $\rightleftharpoons$	CH_3COO^-(aq) +	H^+(aq)
Initial	0.010	–	–
Change	–(0.041)(0.010)	+(0.041)(0.010)	+(0.041)(0.010)
Equilibrium	9.59×10^{-3}	4.10×10^{-4}	4.10×10^{-4}

$$\text{pH} = -\lg[H^+] = -\lg(4.10 \times 10^{-4}) = 3.39$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(4.10 \times 10^{-4})(4.10 \times 10^{-4})}{9.59 \times 10^{-3}} = 1.75 \times 10^{-5}\text{ mol dm}^{-3}.$$

9 Salt Hydrolysis

9.1 Types of salt solution

- A salt may be defined as a compound formed by the reaction of an acid and a base. It contains
  - a cation which originates from the base and
  - an anion which originates from the acid

- Some salts, when dissolved in water, form neutral solutions. Others form acidic or basic solutions due to **salt hydrolysis**, which is a reversible reaction between the salt ions and water.

- Whether a salt solution is neutral, acidic or basic depends on the type of salt. There are four types in this context as summarised in the table below.

Combination of acid and base which gives rise to the type of salt	Example of salt formed	Nature of solution and pH of solution at 25 °C
strong acid + strong base e.g. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$	$NaCl(aq)$	**neutral**, pH = 7
strong acid + weak base e.g. $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$	$NH_4Cl(aq)$	**acidic**, pH < 7
weak acid + strong base e.g. $CH_3COOH + NaOH \rightarrow CH_3COO^-Na^+ + H_2O$	$CH_3COO^-Na^+(aq)$	**basic**, pH > 7
weak acid + weak base e.g. $CH_3COOH + NH_3 \rightarrow CH_3COO^-NH_4^+ + H_2O$	$CH_3COO^-NH_4^+(aq)$	• acidic if K_a of cation > K_b of anion • neutral if K_a of cation = K_b of anion • basic if K_a of cation < K_b of anion

- A salt will undergo hydrolysis (i.e. reaction with water) if
  - its anion is a conjugate base of a weak acid and/or
  - its cation is a conjugate acid of a weak base

- The table on the next page summaries how salt hydrolysis gives rise to acidic or alkaline solution. Note that only ions that are the conjugate bases of weak acids or conjugate acids of weak bases hydrolyse appreciably.

(a)	Salt of a **strong acid** and **strong base**	• Example: **sodium chloride, $NaCl$** • This type of salt dissolves in water to form a **neutral solution**. In the solution, complete dissociation of $NaCl$ occurs. $NaCl(s) + aq. \longrightarrow Na^+(aq) + Cl^-(aq)$ • Both the Na^+ and Cl^- ions are hydrated but they do not undergo hydrolysis. The solution is neutral since $[H^+] = [OH^-]$. • Na^+ does not undergo hydrolysis due to its relatively low charge density (as compared to Mg^{2+} or Al^{3+} ions). • Being the anion of a strong acid (i.e. HCl), Cl^- is a weaker base than water and it does not undergo hydrolysis.
(b)	Salt of a **strong acid** and **weak base**	• Example: **ammonium chloride, NH_4Cl** • This type of salt dissolves in water to form an **acidic solution**. In the solution, complete dissociation of NH_4Cl occurs. $NH_4Cl(s) + aq. \longrightarrow NH_4^+(aq) + Cl^-(aq)$ • Being the anion of a strong acid (i.e. HCl), Cl^- is a weaker base than water and it does not undergo hydrolysis. • Being the cation derived from a weak base, NH_4^+ is a relatively strong conjugate acid (as compared to water) and it undergoes hydrolysis to give H_3O^+ ions. $\boxed{NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)}$ • $[H_3O^+] > [OH^-]$, the slight excess of H_3O^+ ions generated by the hydrolysis reaction causes the solution to be acidic.
(c)	Salt of a **weak acid** and **strong base**	• Example: **sodium ethanoate, $CH_3COO^-Na^+$** • This type of salt dissolves in water to form a **basic solution**. In the solution, complete dissociation of $CH_3COO^-Na^+$ occurs. $CH_3COO^-Na^+(s) + aq. \longrightarrow Na^+(aq) + CH_3COO^-(aq)$ • Na^+ does not undergo hydrolysis due to its low charge density. • Being the anion of a weak acid, CH_3COO^- is a relatively strong conjugate base (as compared to water) and it undergoes hydrolysis to give OH^- ions. $\boxed{CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)}$ • $[OH^-] > [H_3O^+]$, the slight excess of OH^- ions generated by the hydrolysis reaction causes the solution to be alkaline.
(d)	Salt of a **weak acid** and **weak base**	• Example: **ammonium ethanoate, $CH_3COO^-NH_4^+$** • $CH_3COO^-NH_4^+(s)$ dissolves in water to form a very slightly acidic solution. In the solution, complete dissociation of $CH_3COO^-NH_4^+$ occurs. $CH_3COO^-NH_4^+(s) + aq. \longrightarrow NH_4^+(aq) + CH_3COO^-(aq)$ • Both the NH_4^+ and CH_3COO^- ions undergo hydrolysis (see reasons given above). The solution is weakly acidic because the K_a of NH_4^+ is slightly larger than the K_b of CH_3COO^-.

9.2 Calculations involving hydrolysis of a salt

■● Worked Example 16 ●■

The K_a of ethanoic acid is 1.8×10^{-5} mol dm^{-3} at 298 K.
Calculate the pH of a 0.50 mol dm^{-3} sodium ethanoate solution.

Solution

The solution contains ethanoate ions which undergo hydrolysis to give OH^- ions.

$$K_b \text{ of } CH_3COO^- = \frac{K_w}{K_a \text{ of } CH_3COOH} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} \text{ mol dm}^{-3}$$

Let $[OH^-] = [CH_3COOH] = y$ mol dm^{-3} at equilibrium.
Since CH_3COO^- is a weak base with a very small K_b,
assume that at equilibrium, $[CH_3COO^-] = 0.50$ mol dm^{-3}.

$$K_b \text{ of } CH_3COO^- = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} = \frac{y^2}{0.50} = 5.56 \times 10^{-10} \text{ mol dm}^{-3}$$

Conc/mol dm^{-3}	$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons$	$CH_3COOH(aq)$ +	$OH^-(aq)$
Initial	0.50	-	-
Change	$-y$	$+y$	$+y$
Equilibrium	$0.50 - y$	y	y

$y = \sqrt{(5.56 \times 10^{-10})(0.50)} = 1.667 \times 10^{-5}$

$\Rightarrow [OH^-] = 1.667 \times 10^{-5}$ mol dm^{-3}

$pOH = -\lg(1.667 \times 10^{-5}) = 4.78$

$pH = pK_w - pOH = 14 - 4.78 = 9.22$

Note:

K_b of CH_3COO^- is needed here but is <u>not</u> given.

It can be calculated from the given K_a of CH_3COOH.

■● Worked Example 17 ●■

The K_b of NH_3 is 1.74×10^{-5} mol dm^{-3} at 298 K.
Calculate the pH of a 0.10 mol dm^{-3} ammonium chloride solution.

Solution:

The solution contains ammonium ions which undergo hydrolysis to give H_3O^+ ions.

$$K_a \text{ of } NH_4^+ = \frac{K_w}{K_b \text{ of } NH_3} = \frac{1.0 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.75 \times 10^{-10} \text{ mol dm}^{-3}$$

Let $[H_3O^+] = [NH_3] = y$ mol dm^{-3} at equilibrium.
Since NH_4^+ is a weak acid with a very small K_a,
assume that at equilibrium, $[NH_4^+] = 0.10$ mol dm^{-3}.

$$K_a \text{ for } NH_4^+ = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]} = \frac{y^2}{0.10} = 5.75 \times 10^{-10} \text{ mol dm}^{-3}$$

Concentration/mol dm^{-3}	$NH_4^+(aq) + H_2O(l) \rightleftharpoons$	$NH_3(aq)$ +	$H_3O^+(aq)$
initial	0.10	–	–
change	$-y$	$+y$	$+y$
equilibrium	$(0.10 - y)$	y	y

$y = [H_3O^+] = \sqrt{(5.75 \times 10^{-10})(0.10)}$
$= 7.583 \times 10^{-6}$ mol dm^{-3}

$pH = -\lg(7.583 \times 10^{-6}) = \underline{5.12}$

Note:

K_a of NH_4^+ is needed here but is <u>not</u> given.

It can be calculated from the given K_b of NH_3.

10 Buffer Solutions

10.1 Definition

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

- A buffer solution contains both an acidic species and a basic species (both in relatively large amounts) to react respectively with any base or acid added.

  In general, there are two types of buffer solutions:

  ① acidic buffer which consists of a mixture of a weak acid and one of its salt
    - Example: an aqueous mixture of CH_3COOH and $CH_3COO^-Na^+$

  ② alkaline buffer which consists of a mixture of a weak base and one of its salt
    - Example: an aqueous mixture of NH_3 and NH_4Cl

10.2 Acidic buffer

(a) Composition of an acidic buffer

- An acidic buffer solution consists of a mixture of a **weak acid** and a salt containing its **conjugate base.**

- Consider an acidic buffer consisting of a mixture of ethanoic acid and sodium ethanoate.

In this solution, ethanoic acid, being a weak acid, is only partially dissociated:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

On the other hand, sodium ethanoate, a strong electrolyte, is fully dissociated:

$$CH_3COO^-Na^+(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq) \quad \ldots\ldots\ldots\ldots(2)$$

- In accordance with Le Chatelier's principle, the presence of CH_3COO^- ions from the complete dissociation of $CH_3COO^-Na^+$ further suppresses the dissociation of CH_3COOH such that the equilibrium position of reaction (1) lies very much to the left.

- Hence the buffer solution contains relatively high concentrations of both CH_3COOH and CH_3COO^-. The buffer solution is said to contain a large reservoir of CH_3COOH (acidic species) and a large reservoir of CH_3COO^- (basic species).

(b) Action of the acidic buffer solution

- **Addition of a small amount of acid (i.e. H^+ ions)**

  - When a small amount of H^+ ions is added to the solution, the following reaction occurs:

$$CH_3COO^-(aq) + H^+(aq) \longrightarrow CH_3COOH(aq)$$

neutralisation reaction use → , not ⇌

  - The presence of a large reservoir of CH_3COO^- ions in the solution ensures that nearly all the added H^+ ions are removed.
  - Hence $[H^+]$ in the solution changes very little and the pH is kept approximately constant.

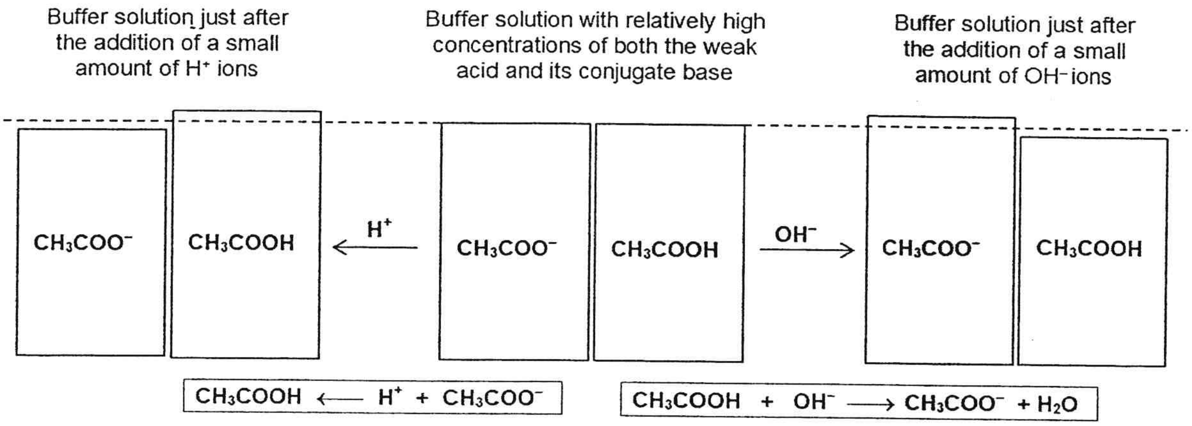
- **Addition of a small amount of base (i.e. OH^- ions)**

  - When a small amount of OH^- ions is added to the solution, the following reaction occurs:

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

  - The presence of a large reservoir of unionised CH_3COOH molecules in the solution ensures that nearly all the added OH^- ions are removed.
  - Hence $[OH^-]$ in the solution changes very little and the pH is kept approximately constant.

(c) Diagrammatic representation of how an acidic buffer works



10.3 Basic buffer

(a) Composition of a basic buffer

- An alkaline buffer solution consists of a mixture of a **weak base** and a salt containing its **conjugate acid**.
- Consider an alkaline buffer consisting of a mixture of ammonia and ammonium chloride.

In this solution, ammonia, being a weak base, is only partially ionised:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad \ldots\ldots\ldots\ldots(1)$$

On the other hand, ammonium chloride, a strong electrolyte, is fully dissociated:

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq) \quad \ldots\ldots\ldots\ldots\ldots(2)$$

- In accordance with Le Chatelier's principle, the presence of NH_4^+ ions from the complete dissociation of NH_4Cl further suppresses the ionisation of NH_3 such that the equilibrium position of reaction (1) lies very much to the left.
- Hence the buffer solution contains relatively high concentrations of both NH_3 and NH_4^+. The buffer solution is said to contain a large reservoir of NH_3 (basic species) and a large reservoir of NH_4^+ (acidic species).

(b) Action of the basic buffer solution

- **Addition of a small amount of acid (i.e. H^+ ions)**

  - When a <u>small amount of H^+ ions</u> is added to the solution, the following reaction occurs:

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

  - The presence of a <u>large reservoir of unionised NH_3 molecules</u> in the solution ensures that nearly all the added H^+ ions are removed.
  - Hence $[H^+]$ in the solution changes very little and the <u>pH is kept approximately constant</u>.

- **Addition of a small amount of base (i.e. OH^- ions)**

  - When a <u>small amount of OH^- ions</u> is added to the solution, the following reaction occurs:

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

  - The presence of a <u>large reservoir of NH_4^+ ions</u> in the solution ensures that nearly all the added OH^- ions are removed.
  - Hence $[OH^-]$ in the solution changes very little and the pH is kept approximately constant.

■● Exercise 4 ●■ [N2003/I/33]

Which of the following could act as buffer solutions?

✓ 1 $NaHCO_3$ and Na_2CO_3
WB (CO_3^{2-}) & conj acid (HCO_3^-)

2 CH_3CO_2H and $NaCl$
WA (CH_3COOH) but no conj base

3 HNO_3 and $NaNO_3$
↓ strong acid.

11 pH Calculations involving Buffer Solutions

11.1 The relationship between pH, pK_a and composition of an acidic buffer

- Consider a buffer solution containing a weak acid HA and a salt of the acid Na^+A^-.

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

conc./mol dm^{-3}	HA(aq) ⇌	H^+(aq) +	A^-(aq)
initial	C_o	–	D_o
change	$-y$	$+y$	$+y$
equilibrium	$C_o - y$ $\approx C_o$	y	$D_o + y$ $\approx D_o$

- HA, being a weak acid, undergoes partial dissociation in the solution. The dissociation of HA is further suppressed by the presence of A^- ions from the complete dissociation of Na^+A^-. <u>Hence at equilibrium, only a very small amount of HA has dissociated</u>.

- Hence **at equilibrium**,

[HA] ≈ initial [HA]	**[A$^-$] ≈ initial [A$^-$]**	**[H$^+$] ≠ [A$^-$]**
In the solution, all the HA molecules can be assumed to remain undissociated.	In the solution, all the A^- ions can be assumed to come from Na^+A^-.	• In the solution, due to the presence of A^- from Na^+A^-, $[H^+] \neq [A^-]$. • *If the solution contains <u>only</u> the weak acid HA (i.e. Na^+A^- is absent), then $[H^+] = [A^-]$.*

- At equilibrium,

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

Taking logarithms to base ten,

$$\lg K_a = \lg [H^+] + \lg \left(\frac{[A^-]}{[HA]}\right)$$

Multiplying by –1,

$$-\lg K_a = -\lg [H^+] - \lg \left(\frac{[A^-]}{[HA]}\right)$$

Substituting pH = $-\lg [H^+]$ and pK_a = $-\lg K_a$,

$$pK_a = pH - \lg \left(\frac{[A^-]}{[HA]}\right)$$

- Rearranging the above expression gives the following expression:

$$\boxed{\mathbf{pH = pK_a + \lg \left(\frac{[A^-]}{[HA]}\right)} \text{ conj base} \qquad \text{or} \qquad \mathbf{pH = pK_a + \lg \left(\frac{[salt]}{[acid]}\right)}}$$

The above expression is called the **Henderson-Hasselbalch equation** for a buffer solution consisting of a weak acid and its salt.

- The **Henderson-Hasselbalch equation** can be used to calculate the following:
  - the pH of a buffer solution,
  - how much acid or salt is needed to make a buffer solution of required pH,
  - the effect on the pH of a buffer solution when a small amount of acid or base is added.

11.2 The relationship between pH, pK_b and composition of a basic buffer

- Consider an alkaline buffer solution containing NH_3 and NH_4Cl.

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- In a similar manner as that in **Section 11.1**, the following expression can be derived.

$$\boxed{\mathbf{pOH = pK_b + \lg \left(\frac{[NH_4^+]}{[NH_3]}\right)} \text{ conj acid.} \qquad \text{or} \qquad \mathbf{pOH = pK_b + \lg \left(\frac{[salt]}{[base]}\right)}}$$

The above expression is called the **Henderson-Hasselbalch equation** for a buffer solution consisting of a weak base and its salt.

11.3 Calculating the pH of buffer solutions

■● Worked Example 18 ●■

Calculate the pH of a solution containing 0.50 mol dm^{-3} of methanoic acid, HCOOH, and 2.5 mol dm^{-3} of potassium methanoate, $HCOO^-K^+$. K_a for HCOOH = 1.6 x 10^{-4} mol dm^{-3}.

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

$[H^+] = \underline{K_a [HCOOH]}$

Solution

$HCOO^-K^+(aq) \longrightarrow HCOO^-(aq) + K^+(aq)$

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

The given solution is an acidic buffer.

For this acidic buffer, $pH = pK_a + \lg\left(\frac{[HCOO^-]}{[HCOOH]}\right) = -\lg(1.6 \times 10^{-4}) + \lg\left(\frac{2.5}{0.50}\right) = \underline{4.49}$

■● Worked Example 19 ●■

Calculate the pH of a solution that is formed by mixing equal volumes of 0.40 mol dm^{-3} $NH_3(aq)$ and 0.20 mol dm^{-3} $NH_4Cl(aq)$. The pK_b of NH_3 is 4.75.

Solution

Let V dm^3 be the volume of each solution, $NH_3(aq)$ and $NH_4Cl(aq)$, used.

At equilibrium in the resultant solution,

$[NH_3] \approx$ initial $[NH_3]$ in the solution after mixing = $\frac{0.40 \times V}{V+V} = \frac{0.40V}{2V} = 0.20$ mol dm^{-3}

$[NH_4^+] \approx$ initial $[NH_4^+]$ in the solution after mixing = $\frac{0.20 \times V}{V+V} = \frac{0.20V}{2V} = 0.10$ mol dm^{-3}

The resultant solution is a basic buffer.

For this buffer solution, $pOH = pK_b + \lg\left(\frac{[NH_4^+]}{[NH_3]}\right) = 4.75 + \lg\left(\frac{0.10}{0.20}\right) = 4.45$

$pH = pK_w - pOH = 14 - 4.45 = 9.55$

■● Worked Example 20 ●■

Calculate the pH of a 1 dm^3 solution prepared by mixing 0.04 mol of NaOH and 0.10 mol of CH_3COOH. The pK_a of CH_3COOH is 4.74.

Solution

Upon mixing, an acid-base reaction occurs: $CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$

Since initial $n(CH_3COOH) > n(OH^-)$ added, some CH_3COOH remains unreacted and the resultant mixture contains both CH_3COOH and CH_3COO^- $\Rightarrow$ an acidic buffer is formed

After mixing,

$n(CH_3COOH)$ left = initial $n(CH_3COOH) - n(CH_3COOH)$ reacted = 0.10 – 0.04 = 0.06 mol

$n(CH_3COO^-) = n(OH^-)$ added = 0.04 mol

$\therefore [CH_3COOH] = 0.06$ mol dm^{-3} and $[CH_3COO^-] = 0.04$ mol dm^{-3}

For this acidic buffer, $pH = pK_a + \lg\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) = 4.74 + \lg\left(\frac{0.04}{0.06}\right) = 4.564 = \underline{4.56}$

11.4 Calculating the change in pH of buffer solutions

■● Worked Example 21 ●■

Calculate the change in pH when 0.001 mol of solid potassium hydroxide is added to 1 dm^3 of water.

Solution

Since water is neutral, pH of water = 7.0 (at 298 K)

After addition of KOH,
$[OH^-]$ in the solution = 1.00×10^{-3} mol dm^{-3}

pOH = $-\lg [OH^-] = -\lg (1.00 \times 10^{-3}) = 3.00$

At 298 K, pH = 14 – pOH = 14 – 3.00 = 11.0

Change in pH = final pH – original pH = 11.0 – 7.0 = $\underline{+ 4.00} \Rightarrow$ increase in pH of 4.00 units

■● Worked Example 22 ●■

Calculate the change in pH when 0.001 mol of solid potassium hydroxide is added to 1 dm^3 of the buffer solution prepared in Worked Example 20.

Solution

pH of the buffer solution = 4.564
Initial amount of CH_3COOH present in the buffer = 0.06 mol
Initial amount of CH_3COO^- present in the buffer = 0.04 mol

Upon the addition of OH^-: $CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$

$n(CH_3COOH)$ left = initial $n(CH_3COOH)$ – $n(CH_3COOH)$ reacted
= 0.06 – 0.001 = 0.0590 mol

$n(CH_3COO^-)$ present = initial $n(CH_3COO^-)$ + $n(CH_3COO^-)$ formed
= 0.04 + 0.001 = 0.0410 mol

At equilibrium in the resultant solution after reaction,
$[CH_3COOH] \approx [CH_3COOH]$ left after reaction = 0.0590 mol dm^{-3}
$[CH_3COO^-] \approx [CH_3COO^-]$ present after reaction = 0.0410 mol dm^{-3}

The resultant solution is an acidic buffer.

$$\text{For this acidic buffer, pH} = pK_a + \lg \left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$= 4.74 + \lg \left(\frac{0.0410}{0.0590}\right) = 4.582$$

Change in pH = final pH – original pH = 4.582– 4.564 = $\underline{+0.018} \Rightarrow$ increase in pH of 0.018 units

- Note: Compare the answers for Worked Examples 21 and 22.

Worked E.g.	Solution	Original pH	pH after addition of 0.001 mol KOH	Change in pH
21	1 dm^3 of water	7.0	11.0	+ 4.00
22	1 dm^3 of buffer	4.564	4.582	+0.018

There is a significantly smaller change in pH when the same small amount of KOH is added to a buffer solution than to water.

12 More on Buffer Solutions

12.1 Buffer capacity and effective buffer range

(a) Buffer capacity

- The buffer capacity of a buffer is **a measure of its ability to resist pH change** and depends on both the absolute and relative component concentrations.

- In absolute terms, the more concentrated the components of a buffer, the greater the buffering capacity.

Consider the following two acidic buffer solutions.

Buffer	Components in a 1 dm^3 solution	pH
❶	1 mol dm^{-3} CH_3COOH and 1 mol dm^{-3} $CH_3COO^-Na^+$	4.74
❷	0.1 mol dm^{-3} CH_3COOH and 0.1 mol dm^{-3} $CH_3COO^-Na^+$	4.74

In this case, buffer ❶ has greater buffer capacity than buffer ❷.

- Adding the same amount of H^+ ions (or OH^- ions) to each buffer will produce a smaller pH change in buffer ❶ than buffer ❷.
- A larger amount of H^+ ions (or OH^- ions) will have to be added to buffer ❶ than buffer ❷ to obtain the same pH change.

- Buffer capacity is also affected by the relative concentrations of the buffer components.

- For a given addition of acid or base, the buffer component ratio (i.e. $\frac{[\text{salt}]}{[\text{acid}]}$ or $\frac{[\text{salt}]}{[\text{base}]}$) changes less (and hence the pH changes less) when the component concentrations are similar than when they are different.

- It follows that a buffer has **maximum buffer capacity** when $\frac{[\text{salt}]}{[\text{acid}]} = 1$ for an acidic buffer or when $\frac{[\text{salt}]}{[\text{base}]} = 1$ for an alkaline buffer.

Acidic buffer	Alkaline buffer
When $\frac{[\text{salt}]}{[\text{acid}]} = 1$, $\text{pH} = \text{p}K_a + \lg\left(\frac{[\text{salt}]}{[\text{acid}]}\right)$ $= \text{p}K_a + \lg 1$ $= \text{p}K_a$	When $\frac{[\text{salt}]}{[\text{base}]} = 1$, $\text{pOH} = \text{p}K_b + \lg\left(\frac{[\text{salt}]}{[\text{base}]}\right)$ $= \text{p}K_b + \lg 1$ $= \text{p}K_b$
Hence maximum buffer capacity is attained at $\boxed{\textbf{pH} = \textbf{p}K_a}$ [salt] = [acid]	Hence maximum buffer capacity is attained at $\boxed{\textbf{pOH} = \textbf{p}K_b}$ [salt] = [base]

- A buffer solution is most effective in resisting changes in pH when the following requirements are met:

  ① The number of moles of both the weak acid (or weak base) and its salt are large relative to that of the acid or base to be added to the buffer solution.

  ② The weak acid (or weak base) to salt concentration ratio is close to 1:1.

(b) Effective buffer range

- The effective buffer range is the pH range over which the buffer acts effectively in keeping pH approximately constant, and it is related to the relative component concentrations.

- In practice, an acidic buffer is effective provided: $0.1 \leq \frac{[\text{salt}]}{[\text{acid}]} \leq 10$

When $\frac{[\text{salt}]}{[\text{acid}]} = 0.1$	**pH** = pK_a + lg 0.1 = **pK_a – 1**
When $\frac{[\text{salt}]}{[\text{acid}]} = 10$	**pH** = pK_a + lg 10 = **pK_a + 1**

- This means that the effective buffer range is from pH = (pK_a – 1) to pH = (pK_a + 1).

Effective buffer range of an acidic buffer = **pK_a ± 1**

12.2 Effect of dilution on the pH of buffer

- For an acidic buffer containing a weak acid HA and its salt Na^+A^-, pH = pK_a + lg $\left(\frac{[A^-]}{[HA]}\right)$.

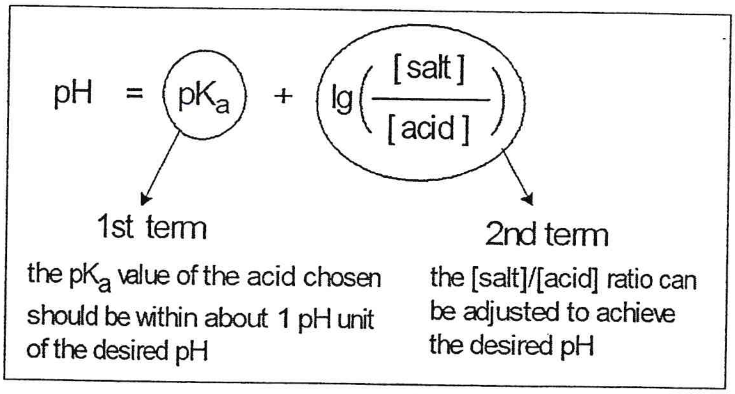
- From the equation, it can be seen that diluting the buffer has no effect on the pH because [HA] and $[A^-]$ are reduced to the same extent (i.e. the value of $\frac{[A^-]}{[HA]}$ is unchanged).

- Similarly, for an alkaline buffer containing a weak base B and its salt BH^+, dilution has no effect on pOH (and hence pH) since [B] and $[BH^+]$ are reduced to the same extent.

- However, note that dilution has a marked effect on buffer capacity. It reduces the ability of the buffer to cope with contaminating acid and base.

12.3 Preparing a buffer solution

- Consider the Henderson-Hasselbalch equation as applied to acidic buffers.



$$\text{pH} = \text{p}K_a + \lg\left(\frac{[\text{salt}]}{[\text{acid}]}\right)$$

- There are two terms on the right-hand side, which determine the final pH of the solution.

- The first term is pK_a, whose value is responsible for the 'coarse selection' of pH.

- The second term involves the ratio [salt]/[acid] and provides the 'fine tuning' to the final desired pH.

■● Worked Example 23 ●■

What mass of sodium ethanoate must be added to 1 dm^3 of 1.0 mol dm^{-3} ethanoic acid to produce a buffer of pH 4.5? The pK_a of ethanoic acid is 4.8.

Solution

$$pH = pK_a + \lg \left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) \quad \text{(Acidic buffer)}$$

$$4.5 = 4.8 + \lg ([CH_3COO^-]/1)$$

$[CH_3COO^-]$ = $10^{-0.3} = 0.501\ mol\ dm^{-3}$

Amount of $CH_3COO^-Na^+$ needed = Amount of CH_3COO^- = $(1\ dm^3)(0.501\ mol\ dm^{-3}) = 0.501\ mol$

Molar mass of $CH_3COO^-Na^+$ = 82 g mol^{-1}
Hence mass of $CH_3COO^-Na^+$ to be added = $(0.501)(82) = 41.1$ g.

12.4 Blood as a biological buffer

- The pH of human blood is maintained between 7.35 and 7.45 even though the concentration of carbon dioxide and thus carbonic acid in the blood varies greatly.

- The pH of blood must be kept approximately constant so that the enzymes in the blood can function. Enzymes only work over a narrow range of pH. Death may result if the pH falls below 6.8 or rises above 7.8.

- The control of pH in the blood is achieved using different buffers: the **H_2CO_3/HCO_3^- buffer**, the **$H_2PO_4^-/HPO_4^{2-}$ buffer**, and **plasma proteins**.

The H_2CO_3/HCO_3^- buffer in blood

- One of the important buffers in human blood is made up of carbonic acid (H_2CO_3) and the hydrogencarbonate ion (HCO_3^-):

$$\boxed{H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)}$$

The carbonic acid in the blood originates from dissolved carbon dioxide. The latter enters the blood from tissues as the by-product of metabolic reactions:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

- If the concentration of H^+ ions in the blood increases (e.g. from lactic acid produced from exercise), the HCO_3^- present reacts with the additional H^+ ions and thus the pH remains virtually unchanged.

$$\boxed{\mathbf{HCO_3^-(aq) + H^+(aq) \longrightarrow H_2CO_3(aq)}}$$

- If the concentration of OH^- ions in the blood increases, H_2CO_3 present reacts with the additional OH^- ions and thus a constant pH is maintained.

$$\boxed{\mathbf{H_2CO_3(aq) + OH^-(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)}}$$

13 Acid-Base Titration and Indicators

13.1 Equivalence point and end-point

- The aim of any titration is to determine the volumes of two solutions which just react with each other completely. This occurs at the equivalence point and it marks the completion of the titration.

- In an acid-base titration, the **equivalence point** is the stage reached when the amount of acid needed to react with the amount of base is precisely that required by the stoichiometric equation.

- In practice, the completion of an acid-base titration can be detected by a distinct colour change brought about by the use of a suitable indicator. The point during titration at which this distinct colour change occurs is called the **end-point** of the titration.

- The use of a suitable indicator will ensure that the end-point of the titration is very close to the equivalence point of the titration.

13.2 Use of indicators during acid-base titrations

- During an acid-base titration, there is a change in pH as the base is added to the acid or vice versa. This change in pH during the course of a titration depends largely upon the strengths of the acid and base used.

- As shown in the table below, there are four main types of acid-base titrations but only three of them can employ suitable indicators to help identify the equivalence point.

- This is essentially because, for the equivalence point of an acid-base titration to be identifiable using an indicator, the pH near the equivalence point must change sharply by several units. This does not occur in the case of a weak acid-weak base titration.

- Types of acid-base titration

Type of titration	Acid	Base	Region of marked pH change	Suitable indicator
strong acid – strong base	$HCl(aq)$	$NaOH(aq)$	4 – 10	methyl orange screened methyl orange thymol blue thymolphthalein phenolphthalein
strong acid – weak base	$HCl(aq)$	$NH_3(aq)$	3.5 – 6.5	methyl orange screened methyl orange
weak acid – strong base	$CH_3COOH(aq)$	$NaOH(aq)$	7.5 – 10.5	thymol blue thymolphthalein phenolphthalein
weak acid – weak base	$CH_3COOH(aq)$	$NH_3(aq)$	no marked change	no suitable indicator

13.3 Acid-base indicators

- Acid-base indicators such as thymolphthalein and methyl orange are substances which change colour according to the hydrogen ion concentration of the solution to which they are added. Consequently, they are used to test for acidity and alkalinity. They are also used to detect the end point in acid-base titrations.

- Acid-base indicators are usually weak acids or weak bases. When dissolved in water, they dissociate slightly forming ions.

(a) Indicators as weak acids

- Consider an indicator which is a weak acid with the general formula HIn. In aqueous solution, the following equilibrium is established:

$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$ acid — conjugate base **colour A** — **colour B**	• The equilibrium constant expression for the reaction is given in the left-hand box below. • It can be used to derive the equation which shows the relationship between pH and $\frac{[In^-]}{[HIn]}$.
$K_{In} = \frac{[H^+][In^-]}{[HIn]}$	$pH = pK_{In} + \lg\left(\frac{[In^-]}{[HIn]}\right)$

- When the indicator is added to an acidic solution, the relatively high $[H^+]$ in the solution causes the equilibrium position of the above reaction to shift to the left.
  ⇒ Colour A will be observed since $[HIn] > [In^-]$.

- When the indicator is added to an alkaline solution, the OH^- ions in the solution react with the H^+ ions from HIn and this causes the equilibrium position to shift to the right.
  ⇒ Colour B will be observed since $[In^-] > [HIn]$.

- Hence the indicator colour that is observed depends on the relative proportions of HIn and In^-. The relative proportions of HIn and In^- in turn is affected by the $[H^+]$ in the solution.

(b) The pH range of an acid-base indicator

- Each acid-base indicator has a pH range over which it changes colour. The colour change of an indicator is due to the change from one coloured form to another.

- Typically, the human eye sees

colour A when $\frac{[HIn]}{[In^-]} \geq 10$	**colour B** when $\frac{[In^-]}{[HIn]} \geq 10$

- Consider a titration experiment in which an indicator HIn(aq) is added to an acid solution in a conical flask and this solution is then titrated against a base placed in the burette. In this case, the indicator will be changing from **colour A** to **colour B** during the titration. This colour change can be summarised as follows:

$[HIn]/[In^-]$	Remark	pH
$[HIn]/[In^-] > 10$	**Colour A** is observed.	
$[HIn]/[In^-] = 10$	Change of colour starts though **colour A** still dominates.	$pH = pK_{In} - 1$
$[HIn]/[In^-] = 1$	Mid-point of colour change. **Observed colour: colour A + colour B**	$pH = pK_{In}$
$[HIn]/[In^-] = 0.1$	Change of colour ends and **colour B** now dominates.	$pH = pK_{In} + 1$
$[HIn]/[In^-] < 0.1$	**Colour B** is observed.	

- From the above table, the **colour-change interval** is accordingly from

  $pH = pK_{In} - 1$ to **$pH = pK_{In} + 1$** (i.e. over approximately two pH units)

$$\boxed{\textbf{pH range} \text{ of an indicator} = pK_{In} \pm 1}$$

- The pH ranges of selected indicators are shown in the table below:

Indicator	pK_{In} at 25 °C	approximate pH range	colour in 'acid' solution	colour in 'basic' solution	colour at end-point
methyl orange	3.7	3.1 – 4.4	red	yellow	orange
screened methyl orange	–	3.1 – 4.4	violet	green	grey
bromothymol blue	7.0	6.0 – 7.6	yellow	blue	green
thymol blue	8.9	8.0 – 9.6	yellow	blue	green
thymolphthalein	9.9	9.3 – 10.5	colourless	blue	light blue (if titrant is alkali) colourless (if titrant is acid)
phenolphthalein	9.2	8.3 – 10.0	colourless	pink	light pink (if titrant is alkali) colourless (if titrant is acid)

(c) The pH at the end-point of a titration

- For the titration experiment described in **(b)**, the end-point of the titration is reached when the indicator used gives a distinct colour change, i.e. from colour A to a colour that results from the combination of colour A and colour B.

- This end-point is reached when the indicator colour observed is a combination of the two extreme colours and this occurs when:

$[HIn(aq)] = [In^-(aq)]$	$\Rightarrow pH = pK_{In} + \lg\left(\frac{[In^-]}{[HIn]}\right) = pK_{In} + \lg 1 = pK_{In}$

- Hence at the end-point of the titration, $\boxed{pH = pK_{In}}$. The pH at the end-point is generally the centre of the pH range of the indicator used.

- **Note:** The end-point is a property of the indicator and does not necessarily show that the reaction between acid and base is complete.

(d) Choice of indicators

- Essential characteristics of a suitable indicator:
  ① The colour change of the indicator must occur when the correct volume of titrant is added from the burette, i.e. the pH range over which the colour change takes place must be such as to indicate when the reaction (as shown by the equation) is complete.
  ② The indicator must give a sharp end-point in the titration, i.e. it must change colour distinctly upon the addition of one drop of the titrant from the burette.

- The choice of an indicator for an acid-base titration depends on the
  - type of titration carried out and
  - pH range of the indicator

- The ideal situation would be to choose an indicator such that the end-point of the titration coincides exactly with the equivalence point of the titration. This occurs if the chosen indicator has a pK_{In} value which is identical to the pH of the resulting solution at the equivalence point. In other words,

A suitable indicator is one where its **pH range coincides with the region of rapid pH change** in the titration curve (i.e. the pH range of the indicator must fall on the vertical portion of the titration curve).

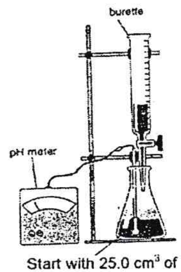
14 Acid-Base Titration Curves

14.1 Types of titration curves

- A titration curve is a graph of pH against volume of an acid or base.
- It shows how the pH of an acid (or base) solution in a conical flask changes as it is neutralised by the addition of a base (or acid) from a burette.
- There are 4 main types of titration curves based on the 4 types of acid-base titration.

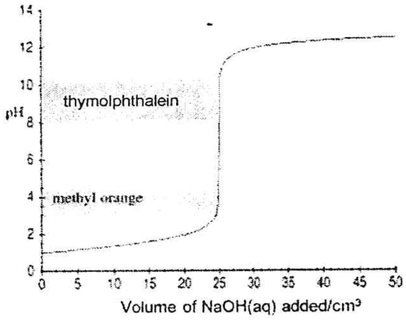
Strong acid – Strong base Titration

Suitable indicators:
phenolphthalein,
methyl orange, etc.



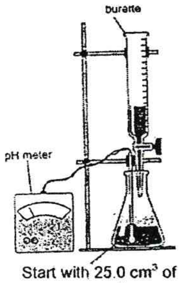
Start with 25.0 cm^3 of 0.10 mol dm^{-3} HCl in the conical flask

Titration of 25.0 cm^3 of 0.10 mol dm^{-3} HCl(aq) against 0.10 mol dm^{-3} NaOH(aq)



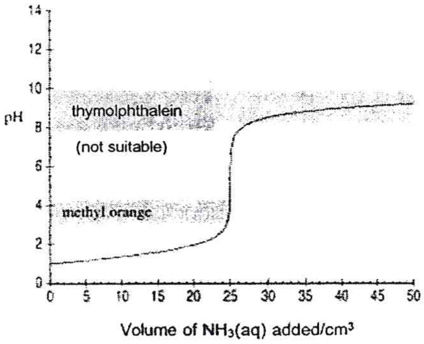
Strong acid – Weak base Titration

Suitable indicator:
methyl orange



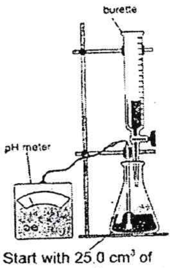
Start with 25.0 cm^3 of 0.10 mol dm^{-3} HCl in the conical flask

Titration of 25.0 cm^3 of 0.10 mol dm^{-3} HCl(aq) against 0.10 mol dm^{-3} NH_3(aq)



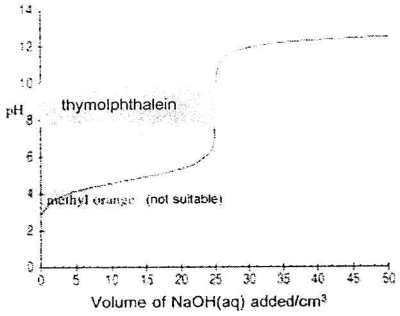
Weak acid – Strong base Titration

Suitable indicator:
phenolphthalein



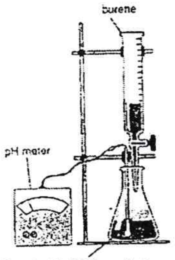
Start with 25.0 cm^3 of 0.10 mol dm^{-3} CH_3COOH in the conical flask

Titration of 25.0 cm^3 of 0.10 mol dm^{-3} CH_3COOH(aq) against 0.10 mol dm^{-3} NaOH(aq)



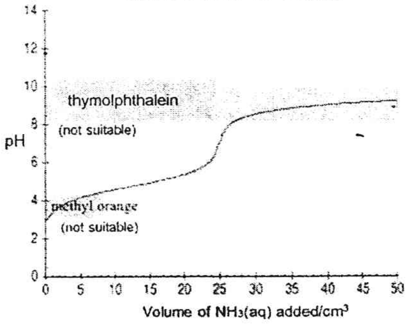
Weak acid – Weak base Titration

No suitable indicator.



Start with 25.0 cm^3 of 0.10 mol dm^{-3} CH_3COOH in the conical flask

Titration of 25.0 cm^3 of 0.10 mol dm^{-3} CH_3COOH(aq) against 0.10 mol dm^{-3} NH_3(aq)



- Important parts of a titration curve

1 initial pH

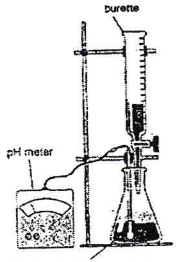
2 (for SA-WB and WA-SB titrations only) region where solution is a buffer solution
  - pH of solution at maximum buffering capacity

3 region near the equivalence point (i.e. region of drastic pH change)
  - pH of solution at equivalence point

4 region after the equivalence point
  - final pH of solution

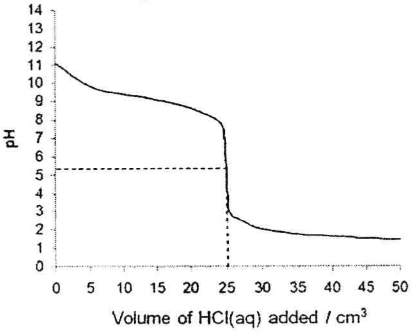
Weak base – Strong acid Titration

Note: The base is in the conical flask.



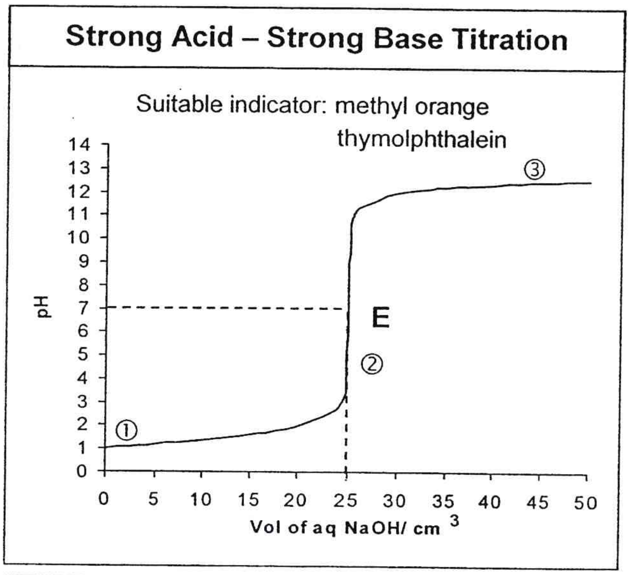
Start with 25.0 cm^3 of 0.10 mol dm^{-3} NH_3 in the conical flask

Titration of 25.0 cm^3 of 0.10 mol dm^{-3} NH_3(aq) against 0.10 mol dm^{-3} HCl(aq)



14.2 Titration curve of a strong acid–strong base titration

The graph below shows the change in pH of the reaction mixture when 0.100 mol dm^{-3} of NaOH was added to 25.0 cm^3 of 0.100 mol dm^{-3} HC*l*: ① not a buffer solution. ② widest range of indicators that can be used.



① The initial pH is low because the acid used is a strong acid.

pH remains low from **0.00** to 25.00 cm^3 as the solution still contains strong acid that has not yet been neutralised.

② This is the region of rapid pH change.

- There is a sudden increase in pH over the equivalence point *(pH 4 to pH 10)* when one or two drops of base are added from the burette.
- At the equivalence point **E**, the pH of the resultant solution containing NaC*l*(aq) is **7**. neutral at 25°C

③ After **E**, excess NaOH is added. The titration curve flattens out at a high pH value since the base used is a strong base.
(pH<13 due to dilution by titrant added)

> **Note:** The equivalence point **E** is found by extrapolating the linear portions of the titration curve (①, ② & ③) and taking the midpoint between the two intersections.

Calculation of pH at various parts of the titration curve:

(i) *Initial pH = pH of strong acid*

Solution is an aqueous solution of strong acid.

$[H^+] = [HCl(aq)]$

$= 0.10$ mol dm^{-3}

$pH = -\lg [H^+] = -\lg (0.10) = 1.00$

(ii) *pH of mixture when 8.00 cm^3 of NaOH(aq) is added. (Before equivalence point E)*

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

$n(OH^-) = 0.008 \times 0.10 = 0.0008$ mol

$n(H^+)_{reacted} = 0.0008$ mol

$n(H^+)_{initial} = 0.025 \times 0.10 = 0.0025$ mol

$\Rightarrow$ H$^+$ is in excess.

$n(H^+)\text{ left} = n(H^+)_{initial} - n(H^+)_{reacted}$

$= 0.0025 - 0.0008 = 0.0017$ mol

Volume of reaction mixture = 25.0 + 8.00 cm^3

= 33.0 cm^3

$[H^+] = \frac{n(H^+)}{V} = \frac{0.0017}{0.033} = 0.05152$ mol dm^{-3}

$pH = -\lg [H^+] = -\lg (0.05152) = 1.29$

(iii) *pH at equivalence point (point E)*

At equivalence point, **HC*l*** has been exactly neutralised by NaOH.

The resultant solution is NaC*l*(aq).

Since Na$^+$ and C*l*$^-$ do not hydrolyse in water, the resultant solution is neutral.

At 25 °C, pH of a neutral solution is 7.

(iv) *pH of mixture when 32.00 cm^3 of NaOH(aq) is added. (After equivalence point E)*

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

$n(OH^-) = 0.032 \times 0.10 = 0.0032$ mol

$n(H^+)_{initial} = 0.025 \times 0.10 = 0.0025$ mol

$\Rightarrow$ OH$^-$ is in excess.

$n(OH^-)_{excess} = n(OH^-) - n(H^+)_{initial}$

$= 0.0032 - 0.0025 = 0.0007$ mol

Volume of reaction mixture = 25.0 + 32.00 cm^3

= 57.0 cm^3

$[OH^-] = \frac{n(OH^-)}{V} = \frac{0.0007}{0.057} = 0.01228$ mol dm^{-3}

$pOH = -\lg [OH^-] = 1.911$

$pH = 14 - pOH = 12.1$

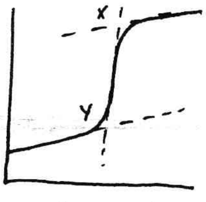
■● Exercise 5 ●■ [N2012/I/11]

A 1 dm^3 solution was made by mixing 0.0040 mol of HC*l*(aq) and 0.0025 mol of NaOH(aq).

What was the pH of the resulting solution?

$pH = -\lg (0.0015)$
$= 2.82$

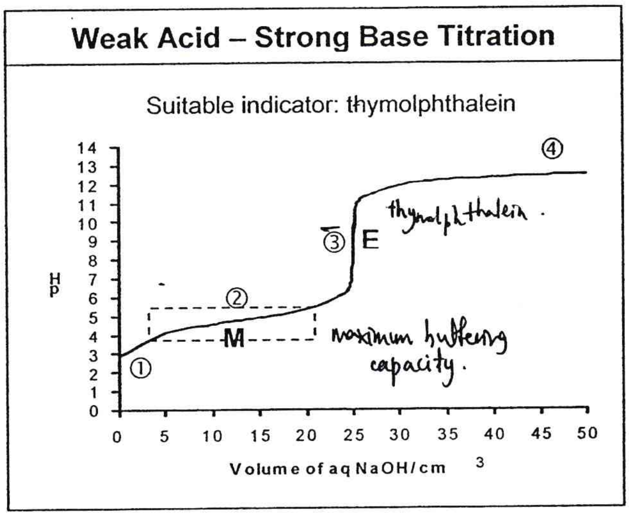
A 2.19 B 2.40 C 2.60 [✓ D] 2.82



- measure length of XY
- midpoint of XY is equivalence point.

14.3 Titration curve of a weak acid–strong base titration

The graph below shows the change in pH of the reaction mixture when 0.100 mol dm^{-3} of NaOH was added to 25.0 cm^3 of 0.100 mol dm^{-3} CH_3COOH (K_a of $CH_3COOH = 1.8 \times 10^{-5}$ mol dm^{-3}):



① The initial pH is not very low (1 < pH < 7) since a weak acid is used. *(pH may be calculated using the formula $[H^+] = \sqrt{K_a C_o}$).*

② Change in pH is fairly constant due to the formation of an <u>effective buffer</u> when large amounts of the weak acid and its salt are present.

***pH at ½ equiv pt* (M)** *(where [HA]=[A⁻])* **= p*K*a**

③ The region of rapid pH change is <u>shorter</u> and occurs at a <u>higher pH range</u> than that for a SA-SB titration.

At equivalence point **E**,

- CH_3COOH is exactly neutralised by NaOH
- The resultant solution is $CH_3COO^-Na^+(aq)$.
- <u>pH > 7</u> as CH_3COO^- hydrolyses in water to give OH^-.

④ After **E**, the base is in excess. The titration curve flattens out at a high alkaline pH value (e.g. pH 12.5) since the excess base present is a strong base.

Calculation of pH at various parts of the titration curve:

(i) *Initial pH = pH of weak acid*

Solution is <u>an aqueous solution of weak acid</u>.

$[H^+] = \sqrt{K_a C_o} = \sqrt{1.8 \times 10^{-5} \times 0.100}$

$= 1.342 \times 10^{-3}$ mol dm^{-3}

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

$= -\lg (1.342 \times 10^{-3})$

$= 2.87$

(ii) *pH of mixture when 8.00 cm³ of NaOH(aq) is added. (region ②)*

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

$n(CH_3COO^-) = n(OH^-) = 0.008 \times 0.10 = 0.0008$ mol

$n(CH_3COOH)_{reacted} = 0.0008$ mol

$n(CH_3COOH)_{left} = n(CH_3COOH)_{initial} - n(CH_3COOH)_{reacted}$

$= (0.025)(0.10) - (0.008)(0.10) = 0.0017$ mol

The resultant mixture is a **<u>buffer</u>** containing CH_3COOH and CH_3COO^-.

$pH = pK_a + \lg\frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a + \lg(\frac{0.0008/V}{0.0017/V})$

$= -\lg (1.8 \times 10^{-5}) + \lg (0.4706)$

$= 4.745 - 0.3272 = 4.42$

(iii) *pH at half-equivalence point (point M)*

Half-equivalence point is the <u>point at which half the volume of NaOH(aq) needed for neutralisation is added</u>.

At this point, CH_3COOH is half–neutralised.

$n(CH_3COOH) = n(CH_3COO^-)$

Hence, $[CH_3COOH] = [CH_3COO^-]$

$pH = pK_a + \lg\frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a + \lg (1) = pK_a = 4.74$

(Note: pH at half-equivalence point = p*K*a)

(iv) *pH at equivalence point (point E)*

At equivalence point, the mixture present is a solution of <u>$CH_3COO^-Na^+$</u>.

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

$n(CH_3COO^-) = 0.025 \times 0.10 = 0.0025$ mol

Volume of reaction mixture = 25.0 + 25.0 cm^3

= 0.050 dm^3

$[CH_3COO^-] = \frac{0.0025}{0.050} = 0.050$ mol dm^{-3}

$[OH^-] = \sqrt{\frac{K_w}{K_a} \times C_o} = \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \times 0.050}$

$= 5.270 \times 10^{-6}$ mol dm^{-3}

$pOH = -\lg [OH^-] = 5.278$, $pH = 14 - pOH = 8.72$

(v) *pH of mixture when 32.00 cm³ of NaOH(aq) is added. (region ④)*

$n(OH^-)$ added $= 0.032 \times 0.10 = 0.00320$ mol, $n(CH_3COOH)$ present initially $= 0.025 \times 0.10 = 0.0025$ mol

$n(OH^-)$ in excess $= 0.0032 - 0.0025 = 0.0007$ mol, $[OH^-] = \frac{0.0007}{0.025 + 0.032} = 0.01228$ mol dm^{-3}

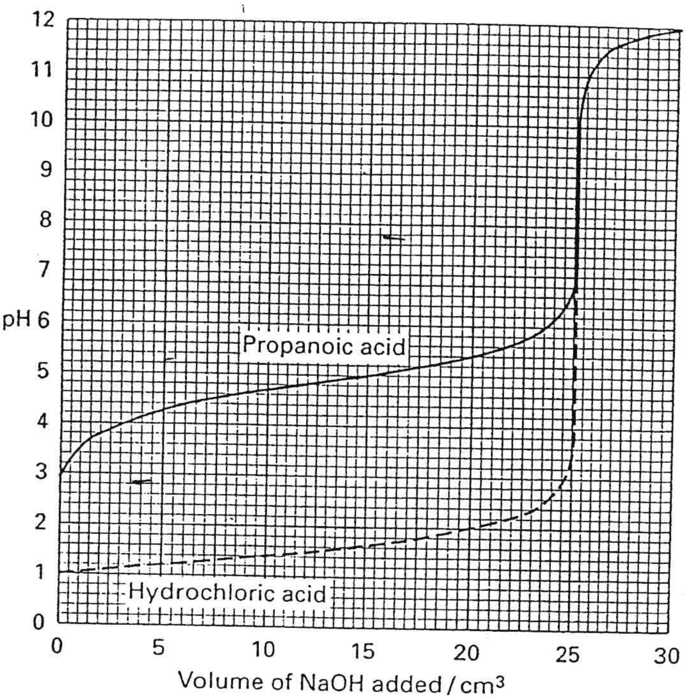
$pOH = -\lg [OH^-] = 1.911$, $pH = 14 - pOH = 12.1$

Worked Example 24

The graphs on the right show the change in pH of the reaction mixture when 0.10 mol dm^{-3} NaOH(aq) is gradually added separately to 25.0 cm^3 of 0.10 mol dm^{-3} CH_3CH_2COOH(aq) and 25.0 cm^3 of 0.10 mol dm^{-3} HC*l*(aq).

(a) State two reasons why the dotted graph is due to HC*l*.

(b) Determine the K_a of propanoic acid using relevant data from the graph.



Solution

(a) Firstly, HC*l*(aq) is a strong acid and ionises completely in aqueous solution.

Thus its initial pH = –lg (0.10) = 1.0

Secondly, HC*l* reacts with NaOH to form NaC*l* which contains ions that do not hydrolyse in water. Thus, for the titration involving HC*l*, pH at equivalence point = 7 which corresponds to the dotted graph.

(b) Method 1: **pH at half-equivalence point = pK_a**

For a weak acid–strong base titration, pH at ½ equivalence (or neutralisation) point = pK_a. Hence pK_a can be found by finding the pH at ½ equivalence point which is the point when ½ the volume of titrant needed for equivalence point is added.

Since volume needed for complete neutralisation is 25.00 cm^3, half-equivalence point is the point at which 12.50 cm^3 of aq NaOH is added.

From graph,
pH when 12.50 cm^3 of aq NaOH is added = 4.80

Thus pK_a = pH at ½ equivalence point = 4.80

$K_a = 10^{-pK_a} = 10^{-4.8} = 1.58 \times 10^{-5}$ mol dm^{-3}

Method 2: **Initial pH of weak acid**

Let HA represents propanoic acid. $HA \rightleftharpoons H^+ + A^-$

From the graph, initial pH of HA = 2.90

Initial $[H^+] = 10^{-2.90} = 0.001259$ mol dm^{-3}

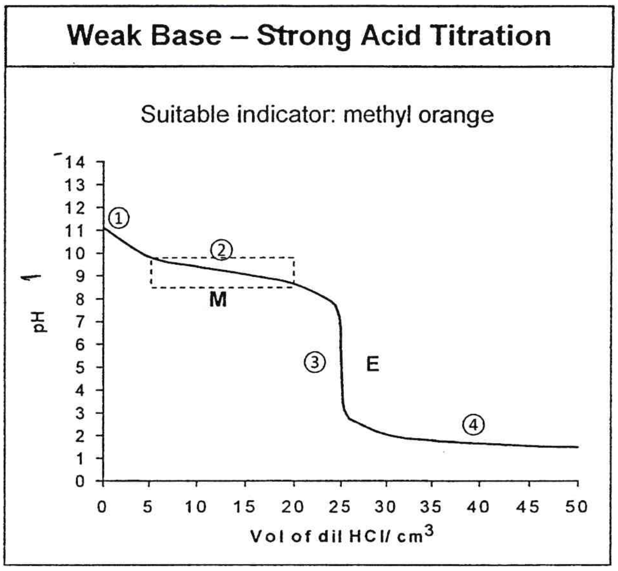
$[A^-] = [H^+] = 0.001259$ mol dm^{-3} and

$[HA] = 0.10 - 0.001259 = 0.09874$ mol dm^{-3}

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} = 1.61 \times 10^{-5} \text{ mol dm}^{-3}$$

14.4 Titration Curve of Weak Base – Strong Acid Reaction

The graph below shows the change in pH of the reaction mixture when 0.100 mol dm^{-3} of HC*l* was added to 25.0 cm^3 of 0.100 mol dm^{-3} NH_3 (K_b of NH_3 = 1.74×10^{-5} mol dm^{-3}).



① The initial pH is not very high (7 < pH < 13) since a weak base is used. *(pOH may be calculated using the formula* $[OH^-] = \sqrt{K_bC_o}$*).*

② Change in pH is fairly constant due to the formation of an <u>effective buffer</u> when large amounts of weak base and its salt are present.

***pOH at ½ Equiv* (pt M)** *(where [B]=[BH$^+$])* = **p*K*$_b$**

③ The region of rapid pH change is <u>shorter</u> and occurs at <u>lower pH range</u> than that for a SA-SB titration.
At equivalence point **E**,

- NH_3 is exactly neutralised by HC*l*
- The resultant solution is NH_4Cl(aq).
- <u>pH < 7</u> as NH_4^+ hydrolyses in water to give H^+.

④ After **E**, the acid is in excess. The titration curve flattens out at a low acidic pH value since the excess acid present is a strong acid.

Calculation of pH at various parts of the titration curve:

(i) *Initial pH = pH of weak base*

Solution is an aqueous solution of <u>weak base.</u>

$[OH^-] = \sqrt{K_bC_o} = \sqrt{1.74 \times 10^{-5} \times 0.100}$

$= 1.319 \times 10^{-3}$ mol dm^{-3}

pOH = –lg [OH$^-$] = –lg (1.319×10^{-3}) = 2.88

pH = 14 – pOH = 11.12

(iii) *pH at half-equivalence point (point M)*

Half-equivalence point is the point at which <u>half the volume of HC*l*(aq) needed for neutralisation is added</u>.

At this point, NH_3 is half–neutralised.

n(NH_3) = n(NH_4^+)

Hence, [NH_3] = [NH_4^+]

pH at half equiv point = pK_a of NH_4^+

pOH at half equiv point = pK_b of NH_3.

$pOH = pK_b + \lg\frac{[NH_4^+]}{[NH_3]} = pK_b + \lg(1) = pK_b = 4.759$

pH = 14 – pOH = 9.24

(ii) *pH of mixture when 14.00 cm^3 of HCl(aq) is added. (region ②)*

$NH_3 + H^+ \rightarrow NH_4^+$

n(NH_4^+) = n(H^+) added = 0.014 x0.10 = 0.0014 mol

n(NH_3) = n(NH_3)$_{initial}$ –n(H^+)

= (0.025)(0.10) – (0.014)(0.10) = 0.0011 mol

The resultant mixture is a <u>buffer</u> containing NH_3 and NH_4^+.

$pOH = pK_b + \lg\frac{[NH_4^+]}{[NH_3]} = pK_b + \lg(\frac{0.0014/V}{0.0011/V})$

= –lg (1.74×10^{-5}) + lg (1.272)

= 4.759 + 0.1047 = 4.864

pH = 14 – pOH = 9.14

(iv) *pH at equivalence point (point E)*

At equivalence point, the mixture present is a solution of <u>NH_4Cl.</u>

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

n(NH_4^+) = 0.025 x 0.10 = 0.0025 mol

Volume of reaction mixture = 25.0 + 25.0 cm^3

= 0.050 dm^3

$[NH_4^+] = \frac{0.0025}{0.050} = 0.050$ mol dm^{-3}

$[H^+] = \sqrt{\frac{K_w}{K_b} \times C_o} = \sqrt{\frac{1.0 \times 10^{-14}}{1.74 \times 10^{-5}} \times 0.050}$

$= 5.361 \times 10^{-6}$ mol dm^{-3}

pH = –lg [H^+] = 5.27

(v) *pH of mixture when 35.00 cm^3 of HCl(aq) is added. (region ④)*

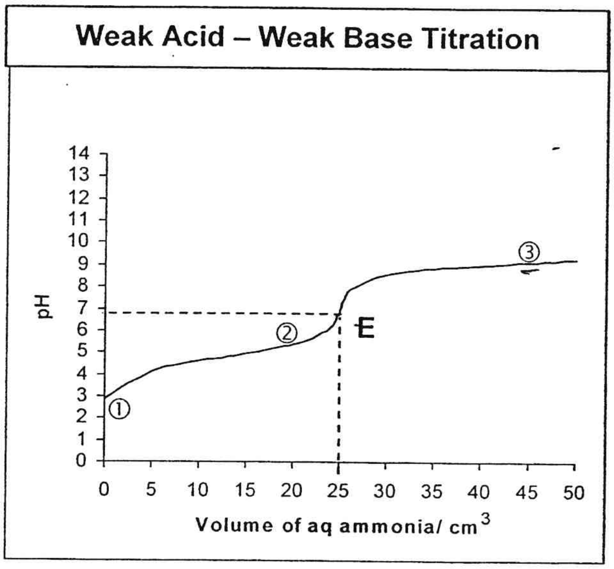
n(H^+) added = 0.035 x 0.10 = 0.00350 mol, n(NH_3) present initially = 0.025 x 0.10 = 0.0025 mol

n(H^+) in excess = 0.0035 – 0.0025 = 0.001 mol, $[H^+] = \frac{0.001}{0.025 + 0.035} = 0.01667$ mol dm^{-3}

pH = –lg [H^+] = 1.78

14.5 Titration Curve of Weak Acid – Weak Base Reaction

The graph below shows the change in pH of the reaction mixture when 0.100 mol dm^{-3} of NH_3 was added to 25.0 cm^3 of 0.100 mol dm^{-3} CH_3COOH:



① Since the acid is weak, the starting pH is a fairly high value.

② There is no straight, vertical section on the graph. This shows that the change in pH at the equivalence point is <u>not as sharp as</u> any of the previous titrations.

- pH at **E** < 7, if K_a of WA > K_b of WB
- pH at **E** > 7, if K_a of WA < K_b of WB

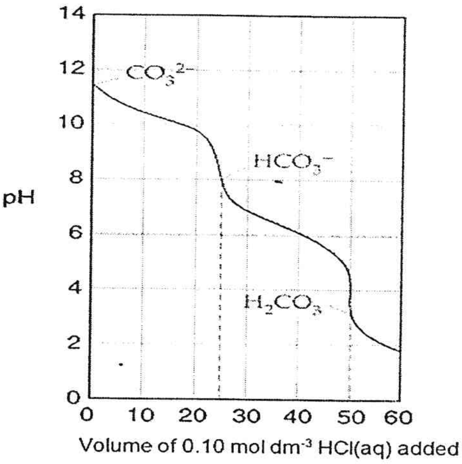
③ Soon after the equivalence point **E** has been passed, the titration curve flattens out at a fairly low alkaline pH value since the excess base present is a weak base.

Note:
There is no suitable indicator for a weak acid–weak base titration as the region of rapid pH change is absent.

14.6 Titration curve of a carbonate-strong acid titration

- Sodium carbonate is a diacidic base.

1	$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$	K_{b1}
2	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$	K_{b2}



- The figure on the right shows how the pH changes during the titration of 25.0 cm^3 of 0.10 mol dm^{-3} $Na_2CO_3(aq)$ with 0.10 mol dm^{-3} $HCl(aq)$. There are <u>two equivalence points</u> in the titration curve.

- The reaction of $Na_2CO_3(aq)$ with $HCl(aq)$ can be represented in two stages:

Stage	Reaction	indicator to indicate completion of reaction
(a)	$Na_2CO_3(aq) + HCl(aq) \longrightarrow NaHCO_3(aq) + NaCl(aq)$	thymolphthalein
(b)	$NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l)$	methyl orange
Overall	$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$	

- If <u>thymolphthalein</u> is used as the indicator, it changes colour from blue to colourless when reaction (a) is completed, i.e. when Na_2CO_3 is only half-neutralised to form $NaHCO_3$.

- If <u>methyl orange</u> is used as the indicator, it changes colour from yellow to orange when reaction (b) is completed, i.e. when Na_2CO_3 is completely neutralised to give CO_2 and H_2O.

- From the stoichiometry of the two reactions, it can be seen that

> - if volume of HC*l* required for reaction (a) = **x** cm³,
> - then volume of HC*l* required for reaction (b) = **x** cm³
>
> and
> - volume of HC*l* required when using thymolphthalein as indicator = **x** cm³
> - volume of HC*l* required when using methyl orange as indicator = **2x** cm³

- The **double indicator method** makes use of this two-stage titration to estimate the Na_2CO_3 in
  - a mixture of Na_2CO_3 and NaOH or
  - a mixture of Na_2CO_3 and $NaHCO_3$

14.7 Titration curve of a polyprotic acid-strong base titration

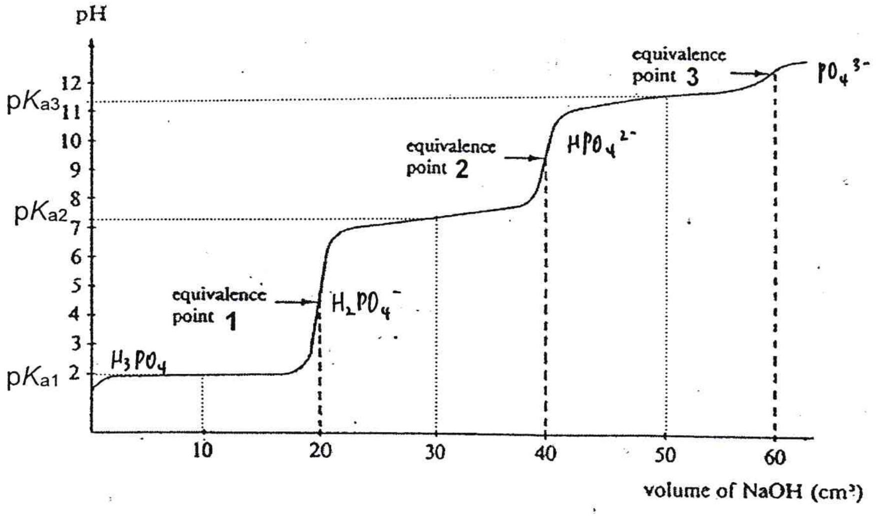
- Phosphoric acid, H_3PO_4, is a triprotic acid.

Dissociation	Equilibrium in aqueous solution	K_a/mol dm^{-3}	pK_a
First	$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$	7.5×10^{-3}	2.1
Second	$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$	6.2×10^{-8}	7.2
Third	$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$	4.2×10^{-13}	12.4

- The following three equations represent the step-wise reactions of H_3PO_4 with NaOH.

$$H_3PO_4(aq) + OH^-(aq) \longrightarrow H_2PO_4^-(aq) + H_2O(l) \quad \text{------------------- (1)}$$
$$H_2PO_4^-(aq) + OH^-(aq) \longrightarrow HPO_4^{2-}(aq) + H_2O(l) \quad \text{------------------- (2)}$$
$$HPO_4^{2-}(aq) + OH^-(aq) \longrightarrow PO_4^{3-}(aq) + H_2O(l) \quad \text{------------------- (3)}$$

- When a solution of phosphoric acid is titrated against sodium hydroxide, the titration curve shows three equivalence points corresponding to the completion of each of the above reactions:



At 10, 30, 50 cm³ (half equi points), pH = pKa.

15 Summary

	Arrhenius theory	Brønsted-Lowry theory	Lewis theory
acid	releases $H^+(aq)$	a proton donor	an electron pair acceptor
base	releases $OH^-(aq)$	a proton acceptor	an electron pair donor

H_3O^+ hydronium ion or hydroxonium ion or oxonium ion	**Note:** For simplicity, we write $H^+(aq)$ instead of $H_3O^+(aq)$.

Conjugate acid-base pairs

$$HA(aq) + B(aq) \rightleftharpoons A^-(aq) + HB^+(aq)$$

acid 1 base 2 base 1 acid 2

A^- is the **conjugate base** of the acid HA.
HB^+ is the **conjugate acid** of the base B.

For a conjugate acid-base pair,
$K_a \times K_b = K_w = 1.0 \times 10^{-14}$ mol² dm⁻⁶
$pK_a + pK_b = pK_w = 14$ (at 298 K)

pH = –lg [H⁺]
pOH = –lg [OH⁻] $pK_a = -\lg K_a$

neutral solution: **[H⁺] = [OH⁻]**
acidic solution: **[H⁺] > [OH⁻]**
alkaline solution: **[H⁺] < [OH⁻]**

K_w: ionic product of water
$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$; $\Delta H > 0$
$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ mol² dm⁻⁶
$pK_w = pH + pOH = 14$ (at 298 K)

α = degree of ionisation
or **α = degree of dissociation**

α can be expressed in fraction or percentage

$$\alpha = \text{fraction of molecules ionised at equilibrium} = \frac{\text{number of moles of molecules ionised at equilibrium}}{\text{initial number of moles of molecules}}$$

For a weak acid, $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(\alpha C_o)(\alpha C_o)}{C_o(1-\alpha)} = \frac{\alpha^2 C_o}{(1-\alpha)}$$

If α << 1 such that (1–α) ≈ 0, $K_a = \alpha^2 C_o$

Strong acid
- **complete dissociation** in aqueous solution
- degree of dissociation, **α = 1**
- $HX(aq) \longrightarrow H^+(aq) + X^-(aq)$
- Note: for monobasic acid,
  [H⁺] = [HX]₀ and **pH = –lg [H⁺]**

Strong base
- **complete ionisation** in aqueous solution
- degree of ionisation, **α = 1**
- $NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$
- Note: for monoacidic base (e.g. NaOH),
  [OH⁻] = [NaOH] and **pOH = –lg [OH⁻]**

pH Calculations

When solutions are mixed, always consider whether a reaction has taken place. Then take note of what species are present in the resultant solution at equilibrium before calculating the pH of the solution.

- strong acid or strong base?
- weak acid or weak base?
- hydrolysis of salt?
- acidic buffer?
- alkaline buffer?
- a mixture of strong acid and weak acid (ignore weak acid)
- a mixture of strong base and weak base (ignore weak base)

Weak acid
- **partial dissociation** in aqueous solution
- $0 < \alpha < 1$
- $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{units: mol dm}^{-3}$$

- K_a is the **acid dissociation constant** of HA.
- The larger the K_a of an acid, the greater is the strength of the acid.

Weak base
- **partial ionisation** in aqueous solution
- $0 < \alpha < 1$
- $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad \text{units: mol dm}^{-3}$$

- K_b is the **base dissociation constant** of B.
- The larger the K_b of a base, the greater is the strength of the base.

Calculating pH of a weak acid:
$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$
$[H^+] \approx \sqrt{K_a[HA]}$
pH = –lg [H⁺]

Calculating pH of salt of weak acid:
$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$

$$[OH^-] \approx \sqrt{\frac{K_w}{K_a\ of\ HA}[A^-]}$$

pOH = –lg [OH⁻]
pH = 14 – pOH

Calculating pH of a weak base:
$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$
$[OH^-] \approx \sqrt{K_b[B]}$
pOH = –lg [OH⁻]
pH = 14 – pOH

Calculating pH of salt of weak base:
$BH^+(aq) \rightleftharpoons H^+(aq) + B(aq)$

$$[H^+] \approx \sqrt{\frac{K_w}{K_b\ of\ B}[BH^+]}$$

pH = –lg [H⁺]

Buffer solution
- definition and composition
- actions of buffer upon adding H⁺ / OH⁻ ions

Acidic buffer
- a mixture of weak acid and its salt
- E.g. mixture of CH_3COOH and $CH_3COO^-Na^+$

$$pH = pK_a + \lg\left(\frac{[salt]}{[acid]}\right)$$

- **maximum buffer capacity** when $\frac{[salt]}{[acid]} = 1$
  and hence **pH = pK_a**
- **effective buffer range:** pH = pK_a ± 1

Alkaline buffer
- a mixture of weak base and its salt
- E.g. mixture of NH_3 and NH_4Cl

$$pOH = pK_b + \lg\left(\frac{[salt]}{[base]}\right)$$

- **maximum buffer capacity** when $\frac{[salt]}{[base]} = 1$
  and hence **pOH = pK_b**
- **effective buffer range:** pOH = pK_b ± 1

Salt hydrolysis
1. salt of a strong acid and a strong base
   e.g. $NaCl(aq)$ – neutral
2. salt of a strong acid and a weak base
   e.g. $NH_4Cl(aq)$ – acidic
   $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
3. salt of a weak acid and a strong base
   e.g. $CH_3COO^-Na^+(aq)$ – alkaline
   $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
4. salt of a weak acid and a weak base
   e.g. $CH_3COO^-NH_4^+(aq)$ – very weakly acidic

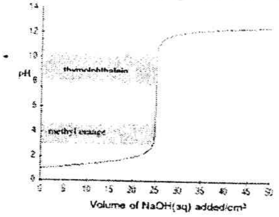
Note: Ions that are conjugate acids of weak bases or conjugate bases of weak acids will under hydrolysis.

Acid-base indicator

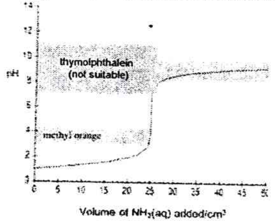
Note: A suitable indicator is one where **its pH range coincides with the region of rapid pH change** in the titration curve (i.e. the pH range of the indicator **must** fall on the vertical portion of the titration curve).

Acid-base Titration Curves

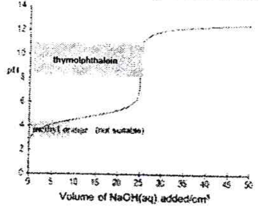
1. strong acid – strong base titration



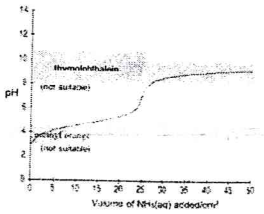
2. strong acid – weak base titration



3. weak acid – strong base titration



4. weak acid – weak base titration



16 Appendix

(1) Calculation of pH after a small amount of H^+/ OH^- to an acidic/ alkaline buffer

<table>
<tr><td colspan="2">(i) Consider an acidic buffer initially containing $n_{HA}{}^o$ mol of HA and $n_{A^-}{}^o$ mol of A^-.
Initial pH = $pK_a + \lg\frac{[A^-]}{[HA]} = pK_a + \lg\frac{n_{A^-}{}^o/V}{n_{HA}{}^o/V} = pK_a + \lg\frac{n_{A^-}{}^o}{n_{HA}{}^o}$</td></tr>
<tr><td>(a) After adding a small amount of H^+, n_{H^+} mol
$A^-(aq) + H^+(aq) \rightarrow HA(aq)$
(A^- is used up while HA is formed)
$n_{A^-} = n_{A^-}{}^o - n_{H^+}$
$n_{HA} = n_{HA}{}^o + n_{H^+}$
pH = $pK_a + \lg\frac{[A^-]}{[HA]} = pK_a + \lg\frac{n_{A^-}/V}{n_{HA}/V}$
$= pK_a + \lg\frac{n_{A^-}{}^o - n_{H^+}}{n_{HA}{}^o + n_{H^+}}$
Since $n_{HA}{}^o$ and $n_{A^-}{}^o$ are large, pH of buffer is similar to its initial pH if n_{H^+} is small.</td><td>(b) After adding of a small amt of OH^-, n_{OH^-} mol
$HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(l)$
(A^- is formed while HA is used up)
$n_{A^-} = n_{A^-}{}^o + n_{OH^-}$
$n_{HA} = n_{HA}{}^o - n_{OH^-}$
pH = $pK_a + \lg\frac{[A^-]}{[HA]} = pK_a + \lg\frac{n_{A^-}/V}{n_{HA}/V}$
$= pK_a + \lg\frac{n_{A^-}{}^o + n_{OH^-}}{n_{HA}{}^o - n_{OH^-}}$
Since $n_{HA}{}^o$ and $n_{A^-}{}^o$ are large, pH of buffer is similar to its initial pH if n_{OH^-} is small.</td></tr>
<tr><td colspan="2">(ii) Consider an alkaline buffer initially containing $n_B{}^o$ mol of B and $n_{BH^+}{}^o$ mol of BH^+.
Initial pOH = $pK_b + \lg\frac{[BH^+]}{[B]} = pK_b + \lg\frac{n_{BH^+}{}^o/V}{n_B{}^o/V} = pK_b + \lg\frac{n_{BH^+}{}^o}{n_B{}^o}$</td></tr>
<tr><td>(a) After adding a small amount of H^+, n_{H^+} mol
$B\ (aq) + H^+\ (aq) \rightarrow BH^+\ (aq)$
(B is used up while BH^+ is formed)
$n_{BH^+} = n_{BH^+}{}^o + n_{H^+}$
$n_B = n_B{}^o - n_{H^+}$
pOH = $pK_b + \lg\frac{[BH^+]}{[B]} = pK_b + \lg\frac{n_{BH^+}/V}{n_B/V}$
$= pK_b + \lg\frac{n_{BH^+}{}^o + n_{H^+}}{n_B{}^o - n_{H^+}}$
Since $n_B{}^o$ and $n_{BH^+}{}^o$ are large, pOH and hence pH of buffer is similar to its initial pH if n_{H^+} is small.</td><td>(b) After adding of a small amt of OH^-, n_{OH^-} mol
$BH^+\ (aq) + OH^-\ (aq) \rightarrow B\ (aq) + H_2O\ (l)$
(B is formed while BH^+ is used up)
$n_{BH^+} = n_{BH^+}{}^o - n_{OH^-}$
$n_B = n_B{}^o + n_{OH^-}$
pOH = $pK_b + \lg\frac{[BH^+]}{[B]} = pK_b + \lg\frac{n_{BH^+}/V}{n_B/V}$
$= pK_b + \lg\frac{n_{BH^+}{}^o - n_{OH^-}}{n_B{}^o + n_{OH^-}}$
Since $n_B{}^o$ and $n_{BH^+}{}^o$ are large, pOH and hence pH of buffer is similar to its initial pH if n_{OH^-} is small.</td></tr>
</table>

(2) Buffer solution made of a salt of weak acid and base

A buffer solution is able to resist changes in pH when a small amount of H^+ or OH^- is added to it. Hence it must contain species that are able to react with both H^+ and OH^-. Besides the common acidic buffer (made of weak acid and its salt) and alkaline buffer (made of weak base and its salt), a solution containing salt of a weak acid and weak base can also function as a buffer as it contains species which react with both H^+ and OH^-.

Consider a solution of ammonium ethanoate, $CH_3COO^-NH_4^+$:

When a small amount of H^+ is added, $CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$
H^+ added is removed by CH_3COO^-. Hence pH is maintained.

When a small amount of OH^- is added, $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$
OH^- added is removed by NH_4^+. Hence pH is maintained.
Large reservoir of CH_3COO^- and NH_4^+ helps the buffer cope with small amount of H^+ and OH^- added.

An aqueous solution of amino acid such as H_2NCH_2COOH is also able to act as a buffer as it is able to react with both H^+ and OH^- as shown by the following equations:
$H_2NCH_2COOH(aq) + H^+(aq) \rightarrow {}^+H_3NCH_2COOH(aq)$
$H_2NCH_2COOH(aq) + OH^-(aq) \rightarrow H_2NCH_2COO^-(aq) + H_2O(l)$