Raffles Institution
Year 6 H2 Chemistry 2023
Lecture Notes 14 – Acid-Base Equilibria

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 and pOH
4 The ionic product of water, K_w
5 pH Calculations for weak acids
6 pH Calculations for weak bases
7 Relationship between K_a and K_b for a conjugate acid-base pair
8 Salt hydrolysis
9 Buffer solutions
10 pH Calculations involving buffer solutions
11 More on buffer solutions
12 Acid-base titration and indicators
13 Acid-base titration curves
14 Summary

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 to produce $H^+(aq)$.	A weak acid is one which undergoes partial dissociation in aqueous solution to produce $H^+(aq)$.
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 $[CH_3COOH]$
Degree of dissociation, α (Ref Chem Eqm)	$\alpha = 1$	$0 < \alpha < 1$

(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.

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

	Number of H atoms ionisable (as H^+ ion) per molecule	Examples
monobasic (or monoprotic) acid	1	HCl, HNO_3 and CH_3COOH
dibasic (or diprotic) acid	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 <u>strong base</u> is one which undergoes <u>complete dissociation</u> in aqueous solution to produce $OH^-(aq)$.

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

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

- A <u>weak base</u> is one which undergoes <u>partial ionisation</u> in aqueous solution to produce $OH^-(aq)$.

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

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

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 releases H^+ ions in aqueous solution.	• A base releases OH^- ions in aqueous solution.
• Example: $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$	• Example: $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

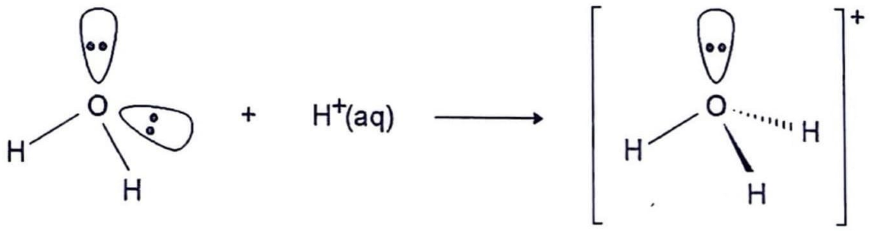
(b) Limitations of Arrhenius theory:

- It restricted acid-base reactions to those which occur in aqueous solutions.
- 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

- 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.
- Therefore, in aqueous solution, a water molecule forms a dative covalent bond to the H^+ ion to produce the <u>hydronium ion (also known as 'hydroxonium ion'), H_3O^+</u>.

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



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.
- 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:

$$\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow H_3NBF_3$$

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

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

- 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.

HA	+	B	$\rightleftharpoons$	A^-	+	HB^+
acid		base		conjugate base of HA		conjugate acid of B

- An acid and its conjugate base are defined as a pair:

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

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

- Examples

loses H^+ (acid → conjugate base)

gains H^+ (base → conjugate acid)

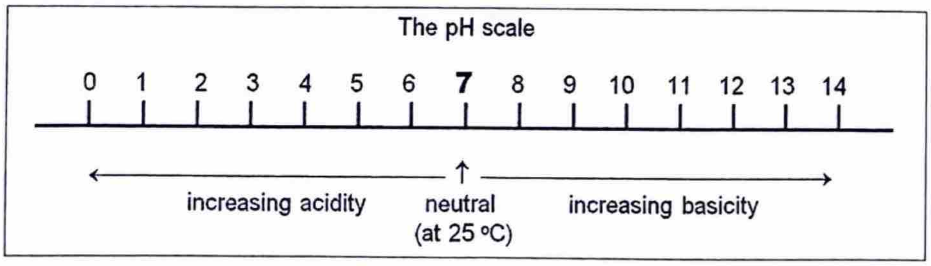
	Reaction (forward reaction)	acid	conjugate base	base	conjugate acid
1	$HCl(aq) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$	HCl	Cl^-	H_2O	H_3O^+
2	$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$	H_2O	OH^-	CH_3NH_2	$CH_3NH_3^+$
3	$NH_3(aq) + CH_3COOH(aq) \rightleftharpoons CH_3COO^-NH_4^+(aq)$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

3 pH and pOH

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

- The concentration of hydrogen ions (in mol dm^{-3}) in solution can also be calculated from pH. $\boxed{[H^+] = 10^{-pH}}$

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.

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} $HCl(aq)$. $HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$ $[H^+] = [HCl(aq)] = 0.200$ mol dm^{-3} $pH = -\lg [H^+] = -\lg (0.200) = \underline{0.699}$	**(b)** Calculate the pH of 1.00 mol dm^{-3} $H_2SO_4(aq)$. $H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$ $[H^+] = 2 \times 1.00 = 2.00$ mol dm^{-3} $pH = -\lg [H^+] = -\lg (2.00) = \underline{-0.30}$

■● 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

3.4 Calculating [H$^+$] from pH

■● Worked Example 2 ●■

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

3.5 Measuring the pH of a solution

- Main methods available to determine the pH (and hydrogen ion concentration) of a solution:
  - ① using universal indicator paper or solution for an approximate pH value.
  - ② using a pH meter for an accurate pH determination.
- The pH values of some familiar aqueous solutions are shown in the diagram below.

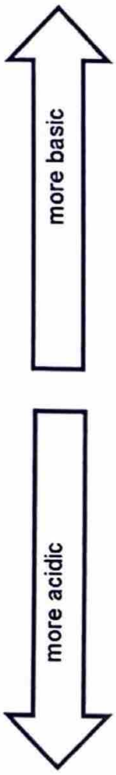
pH values of some familiar substances

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
limewater	11	1×10^{-11}	1×10^{-3}	3
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
rainwater (normal)	6	1×10^{-6}	1×10^{-8}	8
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

3.6 Definition of pOH

- The pOH of a solution is defined as:

$$\boxed{pOH = -\lg [OH^-]}$$

- The concentration of OH^- ions (in mol dm^{-3}) in solution can also be calculated.

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

4 The Ionic Product of Water, K_w

4.1 Deriving the expression for K_w

- Despite water having a simple molecular structure, the electrical conductivity of pure 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.

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \text{----- (1)}$$

or for simplicity:

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

- The equilibrium constant of eq. (2) is $K_c = \dfrac{[H^+][OH^-]}{[H_2O]}$

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

  Since the amount of water ionised is very small, $[H_2O]$ is effectively constant.
  Let $K_w = K_c\,[H_2O]$.

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

  Alternatively, using eq. (1),

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

- K_w is termed the **ionic product of water**. It has **units of $mol^2\ dm^{-6}$**.

- The exact value of K_w depends on temperature.

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

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

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

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

- For pure water (at 25 °C) which is **neutral**.

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

$$\Rightarrow \text{pH} = \text{pOH} = 7 \text{ (at 25 °C)}$$

- 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

4.3 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
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.

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

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

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 2 ●■ [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.

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.

4.4 Relationship between pK_w, pH and pOH

- pK_w is defined as follows:

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

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

$$\begin{aligned} K_w &= [H^+][OH^-] \\ -\lg K_w &= -\lg [H^+] - \lg [OH^-] \\ \Rightarrow pK_w &= pH + pOH \end{aligned}$$

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

- At 25 °C,

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

At 25 °C,

$$\boxed{pK_w = pH + pOH = 14}$$

4.5 Calculating pH and [H⁺] of solution of a strong base

■● Worked Example 3 ●■

(a) Calculate the pH of 0.100 mol dm^{-3} KOH(aq) at 25 °C. $KOH(aq) \longrightarrow K^+(aq) + OH^-(aq)$ $[OH^-] = 0.100$ mol dm^{-3} $pOH = -\lg(0.100) = 1$ $pH = pK_w - pOH = 14 - 1 = \underline{13.0}$	**(b)** Calculate the [H⁺] in 0.020 mol dm^{-3} Ba(OH)$_2$(aq) at 25 °C. $[OH^-] = 2 \times 0.020 = 0.040$ mol dm^{-3} $K_w = [H^+][OH^-]$ $[H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1.00 \times 10^{-14}}{0.040}$ $= 2.50 \times 10^{-13}$ mol dm^{-3}

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$_3$COOH) 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,

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

- Alternatively, using the first chemical equation,

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

- 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 pK_a of an acid is given by:
- The K_a and pK_a values of different acids can be used to compare the strength of the acids.

$$\boxed{\mathbf{p}K_a = -\lg K_a}$$

■● Worked Example 4 ●■

Ethanoic acid is a weak organic acid.
Write down the K_a expression for ethanoic acid.

<u>Solution</u>

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

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

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	
$HF(aq)$	5.6×10^{-4}	3.25	acid strength decreases
$HNO_2(aq)$	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 $\boldsymbol{K_a}$ value, the **stronger** the acid.
- The **larger** (i.e. **more positive**) the **p$\boldsymbol{K_a}$** value, the **weaker** the acid.

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

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

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

Since K_a of HF > K_a of HCN, HF is a stronger acid than HCN.

- For solutions of HF(aq) and HCN(aq) that are of the <u>same concentration</u>,
  - 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).

Note:

Which is the better indicator of the strength of an acid: pH or K_a?

- **K_a is the better 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.

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

- 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 K_a of a weak acid from pH

- When given the pH of a solution of a weak acid of known concentration, you can calculate the K_a value of the acid.

■● Worked Example 5 ●■

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

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	0.3349	0.01514	0.01514

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

5.5 Calculating the pH of a weak acid from K_a

- Conversely, given the K_a value of a weak acid, you can calculate the pH of its solution of known concentration. Note that unlike a strong acid, the [H⁺] of a weak acid is not equal to [HA]. *This method uses the ICE table introduced in the Chemical Equilibria topic (Lecture 7).*

■● Worked Example 6 ●■

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

Solution

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) ≈ 0.200.

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

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

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

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

- Compare the above answer with that of Worked Example 1(a) on page **6**.
- **Note:** The pH of a weak acid is higher (due to lower [H⁺]) than that of a strong acid of the same concentration.

- The following expression derived in the final step of the calculation is an alternative method for calculating [H⁺]:

$x = [H^+] = \sqrt{K_a[HA]_{initial}}$	• Where $[HA]_{initial}$ is the initial concentration of the **weak acid.** • This formula is especially useful for solving multiple-choice questions.

- The assumption used during the calculation is valid as the degree of dissociation of a weak acid is small / negligible, i.e. $x << [HA]_{initial}$ such that $([HA]_{initial} - x) \approx [HA]_{initial}$.

6 pH Calculations for Weak Bases

6.1 Base dissociation constant, K_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, $\boxed{K_b = \dfrac{[BH^+][OH^-]}{[B]}}$

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

Note:

- K_b is a **measure of the basic strength** of the 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 defined as: $\boxed{pK_b = -\lg K_b}$

■● Worked Example 7 ●■

Write the K_b expression for CO_3^{2-} in the following reaction:

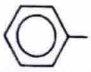
$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq).$$

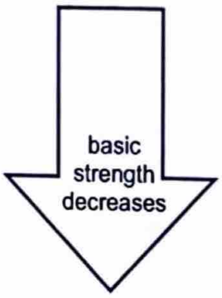
Solution:

$$K_b = \frac{[HCO_3^-]\,[OH^-]}{[CO_3^{2-}]}$$

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 $CH_3CO_2^-$.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \ldots\ldots\ldots\ldots(1)$$
$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) \ldots\ldots\ldots(2)$$

Since K_b of NH_3 > K_b of $CH_3CO_2^-$, NH_3 is a stronger base than $CH_3CO_2^-$.

- For solutions of NH_3(aq) and $CH_3CO_2^-$(aq) that are of the same concentration,
  - 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.

6.3 Calculating the K_b of a weak base

- Similar to weak acids, when given the pH of a solution of a weak base of known concentration, you can calculate the K_b value of the base.

■● Worked Example 8 ●■

The pH of a 0.200 mol dm^{-3} phenylamine, $C_6H_5NH_2$, solution is 8.95. Calculate the K_b of phenylamine.

Solution

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

At 298 K, pOH = 14 – pH = 14 – 8.95 = 5.05

$[OH^-] = 10^{-5.05} = 8.913 \times 10^{-6}$ mol dm^{-3}

Concentration/mol dm^{-3}	$C_6H_5NH_2(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$C_6H_5NH_3^+(aq)$ +	$OH^-(aq)$
initial	0.200	–	–
change	-8.913×10^{-6}	$+8.913 \times 10^{-6}$	$+8.913 \times 10^{-6}$
equilibrium	$0.200 - (8.913 \times 10^{-6})$ $= 0.200$	8.913×10^{-6}	8.913×10^{-6}

$$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{(8.913 \times 10^{-6})^2}{0.200} = \underline{3.97 \times 10^{-10} \text{ mol dm}^{-3}}$$

6.4 Calculating the pH of a weak base from K_b

- Like weak acids, when given the K_b value of a weak base, you can calculate the pH of its solution of known concentration.

■● Worked Example 9 ●■

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

Solution

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

Concentration/mol dm^{-3}	$NH_3(aq)$	$+ H_2O(l) \rightleftharpoons$	$NH_4^+(aq)$ +	$OH^-(aq)$
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.

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

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

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

Therefore,

pOH = – lg (1.319 x 10^{-3}) = 2.88

pH = pK_w – pOH = 14 – 2.88 = 11.1

- Compare the above answer with that of Worked Example 3(a) on page 10.
- **Note:** The pOH of a weak base is higher than that of a strong base of the same concentration.
- Hence, the pH of a weak base is lower than that of a strong base of the same concentration.

- Note: y = **$[OH^-]$** = $\sqrt{K_b[B]_{initial}}$ where $[B]_{initial}$ is the initial concentration of the **weak base**.

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

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

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

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

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

- The relationship can also be expressed in terms of 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 10 ●■

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

Solution

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

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

Solution

K_a of NH_4^+

$$\begin{aligned}&= \frac{K_w}{K_b \text{ of } NH_3}\\ &= \frac{1.0 \times 10^{-14}}{1.74 \times 10^{-5}}\\ &= \underline{\mathbf{5.75 \times 10^{-10} \text{ mol dm}^{-3}}}\end{aligned}$$

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

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

$K_a \times K_b = K_w = 1.0 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$	$K_b = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{K_a}$

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 HX.

- If HA is a stronger acid than HX, then A^- is a weaker base than X^-.

- Reasoning: HA is a stronger acid than HX

$$\Rightarrow \quad K_a \text{ of HA} > K_a \text{ of HX}$$

$$\Rightarrow \quad \frac{K_w}{K_b \text{ of } A^-} > \frac{K_w}{K_b \text{ of } X^-}$$

$$\Rightarrow \quad K_b \text{ of } A^- < K_b \text{ of } X^-$$

$$\Rightarrow \quad A^- \text{ is a weaker base than } X^-$$

- If HA is a stronger acid than HX, the reaction between HA and X^- will occur to a greater extent than that between HX and A^-.

$$\underset{\text{stronger acid}}{HA} + \underset{\text{stronger base}}{X^-} \rightleftharpoons \underset{\text{weaker acid}}{HX} + \underset{\text{weaker base}}{A^-}$$

- 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^-		
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^-		
		H_2CO_3	HCO_3^-		
		H_2S	HS^-		
		NH_4^+	NH_3		
are essentially not acids	weak conjugate acids	H_2O	OH^-	complete protonation	strong bases

- For example, HF is a stronger acid than CH_3COOH (both are weak acids), but CH_3COO^- is a stronger base than F^- (both are weak bases).

8 Salt Hydrolysis

8.1 Types of salt solution

- A salt may be defined as a compound formed by the reaction of an acid and a base.
- 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 (refer to Section 13.5)

- 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 below 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)	**Neutral** salt	• Example: **sodium chloride, $NaCl$** • This type of salt is formed from the reaction of a strong acid and a strong base. In solution, complete dissociation of $NaCl$ occurs. $NaCl(s) + aq. \longrightarrow Na^+(aq) + Cl^-(aq)$ • Both the Na^+ and Cl^- ions do not undergo hydrolysis: • 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^- does not undergo hydrolysis. • The solution is neutral.
(b)	**Acidic** salt	• Example: **ammonium chloride, NH_4Cl** • This type of salt is formed from the reaction of a strong acid (HCl), and a weak base (NH_3). 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^- does not undergo hydrolysis. • Being the conjugate acid of a weak base, NH_4^+ undergoes hydrolysis to give H_3O^+ ions. $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ • The H_3O^+ ions generated by the hydrolysis reaction causes the solution to be acidic.

(c)	**Basic salt**	• Example: **sodium ethanoate, $CH_3COO^-Na^+$** • This type of salt is formed from the reaction of a weak acid (CH_3COOH) and a strong base ($NaOH$). 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 conjugate base of a weak acid, CH_3COO^- undergoes hydrolysis to give OH^- ions. $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$ • The 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 and complete dissociation 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). • Since K_a of NH_4^+ is slightly larger than the K_b of CH_3COO^-, the solution is weakly acidic.

8.2 pH Calculations involving hydrolysis of a salt

- Since acidic and basic salts are themselves, weak acids and weak bases, calculations to determine the pH of a salt solution are similar to previous calculations to determine the pH of a solution from K_a and K_b (refer to Worked Examples 6 and 9).

■● Worked Example 11 ●■

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

Solution

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

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

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

Let $[OH^-]$ = 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

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

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

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

$$pH = pK_w - pOH = 14 - 4.78 = \underline{9.22}$$

■● Worked Example 12 ●■

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}	$NH_4^+(aq)$ + $H_2O(l)$ ⇌	$NH_3(aq)$ +	$H_3O^+(aq)$
initial	0.10	–	–
change	– y	+y	+y
equilibrium	(0.10 – y)	y	y

$$y = [H_3O^+] = \sqrt{(5.75 \times 10^{-10})(0.10)}$$

$$= 7.583 \times 10^{-6} \text{ mol dm}^{-3}$$

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

9 Buffer Solutions

9.1 Definition

A buffer solution is a solution which is able to **resist pH changes** when a **small amount** of an acid or a base is added.

- 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 its conjugate base

  ② alkaline buffer which consists of a mixture of a weak base and its conjugate acid

9.2 Acidic buffer

(a) Composition of an acidic buffer

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

Sodium ethanoate, a strong electrolyte, is fully dissociated:

$$CH_3COO^-Na^+(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq) \quad \text{..................(1)}$$

Ethanoic acid, being a weak acid, is only partially dissociated:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \quad \text{..........................(2)}$$

- 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 (2) 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:

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

Note: An **irreversible arrow '⟶'** should be used for equation showing the action of buffer.

  - 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.

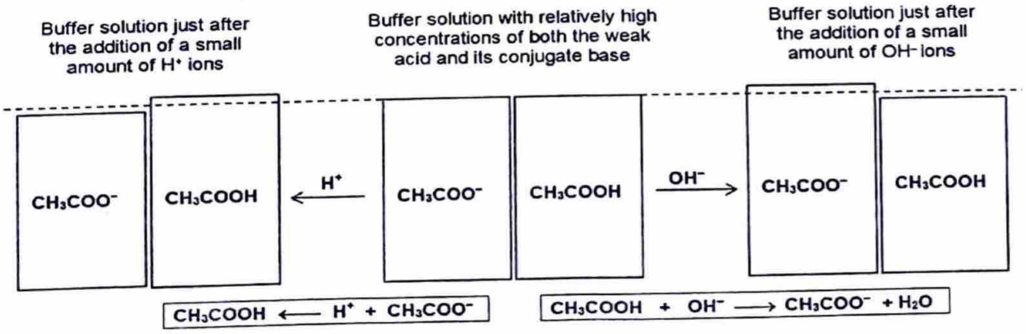
- **Addition of a small amount of base (i.e. OH^- ions)**

  - 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



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9.3 Alkaline buffer

(a) Composition of an alkaline buffer

- Consider an alkaline buffer consisting of a mixture of ammonia and ammonium chloride.

Ammonium chloride, a strong electrolyte, is fully dissociated:

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq) \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Ammonia, being a weak base, is only partially ionised:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad \ldots\ldots\ldots\ldots(2)$$

- 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 (2) 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 alkaline 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:

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

  - The presence of a large reservoir of unionised NH_3 molecules 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:

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

  - The presence of a large reservoir of NH_4^+ ions 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 3** ●■ [N2003/I/33]

Which of the following could act as buffer solutions?

[✓ **1**] $NaHCO_3$ and Na_2CO_3 **2** CH_3CO_2H and $NaCl$ **3** HNO_3 and $NaNO_3$

Hint: In which option(s) are the two species a conjugate acid-base pair?

10 pH Calculations involving Buffer Solutions

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

- Consider a buffer solution containing a weak acid HA (of concentration C_o) and a salt containing the conjugate base of the weak acid, Na^+A^- (of concentration D_o):

$$Na^+A^-(aq) \longrightarrow Na^+(aq) + A^-(aq)$$

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

conc./mol dm^{-3}	HA(aq)	$\rightleftharpoons$ 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^-. Hence at equilibrium, only a very small amount of HA has dissociated.

- **At equilibrium,**

$[HA]_{eqm} \approx [HA]_{initial}$	$[A^-]_{eqm} \approx [A^-]_{initial}$	$[H^+]_{eqm} \neq [A^-]_{eqm}$
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^-, $[H^+]_{eqm} \neq [A^-]_{eqm}$.

- 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:

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

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

- 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.

10.2 The relationship between pH, pK_b and composition of an alkaline buffer

- Consider an alkaline buffer solution containing weak base B and a salt containing the conjugate acid of the base, BH^+Cl^-.

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

- In a similar manner as that in **Section 10.1**, the following expression can be derived.

$$\boxed{\mathbf{pOH = p}K_b \mathbf{+ lg}\left(\frac{[BH^+]}{[B]}\right)}$$

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

10.3 Calculating the pH of buffer solutions

■● Worked Example 13 ●■

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 = 1.6×10^{-4} mol dm^{-3}.

Solution

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

The given solution is an acidic buffer.

$$\text{pH} = \text{p}K_a + \lg\left(\frac{[HCOO^-]}{[HCOOH]}\right)$$
$$= -\lg(1.6 \times 10^{-4}) + \lg\left(\frac{2.5}{0.5}\right)$$
$$= \underline{4.49}$$

Alternative method

Note: In a buffer solution, take note of the initial concentrations of the weak acid and its conjugate base. The rest of the method is similar to those shown in Worked Examples 6, 9, 11 and 12.

Let [H$^+$] = y mol dm^{-3} at equilibrium. Since HCOOH is a weak acid with a small K_a, assume that y is very small and [HCOOH] = 0.5 mol dm^{-3} and [HCOO$^-$] = 2.5 mol dm^{-3} at equilibrium.

conc./mol dm^{-3}	HCOOH(aq)	⇌	H$^+$(aq)	+	HCOO$^-$(aq)
initial	0.5		–		2.5
change	–y		+y		+y
equilibrium	0.5 – y ≈ 0.5		y		2.5 + y ≈ 2.5

$$K_a \text{ for HCOOH} = \frac{[HCOO^-][H^+]}{[HCOOH]} = \frac{2.5y}{0.5} = 1.6 \times 10^{-4}$$

y = [H$^+$] = 3.20×10^{-5} mol dm^{-3}

pH = – lg (3.20×10^{-5}) = $\underline{4.49}$

■● Worked Example 14 ●■

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,

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

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

The resultant solution is an alkaline buffer.

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

$\text{pH} = \text{p}K_w - \text{pOH} = 14 - 4.45 = \underline{9.55}$

10.4 Calculating the change in pH of buffer solutions

■● Worked Example 15 ●■

(a) 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, $\text{pH} = \text{p}K_a + \lg\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) = 4.74 + \lg\left(\frac{0.04}{0.06}\right) = 4.564 = \underline{4.56}$

(b) 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 part (a).

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

0.059 = 0.06 − 0.001

$n(CH_3COO^-)$ present = initial $n(CH_3COO^-)$ + $n(CH_3COO^-)$ formed

0.041 = 0.04 + 0.001

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 <u>an acidic buffer</u>.

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

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

Change in pH = final pH – original pH = 4.582– 4.564 = <u>+0.018</u> ⇒ <u>increase in pH of 0.018 units</u>

Extension: consider what happens when the same amount of KOH is added to water (note: water is not a buffer).

11 More on Buffer Solutions

11.1 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.**
- An acidic 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 and its conjugate base are <u>large</u> relative to the amount of H^+ or OH^- to be added to the buffer solution.
  ② The weak acid to its conjugate base <u>concentration ratio is 1:1</u>.

  Note: the same applies to alkaline buffers.

- A buffer has **maximum buffer capacity** when $\frac{[A^-]}{[HA]} = 1$ for an acidic buffer or when $\frac{[BH^+]}{[B]} = 1$ for an alkaline buffer.

<u>Acidic buffer</u>	<u>Alkaline buffer</u>
When $\frac{[A^-]}{[HA]} = 1$, $\text{pH} = \text{p}K_a + \lg\left(\frac{[A^-]}{[HA]}\right)$ $= \text{p}K_a + \lg 1$ $= \text{p}K_a$	When $\frac{[BH^+]}{[B]} = 1$, $\text{pOH} = \text{p}K_b + \lg\left(\frac{[BH^+]}{[B]}\right)$ $= \text{p}K_b + \lg 1$ $= \text{p}K_b$
Hence <u>maximum buffer capacity</u> is attained at $\boxed{\textbf{pH} = \textbf{p}K_a}$	Hence <u>maximum buffer capacity</u> is attained at $\boxed{\textbf{pOH} = \textbf{p}K_b}$

- Diluting a buffer would decrease its buffer capacity but not change its pH. (Why is this so?)

For same volume of buffer used, the diluted buffer has less **HA** and **A^-** to cope with addition of OH^- and H^+
⇒ dilution ↓ **buffering capacity**

(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: $0.1 \le \frac{[A^-]}{[HA]} \le 10$

When $\frac{[A^-]}{[HA]} = 0.1$	$\mathbf{pH} = pK_a + \lg 0.1 = \mathbf{pK_a - 1}$
When $\frac{[A^-]}{[HA]} = 10$	$\mathbf{pH} = pK_a + \lg 10 = \mathbf{pK_a + 1}$

- 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 = $\mathbf{pK_a \pm 1}$

11.2 Preparing a buffer solution

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

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

The pK_a value of the acid chosen should be within ± 1 pH unit of the desired pH of the buffer.

The $[A^-]/[HA]$ ratio can be adjusted to achieve the desired pH.

- 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 $[A^-]/[HA]$ and provides the 'fine tuning' to the desired pH of the buffer.

■● Worked Example 16 ●■

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

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

11.3 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.

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

12 Acid-Base Titration and Indicators

12.1 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.

12.2 Choice of Indicators

(Refer to Section 1.7 of Guide to Volumetric Analysis and Section 2 of Planning Experiments – Introduction)

- Essential characteristics of a suitable indicator:
  - 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.
  - 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.

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).

- The type of acid-base titration and the suitable indicators, as well as the colour change at the end point of the different indicators are given below.

	Type	Marked pH change	Suitable indicator
1	strong acid – strong base	4 – 10	thymolphthalein, thymol blue, methyl orange, screened methyl orange
2	strong acid – weak base	3.5 – 6.5	methyl orange, screened methyl orange
3	weak acid – strong base	7.5 – 10.5	thymolphthalein, thymol blue
4	weak acid – weak base	no marked change	No suitable indicator

Indicator	Approximate pH range	Colour		
		in 'acidic' solution	at end–point	in 'alkaline' solution
Methyl orange	3.2 – 4.4	red	orange	yellow
Screened methyl orange	3.2 – 4.4	violet	grey	green
Thymol blue	8.0 – 9.6	yellow	green	blue
Thymolphthalein	9.4 – 10.6	colourless	light blue (if titrant is alkali) colourless (if titrant is acid)	blue
Bromothymol blue	6.0 – 7.6	yellow	green	blue
Phenolphthalein **Note:** Not used in school labs due to potential risk of carcinogenicity.	8.3 – 10.0	colourless	light pink (if titrant is alkali) colourless (if titrant is acid)	pink

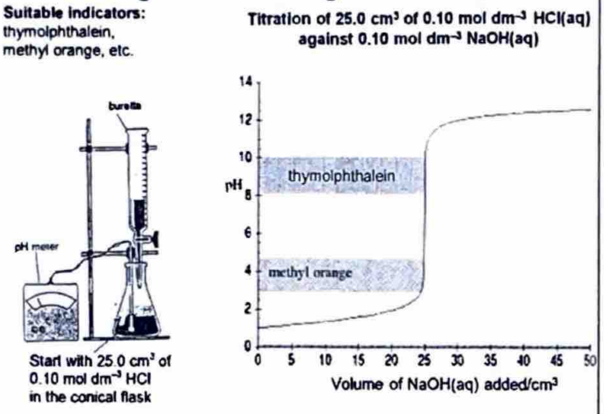
13 Acid-Base Titration Curves

13.1 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 the solution in a conical flask changes as an acid (or a base) is added from a burette.

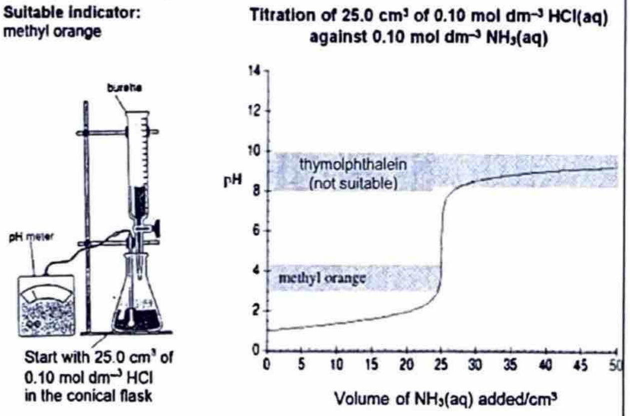
Strong acid – Strong base Titration

Suitable indicators:
thymolphthalein,
methyl orange, etc.



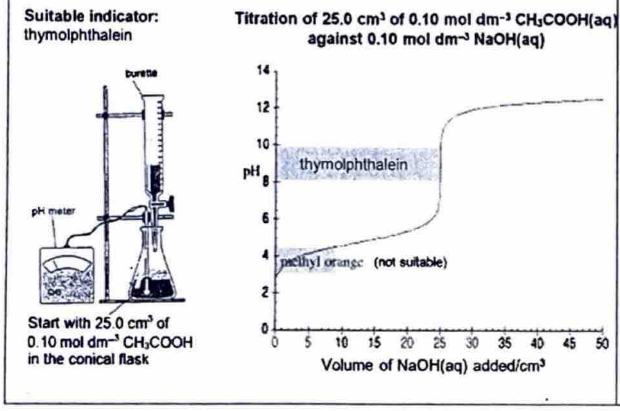
Strong acid – Weak base Titration

Suitable indicator:
methyl orange



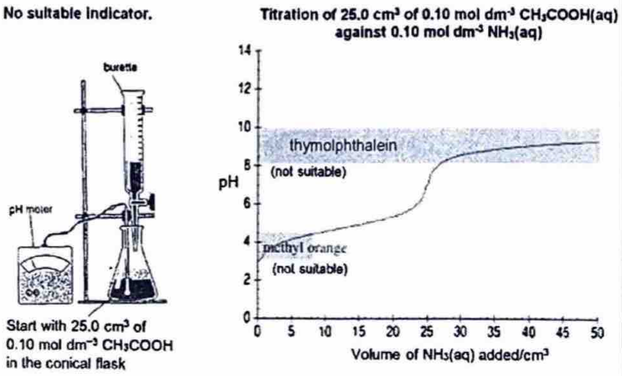
Weak acid – Strong base Titration

Suitable indicator:
thymolphthalein



Weak acid – Weak base Titration

No suitable indicator.

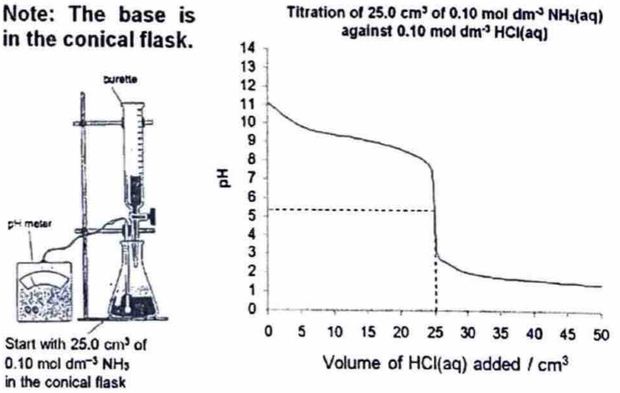


- Important parts of a titration curve

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

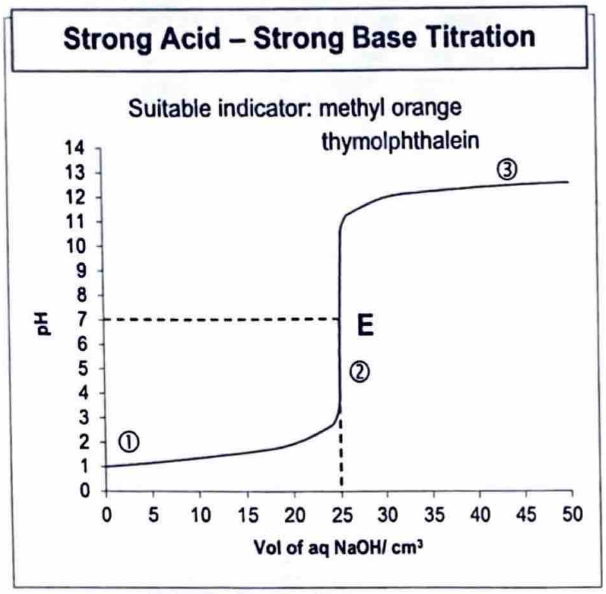
Weak base – Strong acid Titration

Note: The base is in the conical flask.



13.2 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 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**.

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 effect)

Calculation of pH at various parts of the titration curve:

(i) *Initial pH = pH of strong acid*	(ii) *pH at equivalence point (point **E**)*
Solution is <u>an aqueous solution of strong acid</u>. $[H^+] = [HCl(aq)]$ $= 0.10$ mol dm^{-3} $pH = -lg\,[H^+] = -lg\,(0.10) = 1.00$	At equivalence point, HC*l* has been exactly neutralised by NaOH. The resultant solution is NaC*l*(aq). Since Na^+ and Cl^- do not hydrolyse in water, the resultant solution is <u>neutral</u>. At 25 °C, pH of a neutral solution is 7.

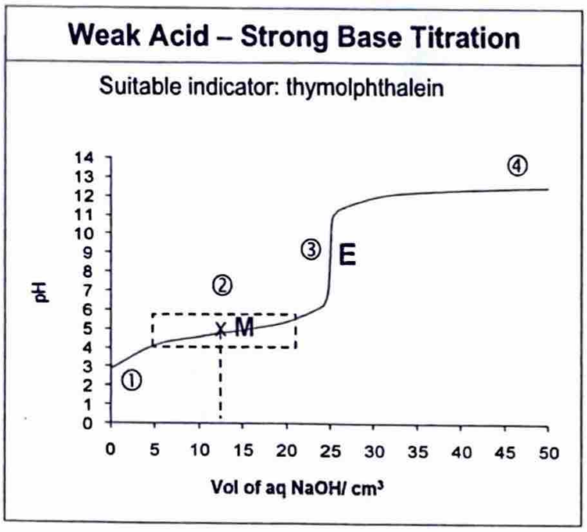
■● Exercise 4 ●■ [N2012/I/11]

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?

A 2.19 **B** 2.40 **C** 2.60 [✓ **D**] 2.82

13.3 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 x 10^{-5} mol dm^{-3}):


Weak Acid – Strong Base Titration

Suitable indicator: thymolphthalein

① The initial pH is not very low (1 < pH < 7) since a weak acid is used.
(pH may be calculated from K_a of weak acid.)

② pH is fairly constant due to the formation of an <u>effective buffer</u> when pH = pK_a ± 1.

When [HA]=[A$^-$] at point **M**, **pH = pK$_a$**

③ 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>.

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(x)(x)}{(0.100 - x)} = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

Since CH_3COOH is a weak acid with a relatively small K_a, assume x << 0.100. Then (0.100 – x) = 0.100.

$$x = [H^+] = \sqrt{(1.8 \times 10^{-5})(0.100)} = 1.342 \times 10^{-3} \text{ mol dm}^{-3}$$

pH = –lg [H$^+$]

= –lg (1.342 x 10^{-3})

= 2.87

(ii) *pH when [HA] = [A$^-$] (point **M**)*

In this case, exactly half of HA has been neutralised when half the volume of NaOH(aq) needed for neutralisation was added. This is the half-equivalence point of this titration.

Since [CH_3COOH] = [CH_3COO^-],

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

pH = –lg [H$^+$] = –lg (1.8 x 10^{-5}) = 4.74

Alternatively,

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

$= pK_a$

= –lg (1.8 x 10^{-5}) = 4.74

(iii) *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 x 0.10 = 0.0025 mol

Volume of reaction mixture = 25.0 + 25.0 cm^3

= 0.050 dm^3

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

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

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{y^2}{(0.050 - y)} = \frac{K_w}{K_a} = 5.56 \times 10^{-10}$$

Since CH_3COO^- is a weak base with a relatively small K_b, assume y << 0.050. Then (0.050 – y) ≈ 0.050.

$$y = [OH^-] = \sqrt{(5.56 \times 10^{-10})(0.050)}$$

= 5.270 x 10^{-6} mol dm^{-3}

pOH = –lg [OH$^-$] = –lg (5.270 x 10^{-6})

= 5.278

pH = 14 – pOH = 14 – 5.278

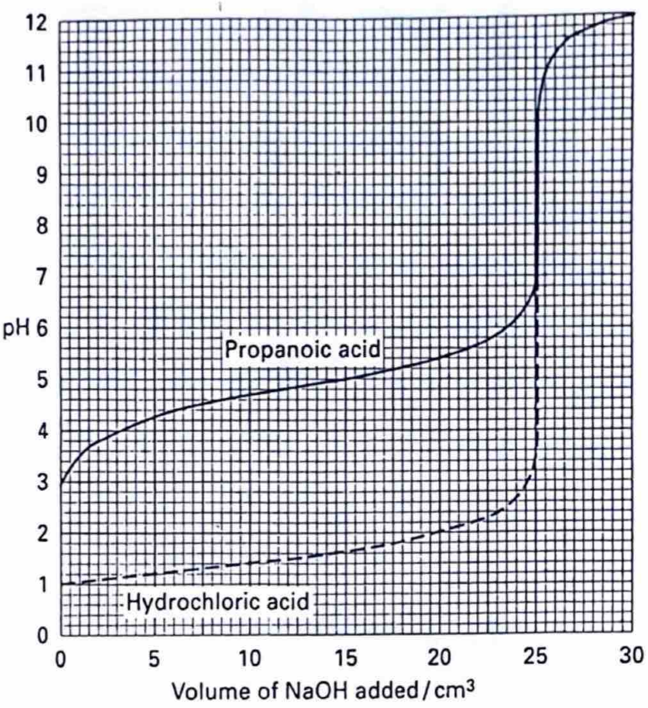
= 8.72

■● Worked Example 17●■

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 dissociates 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.

Note: The equivalence point **E** is found by extrapolating the linear portions of the titration curve and taking the midpoint between the two intersections.

(b) Method 1: when [HA] = [A$^-$], **pH = pK_a**

Since volume needed for complete neutralisation is 25.00 cm^3, [HA] = [A$^-$] when 12.50 cm^3 of aq NaOH was added.

From graph,

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

Thus pK_a = pH at half-equivalence point = 4.80

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

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

Let HA represents propanoic acid.

From the graph, initial pH of HA = 2.90

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

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

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

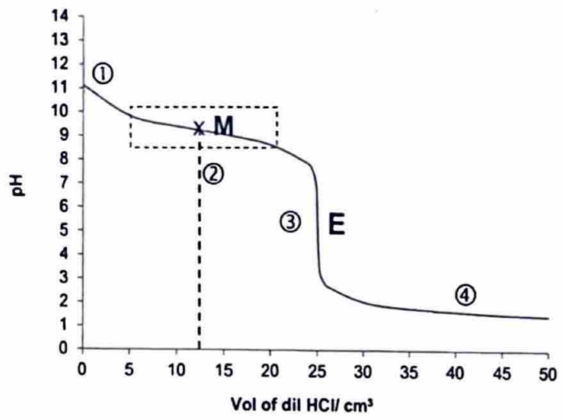
$$K_a = \frac{[H^+]\,[A^-]}{[HA]} = \frac{(0.001259)(0.001259)}{(0.09874)} = 1.61 \times 10^{-5} \text{ mol dm}^{-3}$$

13.4 Titration curve of weak base–strong acid titration

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}).

Weak Base – Strong Acid Titration

Suitable indicator: methyl orange



① The initial pH is not very high (7 < pH < 13) since a weak base is used.
(pOH may be calculated from K_b of weak base.)

② pH is fairly constant due to the formation of an effective buffer when large amounts of weak base and its salt (containing the conjugate acid) are present.

*When $[B]=[BH^+]$ at point **M**, **pOH = pK_b***

③ At equivalence point **E**,
- NH_3 is exactly neutralised by HC*l*
- The resultant solution is NH_4Cl(aq).
- pH < 7 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 weak base.

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

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

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

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

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

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

(ii) *pH when $[B] = [BH^+]$ (point **M**)*

In this case, exactly half of B has been neutralised when half the volume of HC*l*(aq) needed for neutralisation was added. This is the half-equivalence point of this titration.

Since $[NH_3] = [NH_4{}^{+-}]$,

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

$pOH = -\lg [OH^-] = -\lg (1.74 \times 10^{-5}) = 4.759$

$pH = 14 - pOH = 14 - 4.759 = 9.24$

Alternatively,

$$pOH = pK_b + \lg\frac{[NH_4^+]}{[NH_3]} = pK_b + \lg (1)$$
$$= pK_b$$
$$= -\lg (1.8 \times 10^{-5})$$
$$= 4.759$$

$pH = 14 - pOH = 14 - 4.795 = 9.24$

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

At equivalence point, the mixture present is a solution of NH_4Cl.

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

$n(NH_4^+) = 0.025 \times 0.10 = 0.0025$ mol

Volume of reaction mixture = 25.0 + 25.0 cm^3
= 0.050 dm^3

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

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

$$K_a = \frac{[NH_3]\,[H^+]}{[NH_4^+]} = \frac{x^2}{(0.050 - x)} = \frac{K_w}{K_b} = 5.75 \times 10^{-10}$$

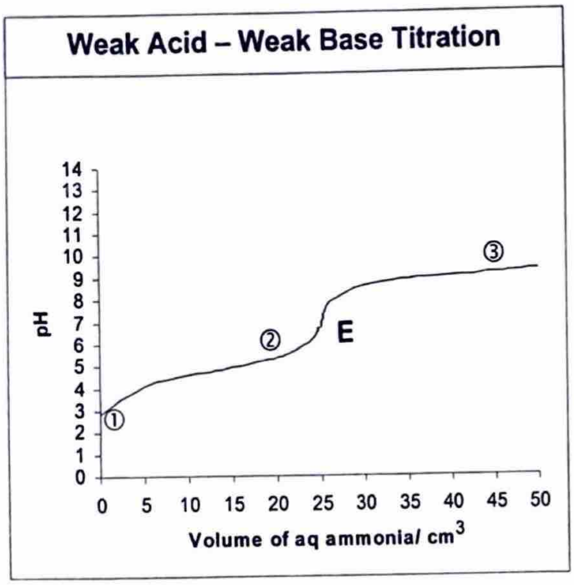
Since NH_4^+ is a weak acid with a relatively small K_a, assume x << 0.050. Then, (0.050 – x) ≈ 0.050.

$$x = [H^+] = \sqrt{(5.75 \times 10^{-10})(0.050)}$$
$$= 5.361 \times 10^{-6} \text{ mol dm}^{-3}$$

$pH = -\lg [H^+] = -\lg (5.361 \times 10^{-6}) = 5.27$

13.5 Titration curve of weak acid–weak base titration

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 not as sharp as 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.

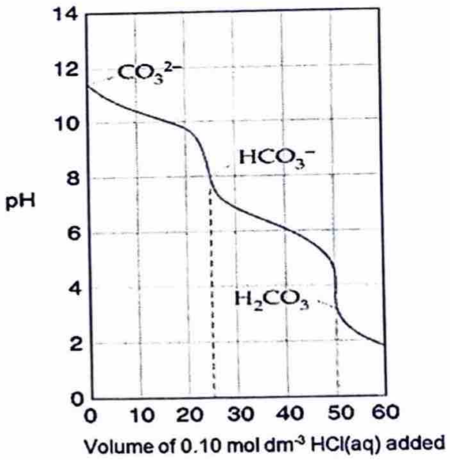
Note:
There is no suitable indicator for a weak acid – weak base titration as the region of rapid pH change is absent.

13.6 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 two equivalence points 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 thymolphthalein 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 methyl orange 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** cm^3,
  - then volume of HC*l* required for reaction (b) = **x** cm^3

  and

  - volume of HC*l* required when using thymolphthalein as indicator = **x** cm^3
  - volume of HC*l* required when using methyl orange as indicator = **2x** cm^3

- 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 $NaHCO_3$

13.7 Titration curve of a polyprotic acid–strong base titration

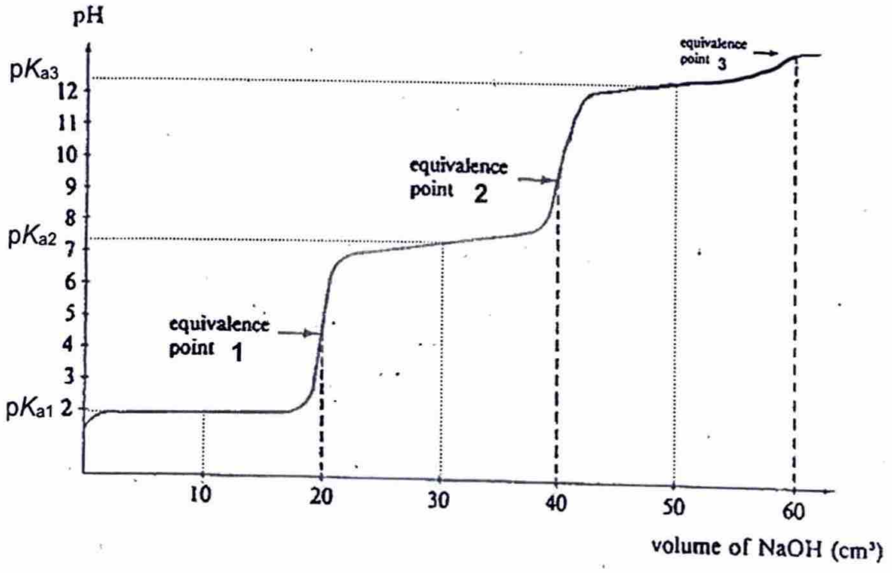
- Phosphoric acid, H_3PO_4, is a triprotic acid.

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 <u>three equivalence points</u> corresponding to the completion of each of the above reactions:



14 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	**Note:** For simplicity, we write $H^+(aq)$ instead of $H_3O^+(aq)$.

Conjugate acid-base pairs

$$\underset{\text{acid 1}}{HA(aq)} + \underset{\text{base 2}}{B(aq)} \rightleftharpoons \underset{\text{base 1}}{A^-(aq)} + \underset{\text{acid 2}}{HB^+(aq)}$$

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

For a conjugate acid-base pair,
$K_a \times K_b = K_w = 1.0 \times 10^{-14}\ mol^2\ dm^{-6}$
$pK_a + pK_b = pK_w = 14$ (at 298 K)

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

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

neutral solution: $[H^+] = [OH^-]$
acidic solution: $[H^+] > [OH^-]$
alkaline solution: $[H^+] < [OH^-]$

K_w: ionic product of water
$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$; $\Delta H > 0$
$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}\ mol^2\ dm^{-6}$
$pK_w = pH + pOH = 14$ (at 298 K)

pH Calculations

When solutions of acids and bases are mixed, always consider what species are present in the resultant solution at equilibrium before calculating the pH of the solution using the correct **K_a or K_b** value.

- strong acid/base or weak acid/base?
- acidic, basic or neutral salt? (hydrolysis)
- acidic buffer? (identify the acid and its conjugate base)
- alkaline buffer? (identify the base and its conjugate acid)

Strong acid
- **complete dissociation** in aqueous solution
- degree of dissociation, $\alpha = 1$
- $HX(aq) \longrightarrow H^+(aq) + X^-(aq)$
- Note: for monobasic acid, **$[H^+] = [HX]_0$** and **$pH = -lg\,[H^+]$**

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

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:

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

$$K_a = \frac{x^2}{[HA]_{initial}} \text{ where } [H^+] = x$$

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

Calculating pH of conjugate base of weak acid (basic salts):

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

$$\frac{K_w}{K_a\ of\ HA} = \frac{y^2}{[A^-]} \text{ where } [OH^-] = y$$

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

Calculating pH of a weak base:

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

$$K_b = \frac{y^2}{[B]_{initial}} \text{ where } [OH^-] = y$$

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

Calculating pH of conjugate acid of weak base (acidic salts):

$BH^+(aq) \rightleftharpoons H^+(aq) + B(aq)$

$$\frac{K_w}{K_b\ of\ B} = \frac{x^2}{[BH^+]} \text{ where } [H^+] = x$$

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

Acidic buffer
- comprises a weak acid, HA, and its conjugate base, A^-

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

- **maximum buffer capacity** when $\frac{[A^-]}{[HA]} = 1$ and hence **$pH = pK_a$**
  effective buffer range: $pH = pK_a \pm 1$

Alkaline buffer
- comprises a weak base, B, and its conjugate acid, BH^+

$$pOH = pK_b + lg\left(\frac{[BH^+]}{[B]}\right)$$

- **maximum buffer capacity** when $\frac{[BH^+]}{[B]} = 1$ and hence **$pOH = pK_b$**
- **effective buffer range:** $pOH = pK_b \pm 1$

Salt hydrolysis

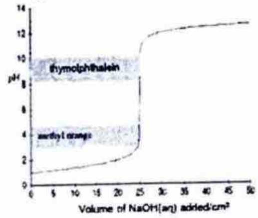
1. **neutral** salts – both cation and anion do not undergo hydrolysis
   e.g. NaC*l*(aq)

2. **acidic** salts – cation (usually the conjugate acid of a weak base) undergoes hydrolysis
   e.g. $NH_4Cl(aq)$
   NH_4^+ is the conjugate acid of NH_3
   $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

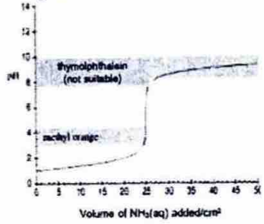
3. **basic** salts – anion (usually the conjugate base of a weak acid) undergoes hydrolysis
   e.g. $CH_3COO^-Na^+(aq)$
   CH_3COO^- is the conjugate base of CH_3COOH
   $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

Acid-base Titration Curves

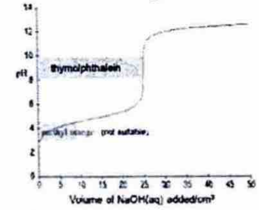
1. strong acid – strong base titration



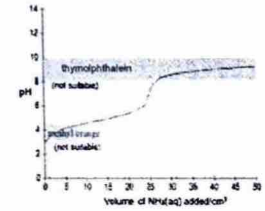
2. strong acid – weak base titration



3. weak acid – strong base titration



4. weak acid – weak base titration



Acid-base indicator

Note: A suitable indicator is one where **its pH range** <u>coincides</u> 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).

Raffles Institution
Year 6 H2 Chemistry 2023
Tutorial 14 – Acid-Base Equilibria

Self-Check Questions

1 (a) (i) Outline the Brønsted–Lowry theory of acids and bases.

(ii) Identify the conjugate acid–base pairs in the following reactions:

I. $CH_3COOH + H_2SO_4 \rightleftharpoons CH_3COOH_2^+ + HSO_4^-$

II. $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

III. $HNO_2(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + NO_2^-(aq)$

(b) (i) Outline the Lewis theory of acids and bases.

(ii) Identify the Lewis acid and base in each of the following reactions:

I. $(CH_3)_3N(g) + BF_3(g) \rightleftharpoons (CH_3)_3NBF_3(s)$

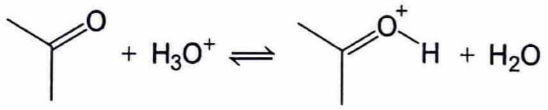
II. $Al(OH)_3(s) + OH^-(aq) \rightleftharpoons [Al(OH)_4]^-(aq)$

(c) Identify the acid and base present in the following reactions, in terms of the Brønsted–Lowry theory, the Lewis theory, or both, as appropriate.

(i) $HBr(g) + H_2O(l) \rightarrow H_3O^+(aq) + Br^-(aq)$

(ii) $HIO + NH_2^- \rightleftharpoons NH_3 + IO^-$

(iii)



2 Calculate the pH of the following solutions at 298 K.

(a) 0.010 mol dm^{-3} H_2SO_4

(b) 0.40 g dm^{-3} NaOH

(c) A solution formed by mixing 14.00 cm^3 of 0.10 mol dm^{-3} H_2SO_4 with 20.00 cm^3 of 0.10 mol dm^{-3} NaOH.

(d) 0.30 mol dm^{-3} CH_3CH_2COOH ($pK_a = 4.89$)

(e) 2.00 mol dm^{-3} $CH_3CH_2NH_2$ (K_b of $CH_3CH_2NH_2 = 5.1 \times 10^{-4}$ mol dm^{-3})
[Note: $CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$]

(f) 0.015 mol dm^{-3} potassium benzoate, $C_6H_5COO^-K^+$
(K_a of benzoic acid, $C_6H_5COOH = 6.5 \times 10^{-5}$ mol dm^{-3})

(g) 0.25 mol dm^{-3} methylammonium nitrate, $CH_3NH_3^+ NO_3^-$
(K_b of methylamine $CH_3NH_2 = 4.4 \times 10^{-4}$ mol dm^{-3})
[Note: $CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$]

(h) A solution containing 0.50 mol dm^{-3} $CH_3CH_2COOH(aq)$ and 0.35 mol dm^{-3} $CH_3CH_2COO^-K^+(aq)$.
(K_a of $CH_3CH_2COOH = 1.3 \times 10^{-5}$ mol dm^{-3})

(i) A solution containing 0.060 mol dm^{-3} of NH_3 and 0.080 mol dm^{-3} of NH_4Cl.
(K_b of $NH_3 = 1.74 \times 10^{-5}$ mol dm^{-3})

3 (a) A solution of 1.00×10^{-3} mol dm^{-3} HX has a pH of 3.25. Calculate the acid dissociation constant of HX.

(b) A solution of 1.00×10^{-2} mol dm^{-3} sodium ethanoate has a pH of 8.37. Calculate the pK_a of ethanoic acid.

(c) A solution of 0.050 mol dm^{-3} ammonium sulfate solution has a pH of 5.12 at 298 K. Calculate the pK_b of ammonia.

4 [N2009/1/6]

What is a property of a solution of dry hydrogen chloride in dry methylbenzene?

A It has a pH less than 7.

B It is a non-conductor of electricity.

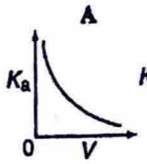
C It reacts with magnesium to give hydrogen.

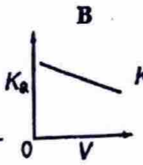
D It reacts with anhydrous sodium carbonate to give carbon dioxide.

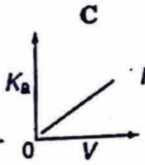
5 [N2008/1/11]

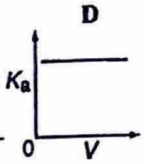
A 1 mol sample of ethanoic acid is diluted at constant temperature to a volume V.

Which diagram shows how K_a, the acid dissociation constant, varies with V?









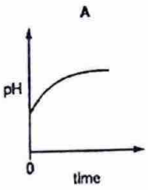
6 [N2010/I/12]

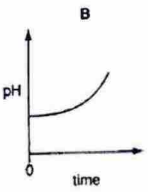
Sulfur dioxide gas is converted to sulfate ions when it is bubbled into aqueous manganate(VII) ions.

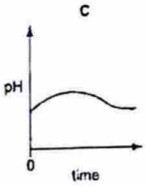
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

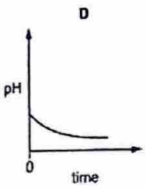
$$SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$

Which graph shows how the pH changes as sulfur dioxide is bubbled at a constant rate into a well-stirred solution of managate(VII) ions until its colour just fades?









7 [N2002/1/8]

Use of the Data Booklet is relevant to this question.

Water dissociates as shown.

$$H_2O \rightleftharpoons H^+ + OH^-$$

At 25 °C, the equilibrium value of [H$^+$] is 10^{-7} mol dm^{-3}; $[H_2O] = \frac{1000}{18}$ mol dm^{-3}.

What is the order of increasing numerical value of pH, pK_a and pK_w for this equilibrium at this temperature?

[pK_w = –log K_w]

	smallest		largest
A	pH	pK_a	pK_w
B	pH	pK_w	pK_a
C	pK_a	pK_w	pH
D	pK_w	pK_a	pH

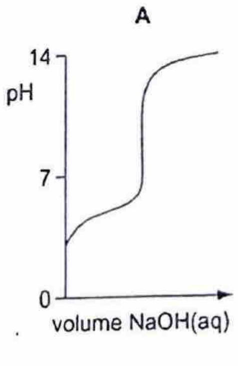
8 [N2012/1/9]

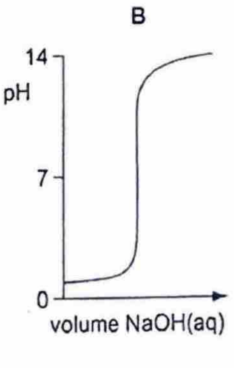
Pyruvic acid is a weak acid that is an important intermediate in many biochemical processes.

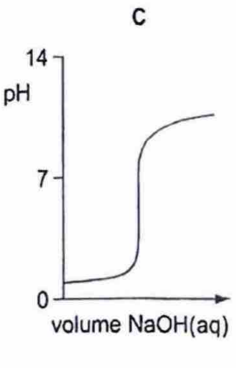
CH_3COCO_2H

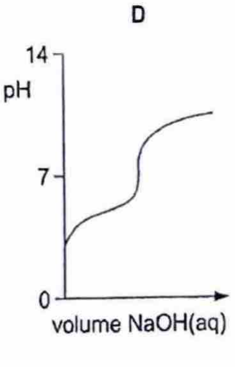
pyruvic acid

Which graph best represents the change in pH that occurs when a sample of pyruvic acid is titrated with NaOH(aq)?









Practice Questions

1 A sample of apple juice has a pH of 3.50. When 25.0 cm^3 of this apple juice sample is titrated against 0.100 mol dm^{-3} sodium hydroxide using thymolphthalein as the indicator, the average titre value is 27.50 cm^3.

(a) Define pH and calculate the molar concentration of hydrogen ions in apple juice.

(b) Assuming that apple juice contains a single acid HA which is monobasic, calculate the molar concentration of HA in apple juice and hence explain whether HA is a strong or weak acid.

(c) Calculate the degree of dissociation and the acid dissociation constant of the acid HA.

(d) A sample of hydrochloric acid has the same pH as the sample of apple juice. Explain why if 1 dm^3 each of apple juice and this hydrochloric acid were treated separately with the same excess amount of zinc powder, the apple juice would yield a larger volume of hydrogen gas at room temperature.

2 The pK_a for ethanoic acid at 25 °C is 4.74.

(a) (i) Calculate the pH of an aqueous solution of 0.50 mol dm^{-3} ethanoic acid.

(ii) Calculate the pH of the resultant solution when equal volumes of 0.50 mol dm^{-3} ethanoic acid and 0.20 mol dm^{-3} sodium hydroxide are mixed.

(b) A solution that contains only sodium ethanoate of concentration 0.050 mol dm^{-3} has a pH that is above 7.

(i) Write an equation involving the ethanoate ion and explain why the pH of the solution is above 7.

(ii) Write an expression for the base dissociation constant K_b for the ethanoate ion and calculate the value of K_b for the ethanoate ion.

(iii) Hence, calculate the pH of a 0.050 mol dm^{-3} sodium ethanoate solution.

(c) A laboratory assistant wanted to prepare a buffer solution containing ethanoic acid and sodium ethanoate. Find the volume of 0.10 mol dm^{-3} of sodium ethanoate that is needed to be added to 25.0 cm^3 of 0.12 mol dm^{-3} $CH_3COOH(aq)$ to form a buffer solution of pH 5.00.

3 (a) A buffer solution is prepared by mixing 750 cm^3 of 0.20 mol dm^{-3} ammonium chloride solution and 500 cm^3 of 0.10 mol dm^{-3} aqueous ammonia. Calculate the pH of this buffer solution. (K_a for the ammonium ion = 6.00×10^{-10} mol dm^{-3} at 25 °C)

(b) Calculate the change in pH of the buffer solution prepared in (a) after the addition of

(i) 0.002 mol of solid sodium hydroxide,
(ii) 1.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid.

4 Blood plasma is a biological fluid that maintains pH in the blood. In the blood plasma, the following equilibrium between carbonic acid, H_2CO_3(aq) and hydrogencarbonate ions, HCO_3^-(aq) is established:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a_1} = 7.90 \times 10^{-7} \text{ mol dm}^{-3}$$

At body temperature, the pH of the arterial blood plasma is 7.40. If the pH falls below this normal value, a condition termed acidosis is produced. If the pH rises above this normal value, the condition termed alkalosis is produced. The concentration of H_2CO_3(aq) is controlled by respiration through the lungs. H_2CO_3(aq) is in equilibrium with dissolved CO_2.

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

In the lungs, excess dissolved CO_2(aq) is exhaled as CO_2(g).

$$CO_2(aq) \rightleftharpoons CO_2(g)$$

During heavy exercise, lactic acid is released into the blood. This eventually leads to an increase in CO_2(aq) concentration and stimulates increased breathing.

(a) Explain what is meant by the term *buffer solution*. With the aid of equations, explain how blood plasma helps to maintain the pH of blood plasma.

(b) Determine the ratio of the concentration of HCO_3^-(aq) to H_2CO_3(aq) in the blood plasma Based on your answer, comment on the buffering capacity of the buffer in blood plasma.

(c) Explain why the rate of breathing increases when lactic acid is released into blood.

[2022 RI Prelim P1 Q17]

5 The K_a of lactic acid is 1.4×10^{-4} mol dm^{-3} at 298 K.

A buffer solution contains 1.5 mol dm^{-3} lactic acid and 0.5 mol dm^{-3} sodium lactate.

Which statement correctly describes the buffer solution?

A The pH of the buffer solution is 4.33.

B The pH of the buffer solution decreases upon dilution with water.

C The buffering capacity of the buffer solution increases upon dilution with water.

D The buffer solution has a greater buffering capacity against a base compared to an acid.

6 The major acidic component of soured milk is lactic acid, $CH_3CH(OH)CO_2H$. When 10.0 cm^3 of solution of lactic acid was titrated against 0.050 mol dm^{-3} sodium hydroxide the following pH readings were obtained:

Volume of NaOH added /cm^3	0	2	4	6	8	10	12	14	16	18	20
pH	2.5	3.1	3.4	3.7	3.9	4.1	4.4	4.7	9.1	11.6	11.8

(a) Plot a graph of these results with pH on the y–axis and volume of NaOH added on the x–axis. Comment on the shape of the curve before, at and after neutralisation.

(b) (i) Suggest a suitable indicator for this titration, giving a reason for your choice.

(ii) For the indicator chosen, state the colour change at the end–point of the titration.

(c) Calculate the molar concentration of the lactic acid in the solution.

(d) Deduce from the graph the K_a value for lactic acid.

(e) Explain why, at the equivalence–point of this titration, the resulting solution is basic.

(f) Indicate clearly on your graph the region within which the mixture is acting as an acidic buffer solution, labelling the point in which the mixture has maximum buffer capacity.

7 Phenylboronic acid, $C_6H_5B(OH)_2$, and benzoic acid, $C_6H_5CO_2H$, are both monoprotic (monobasic) acids, with pK_a values of 8.86 and 4.20 respectively.

(a) Give the equation which represents the dissociation of benzoic acid.

(b) Calculate the pH of 0.010 mol dm^{-3} benzoic acid.

(c) Which is the stronger of the two acids? Explain your reasoning.

(d) A 10.0 cm^3 sample of **X**, a solution containing both of these acids, was titrated against 0.050 mol dm^{-3} NaOH using a mixture of two indicators, bromothymol blue and thymolphthalein. It was found that 8.6 cm^3 of NaOH(aq) were needed to change the colour of the first indicator and a further 7.1 cm^3 were needed to change the colour of the second indicator.

(i) Using the above information, sketch a labelled graph to show how pH changes with the addition of NaOH(aq) for this titration.

(ii) Use the data to calculate the concentration of each of the two acids in **X**.
(hint: the NaOH added will first react with the stronger acid in the titration.)