ANDERSON SERANGOON JUNIOR COLLEGE
JC2 H2 CHEMISTRY

ACID–BASE EQUILIBRIA

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Content

(i) Acid dissociation constants, K_a and the use of pK_a
(ii) Base dissociation constants, K_b and the use of pK_b
(iii) The ionic product of water, K_w
(iv) pH: choice of pH indicators
(v) Buffer solutions

Learning Outcomes

Students should be able to:

(a) explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation
(b) explain the terms pH; K_a; pK_a; K_b; pK_b; K_w and apply them in calculations, including the relationship $K_w = K_aK_b$
(c) calculate $[H^+(aq)]$ and pH values for strong acids, weak monobasic (monoprotic) acids, strong bases, and weak monoacidic bases
[Calculations involving weak acids/bases will **not** require solving of quadratic equations]
(d) describe the changes in pH during acid–base titrations and explain these changes in terms of the strengths of the acids and bases
(e) explain the choice of suitable indicators for acid–base titrations, given appropriate data
(f) (i) explain how buffer solutions control pH
(ii) describe and explain their uses, including the role of H_2CO_3/HCO_3^- in controlling pH in blood
(g) calculate the pH of buffer solutions, given appropriate data

References

1. Chemistry for Advanced Level, Cann and Hughes, Murray
2. Chemistry, The Molecular Nature of Matter and Change (Fourth Edition), Silberberg, McGraw Hill
3. Chemistry & Chemical Reactivity (Sixth Edition), Kotz, Treichel and Weaver, Thomson
4. Chemistry The Central Science (Ninth Edition), Brown, LeMay, Bursten, Prentice Hall
5. Understanding Advanced Physical Inorganic Chemistry, The Learner's Approach, Jeanne Tan, Kim Seng Chan, WS Education

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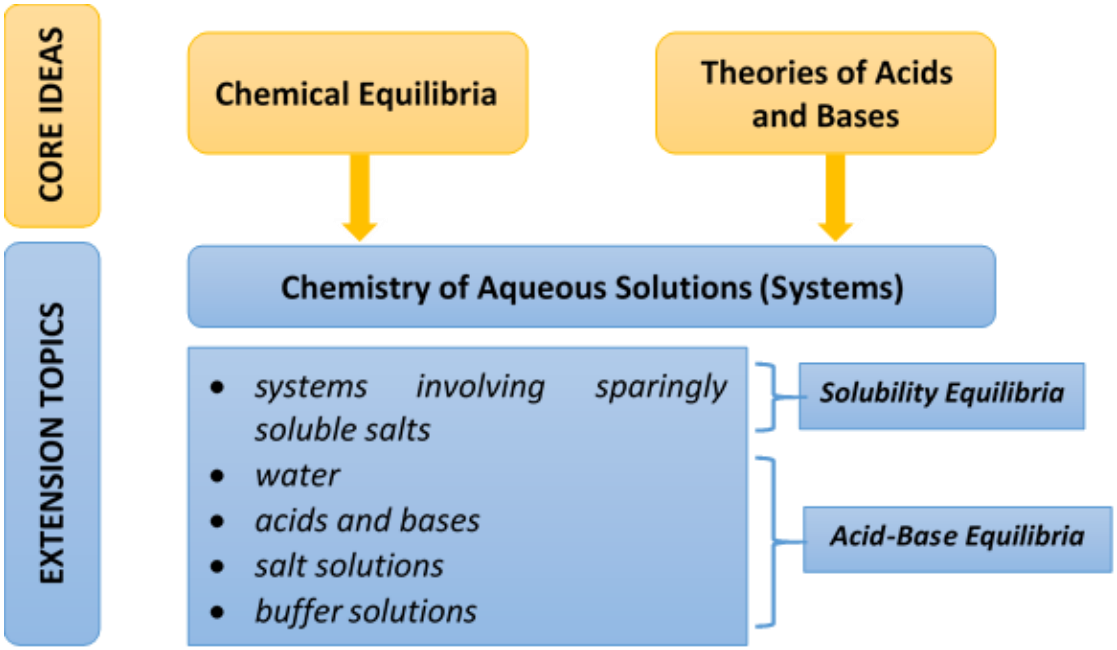
Content Map



1 Theories of Acids and Bases

1.1 Arrhenius Theory of Acids & Bases

- An **Arrhenius acid** is a substance that **releases H^+ ions** and an **Arrhenius base** is a substance that **releases OH^-** when they are dissolved in water.
- An acid–base reaction occurs when H^+ reacts with OH^- to produce H_2O. This reaction is also known as neutralisation.
- Example:

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

1.2 Brønsted–Lowry Theory of Acids & Bases

- A **Brønsted acid** is a proton (H^+) **donor**.
- A **Brønsted base** is a proton (H^+) **acceptor**.
- An acid–base reaction involves **transfer** of **proton** (H^+) from the acid to the base.
- Example:

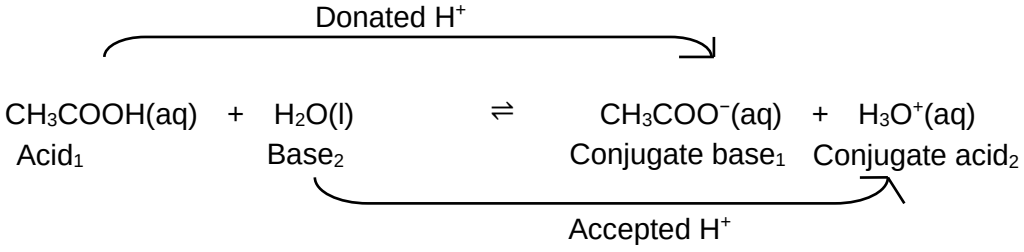
$$HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

1.2.1 Conjugate Acid-Base Pairs

$$\underset{\text{acid}}{HA(aq)} + \underset{\text{base}}{:B(aq)} \rightarrow \underset{\text{conjugate base}}{A^-(aq)} + \underset{\text{conjugate acid}}{BH^+(aq)}$$

- When a Brønsted–Lowry acid, HA, loses a proton, the resulting product, **A^-**, is called the **conjugate base of HA**.
- When a Brønsted–Lowry base, B, accepts a proton, the resulting product, **BH^+**, is called the **conjugate acid of B**.

- Consider the following equilibrium:



- **An acid and a base** such as CH_3COOH and CH_3COO^-, **which differ from each other by only one proton, H^+,** are referred to as a **conjugate acid-base pair**.

Exercise

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

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

acid base conjugate base conjugate acid

(b) $HCOOH(aq) + OH^-(aq) \rightarrow HCOO^-(aq) + H_2O(l)$

conjugate _____ conjugate _____

(c) $NH_4^+(aq) + S^{2-}(aq) \rightarrow HS^-(aq) + NH_3(aq)$

conjugate _____ conjugate _____

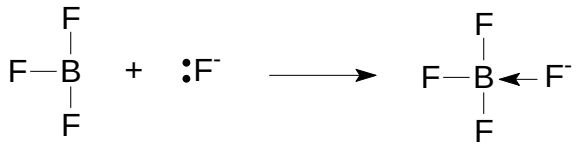
2. Circle the conjugate acid-base pairs from the following sets of substances.

(a) NH_4^+ NH_3 NH_2^+

(b) CH_3O^+ CH_3OH CH_3O^-

1.3 Lewis Theory of Acids & Bases

- A **Lewis acid is an <u>electron–pair acceptor</u>**.
- A **Lewis base is an <u>electron–pair donor</u>**.
- An acid–base reaction involves **the donation of an electron pair by a Lewis base to a Lewis acid to form a covalent bond**.
- Example: BF_3 acts as a Lewis acid and F^- acts as a Lewis base to form BF_4^-.

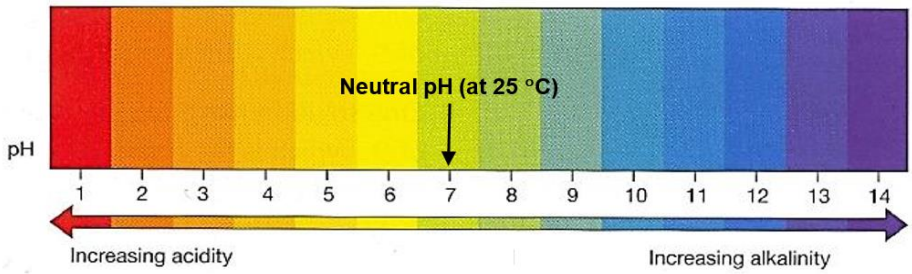


Summary

	ACID	BASE
Arrhenius	**releases H^+ ions in aqueous solution**	**releases OH^- in aqueous solution**
Brønsted–Lowry	**proton (H^+) donor**	**proton (H^+) acceptor**
Lewis	**electron–pair acceptor**	**electron–pair donor**

This topic deals with acid–base equilibria in **<u>aqueous solutions</u>**. Hence, the **<u>Brønsted–Lowry</u>** definitions of acid/base are primarily used in the understanding of the pH of solutions.

2 THE pH SCALE



The pH scale was developed to measure the acidity of solutions based on the concentration of hydrogen ions, H^+ (or hydronium ions, H_3O^+) in the solution.

Experimentally, the pH value is found to lie between 0 and 14 for most aqueous solutions at **298 K** (**25 °C**).

The pH of a solution is defined as:

$$\mathbf{pH = -\log_{10}[H^+] \quad or \quad -\log_{10}[H_3O^+]}$$

Conversely, pOH is a measure of the concentration of hydroxide ions, OH^- in an aqueous system.

pOH is defined as:

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

3 The Ionic Product of Water (K_w)

Pure water conducts electricity slightly as it is **ionised** (or **dissociated**) to a small extent, to form proton and hydroxide ion.

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

Since H^+ has a very high charge density, it attracts another water molecule, forming H_3O^+ and the dissociation equation can also be represented by equation below.

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The above reaction is also known as the **auto–ionisation of water**, and the K_c expression is:

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Since $[H_2O(l)]$ is a constant, we can incorporate it into the equilibrium constant, K_c, and define a new constant, K_w:

$$K_c \times [H_2O]^2 = [H_3O^+][OH^-]$$
$$K_w = [H_3O^+][OH^-]$$

The constant K_w is known as the **ionic product of water**.

$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$ mol^2 dm^{-6}	at 298 K (25 °C)

Taking $-\log_{10}$ on both sides of the K_w expression above:

$pK_w = pH + pOH = 14$	at 298 K (25 °C)

Effect of temperature on K_w:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \Delta H = +58 \text{ kJ mol}^{-1}$$

The dissociation of $H_2O(l)$ is endothermic.

When temperature increases, the forward endothermic reaction is favoured. Thus, the position of equilibrium shifts to the right to absorb the excess heat.
Both $[H_3O^+]$ and $[OH^-]$ increase by the same extent and K_w increases.

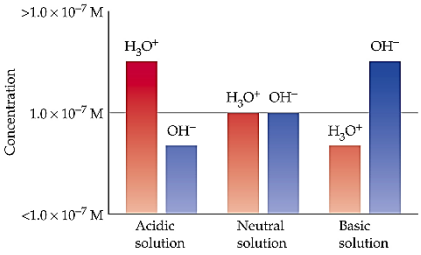
temperature / K	K_w / mol^2 dm^{-6}	pK_w	in a neutral solution (or pure water)	
			$[H_3O^+] = [OH^-]$ / mol dm^{-3}	pH
273	0.11×10^{-14}	15.0	3.32×10^{-8}	7.48
298	**1.00×10^{-14}**	**14.0**	**1.00×10^{-7}**	**7.00**
373	51.3×10^{-14}	12.3	7.16×10^{-7}	6.14

Based on the above data, does pure water become acidic at higher temperatures and basic at lower temperatures?

No! Pure water does NOT become acidic at higher temperature and basic at lower temperature. It is still neutral as water ionises to give **equal** concentration of $[H_3O^+]$ and $[OH^-]$.

Note that a solution is considered:

- neutral if $[H_3O^+] = [OH^-]$
- acidic if $[H_3O^+] > [OH^-]$
- alkaline if $[H_3O^+] < [OH^-]$



What can we conclude from the table above?

- Pure water will only be pH 7 at 298K. It is still neutral but have different pH values at other temperatures.
- We should not use pH alone to conclude if a solution is neutral. Instead, we should compare relative $[H_3O^+]$ and $[OH^-]$.

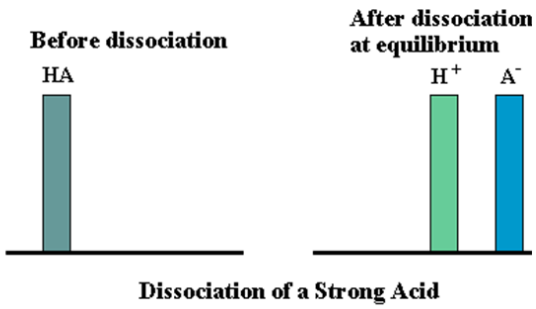
4 Strength of Acids & Bases

Acids and bases can be classified as strong or weak.

	Strong Acid	**Strong Base**
Definition	A **strong acid** is one which **dissociates <u>fully</u>** in aqueous solution to give **protons (H^+)**	A **strong base** is one which **dissociates <u>fully</u>** in aqueous solution to give **hydroxide ions (OH^-)**
Percentage dissociation	**100%**	**100%**
Type of arrow *used in* ***dissociation equation***	$\longrightarrow$ (full arrow)	$\longrightarrow$ (full arrow)
Equilibrium constant, K	Nil	Nil
Example:	$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$	$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

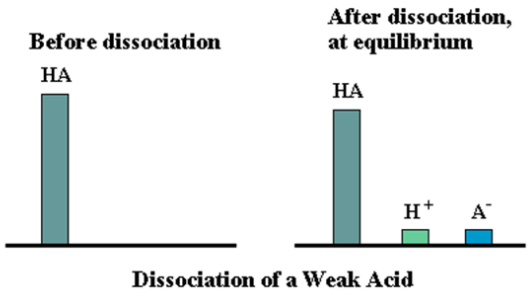
	Weak Acid	**Weak Base**
Definition	A **weak acid** is one which **dissociates <u>partially</u>** in aqueous solution to give **protons (H^+)**	A **weak base** is one which **dissociates <u>partially</u>** in aqueous solution to give **hydroxide ions (OH^-)**
Percentage dissociation	**<< 100%**	**<< 100%**
Type of arrow *used in* ***dissociation equation***	$\rightleftharpoons$ (reversible arrow)	$\rightleftharpoons$ (reversible arrow)
Equilibrium constant, K	**Acid Dissociation Constant, K_a**	**Base Dissociation Constant, K_b**
Example	$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Strong Acid
Percentage dissociation: 100%



Dissociation of a Strong Acid

Weak Acid
Percentage dissociation: << 100%



Dissociation of a Weak Acid

4.1 Calculations involving a Strong Acid or Strong Alkali

A **strong acid** or a **strong alkali** is one which dissociates **completely** in water.

In an aqueous solution of the strong acid, e.g. HC*l*: $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

$$\mathbf{[H_3O^+]_{produced} = [HCl]_{initial}}$$

If the pH of the solution is given, $[H_3O^+]$ can be found and vice versa by using the formulae:

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

In aqueous acid solutions, H_3O^+ ions are contributed by both the auto–ionisation of water and the dissociation of acid. However, the amount of H_3O^+ ions from water is insignificant if the concentration of the acid solution is greater than 10^{-6} mol dm^{-3}.

Therefore, in most cases we only consider $[H_3O^+]$ from the acid in the calculation of pH of the acid solution.

Exercises

Calculate the pH of the following solutions at 25 °C.

(a) 5.0 x 10^{-3} mol dm^{-3} HC*l*

$1HCl + H_2O \longrightarrow 1H_3O^+ + Cl^-$

$[H_3O^+] = 5.00 \times 10^{-3}$ mol dm^{-3}

pH = −lg(5.00 x 10^{-3}) = 2.30 (3sf)

(b) 0.25 mol dm^{-3} H_2SO_4 solution

$1H_2SO_4 + 2H_2O \longrightarrow 2H_3O^+ + SO_4^{2-}$

$[H_3O^+] = 2 \times 0.25 = 0.500$ mol dm^{-3}

pH = −lg(0.500) = 0.301 (3sf)

(c) 1.25 x 10^{-2} mol dm^{-3} NaOH

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

pOH = −lg( ) = 1.90

pH = = 12.1 (3sf)

(d) 0.1 mol dm^{-3} $Ba(OH)_2$ solution

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

pOH = −lg( ) = 0.699

pH = = 13.3 (3sf)

(e) 1.0 x 10^{-8} mol dm^{-3} HC*l*

$[H_3O^+]$

= (contribution from water)

= 1.10 x 10^{-7} mol dm^{-3}

pH = −lg(1.10 x 10^{-7}) = 6.96

**$[HCl]$ is lesser than 10^{-6} mol dm^{-3}

pH_{water}	$[H_3O^+] = [OH^-]$ / mol dm^{-3}
7.00	1.00 x 10^{-7}

4.2 WEAK ACIDS AND WEAK BASES

4.2 (A) Strength of Acids and Bases & Dissociation Constants

The strength of an acid or a base depends on its extent of dissociation in aqueous solution. The **extent of dissociation** of a weak acid or a weak base can be quantified using the concept of dissociation constants.

(i) Acid dissociation constant, K_a

A **weak** acid (HA) is one which dissociates **partially** in water to produce H_3O^+.

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

Applying the Equilibrium Law, we can write the equilibrium constant as:

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

In dilute aqueous solutions, $[H_2O(l)]$ is essentially constant and it can be incorporated into the equilibrium constant, K_c, and a new constant can be defined, called the **acid dissociation constant**, K_a, as follows:

$$K_c \times [H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

$$\boldsymbol{K_a = \frac{[H_3O^+][A^-]}{[HA]}} \qquad \text{units: } \textbf{mol dm}^{\textbf{-3}}$$

Like K_c, $\boldsymbol{K_a}$ is temperature dependent, i.e. they are **constants that only vary when temperature changes.**

A **stronger acid** dissociates to a greater extent and hence its $\boldsymbol{K_a}$ value is **larger**

Polyprotic acids

- The basicity of an acid refers to the number of H^+ ion per molecule that can be donated by one acid molecule. If an acid is able to donate more than one H^+ ion per molecule to a base, it is called a polybasic (or polyprotic) acid.
  - a monobasic (or monoprotic) acid, such as CH_3COOH, can donate 1 H^+ ions per molecule and
  - a dibasic (or diprotic) acid, such as H_2CO_3, can donate 2 H^+ ions per molecule and
  - a tribasic (or triprotic) acid, such as H_3PO_4, can donate 3 H^+ ions per molecule to a base.

Consider a dibasic acid H_2A

$$H_2A(aq) \rightleftharpoons HA^-(aq) + H^+(aq) \qquad K_{a1}$$
$$HA^-(aq) \rightleftharpoons A^{2-}(aq) + H^+(aq) \qquad K_{a2}$$

1st Dissociation constant, $K_{a1} = \dfrac{[H^+][HA^-]}{[H_2A]}$

2nd Dissociation constant, $K_{a2} = \dfrac{[H^+][A^{2-}]}{[HA^-]}$

- Value of successive K_a decreases significantly, e.g. $K_{a1} >> K_{a2}$
  - The first dissociation proceeds more readily than the second since it is easier to remove the positively charged proton from the neutral acid molecule than from the negatively charged anion with which the proton experiences greater attraction.

(ii) Base dissociation constant, K_b

A **weak** base (B) is one which dissociates **partially** in water to produce OH^-.

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

Its base dissociation constant, K_b, expression can be written as:

$$\boldsymbol{K_b = \dfrac{[BH^+][OH^-]}{[B]}} \qquad \text{units: } \textbf{mol dm}^{\textbf{-3}}$$

$\boldsymbol{K_b}$ is temperature dependent, i.e. they are **constants that only vary when temperature changes**

A **stronger base** dissociates to a greater extent and hence its $\boldsymbol{K_b}$ value is **larger**

<u>Exercises</u>

Write expressions for the dissociation constant for each of the following acids and bases.

(a) K_a of CH_3CO_2H

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

(b) K_{a1} and K_{a2} of H_2CO_3

$$K_{a1} = \qquad K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$$

(c) K_b of NH_3

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

(d) K_b of CH_3NH_2

$$K_b =$$

(iii) pK_a and pK_b

Although the magnitude of K_a (or K_b) serves to measure the strength of acids (or bases), it is more convenient to use the corresponding pK_a (or pK_b) value for comparison.

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

The **larger** the value of K_a (or K_b), the **smaller** the value of pK_a (or pK_b).

4.2 (B) Calculations involving a Weak Acid or Weak Alkali

A **weak** acid (or weak alkali) dissociates **partially** in water. Hence the $[H_3O^+]$ (or $[OH^-]$) will be much lower than the initial concentration of the acid (or alkali).

Hence the $[H_3O^+]$ (or $[OH^-]$) must be calculated using the K_a (or K_b) value.

In calculations involving a **weak acid (HA)**, there are usually 3 terms involved:

- pH (derived from $[H_3O^+]$)
- K_a
- initial [acid]

2 of these will be given while the 3rd has to be calculated.
The 3 general types of questions centered on the K_a expression:

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

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

$$K_a = \frac{[H_3O^+]^2}{[HA]} \quad \text{(for solution with weak acid only)}$$

- ☞ Given initial [HA] and K_a, calculate pH (see Example 1)
- ☞ Given initial [HA] and pH, calculate K_a (see Example 2)
- ☞ Given K_a and pH, calculate initial [HA] (see Example 3)

Shortcut formula to find $[H_3O^+]$ and $[OH^-]$ for weak acids and bases:

$$[H_3O^+] = \sqrt{K_a \times [acid]_{initial}}$$
$$[OH^-] = \sqrt{K_b \times [base]_{initial}}$$

Example 1a (Given initial [HA] and K_a, calculate pH)

Calculate the pH of a 0.10 mol dm^{-3} solution of ethanoic acid given its acid dissociation constant, K_a = 1.8 x 10^{-5} mol dm^{-3}.

Step 1: Write the partial dissociation equation

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

Step 2:
- Use an 'I.C.E' table;
- Ignore H_3O^+ from auto–ionisation of water, $[CH_3COO^-] = [H_3O^+] = x$

initial	0.10	0	0
change	– x	+ x	+ x
equilibrium	0.10 – x	x	x

Solve for x using the K_a expression:

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]_{eqm}} = \frac{[H_3O^+]^2}{[CH_3COOH]_{eqm}} \approx \frac{[H_3O^+]^2}{[CH_3COOH]_{initial}}$$

Step 3: Solve for x

Assuming $[CH_3COOH]_{eqm} \approx [CH_3COOH]_{initial}$

Thus,

$$K_a \approx \frac{[H_3O^+]^2}{[HA]_{initial}}$$

and $[H_3O^+] = \sqrt{K_a \times [HA]_{initial}}$

$$K_a = \frac{[H_3O^+]^2}{[CH_3COOH]_{initial}}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.10}$$

$$x = \sqrt{1.8 \times 10^{-5}(0.10)}$$

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

$$[H_3O^+] = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$$

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

$$= \underline{\mathbf{2.87}}$$

Note that only Step 3 onwards needs to be shown in presented answers!
Steps 1 & 2 are visual guides to help in your understanding.

Why is the following assumption $[CH_3COOH]_{eqm} \approx [CH_3COOH]_{initial}$ valid?
Reason:

CH_3COOH is a weak acid with a small K_a, we can assume x << 0.10 such that (0.10 – x) ≈ 0.10

Example 1b (Given initial [B] and K_b, calculate pH)

Calculate the pH, at 298 K, of a 0.20 mol dm^{-3} aqueous solution of ammonia given K_b of NH_3 = 1.8 x 10^{-5} mol dm^{-3}

Step 1: Write the partial dissociation equation

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

Step 2:
- Use an 'I.C.E' table;
- Ignore OH^- from auto–ionisation of water, $[NH_4^+] = [OH^-] = y$

	NH_3		NH_4^+	OH^-
initial	0.20		0	0
change	– y		+ y	+ y
equilibrium	0.20 – y		y	y

Solve for y using the K_b expression:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]_{eqm}} = \frac{[OH^-]^2}{[NH_3]_{eqm}} \approx \frac{[OH^-]^2}{[NH_3]_{initial}}$$

Step 3: Solve for y

Assuming,

$[NH_3]_{eqm} \approx [NH_3]_{initial}$,

Thus $K_b \approx \frac{[OH^-]^2}{[B]_{initial}}$

and $[OH^-] = \sqrt{K_b \times [B]_{initial}}$

$$K_b = \frac{[OH^-]^2}{[NH_3]_{initial}}$$

$$1.8 \times 10^{-5} = \frac{y^2}{0.20}$$

$$y = \sqrt{1.8 \times 10^{-5}(0.20)}$$

$$= 1.90 \times 10^{-3}$$

$$[OH^-] = 1.90 \times 10^{-3} \text{ mol dm}^{-3}$$

Note that only Step 3 onwards needs to be shown in presented answers!
Steps 1 & 2 are visual guides to help in your understanding.

Note:
pH + pOH = 14

$$pH = 14 - pOH$$
$$= 14 - [-\log_{10}(1.90 \times 10^{-3})]$$
$$= \mathbf{\underline{11.3}}$$

(**$[NH_3]_{eqm} \approx [NH_3]_{initial}$** since NH_3 is a weak base with a small K_b, we can assume y << 0.20 such that (0.20 – y) ≈ 0.20)

Example 2 (Given initial [HA] and pH or degree of dissociation, calculate K_a or pK_a)

A 0.20 mol dm^{-3} aqueous solution of an acid HX is 1% dissociated. Calculate the

(i) pH of the solution

(ii) pK_a of the acid HX

(i) $[H_3O^+] = \frac{1}{100} \times 0.20 = 0.00200$ mol dm^{-3}

pH = $-\log_{10} 0.002$ = **2.70**

$\alpha = \frac{[H_3O^+]}{[acid]_{initial}}$

(ii) $K_a = \frac{[H_3O^+][X^-]}{[HX]} \approx \frac{0.002^2}{0.20} = 2.00 \times 10^{-5}$ mol dm^{-3}

$K_a \approx \frac{[H_3O^+]^2}{[HA]_{initial}}$

pK_a = $-\log_{10} (2 \times 10^{-5})$ = **4.70**

Example 3 (Given initial [HA] and pH, calculate K_a)

The pH of a 0.10 mol dm^{-3} solution of a weak monobasic acid, HA, is 2.43 at 298 K. Calculate the value of the dissociation constant, K_a, at 298 K.

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

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

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

Given pH = 2.43,

$[H_3O^+] = 10^{-2.43}$

$= 3.72 \times 10^{-3}$ mol dm^{-3}

Method 1: Apply assumption

$K_a \approx \frac{[H_3O^+]^2}{[HA]_{initial}}$

Method 2: Calculate accurately using

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

$K_a \approx \frac{[A^-][H_3O^+]}{[HA]_{initial}} = \frac{(3.72 \times 10^{-3})^2}{0.10}$

= **1.38 x 10^{-4} mol dm^{-3}**

OR

$K_a = \frac{[A^-][H_3O^+]}{[HA]_{eqm}} = \frac{(3.72 \times 10^{-3})^2}{0.10 - 3.72 \times 10^{-3}}$

= **1.44 x 10^{-4} mol dm^{-3}**

Both methods are acceptable.

Is pH a good indicator of acid strength?

Consider these two acids **X** (1 x 10^{-3} mol dm^{-3}) and **Y** (5.56 x 10^{-2} mol dm^{-3}), both of which have a pH value of 3. Determine if **X** and **Y** are strong or weak acids.

[Hint: Check if the acid has dissociated fully or partially (see definitions on page 7 of the lecture notes). This can be done by comparing [H$^+$] produced and original [acid] in solution.]

X is a strong acid and **Y** is a weak acid.

pH is not a good indicator! Both strong and weak acids may have the same pH due to different initial concentration of acids. K_a is a better indicator of acid strength.

4.3 Complementary Strengths of a Conjugate Acid–base Pair – Relationship between K_a, K_b and K_w

- An acid, after donating a proton forms its conjugate base.
- A base, after accepting a proton forms its conjugate acid.

For a **conjugate acid–base pair** (e.g. CH_3COOH/CH_3COO^- & NH_4^+/NH_3),

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

Taking $-\log_{10}$ on both sides,

$$\boldsymbol{pK_a + pK_b = pK_w}$$

Given that at **298 K** (**25 °C**), $K_w = 1 \times 10^{-14}$ mol^2 dm^{-6},

$$\boldsymbol{K_a \times K_b = K_w = 1 \times 10^{-14} \quad \Rightarrow \quad pK_a + pK_b = pK_w = 14}$$

Hence it allows us to determine the value of K_a of an acid, given K_b of its conjugate base and vice versa.

FYI: How is the expression $K_a \times K_b = K_w$ derived?

For a conjugate acid–base pair of HA/A^-, its K_a and K_b can be expressed as:

$$K_a(HA) = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{and} \quad K_b(A^-) = \frac{[HA][OH^-]}{[A^-]}$$

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

Multiplying K_a with K_b, we get:

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

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

$\therefore \quad K_a \times K_b = K_w$

Recall:
$K_w = [H_3O^+][OH^-]$

Exercise

Complete the following table.

acid	conjugate base	K_a (acid) / mol dm^{-3}	K_b (conjugate base) / mol dm^{-3}	pK_a	pK_b
CH_3COOH		1.80×10^{-5}			9.26
NH_4^+			1.80×10^{-5}	9.26	

The conjugate base of a weak acid is also a weak base!

K_a(acid)	acid	conjugate base	K_b(conjugate base)
1.80×10^{-5}	CH_3CO_2H	$CH_3CO_2^-$	5.60×10^{-10}
4.30×10^{-7}	H_2CO_3	HCO_3^-	2.30×10^{-8}

From the data above, we can conclude the following:

- The conjugate bases of the two weak acids are considered to be weak (as inferred from their small K_b values).
- Since the K_b value of the conjugate base, HCO_3^-, is larger than that of $CH_3CO_2^-$, HCO_3^- is a stronger base than $CH_3CO_2^-$.

Comparing the two weak acids, the stronger acid produces a weaker conjugate base.

5 SALT SOLUTIONS

5.1 Salt hydrolysis

When an acid and a base react, a salt is formed.

When salts dissolve in water, the ions are hydrated. **Hydration** occurs when the ions are attracted to surrounding water molecules through ion–dipole interactions.

Not all salts are neutral. There are certain salts, when dissolved in water, dissociate into ions which then react with water to produce either acidic or alkaline solutions. This phenomenon is known as **salt hydrolysis**.

Salt hydrolysis is a reversible reaction. The pH of a salt solution can be predicted qualitatively by considering the ions of the salt that hydrolyse in water.

(i) Salt formed from Strong Acid (e.g. HC*l*) and Strong Base (e.g. NaOH)

Dissociation of salt: $NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$

NaC*l* is a salt formed from a strong base, NaOH and strong acid, HC*l*.
The Na^+ and Cl^- ions are merely hydrated, and will **not** undergo hydrolysis.
Hence, it gives a neutral solution.

(ii) Salt formed from Weak Acid (e.g. CH_3COOH) and Strong Base (e.g. NaOH)

Dissociation of salt: $CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$

Hydrolysis: $\mathbf{CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)}$

CH_3COO^- is the conjugate base of the weak acid, CH_3COOH, hence it behaves as a weak base in water and will undergo hydrolysis in water to liberate OH^- ions.
As **$[OH^-] > [H_3O^+]$, pH of salt solution > 7** at **298 K** (**25 °C**).

(iii) Salt formed from Strong Acid (e.g. HC*l*) and Weak Base (e.g. NH_3)

Dissociation of salt: $NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$

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

NH_4^+ is the conjugate acid of the weak base, NH_3, hence it behaves as a weak acid in water and will undergo hydrolysis in water to liberate H_3O^+ ions.
As **$[H_3O^+] > [OH^-]$, pH of salt solution < 7** at **298 K** (**25 °C**).

Hence, whether the salt dissolves to form a neutral, acidic or alkaline solution depends on the acid and the base which react to give the salt. This is summarised as below:

Reaction between		**Example of Salt**	**Ion that undergoes hydrolysis**	**pH of solution (at 25 °C)**
strong acid	strong base	NaC*l*, K_2SO_4	None	= 7
weak acid	strong base	$CH_3COO^-Na^+$	CH_3COO^-	> 7
strong acid	**weak base**	$NH_4^+C\mathit{l}^-$	NH_4^+	< 7
weak acid	**weak base**	$CH_3COO^-NH_4^+$	CH_3COO^-, NH_4^+	< 7 if $K_b < K_a$ ≈ 7 if $K_a \approx K_b$ > 7 if $K_b > K_a$

* K_a and K_b in this table are referring to those of the ions in the salt formed, i.e. K_a of NH_4^+ and K_b of CH_3COO^-.

5.2 Calculation of pH of salt solution

Example (Given concentration of salt solution, determine pH of solution)

1. Find the pH of an aqueous solution of ammonium chloride, $NH_4C\mathit{l}$, of concentration 0.100 mol dm^{-3}, given that the K_b of ammonia, NH_3 is 1.8 x 10^{-5} mol dm^{-3}.

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

Step 1: Identify the ion undergoing hydrolysis and write the partial dissociation equation to illustrate hydrolysis of ion.
Salt formed from SA and WB behaves as a weak acid in water

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8\times10^{-5}} = 5.56 \times 10^{-10}$$

Step 2: Write the K_a or K_b expression. E.g. since the hydrolysis of NH_4^+ gives an acidic solution, we determine the value of K_a from the K_b value using $K_a = \frac{K_w}{K_b}$.

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \approx \frac{[H_3O^+]^2}{0.100}$$

$[H_3O^+] = 7.45 \times 10^{-6}$

$pH = -\log_{10}[H_3O^+] = 5.13$

Step 3:
- Determine $[H^+]$ (or $[OH^-]$) from K_a or K_b expression.
- Here, since we are finding pH of acidic solution, we use:

$K_a \approx \frac{[H_3O^+]^2}{[HA]_{initial}}$; $pH = -\log_{10}[H_3O^+]$

Example 2 (Given reaction mixture, determine pH of final solution)

Calculate the pH of the following solution at 298K:

20.00 cm^3 of 0.030 mol dm^{-3} C_6H_5COOH (K_a = 6.46 x 10^{-5}) is added to 20 cm^3 of 0.030 mol dm^{-3} KOH.

$C_6H_5COOH + KOH \longrightarrow C_6H_5COO^-K^+ + H_2O$

Amt of C_6H_5COOH = 20/1000 x 0.030 = 0.000600 mol

Amt of KOH = 20/1000 x 0.030 = 0.000600 mol

Both reactants are used up completely.

Step 1: Determine the limiting reagent and identify the species present at the end of reaction (if any).

$C_6H_5COO^-$ undergoes hydrolysis.

$C_6H_5COO^-(aq) + H_2O(l) \rightleftharpoons C_6H_5COOH(aq) + OH^-(aq)$

Step 2: Identify the ion undergoing hydrolysis, write the partial dissociation equation to illustrate hydrolysis of ion.
Salt formed from WA and SB behaves as a weak base in water

$$K_b = \frac{[C_6H_5COOH][OH^-]}{[C_6H_5COO^-]} = \frac{K_w}{K_a} = \frac{10^{-14}}{6.46 \times 10^{-5}} = 1.548 \times 10^{-10}$$

Step 3: Write the K_a or K_b expression.
Since the hydrolysis of $C_6H_5COO^-$ gives an alkaline solution, we determine the value of K_b using $K_b = \frac{K_w}{K_a}$.

Amt of $C_6H_5COO^-K^+$ formed = 0.000600 mol

$$[C_6H_5COO^-] = \frac{\frac{0.0006}{20+20}}{1000} = 0.0150 \text{ mol dm}^{-3}$$

$$K_b = \frac{[C_6H_5COOH][OH^-]}{[C_6H_5COO^-]} \approx \frac{[OH^-]^2}{0.0150}$$

$[OH^-] = \sqrt{1.548 \times 10^{-10} \times 0.015} = 1.5238 \times 10^{-6}$

$pOH = -\log_{10}(1.5238 \times 10^{-6}) = 5.817$

$pH = 14 - 5.817 = \mathbf{8.18}$

Step 4:

- Determine $[H^+]$ (or $[OH^-]$) from K_a or K_b expression
- Here since we are finding OH^-, we use

$$K_b \approx \frac{[OH^-]^2}{[B]_{initial}}$$

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

$pH = 14 - pOH$

Exercise

1. Find the pH of 2.00 mol dm^{-3} sodium ethanoate, $CH_3COO^-Na^+$, given that the K_a of ethanoic acid, CH_3COOH, is 1.80 x 10^{-5} mol dm^{-3}. [Answer: 9.52]

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

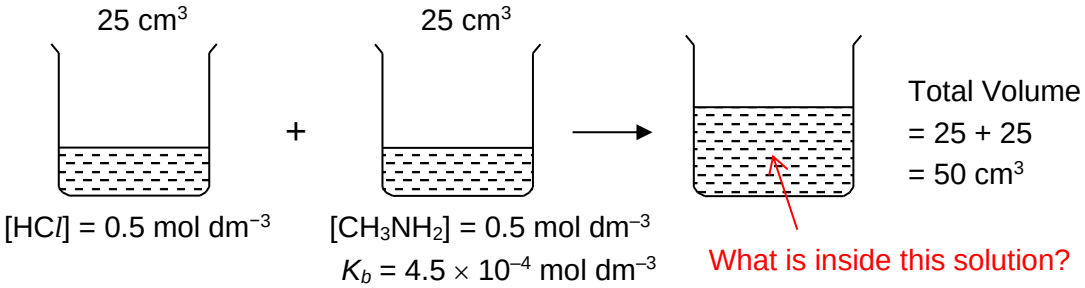
Salt formed from WA and SB behaves as a weak base in water

$$K_w / K_a = K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \approx \frac{[OH^-]^2}{2.00} =$$

$[OH^-] = 3.33 \times 10^{-5}$ mol dm^{-3} $\Rightarrow$ pOH = $-\log_{10}[OH^-]$ =

$\Rightarrow$ pH = = **9.52**

2. Calculate the pH of the solution that results when 25.0 cm^3 of 0.5 mol dm^{-3} CH_3NH_2, with $K_b = 4.5 \times 10^{-4}$ mol dm^{-3}, reacts with 25.00 cm^3 of 0.5 mol dm^{-3} of HC*l*. [Answer: 5.63]



	CH_3NH_2 +	HC*l* →	$CH_3NH_3^+Cl^-$
Initial amt / mol	$\frac{25}{1000}$ x 0.5	$\frac{25}{1000}$ x 0.5	0
change amt / mol	–0.0125	–0.0125	+0.0125
End amt / mol	0	0	0.0125

$\Rightarrow$ Resulting solution is **salt solution of $CH_3NH_3^+Cl^-$**

$CH_3NH_3^+$ undergoes hydrolysis.

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

Salt formed from SA and WB behaves as a weak acid in water

Amt of $CH_3NH_3^+Cl^-$ produced = mol

$[CH_3NH_3^+Cl^-] = \frac{\text{Amt of salt}}{\text{total volume}} =$ = 0.250 mol dm^{-3}

$$K_a = K_w / K_b = 2.222 \times 10^{-11} \text{ mol dm}^{-3}$$

$[H^+] =$ (since $CH_3NH_3^+$ is a conjugate acid)

$pH = -\log_{10}[H^+] = -\log_{10}(2.3569 \times 10^{-6}) =$ **5.63**

6 BUFFER SOLUTIONS

6.1 Types of Buffer Solutions

A buffer solution is one whose **pH remains ALMOST constant** when **small** amounts of acid (H^+) or alkali (OH^-) are added to it.

There are two types of buffer solutions:

Types of buffer		acidic	alkaline
pH		< 7	> 7
composition		weak acid and its salt (sodium/potassium salt)	weak base and its salt
example		CH_3COOH and $CH_3COO^-Na^+$	NH_3 and $NH_4^+Cl^-$
conjugate acid–base pair	**acid component**	CH_3COOH	NH_4^+
	base component	CH_3COO^-	NH_3

(i) Acidic buffer

Example: A solution of ***CH_3COOH*** *&* ***$CH_3COO^-Na^+$***

The **weak acid** undergoes **partial** dissociation:

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

The **salt** undergoes **complete** dissociation:

$$CH_3COO^-Na^+ \longrightarrow CH_3COO^- + Na^+$$

By *Le Chatelier's Principle*, the large amount of CH_3COO^- from $CH_3COO^-Na^+$ suppresses the dissociation of CH_3COOH (common ion effect – recall concept from Solubility Equilibria).

The resultant solution thus contains high concentrations of both **CH_3COOH** (acid) and **CH_3COO^-** (base).

(ii) Alkaline buffer

*Example: A solution of **NH_3** and **NH_4Cl***

The **weak base** undergoes **partial** dissociation:

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

The **salt** undergoes **complete** dissociation:

$NH_4Cl \longrightarrow NH_4^+ + Cl^-$

By *Le Chatelier's Principle*, the large amount of NH_4^+ from NH_4Cl suppresses the dissociation of NH_3 (common ion effect – recall concept from Solubility Equilibria).

The resultant solution thus contains high concentrations of both **NH_3** (base) and **NH_4^+** (acid).

6.2 How a Buffer System Controls pH

(i.e. How does a buffer system resist significant changes in pH when a small amount of an acid or a base is added to it?)

(i) Acidic buffer

Explain how a given solution containing a weak acid, CH_3COOH and its sodium salt, $CH_3COO^-Na^+$, acts as an acidic buffer.

Answer:
The solution contains high concentration of both CH_3COOH and CH_3COO^-.

CH_3COOH(aq) ⇌ CH_3COO^-(aq) + H^+(aq)
$CH_3COO^-Na^+$(aq) → **CH_3COO^-(**aq) + Na^+(aq)

When a **small amount of acid, H^+** is added:	When a **small amount of base, OH^-** is added:
CH_3COO^-(aq) + **H^+**(aq) → CH_3COOH(aq)	CH_3COOH(aq) + **OH^-(**aq) → CH_3COO^-(aq) + H_2O(l)
The large amount of CH_3COO^- ions present ensures that the added H^+ ions are removed as **CH_3COOH(aq)**.	The large amount of CH_3COOH molecules present ensures that the added OH^- ions are removed as **CH_3COO^-(aq) and H_2O(l).**
Hence pH **remains fairly constant.**	Hence pH **remains _____ constant.**

(ii) Alkaline buffer

<table>
<tr><td colspan="2">Explain how a given solution containing a weak base, NH_3 and its salt, NH_4Cl, acts as a basic buffer.
Answer:
The solution contains <u>high concentration</u> of both NH_3 and NH_4^+.

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

$NH_4Cl(aq) \rightarrow \mathbf{NH_4^+}(aq) + Cl^-(aq)$</td></tr>
<tr><td>When a small amount of acid, H^+ is added:

<u>$NH_3(aq) + \mathbf{H^+}(aq) \rightarrow NH_4^+(aq)$</u>

The large amount of NH_3 molecules present ensures that the added H^+ ions are removed as <u>$NH_4^+(aq)$.</u>

Hence pH <u>remains fairly constant</u>.</td><td>When a small amount of base, OH^- is added:

<u>$NH_4^+(aq) + \mathbf{OH^-}(aq) \rightarrow NH_3(aq) + H_2O(l)$</u>

The large amount of NH_4^+ ions present ensures that the added OH^- ions are removed as <u>$NH_3(aq)$ and $H_2O(l)$.</u>

Hence pH <u>remains fairly constant</u>.</td></tr>
</table>

6.3 Calculating pH of Buffer Solutions

(i) Acidic buffer

For any **weak acid and its salt** in an acidic buffer, e.g. HA / NaA

In general for an acidic buffer, $$K_a \approx \frac{[A^-]_{salt}[H_3O^+]}{[HA]_{initial}}$$

Example

Calculate the pH of a solution that contains 0.05 mol dm^{-3} of the weak acid, HA, and 0.15 mol dm^{-3} of the sodium salt, NaA (given K_a of HA = 7.5 x 10^{-4} mol dm^{-3}).

Step 1: Identify the salt and weak acid present in the buffer system. Write an equation to show how the weak acid dissociates to give H_3O^+.

$$NaA \longrightarrow A^- + Na^+$$

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

'I.C.E' table

	HA	H_2O	A^-	H_3O^+
initial	0.05		0.15	0
change	– x		+ x	+ x
equilibrium	0.05 – x ≈ 0.05		0.15 + x ≈ 0.15	x

Note that at equilibrium, **$[H_3O^+] \neq [A^-]$** for a buffer solution. This is unlike the case when pure HA is added to water whereby at equilibrium, $[H_3O^+] = [A^-]$.

FYI: Recall that the large amount of A^- from the complete dissociation of NaA suppresses the dissociation of the weak acid HA to such a large extent that the following **assumptions** can be made:

$$[A^-]_{eqm} = [A^-]_{HA} + [A^-]_{NaA} \approx [A^-]_{NaA}, \quad \text{i.e.} \quad (x + 0.15) \approx 0.15$$

$$[HA]_{eqm} = [HA]_{initial} - [HA]_{ionised} \approx [HA]_{initial}, \quad \text{i.e.} \quad (0.05 - x) \approx 0.05$$

Step 2: Write the K_a expression since the system is an acidic buffer.

$$K_a \approx \frac{[A^-]_{NaA}[H_3O^+]_{eqm}}{[HA]_{initial}}$$

Step 3: Substitute the concentration of the species into the K_a expression and solve.

$$7.5 \times 10^{-4} \approx \frac{0.15 \times [H_3O^+]}{0.05}$$

$$[H_3O^+] = 2.50 \times 10^{-4} \text{ mol dm}^{-3}$$

$$pH = -\log_{10}(2.50 \times 10^{-4})$$

$$= \underline{\mathbf{3.60}}$$

Note that only working in Steps 2 & 3 needs to be shown in presented answers!
The I.C.E table and FYI above are visual guides to help in your understanding.

Alternatively, the pH of an acidic buffer solution can be obtained by taking $-\log_{10}$ on both sides of the K_a equation:

$$-\log_{10}K_a = -\log_{10}\frac{[A^-]_{salt}}{[HA]_{initial}} + (-\log_{10}[H_3O^+])$$

$$pK_a = -\log_{10}\frac{[A^-]_{salt}}{[HA]_{initial}} + pH$$

$$\mathbf{pH = pK_a + \log_{10}\frac{[A^-]_{salt}}{[HA]_{initial}}} \qquad \textbf{or } pH = pK_a + \lg\frac{[salt]}{[acid]}$$

The above equation is also known as the *Henderson–Hasselbalch Equation*.

(ii) Alkaline buffer

For an alkaline buffer solution containing a weak base B and a salt of the base with BH^+, e.g. NH_3 / NH_4^+ Cl^-

In general for an alkaline buffer, $$K_b \approx \frac{[BH^+]_{salt}[OH^-]}{[B]_{initial}}$$

Example

Calculate the pH of a solution that contains 0.10 mol dm^{-3} of ammonium chloride and 0.05 mol dm^{-3} of aqueous ammonia (given K_b of NH_3 = 1.8 x 10^{-5} mol dm^{-3} at 25 °C).

$NH_4Cl \longrightarrow NH_4^+ + Cl^-$

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

Step 1: Identify the salt and weak base present in the buffer system. Write an equation to show how the weak base undergoes hydrolysis to give hydroxide.

$$K_b \approx \frac{[NH_4^+]_{salt}[OH^-]}{[NH_3]_{initial}}$$

Step 2: Write the K_a or K_b expression. Since the system is an alkaline buffer, write the K_b expression.

$$1.8 \times 10^{-5} \approx \frac{0.10 \times [OH^-]}{0.05}$$

Step 3: Substitute the concentration of the species into the K_b expression. Solve for $[OH^-]$ and hence pH.

$[OH^-] = 9.00 \times 10^{-6}$ mol dm^{-3}

$pOH = -\log_{10}(9.00 \times 10^{-6}) = 5.05$

$pH = 14 - 5.05 = \underline{\mathbf{8.95}}$

Alternatively, the pOH of an alkaline buffer solution can be obtained by taking $-\log_{10}$ on both sides of the K_b equation:

$$-\log_{10}K_b = -\log_{10}\frac{[BH^+]_{salt}}{[B]_{initial}} + (-\log_{10}[OH^-])$$

$$pK_b = -\log_{10}\frac{[BH^+]_{salt}}{[B]_{initial}} + pOH$$

$$\mathbf{pOH = pK_b + \log_{10}\frac{[BH^+]_{salt}}{[B]_{initial}}} \quad \textbf{or } pOH = pK_b + \lg\frac{[salt]}{[base]}$$

The above equation is also known as the *Henderson–Hasselbalch Equation*.

Exercises

Buffer involving mixing of 2 solutions.

1. A buffer solution is made by mixing 10 cm^3 of 0.090 mol dm^{-3} HA and 20 cm^3 of 0.15 mol dm^{-3} NaA. Calculate the pH of the buffer solution.
(K_a of HA = 4.7 x 10^{-6} mol dm^{-3} at 25 °C)

(Hint: Upon mixing, the resulting buffer solution now has a combined volume of 30cm^3)

$$[\text{HA}] \text{ in buffer} = \frac{10 \times 0.090}{10 + 20} = 0.0300 \text{ mol dm}^{-3}$$

$[\text{species}]_{new} = \dfrac{[\text{species}]_{initial} \times \text{volume of species}}{\text{new total volume}}$

$$[\text{NaA}] \text{ in buffer} = \frac{20 \times 0.15}{30} = 0.100 \text{ mol dm}^{-3} = [\text{A}^-]$$

Total volume after mixing
= 10 + 20 = 30 cm^3

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$$

Step 1: Identify the salt and weak acid present in the buffer system. Write an equation to show how the weak acid undergoes hydrolysis to give its salt (conjugate base).

Using $K_a \approx \dfrac{[\text{A}^-]_{salt}[\text{H}_3\text{O}^+]}{[\text{HA}]_{initial}}$

Step 2: Write the K_a or K_b expression.
Since the system is an acidic buffer, write the K_a expression.

$[\text{H}_3\text{O}^+]$ = 4.7 x 10^{-6} x 0.0300 / 0.100
= 1.41 x 10^{-6} mol dm^{-3}
pH = $-\log_{10}(1.41 \times 10^{-6})$
= **5.85**

Step 3: Substitute the NEW concentration of the species upon mixing into the K_a expression. Solve.

Buffer involving mixing of solution and solid.

2. A buffer solution is made by mixing 500 cm^3 of a 0.24 mol dm^{-3} NH_3 solution and 4.815 g of NH_4Cl. (K_b of NH_3 = 1.8 x 10^{-5} mol dm^{-3} at 25 °C)
   (a) Calculate the pH of the buffer solution.
   (b) Write an equation for the reaction that occurs when a drop of HC*l* is added to this buffer.

(a) $[NH_4Cl]$ = = 0.180 mol dm^{-3} = $[NH_4^+]$

Total volume after mixing remains at 0.5 dm^3 since there is no change in volume when salt is added to solution.

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

Step 1: Identify the salt and weak base present in the buffer system. Write an equation to show how the weak base undergoes hydrolysis to give hydroxide.

Using $K_b \approx \dfrac{[\text{NH}_4^+]_{salt}[\text{OH}^-]}{[\text{NH}_3]_{initial}}$

Step 2: Write the K_a or K_b expression.
Since the system is an alkaline buffer, write the K_b expression.

$[\text{OH}^-]$ =
= 2.40 x 10^{-5} mol dm^{-3}

Step 3: Substitute the concentration of the species upon mixing into the K_b expression. Solve.

pOH = $-\log_{10}(2.40 \times 10^{-5})$
= 4.62

pH = 14 – 4.62
= **9.38**

(b) $NH_3 + H_3O^+ \longrightarrow NH_4^+ + H_2O$

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

Buffer formed when excess WA is mixed with SB.

3. Calculate pH of the solution made up of 50 cm^3 of 0.200 mol dm^{-3} propanoic acid and 35 cm^3 of 0.200 mol dm^{-3} sodium hydroxide solution.
K_a of CH_3CH_2COOH = 1.34 x 10^{-5} mol dm^{-3}

Acid-base reaction occurs upon mixing.
CH_3CH_2COOH will be in excess and its salt $CH_3CH_2COO^-$ will be formed $\Rightarrow$ Buffer!

Step 1: Write the equation for the reaction

	CH_3CH_2COOH	+	OH^-	$\rightarrow$	$CH_3CH_2COO^-$	+	H_2O
Initial amt / mol	0.01		0.007		0		0
Δ amt / mol							
End amt / mol	0.003		0		0.007		0.007

Step 2: Use an ICE table to calculate the **resulting** concentrations of the acid & base components of the buffer.

4. Total volume = 50 cm^3 propanoic acid + 35 cm^3 sodium hydroxide solution = 85 cm^3

Step 3: Substitute the NEW concentration of the species upon mixing into the K_a expression.
Or use $pH = pK_a + \log_{10}\frac{[A^-]}{[HA]}$

$$pH = pK_a + \log_{10}\frac{[A^-]}{[HA]}$$

$$pH = -\log_{10}(1.34 \times 10^{-5}) + \log_{10}\left(\frac{\frac{0.007}{85/1000}}{\frac{0.003}{85/1000}}\right) = \mathbf{\underline{5.24}}$$

4.

(a) Use the relationship $pH = pK_a - \log_{10}\frac{[acid]}{[salt]}$

to calculate the pH of a solution which is 0.40 mol dm^{-3} with respect to ethanoic acid and 0.20 mol dm^{-3} with respect to sodium ethanoate.

[Take K_a for ethanoic acid as 1.80×10^{-5} mol dm^{-3}]

(b) Calculate the change in pH of 1.0 dm^3 of the solution in (a) when 0.050 mol of solid sodium hydroxide is added (assume no change in volume).

(c) What is the change in pH when 0.050 mol of sodium hydroxide is added to 1.0 dm^3 of water?

(a) $pH = -\log_{10}(1.80 \times 10^{-5}) - \log_{10}(\frac{0.40}{0.20}) =$ **<u>4.44</u>**

(b) When NaOH is added to the buffer, the following reaction takes place:

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

Step 1: Write the equation for the reaction that takes place.

Hence,

$[CH_3COOH]$ = = 0.350 mol dm^{-3}

$[CH_3COO^-]$ = = 0.250 mol dm^{-3}

Step 2: Calculate the **resulting** concentrations of the acid & base components of the buffer.

Using the given relationship: $pH = pK_a - \log_{10}\frac{[acid]}{[salt]}$

$pH = -\log_{10}(1.80 \times 10^{-5}) - \log_{10}(\frac{0.350}{0.250})$

= **<u>4.60</u>**

Step 3: Substitute the NEW concentration of the species upon mixing into the K_a expression.

Or use $pH = pK_a - \log_{10}\frac{[acid]}{[salt]}$

$\Rightarrow$ change in pH = 4.60 – 4.44 = **<u>0.16</u>**

(c) When 0.0500 mol of NaOH is added to 1.0 dm^3 of water,

$[OH^-]$ = 0.0500 mol dm^{-3}

pH = $14 - (-\log_{10} 0.050) = 12.7$

pH = 14 – pOH

$\Rightarrow$ change in pH = 12.7 – 7 = **<u>5.7</u>**

Notice how the buffer helps to <u>remove the added alkali</u> and keeps the pH of the solution almost constant!

6.4 Buffer Capacity and Buffer Range

The *capacity of a buffer* is the quantity of H_3O^+ or OH^- it can remove before its pH changes drastically.

A buffer is at its **maximum buffer capacity** (most effective) when **[salt] = [acid]** (for an acidic buffer) or when **[salt] = [base]** (for an alkaline buffer).

At this point, **$pH = pK_a$ or $pOH = pK_b$**

Since:

$$pH = pK_a + \log_{10}\frac{[salt]}{[acid]}$$

$$pOH = pK_b + \log_{10}\frac{[salt]}{[base]}$$

When selecting an appropriate buffer to control the pH of a solution, the selected buffer should have a **($pK_a \pm 1$)** range coinciding with the pH that needs to be maintained.

For instance, if you want to keep the pH constant at 4.5, then you should select a weak acid such that its ($pK_a \pm 1$) value coincides with pH 4.5. This ($pK_a \pm 1$) range is known as the ***effective buffer range***, which is the range over which the buffer is effective in maintaining its pH.

6.5 Uses of Buffer

(i) pH control in blood

Human blood is slightly basic with a normal pH of 7.35 – 7.45. Its pH must be maintained for the effective transportation of oxygen.

The major buffer system used to control the pH of blood is the carbonic acid and hydrogen carbonate buffer system (H_2CO_3/HCO_3^-).

CO_2 is formed in tissue cells and it dissolves in water to form carbonic acid, H_2CO_3:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad \text{——————} \ (*)$$

- When blood becomes too acidic, the additional H_3O^+ ions are removed by HCO_3^-, thus pH is maintained.

$$HCO_3^- + H_3O^+ \longrightarrow H_2CO_3 + H_2O$$

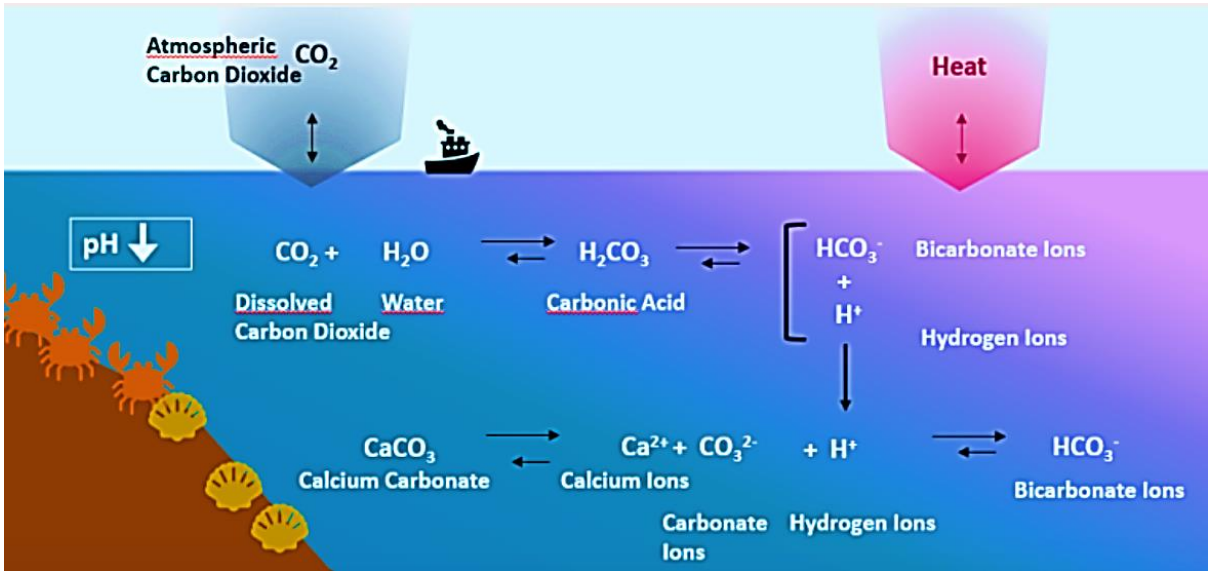
The excess H_2CO_3 produced is removed by an increase in the rate of respiration and the expulsion of CO_2 rapidly from the lungs. Position of equilibrium (*) shifts to the left.

- When blood becomes too alkaline, the additional OH^- ions are removed by H_2CO_3, thus maintaining the pH.

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

Another buffer system used to control the pH of blood includes the phosphoric acid (H_3PO_4) and dihydrogen phosphate ($H_2PO_4^-$) system but it plays a less major role than the carbonic acid and hydrogen carbonate buffer system (H_2CO_3/HCO_3^-).

(ii)maintaining pH in oceans (Self-directed Learning)



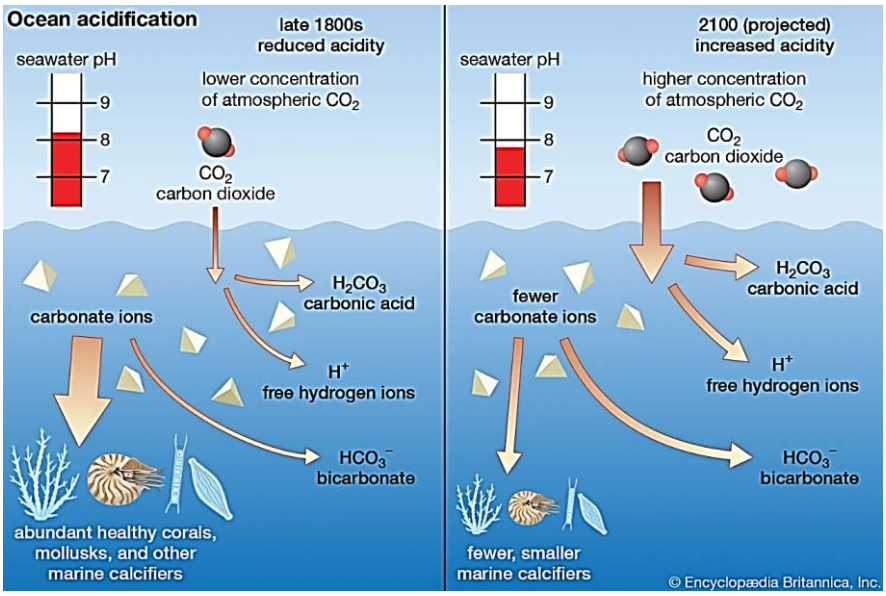
- CO_2 dissolves in water to produce carbonic acid, H_2CO_3

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

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \text{ ---- source of } H_3O^+$$

- When sea water in ocean becomes too acidic, the additional H_3O^+ ions are removed by CO_3^{2-}, thus pH is maintained.

$$CO_3^{2-}(aq) + H_3O^+(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$



- Rapid increase in atmospheric carbon dioxide gas will lead to ocean acidification.

- Ocean acidification affects organisms like oysters and corals that make hard shells and skeletons by combining calcium ions and carbonate ions from seawater.

- When ocean acidification increases, $[H^+]$ increases. $[CO_3^{2-}]$ will decrease as CO_3^{2-} reacts with H^+, resulting in fewer CO_3^{2-} available for calcifying organisms to build and maintain their shells, skeletons, and other calcium carbonate structures.

- If the pH gets too low, shells and skeletons can even begin to dissolve.

- The fish that depend on coral reef will also suffer, as do the human population who rely on the fish for food and economy.

(iii)pH control in industries (Self-directed Learning)

Buffers are used extensively in:

(1) food production
   - ☞ synthetic and processed food are prepared in a buffered form so that the food can be consumed without undue changes in pH

(2) fermentation process
   - ☞ fermenting organisms may die when pH changes too drastically

(3) manufacture of dyes, photographic materials and leather

(4) electroplating

(5) medicine
   - ☞ intravenous injections need to be carefully buffered

(6) research laboratories
   - ☞ buffer solutions are used to calibrate pH meters, and in research works involving bacteria and enzymes

7 Acid–Base Titration

7.1 Indicators

(i) How do indicators work?

An indicator is a substance that changes colour in response to pH changes of the solution it is added to. An indicator is a weak acid, whose acid form, HIn, has a different colour from its ionised form (conjugate base), In^-.

e.g. $HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$ (1)

HIn(aq): weak acid (colour A); $In^-(aq)$: conjugate base colour B

The acid dissociation constant of an indicator is termed K_{In}:

similar to the idea of K_a

$$K_{In} = \frac{[In^-][H_3O^+]}{[HIn]} \quad \text{and} \quad pH = pK_{In} + \log_{10}\frac{[In^-]}{[HIn]}$$

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

In acidic solutions, $[H_3O^+]$ is high. The position of equilibrium (1) shifts to the left, resulting in a large proportion of HIn.

In alkaline solutions, $[H_3O^+]$ is very low. The position of equilibrium (1) shifts to the right, resulting in a large proportion of In^-.

For the 2 colours to be distinguishable, one form must be about <u>10 times more concentrated</u> than the other form, i.e. in the ratio 1:10. In general,

If $\frac{[In^-]}{[HIn]} = 0.1$, colour A is observed $\Rightarrow$ $pH = pK_{In} - 1$

If $\frac{[In^-]}{[HIn]} = 10$, colour B is observed $\Rightarrow$ $pH = pK_{In} + 1$

If $[In^-] = [HIn]$, colour observed is a combination of A and B $\Rightarrow$ $pH = pK_{In}$

Hence, an indicator is found to change colour over an <u>approximate</u> pH range of $\mathbf{pK_{In} \pm 1}$, which is called the **<u>working pH range</u>** of the indicator.

(ii) Working pH range of Indicators

The working pH range of some indicators can be found in the table below.

indicator	colour of HIn (in acidic solution)	colour of In^- (in alkaline solution)	pK_{In}	pH range
methyl orange	**red**	**yellow**	**3.7**	**3.1 – 4.4**
methyl red	red	yellow	5.1	4.2 – 6.3
litmus	red	blue	6.5	6.0 – 8.0
bromothymol blue	yellow	blue	7.0	6.0 – 7.6
thymolphthalein	colourless	blue	9.9	9.3 – 10.5
phenolphthalein	**colourless**	**pink**	**9.5**	**8.3 – 10.0**

What is the difference between equivalence point and end–point of a titration?

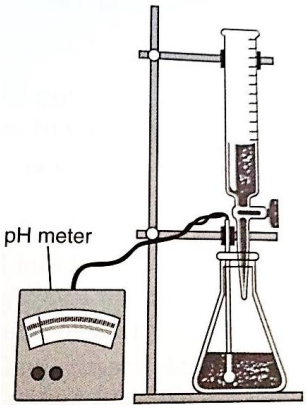
Equivalence point is the point at which stoichiometric amounts of acid and base react completely. It is the mid–point of the region of rapid pH change during the titration.

End–point is an experimentally determined value and it is reached when the first drop of titrant changes the colour of the indicator permanently.

When an appropriate indicator is chosen, the end–point will be close to the equivalence point.

7.2 Titration Curves

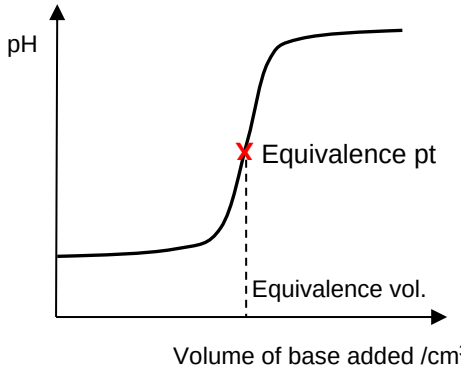
These are graphs showing how the pH changes with the volume of solution added from the burette (the titrant) during a titration. The graphs can be obtained by monitoring the pH of a titration using a pH meter.



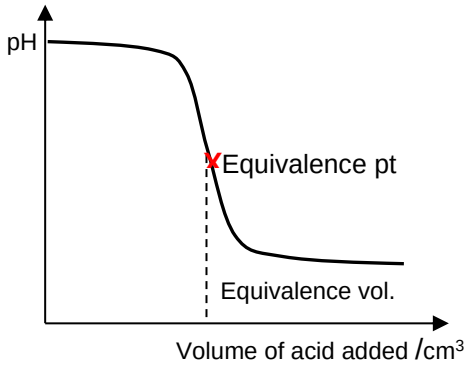
Source: Understanding Advanced Physical Inorganic Chemistry, The Learner's Approach

There are generally 2 types of shapes of titration curves as shown below:

Acid in conical flask, base in burette



Base in conical flask, acid in burette



Due to different combinations of strong/weak acids and bases, there are 4 types of acid–base titration (with single equivalence point) and the indicator suitable for each type of titration is shown below.

An indicator is suitable for a titration if

- the working pH range of the indicator (pH range for colour change) **lies within** the range of rapid pH change for the titration.

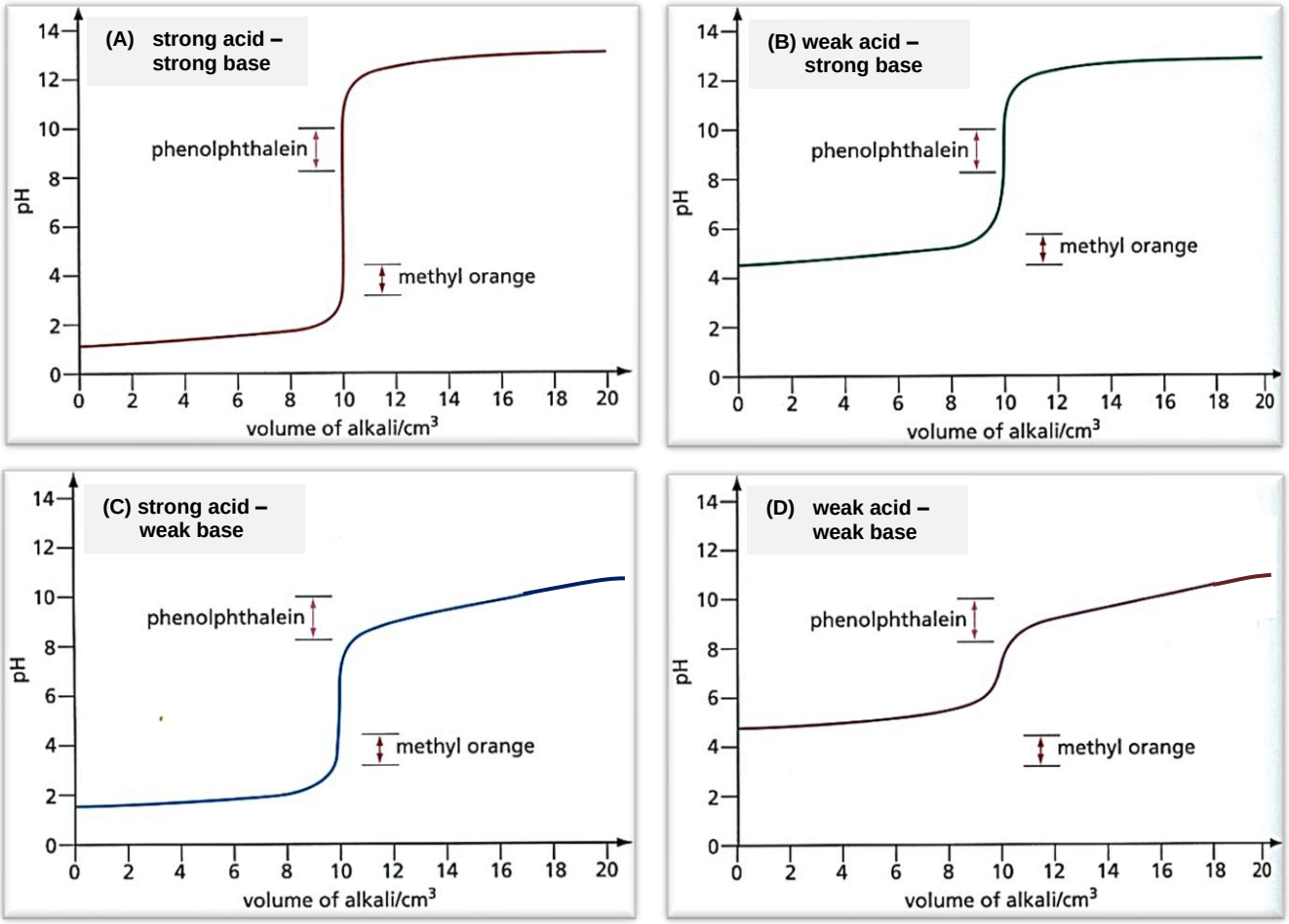
OR

- pH at equivalence point for the titration occurs within the working pH range of the indicator.

type	range of rapid pH change	examples of suitable indicator*
(A) strong acid – strong base	3 – 11	methyl orange or phenolphthalein
(B) strong acid – weak base	3 – 7	methyl orange
(C) weak acid – strong base	6 – 11	phenolphthalein
(D) weak acid – weak base	nil	no suitable indicator

**refer to the table on page 33 for the working pH range of the indicators*

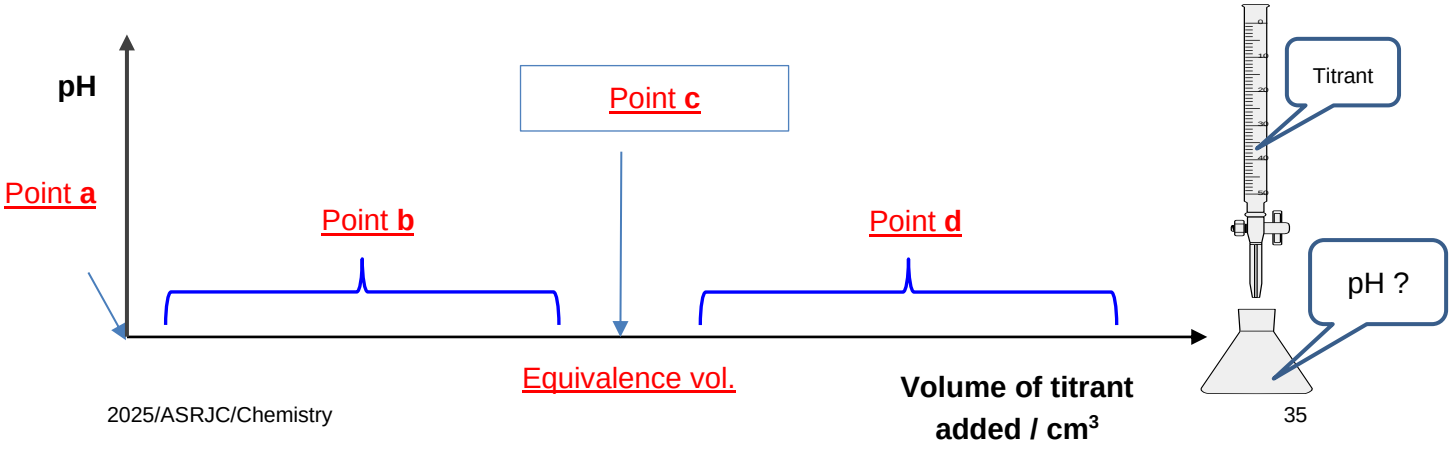
The diagrams below show the 4 possible titration curves that can be obtained when **base (burette) is added to acid (conical flask)**. The pH ranges over which methyl orange and phenolphthalein change colour are also shown.



*Titration curves **(A)–(D)** showing the pH changes as 1.0 mol dm^{-3} alkali (base) is added into 100 cm^3 of 0.10 mol dm^{-3} acid*

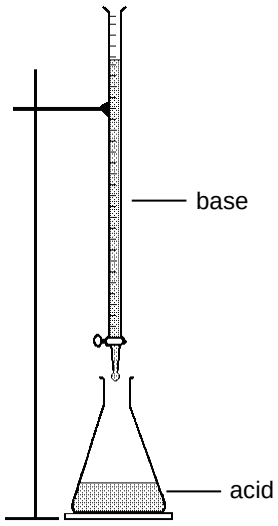
4 Important points to consider in a Titration Curve

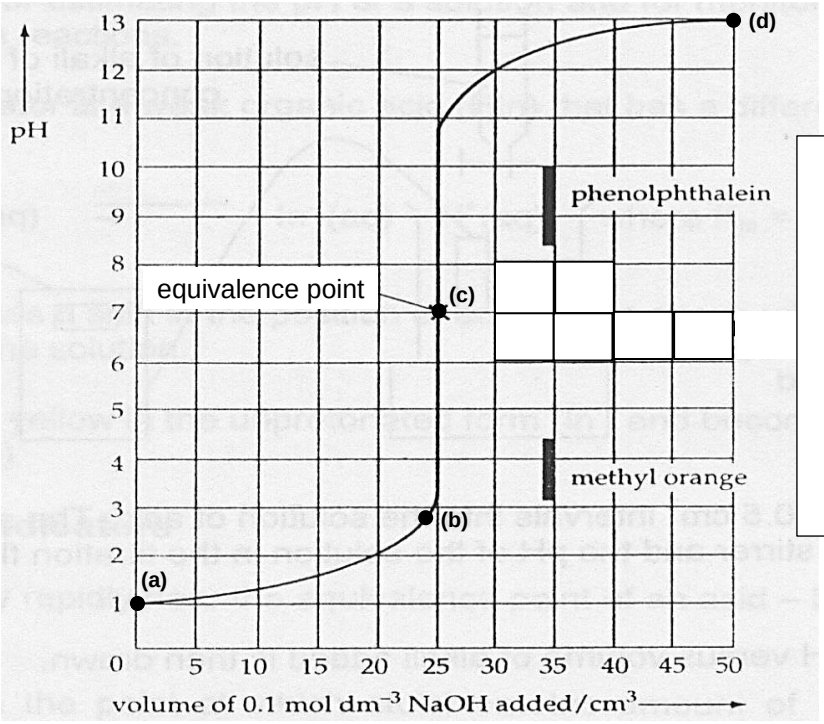
Point	Species present	Calculation required
a	species in conical flask	Initial pH of species in the flask
b	species + salt	Any Buffer region? If yes, what is MBC pH? Vol. of titrant to reach MBC?
c	salt only	Volume of titrant required + pH at equivalence pt
d	salt and excess titrant	Any Buffer region? If yes, what is MBC pH? Vol. of titrant to reach MBC? Final pH?



(A) Strong acid – strong base (SA–SB) titration

Example: 25.0 cm^3 0.10 mol dm^{-3} HC*l* titrated against 0.10 mol dm^{-3} NaOH
Range of rapid pH change: pH 3 to 11
Indicator: methyl orange or phenolphthalein





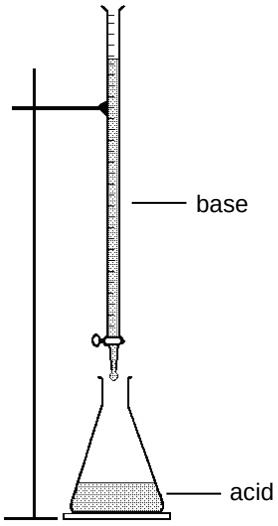
How do we obtain the pH values at different points of the titration curve? See the table below for details in calculation!

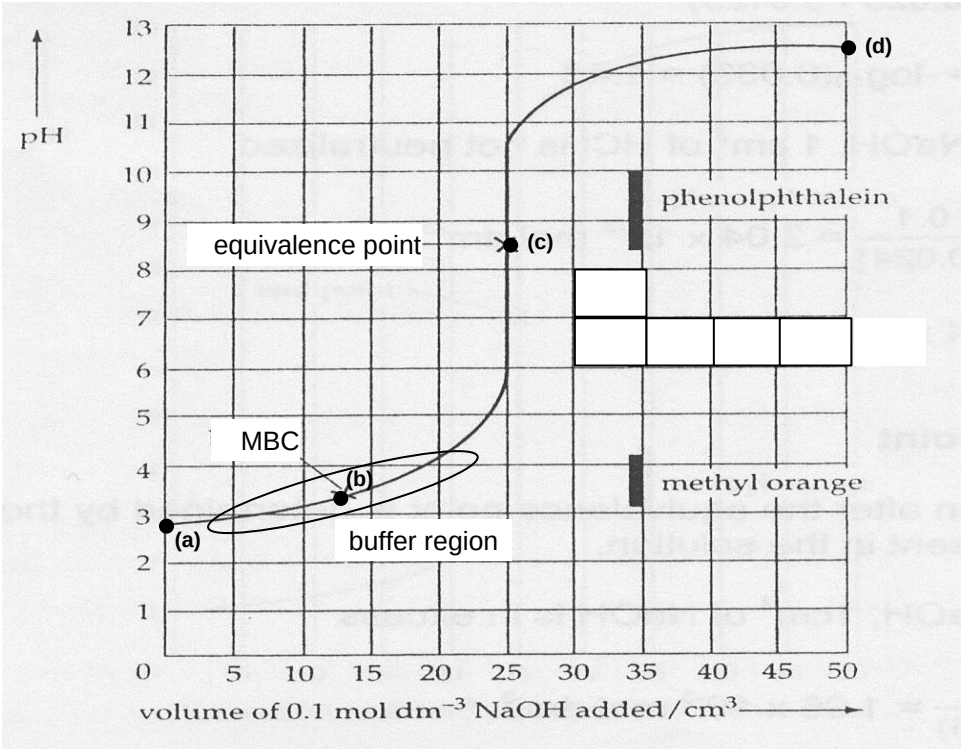
Volume of NaOH added	Species in the solution	pH changes at that point	pH
(a) 0.00 cm^3 ***Case 1*** **see p52 for cases of pH calculations*	<u>Only the strong acid HC*l* is present</u> 0.10 mol dm^{-3} HC*l* HC*l* $\longrightarrow$ $H^+ + Cl^-$ $[H^+]$ = 0.10 mol dm^{-3} $\therefore$ pH = $-\log_{10}(0.10)$ = 1.00	Initial pH	1
(b) 24.00 cm^3 ***Case 1***	<u>NaC*l* & **excess** HC*l* are present</u> NaOH + HC*l* $\longrightarrow$ NaC*l* + H_2O **Total volume = 49.00 cm^3** $n(HCl)_{remaining}$ = $\frac{25.0}{1000}(0.10) - \frac{24.00}{1000}(0.10)$ = 1.00 x 10^{-4} mol $[H^+] = \frac{1\times10^{-4}}{49.00/1000}$ = 2.04 x 10^{-3} mol dm^{-3} pH = $-\log_{10}(2.04 \times 10^{-3})$ = 2.69	Gradual increase in pH as NaOH is added from the burette. The amount of HC*l* decreases and total volume of solution increases. To determine the pH at any other point **<u>before</u>** equivalence point, the same method can be applied but need to take note of the **<u>total volume</u>** at that point.	2.69

(c) 25.00 cm^3	Only NaC*l* is present **Neutral** salt solution because NaC*l* does not undergo hydrolysis in water.	HC*l* is completely neutralised at the **equivalence point**. Sharp increase in pH just before and at equivalence point. The pH at equivalence point is at the mid–point of the vertical section (region of large rapid pH change). pH = pH of water	7
(d) 50.00 cm^3 ***Case 1***	NaC*l* and **excess** NaOH are present **Total volume = 75.00 cm^3** $n(NaOH)_{excess} = \frac{25.00}{1000}(0.10)$ $= 2.50 \times 10^{-3}$ mol $[NaOH] = [OH^-] = \frac{2.50 \times 10^{-3}}{75.00/1000}$ $= 3.33 \times 10^{-2}$ mol dm^{-3} $pOH = -\log_{10}(3.33 \times 10^{-2}) = 1.48$ $\therefore$ pH = 14 – 1.48 = 12.5	Upon infinite addition of NaOH, solution resembles that of 0.10 mol dm^{-3} of NaOH which fully ionises in water. The pH approaches but will never reach 13 (initial pH of NaOH) due to dilution.	12.5

(B) Weak acid – strong base (WA–SB) titration

Example: 25.0 cm^3 0.10 mol dm^{-3} CH_3COOH titrated against 0.10 mol dm^{-3} NaOH
Range of rapid pH change: pH 6 to 11
Indicator: phenolphthalein





Features of the titration curve (with detailed calculations):

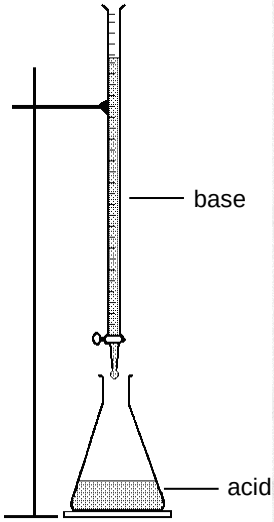
Volume of NaOH added	Species in the solution	pH changes at that point	pH
(a) 0.00 cm^3 ***Case 2*** **see p52 for cases of pH calculations*	<u>Only the weak acid CH_3COOH is present</u> 0.10 mol dm^{-3} CH_3COOH Given K_a of CH_3COOH = 1.8 x 10^{-5} mol dm^{-3}, $K_a \approx \frac{[H_3O^+]^2}{[CH_3COOH]_{initial}}$ $[H_3O^+] = \sqrt{K_a \times 0.10} = 1.34 \times 10^{-3}$ pH = $-\log_{10}(1.34 \times 10^{-3})$ = 2.87	Initial pH	2.87

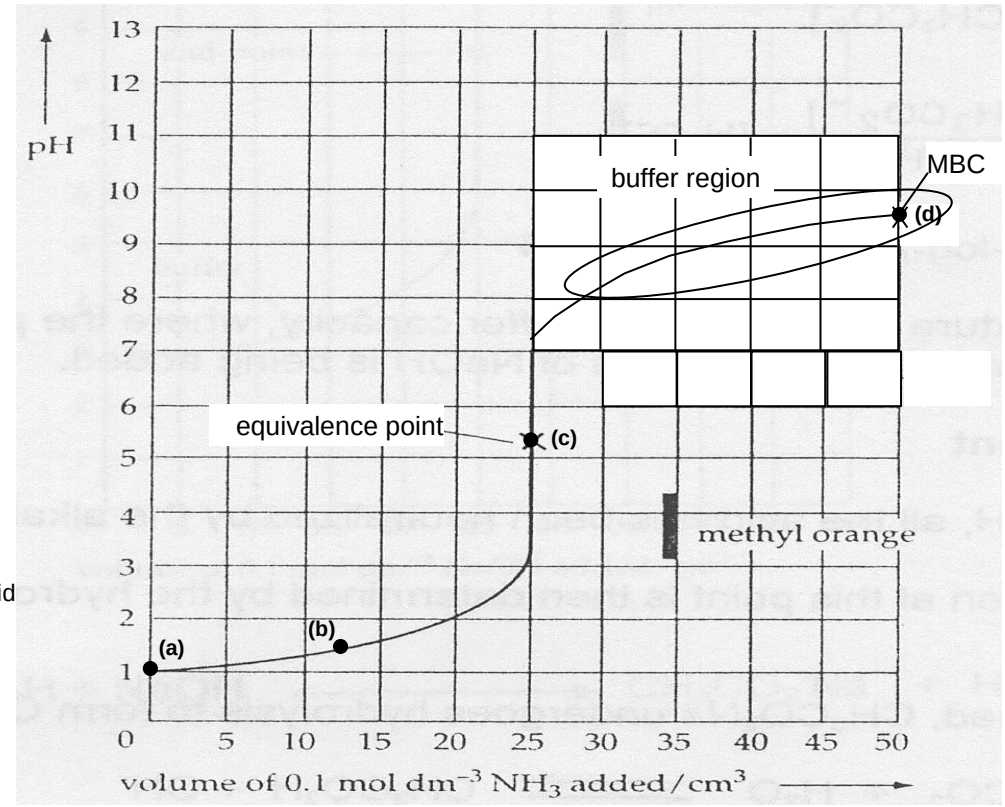
Think!
What happens to the titration curve if the weak acid is placed in the burette while the strong base is in the conical flask? Turn to page 48 to find out more later.

Volume of NaOH added	Species in the solution	pH changes at that point	pH
(b) 12.50 cm^3 ***Case 4*** *Try to work out!*	<u>$CH_3COO^-Na^+$ and **excess** CH_3COOH are present</u> $CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$ **(Presence of weak acid & its conjugate base ⇒ acidic buffer)** From calculations, $[CH_3COOH] = 0.0333$ mol dm^{-3} $[CH_3COO^-Na^+] = 0.0333$ mol dm^{-3} **$[CH_3COO^-Na^+] = [CH_3COOH]$** i.e. **[salt] = [acid]** ⇒ **$pH = pK_a$** $= -\log_{10}(1.8 \times 10^{-5})$ $= 4.74$	This is the pH at which the **maximum buffer capacity (MBC)** occurs. *Notice that the volume of NaOH required to reach equivalence point is 25.00 cm^3. Hence, when 12.50 cm^3 (**HALF** of 25.00 cm^3) of NaOH is added, the resulting solution is an acidic buffer at maximum buffer capacity (MBC) with $[CH_3COO^-Na^+] = [CH_3COOH]$* Recall: $pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$	4.74
(c) 25.00 cm^3 ***Case 3*** *Try to work out!*	<u>Only $CH_3COO^-Na^+$ is present</u> CH_3COO^- undergoes hydrolysis in water. $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ $K_b(CH_3COO^-) = K_w/K_a = 5.56 \times 10^{-10}$ mol dm^{-3} From calculations, $[CH_3COO^-] = 0.0500$ mol dm^{-3} $K_b \approx \frac{[OH^-]^2}{[CH_3COO^-]_{initial}}$ $[OH^-] = \sqrt{(5.56 \times 10^{-10}(0.0500)}$ $= 5.27 \times 10^{-6}$ mol dm^{-3} $pH = 14 - [-\log_{10}(5.27 \times 10^{-6})] = 8.72$	CH_3COOH is completely neutralised at the **equivalence point**. The pH at equivalence point is higher (> 7) as compared to SA–SB titration. This is due to the hydrolysis of CH_3COO^- in water to give OH^- ions.	> 7 (8.72)
(d) 50.00 cm^3 ***Case 1***	<u>$CH_3COO^-Na^+$ and **excess** NaOH are present</u> **Total volume = 75.00 cm^3** $n(NaOH)_{excess} = \frac{25.00}{1000}(0.10)$ $= 2.50 \times 10^{-3}$ mol $[NaOH] = [OH^-] = \frac{2.50 \times 10^{-3}}{75.00/1000}$ $= 3.33 \times 10^{-2}$ mol dm^{-3} $pOH = -\log_{10}(3.33 \times 10^{-2}) = 1.48$ $\therefore pH = 14 - 1.48 = 12.5$	The base is in excess. The titration curve flattens out at high pH since the excess base present is a strong base. The hydrolysis of CH_3COO^- is suppressed by the addition of excess strong base! *Why is this so?*	12.5

(C) Strong acid – weak base (SA–WB) titration

Example: 25.0 cm^3 0.10 mol dm^{-3} HC*l* titrated against 0.10 mol dm^{-3} NH_3(aq)
Range of rapid pH change: pH 3 to 7
Indicator: methyl orange





Features of the titration curve (with detailed calculations):

Volume of NH_3 added	Species in the solution	pH changes at that point	pH
(a) 0. 00 cm^3 ***Case 1*** **see p52 for cases of pH calculations*	<u>Only the strong acid HC*l* is present</u> 0.10 mol dm^{-3} HC*l* $[H^+]$ = 0.10 mol dm^{-3} pH = $-\log_{10}(0.10)$ = 1.00	Initial pH	1
(b) 12.50 cm^3 ***Case 1***	<u>NH_4Cl and **excess** HC*l* are present</u> $NH_3 + HCl \longrightarrow NH_4Cl$ $[HCl]_{remaining} = \frac{12.5}{37.5} \times 0.10$ = 0.0333 mol dm^{-3} pH = $-\log_{10}(0.0333)$ = 1.48	Gradual increase in pH as NH_3 is added from the burette. The amount of HC*l* decreases and total volume of solution increases. pH is due to $[HCl]_{remaining}$ since contribution of H^+ from NH_4^+ is negligible compared to H^+ from HC*l*.	< 7 (1.48)

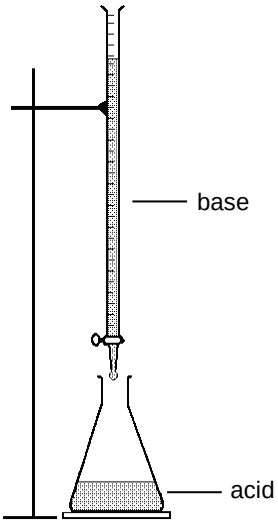
Volume of NH_3 added	Species in the solution	pH changes at that point	pH
(c) 25.00 cm^3 ***Case 3***	<u>Only NH_4Cl is present</u> NH_4^+ undergoes **hydrolysis** in water. $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ Given $K_b(NH_3) = 1.8 \times 10^{-5}$, $K_a(NH_4^+) = K_w / K_b(NH_3)$ $= \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$ $= 5.56 \times 10^{-10}$ mol dm^{-3} $[NH_4^+] = \frac{25.0(0.10)}{25.0 + 25.00}$ $= 0.0500$ mol dm^{-3} $K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \approx \frac{[H_3O^+]^2}{[NH_4^+]_{initial}}$ $[H_3O^+] = \sqrt{K_a \times [NH_4^+]_{initial}}$ $= 5.27 \times 10^{-6}$ mol dm^{-3} $pH = -\log_{10}(5.27 \times 10^{-6}) = 5.28$	HC*l* is completely neutralised at the **equivalence point**. The pH at equivalence point is lower (< 7) as compared to SA–SB titration. This is due to the hydrolysis of NH_4^+ in water to give H_3O^+ ions.	< 7 (5.28)
(d) 50.00 cm^3 ***Case 4***	<u>NH_4Cl and **excess** NH_3 are present</u> **(Presence of weak base & its conjugate acid ⇒ alkaline buffer)** $[NH_3] = \frac{25.00(0.10)}{25.0 + 50.00}$ $= 0.0333$ mol dm^{-3} $[NH_4^+] = \frac{25.0(0.10)}{25.0 + 50.00}$ $= 0.0333$ mol dm^{-3} **$[NH_4^+] = [NH_3]$** , i.e. **[salt] = [base]** ⇒ **$pOH = pK_b$** $= -\log_{10}(1.8 \times 10^{-5})$ $= 4.74$ ∴ $pH = 14 - 4.74 = 9.26$	This is the pH at which the **maximum buffer capacity (MBC)** occurs. *Notice that the volume of NH_3 required to reach equivalence point is 25.00 cm^3. Hence, when 50.00 cm^3 (**TWICE** of 25.00 cm^3) of NH_3 is added, the resulting solution is an alkaline buffer at maximum buffer capacity (MBC) with $[NH_4^+] = [NH_3]$.* Since $pOH = pK_b + \log_{10} \frac{[salt]}{[base]}$	9.26

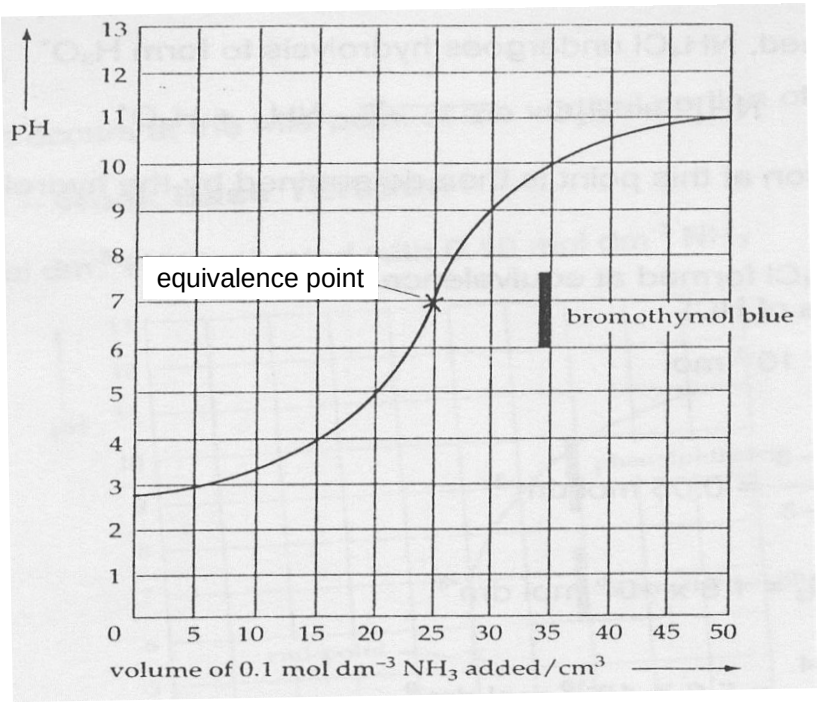
Think!
What happens to the titration curve if the strong acid is placed in the burette while the weak base is in the conical flask? Turn to page 42 to find out more.

(D)Weak acid – weak base (WA–WB) titration (Not in Syllabus)

***Just make sure you know the underlined parts to complete the understanding of titration curves.**

Example: 25.0 cm^3 0.10 mol dm^{-3} CH_3COOH titrated against 0.10 mol dm^{-3} $NH_3(aq)$
Range of rapid pH change: none because gradual change
Indicator: No suitable one because there is no rapid pH change at equivalence point

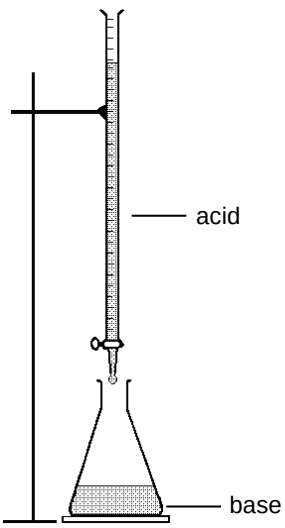


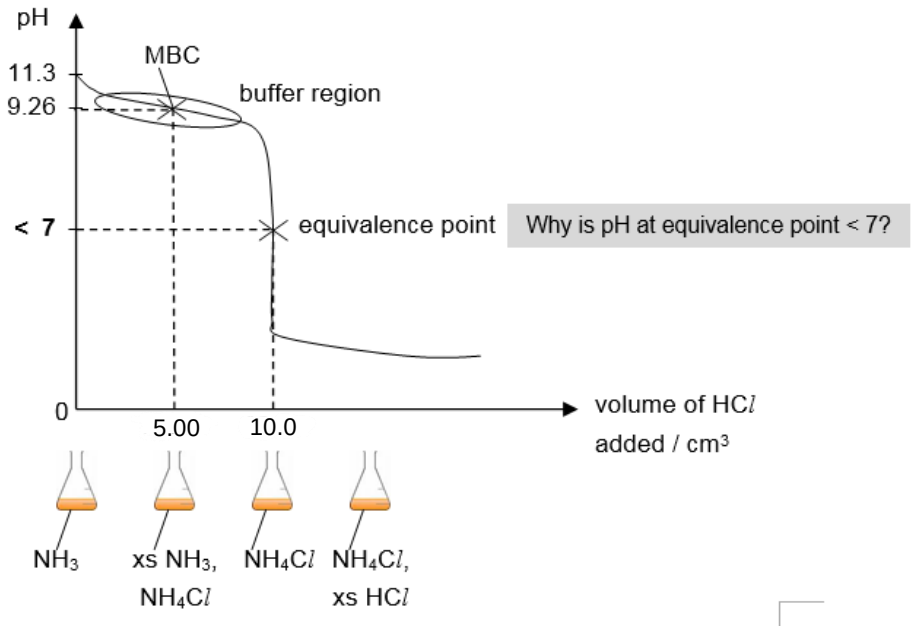


Examples on sketching of titration curves

1) Titration curve of a weak base–strong acid (WB–SA) titration

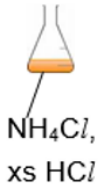
Sketch the titration curve when 10.0 cm^3 of 0.20 mol dm^{-3} NH_3(aq) is titrated against 0.20 mol dm^{-3} HC*l*(aq). [$K_b(NH_3) = 1.8 \times 10^{-5}$]





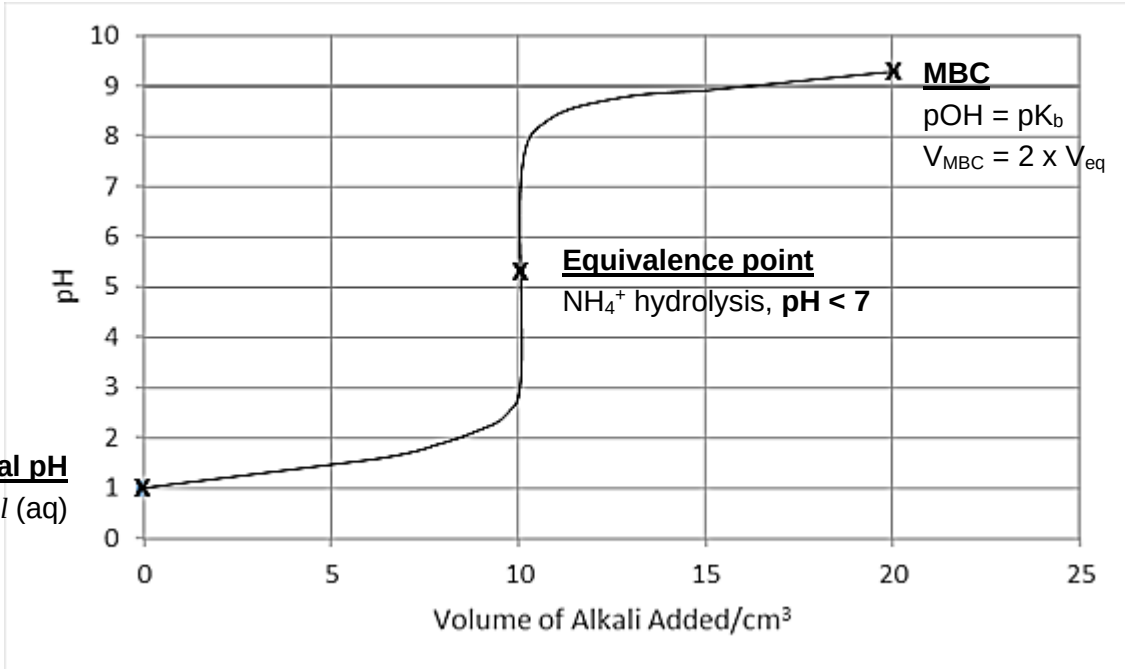
Pts	*Things to consider*	*Detailed calculation*
1	determine the initial pH [Case 1 or 2]  NH_3	NH_3 is in the flask. [Case 2] $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ $K_b \approx \frac{[OH^-]^2}{[NH_3]_{initial}}$; $[OH^-] = \sqrt{K_b \times [NH_3]} = 1.897 \times 10^{-3}$ mol dm^{-3} initial pH = $14 - [-\log_{10}(1.897 \times 10^{-3})]$ = **<u>11.3</u>**
2	identify the **buffer region** (if any)	<u>Before</u> the equivalence point where there is a mixture of NH_3 and NH_4Cl.
3	determine the volume at which maximum buffer capacity (MBC) occurs (if any) and determine the pH at MBC  $[NH_3] = [NH_4^+]$	At MBC, $[NH_3] = [NH_4^+]$ $pOH = pK_b = -\log_{10}(1.8 \times 10^{-5}) = 4.74$; pH = 14 – 4.74 = **<u>9.26</u>** Volume of HC*l* required for complete neutralisation = (10 x 0.20) / 0.20 = **<u>10.00 cm^3</u>** = equivalence volume Volume at which MBC occurs is <u>half</u> the equivalence volume = **<u>5.00 cm^3</u>**.

Pts	***Things to consider***	***Detailed calculation***
4	determine the **equivalence volume** and indicate **pH** (=7, >7 or <7) at **equivalence point**	$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$ **Salt formed from SA and WB** behaves as a <u>weak acid</u> in water. NH_4Cl is the salt of a weak base; **$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$** pH **<u>< 7</u>**
5	determine the pH at equivalence point (if asked) [Case 3]  	Amt of HCl = 10/1000 x 0.200 = 2.00×10^{-3} mol Amt of NH_4Cl formed = amt of titrant used = 2.00×10^{-3} mol Total volume at equivalence point = Initial vol of NH_3 in flask + equivalence vol of HCl = 10.0 + 10.00 = 20.00 cm^3 Concentration of salt (NH_4Cl) at equivalence point = 2.00×10^{-3} / 0.02 = **0.100 mol dm^{-3}** NH_4^+ undergoes salt hydrolysis. (since NH_4^+ is a conjugate acid) $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$ $K_w = K_a \times K_b$ $K_a = 5.55 \times 10^{-10}$ mol dm^{-3} $K_a = \frac{[H_3O^+]^2}{[NH_4^+]_{initial}}$ $[H_3O^+] = \sqrt{5.55 \times 10^{-10} \times 0.10} = 7.453 \times 10^{-6}$ mol dm^{-3} $pH = -\log_{10}[H^+] = -\log_{10}(7.453 \times 10^{-6})$ = **<u>5.13</u>**

Pts	***Things to consider***	***Detailed calculation***
6	*determine the final pH* (if asked)  	*If the question states that 20.00 cm^3 of HCl was added* Volume of excess HC*l* = 20.00 – 10.00 = 10.00 cm^3 of HC*l* HC*l* (aq) → H^+ (aq) + Cl^- (aq) HC*l* ≡ H^+ Amt of H^+ = $\frac{10.00}{1000}$ x 0.200 = 0.00200 mol Total volume of solution when *20.00 cm^3 of HCl was added* = Initial vol of NH_3 in conical flask + vol of HC*l* added = 10.0 + 20.00 = 30.00 cm^3 $[H^+]$ = $\frac{n}{V}=\frac{0.00200}{(0.03)}$=0.06667 mol dm^{-3} pH = $-\log_{10}[H^+] = -\log_{10}(0.06667)$ = **<u>1.17</u>**
7	identify a suitable indicator (if asked)	Methyl Orange

2) Titration curve of a strong acid–weak base (SA–WB) titration

Sketch the titration curve when 10.0 cm^3 of 0.10 mol dm^{-3} HC*l* (aq) is titrated against 0.10 mol dm^{-3} NH_3 (aq). [$K_b(NH_3) = 1.8 \times 10^{-5}$]



HC*l*

NH_4Cl formed

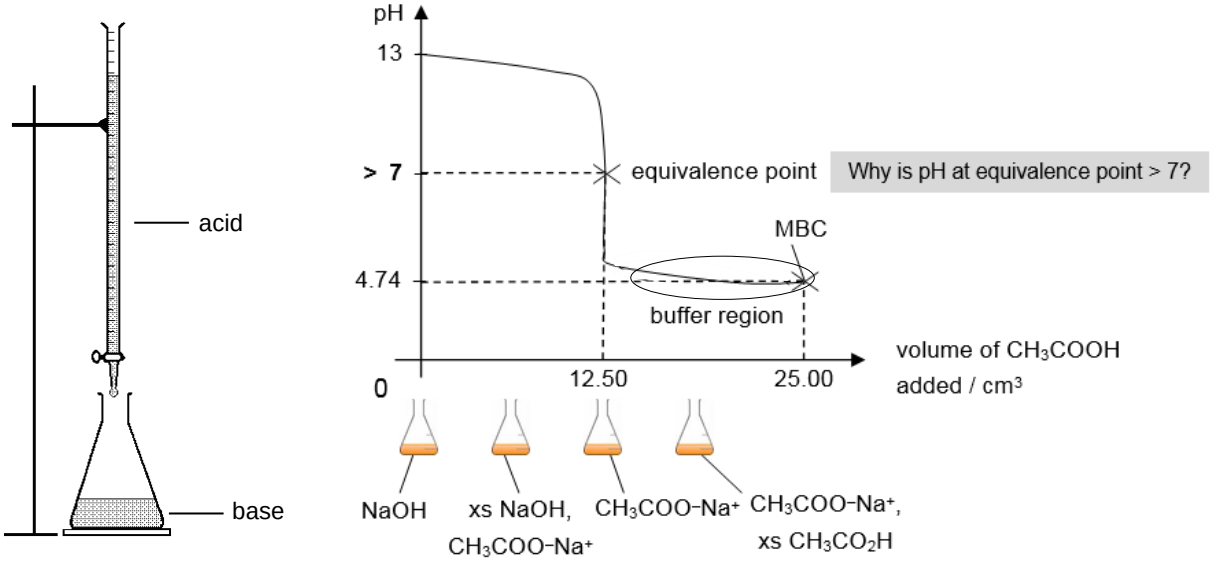
NH_4Cl, xs NH_3 (alkaline buffer)

Pts	***Things to consider***	***Detailed calculation***
1	determine the initial pH [Case 1 or 2]	pH = – $\log_{10}$ (0.10) = **1.00** [Case 1]
2	identify the **buffer region** (if any)	**No buffer region** occurs **before** equivalence point since there is absence of weak acid or base. After the equivalence point where there is a mixture of NH_4Cl and NH_3.
3	determine the volume at which maximum buffer capacity (MBC) occurs (if any) and determine the pH at MBC	Volume of NH_3 required for complete neutralisation = (10 x 0.10) / 0.10 = **10.00 cm^3** = equivalence volume Volume at which MBC occurs is **twice** the equivalence volume, i.e. 2 x 10.00 = **20.00 cm^3** pOH = pK_b = 4.74 pH = **9.26**

Pts	*Things to consider*	*Detailed calculation*
4	determine the **equivalence volume** and indicate **pH** (=7, >7 or <7) at **equivalence point**	$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$ NH_4Cl is the salt of a weak base; **$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$** pH **<u>< 7</u>**
5	determine the pH at equivalence point (if asked) [Case 3]	Amt of NH_3 = 10/1000 x 0.100 = 1.00×10^{-3} mol Amt of NH_4Cl formed = amt of titrant used = 1.00×10^{-3} mol Total volume at equivalence point = Initial vol of NH_3 in flask + equivalence vol of HCl = 10.0 + 10.00 = 20.00 cm^3 Concentration of salt (NH_4Cl) at equivalence point = 1.00×10^{-3} / 0.02 = **0.0500 mol dm^{-3}** NH_4^+ undergoes salt hydrolysis. (since NH_4^+ is a conjugate acid) $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$ $K_w = K_a \times K_b$ $K_a = 6.25 \times 10^{-10}$ mol dm^{-3} $K_a = \frac{[H_3O^+]^2}{[NH_4^+]_{initial}}$ $[H_3O^+] = \sqrt{(10^{-9.25}) \times 0.05} = 5.30 \times 10^{-6}$ mol dm^{-3} pH = $-\log_{10}[H^+] = -\log_{10}(5.30 \times 10^{-6})$ = **<u>5.28</u>**

3) Titration curve of a strong base–weak acid (SB–WA) titration

Sketch the titration curve when 25.0 cm^3 of 0.10 mol dm^{-3} NaOH is titrated against 0.20 mol dm^{-3} CH_3COOH. [$K_a(CH_3COOH) = 1.8 \times 10^{-5}$]



Pts	*Things to consider*	*Detailed calculation*
1	determine the initial pH	$NaOH \longrightarrow Na^+ + OH^-$ [Case 1] $[NaOH] = [OH^-] = 0.10$ mol dm^{-3} initial pH = 14 – pOH = 14 – [– $\log_{10}$ (0.10)] = **13.0**
2	identify the **buffer region** (if any)	No buffer region occurs before equivalence point since there is absence of weak acid or base. After the equivalence point where there is a mixture of CH_3COOH and $CH_3COO^-Na^+$. Volume at which MBC occurs is **twice** the equivalence volume, i.e. 2 x 12.50 = **25.00 cm^3**
3	determine the volume at which maximum buffer capacity (MBC) occurs (if any) and determine the pH at MBC	At MBC, $[CH_3COOH] = [CH_3COO^-]$ $pH = pK_a$ $pH = -\log_{10}(1.8 \times 10^{-5})$ = **4.74**
4	determine the **equivalence volume** and indicate **pH** (=7, >7 or <7) at **equivalence point**	$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COO^-Na^+(aq) + H_2O(l)$ volume of CH_3COOH required = 25.0 x 0.10/ 0.20 = **12.50 cm^3** ; $CH_3COO^-Na^+$: salt of a weak acid, pH **> 7**

Pts	***Things to consider***	***Detailed calculation***
5	determine the pH at equivalence point (if asked)	Amt of CH_3COOH = 25/1000 x 0.100 = 2.50 x 10^{-3} mol Amt of $CH_3COO^-Na^+$ formed = amt of titrant used = 2.50 x 10^{-3} mol Total volume at equivalence point = Initial vol of NaOH in flask + equivalence vol of CH_3COOH = 25.0 + 12.50 = 37.50 cm^3 Concentration of salt ($CH_3COO^-Na^+$) at equivalence point = 2.50 x 10^{-3} / 0.0375 = **0.0667 mol dm^{-3}** CH_3COO^- undergoes salt hydrolysis. (since CH_3COO^- is a conjugate base) $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ $K_b(CH_3COO^-) = K_w/K_a$ = 5.56 x 10^{-10} mol dm^{-3} $K_b \approx \frac{[OH^-]^2}{[CH_3COO^-]_{initial}}$ $[OH^-] = \sqrt{(5.56 \times 10^{-10}(0.0667)}$ = 6.09 x 10^{-6} mol dm^{-3} pH = 14 – [– $\log_{10}$ (6.09 x 10^{-6})] = **<u>8.78</u>**

(E) Titration involving polybasic acids (with multiple equivalence points)

For **polybasic** (or **polyprotic**), the difference between the K_a values for each dissociation, causes the protons (H^+) in these acids to react in a **step–wise manner** and the titration will involve more than one equivalence point.

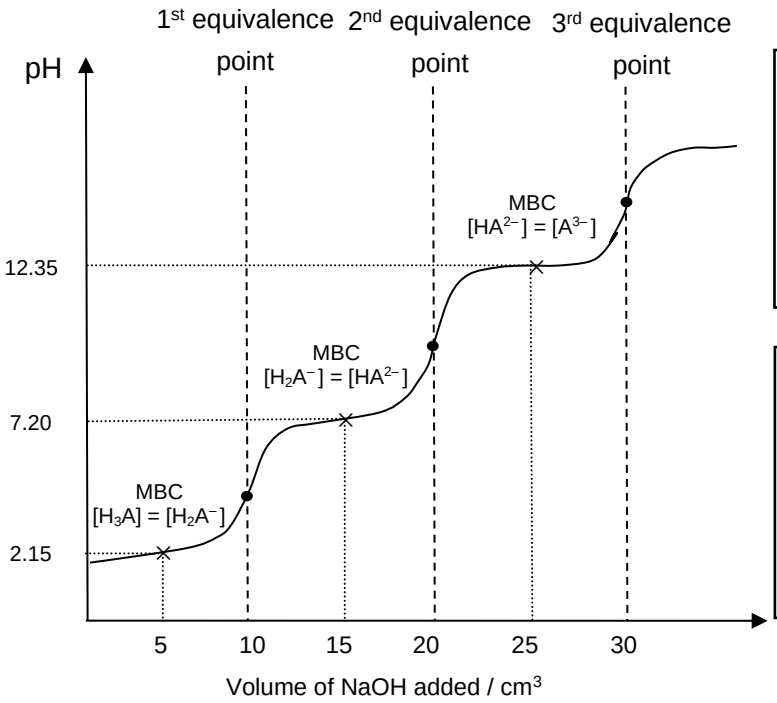
The table below shows the acid dissociation constants for some of the polybasic acids.

acid	H^+	K_a / mol dm^{-3}	pK_a
H_2CO_3	1st	4.5×10^{-7}	6.35
	2nd	4.7×10^{-11}	10.33
H_3PO_4	1st	7.1×10^{-3}	2.15
	2nd	6.3×10^{-8}	7.20
	3rd	4.5×10^{-13}	12.35
H_2SO_3	1st	1.5×10^{-2}	1.82
	2nd	6.6×10^{-7}	7.18

Example

10.0 cm^3 of 0.50 mol dm^{-3} of a weak tribasic acid, H_3PO_4, is titrated against 0.50 mol dm^{-3} of a strong base, NaOH. Indicate, on the titration curve, the pH at which each MBC occurs and the equivalence volume at each equivalence point.
(Use H_3A to represent H_3PO_4)

$$H_3A(aq) + 3NaOH(aq) \longrightarrow Na_3A(aq) + 3H_2O(l)$$



The **step–wise** dissociation of the weak tribasic acid, H_3A is as follows:

(i) $H_3A + H_2O \rightleftharpoons H_2A^- + H_3O^+$ (K_{a1})

(ii) $H_2A^- + H_2O \rightleftharpoons HA^{2-} + H_3O^+$ (K_{a2})

(iii) $HA^{2-} + H_2O \rightleftharpoons A^{3-} + H_3O^+$ (K_{a3})

The 3 equivalence points correspond to the **step–wise** completion of the following reactions:

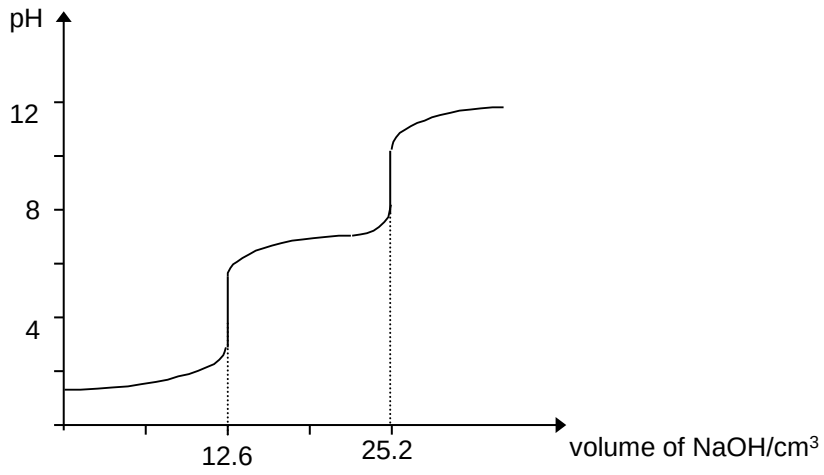
(i) $H_3A + OH^- \longrightarrow H_2A^- + H_2O$

(ii) $H_2A^- + OH^- \longrightarrow HA^{2-} + H_2O$

(iii) $HA^{2-} + OH^- \longrightarrow A^{3-} + H_2O$

Example

During the titration of 20 cm^3 of saturated aqueous sulfur dioxide against 1.0 mol dm^{-3} aqueous sodium hydroxide, the pH was determined.



***Note:* In saturated aqueous sulfur dioxide, H_2SO_3 is formed.**

(a) Write balanced equations for the reactions which occur during the titration.

$H_2SO_3 + OH^- \longrightarrow HSO_3^- + H_2O$ (1)

(2)

(b) Calculate the concentration in mol dm^{-3} of sulfur dioxide in the initial solution.

Using Eqn. (1),

$[H_2SO_3]$ = = **0.630 mol dm^{-3}**

(c) Estimate from the figure above, a value for the **first** dissociation constant of ***H_2SO_3***.

$H_2SO_3 + H_2O \rightleftharpoons HSO_3^- + H_3O^+$ K_{a1}

$$K_{a1} = \frac{[H_3O^+][HSO_3^-]}{[H_2SO_3]}$$

From the graph, at **6.3 cm^3** *(half of 1st equivalence volume)* where $[HSO_3^-] = [H_2SO_3]$,

pH ≈ 1.5

pH = pK_{a1} (at MBC)

$K_{a1} = [H_3O^+] = 10^{-1.5}$ = **3.16 x 10^{-2} mol dm^{-3}**

(d) Suggest an indicator which would change colour when the following volumes of NaOH was added. State the colour change in each case.

(i) 12.6 cm^3;
methyl orange; red to orange

(ii) 25.2 cm^3 of 1.0 mol dm^{-3}.
phenolphthalein; colourless to pink

In summary, when you are asked to <u>sketch</u> a titration curve,

<table>
<tr><th>Pts</th><th>You must be able to:</th><th>Strategy</th></tr>
<tr><td>1</td><td>determine the initial pH</td><td>Case 1 or Case 2</td></tr>
<tr><td>2</td><td>identify the buffer region (if any)</td><td>Look out for unreacted WA or WB</td></tr>
<tr><td>3</td><td>determine the volume at which maximum buffer capacity (MBC) occurs (if any) and determine the pH at MBC</td><td>☞ If buffer region is <u>before</u> equivalence point, MBC occurs at <u>half</u> the equivalence volume.
☞ If buffer region is <u>after</u> equivalence point, MBC occurs at <u>twice</u> the equivalence volume.

☞ $pH = pK_a$
$pOH = pk_b$ (pH = 14 – pOH)</td></tr>
<tr><td>4</td><td>determine the equivalence volume and indicate pH (=7, >7 or <7) at equivalence point</td><td>☞ VA calculation.
☞ Salt of weak acid → pH >7
☞ Salt of weak base → pH <7</td></tr>
<tr><td>5</td><td>determine the pH at equivalence point</td><td>Case 3</td></tr>
<tr><td>6</td><td>determine the final pH</td><td>☞ Determine [species] unreacted
☞ Apply Case 1 or Case 2.</td></tr>
<tr><td>7</td><td>identify a suitable indicator (if asked)</td><td><table><tr><th>type</th><th>examples of suitable indicator*</th></tr><tr><td>SA–SB</td><td>methyl orange or phenolphthalein</td></tr><tr><td>SA–WB</td><td>methyl orange</td></tr><tr><td>WA–SB</td><td>phenolphthalein</td></tr><tr><td>WA–WB</td><td>no suitable indicator</td></tr></table></td></tr>
</table>

Useful equations learnt so far…

Case 1: To calculate pH of **strong** monoprotic acid (HX) and **strong** monoprotic base (MOH)

$[H_3O^+] = [HX]$

$pH = -\log_{10}[HX]$

$[OH^-] = [MOH]$

$pOH = -\log_{10}[MOH]$; $pH = 14 - pOH$

Case 2: To calculate pH of **weak** acid (HA) and **weak** base (B)

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

$K_a = \dfrac{[A^-][H_3O^+]}{[HA]} \approx \dfrac{[H_3O^+]^2}{[HA]_{initial}}$

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

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

$K_b = \dfrac{[BH^+][OH^-]}{[B]} \approx \dfrac{[OH^-]^2}{[B]_{initial}}$

$pOH = -\log_{10}[OH^-]$; $pH = 14 - pOH$

Case 3: To calculate pH of **salt** solutions which undergo salt hydrolysis

** **Identify the ion** that undergoes salt hydrolysis (i.e. cation or anion must be from a weak acid / base

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

$K_b = K_w/K_a = \dfrac{[HA][OH^-]}{[A^-]} \approx \dfrac{[OH^-]^2}{[A^-]_{initial}}$

$pOH = -\log_{10}[OH^-]$; $pH = 14 - pOH$

$BH^+(aq) + H_2O(l) \rightleftharpoons B(aq) + H_3O^+(aq)$

$K_a = K_w/K_b = \dfrac{[B][H_3O^+]}{[BH^+]} \approx \dfrac{[H_3O^+]^2}{[BH^+]_{initial}}$

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

Case 4: To calculate pH of **buffer** solutions

acidic buffer (HA / A^-)

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

$K_a \approx \dfrac{[A^-]_{salt}[H_3O^+]}{[HA]_{initial}}$

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

alkaline buffer (B / BH^+)

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

$K_b \approx \dfrac{[BH^+]_{salt}[OH^-]}{[B]_{initial}}$

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

$pH = 14 - pOH$

** If there is a mixing of 2 solutions, re–calculate the concentration of the species.

$$[species]_{new} = \frac{[species]_{initial} \times \text{volume of species}}{\text{new total volume}}$$

A buffer at its ***maximum buffer capacity*** when [HA] = [salt] or [B] = [salt]:

acidic buffer: pH = pK_a of weak acid

alkaline buffer: pOH = pK_b of weak base