eunoia
JUNIOR COLLEGE

2023 JC2 H2 CHEMISTRY (9729)
EXTENSION TOPIC: CHEMISTRY OF AQUEOUS SOLUTIONS
ACID-BASE EQUILIBRIA

Name: ____ Civics Group: 22 – ____

Learning Outcomes

Students 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 require solving of quadratic equations]
(g) describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases
(h) explain the choice of suitable indicators for acid-base titrations, given appropriate data
(i) (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
(j) calculate the pH of buffer solutions, given appropriate data

REFERENCES

1.	Chemistry (for CIE AS & A Level) by Peter Cann & Peter Hughes	540 CAN
2.	Chemistry: The Molecular Nature of Matter & Change by Martin S. Silberberg	540 SIL
3.	Calculations in A Level Chemistry (4th Edition) by E.N. Ramsden	540 RAM
4.	Calculations for AS/A Level Chemistry by Jim Clark	540 CLA

LECTURE CONTENT

1 Theories of Acids and Bases

LO (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).

The concept of acids and bases has developed over time as chemists sought a model that could accurately classify, rationalise and predict acid-base chemistry. The Greeks first identified acids based on properties such as having a sour taste (the Latin word for sour is *Acidus*) and whether the substance could change the colour of some plant extracts.

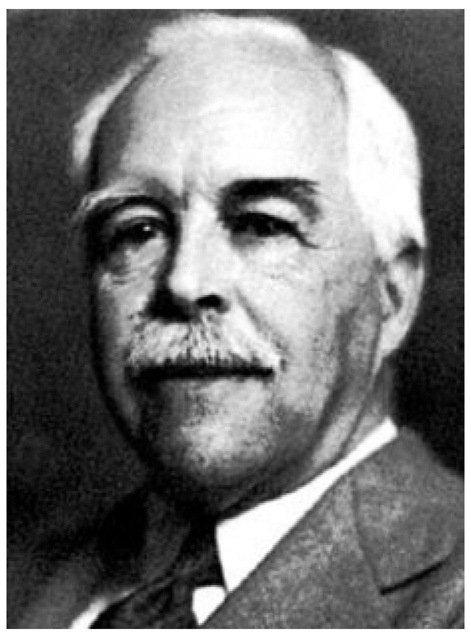
The first historical concept developed came from Antoine Lavoisier, who proposed that all acids contain oxygen (e.g. HNO_3). This was refuted by Humphry Davy, who found that hydrochloric acid has acidic properties, even though it does not contain oxygen. The next significant concept came from Justus von Liebig, who analysed empirical data and proposed that acids contained hydrogen, which is replaced by a metal, producing hydrogen gas (acid-metal reaction).

This was the paradigm for about 50 years until Svante Arrhenius put forth his theory of acids and bases in 1884. This became the foundation of the modern idea of acids and bases, which was further advanced by Johannes Brønsted, Thomas Lowry and Gilbert Newton Lewis. The findings of these chemists brought us to our current understanding of acids and bases.


Svante Arrhenius


Johannes Brønsted

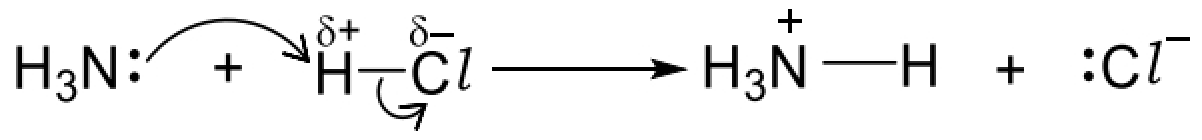
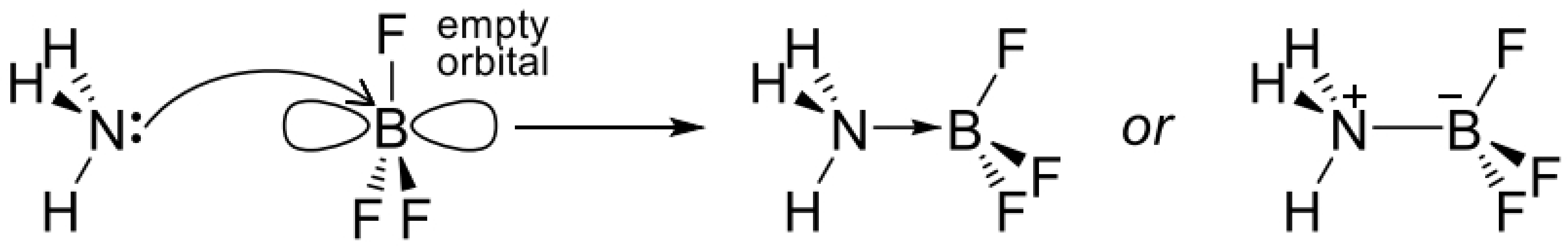
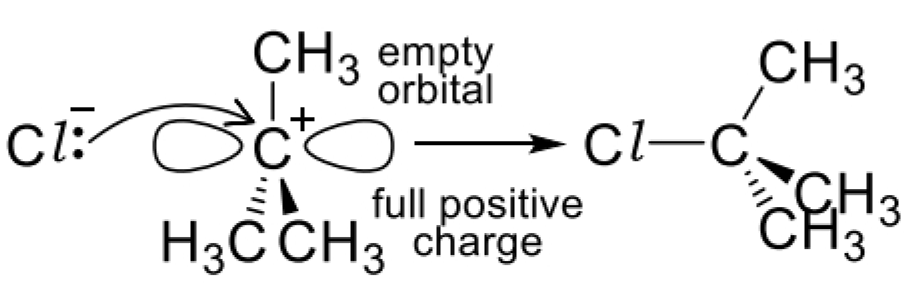
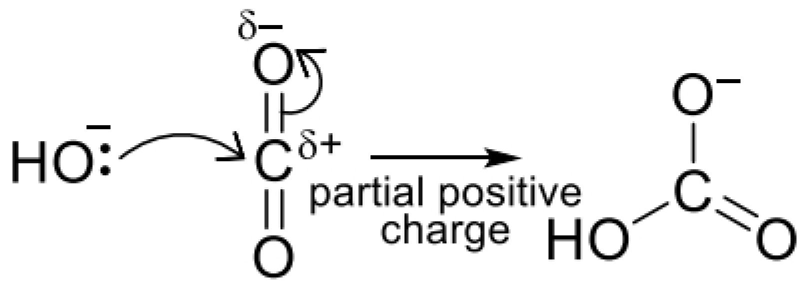

Thomas Lowry


Gilbert Newton Lewis

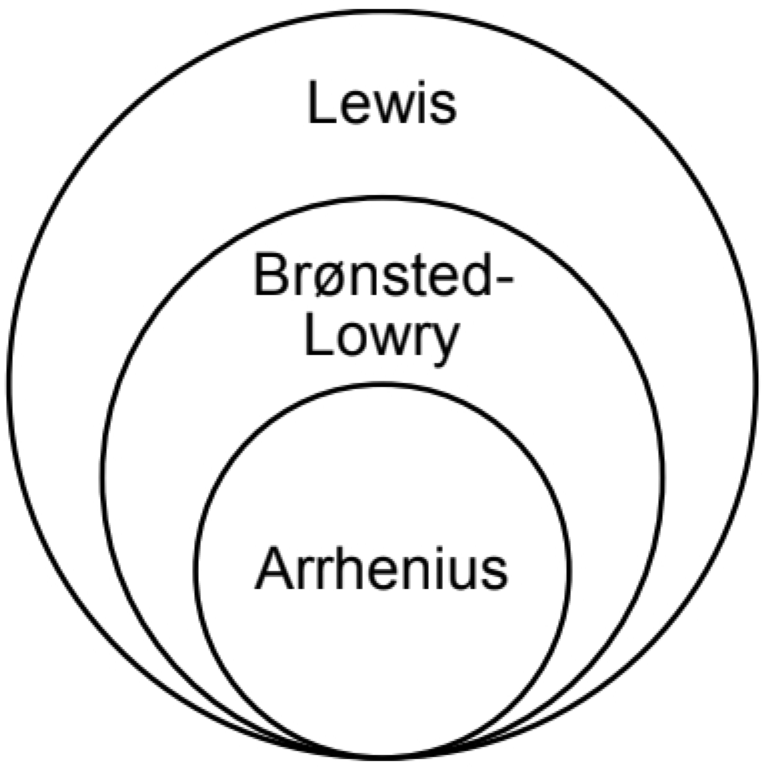
We will explore the strengths and limitations of the different models proposed to explain the characteristics of acids and bases, namely the Arrhenius Theory, the Brønsted-Lowry Theory, and the Lewis Theory.

Each theory starts off with either the proposal of a hypothesis to explain empirical data, or to address the limitations of a previous theory. With each iteration, we obtain a better understanding of the science behind acids and bases. This is the nature of scientific knowledge.

1.1 The Three Theories of Acids and Bases

Theory		**Acid**	**Base**
Arrhenius	**Definition**	A substance that **dissociates in water to form hydrogen ions** (*i.e.* $H^+(aq)$)	A substance that **dissociates in water to form hydroxide ions** (*i.e.* $OH^-(aq)$)
	Example	$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$	$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$
	Acid-base reaction	$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	
	Limitations	- Acid-base reactions are restricted to those which occur in aqueous solutions. However, there are acid-base reactions that occur in non-aqueous media. *E.g.* $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$ - Substances that do not have a OH (hydroxyl) group are not considered to be Arrhenius bases. However, there are bases that do not contain a OH group, such as ammonia and amines.	
Brønsted-Lowry	**Definition**	A **proton (H^+) donor**	A **proton (H^+) acceptor**
	Example	H_2O, HCl, H_2SO_4, HNO_3, CH_3CO_2H	H_2O, NH_3, CO_3^{2-}
	Acid-base reaction	The acid (HA) transfers a proton (H^+) to the base (B):  $B: + \overset{\delta+}{H}-\overset{\delta-}{A} \longrightarrow \overset{+}{B}-H + A^-$ *E.g.* $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$ *or* $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$  $H_3N: + \overset{\delta+}{H}-\overset{\delta-}{Cl} \longrightarrow H_3\overset{+}{N}-H + :Cl^-$	
	Limitations	While the Brønsted-Lowry Theory addresses some of the limitations of the Arrhenius Theory, it is still inadequate in explaining why non-protic substances such as CO_2 and $AlCl_3$ can exhibit acidic properties. Therefore, a more comprehensive model is required to account for these observations.	
Lewis (not in H1 syllabus)	**Definition**	An **electron-pair acceptor**	An **electron-pair donor**
	Example	BF_3, $AlCl_3$, CO_2, $(CH_3)_3C^+$	NH_3, Cl^-, HO^-
	Acid-base reaction	The Lewis base (B) donates a pair of electrons to the Lewis acid (A): *E.g.*    	
	Limitations	The Lewis theory of acids and bases extends the range of acid-base reactions to include those which do not involve protons. However, the Lewis theory has its own limitations as well. For example, it could not explain the behaviour of protic acids like HCl which do not form coordination compounds with bases.	

Notice that the Arrhenius classification is based on the ions (H^+(aq) or OH^-(aq)) that is produced [*absolute*], while the Brønsted-Lowry and Lewis classification is based on the reaction between two substances, one is the acid and the other the base [*relative*]. (see **Example 1A**, **1**)

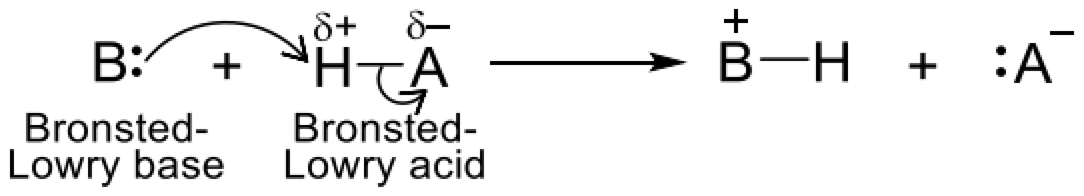


You will realise that the Arrhenius theory is a sub-set of the Brønsted-Lowry theory. The concept of the generation of H^+ and OH^- ions in the Arrhenius theory is linked to the concept of proton donors (H^+ generated) and proton acceptors (OH^- generated to accept H^+) in the Brønsted-Lowry theory. The Brønsted-Lowry theory too is a sub-set of the Lewis theory, which involves electron pair-donors (OH^- donates its lone pair to H^+) and acceptors (H^+ accepts a lone pair from OH^-).

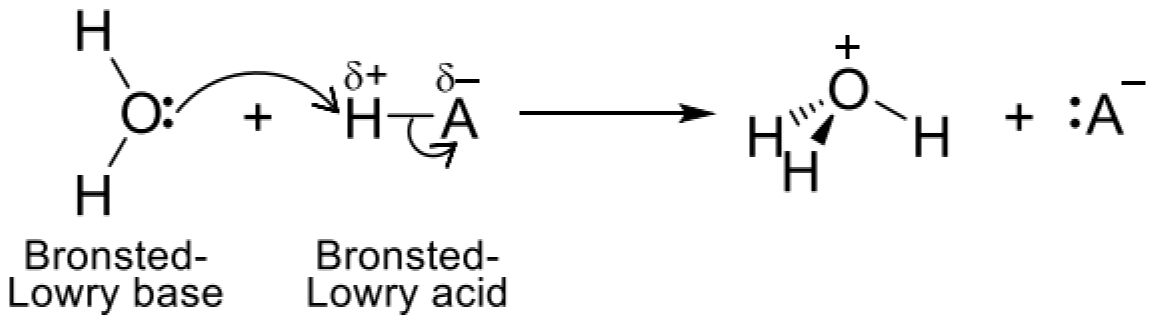
1.2 The Hydrogen Ion

Central to the Arrhenius and Brønsted-Lowry definition of an acid is the hydrogen ion or **proton**, a fundamental particle. It is very small (10^{-15} m diameter) compared to other cations (around 10^{-10} m diameter), and thus has a very **high charge density** (charge density $\propto \frac{q_+}{r_+}$). As such the proton does not exist on its own and a Brønsted-Lowry acid does not dissociate to give an isolated H^+.

Rather a Brønsted-Lowry acid attracts a lone pair of electrons of a particle, the Brønsted-Lowry base, and transfer the H^+ to (*i.e. protonate*) the base:



An Arrhenius acid is thus a special case of a Brønsted-Lowry acid in *aqueous medium*, where water serves as the Brønsted-Lowry base to generate the **hydronium ion, H_3O^+** ion:



It is important to note that both symbols, **H^+(aq)** and **H_3O^+(aq)** can be used to represent the hydronium ion, H_3O^+, and are often used interchangeably. H^+(aq) is more commonly used for simplicity's sake. H_3O^+ is also sometimes referred to as the 'hydroxonium ion' or 'oxonium ion'.

For the rest of this topic of Acid-Base Equilibria, we will be concerned primarily with Brønsted-Lowry acids and bases in water.

Example 1A

1 Most commercially available concentrated nitric acid has a concentration of 68% in water.

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

When mixed with concentrated sulfuric acid, it reacts to form the nitronium ion, NO_2^+:

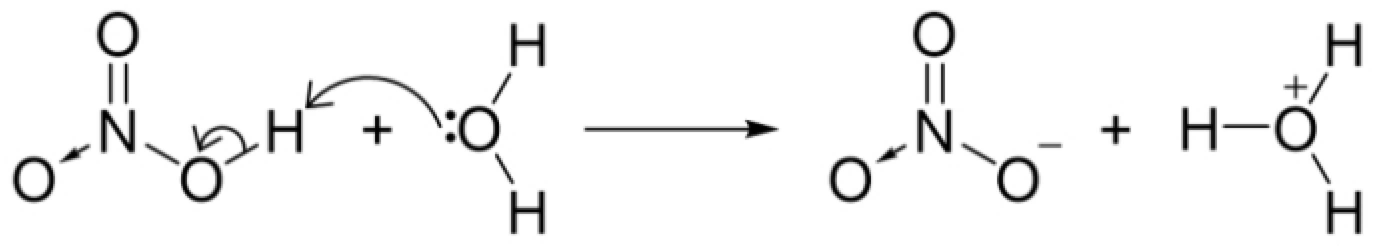
$$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$$

$$H_2NO_3^+ + H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + HSO_4^-$$

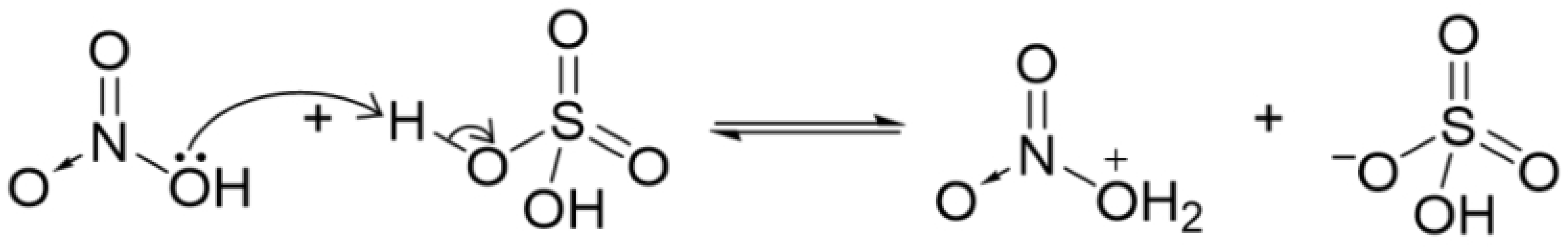
Explain whether HNO_3 is a Brønsted-Lowry acid, base, or both.

HNO_3 can be ____________________________________, depending on *what it reacts with*.

- HNO_3 acts as a Brønsted-Lowry __________ when reacting with water as it ____________ a proton to water (*i.e.* the Brønsted-Lowry base) to give H_3O^+.



- HNO_3 acts as a Brønsted-Lowry __________ when reacting with H_2SO_4 as it ___________ a proton from H_2SO_4 (*i.e.* the Brønsted Lowry acid) to give $H_2NO_3^+$.



2 An aqueous solution of boric acid is weakly acidic:

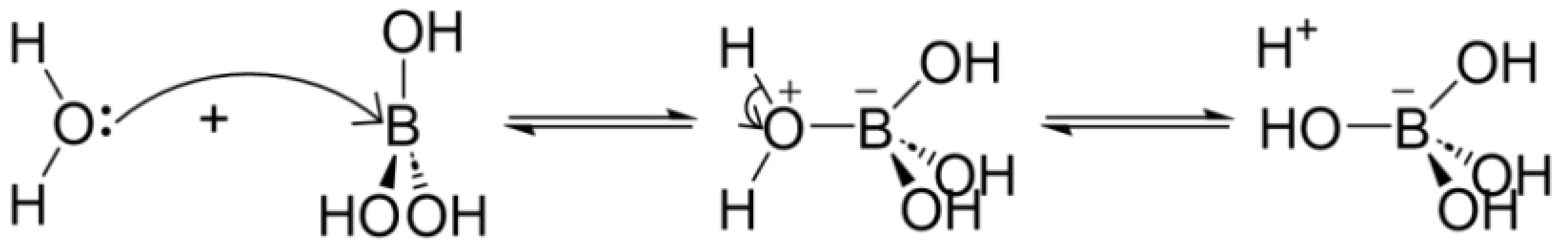
$$B(OH)_3(aq) + H_2O(l) \rightleftharpoons H^+(aq) + [B(OH)_4]^-(aq)$$

Explain which type of acid (Arrhenius, Brønsted-Lowry or Lewis) boric acid belongs to.

Boric acid is _______________________ since the H^+(aq) produced does not originate from $B(OH)_3$ itself, but from the H_2O it reacts with.

Boric acid is _______________________ since it does not donate a proton.

Boric acid is _______________________ since it accepts a lone pair of electrons from O of H_2O to give $H^+[B(OH)_4]^-$ which then dissociates to give H^+(aq).



Self Check 1A

1 Which of the following can act as a Brønsted-Lowry acid?
(There may be more than one correct answer.)

(a) H_3O^+ **(b)** NH_4^+ **(c)** H_2O

2 Describe the following reaction in terms of the Lewis theory of acids and bases:

$$I_2(aq) + I^-(aq) \rightarrow I_3^-(aq)$$

Checkpoint for Section 1

At the end of this section, you should know that:

1. An Arrhenius acid dissociates and releases hydrogen ions when dissolved in water.
2. An Arrhenius base dissociates and releases hydroxide ions when dissolved in water.
3. A Brønsted-Lowry acid is a proton donor.
4. A Brønsted-Lowry base is a proton acceptor.
5. A Brønsted-Lowry acid-base reaction involves transferring of a proton from an acid to a base.
6. A Brønsted-Lowry base must have at least one lone pair of electrons.
7. A Lewis acid is an electron-pair acceptor.
8. A Lewis acid usually contains either empty orbitals or a partial/whole positive charge.
9. A Lewis base is an electron-pair donor.
10. A Lewis acid-base reaction involves transferring of a pair of electrons from a base to an acid.

2 Brønsted-Lowry Acids and Bases

In this section, we will utilise our knowledge of the **Brønsted–Lowry theory** to help us understand the different relationships between the different types of acids and bases in aqueous solutions and their respective pH.

2.1 Conjugate Acid-Base Pairs

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

Consider the following reversible proton-transfer reaction (which can happen in both aqueous and non-aqueous mediums):

$$B + HA \rightleftharpoons HB^+ + A^-$$

We can identify two acids and two bases:

	Brønsted-Lowry Acid (proton donor)	**Brønsted-Lowry Base** (proton acceptor)
In the **forward** reaction	**HA**	**B**
In the **backward** reaction	**HB^+**	**A^-**

- Two substances which **differ from each other by only one H^+** are known collectively as a **conjugate acid-base pair**.
- Every **acid** has a **conjugate base**; this is the substance formed after the acid donates its proton. A conjugate base has one H^+ fewer than its acid.
- Every **base** has a **conjugate acid**; this is the substance formed after the base accepts a proton. A conjugate acid has one H^+ more than its base.

In other words,

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

conjugate acid-base pair

$$B + HA \rightleftharpoons HB^+ + A^-$$

conjugate acid-base pair

Example 2A

Identify the conjugate acid-base pairs in the reaction between ammonia and hydrofluoric acid in aqueous solution.

$$NH_3(aq) + HF(aq) \rightleftharpoons NH_4^+(aq) + F^-(aq)$$

The conjugate acid-base pairs are

Self Check 2A

1 Which of the following is a conjugate acid-base pair?

A H_3PO_4 / HPO_4^{2-} **B** H_2SO_4 / HSO_4^- **C** H_3PO_4 / PO_4^{3-} **D** H_2SO_4 / SO_4^{2-}

2 For the equilibrium, $HNO_3(l) + H_2SO_4(l) \rightleftharpoons H_2NO_3^+(l) + HSO_4^-(l)$

Which set is a conjugate Brønsted-Lowry acid-base pair?

	Brønsted-Lowry Base	Conjugate Acid
A	HNO_3	HSO_4^-
B	HNO_3	$H_2NO_3^+$
C	H_2SO_4	HSO_4^-
D	H_2SO_4	$H_2NO_3^+$

2.2 Basicity or Proticity of Acids

Acids which can donate one H^+ each to a base are called **monobasic** (or monoprotic) acids. Others which can donate two, three or more protons are called **dibasic** (or diprotic), **tribasic** (or triprotic) and **polybasic** (or polyprotic) acids respectively.

Examples of acids of different basicities:

monobasic acid	HCl, HNO_3, CH_3CO_2H
dibasic acid	H_2SO_4, $H_2C_2O_4$
tribasic acid	H_3PO_4

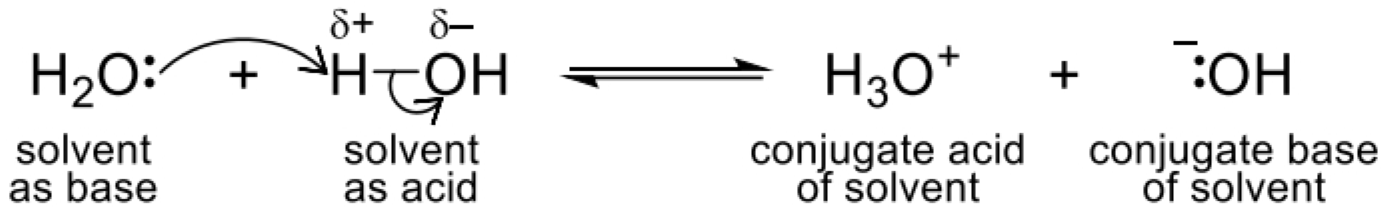
Checkpoint for Section 2

At the end of this section, you should know that:

1. Two substances that differ from each other by only one H^+ are known as a conjugate acid-base pair.
2. Every acid has a conjugate base and every base has a conjugate acid.
3. The basicity of an acid refers to its ability to donate H^+.

3 Water as Solvent

Water can act as both a Brønsted-Lowry acid and a Brønsted-Lowry base. In the process called **auto-ionisation**, water can react with itself in a reversible acid-base reaction represented by the following equation:



From the auto-ionisation, we can see that water gives $H_3O^+(aq)$ as its conjugate acid, and $OH^-(aq)$ as its conjugate base. Hence, **when water is used as the solvent, all acids produce $H_3O^+(aq)$, while all bases produce $OH^-(aq)$**. In this way, the Brønsted-Lowry definition of acids and bases corresponds to that of Arrhenius.

3.1 Ionic Product of Water, K_w

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

At equilibrium, the equilibrium constant K_c for the auto-ionisation of water is represented by

$$K_c = \left[H_3O^+\right]_{eqm}\left[OH^-\right]_{eqm}$$

Due to the ubiquitous nature of water in chemical systems, this equilibrium constant is given a special name, called the **ionic product of water**, $\boldsymbol{K_w}$.

$$\boxed{K_w = \left[H_3O^+\right]_{eqm}\left[OH^-\right]_{eqm} \qquad \text{units: mol}^2\text{ dm}^{-6}}$$

For **pure water at 298K (25 °C)**, the ionic product of water, $\boldsymbol{K_w = \underline{10^{-14}\text{ mol}^2\text{ dm}^{-6}}}$.
At this temperature, the **concentration of H_3O^+ ions** in water can be calculated in the following way:
Since $[H_3O^+] = [OH^-]$ in pure H_2O,

$$K_w = \left[H_3O^+\right]\left[OH^-\right] = 10^{-14}$$

$$\left[H_3O^+\right] = \left[OH^-\right] = \sqrt{10^{-14}}$$

$$= \underline{\mathbf{10^{-7}\ mol\ dm^{-3}}}$$

Since K_w is an equilibrium constant, **its value will change when temperature changes**. The variation of K_w values of pure water with temperature, T, is shown in the table below:

T /°C	K_w /mol² dm⁻⁶	T /°C	K_w /mol² dm⁻⁶
0	0.114×10^{-14}	40	2.916×10^{-14}
10	0.293×10^{-14}	50	5.476×10^{-14}
20	0.681×10^{-14}	100	51.3×10^{-14}

When the temperature increases, the forward endothermic reaction is favoured to absorb the extra heat energy. Hence, water dissociates more at higher temperatures, and both $[H_3O^+]$ and $[OH^-]$ at equilibrium increases, leading to larger values of K_w. We will examine the consequences of this in the next section.

3.2 pH and pOH

LO (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

pH is a measure of the concentration of hydrogen ions in a solution, and is defined as the negative logarithm of the hydrogen ion concentration in mol dm^{-3}.

$$\boxed{\text{pH} = -\lg\left[H_3O^+\right] \qquad \text{Note: pH does } \textbf{not} \text{ have units}}$$

A solution that has a **lower pH** has a **higher [H_3O^+]** than a solution with a higher pH.

pOH on the other hand is a measure of the concentration of hydroxide ions in a solution. It is defined as the negative logarithm of the hydroxide ion concentration in mol dm^{-3}.

$$\boxed{\text{pOH} = -\lg\left[OH^-\right] \qquad \text{Note: pOH does } \textbf{not} \text{ have units}}$$

A solution that has a **lower pOH** has a **higher [OH^-]** than a solution with a higher pOH.

Relationship between pH and pOH

For **aqueous** solutions at **298 K**,

$$K_w = \left[H_3O^+\right]\left[OH^-\right] = 10^{-14}$$

$$-\lg\left(\left[H_3O^+\right]\left[OH^-\right]\right) = -\lg\left(10^{-14}\right)$$

$$\left(-\lg\left[H_3O^+\right]\right) + \left(-\lg\left[OH^-\right]\right) = -\lg\left(10^{-14}\right)$$

Therefore,

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

Think about this…

In secondary school, you learnt that the pH of **pure water at 298 K (25 ºC)** is **7**. How was this value derived?

On page 10, we calculated that for pure water at 298 K, **$[H_3O^+]$** = $\sqrt{10^{-14}}$ = **10^{-7} mol dm^{-3}**. Hence, pH in this situation is –lg(10^{-7}) **= 7**.

Now, let's calculate the pH of **pure water at 373 K (100 ºC)**, using the K_w value at that temperature of 51.3 × 10^{-14} mol^2 dm^{-6}.

$$K_w = [H_3O^+][OH^-] = 51.3 \times 10^{-14}$$
$$[H_3O^+] = [OH^-] = \sqrt{51.3 \times 10^{-14}}$$
$$= 7.16 \times 10^{-7} \text{ mol dm}^{-3}$$
$$\text{pH} = -\lg(7.16 \times 10^{-7}) = \underline{\mathbf{6.14}}$$

Since the pH of water at 373 K is below 7, does it mean that water is acidic at its boiling point?

NO!

Important:
pH is a measure of concentration of hydrogen ions in the solution. It does not always tell us the acidity or basicity of a solution. Rather,
A solution is **acidic** if $[H_3O^+]$ **>** $[OH^-]$.
A solution is **neutral** if $[H_3O^+]$ **=** $[OH^-]$.
A solution is **basic** if $[H_3O^+]$ **<** $[OH^-]$.

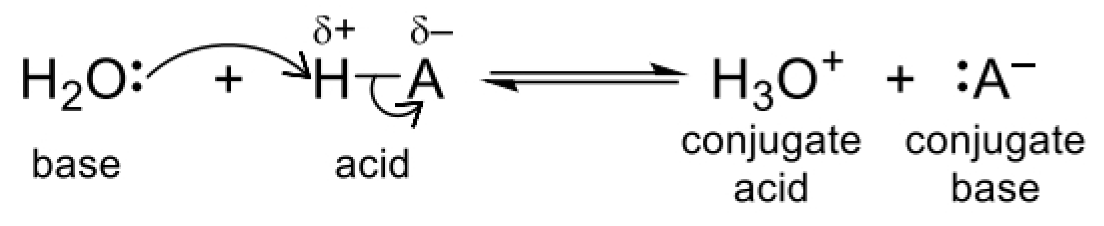
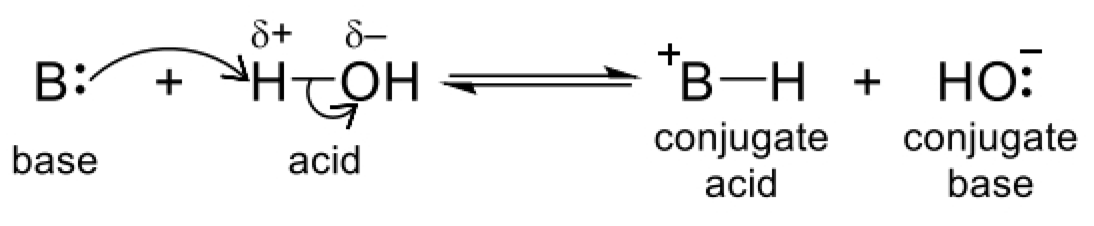
For water at 373 K, the solution **remains neutral** as $[H_3O^+]$ and $[OH^-]$ are the same. The decrease in pH is merely a consequence of the higher $[H_3O^+]$ due to the larger extent of dissociation of water. So, both the pH and pOH of pure water decrease as temperature increases because the K_w of water increases.

3.3 Strength of Acids and Bases

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

In the following discussion, we will focus on Brønsted-Lowry acids and bases in aqueous medium. However, the concept is applicable to non-aqueous medium as well.

In water, the strength of an acid or base in water depends on the **position** of the following equilibria:

	Acid, HA	**Base, B:**
solvent role	solvent (water) as base	solvent (water) as acid
equilibrium		
factors affecting strength	- stability of conjugate base, A^- ***(hydroxy cpds & carboxylic acids)*** - strength of H–A bond ***(Group 17)***	- stability of conjugate acid, ^+BH - availability of lone pair on B for donation ***(nitrogen compounds)***

Strong Acid	**Weak Acid**
A strong acid **dissociates (or ionises) completely** in water to form $H_3O^+(aq)$. For example, $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$ In an aqueous solution of the strong acid, HCl, $[H_3O^+]_{produced} = [Cl^-]_{produced} = [HCl]_{initial}$ Other examples of strong acids include: - sulfuric acid, H_2SO_4 - nitric acid, HNO_3	A weak acid **dissociates (or ionises) partially** in water to form $H_3O^+(aq)$. For example, $CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$ In an aqueous solution of the weak acid, CH_3CO_2H, $[H_3O^+]_{produced} = [CH_3CO_2^-]_{produced} \ll [CH_3CO_2H]_{initial}$ Other examples of weak acids include: - carbonic acid, H_2CO_3 - phosphoric acid, H_3PO_4 - hydrofluoric acid, HF - many organic acids
Strong Base	**Weak Base**
A strong base **dissociates (or ionises) completely** in water to form $OH^-(aq)$. For example, $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$ In an aqueous solution of the strong base, NaOH, $[OH^-]_{produced} = [Na^+]_{produced} = [NaOH]_{initial}$ Examples: - potassium hydroxide, KOH - calcium hydroxide, $Ca(OH)_2$	A weak base **dissociates (or ionises) partially** in water to form $OH^-(aq)$. For example, $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ In an aqueous solution of the weak base, NH_3, $[OH^-]_{produced} = [NH_4^+]_{produced} \ll [NH_3]_{initial}$ Examples: - Most organic amines, *e.g.* ethylamine, $CH_3CH_2NH_2$

Notice that a **strong acid HA**, where the position of equilibrium ($HA + H_2O \rightleftharpoons H_3O^+ + A^-$) lies essentially to the right, will give a **weak conjugate base A^-** as the backward reaction involving protonation of A^- is not favourable, and *vice versa*. Similarly, a strong base B will give a weak conjugate acid BH^+, and *vice versa*. (See Section 4.4 on page 18)

Checkpoint for Section 3

At the end of this section, you should know that:

1. The ionic product of water, $K_w = [H^+]_{eqm}\,[OH^-]_{eqm} = 10^{-14}$ mol² dm⁻⁶ at 298 K.
2. $pK_w = 14$ at 298 K (25 °C).
3. pH is a measure of $[H^+]$ and is calculated by $pH = -lg\,[H^+]$.
4. pOH is a measure of $[OH^-]$ and is calculated by $pOH = -lg\,[OH^-]$.
5. Strength of an acid, HA, depends on the position of the equilibrium:
$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
6. Strength of a base, B, depends on the position of the equilibrium:
$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$
7. A strong acid dissociates completely in water to form $H_3O^+(aq)$.
8. A weak acid dissociates partially in water to form $H_3O^+(aq)$.
9. A strong base dissociates completely in water to form $OH^-(aq)$.
10. A weak base dissociates partially in water to form $OH^-(aq)$.

4 Comparing the Strength of Acids and Bases

4.1 pH

Is pH a good measure of the strength of acids and bases in water?

The pH of 1 mol dm^{-3} ethanoic acid, $CH_3CO_2H(aq)$, is approximately pH 2.4.

$$\left[H^+(aq)\right] = 10^{-2.4} \approx 4 \times 10^{-3}\ \text{mol dm}^{-3} \ll \left[CH_3CO_2H\right]_{\text{initial}}$$

The pH of 1 × 10^{-3} mol dm^{-3} hydrochloric acid, $HCl(aq)$, is pH 3.

$$\left[H^+(aq)\right] = 10^{-3.0} = 1 \times 10^{-3}\ \text{mol dm}^{-3} = \left[HCl\right]_{\text{initial}}$$

We know that

- CH_3CO_2H is a weak acid as $\left[H^+(aq)\right] \ll \left[CH_3CO_2H(aq)\right]_{\text{initial}}$, *i.e.* CH_3CO_2H partially dissociates,
- HCl is a strong acid as $\left[H^+(aq)\right] = \left[HCl(aq)\right]_{\text{initial}}$, *i.e.* HCl fully dissociates

in water

However, the pH of aqueous solution of the weak acid is lower, *i.e.* more acidic, than that of the strong acid! The reason is pretty obvious. The concentration of the ethanoic acid (1 mol dm^{-3}) is much higher than that of the strong acid (1 × 10^{-3} mol dm^{-3}).

pH is **not** a good measure of the strength of acids and bases in water. pH will give an indication of the strength of the acid **only if** the acids compared have the **same initial concentration**, **same proticity/basicity** and are at the **same temperature**. In this situation, the acid with a lower pH will be a stronger acid.

So, the pH of 1 × 10^{-3} mol dm^{-3} CH_3CO_2H is approximately 3.9, which is higher than for of HCl of the same concentration, showing that CH_3CO_2H is a weaker acid than HCl.

Think about this…

In 1 × 10^{-3} mol dm^{-3} HCl, at pH 3.0, $\left[H^+(aq)\right] = 10^{-3.0} = 1 \times 10^{-3}\ \text{mol dm}^{-3}$, while

in 1 × 10^{-3} mol dm^{-3} CH_3CO_2H, at pH 3.9, $\left[H^+(aq)\right] = 10^{-3.9} = 1.3 \times 10^{-4}\ \text{mol dm}^{-3}$.

Does it mean that the 25.0 cm^3 of 1 × 10^{-3} mol dm^{-3} of HCl will require more NaOH for complete neutralisation, compared to 25.0 cm^3 of 1 × 10^{-3} mol dm^{-3} of CH_3CO_2H?

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

NO!

Removal of $H^+(aq)$ by $OH^-(aq)$ will cause the equilibrium $CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$ to shift to the right, until eventually all the CH_3CO_2H dissociates and reacts with NaOH fully!

We have seen in Section 3.3 that the strength of an acid depends on the *position* of the equilibrium

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

Hence, the equilibrium constant, K_c, which measures the extent of an equilibrium reaction *independent of the initial concentrations* is a more appropriate measure of the strength of an acid.

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

4.2 Acid Dissociation Constant, K_a

Consider the partial dissociation of a weak monobasic acid, HA(aq):

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

Since water is the solvent in the system, we can write the equilibrium constant, which is known as the **acid dissociation constant**, **K_a**.

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

Since K_a is an equilibrium constant, it is **constant** at **constant temperature**.

The K_a values of different acids can be used to compare the **strength** of weak acids as it gives us a quantitative indication of the extent to which the acid is dissociated. However, as K_a values are typically very small for weak acids, it is usually more convenient to compare the acid strength using **pK_a** values.

$$pK_a = -\lg K_a \qquad \text{Note: p}K_a \text{ does } \textbf{not} \text{ have units}$$

The dissociation constants of some weak acids in water at 25 °C are given in the table below:

acids	K_a / mol dm^{-3}	pK_a
HF(aq)	6.76×10^{-4}	3.17
$C_6H_5CO_2H$(aq)	6.31×10^{-5}	4.20
CH_3CO_2H(aq)	1.75×10^{-5}	4.76
HCN(aq)	6.17×10^{-10}	9.21
C_6H_5OH(aq)	1.12×10^{-10}	9.95

Note: **Larger** K_a value or **smaller** pK_a value $\Rightarrow$ **Stronger** acid, and *vice versa*.

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

dissociation	**equilibrium**	**K_a / mol dm^{-3}**	**pK_a**
first, K_{a1}	$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$	7.08×10^{-3}	2.15
second, K_{a2}	$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$	6.31×10^{-8}	7.20
third, K_{a3}	$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$	4.47×10^{-13}	12.35

From the table, you will notice that the value of K_a decreases upon each dissociation, *i.e.* $K_{a2} < K_{a1}$ and $K_{a3} < K_{a2}$. This is because it is **more difficult to lose a proton** due to the **stronger electrostatic forces of attraction** between the **increasingly negatively charged conjugate base and the proton**.

4.3 Base Dissociation Constant, K_b

Consider the partial dissociation of a weak monoacidic base, B(aq):

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

Like how K_a is derived, we can derive the **base dissociation constant, K_b** and **pK_b** of a weak base:

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

$$\boxed{pK_b = -\lg K_b \qquad \text{Note: p}K_b \text{ does \textbf{not} have units}}$$

K_b and pK_b values can be used to compare the strength of the weak bases.

The dissociation constants of some weak bases in water at 25 °C are given in the table below:

bases	**formula**	**K_b / mol dm^{-3}**
ethylamine	$CH_3CH_2NH_2$	5.62×10^{-4}
methylamine	CH_3NH_2	4.54×10^{-4}
ammonia	NH_3	1.74×10^{-5}
phenylamine	$C_6H_5NH_2$	4.27×10^{-10}

Note: **Larger** K_b value or **smaller** pK_b value $\Rightarrow$ **Stronger** base, and *vice versa*.

4.4 Relationship between K_a, K_b and K_w (not in H1 syllabus)

Consider the dissociation of a weak acid, HA in water.

$$HA(aq) + H_2O(\mathit{l}) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{\left[H_3O^+\right]\left[A^-\right]}{[HA]} \text{ ------------------- (1)}$$

For its conjugate base, A^-,

$$A^-(aq) + H_2O(\mathit{l}) \rightleftharpoons HA(aq) + OH^-(aq) \qquad K_b = \frac{[HA]\left[OH^-\right]}{\left[A^-\right]} \text{ --------------------- (2)}$$

Taking (1) × (2),

$$\begin{aligned} K_a \times K_b &= \frac{\left[H_3O^+\right]\left[A^-\right]}{[HA]} \times \frac{[HA]\left[OH^-\right]}{\left[A^-\right]} \\ &= \left[H_3O^+\right]\left[OH^-\right] \\ &= K_w \end{aligned}$$

$$\boxed{K_a \times K_b = K_w \qquad K_w = 10^{-14} \text{ at } 298 \text{ K}}$$

If we take the negative logarithm on both sides,

$$\begin{aligned} -\lg\left(K_a \times K_b\right) &= -\lg K_w \\ -\lg K_a - \lg K_b &= -\lg K_w \end{aligned}$$

$$\boxed{pK_a + pK_b = pK_w \qquad pK_w = 14 \text{ at } 298 \text{ K}}$$

Since K_w is a constant at constant temperature, the higher the K_a, the lower the K_b. This would mean that **a stronger acid will always give a weaker conjugate base, and *vice versa***.

For example, $C\mathit{l}^-$ is essentially non-basic as $HC\mathit{l}$ is a very strong acid, while CN^- is a relatively strong base as HCN is a weak acid.

Useful conversion:
At 298 K or 25 °C,

$$\begin{tikzcd}[row sep=huge, column sep=huge]
{[H^+]} \arrow[r, shift left, "-\lg\left[H^+\right]"] \arrow[d, shift left, "\frac{10^{-14}}{\left[H^+\right]}"] & pH \arrow[l, shift left, "10^{-pH}"] \arrow[d, shift left, "14-pH"] \\
{[OH^-]} \arrow[r, shift left, "-\lg\left[OH^-\right]"] \arrow[u, shift left, "\frac{10^{-14}}{\left[OH^-\right]}"] & pOH \arrow[l, shift left, "10^{-pOH}"] \arrow[u, shift left, "14-pOH"]
\end{tikzcd}
\qquad
\begin{tikzcd}[row sep=huge, column sep=huge]
K_a \arrow[r, shift left, "-\lg K_a"] \arrow[d, shift left, "\frac{10^{-14}}{K_a}"] & pK_a \arrow[l, shift left, "10^{-pK_a}"] \arrow[d, shift left, "14-pK_a"] \\
K_b \arrow[r, shift left, "-\lg K_b"] \arrow[u, shift left, "\frac{10^{-14}}{K_b}"] & pK_b \arrow[l, shift left, "10^{-pK_b}"] \arrow[u, shift left, "14-pK_b"]
\end{tikzcd}$$

4.5 Degree of Dissociation, α (not in H1 syllabus)

The fraction of acid or base molecules which is dissociated into ions in water, is known as the **degree of dissociation, α**.

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

In general, the degree of dissociation is **close to 1** for **strong** acids and bases, and **≪1** for **weak** acids and bases. The degree of dissociation is sometimes represented by a percentage, *i.e.* close to 100% for strong acids and bases, and ≪100% for weak acids and bases.

Consider a weak acid, HA with concentration *c* mol dm^{-3}, and a degree of dissociation α:

	$HA(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$A^-(aq)$
initial concentration/ mol dm^{-3}	c				0		0
change in concentration/ mol dm^{-3}	$-c\alpha$				$+c\alpha$		$+c\alpha$
equilibrium concentration/ mol dm^{-3}	$c(1-\alpha)$				$c\alpha$		$c\alpha$

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

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

For a weak acid, since $\alpha \ll 1$, hence, $1-\alpha \approx 1$

$$K_a = \alpha^2 c \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}}$$

Since $c = [HA]_{initial}$,

$$\boxed{K_a = \alpha^2 [HA]_{initial} \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{[HA]_{initial}}}}$$

Similarly for bases,

$$\boxed{K_b = \alpha^2 [B]_{initial} \quad \text{or} \quad \alpha = \sqrt{\frac{K_b}{[B]_{initial}}}}$$

From the equations, we can see that **α is dependent on the initial concentration of the acid or base**. The more dilute the acid or base, the more it dissociates. For example, the value of α is 0.00417 (*i.e.* 0.4% dissociated) for 1 mol dm^{-3} CH_3CO_2H, but 0.0417 (*i.e.* 4.2% dissociated) for 0.01 mol dm^{-3} CH_3CO_2H, and 0.417 (*i.e.* 41.7% dissociated) for 0.0001 mol dm^{-3} CH_3CO_2H.

This phenomenon can also be understood using Le Châtelier's Principle. When water is added to a solution of a weak acid in water:

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

The concentration of all the aqueous species, HA(aq), H_3O^+(aq) and A^-(aq) decreases. However, there are *more concentration terms* on the right-hand side of the equilibrium and so the overall decrease in concentration is more severe for the right-hand side. By Le Châtelier's Principle, the system would attempt to counter this change by increasing the [H_3O^+(aq)] and [A^-(aq)], shifting the position of equilibrium to the right, favouring the dissociation of HA.

Think about this…

If water is continuously added to a solution of acid, does the solution become more acidic (*i.e.* does the pH of the solution decrease), since the acid dissociates to a larger extent?

Not necessarily! This is because pH = –lg [H^+], which can also be expressed as $\mathrm{pH} = -\lg\left(\dfrac{\text{amount of H}^+}{\text{volume of solution}}\right)$. As we add water to a solution of acid, the **amount of H^+** does increase since more of the weak acid dissociates. However, the **volume of solution** increases more significantly than the amount of H^+. As a result, the [H^+] decreases, which causes an increase in the pH of the solution, *i.e.* the solution becomes **less** acidic.

Checkpoint for Section 4

At the end of this section, you should know that:

1. pH is not a good measure of strength of acids and bases, unless the initial concentrations are the same.
2. The dissociation of an acid can be expressed as $K_a = \dfrac{\left[\mathrm{H_3O^+}\right]_{\mathrm{eqm}}\left[\mathrm{A^-}\right]_{\mathrm{eqm}}}{\left[\mathrm{HA}\right]_{\mathrm{eqm}}}$, where K_a is the acid dissociation constant.
3. pK_a is normally used to compare acid strength and is calculated by pK_a = –lg K_a.
4. The larger the magnitude of pK_a, the weaker the acid.
5. The dissociation of a base can be expressed as $K_b = \dfrac{\left[\mathrm{BH^+}\right]_{\mathrm{eqm}}\left[\mathrm{OH^-}\right]_{\mathrm{eqm}}}{\left[\mathrm{B}\right]_{\mathrm{eqm}}}$, where K_b is the base dissociation constant.
6. pK_b is normally used to compare acid strength and is calculated by pK_b = –lg K_b.
7. The larger the magnitude of pK_b, the weaker the base.
8. $K_w = K_a \bullet K_b$ or pK_a + pK_b = pK_w for a conjugate acid-base pair.
9. A stronger acid will give a weaker conjugate base, and vice versa.
10. The degree of dissociation of an acid or a base can be expressed as $\alpha = \sqrt{\dfrac{K_a}{[\mathrm{HA}]_{\mathrm{initial}}}}$ and $\alpha = \sqrt{\dfrac{K_b}{[\mathrm{B}]_{\mathrm{initial}}}}$ respectively.

5 Calculating the pH of Acids and Bases

5.1 Strong Acids and Bases

Example 5A – pH of strong acid

Calculate the pH of 10^{-2} mol dm^{-3} nitric acid.

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

Example 5B – pH of strong base

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

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

$[OH^-]$ =

Since $[H_3O^+][OH^-] = 10^{-14}$, *or*

Self Check 5A

1 Calculate the pH of solutions with the following H_3O^+ concentrations in mol dm^{-3}:
(a) 6.8×10^{-3} **(b)** 3.2×10^{-9}

2 Calculate the pH of solutions with the following OH^- concentrations in mol dm^{-3}:
(a) 3.7×10^{-10} **(b)** 6.4×10^{-5}

3 Calculate the H_3O^+ and OH^- concentrations in solutions with the following pH values:
(a) 9.21 **(b)** 13.7

4 Calculate the pH and pOH of the following solutions:
(a) 25 cm^3 of 0.200 mol dm^{-3} of hydrochloric acid made up to 500 cm^3 of solution
(b) 0.90 g of $HClO_4$ (strong monobasic acid) dissolved in 100 cm^3 of water
(c) 20 cm^3 of 0.100 mol dm^{-3} of potassium hydroxide made up to 100 cm^3 of solution
(d) 1.00 g of calcium hydroxide dissolved in water and made up to 250 cm^3 of solution

5.2 Weak Acids and Bases (not in H1 syllabus)

For a weak monobasic acid, HA, of concentration *c* mol dm^{-3}, in pure water.

Let the [H_3O^+] at equilibrium be *x* mol dm^{-3}.

	$HA(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$A^-(aq)$
initial concentration/ mol dm^{-3}	c				0		0
change in concentration/ mol dm^{-3}	$-x$				$+x$		$+x$
equilibrium concentration/ mol dm^{-3}	$c-x$				x		x

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

Since dissociation of weak acids occurs to a very small extent, **$c \gg x$**.

Hence, we can assume that $c - x \approx c$

$$\textit{i.e.} \quad [HA]_{eqm} \approx [HA]_{intial}$$

$$\text{Hence,} \quad K_a \approx \frac{\left(\left[H_3O^+\right]_{eqm}\right)^2}{[HA]_{initial}}$$

$$\boxed{\left[H_3O^+\right]_{eqm} = \sqrt{K_a[HA]_{initial}} \qquad \text{for a } \textbf{weak monobasic acid}}$$

For a weak monoacidic base, B, of concentration *c* mol dm^{-3}, in pure water.

Let the [OH^-] at equilibrium be *x* mol dm^{-3}.

	$B(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$BH^+(aq)$	+	$OH^-(aq)$
initial concentration/ mol dm^{-3}	c				0		0
change in concentration/ mol dm^{-3}	$-x$				$+x$		$+x$
equilibrium concentration/ mol dm^{-3}	$c-x$				x		x

$$K_b = \frac{\left[OH^-\right]_{eqm}\left[BH^+\right]_{eqm}}{[B]_{eqm}}$$

Since dissociation of weak bases occurs to a very small extent, ***c* ≫ *x***.

Hence, we can assume that $c - x \approx c$

$$\textit{i.e.} \quad [B]_{eqm} \approx [B]_{intial}$$

$$\text{Hence,} \quad K_b \approx \frac{\left(\left[OH^-\right]_{eqm}\right)^2}{[B]_{initial}}$$

$$\boxed{\left[OH^-\right]_{eqm} = \sqrt{K_b[B]_{initial}} \qquad \text{for a } \textbf{weak monoacidic base}}$$

Example 5C – pH of weak acid

Hypochlorous acid, HOC*l*, is a weak acid. Given that its acid dissociation constant, K_a, is 2.0×10^{-8} mol dm^{-3}, calculate

(a) pH of a 1.5 mol dm^{-3} aqueous solution of hypochlorous acid.

(b) degree of dissociation of hypochlorous acid.

Let the $[H_3O^+]$ at equilibrium be x mol dm^{-3}.

	$HOCl(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$ClO^-(aq)$
initial concentration/ mol dm^{-3}	1.5				0		0
change in concentration/ mol dm^{-3}	$-x$				$+x$		$+x$
equilibrium concentration/ mol dm^{-3}	$1.5-x$				x		x

(a) $$K_a = \frac{\left[H_3O^+\right]_{eqm}\left[A^-\right]_{eqm}}{\left[HA\right]_{eqm}} = \frac{x^2}{1.5-x}$$

Since $x \ll 1.5$,

What happens if we do not make the approximation that $[HA]_{eqm} \approx [HA]_{initial}$?

$$2.0 \times 10^{-8} = \frac{x^2}{1.5-x}$$

$$\left[H_3O^+\right] = x = \frac{-\left(2\times10^{-8}\right) \pm \sqrt{\left(2\times10^{-8}\right)^2 - 4\left(-3\times10^{-8}\right)}}{2}$$

$$= 1.732 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg\left[H_3O^+\right] = 3.76$$

Since x is so much smaller than the initial concentration of the acid, doing the approximation does not result in any significant impact on the final answer. Hence, it is safe to make the approximation.

(b) $$\alpha = \frac{\text{amount dissociated}}{\text{total initial amount}} \quad \textit{or} \quad \alpha = \sqrt{\frac{K_a}{[HA]_{initial}}}$$

Example 5D – pK_a of weak acid

The pH of a 0.01 mol dm^{-3} ethanoic acid is 3.34. Find the K_a of ethanoic acid.

$[H_3O^+] = 10^{-3.34} = 4.571 \times 10^{-4}$ mol dm^{-3}

	CH_3CO_2H (aq)	+	$H_2O(l)$	$\rightleftharpoons$	H_3O^+(aq)	+	$CH_3CO_2^-$(aq)
initial conc/ mol dm^{-3}	0.01				0		0
change in conc/ mol dm^{-3}	-4.571×10^{-4}				$+4.571\times10^{-4}$		$+4.571\times10^{-4}$
equilibrium conc/ mol dm^{-3}	$0.01-4.571\times10^{-4}$				4.571×10^{-4}		4.571×10^{-4}

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

Example 5E – pH of weak base

Calculate the pH of a 0.2 mol dm^{-3} ammonia solution, given that its $K_b = 1.8 \times 10^{-5}$ mol dm^{-3}.

Let the $[OH^-]$ at equilibrium be x mol dm^{-3}.

	NH_3(aq)	+	$H_2O(l)$	$\rightleftharpoons$	NH_4^+(aq)	+	OH^-(aq)
initial conc/ mol dm^{-3}	0.2				0		0
change in conc/ mol dm^{-3}	$-x$				$+x$		$+x$
equilibrium conc/ mol dm^{-3}	$0.2-x$				x		x

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

Self Check 5B

1. Calculate the K_a of the weak monobasic acids listed below:
   (a) a solution of 0.0100 mol dm^{-3} CH_3CO_2H has a pH of 3.38.
   (b) a solution of 0.200 mol dm^{-3} HCN has a pH of 5.05

2. Calculate the K_b of the weak monoacidic bases listed below:
   (a) a solution of 0.0100 mol dm^{-3} CH_3NH_2 has [OH^-] of 4.78 × 10^{-7} mol dm^{-3}.
   (b) a solution of 0.0500 mol dm^{-3} $C_6H_5NH_2$ has [OH^-] of 9.65 × 10^{-5} mol dm^{-3}.

3. Calculate the pH and pOH of the following solutions:
   (a) 100 cm^3 of 0.001 mol dm^{-3} of nitrous acid, HNO_2
   (Given: K_a of HNO_2 = 7.1 × 10^{-4} mol dm^{-3})
   (b) 10 cm^3 of 0.300 mol dm^{-3} of $HOCH_2CH_2NH_2$ solution
   (Given: K_b of $HOCH_2CH_2NH_2$ = 3.24 × 10^{-5} mol dm^{-3})
   (c) 25 cm^3 of 0.200 mol dm^{-3} of propanoic acid, $C_2H_5CO_2H$, added with 20 cm^3 of water
   (Given: K_a of C_2H_5COOH = 1.3 × 10^{-5} mol dm^{-3})
   (d) 50 cm^3 of 0.100 mol dm^{-3} of propanoic acid, $C_2H_5CO_2H$, added to an equal volume of water (Given: K_a of C_2H_5COOH = 1.3 × 10^{-5} mol dm^{-3})
   (e) 20 cm^3 of 0.100 mol dm^{-3} of nitrous acid, HNO_2, made up to 100 cm^3 of solution.
   (Given: pK_a of HNO_2 = 3.15)

4. Calculate the degree of ionisation of each of the following in aqueous solution:
   (a) 2.00 × 10^{-3} mol dm^{-3} HCN (pK_a = 9.40)
   (b) 1.00 × 10^{-3} mol dm^{-3} $(CH_3)_3N$ (pK_b = 9.80)

5.3 Effect of Concentration on Calculation of pH (Extra)

Imagine starting with 1 mol dm^{-1} each of aqueous phenol (C_6H_5OH), ethanoic acid (CH_3CO_2H) and hydrochloric acid (HCl) and performing serial dilution ten times to get a series of solutions with concentrations of 1×10^{-n} mol dm^{-3} for n = 1 to 10. The concentration of $H^+(aq)$ and pH of the series of $C_6H_5OH(aq)$, $CH_3CO_2H(aq)$ and $HCl(aq)$ resulting are as shown in the table below.

initial conc.	**C_6H_5OH (pK_a = 9.95)**			**CH_3CO_2H (pK_a = 4.756)**			**HCl**	
	$\sqrt{K_a \times [C_6H_5OH]}$	**actual [H^+]**	**pH**	$\sqrt{K_a \times [CH_3CO_2H]}$	**actual [H^+]**	**pH**	**actual [H^+]**	**pH**
1	1.059×10^{-5}	1.059×10^{-5}	4.97	4.188×10^{-3}	4.178×10^{-3}	2.38	1.000	0.00
1×10^{-1}	3.350×10^{-6}	3.351×10^{-6}	5.47	1.324×10^{-3}	1.316×10^{-3}	2.88	1.000×10^{-1}	1.00
1×10^{-2}	1.059×10^{-6}	1.064×10^{-6}	5.97	4.188×10^{-3}	4.101×10^{-3}	3.39	1.000×10^{-2}	2.00
1×10^{-3}	3.350×10^{-7}	3.495×10^{-7}	6.46	1.324×10^{-4}	1.240×10^{-4}	3.91	1.000×10^{-3}	3.00
1×10^{-4}	1.059×10^{-7}	1.456×10^{-7}	6.84	4.188×10^{-5}	3.402×10^{-5}	4.47	1.000×10^{-4}	4.00
1×10^{-5}	3.350×10^{-8}	1.055×10^{-7}	6.98	1.324×10^{-5}	7.115×10^{-6}	5.15	1.000×10^{-5}	5.00
1×10^{-6}	1.059×10^{-8}	1.006×10^{-7}	7.00	4.188×10^{-6}	9.586×10^{-7}	6.02	1.001×10^{-6}	6.00
1×10^{-7}	3.350×10^{-9}	1.001×10^{-7}	7.00	1.324×10^{-6}	1.611×10^{-7}	6.79	1.618×10^{-7}	6.79
1×10^{-8}	1.059×10^{-9}	1.000×10^{-7}	7.00	4.188×10^{-7}	1.051×10^{-7}	6.98	1.051×10^{-7}	6.98
1×10^{-9}	3.350×10^{-10}	1.000×10^{-7}	7.00	1.324×10^{-7}	1.005×10^{-7}	7.00	1.005×10^{-7}	7.00
1×10^{-10}	1.059×10^{-10}	1.000×10^{-7}	7.00	4.188×10^{-8}	1.001×10^{-7}	7.00	1.000×10^{-7}	7.00

These are some general observations:

For initial concentration of 1×10^{-6} mol dm^{-3} and *higher*,

- [H^+] = [HCl]$_{\text{initial}}$ since HCl is a strong acid which fully dissociates in aqueous solution.
- [H^+] is higher and hence pH is lower for the same initial concentration of HCl compared to C_6H_5OH and CH_3CO_2H. This is because C_6H_5OH and CH_3CO_2H are weak acid which partially dissociates in aqueous solution, hence [H^+] < [C_6H_5OH]$_{\text{initial}}$ and [H^+] < [CH_3CO_2H]$_{\text{initial}}$.

For initial concentration of 1×10^{-7} mol dm^{-3} and *lower*,

- [H^+] is significantly higher than initial [acid]! This is because the auto-ionisation of water (see Section 3)

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

  is no longer suppressed, and cannot be ignored, due to the low [$H^+(aq)$] from the acid. In other words, the H_2O solvent contributes significantly to the total [$H^+(aq)$].
- The [H^+] and pH for $CH_3CO_2H(aq)$ and $HCl(aq)$ are almost identical, despite CH_3CO_2H being a weak acid. We have seen earlier in Section 4.5 (page 19) that the degree of dissociation, α, increases with dilution. In this case, for concentration of 1×10^{-7} mol dm^{-3} and lower, CH_3CO_2H is essentially *completely ionised* in water, just like HCl.

For *weak acid*, at initial concentration between 1×10^{-4} mol dm^{-3} and 1×10^{-6} mol dm^{-3},

- For CH_3CO_2H, $\sqrt{K_a \times [CH_3CO_2H]} > [H^+]$ as the approximation that $[CH_3CO_2H]_{eqm} \approx [CH_3CO_2H]_{initial}$ (see Section 5.2) breaks down, because the degree of dissociation, α, increases with dilution. So $[CH_3CO_2H]_{eqm} \approx [CH_3CO_2H]_{initial} - [H^+]$ instead.
- For the even weaker acid, C_6H_5OH, $\sqrt{K_a \times [C_6H_5OH]} < [H^+]$ as $[H^+]$ from the acid is too low to suppress the auto-ionisation of water and H^+ from water contributes significantly to the total $[H^+]$ at concentration of 1×10^{-4} mol dm^{-3} and lower.

For simplicity, $H^+(aq)$ from auto-ionisation of the water solvent is taken into considerations if the **initial concentration of the acid is *lower* than 1×10^{-7} mol dm^{-3}**.

So, for *dilute solutions* (< 1×10^{-7} mol dm^{-3}) of

- strong acids, H^+ from the water solvent is taken into considerations by simply **adding 1×10^{-7} mol dm^{-3}** to the $[H^+]$ from the strong acid itself.
- weak acids, we assume that the weak acid is **fully ionised**, behaving just like a strong acid, and can be treated in the same way by **adding 1×10^{-7} mol dm^{-3}** to the $[H^+]$ from the weak acid itself.

Example 5F – pH of dilute strong acid

Calculate the pH of 10^{-8} mol dm^{-3} nitric acid.

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

Due to the **low concentration** (*i.e.* **$<10^{-7}$ mol dm^{-3}**) of HNO_3, contribution of **H_3O^+** from the **auto-ionisation of water** is **significant** and should not be ignored.

Checkpoint for Section 5

At the end of this section, you should know that:

1. For a weak monobasic acid, $[H^+]_{eqm} = \sqrt{K_a [HA]_{initial}}$.
2. For a weak monoacidic base, $[OH^-]_{eqm} = \sqrt{K_b [B]_{initial}}$.

6 Acid and Base Properties of Salt Solutions

A salt is formed by the reaction of an acid and a base. It is made up of a cation which comes from the base and an anion which comes from the acid. For example, ammonium ethanoate, $CH_3CO_2^-NH_4^+$ comes from CH_3CO_2H and NH_3.

Salts can be very soluble, sparingly soluble or insoluble in water. Soluble salts dissociate completely in water, forming hydrated ions. If the ions do not undergo *hydrolysis*, the solution will remain neutral. If the ions undergo *salt hydrolysis*, they will form either acidic or alkaline solutions. As such, these salts can be classified as either acidic or basic respectively.

6.1 Salt Hydrolysis

	strong acid *e.g.* $\mathrm{HC}l$	**weak acid** *e.g.* CH_3CO_2H
strong base *e.g.* NaOH	$\mathrm{NaOH} + \mathrm{HC}l \rightarrow \mathbf{NaC}\boldsymbol{l} + \mathrm{H_2O}$	$\mathrm{NaOH} + \mathrm{CH_3CO_2H} \rightarrow \mathbf{CH_3CO_2Na} + \mathrm{H_2O}$
	$OH^- + H^+ \rightarrow H_2O$	$OH^- + CH_3CO_2H \rightarrow CH_3CO_2^- + H_2O$
	$\mathrm{Na^+C}l^-\mathrm{(aq)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{C}l^-\mathrm{(aq)}$	$\mathrm{CH_3CO_2^-Na^+(aq)} \rightarrow \mathrm{Na^+(aq)} + \mathbf{CH_3CO_2^-\ (aq)}$
	Na^+ has a very low charge density, while $\mathrm{C}l^-$ is a very weak conjugate base of the strong acid $\mathrm{HC}l$. Both do not undergo hydrolysis.	$Na^+(aq)$ does not undergo hydrolysis; $CH_3CO_2^-$ being the conjugate base of the weak acid, CH_3CO_2H, undergoes hydrolysis: $CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$
	pH = 7 (neutral)	**pH > 7** (alkaline)
weak base *e.g.* NH_3	$\mathrm{NH_3} + \mathrm{HC}l \rightarrow \mathbf{NH_4C}\boldsymbol{l}$	$\mathrm{NH_3} + \mathrm{CH_3CO_2H} \rightarrow \mathbf{CH_3CO_2NH_4}$
	$NH_3 + H^+ \rightarrow NH_4^+$	$NH_3 + CH_3CO_2H \rightarrow CH_3CO_2^- + NH_4^+$
	$\mathrm{NH_4^+C}l^-\mathrm{(aq)} \rightarrow \mathbf{NH_4^+(aq)} + \mathrm{C}l^-\mathrm{(aq)}$	$\mathrm{CH_3CO_2^-NH_4^+(aq)} \rightarrow \mathbf{NH_4^+(aq)} + \mathbf{CH_3CO_2^-\ (aq)}$
	$\mathrm{C}l^-\mathrm{(aq)}$ does not undergo hydrolysis; NH_4^+ being the conjugate acid of the weak base, NH_3, undergoes hydrolysis: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$	Both $CH_3CO_2^-$ and NH_4^+ undergo hydrolysis: $CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$ $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
	pH < 7 (acidic)	K_a of cation > K_b of anion : pH < 7 (acidic) K_a of cation < K_b of anion : pH > 7 (alkaline) K_a of cation ≈ K_b of anion : pH ≈ 7 (neutral) $K_a(NH_4^+) = 5.6\times10^{-10} \approx K_b(CH_3CO_2^-) = 5.7\times10^{-10}$, the solution is neutral

6.2 Calculating pH of Salt Solutions

Example 6A

Calculate the pH of 0.10 mol dm^{-3} NH_4Cl, given K_a of NH_4^+ = 5.75 × 10^{-10} mol dm^{-3}.

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

	$NH_4^+(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_3(aq)$	+	$H_3O^+(aq)$
initial conc/ mol dm^{-3}	0.10				0		0
change in conc/ mol dm^{-3}	$-x$				$+x$		$+x$
equilibrium conc/ mol dm^{-3}	$0.10-x$				x		x

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

(Note: Do you see that this calculation is similar to Example 5C?)

Consider the salt ammonium chloride, NH_4Cl, wherein the NH_4^+ ion hydrolyses to give an acidic solution:

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

The acid dissociation constant, K_a of the conjugate acid can be derived from the base dissociation constant, K_b of the base it was formed from using K_w (refer to Section 4.4)

i.e. $$\boldsymbol{K_a(NH_4^+) \times K_b(NH_3) = K_w}$$

Similarly, for a basic salt such as sodium ethanoate, wherein the $CH_3CO_2^-$ ion hydrolyses to give a basic solution:

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

the base dissociation constant, K_b of the conjugate base can be derived from the acid dissociation constant, K_a of the acid it was formed from using K_w (refer to Section 4.4)

i.e. $$\boldsymbol{K_b(CH_3CO_2^-) \times K_a(CH_3CO_2H) = K_w}$$

Example 6B

When 25.0 cm^3 of 1 mol dm^{-3} NaOH is added to 25.0 cm^3 of 1 mol dm^{-3} CH_3CO_2H, complete neutralisation occurs. Given that K_a of CH_3CO_2H is 1.8×10^{-5} mol dm^{-3}, calculate the pH of the resultant solution.

	$CH_3CO_2H(aq)$	+	$NaOH(aq)$	$\rightarrow$	$CH_3CO_2^-Na^+(aq)$	+	$H_2O(l)$
amt before mixing/mol	0.025		0.025		0		0
change in amt/mol	–0.025		–0.025		+0.025		+0.025
amt after mixing/mol	0		0		0.025		0.025

The final solution contains only ________________________________.

$[CH_3CO_2Na]$ after mixing =

$CH_3CO_2^-$ is a __________________ of CH_3CO_2H and it hydrolyses in water, forming OH^-.

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

	$CH_3CO_2^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$CH_3CO_2H(aq)$	+	$H_3O^+(aq)$
initial conc/ mol dm^{-3}	0.500				0		0
change in conc/ mol dm^{-3}	$-x$				$+x$		$+x$
equilibrium conc/ mol dm^{-3}	$0.500-x$				x		x

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]}$$

Checkpoint for Section 6

At the end of this section, you should know that:

1. The salt formed from a reaction between a strong acid and a strong base will dissolve in water to give a neutral solution, as neither the cation nor the anion undergoes hydrolysis.
2. The salt formed from a reaction between a strong acid and a weak base will dissolve in water to form an acidic solution, as the cation is a moderately strong conjugate acid that hydrolyses in water.
3. The salt formed from a reaction between a weak acid and a strong base will dissolve in water to form an alkaline solution, as the anion is a moderately strong conjugate base that hydrolyses in water.
4. Both the cation and anion of a salt formed from a reaction between a weak acid and a weak base will hydrolyse in water.

7 Buffer Solutions

LO (i) (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
(j) calculate the pH of buffer solutions, given appropriate data

A buffer solution is a solution which is able to **resist a change in pH** (*i.e.* pH remains **almost** unchanged) when a **small amount** of acid or base is added to it.

In general, there are two types of buffers:

acidic buffer	**basic buffer**
A solution containing a **weak acid** and its **salt** (**conjugate base** of the acid) *e.g.* a mixture of CH_3CO_2H and CH_3CO_2Na	A solution containing **weak base** and its **salt** (**conjugate acid** of the base) *e.g.* a mixture of NH_3 and NH_4Cl
pH < 7	pH > 7

Note: Regardless of whether a buffer is acidic or basic, it contains a conjugate acid-base pair!

A buffer solution must contain a **high concentration** of a **conjugate acid-base pair** for it to function effectively as a buffer.

7.1 Acidic Buffer

Consider a mixture of a weak acid and its salt, CH_3CO_2H and CH_3CO_2Na.

- **CH_3CO_2H** – weak acid
- **CH_3CO_2Na** – basic salt, contains $CH_3CO_2^-$, the conjugate base of the weak acid

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

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq) \quad \text{----------------------------- (1)}$$

On the other hand, sodium ethanoate is **fully dissociated**:

$$CH_3CO_2^-Na^+(aq) \rightarrow CH_3CO_2^-(aq) + Na^+(aq) \quad \text{----------------------------- (2)}$$

According to **Le Châtelier's principle**, the presence of **$CH_3CO_2^-$ ions** from the complete dissociation of sodium ethanoate **suppresses the dissociation of ethanoic acid** in (1).

Hence the buffer solution contains a **relatively high concentration of the undissociated ethanoic acid** (a weak acid) **and the ethanoate ions** (the conjugate base of the weak acid). These relatively high concentrations of both the ethanoic acid and ethanoate ions enable the solution to function as a buffer solution.

On adding a small amount of H_3O^+ or H^+, the large amount of $CH_3CO_2^-$ ions present removes the added H_3O^+ or H^+ ions. Thus, $[H_3O^+]$ or $[H^+]$ in the aqueous system does not change much and the pH remains **almost unchanged**.

$$H_3O^+(aq) + CH_3CO_2^-(aq) \rightarrow CH_3CO_2H(aq) + H_2O(l)$$

or $$H^+(aq) + CH_3CO_2^-(aq) \rightarrow CH_3CO_2H(aq)$$

On adding a small amount of OH^-, the large amount of CH_3CO_2H present removes the added OH^- ions. Thus, $[OH^-]$ in the aqueous system does not change much and the pH remains **almost unchanged**.

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

Note:
The ***removal* of H_3O^+/H^+ and OH^-** is illustrated using a **single arrow** '→' rather than an equilibrium arrow '$\rightleftharpoons$' to signify the essentially ***complete* removal** of the small amount of acid or base added.

7.2 Basic Buffer

Consider a mixture of a weak base and its salt, NH_3 and NH_4Cl.

- **NH_3** – weak base
- **NH_4Cl** – acidic, contains NH_4^+, the conjugate acid of the weak base

In this solution, aqueous ammonia being a weak base, is only **partially dissociated**:

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

On the other hand, ammonium chloride is **fully dissociated**:

$$NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq) \quad \text{----------------------------- (2)}$$

According to **Le Châtelier's principle**, the presence of **NH_4^+ ions** from the complete dissociation of ammonium chloride **suppresses the ionisation of aqueous ammonia** in (1).

Hence, the buffer solution contains a **relatively high concentration of aqueous ammonia** (a weak base) **and the ammonium ions** (the conjugate acid of the weak base). These relatively high concentrations of both aqueous ammonia and ammonium ion enable the solution to function as a buffer.

On adding a small amount of H_3O^+, the large amount of NH_3 present removes the added H_3O^+ ions. Thus, $[H_3O^+]$ in the aqueous system does not change much and the pH remains **almost unchanged**.

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

On adding a small amount of OH^-, the large amount of NH_4^+ ions present removes the added OH^- ions. Thus, $[OH^-]$ in the aqueous system does not change much and the pH remains **almost unchanged**.

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

7.3 pH of a Buffer (not in H1 syllabus)

Consider an acidic buffer containing an acid, HA, and its conjugate base, A^-,

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

$$NaA(aq) \rightarrow Na^+(aq) + A^-(aq)$$

HA, being a weak acid, undergoes slight dissociation in aqueous solution. Its dissociation is suppressed by the high concentration of A^- ions from the complete dissociation of the salt, NaA. This is in accordance with Le Châtelier's Principle.

Hence, $\mathbf{[HA]_{eqm} = [HA]_{initial} - [A^-]_{from\ HA}}$

$\mathbf{\approx [HA]_{initial}}$

$\mathbf{[A^-]_{eqm} = [A^-]_{from\ NaA} + [A^-]_{from\ HA}}$

$\mathbf{\approx [A^-]_{from\ NaA}}$

Hence for an acidic buffer solution,

Note:
Unlike weak acids, $[H_3O^+] \neq [A^-]$ for buffers.

$$K_a(HA) = \frac{[H_3O^+][A^-]_{from\ NaA}}{[HA]_{initial}}$$

$$[H_3O^+] = K_a(HA)\frac{[HA]_{initial}}{[A^-]_{from\ NaA}}$$

$$-\lg[H_3O^+] = -\lg K_a(HA) - \lg\frac{[HA]_{initial}}{[A^-]_{from\ NaA}}$$

$$pH = pK_a(HA) + \lg\frac{[A^-]_{from\ NaA}}{[HA]_{initial}}$$

Consider a basic buffer containing a base, B, and its conjugate acid, BH^+,

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

$$BHCl(aq) \rightarrow BH^+(aq) + Cl^-(aq)$$

B, being a weak base, undergoes slight dissociation in aqueous solution. Its dissociation is suppressed by the high concentration of BH^+ ions from the complete dissociation of the salt, $BHCl$. This is in accordance with Le Châtelier's Principle.

Hence, $\mathbf{[B]_{eqm} = [B]_{initial} - [BH^+]_{from\ B}}$

$\mathbf{\approx [B]_{initial}}$

$\mathbf{[BH^+]_{eqm} = [BH^+]_{from\ BHCl} + [BH^+]_{from\ B}}$

$\mathbf{\approx [BH^+]_{from\ BHCl}}$

Considering dissociation of the conjugate acid, BH^+, of the weak base, B:

$$BH^+(aq) + H_2O(l) \rightleftharpoons B(aq) + H_3O^+(aq) \qquad K_a(BH^+) = \frac{K_w}{K_b(B)}$$

Hence for a basic buffer solution,

Note:
Unlike weak acid, $[H_3O^+] \neq [B]$ for buffer

$$K_a\left(BH^+\right) = \frac{\left[H_3O^+\right][B]_{\text{initial}}}{\left[BH^+\right]_{\text{from BHC}l}}$$

$$\left[H_3O^+\right] = K_a\left(BH^+\right)\frac{\left[BH^+\right]_{\text{from BHC}l}}{[B]_{\text{initial}}}$$

$$-\lg\left[H_3O^+\right] = -\lg K_a\left(BH^+\right) - \lg\frac{\left[BH^+\right]_{\text{from BHC}l}}{[B]_{\text{initial}}}$$

$$\text{pH} = \text{p}K_a\left(BH^+\right) + \lg\frac{[B]_{\text{initial}}}{\left[BH^+\right]_{\text{from BHC}l}}$$

Henderson-Hasselbalch equation for buffers:

$$\text{pH} = \text{p}K_a(\text{HA}) + \lg\frac{\left[A^-\right]_{\text{from NaA}}}{[\text{HA}]_{\text{initial}}} = \text{p}K_a\left(BH^+\right) + \lg\frac{[B]_{\text{initial}}}{\left[BH^+\right]_{\text{from BHC}l}} \quad \text{or}$$

$$\boxed{\mathbf{pH = pK_a + \lg\frac{[(conjugate)\ \ base]}{[(conjugate)\ \ acid]}}}$$

7.4 Buffering Capacity

Buffering capacity refers to the amount of acid or base that may be added to a buffer solution before its pH changes appreciably. It represents the ability of a buffer to resist changes in pH.

For a buffer to be effective, $0.1 \leq \frac{[(\text{conjugate})\ \text{base}]}{[(\text{conjugate})\ \text{acid}]} \leq 10$

Hence, $\text{p}K_a + \lg 0.1$ to $\text{p}K_a + \lg 10$

i.e. $\text{p}K_a - 1$ to $\text{p}K_a + 1$

The **effective buffer range** of a buffer is about one pH unit on either side of the pK_a value *i.e.* **pK_a ± 1**. Beyond this range, the pH of the solution changes appreciably upon the addition of small amounts of acid or base.

A buffer solution is **most effective** in resisting changes in pH when:

1. The amount of both the weak acid (or base) and its conjugate base (or acid) are **large** relative to that of the acid or base to be added to the buffer solution.
2. The ratio of the concentrations of the conjugate acid and its conjugate base is close to **1 : 1**.

When the ratio of the concentrations of the acid and its conjugate base is 1 : 1,

$$\begin{aligned}\text{pH} &= \text{p}K_a + \lg\frac{[(\text{conjugate})\ \text{base}]}{[(\text{conjugate})\ \text{acid}]}\\ &= \text{p}K_a + \lg 1\\ &= \text{p}K_a\end{aligned}$$

Hence we usually try to select a **buffer** whose acid form has a **pK_a close to the desired pH** to ensure effectiveness.

Example 7A

Phosphoric acid is a tribasic acid.

$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$ $\qquad pK_{a1} = 2.15$

$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$ $\qquad pK_{a2} = 7.20$

$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$ $\qquad pK_{a3} = 12.35$

Suggest how a buffer at pH 6.80 can be prepared from 1.00 mol dm^{-3} NaOH and 1 dm^3 of 1.00 mol dm^{-3} H_3PO_4.

The effective buffer range is approximately **$\underline{pK_a \pm 1}$**. Hence for a buffer at pH 6.80, we will choose the ____________________ conjugate acid-base pair as ______________________________.

$$\text{pH} = \text{p}K_a + \lg\frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$6.80 = 7.20 + \lg\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 10^{-0.40} = 0.3981$$

$$n_{HPO_4^{2-}} = 0.3981 n_{H_2PO_4^-}$$

Both HPO_4^{2-} and $H_2PO_4^-$ are obtained by reacting H_3PO_4 with an appropriate amount of NaOH:

$H_3PO_4(aq) + NaOH(aq) \rightarrow NaH_2PO_4(aq) + H_2O(l)$

$H_3PO_4(aq) + 2NaOH(aq) \rightarrow Na_2HPO_4(aq) + 2H_2O(l)$

$$\begin{aligned} n_{HPO_4^{2-}} + n_{H_2PO_4^-} &= n_{H_3PO_4} = 1.00 \text{ mol} \\ 0.3981 n_{H_2PO_4^-} + n_{H_2PO_4^-} &= 1.00 \\ n_{H_2PO_4^-} &= 0.7153 \text{ mol} \\ \text{so, } n_{HPO_4^{2-}} &= 0.2847 \text{ mol} \end{aligned}$$

$$\begin{aligned} n_{NaOH} \text{ required} &= 2n_{HPO_4^{2-}} + n_{H_2PO_4^-} \\ &= 2 \times 0.2847 + 0.7153 \\ &= 1.285 \text{ mol} \end{aligned}$$

Hence, a buffer at pH 6.80 can be obtained by adding __________ of 1.00 mol dm^{-3} NaOH to ____________ of 1.00 mol dm^{-3} H_3PO_4.

7.5 Uses of Buffers

Buffer solutions are used in situations in which it is necessary to maintain a constant pH.
A few examples are given below:

1) Buffers are used widely to control chemical processes including electroplating, manufacture of dyes, photographic materials and leather.
2) Chemists use buffers in analysis e.g. in calibration of pH meters.
3) Analytical biochemists use buffers to determine the number and type of amino acids present in proteins by electrophoresis, a technique which involves the migration of charged particles in solution through an electric field.
4) Many biological systems in which a change in pH can have a great effect on the functioning of a cell are buffered. For example, all intravenous injections and eye drops are buffered as human blood and tears have specific pH.
5) In bacteriological research, a buffer solution is used to maintain the pH of culture media used for the growth of bacteria.
6) In agriculture, buffers are used to maintain the pH of soils for growth of certain plants *e.g.* azalea, rhododendron – pH 4

<u>Blood Buffer System</u>

The pH of human blood must be maintained within a narrow range of 7.35 – 7.45. It is important for the pH of blood to be kept constant so that enzymes in the blood which only work within a small pH range can function properly.

In a healthy person, the pH of blood never deviates more than approximately 0.2 pH unit from the average value. If the pH of blood falls below 6.8 or rises above 7.8, death may result.

The buffer in blood mainly consists of proteins, a mixture of phosphates ($HPO_4^{2-}/H_2PO_4^-$) and a mixture carbonates (HCO_3^-/H_2CO_3).

1) The proteins are made up of amino acids containing acidic and basic side chains, which act as buffers (*e.g.* lysine, arginine, aspartic acid)

2) CO_2 produced as the by-product of metabolic reactions in the body, dissolves to form carbonic acid which dissociates partially to give hydrogen carbonate (or bicarbonate) ion, HCO_3^-.

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

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

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

If the concentration of H_3O^+ increases (*e.g.* from lactic acid which is produced during exercise), HCO_3^- present reacts with and removes the additional H_3O^+ ions to resist changes in pH.

$$H_3O^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq)$$

When $[OH^-]$ increases, H_2CO_3 present reacts with and removes the additional OH^- ions to resist changes in pH.

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

Hydrogen carbonate buffer is constantly replenished in the body through the dissolved carbon dioxide produced during normal metabolism.

3) Phosphate ($HPO_4^{2-}/H_2PO_4^-$) buffer in blood

$$\underset{\text{acid}}{H_2PO_4^-(aq)} + H_2O(l) \rightleftharpoons \underset{\text{conjugate base}}{HPO_4^{2-}(aq)} + H_3O^+(aq) \qquad K_a = 6.2 \times 10^{-8}\ \text{mol dm}^{-3}$$

With excess H_3O^+: $HPO_4^{2-} + H_3O^+ \rightarrow H_2PO_4^- + H_2O$

With excess OH^-: $H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

Think about this…

From the Henderson- Hasselbalch equation

$$\text{pH} = \text{p}K_a + \lg\frac{[(\text{conjugate})\ \text{base}]}{[(\text{conjugate})\ \text{acid}]}$$

if we add water to a buffer, the ratio $\frac{[(\text{conjugate})\ \text{base}]}{[(\text{conjugate})\ \text{acid}]}$ remains the same since both the conjugate acid-base pair are diluted to the same extent. Hence we would expect the pH of the buffer to remains the same.

However, common sense also tells us that if we add enough water to any solution to dilute it sufficiently, it becomes essentially “pure” water, with a pH of 7!

What is wrong with the logic here?

Checkpoint for Section 7

At the end of this section, you should know that:

1. An acidic buffer contains a weak acid and its salt (conjugate base).
2. A basic buffer contains a weak base and its salt (conjugate acid).
3. A buffer must contain a large concentration of a conjugate acid-base pair to function effectively.
4. When a small amount of acid or base is added to a buffer, it will be neutralised by the basic component or acidic component of the buffer, respectively.
5. When a small amount of acid or base is added to a buffer, the pH of the buffer remains almost unchanged.
6. The pH of a buffer can be calculated by the formula $\text{pH} = \text{p}K_\text{a} + \lg\dfrac{[(\text{conjugate})\ \text{base}]}{[(\text{conjugate})\ \text{acid}]}$.
7. The effective buffer range of any buffer is $\text{p}K_\text{a} \pm 1$.
8. A buffer solution is most effective when [(conjugate) acid] = [(conjugate) base], and the amount of conjugate acid-base pair is large as compared to the amount of acid or base added

8 Indicators

An indicator is a substance that changes colour in response to pH changes of the solution it is added to. Most indicators are usually weak acids or bases, which change colour depending on the pH of the solution. Different colours will be exhibited by their dissociated and un-dissociated forms. Indicators are used to detect the end-point in acid-base titrations.

Let the formula of the undissociated indicator be HIn.
At equilibrium,

$$\underset{\substack{\text{weak acid}\\\text{(colour A)}}}{HIn(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \underset{\substack{\text{conjugate base}\\\text{(colour B)}}}{In^-(aq)}$$

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

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]} \qquad pH = pK_{In} + \lg\frac{[In^-]}{[HIn]}$$

At different pH, the proportion of HIn to In^- is different, giving rise to different colours.
At **low pH**, $[H_3O^+]$ is high, the equilibrium position shifts to the **left**. Hence, there is a larger proportion of **HIn** and **colour A** is observed.
At **high pH**, $[H_3O^+]$ is low (as large amounts of H_3O^+ is consumed during the titration), the equilibrium position shifts to the **right**. Hence there is a larger proportion of **In^-** and **colour B** is observed.

For the 2 colours to be distinguishable by the human eye, one form must be about **10 times more concentrated** than the other form, *i.e.* in the ratio of 1 : 10.

i.e. 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 changed observed is a combination of A and B $\Rightarrow$ pH = pK_{In}

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

Choice of indicator

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**.

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

indicator	**colour**		pK_{In}	**pH range/ working range**
	HIn (acidic)	**In⁻ (alkaline)**		
thymol blue^	red	yellow	1.6	1.2 – 2.8
methyl orange	red	yellow	3.4	3.1 – 4.4
screened methyl orange*	violet	green	3.4	3.1 – 4.4
methyl red	red	yellow	5.1	4.2 – 6.3
litmus	red	blue	6.5	6.0 – 8.0
thymol blue^	yellow	blue	8.9	8.0 – 9.6
phenolphthalein	colourless	pink	9.3	8.2 – 10.0
thymolphthalein	colourless	blue	9.9	9.3 – 10.5

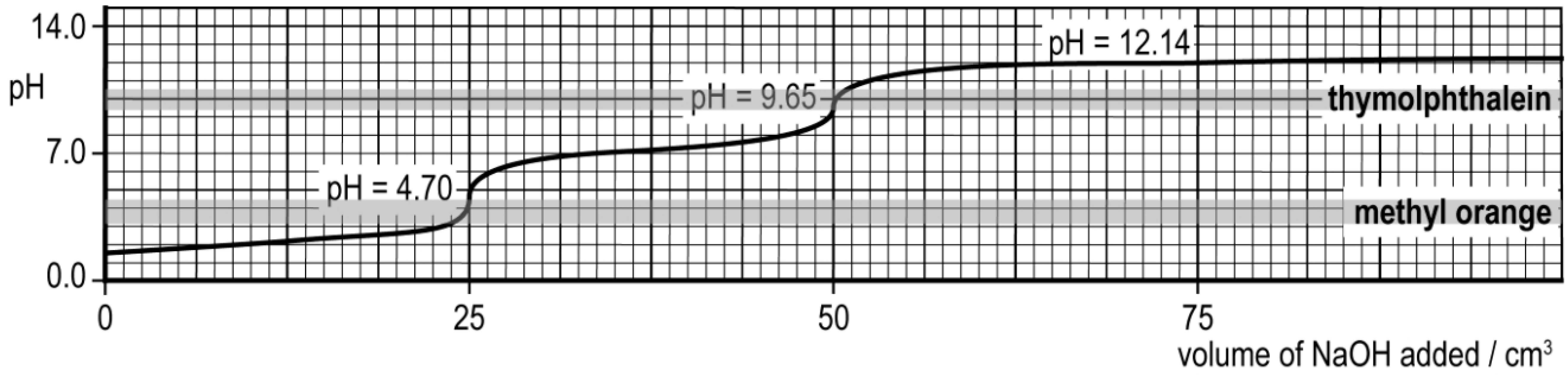
^ Thymol blue is a dibasic acid and there are three forms: H_2In (red), HIn^- (yellow) and In^{2-} (blue).

* Screened methyl orange is a mixture of methyl orange and an inert blue dye, xylene cyanole FF, to make the end-point more prominent.

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**.
- **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**. Hence, the end-point of titration depends on the indicator being used.



For example, in the titration of 25.0 cm³ of 0.100 mol dm⁻³ H_3PO_4 against 0.100 mol dm⁻³ NaOH shown above, thymolphthalein is a good indicator for the second end-point, but methyl orange is not a good indicator for the first end-point. There is no suitable indicator for the third end-point.

9 Titration Curves

LO (g) describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases
(h) explain the choice of suitable indicators for acid-base titrations, given appropriate data

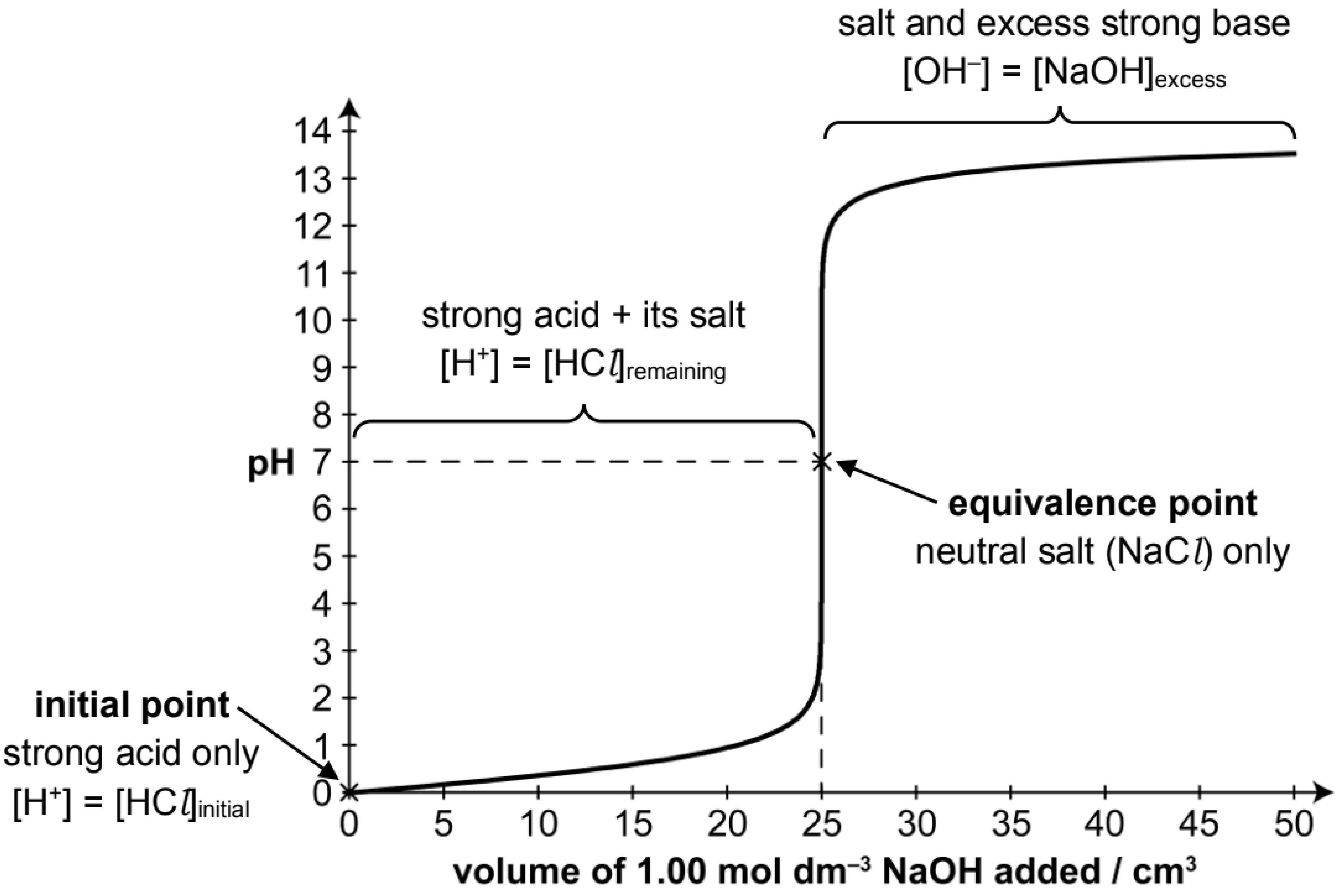
A titration curve is a graph of pH against volume of an acid or base. It shows how the pH of the solution in the conical flask changes with the volume of solution added from the burette (the titre) during a titration. This change in pH during a titration depends largely upon the strength of the acid and base used. The graphs can be obtained by monitoring the pH of a titration using a pH meter. There are 4 types of acid-base titration and the indicator suitable for each type of titration is shown below.

type of titration	range of rapid pH change	examples of suitable indicator
strong acid – strong base	3 – 11	screened methyl orange, methyl orange, thymolphthalein or phenolphthalein
strong acid – weak base	3 – 7	screened methyl orange or methyl orange
weak acid – strong base	7 – 11	thymolphthalein or phenolphthalein
weak acid – weak base	nil	no suitable indicator

9.1 Strong Acid – Strong Base Titration

Consider a titration of a strong acid, 25.0 cm^3 of 1.00 mol dm^{-3} HCl, with a strong base, 1.00 mol dm^{-3} NaOH.

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



(a) Before titration (at initial point)

- At the initial point, the solution contains only **strong acid**. The pH of the solution is caused by the strong acid present.

$[H^+] = [HCl] = 1.00$ mol dm^{-3}

pH = $-\lg(1.00)$ = **<u>0.00</u>**

(b) When acid is partially neutralised (after initial, before equivalence point)

- pH gradually increases as the acid is gradually neutralised by the added base.
- In this region, the mixture consists of the remaining **strong acid** and the **salt** formed from neutralisation. The pH of the mixture is caused by the remaining strong acid present, as the salt formed is neutral.

<u>When 10.00 cm^3 of 1.00 mol dm^{-3} NaOH is added to 25.0 cm^3 of 1.00 mol dm^{-3} HCl,</u>

	$HCl(aq)$	+	$NaOH(aq)$	→	$NaCl(aq)$	+	$H_2O(l)$
initial amt/mol	$0.025 \times 1 = 0.025$		$0.01 \times 1 = 0.01$		0		
change in amt/mol	-0.01		-0.01		$+0.01$		
final amt/mol	0.015		0		0.01		
final conc/mol dm^{-3}	$0.015 \div \frac{35}{1000}$		0		$0.01 \div \frac{35}{1000}$		

$[H^+] = [HCl] = 0.015 \div \frac{35}{1000} = 0.429$ mol dm^{-3}

pH = $-\lg(0.0429)$ = **<u>0.37</u>**

<u>When 24.90 cm^3 of 1.00 mol dm^{-3} NaOH is added to 25.0 cm^3 of 1.00 mol dm^{-3} HCl,</u>

	$HCl(aq)$	+	$NaOH(aq)$	→	$NaCl(aq)$	+	$H_2O(l)$
initial amt/mol	$0.025 \times 1 = 0.025$		$0.0249 \times 1 = 0.0249$		0		
change in amt/mol	-0.0249		-0.0249		$+0.0249$		
final amt/mol	10^{-4}		0		0.0249		
final conc/mol dm^{-3}	$10^{-4} \div \frac{49.90}{1000}$		0		$0.0249 \div \frac{49.90}{1000}$		

$[H^+] = [HCl] = 10^{-4} \div \frac{49.90}{1000} = 2.00 \times 10^{-3}$ mol dm^{-3}

pH = $-\lg(2.00 \times 10^{-3})$ = **<u>2.70</u>**

(c) At equivalence point

- This is the **region of rapid pH change**. A single drop of alkali to either side of the equivalence point produces a large pH change. The region of rapid pH change generally lies between 3 and 11.
- The equivalence point occurs when the amount of alkali added **just neutralises** the amount of acid present.
- At this point, the mixture contains only the **salt** and **water** formed. Since the salt formed is **neutral**, the pH at this point is expected to be **<u>7</u>**.

(d) When excess base is added (after equivalence point)

- From now on, the base added has nothing to react with, so the pH rises towards a final value of 14.
- When excess base is added, the mixture contains excess **strong base** and the **salt** formed. The pH of the mixture is due to the strong base since the salt formed is neutral.

<u>When 25.10 cm^3 of 1.00 mol dm^{-3} NaOH have been added to 25 cm^3 of 1.00 mol dm^{-3} HCl,</u>

	$HCl(aq)$	+	$NaOH(aq)$	→	$NaCl(aq)$	+	$H_2O(l)$
initial amt/mol	$0.025\times1 = 0.025$		$0.0251\times1 = 0.0251$		0		
change in amt/mol	-0.025		-0.025		$+0.025$		
final amt/mol	0		10^{-4}		0.025		
final conc/mol dm^{-3}	0		$10^{-4}\div\dfrac{50.10}{1000}$		$0.025\div\dfrac{50.10}{1000}$		

$[OH^-] = [NaOH] = 10^{-4}\div\dfrac{50.10}{1000} = 2.00\times10^{-3}$ mol dm^{-3}

pOH = $-\lg(2.00\times10^{-3}) = 2.7$

pH = 14 – 2.70 = <u>**11.3**</u>

The pH changes rapidly near the equivalence point (from 2.70 at 24.90 cm^3 of base to 11.3 at 25.10 cm^3 of base in this case).

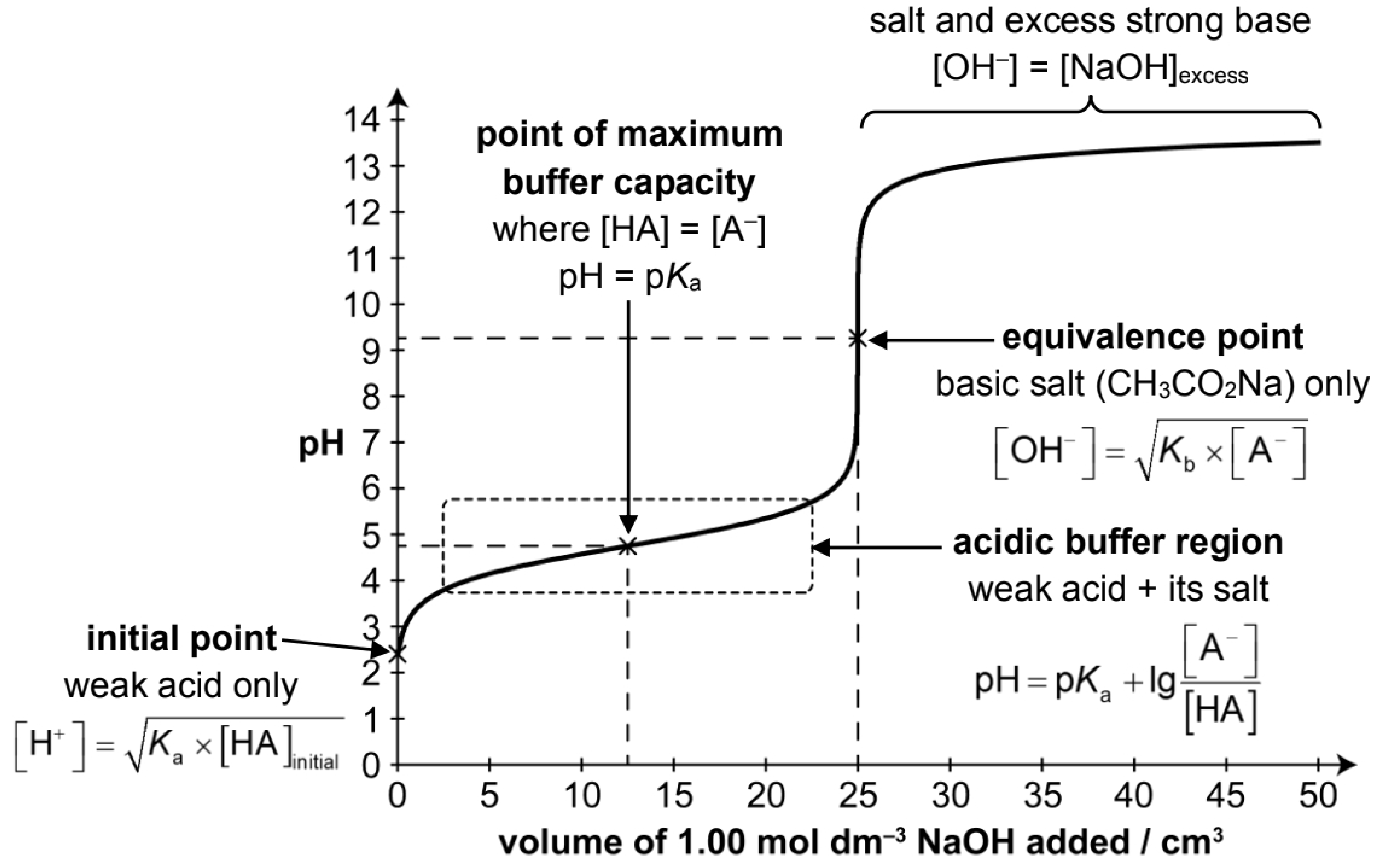
***<u>Suitable Indicators</u>*:**

Suitable indicators for a strong acid-strong base titration: **methyl orange/screened methyl orange and thymolphthalein/phenolphthalein**.

9.2 Weak Acid – Strong Base Titration

Consider a titration of a weak acid, 25.0 cm^3 of 1.00 mol dm^{-3} CH_3CO_2H (K_a = 1.74 × 10^{-5} mol dm^{-3}), with a strong base, 1.00 mol dm^{-3} NaOH.

$$CH_3CO_2H(aq) + NaOH(aq) \rightarrow CH_3CO_2Na(aq) + H_2O(l)$$



(a) Before titration (at initial point)

- At the initial point, the solution contains only weak acid. The pH of the solution is caused by the weak acid present.

$\left[H^+\right] = \sqrt{K_a \times [HA]_{initial}}$ = 4.17 × 10^{-3} mol dm^{-3}

pH = –lg(4.17 × 10^{-3}) = **2.38**

(b) When acid is partially neutralised (after initial, before equivalence point)

- pH gradually increases as the weak acid is being neutralised by added base.
- In this region, the mixture consists of the remaining **weak acid** and the **conjugate base** formed from neutralisation, forming an **acidic buffer**.

When 10.00 cm^3 of 1.00 mol dm^{-3} NaOH is added to 25.0 cm^3 of 1.00 mol dm^{-3} CH_3CO_2H,

	$CH_3CO_2H(aq)$	+	$NaOH(aq)$	$\rightarrow$	$CH_3CO_2Na(aq)$ + $H_2O(l)$
initial amt/mol	0.025×1 = 0.025		0.010×1 = 0.01		0
change in amt/mol	–0.01		–0.01		+0.01
final amt/mol	0.015		0		0.01
final conc/mol dm^{-3}	$0.015 \div \frac{35}{1000}$		0		$0.01 \div \frac{35}{1000}$

Solution is an **acidic buffer** as a weak acid, CH_3COOH and its conjugate base, CH_3COONa salt is present.

$$\mathrm{pH} = \mathrm{p}K_a + \lg\frac{[\text{conjugate base}]}{[\text{acid}]} = -\lg(1.74\times10^{-5}) + \lg\frac{0.01\div\frac{35}{1000}}{0.015\div\frac{35}{1000}}$$

$$= \underline{\mathbf{4.58}}$$

<u>When 12.50 cm³ of 1.00 mol dm⁻³ NaOH is added to 25.0 cm³ of 1.00 mol dm⁻³ CH_3CO_2H,</u>
<u>Half-equivalence point:</u> where half of the acid present in the reaction mixture is neutralised

i.e. volume at half-equivalence point = $\frac{\mathbf{1}}{\mathbf{2}}\times$ **volume at equivalence point**

At this point,

- [weak acid] = [conjugate base]
- **Buffer is at its maximum buffer capacity**
- **pH = pK_a** (because pH = pK_a + lg 1, and lg 1 = 0)

pH = pK_a = **<u>4.76</u>**

(c) At equivalence point

- The pH at equivalence point is **> 7** due to the hydrolysis of CH_3CO_2Na salt.

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

$$[CH_3CO_2^-] = 0.025 \div 0.05 = 0.5 \text{ mol dm}^{-3}$$

$$K_b(CH_3CO_2^-) = \frac{K_w}{K_a(CH_3CO_2H)} = 5.75\times10^{-10} \text{ mol dm}^{-3}$$

$$[OH^-] = \sqrt{K_b[CH_3CO_2^-]} = \sqrt{5.75\times10^{-10}\times0.5}$$

$$= 1.70\times10^{-5} \text{ mol dm}^{-3}$$

pOH = $-\lg(1.70\times10^{-5})$ = 4.77

pH = 14 – 4.77 = **<u>9.23</u>**

(d) When excess base is added (after equivalence point)

- From now on, the base added has nothing to react with, so the pH rises towards a final value of 14 (*i.e.* the pH of 0.1 mol dm⁻³ NaOH).
- When excess base is added, the mixture contains excess strong base and the salt formed. The pH of the mixture is due to the strong alkali since the $[OH^-]_{salt}$ produced from the hydrolysis of the salt is much smaller than the excess $[OH^-]_{base}$ added.

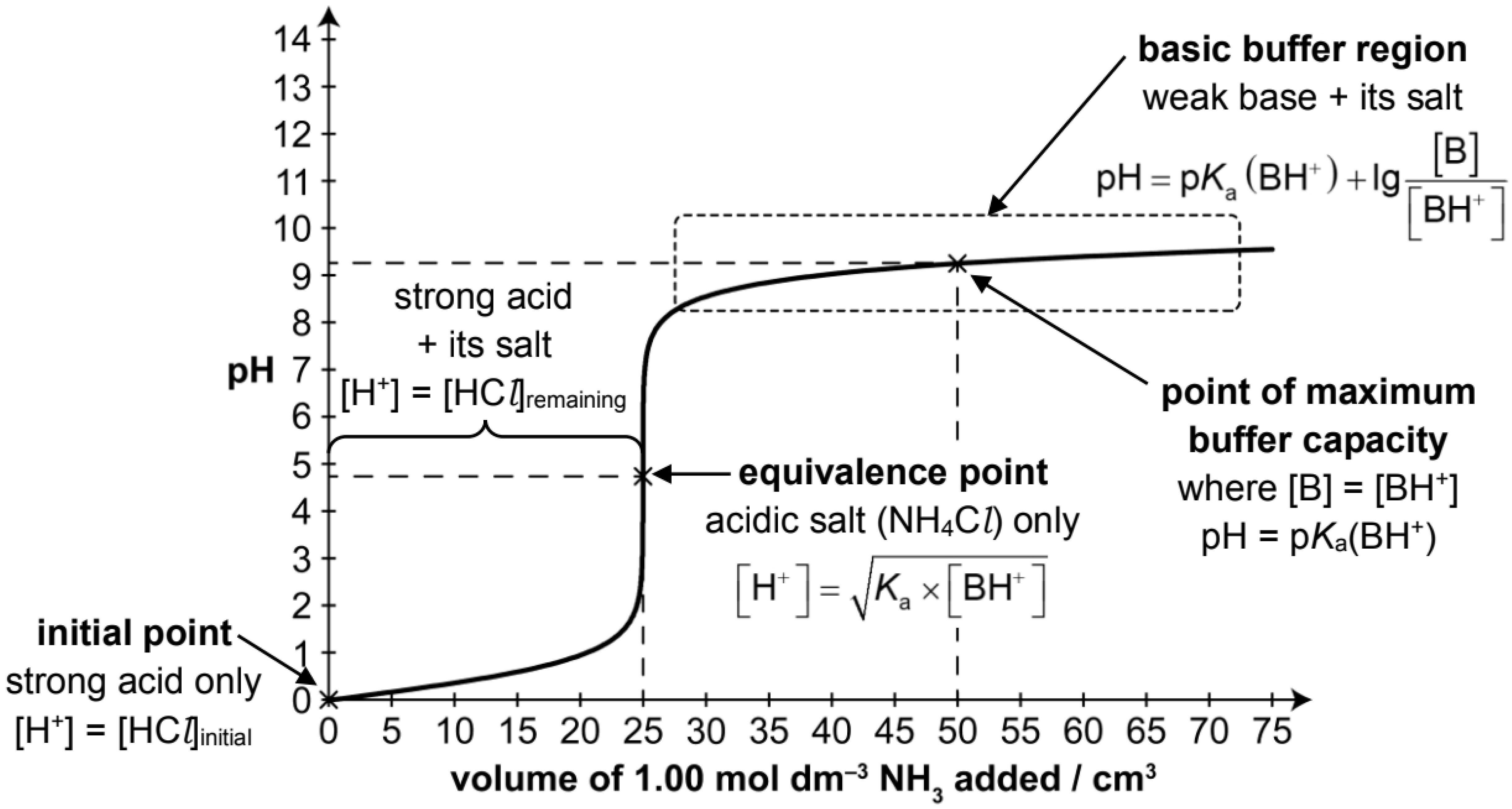
***<u>Suitable Indicators</u>*:**

- The region of rapid pH change lies between <u>7 and 11</u>.
- Any indicator which changes colour over the range of pH 7 to 11 can be used to gauge the equivalence point.
- Suitable indicators: **thymolphthalein/phenolphthalein**.

9.3 Strong Acid – Weak Base Titration

Consider a titration of a strong acid, 25.0 cm^3 of 1.00 mol dm^{-3} HC*l*, with a weak base, 1.00 mol dm^{-3} NH$_3$ (K_b = 1.77 × 10^{-5} mol dm^{-3}).

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



(a) Before titration (at initial point)

- Only strong acid present
- [H$^+$] contributed by the strong acid
- pH caused by strong acid present

(b) When acid is partially neutralised (after initial, before equivalence point)

- pH gradually increases.
- Acid is being neutralised by added base.
- Mixture contains remaining strong acid and the conjugate acid formed (NH_4^+) from the neutralisation.
- [H$^+$] contributed by the conjugate acid is much smaller than [H$^+$] contributed by the strong acid.
- pH of mixture caused by remaining strong acid.

(c) At equivalence point

- The pH at equivalence point is **< 7** due to the hydrolysis of NH$_4$C*l*.

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

$$[NH_4^+] = 0.025 \div 0.05 = 0.5 \text{ mol dm}^{-3}$$

$$K_a(NH_4^+) = \frac{K_w}{K_b(NH_3)} = 5.00 \times 10^{-10} \text{ mol dm}^{-3}$$

$$[H^+] = \sqrt{K_a[NH_4^+]} = \sqrt{5.00 \times 10^{-10} \times 0.5}$$

$$= 1.58 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pH = \underline{\mathbf{4.80}}$$

(d) When excess base is added (after equivalence point)

- pH gradually increases but resists pH change near maximum buffer capacity.
- In this region, the mixture consists of the additional **weak base** and the **conjugate acid** formed from neutralisation, forming a **basic buffer**.

When 50.00 cm^3 of 1.00 mol dm^{-3} NH_3 is added to 25.0 cm^3 of 1.00 mol dm^{-3} HCl,

- **Maximum buffer capacity** occurs when **[weak base] = [conjugate acid]**
- **pH = pK_a** (where K_a is for NH_4^+)
- This point occurs at **2*V* cm^3** where *V* cm^3 is the volume of base required to neutralise the acid completely. 1 *V* = amount of base needed for neutralisation and 1 *V* = amount of base added equal to the amount of salt present.

	$HCl(aq)$	+	$NH_3(aq)$	$\rightarrow$	$NH_4Cl(aq)$
initial amt/mol	0.025×1 = 0.025		0.050×1 = 0.050		0
change in amt/mol	–0.025		–0.025		+0.025
final amt/mol	0		0.025		0.025

$\text{pH} = \text{p}K_a(NH_4^+)$ OR $\text{pOH} = \text{p}K_b(NH_3) = 4.70$

$= -\lg(5.00 \times 10^{-10}) = \underline{\mathbf{9.30}}$ $\text{pH} = 14 - 4.70 = \underline{\mathbf{9.30}}$

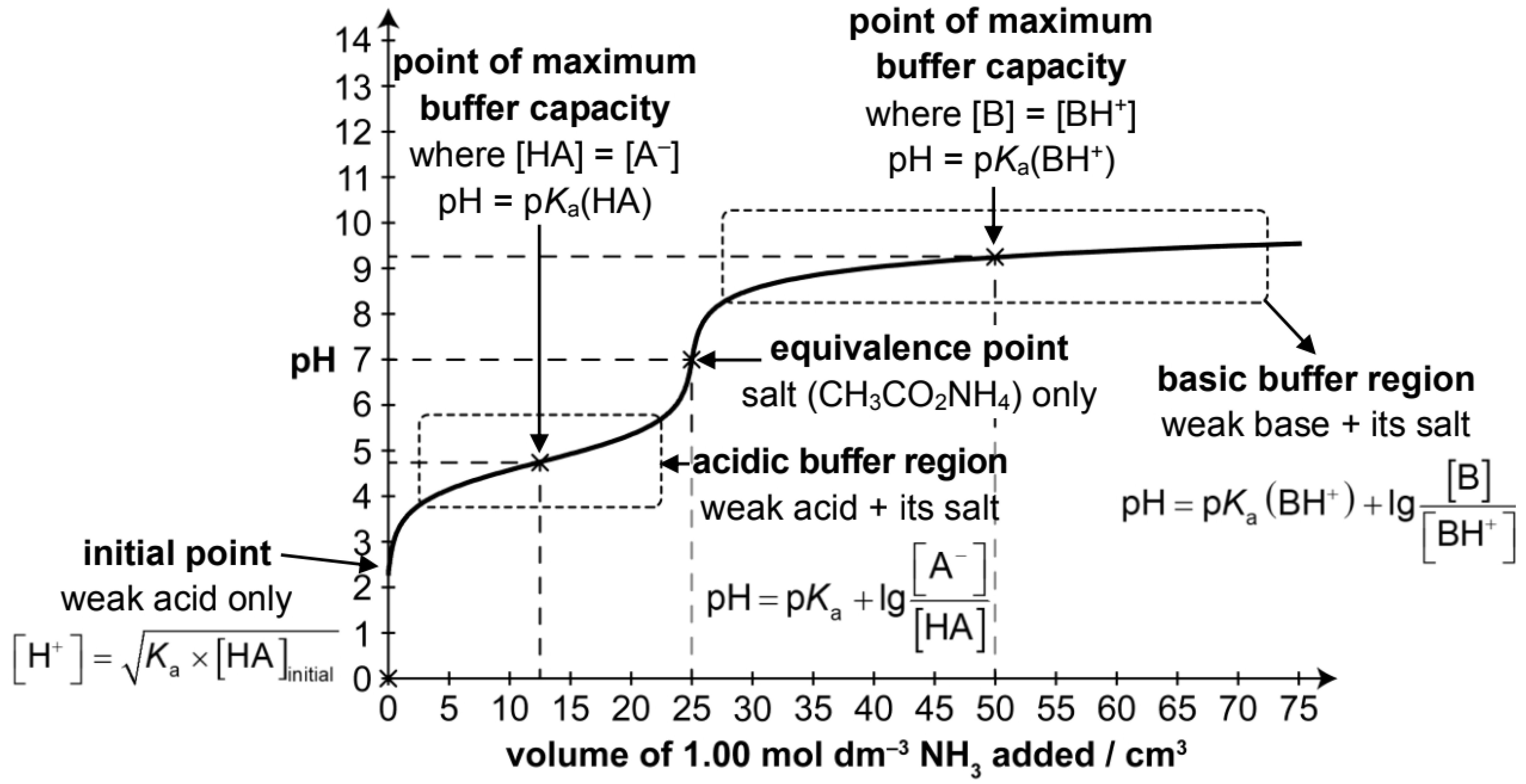
***<u>Suitable Indicators</u>*:**

- The region of rapid pH change generally lies between <u>3 and 7</u>.
- Any indicator which changes colour over the range of pH 3 to 7 can be used to gauge the equivalence point.
- Suitable indicators: **methyl orange/screened methyl orange**.

9.4 Weak Acid – Weak Base Titration (not required to know)

Consider a titration of 25.0 cm^3 of a weak acid, 1.00 mol dm^{-3} CH_3CO_2H (K_a = 1.74 × 10^{-5} mol dm^{-3}) with weak base, 1.00 mol dm^{-3} NH_3 (K_b = 1.77 × 10^{-5} mol dm^{-3}).

$$CH_3CO_2H(aq) + NH_3(aq) \rightarrow CH_3CO_2NH_4(aq)$$



(a) Before titration (at initial point)

- At the initial point, the solution contains only weak acid. The pH of the solution is caused by the weak acid present.

$[\text{H}^+] = \sqrt{K_a \times [\text{HA}]_{\text{initial}}}$ = 4.17 × 10^{-3} mol dm^{-3}

pH = –lg(4.17 × 10^{-3}) = <u>**2.38**</u>

(b) When acid is partially neutralised (after initial, before equivalence point)

- pH gradually increases as the weak acid is being neutralised by added weak base.
- In this region, the mixture consists of the remaining **weak acid** (CH_3CO_2) and the **conjugate base** ($CH_3CO_2^-$) formed from neutralisation, forming an **acidic buffer**.
- The conjugate acid of the weak base, NH_4^+, does not contribute significant to the [H$^+$] as it is a much weaker acid than CH_3CO_2H. $K_a(\text{NH}_4^+) = \frac{K_w}{K_b(\text{NH}_3)} = 5.65 \times 10^{-10}$ mol dm^{-3} .

<u>When 12.50 cm^3 of 1.00 mol dm^{-3} NH_3 is added to 25.0 cm^3 of 1.00 mol dm^{-3} CH_3CO_2H,</u>
<u>**Half-equivalence point:**</u> where half of the acid present in the reaction mixture is neutralised

i.e. volume at half-equivalence point = $\frac{1}{2}$ × **volume at equivalence point**

At this point,

- [weak acid] = [conjugate base]
- **Buffer is at its maximum buffer capacity**
- **pH = pK_a = <u>4.76</u>** (because pH = pK_a + lg 1, and lg 1 = 0)

(c) At equivalence point

- The equivalence point occurs when 25.00 cm^3 of aqueous ammonia is added.
- The pH at equivalence point is 7 as both ammonium and ethanoate ions hydrolyse to the same extent (K_a of NH_4^+ $\approx$ K_b of $CH_3CO_2^-$).

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad K_a(NH_4^+) = 5.65 \times 10^{-10} \text{ mol dm}^{-3}$$

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) \qquad K_b(CH_3CO_2^-) = 5.75 \times 10^{-10} \text{ mol dm}^{-3}$$

(d) When excess base is added (after equivalence point)

- pH gradually increases but resists pH change near maximum buffer capacity.
- In this region, the mixture consists of the additional **weak base** (NH_3) and the **conjugate acid** (NH_4^+) formed from neutralisation, forming a **basic buffer**.
- The conjugate base of the weak acid, $CH_3CO_2^-$, does not contribute significant to the [OH^-] as it is a much weaker acid than NH_3. $K_b(CH_3CO_2^-) = \dfrac{K_w}{K_a(CH_3CO_2H)} = 5.75 \times 10^{-10} \text{ mol dm}^{-3}$.

<u>When 50.00 cm^3 of 1.00 mol dm^{-3} NH_3 is added to 25.0 cm^3 of 1.00 mol dm^{-3} CH_3CO_2H,</u>

- **Maximum buffer capacity** occurs when **[weak base] = [conjugate acid]**
- **pH = pK_a** (where K_a is for NH_4^+)
- This point occurs at **2*V* cm^3** where *V* cm^3 is the volume of base required to neutralise the acid completely. 1 *V* = amount of base needed for neutralisation and 1 *V* = amount of base added equal to the amount of salt present

	$CH_3CO_2H(aq)$	+	$NH_3(aq)$	$\rightarrow$ $CH_3CO_2NH_4(aq)$
initial amt/mol	0.025×1 = 0.025		0.050×1 = 0.050	0
change in amt/mol	–0.025		–0.025	+0.025
final amt/mol	0		0.025	0.025

pH = pK_a(NH_4^+)
= −lg (5.00 × 10^{-10}) = **<u>9.30</u>**

OR

pOH = pK_b(NH_3) = 4.70
pH = 14 – 4.70 = **<u>9.30</u>**

***<u>Suitable Indicators</u>*:**

- There is **no** region of rapid pH change
- No sharp increase of pH at the end-point. **No indicator is suitable for this type of titration since colour change would be gradual to a lack of a sharp pH change.**

9.5 Polyprotic (polybasic) Acid – Strong Base Titration

Polyprotic acids contain more than one ionisation proton. In a solution of a polyprotic acid, one proton at a time dissociates from the acid molecule, and each dissociation step has a different K_a. For example, phosphoric acid is a triprotic acid, and has three pK_a values:

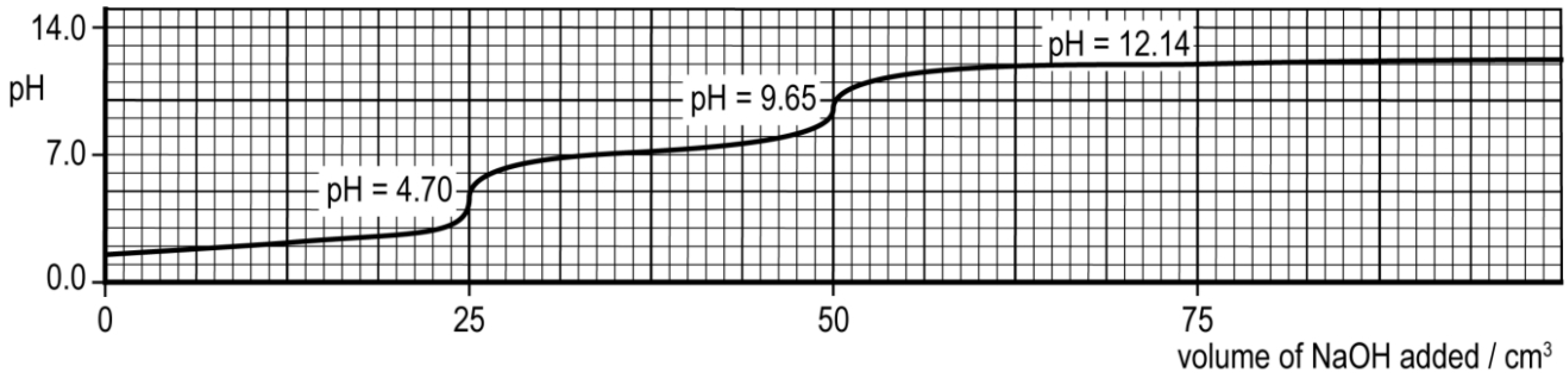
$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq) \qquad pK_{a1} = 2.15$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq) \qquad pK_{a2} = 7.20$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq) \qquad pK_{a3} = 12.35$$

The pK_a values increase from each dissociation step for phosphoric acid. This implies that H_3PO_4 is a much stronger acid than $H_2PO_4^-$, which is in turn stronger than HPO_4^{2-}.

Theoretically, we would expect **three equivalence points** in the titration of H_3PO_4 against NaOH. However, the titration of H_3PO_4 is an interesting case. The pH curve obtained when 25.0 cm^3 of 0.100 mol dm^{-3} H_3PO_4 is titrated against 0.100 mol dm^{-3} NaOH is shown below.



The titration curve contains only **two inflection points** and phosphoric acid can be titrated either as a *monoprotic acid* or as a *diprotic acid*.

- In the first case, the acid has to be titrated with an indicator that changes colour at around pH 4.70 (methyl orange and screened methyl orange are actually not good indicators as their working range is pH 3.1 – 4.4);
- In the second case – the acid is titrated with an indicator that changes colour at around pH 9.65 (for example thymolphthalein, working range 9.3 – 10.5). Phenolphthalein cannot be used, as it starts to change colour around pH 8.2, when phosphoric acid is titrated in about 95%.

It is interesting to mention, that phosphoric acid can be titrated as triprotic – if the PO_4^{3-} anion is precipitated first using a suitable metal ions (for example Ca^{2+} or Ag^+):

$$2H_3PO_4(aq) + 3CaCl_2(aq) \rightarrow Ca_3(PO_4)_2\mathbf{(s)} + 6HCl(aq)$$

After precipitation HCl can be titrated against NaOH.

Think about this…

How many equivalence point(s) will there be, if NaOH(aq) [in the conical flask] is titrated against H_3PO_4(aq) [from the burette] instead?

9.6 Double Indicator Titrations

The use of two different acid-base indicators (which change colour at different pH from one another) can be applied to determine the composition of mixtures of weak and strong bases (or acids), or in the titration of polyprotic substances with two equivalence points or more. Some common examples are:

- Acid-carbonate titrations
- Titration of a mixture of carbonate and hydrogen carbonate solution

Titration of sodium carbonate solution against strong acid

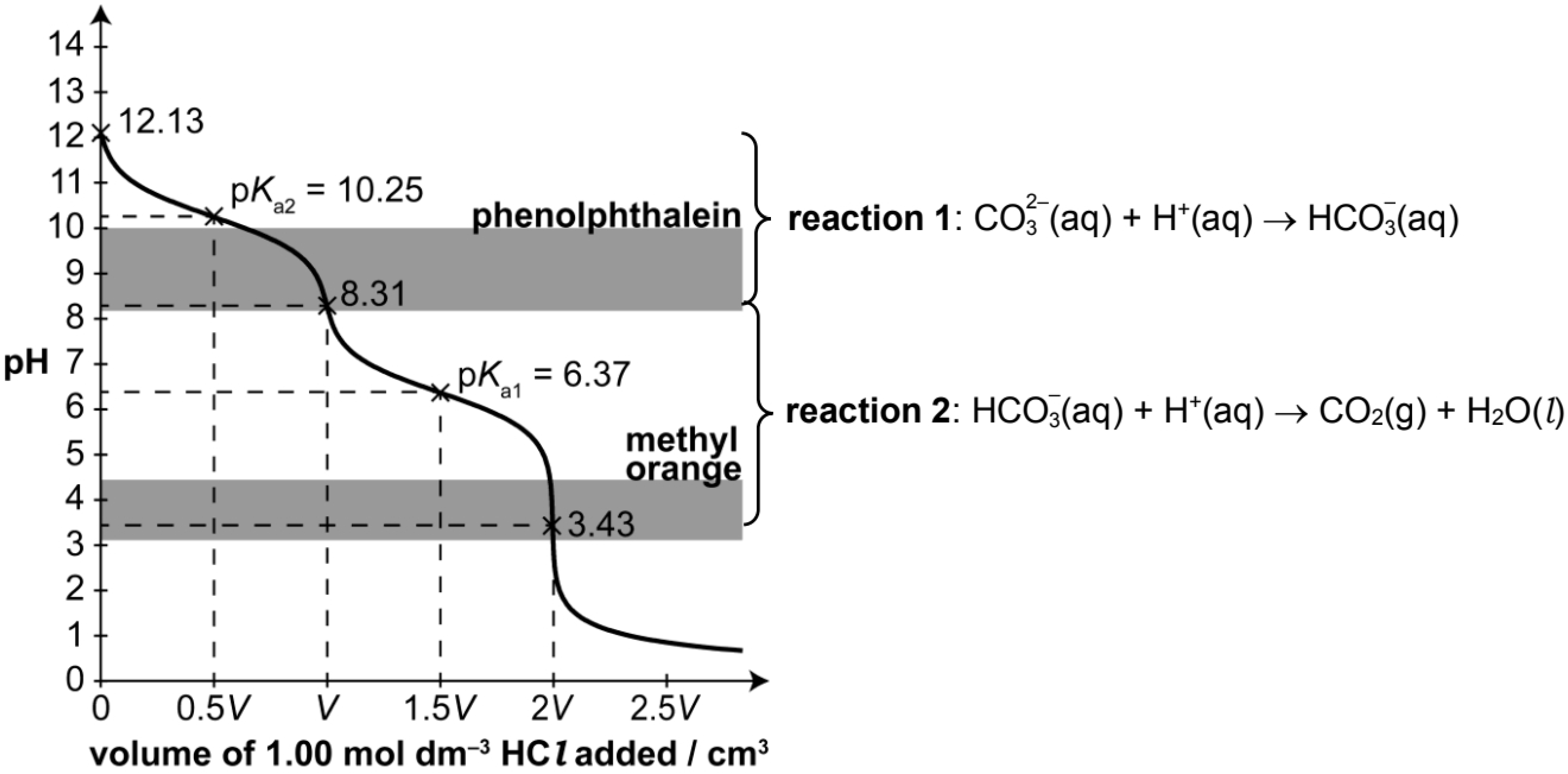
The reaction of CO_3^{2-} with acids occurs in 2 steps:

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

Step 2: $\mathbf{HCO_3^-(aq) + H^+(aq) \rightarrow CO_2(g) + H_2O(\mathit{l})}$

Overall: $\mathbf{CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(\mathit{l})}$

This implies that there are two sharp changes observed in the titration, as illustrated below for the titration of V cm^3 of 1.00 mol dm^{-3} Na_2CO_3 against 1.00 mol dm^{-3} HCl:



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

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

When HCl is first added to Na_2CO_3, **reaction 1** will occur and an indicator, such as phenolphthalein can be used to detect the first end-point since the working pH range of phenolphthalein (*i.e.* pH 8.2 – 10.0) coincides with the sharp pH change of the equivalence point of **reaction 1**.

Similarly, when **reaction 2** starts to occur, methyl orange or screened methyl orange can be used to detect the second end-point, since the working pH range of methyl orange (*i.e.* 3.1 – 4.4) coincides with the sharp pH change of the equivalence point of **reaction 2**.

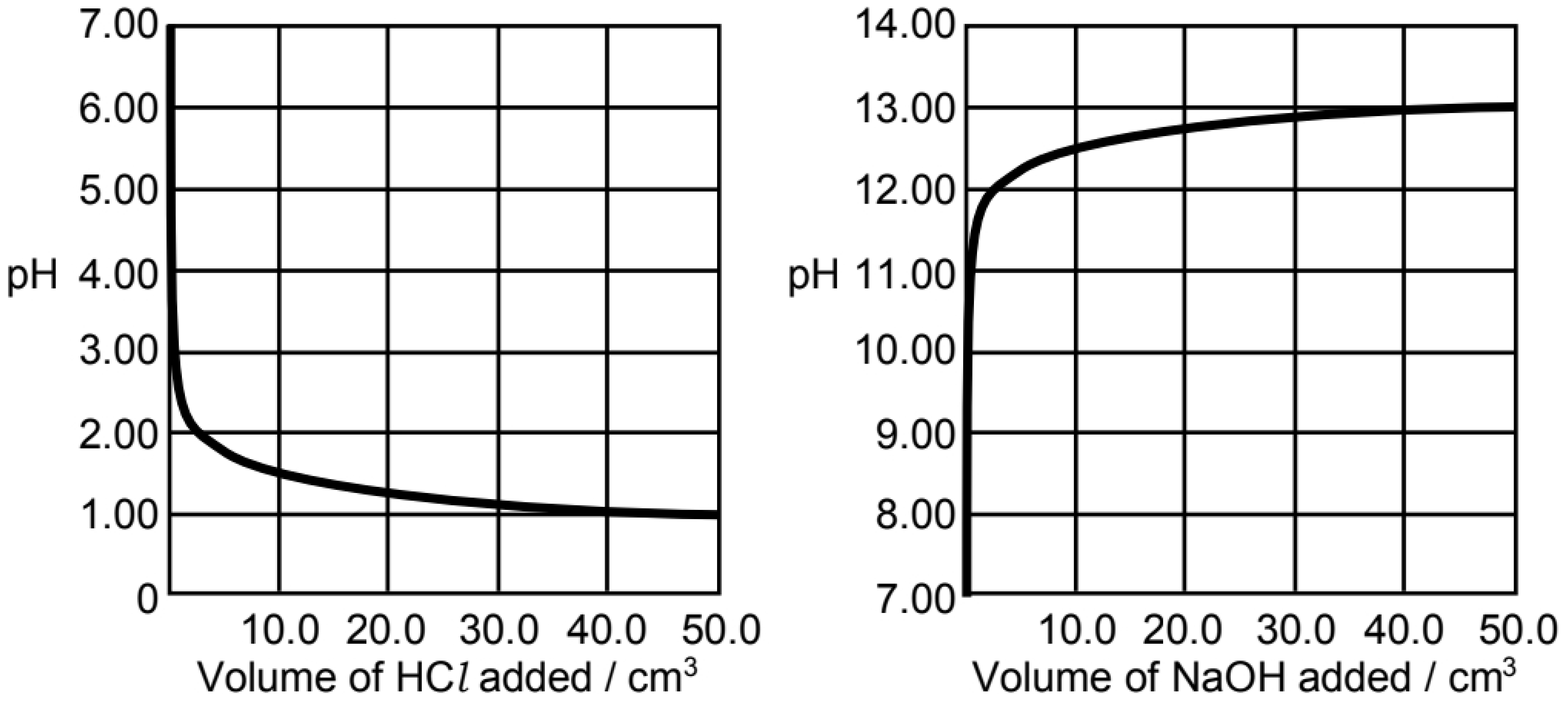
Checkpoint for sections 8 and 9

At the end of these two sections, you should know that:

1. At low pH, a larger proportion of HIn is present and the colour corresponding to the acidic form is observed.
2. At high pH, a larger proportion of In^- is present and the colour corresponding to the basic form is observed.
3. When [HIn] = $[In^-]$, the colour observed is a mixture of both the acidic and basic form, where pH = pK_{In}.
4. An indicator changes colour over an approximate pH range of $pK_{In} \pm 1$, which is the working pH range of the indicator.
5. An indicator is suitable for use if the working pH range of the indicator lies within the range of rapid pH change for the titration.
6. For a strong acid-strong base titration, the pH of the solution at equivalence point is 7 because the salt does not hydrolyse.
7. For a weak acid-strong base titration, the pH of the solution at equivalence point is > 7 because the anion of the salt formed (conjugate base) hydrolyses to give an alkaline solution.
8. For a strong acid-weak base titration, the pH of the solution at equivalence point is < 7 because the cation of the salt formed (conjugate acid) hydrolyses to give an acidic solution.
9. For a weak acid-weak base titration, the pH of the solution at equivalence point depends on the K_a and K_b of the conjugate acid and conjugate base formed.
10. If a titration has more than one equivalence point, then each equivalence point can be determined by a different indicator as long as a sharp change in pH occurs at that equivalence point.

10 APPENDIX: The Levelling Effect of Water

Let us consider the scenarios where we introduce a strong acid (such as 0.20 mol dm^{-3} HCl) or strong base (such as 0.20 mol dm^{-3} NaOH) to water, the changes in pH of the solution tends to follow the curve in **Fig. A1.1**.



(a) Water with strong acid added **(a) Water with strong base added**

Fig. A1.1: (a) When 0.20 mol dm^{-3} HCl is added to 50.0 cm^3 of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 mol dm^{-3} HCl. (b) Conversely, when 0.20 mol dm^{-3} NaOH is added to 50.0 cm^3 of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 mol dm^{-3} NaOH

As we can see from the figure, the changes to pH tends to "level off" at a certain value after a large enough quantity of acid or base is added. In the case where an *infinite* volume of 0.20 mol dm^{-3} of HCl is introduced to 50 cm^3 of water, the effective concentration of H_3O^+ approaches 0.20 mol dm^{-3}, and the measured pH of the solution tends to be –lg (0.20) = **0.699**. Similarly, if another hydrohalic acid, such as HBr, is used, the measured pH will have the same values. This is **counter-intuitive**, especially if we were to taken into consideration that the K_a values of HCl and HBr are 1.3×10^6 and 1.0×10^9 respectively. It suggests that the pH value is independent of the identity of the (strong) acid added.

This observed phenomenon is due to the **levelling effect**, which suggests that:

- An acid stronger than the conjugate acid of the solvent cannot exist in any appreciable concentration in that solvent, and
- A base stronger than the conjugate base of the solvent cannot exist in any appreciable concentration in that solvent,

which arises due to the acid/ base dissociating completely in the solvent.

To rank strong acids in terms of their relative strength, the acids must be dissolved in a solvent that is a weaker base than water. This is illustrated by the solvation of hydrohalic acids in ethanoic acid:

$$HCl(g) + CH_3CO_2H(l) \rightleftharpoons Cl^-(acet) + CH_3CO_2H_2^+(acet) \qquad K_a = 1.3 \times 10^6$$

$$HBr(g) + CH_3CO_2H(l) \rightleftharpoons Br^-(acet) + CH_3CO_2H_2^+(acet) \qquad K_a = 1.0 \times 10^9$$

$$HI(g) + CH_3CO_2H(l) \rightleftharpoons I^-(acet) + CH_3CO_2H_2^+(acet) \qquad K_a = 3.2 \times 10^9$$

The strength of the H–X bond is inversely proportional to the strength of the acid. In the case of ethanoic acid, which is a weaker base than water, the acids protonate ethanoic acid to different extents. Measurements shows that HI protonates ethanoic acid to a greater extent than HBr, and HBr more than HCl. In this case, ethanoic acid serves as a differentiating solvent. Similarly, the relative strength of strong bases may be determined using a weaker acid than water, such as liquid NH_3.