18.1 Further Aspects of Acids & Bases
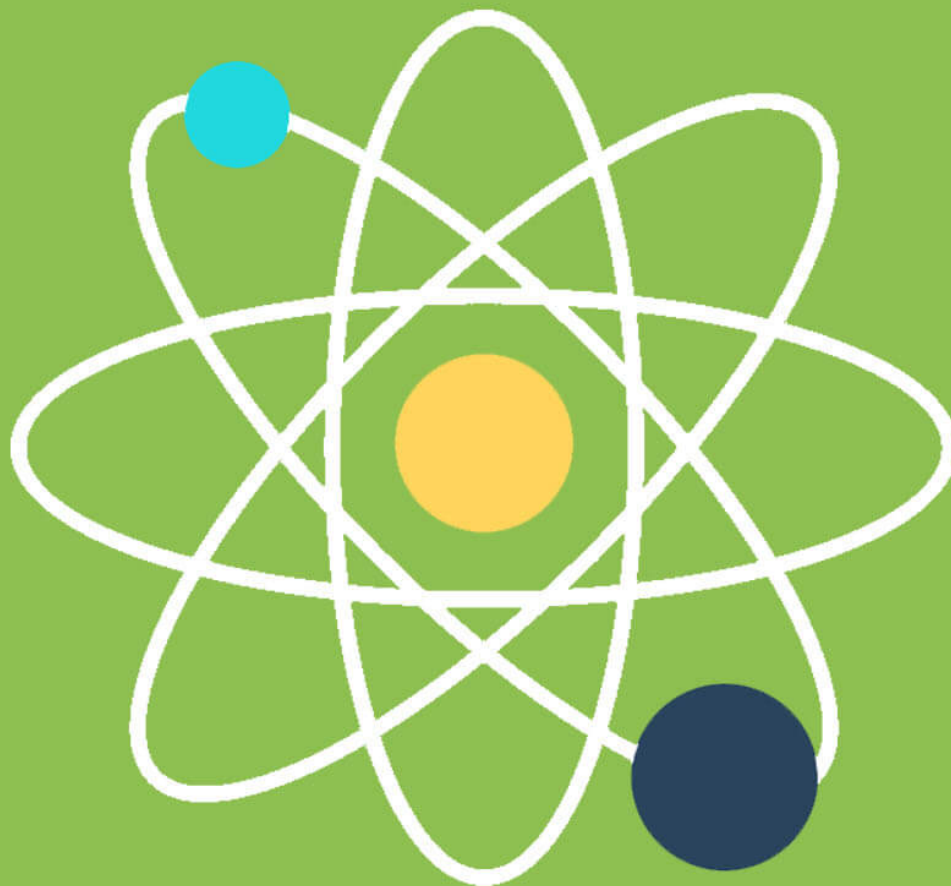
IB Chemistry - Revision Notes

18.1.1 Lewis Theory

Lewis Theory of Acids & Bases

- A more general definition of acids and bases was given by G.N. Lewis who defined them as:
  - A Lewis **acid** is an **electron pair acceptor**
  - A Lewis **base** is an **electron pair donor**

$$A^+ \quad + \quad :B^- \quad \longrightarrow \quad A\leftarrow:B$$

LEWIS ACID   LEWIS BASE   COORDINATE
(ELECTRON ACCEPTOR)   (ELECTRON DONOR)   BOND

General mechanism for Lewis acids and bases

- This enabled a wider range of substances to be classed as acids or bases
- This can be shown in the following examples in which a hydroxide ion, OH^-, and ammonia, NH_3, donate a pair of electrons to a hydrogen ion
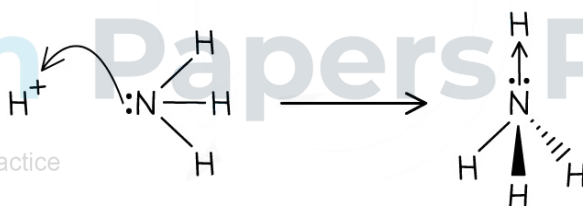
The OH^- ion and ammonia act as Lewis bases in both examples by donating an electron pair

Brønsted–Lowry Acids and Bases

- A **Brønsted–Lowry acid** is a species that can donate a proton
  - For example, hydrogen chloride (HCl) is a Brønsted–Lowry acid as it can lose a proton to form a hydrogen (H^+) and chloride (Cl^-) ion

$$HCl\,(aq) \rightarrow H^+\,(aq) + Cl^-\,(aq)$$
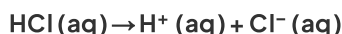
- A **Brønsted–Lowry base** is a species that can accept a proton
  - For example, a hydroxide (OH^-) ion is a Brønsted–Lowry base as it can accept a proton to form water

$$OH^-\,(aq) + H^+\,(aq) \rightarrow H_2O\,(l)$$
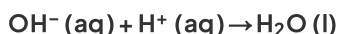
Weak acids dissociating

- In an equilibrium reaction, the products are formed at the same rate as the reactants are used
- This means that at equilibrium, both reactants and products are present in the solution
- For example, ethanoic acid (CH_3COOH) is a weak acid that partially dissociates in solution
- When equilibrium is established there are CH_3COOH, H_2O, CH_3COO^- and H_3O^+ ions present in the solution

Lewis Acid, Lewis Base, Brønsted–Lowry acid or Brønsted–Lowry base

A point to consider when thinking about Lewis acids and bases as well as Brønsted–Lowry acids and bases is the donating and accepting of protons

- Brønsted–Lowry acid and base theory considers acids as **proton donors only**
- This does not of course occur in every reaction
- For example:
  - The lone pair on the nitrogen atom in ammonia, NH_3, can be donated to the boron atom in boron trifluoride, BF_3, creating a molecule of NH_3BF_3
  - In this case, neither compound reacts as an Brønsted–Lowry acid or Brønsted–Lowry base as no protons (H^+ ions) are being donated or accepted
  - Only electron pairs are being donated and accepted
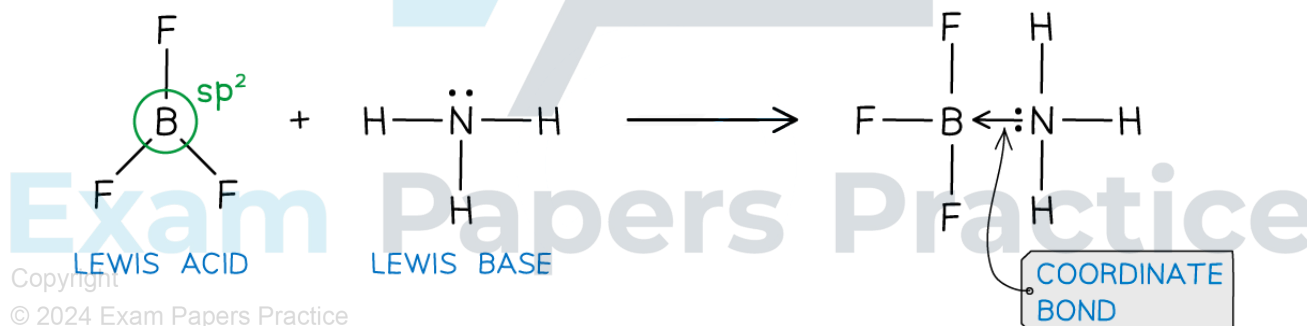
*Ammonia donates a lone pair of electrons to form a coordinate bond*

- Here boron forms three sp^2 hybridised orbitals leaving a vacant $2p_z$ orbital which allows the lone pair on the nitrogen atom to form a dative covalent bond

SPACE FOR A LONE PAIR TO FORM COORDINATE BOND

2p ↑ ↑

HYBRIDISE →

2p² [ ]

2s ↑

2sp² ↑ ↑ ↑

1s ↑↓

1s ↑↓

EXCITED STATE
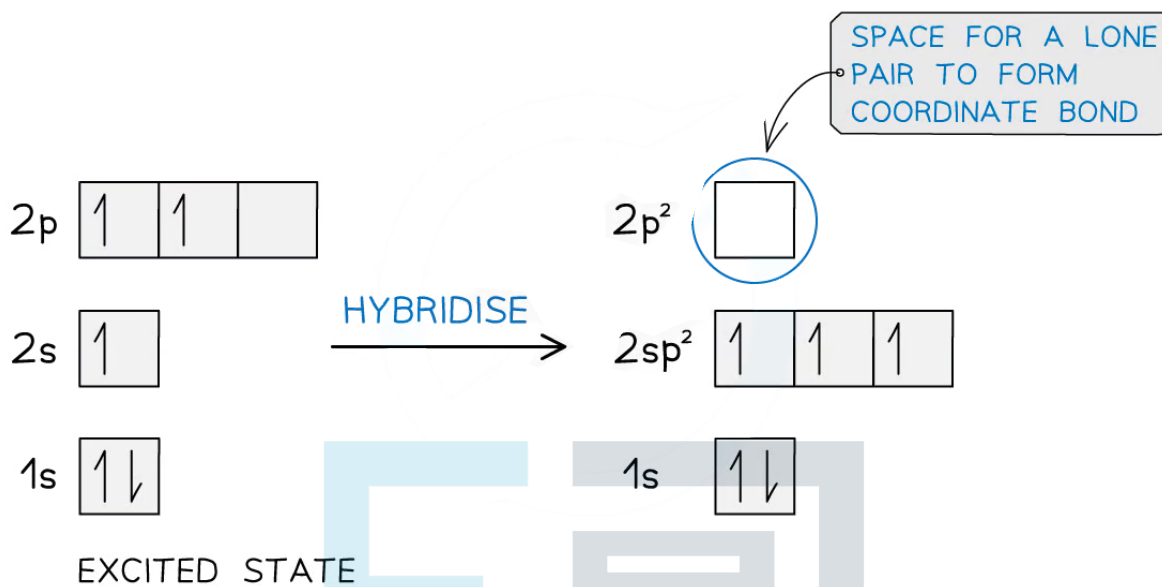
Hybridisation of the boron atom

- The following molecules can behave as either Lewis bases and Brønsted-Lowry bases
  - Lewis bases as they can donate an electron pair
  - Brønsted-Lowry base as they can accept a proton

$:\overset{..}{\underset{..}{O}} — H$ $:C \equiv N$ $CH_3\overset{..}{N}H_2$
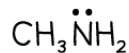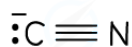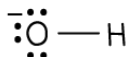
Examples of molecules that can behave both as Lewis bases and Brønsted–Lowry base

Identifying Lewis Acids & Bases

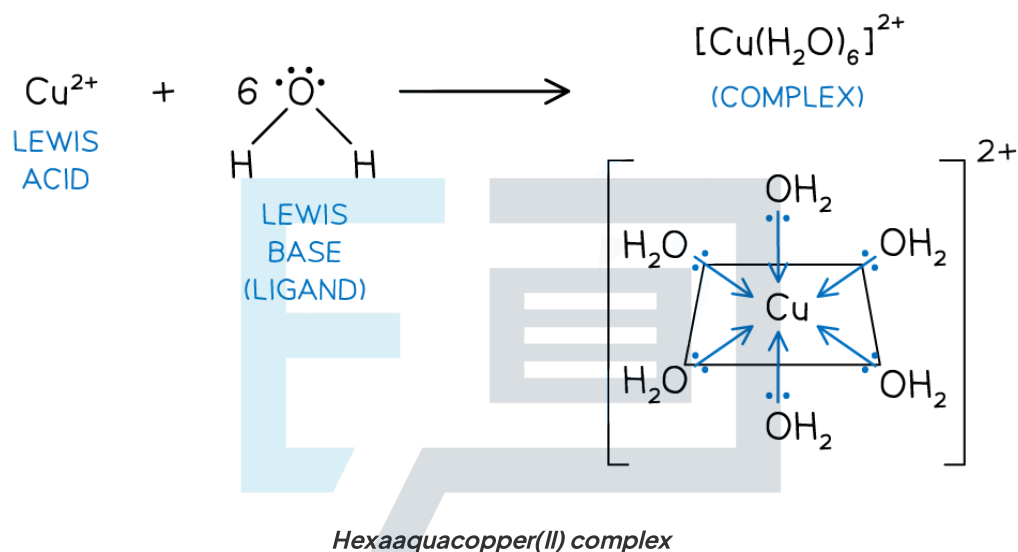- In the case of a complex ion, such as hexaaquacopper(II), the water molecule is acting as a Lewis base and the metal ion is acting as a Lewis acid
  - Copper(II), like other transition metals, can form a complex due to a partially occupied d subshell
  - $Cu^{2+}(aq) + 6H_2O(l) \rightarrow [Cu(H_2O)_6]^{2+}(aq)$

Hexaaquacopper(II) complex

- Given that Lewis acids can accept a pair of electrons, they can be classed as electrophiles
  - An electrophile is a electron-deficient species that can accept a lone pair from a nucleophile, in the same way the Cu^{2+} ion accepts electron pairs from water
  - The cyanide ion, ^-CN, water, H_2O, ammonia, NH_3, are examples of Lewis bases and they can also act as nucleophiles
    - Nucleophiles are electron rich species with at least on pair of lone electrons

✎ Worked example

Identify the Lewis acid and Lewis base in the following reaction
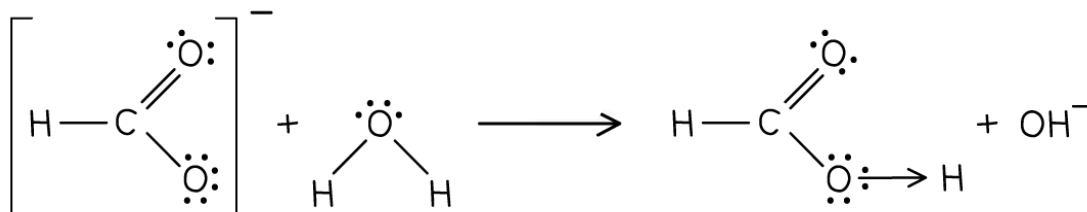
Methanoate ion reacting with water

Answer

- The Lewis acid is water, H_2O
    - The hydrogen in the water molecule is accepting a pair of electrons leaving an OH^- ion

- The Lewis base is the methanoate ion, $HCOO^-$
    - The lone pair of electrons in the methanoate ion forms a coordinate bond with one of the hydrogens from the water molecule

We have seen previously that water can act as a Brønsted–Lowry acid or base, so it should be no surprise that water can act as both a Lewis acid or base depending on how it is interacting with other species

18.1.2 pH Curves

pH Curves

- During a titration, a pH meter can be used and a pH curve plotted
- A pH curve is a graph showing how the pH of a solution changes as the acid (or base) is added
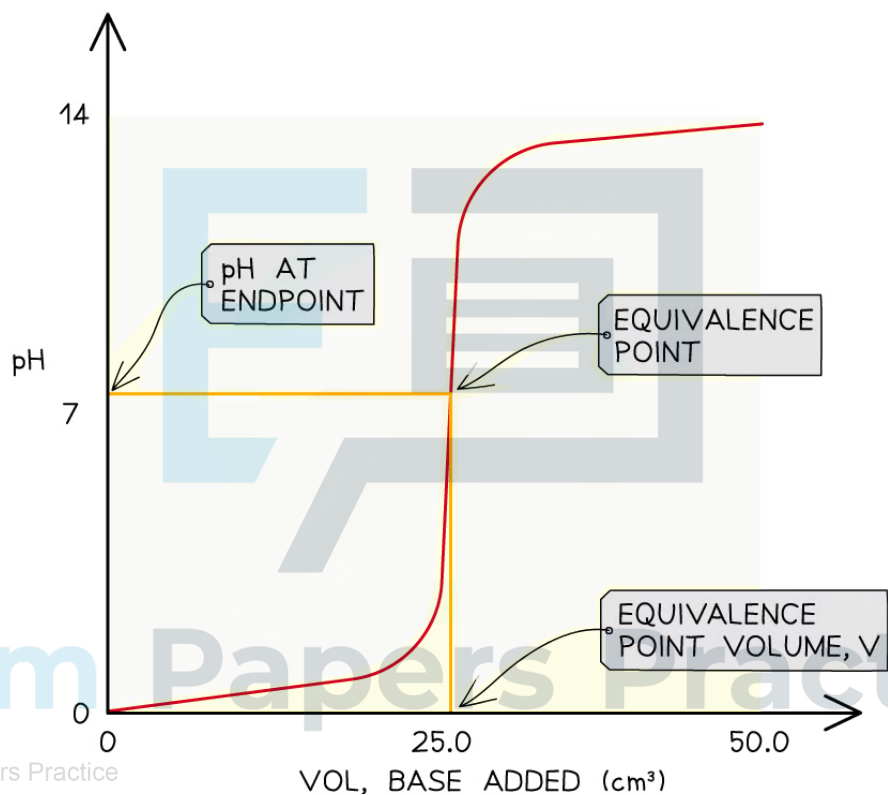
The features of a pH curve

- All pH curves show an s-shape curve
- pH curves yield useful information about how the acid and alkali react together with stoichiometric information
- The midpoint of the inflection is called the **equivalence** or **stoichiometric point**
- From the curves you can:
  - Determine the pH of the acid by looking where the curve starts on the y-axis
  - Find the pH at the equivalence point
  - Find volume of base at the equivalence point

- Obtain the range of pH at the vertical section of the curve

Four Types of Acid–Base Titrations

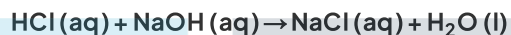- There are four combinations of acids and alkalis that you should know about:
  - strong acid + strong base
  - weak acid + strong base
  - weak base + strong acid
  - weak acid + weak base

Strong Acid + Strong Base

- In this example, sodium hydroxide, NaOH (aq), is being added to hydrochloric acid, HCl (aq)

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

- The pH intercept on the y axis starts at a low pH, roughly 1, due to the relative strength of the hydrochloric acid
- As the NaOH (aq) is added, there is a gradual rise in pH until the titration approaches the equivalence point
- In this case, the pH at equivalence is 7
  - The equivalence point is in the middle of the vertical section of the pH curve

- Once all of the acid has been neutralised, the curve flattens out and continues to rise gradually
- At the end of the titration, the pH will be high due to the relative strength of the sodium hydroxide
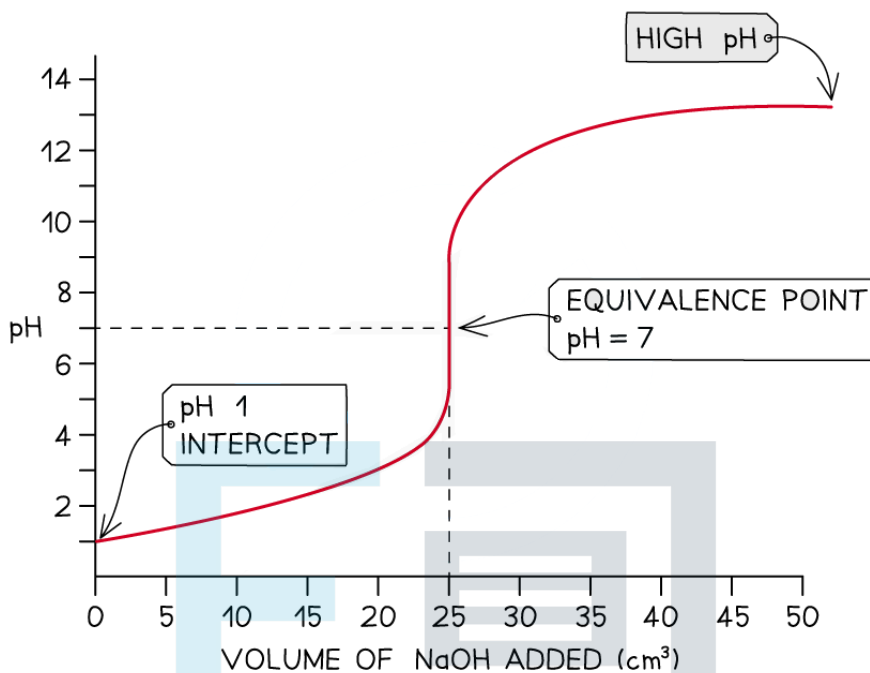
Strong acid – strong base pH curve

Weak Acid + Strong Base

- In this example, strong sodium hydroxide, $NaOH$ (aq), is being added to weak ethanoic acid, CH_3COOH (aq)

$$NaOH\,(aq) + CH_3COOH\,(aq) \rightarrow CH_3COONa\,(aq) + H_2O\,(l)$$

- The pH on the intercept on the y axis starts at roughly 3 due to the relative strength of the ethanoic acid
- The initial rise in pH is steep as the neutralisation of the weak acid by the strong base is rapid
- Ethanoate ions (conjugate base to ethanoic acid) are formed which then creates a buffer
  - A buffer consists of a weak acid and its conjugate base or a weak base and its conjugate acid

- At this point, the buffer formed will resist changes in pH so the pH rises gradually as shown in the **buffer region**
- The **half equivalence point** is the stage of the titration at which exactly half the amount of weak acid has been neutralised
  - **$[CH_3COOH\,(aq)] = [CH_3COO^-\,(aq)]$**
  - At this point, it is important to note that the pK_a of the acid is equal to the pH
    - **pK_a = pH** at **half equivalence**

- The equivalence point in a weak acid – strong base titration is **above 7**
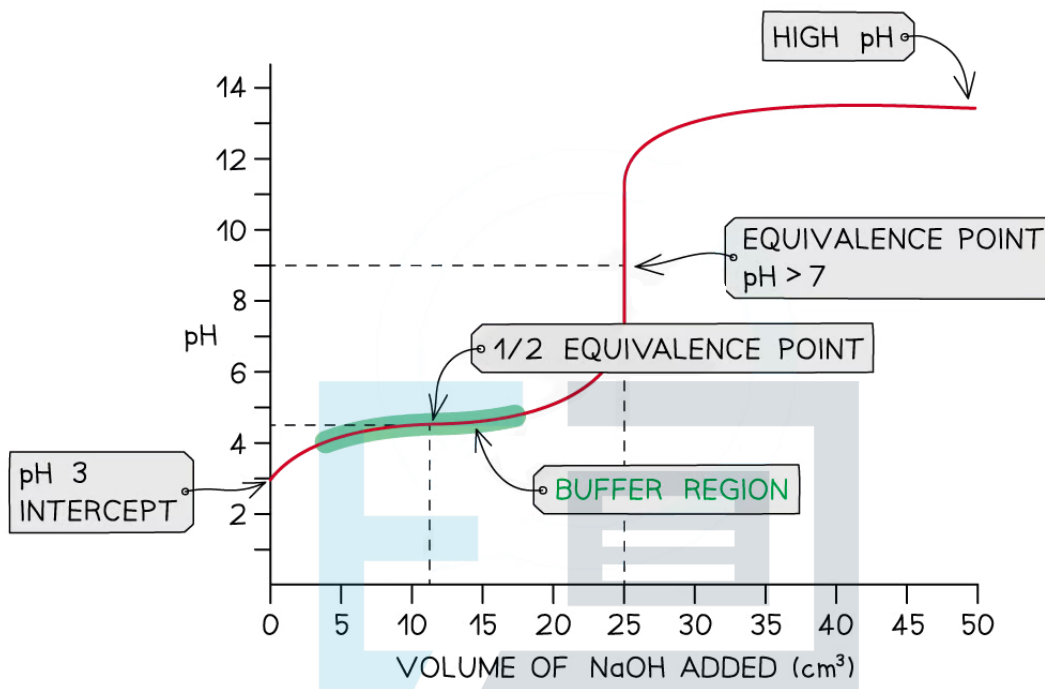
Weak acid – strong base pH curve

Weak Base + Strong Acid

- In this example, strong hydrochloric acid, HCl (aq), is being added to weak ammonia, NH₃ (aq)

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

- The pH on the intercept on the y axis starts at roughly 11 due to the relative strength of the ammonia
- The pH will fall as the ammonia begins to be neutralised and the conjugate acid, NH_4^+ (aq), is produced
- This again creates a buffer region so the pH will only fall gradually
- The **half equivalence point** is the stage of the titration at which exactly half the amount of weak base has been neutralised
    - **[NH₃ (aq)] = [NH₄⁺ (aq)]**
    - At this point it is important to note that the pK_b of the base is equal to the pOH
        - pK_b = pOH at **half equivalence**

- The pH at equivalence for a weak base–strong acid is **below 7**

Weak base – strong acid pH curve
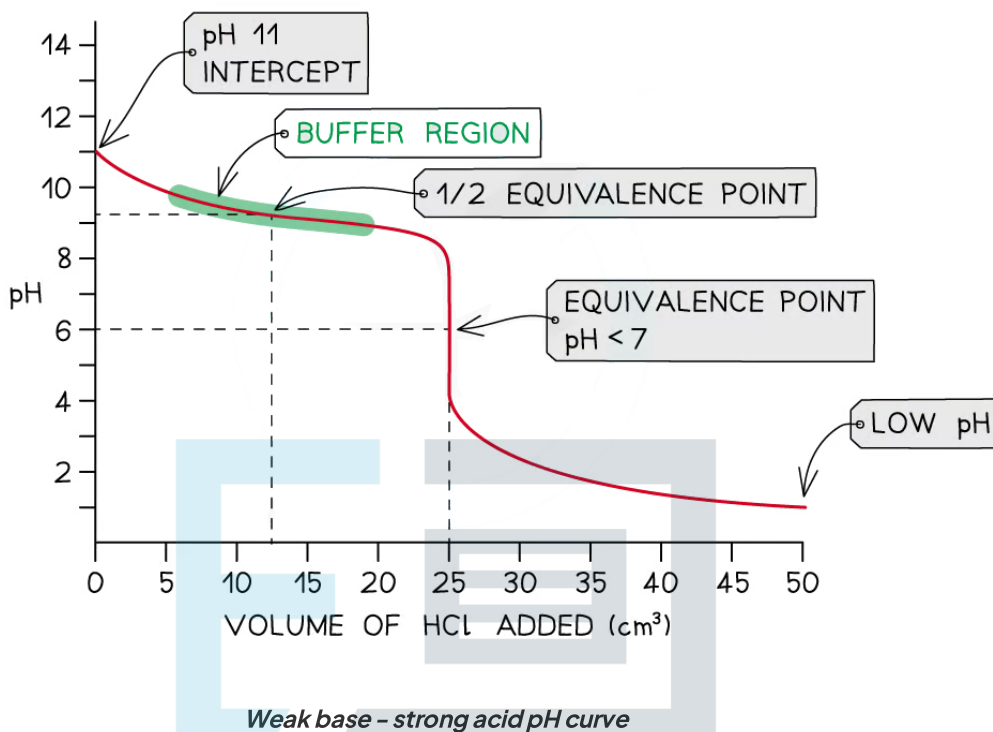
Weak Acid + Weak Base

- In this example, weak ethanoic acid, CH_3COOH (aq), is being added to weak ammonia, NH_3 (aq)

$$NH_3 \text{ (aq)} + CH_3COOH \text{ (aq)} \rightarrow CH_3COONH_4 \text{ (aq)}$$

- The starting pH of roughly 11 for the weak base will fall as it begins to neutralise
- The change in pH for this titration is very gradual
    - Note the that the vertical section of this pH curve is not steep as with other three so the equivalence point is difficult to determine
    - Therefore this titration is not performed

- The pH at equivalence for a weak acid – weak base is **roughly 7 but is difficult to determine**
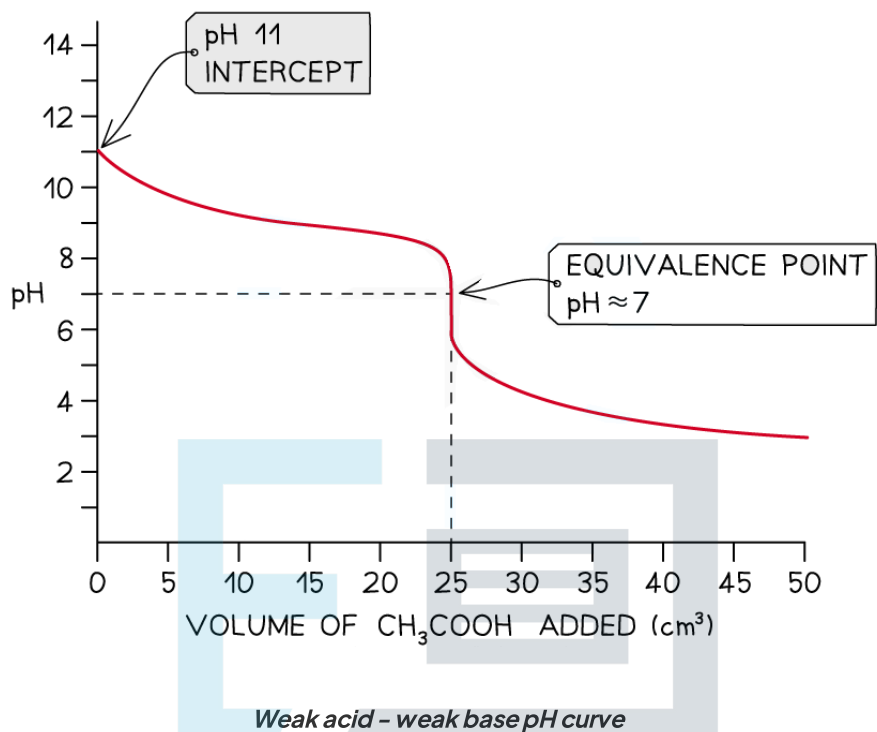
Weak acid – weak base pH curve

18.1.3 Indicators

Indicators

- An **acid–base** indicator is a weak acid which dissociates to give an anion of a different colour
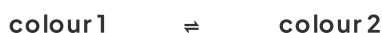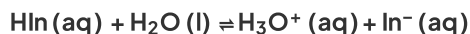- Consider a weak acid, HIn:

$$HIn\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + In^-\,(aq)$$

$$colour\,1 \qquad \rightleftharpoons \qquad colour\,2$$

- HIn and its conjugate base In⁻ are different colours
- The colour of the solution depends on the relative concentrations of the two species
- If the solution is **acidic**, the above equilibrium will be shifted to the left and more HIn will be present
  - Colour 1 will dominate

- If the solution is **alkaline**, the above equilibrium will shift to the right and more In⁻ will be present
  - Colour 2 will dominate

- The colour of the indicator depends on the pH of the solution
  - The colour does not change suddenly at a certain pH, but changes gradually over a pH range
  - The colour of the indicator depends on the ratio of [HIn] to [In⁻]

- The pH at which these transitions will occur depends on the K_a of the indicator

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

- The endpoint of the reaction is where there is a balance between [HIn] and [In⁻]. At this point these two concentrations are equal:

$$K_a = \frac{[H^+][\cancel{In^-}]}{[\cancel{HIn}]} = [H^+]$$
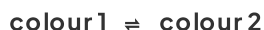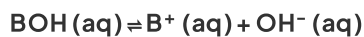
- Taking negative logs of both sides:

$$pK_a = pH$$

- This means the pK_a of an indicator is the same as the pH of its endpoint
- The colour change for most indicators takes place over a range of **$pH = pK_a \pm 1$**

Weak bases as indicators

- An indicator can also be a weak base:

$$BOH\,(aq) \rightleftharpoons B^+\,(aq) + OH^-\,(aq)$$

$$\text{colour 1} \rightleftharpoons \text{colour 2}$$

- For such indicators:
    - Colour 1 is observed in alkaline conditions
    - Colour 2 is observed in acidic conditions

Choosing a suitable indicator

- Around the equivalence point of a titration, the pH changes very rapidly
- **Indicators** change colour over a narrow pH range, approximately centred around the pK_a of the indicator
- An indicator will be appropriate for a titration if the pH range of the indicator falls within the rapid pH change for that titration

Common Indicators and their colours table

Indicator	Colour in acid	Colour in alkali	pK$_a$	pH range of colour change
Thymol blue	red	yellow	1.7	1.2 – 2.8
Methyl orange	red	yellow	3.7	3.1 – 4.4
Bromophenol blue	yellow	blue	4.1	3.4 – 4.6
Methyl red	red	yellow	5.1	4.4 – 6.2
Phenolphthalein	colourless	pink	9.3	8.3 – 10.0

Strong acid – strong base

- In strong acid – strong base titrations, the pH changes from 4 to 10 at the end-point so a suitable indicator must change colour within this range
    - **Methyl red** and **phenolphthalein** are suitable indicators for these titrations

- **Methyl orange** is not ideal but it shows a significant enough colour change at the end point so is widely used

Weak acid – strong base

- In weak acid – strong base titrations, the pH changes from 7 to 10 at the end-point so a suitable indicator must change colour within this range
  - **Phenolphthalein** is the only suitable indicator for weak acid – strong base titrations that is widely available

Strong acid – weak base

- In strong acid – weak base titrations, the pH changes from 4 to 7 at the end-point so a suitable indicator must change colour within this range
  - **Methyl red** is the most suitable indicator for these titrations
  - However, **methyl orange** is often used since it shows a significant enough colour change at the end-point and is more widely available than methyl red

Weak acid – weak base

- In weak acid – weak alkali titrations, there is **no sudden pH change** at the end-point and thus there are **no suitable indicators** for these titrations
  - The end-points of these titrations cannot be easily determined
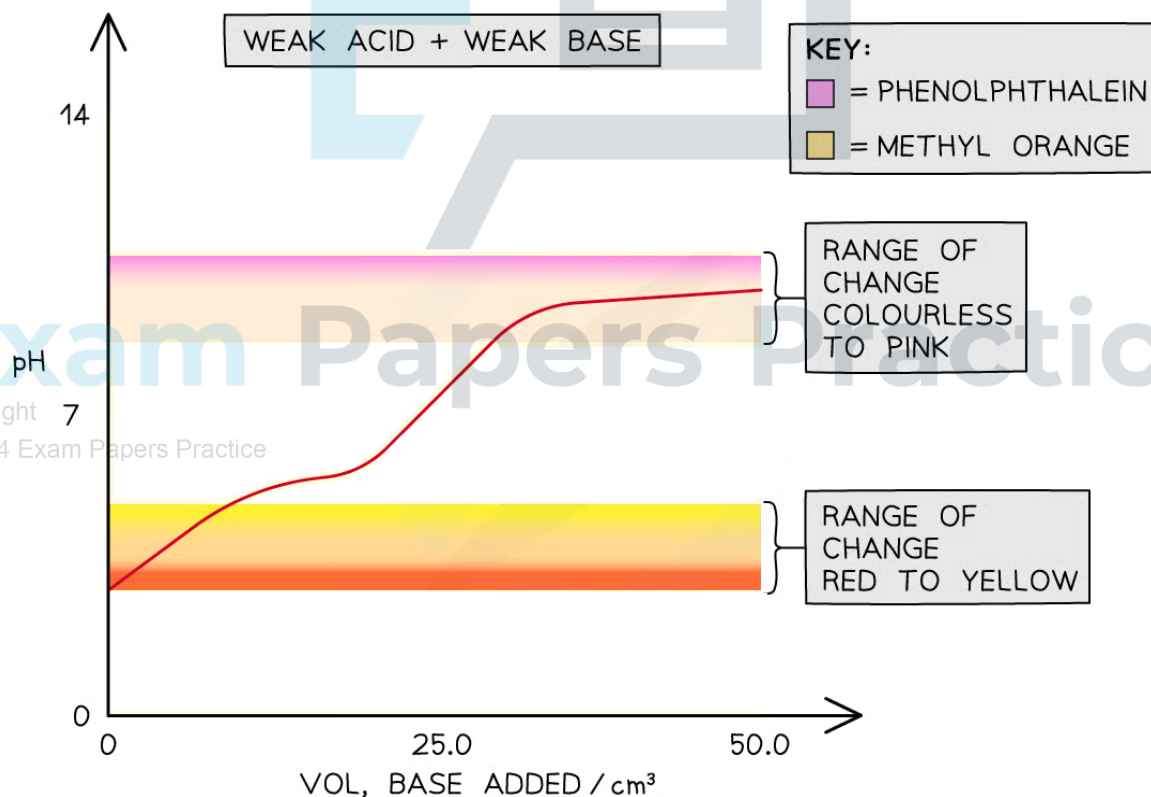
The overlay on the graph shows that both phenolphthalein and methyl orange would change colour outside the point of inflection in a weak acid–weak base titration so they would not be able to show the equivalence point of the titration
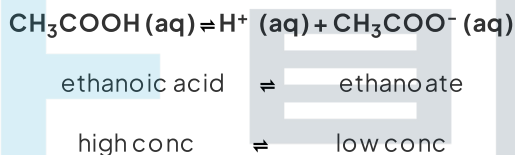
18.1.4 Buffers

Buffers

- A **buffer solution** is a solution which resists changes in pH when small amounts of acid or base are added
  - A buffer solution is used to keep the pH almost constant
  - A buffer can consist of **weak acid – conjugate base** or **weak base – conjugate acid**

Ethanoic acid & sodium ethanoate as a buffer

- A common buffer solution is an **aqueous mixture** of ethanoic acid and sodium ethanoate
- Ethanoic acid is a **weak acid** and partially ionises in solution to form a relatively low concentration of **ethanoate ions**

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

| ethanoic acid | $\rightleftharpoons$ | ethanoate |
| high conc | $\rightleftharpoons$ | low conc |

- Sodium ethanoate is a **salt** which fully ionises in solution

$$CH_3COONa + aq \rightarrow Na^+\,(aq) + CH_3COO^-\,(aq)$$

| sodium ethanoate | $\rightarrow$ | ethanoate ion |
| low conc. | $\rightarrow$ | high conc. |

- There are **reserve supplies** of the acid (CH_3COOH) and its conjugate base (CH_3COO^-)
- The buffer solution contains relatively high concentrations of CH_3COOH (due to the partial ionisation of ethanoic acid) and CH_3COO^- (due to the full ionisation of sodium ethanoate)

- In the **buffer solution**, the ethanoic acid is in **equilibrium** with hydrogen and ethanoate ions

$$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq)$$
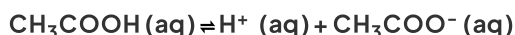
| high conc. | | high conc. |

Adding H⁺ ions to a buffer solution:

- The equilibrium position shifts to the **left** as H⁺ ions react with CH_3COO^- ions to form more CH_3COOH until equilibrium is re-established
- As there is a large reserve supply of CH_3COO^-, the concentration of CH_3COO^- in solution doesn't change much as it reacts with the added H⁺ ions

- As there is a large reserve supply of CH_3COOH, the concentration of CH_3COOH in solution doesn't change much as CH_3COOH is formed from the reaction of CH_3COO^- with H^+
- As a result, the pH remains reasonably constant

> ETHANOATE IONS IN THE BUFFER SOLUTION REACT WITH THE ADDED H^+ IONS TO PREVENT THE pH FROM DECREASING

$$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(aq)$$
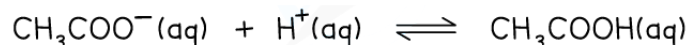
When hydrogen ions are added to the solution the pH of the solution would decrease. However, the ethanoate ions in the buffer solution react with the hydrogen ions to prevent this and keep the pH constant

Adding OH^- ions to a buffer solution:
- The OH^- reacts with H^+ to form water

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$
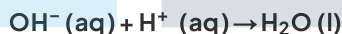
- The H^+ concentration **decreases**
- The equilibrium position shifts to the **right** and more CH_3COOH molecules ionise to form more H^+ and CH_3COO^- until equilibrium is re-established
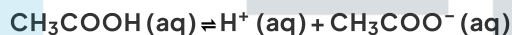
$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

- As there is a large reserve supply of CH_3COOH, the concentration of CH_3COOH in solution doesn't change much when CH_3COOH dissociates to form more H^+ ions
- As there is a large reserve supply of CH_3COO^-, the concentration of CH_3COO^- in solution doesn't change much
- As a result, the pH remains reasonably constant

> EQUILIBRIUM MOVES TO REPLACE THE REMOVED HYDROGEN IONS

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$
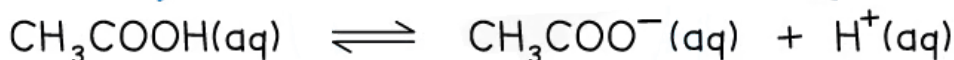
> HYDROXIDE IONS COMBINE WITH THESE TO MAKE WATER

When hydroxide ions are added to the solution, the hydrogen ions react with them to form water; The decrease in hydrogen ions would mean that the pH would increase however the equilibrium moves to the right to replace the removed hydrogen ions and keep the pH constant

> 💡 **Exam Tip**
>
> Remember that buffer solutions cannot cope with **excessive addition** of acids or alkalis as their pH will change significantly. The pH will only remain relatively constant if **small amounts** of acids or alkalis are added.

The Buffer Region

- These are seen on a pH curve and represent the region where small additions in acid or base result in little change in the overall pH of the solution
- For a weak acid – strong base titration between sodium hydroxide, NaOH (aq), and ethanoic acid, CH_3COOH (aq)
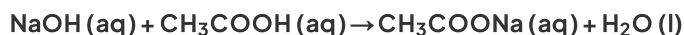
$$NaOH \, (aq) + CH_3COOH \, (aq) \rightarrow CH_3COONa \, (aq) + H_2O \, (l)$$

- The initial rise in pH is steep as the neutralisation of the weak acid by the strong base is rapid
- Sodium ethanoate is then formed which creates a buffer that will resist changes in pH so the pH rises gradually
  - A buffer consists of a weak acid and its conjugate salt

- This section of the curve is known as the **buffer region**
- Only small increases in pH are seen when the strong base is added in this part of the titration curve
- At this point, the acid is in equilibrium with the salt ion
  - $CH_3COOH \, (aq) + H_2O \, (l) \rightleftharpoons CH_3COO^- + H_3O^+ (aq)$

- Continuing to add the strong base will 'use up' all of the acid so the forward reaction will then be favoured

Buffer region shown is a weak acid – strong base titration curve
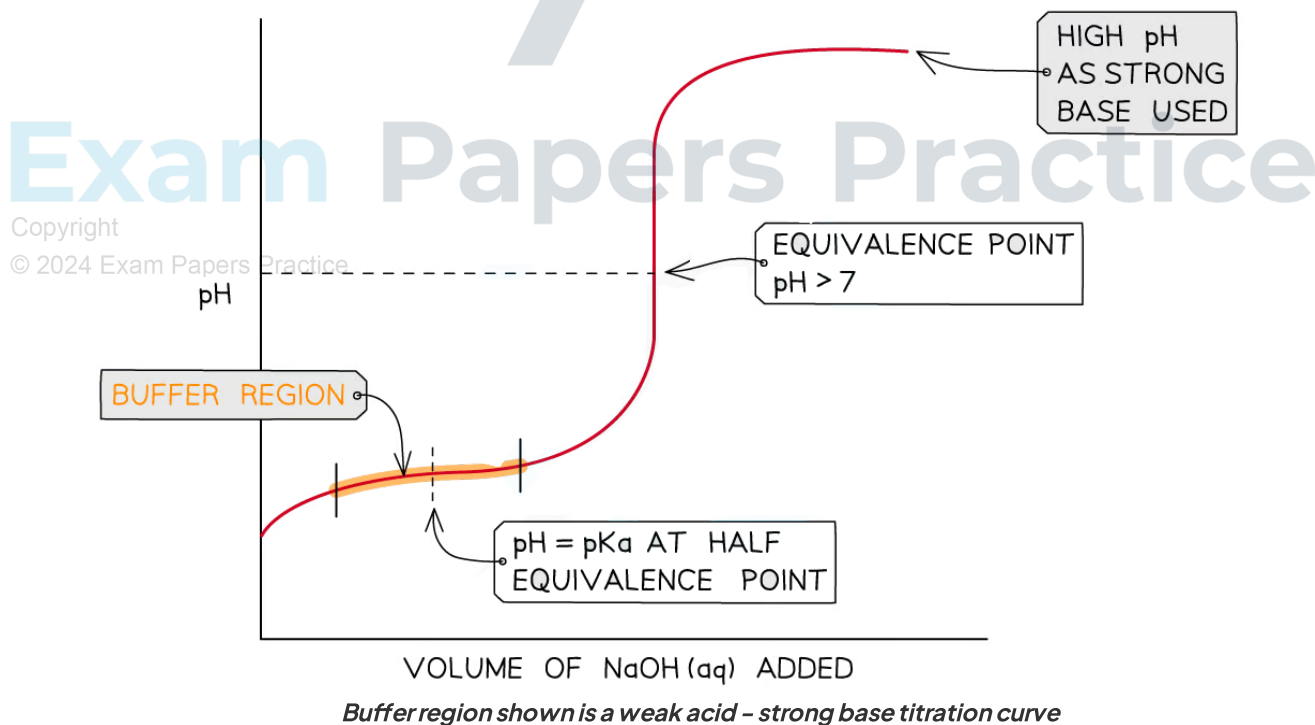
- A buffer region is also observed during a weak base – strong acid titration
  - Ammonia, NH_3 (aq), and hydrochloric acid, HCl (aq), is a common example

$$NH_3 \text{ (aq)} + HCl \text{ (aq)} \rightarrow NH_4Cl \text{ (aq)}$$

- The starting pH of the weak base will fall as it begins to be neutralised and the conjugate acid, NH_4^+ (aq), will be produced
- This results in a buffer that resists change in pH
- Due to this, the pH will only fall gradually
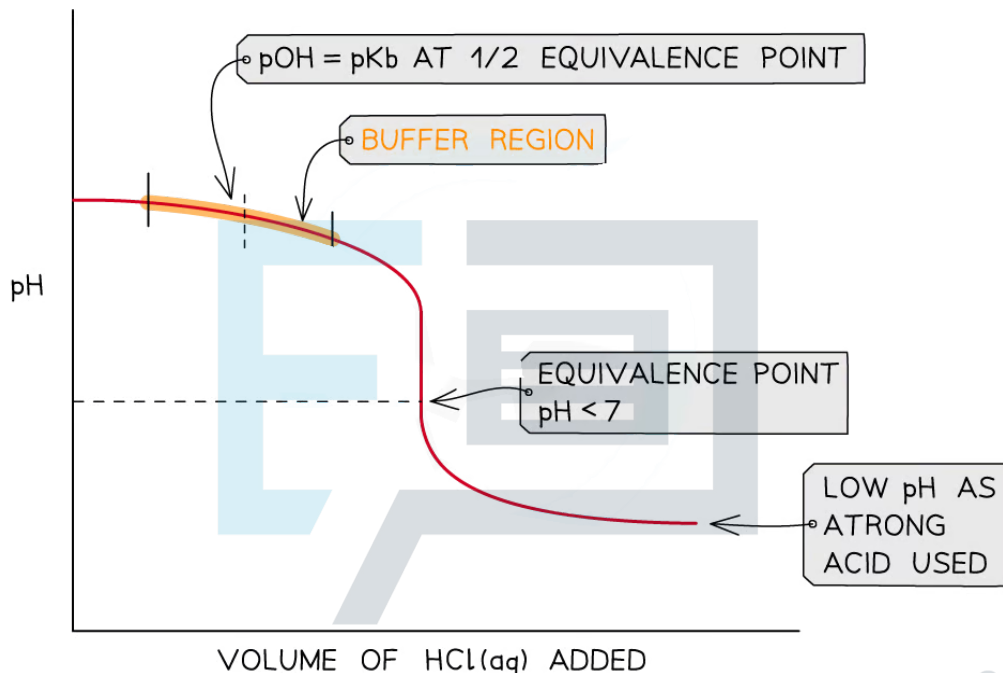
Buffer region shown is a weak base – strong acid titration curve

18.1.5 Salt Hydrolysis

Salt Hydrolysis

- An ionic salt is formed from the neutralisation reaction of an acid and base

$$HA + MOH \xrightarrow{\text{NEUTRALISATION}} M^+A^- + H_2O$$

PARENT ACID   PARENT BASE   SALT

Neutralisation

- The ionic salt, MA, formed will dissociate in water
  - **Hydrolysis** is where water is used to break a bond within a compound, which results in the aqueous ions for an ionic salt

- The reaction of the salt will vary depending on the strength of the acids and bases used in the neutralisation reaction
- The use of the differing strengths of the acids and bases will directly influence the type of salt hydrolysis and the pH of the final solution

Strong Acids and Strong Bases

- A common example of this is the reaction between hydrochloric acid, HCl (aq), and sodium hydroxide (aq):

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

- The Na^+ and Cl^- ions do not act as Brønsted-Lowry acids or bases as they can not release or accept H^+ ions
- Therefore, they do not affect the pH

Strong Acid and Weak Base

- The salt formed by a strong acid such as hydrochloric acid, HCl (aq), and a weak base such as ammonia, NH_3 (aq), will form an acidic solution:

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

- In this reaction, the conjugate acid of ammonia is formed, NH_4^+, and can react with water to produce H_3O^+

$$NH_4^+ \text{ (aq)} + H_2O \text{ (l)} \rightarrow H_3O^+ \text{ (aq)} + NH_3 \text{ (aq)}$$
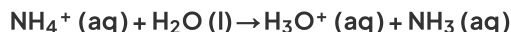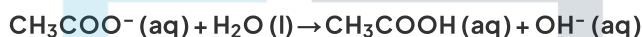
- Therefore, the solution becomes more acidic
- The hydrolysis of this salt demonstrates why the equivalence point of a strong acid – weak base pH curve is below 7

Strong Base and Weak Acid

- The salt formed by a strong base such as sodium hydroxide, NaOH (aq), and a weak acid such as ethanoic acid, CH_3COOH (aq), will form an alkaline solution:

$$NaOH \text{ (aq)} + CH_3COOH \text{ (aq)} \rightarrow CH_3COONa \text{ (aq)} + H_2O \text{ (l)}$$
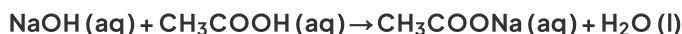
- In this reaction, the conjugate base of ethanoic acid is produced, $\mathbf{CH_3COO^-}$ **(aq)**, and this will react with water to form hydroxide ions, $\mathbf{OH^-}$ (aq)

$$CH_3COO^- \text{ (aq)} + H_2O \text{ (l)} \rightarrow CH_3COOH \text{ (aq)} + OH^- \text{ (aq)}$$
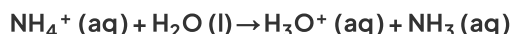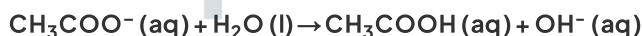
- Therefore, the solution becomes more basic
- The hydrolysis of this salt demonstrates why the equivalence point of a strong base – weak acid pH curve is above 7

Weak Acid and Weak Base

- In order to determine the pH of the resulting solution of a reaction between a weak acid and weak base we must take into account the K_a and K_b values
- Using the reaction between ammonia, NH_3 (aq), and ethanoic acid, CH_3COOH (aq), as an example:

$$NH_3 \text{ (aq)} + CH_3COOH \text{ (aq)} \rightarrow CH_3COONH_4 \text{ (aq)}$$

- Both the cation (positive ion) and anion ion (negative) produced will have acid–base properties

$$CH_3COO^- \text{ (aq)} + H_2O \text{ (l)} \rightarrow CH_3COOH \text{ (aq)} + OH^- \text{ (aq)}$$

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

$$K_a \text{(CATION)} = \frac{K_w}{K_b \text{ (PARENT BASE)}}$$

$$K_b \text{(ANION)} = \frac{K_w}{K_a \text{ (PARENT ACID)}}$$

*How to calculate the vales for the values of K_a (cation) and K_b (anion)*

- If the K_a is larger, the solution will be acidic
- If the K_b is larger the solution will be basic
- If $K_a = K_b$, then the pH will be 7

Metals

- Small metal ions that have a high charge will exhibit a high charge density
  - An example is Al^{3+}

- This makes the highly charged metal ions ideal for forming complexes as they can coordinately bond with ligands
- The complex formed can then act as a weak acid by releasing hydrogen ions when hydrolysed, H^+
- The high charge density of the metal ion increases the polarity of the water molecule pulling the electrons towards itself, until the O–H bond finally breaks

$$[Al(H_2O)_6]^{3+} \text{ (aq)} \rightarrow [Al(H_2O)_5(OH)]^{2+} \text{ (aq)} + H^+ \text{ (aq)}$$

- The metal ion must have a high enough charge and small radius for this to occur, consequently, 1+ and 2+ ions will not release H^+ ions and therefore decrease the pH of a solution
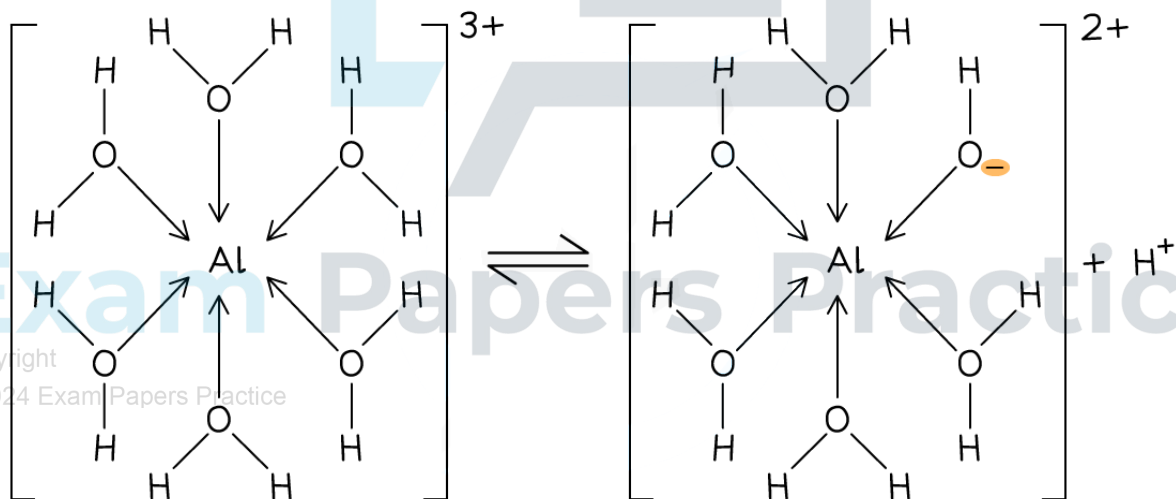
The $[Al(H_2O)_6]^{3+}$ (aq) releases an H+ ion decreasing the pH of the solution