HL IB Chemistry

Your notes

Proton Transfer Reactions

Contents

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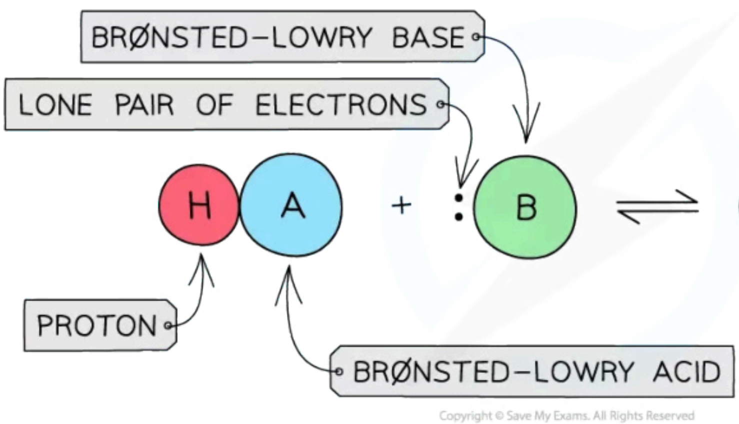
Brønsted–Lowry Acids & Bases

Brønsted–Lowry Acids & Bases

What are Brønsted–Lowry acids and bases?

- **The Brønsted–Lowry Theory** defines acids and bases in terms of proton transfer between chemical compounds
  - A **Brønsted–Lowry acid** is a species that **gives away** a **proton** (H^+)
  - A **Brønsted–Lowry base** is a species that **accepts** a proton (H^+) using its **lone pair of electrons**

Equilibrium of a Brønsted–Lowry acid and base

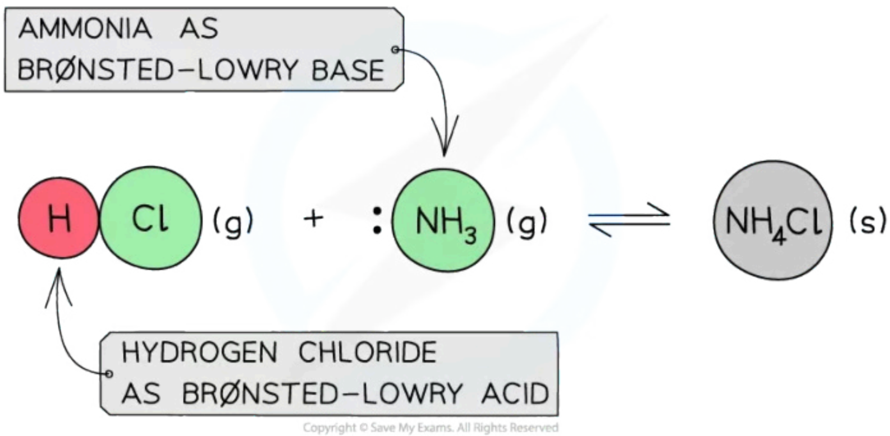


The diagram shows a Brønsted–Lowry acid which donates the proton to the Brønsted–Lowry base that accepts the proton using its lone pair of electrons

- The Brønsted-Lowry Theory is not limited to aqueous solutions only and can also be applied to reactions that occur in the gas phase

Diagram to show how hydrochloric acid acts as a Brønsted–Lowry acid and ammonia acts as a Brønsted–Lowry base

Your notes



Example of a Brønsted-Lowry acid and base reaction in the gas state

Worked example

Identify the correct role of the species in the following reaction:

$$H_2PO_4^-(aq) + H_2O(l) \rightarrow HPO_4^{2-}(aq) + H_3O^+(aq)$$

	Brønsted-Lowry acid	Brønsted-Lowry base
A	$H_2PO_4^-$	H_2O
B	$H_2PO_4^{2-}$	$H_2PO_4^-$
C	$H_2PO_4^-$	H_3O^+
D	H_2O	$H_2PO_4^-$

Answer:

- The correct option is **A**.
  - $H_2PO_4^-$ is donating a proton to H_2O
  - So, $H_2PO_4^-$ must be an acid and H_2O must be a base

Examiner Tip

- An atom of hydrogen contains 1 **proton**, 1 electron and 0 neutrons
- When hydrogen loses an electron to become **H^+** only a **proton** remains, which is why a H^+ ion is also called a proton.

Your notes

Conjugate Acids & Bases

Your notes

Conjugate Acids & Bases

- A **Brønsted-Lowry acid** is a species that can donate a proton
- A **Brønsted-Lowry base** is a species that can accept a proton
- In an equilibrium reaction, the products are formed at the same rate as the reactants are used

$$\underset{\text{acid}}{CH_3COOH\,(aq)} + \underset{\text{base}}{H_2O\,(l)} \rightleftharpoons \underset{\text{conjugate base}}{CH_3COO^-\,(aq)} + \underset{\text{conjugate acid}}{H_3O^+\,(aq)}$$

- The reactant CH_3COOH is linked to the product CH_3COO^- by the transfer of a **proton** from the acid to the base
  - Similarly, the H_2O molecule is linked to H_3O^+ ion by the transfer of a proton
- These pairs are therefore called **conjugate acid-base pairs**
  - A **conjugate acid-base pair** is two species that are different from each other by a H^+ ion
    - **Conjugate** here means related
    - In other words, the acid and base are related to each other by one proton difference

Worked example

In the equilibrium reaction shown below, which species are a conjugate acid-base pair?

$$\mathbf{CH_3CH_2CH_2COOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CH_2CH_2COO^-\,(aq) + H_3O^+\,(aq)}$$

A. $CH_3CH_2CH_2COOH$ and H_2O

B. H_2O and H_3O^+

C. H_2O and $CH_3CH_2CH_2COO^-$

D. $CH_3CH_2CH_2COO^-$ and H_3O^+

Answer:

- The correct option in **B**
  - A conjugate acid-base pair differ only by an H^+ ion

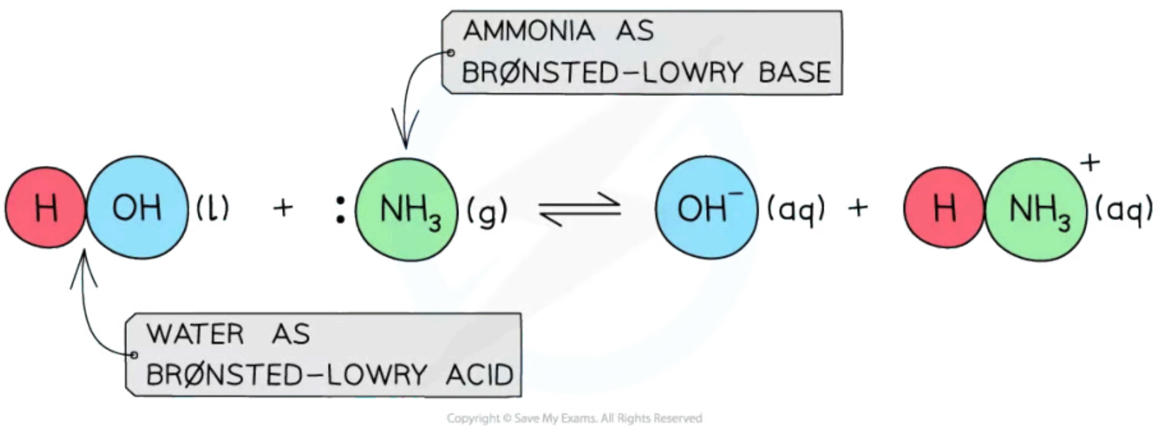
Amphiprotic Species

Amphiprotic Species

- Species that can act both as proton donors and acceptors are called **amphiprotic**

Water as a Brønsted-Lowry acid

Diagram to show how water is amphiprotic

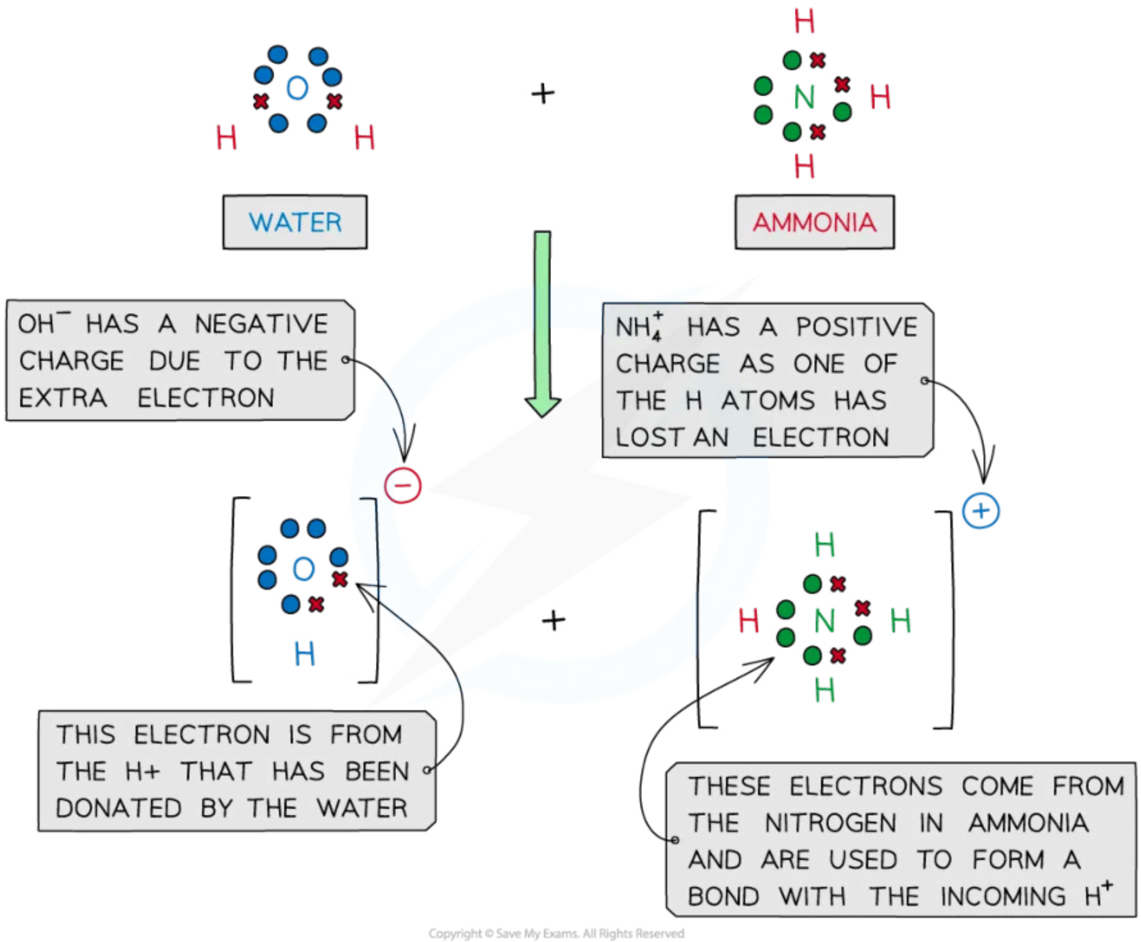


The diagram shows water acting as a Brønsted-Lowry acid by donating a proton to ammonia which accepts the proton using its lone pair of electrons

Lewis diagram for the reaction between water and ammonia

Your notes

Your notes

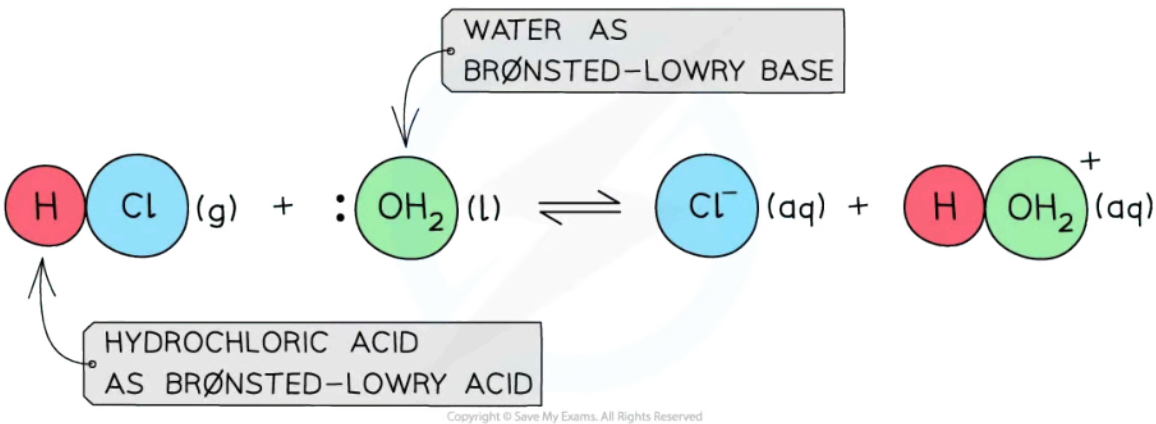


The Lewis diagram for the reaction of water with ammonia to show how water acts as a Brønsted-Lowry acid and ammonia as a Brønsted-Lowry base

Water as a Brønsted-Lowry base

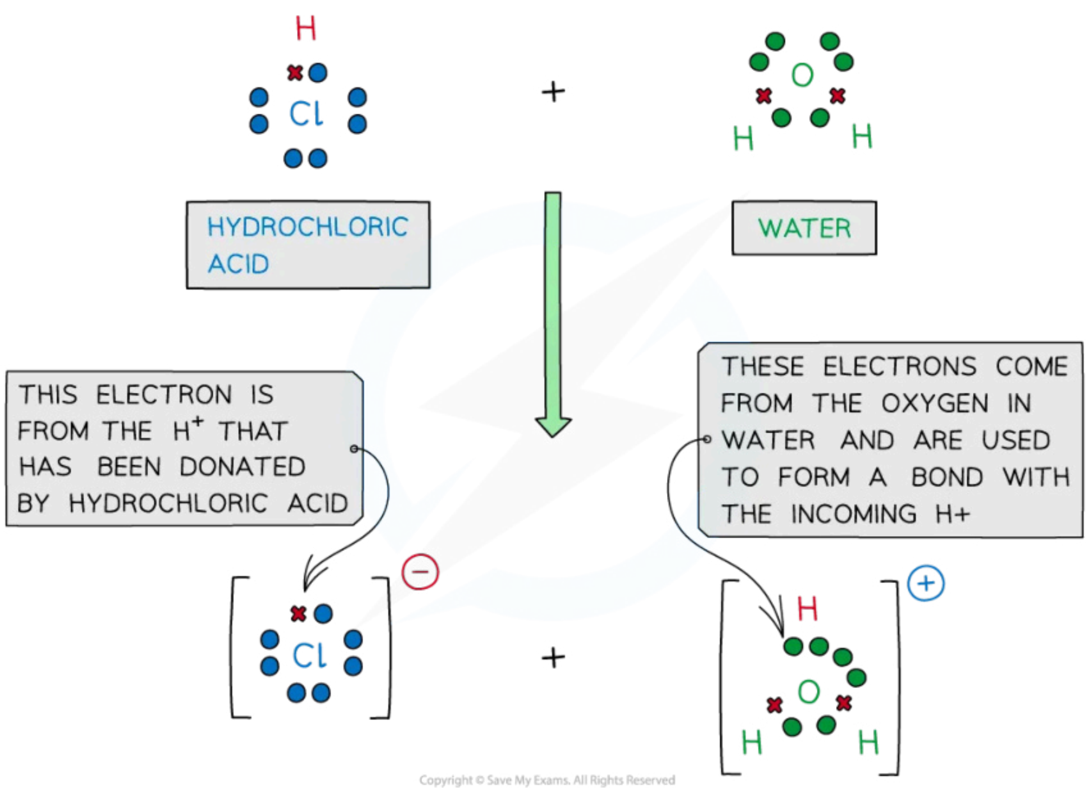
Diagram to show how water is amphiprotic

Your notes



The diagram shows water acting as a Brønsted-Lowry base by accepting a proton from hydrochloric acid proton using its lone pair of electrons

Lewis diagram for the reaction between water and hydrochloric acid



The Lewis diagram for the reaction of water with hydrochloric acid to show how water acts as a Brønsted-Lowry base and ammonia as a Brønsted-Lowry acid

What is the difference between amphiprotic and amphoteric?

Your notes

- A compound that is **amphoteric** means it has both basic and acidic character
  - When the compound reacts with an acid, it shows that it has basic character
  - When it reacts with a base, it shows that it's acidic
  - An example of this is aluminium oxide which reacts with both hydrochloric acid and sodium hydroxide:

$$Al_2O_3\,(s) + 6HCl\,(aq) \rightarrow 2AlCl_3\,(aq) + 3H_2O\,(l)$$

$$Al_2O_3\,(s) + 2NaOH\,(aq) + 3H_2O\,(l) \rightarrow 2NaAl(OH)_4\,(aq)$$

- When a compound is **amphiprotic**, it means it can act as a proton donor and as a proton acceptor
- Aluminium oxide is not amphiprotic, even though it is amphoteric

Amphiprotic versus Amphoteric Table

Amphiprotic	Amphoteric
The term amphiprotic describes a substance that can both accept and donate a proton or H^+	The term amphoteric refers to the ability to act as both an acid and a base
Amphiprotic substances can both accept or donate protons	Amphoteric substances can act as both an acid and a base
All amphiprotic substances are amphoteric	Not all amphoteric substances are amphiprotic

The pH Scale

Your notes

The pH Scale

- The acidity of an aqueous solution depends on the number of **H^+** (**H_3O^+**) ions in the solution
- **pH** is defined as:

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

  - Where $[H^+]$ is the concentration of H^+ in mol dm^{-3}
- The pH scale is a logarithmic scale with base 10
- This means that each value is 10 times the value below it
  - For example, pH 5 is 10 times more acidic than pH 6.
- pH values are usually given to 2 decimal places
- The relationship between concentration is easily seen in the following table:

pH & $[H^+]$ Table

$[H^+]$	Scientific notation	pH
1.0	10^0	0
0.1	10^{-1}	1
0.01	10^{-2}	2
0.001	10^{-3}	3
0.0001	10^{-4}	4
-	10^{-x}	x

Worked example

10.0 cm^3 of an aqueous solution of nitric acid of pH = 1.0 is mixed with 990.0 cm^3 of distilled water. What is the pH of the final solution?

A. 1

B. 2

C. 3

D. 10

Answer:

- The correct option is **C**.
  - The total volume after dilution is 1000.0 cm^3
  - So, the concentration of H^+ has been **reduced** by a factor of 100 or 10^{-2}
  - This means an increase of 2 pH units
  - Therefore, the final solution is **pH 3**

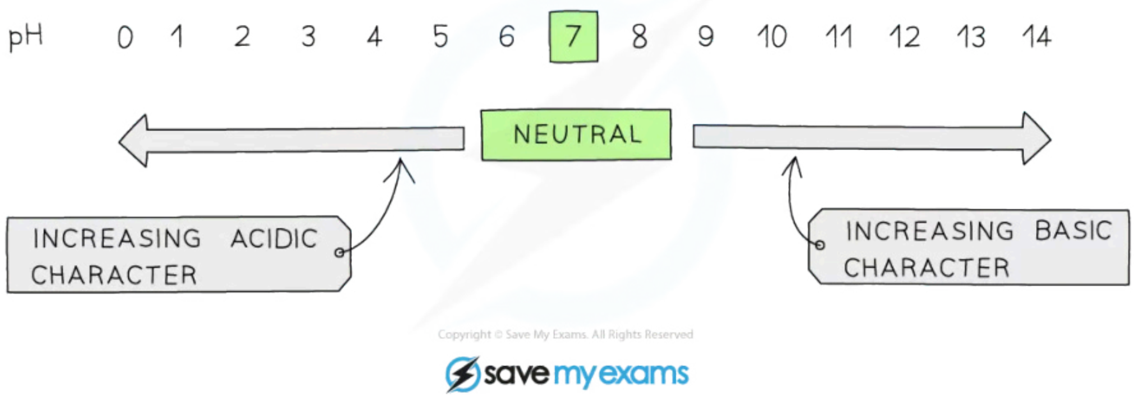
Examiner Tip

- Make sure you know how to use the antilog (base 10) feature on your calculator
  - On most calculators, it is the 10^x button
  - But on other models, it could be LOG^{-1}, ALOG or even a two-button sequence such as INV + LOG

- The pH scale is a numerical scale that shows how **acidic** or **alkaline** a solution is
- The values on the pH scale go from 0 - 14 (extremely acidic substances have values of below 0)
- All acids have pH values **below** 7, all alkalis have pH values **above** 7
  - The **lower** the pH then the **more acidic** the solution is
  - The **higher** the pH then the **more alkaline** the solution is

The pH scale

Your notes



The pH scale showing acidity, neutrality and alkalinity

pH of acids

- **Acidic** solutions (strong or weak) **always** have more H^+ than OH^- ions
- Since the concentration of $\mathbf{H^+}$ is always **greater** than the concentration of $\mathbf{OH^-}$ ions, $[H^+]$ is always **greater** than 10^{-7} mol dm^{-3}
- Using the pH formula, this means that the **pH of acidic solutions** is always **below** 7
- The higher the $[H^+]$ of the acid, the lower the pH

pH of bases

- **Basic** solutions (strong or weak) **always** have more OH^- than H^+ ions
- Since the concentration of $\mathbf{OH^-}$ is always **greater** than the concentration of $\mathbf{H^+}$ ions, $[H^+]$ is always **smaller** than 10^{-7} mol dm^{-3}
- Using the pH formula, this means that the **pH of basic solutions** is always **above** 7
- The higher the $[OH^-]$ of the base, the higher the pH

pH of water

- Water at 298K has **equal amounts** of $\mathbf{OH^-}$ and $\mathbf{H^+}$ **ions** with concentrations of $\mathbf{10^{-7}}$ **mol** $\mathbf{dm^{-3}}$
- To calculate the pH of water, the following formula should be used:

$$pH = -\log_{10}[H^+(aq)]$$

$$[H^+(aq)] = \text{concentration of } H^+/H_3O^+ \text{ ions}$$

$$pH = -\log(10^{-7}) = 7$$

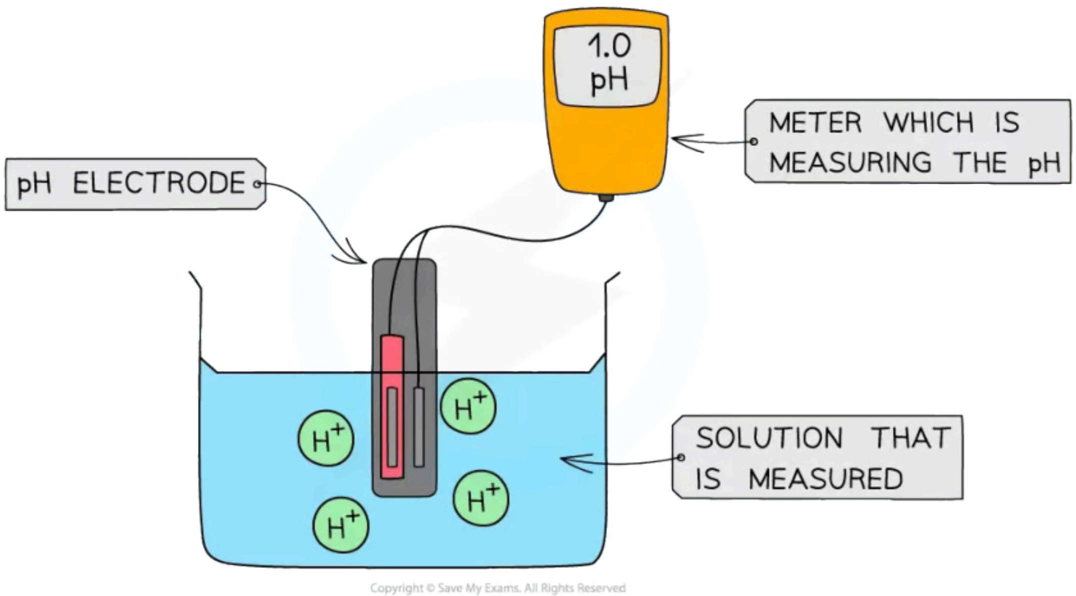
- Thus, water has a pH of 7 at 298 K

How to measure pH

- The most **accurate** way to determine the pH is by reading it off a **pH meter**
- The pH meter is connected to the **pH electrode** which shows the pH value of the solution

Using a pH meter

Your notes

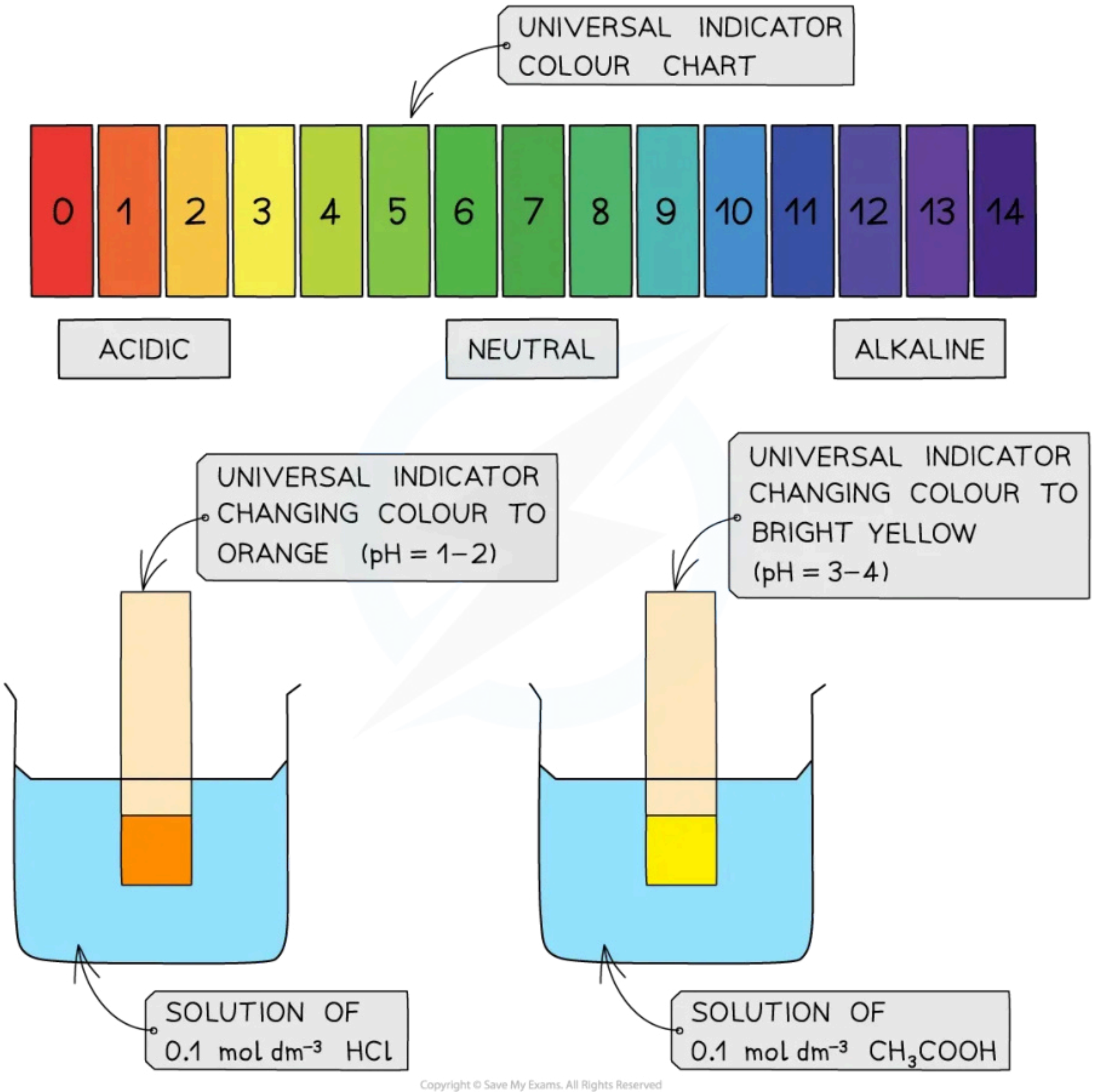


The diagram shows a digital pH meter that measures the pH of a solution using a pH electrode

- A less accurate method is to measure the pH using universal indicator paper
- The universal indicator paper is dipped into a solution of acid upon which the paper changes colour
- The colour is then compared to those on a chart which shows the colours corresponding to different pH values

Using universal indicator

Your notes



The diagram shows the change in colour of the universal indicator paper when dipped in a strong (HCl) and weak (CH_3COOH) acid. The colour chart is used to read off the corresponding pH values which are between 1–2 for HCl and 3–4 for CH_3COOH

The Ion Product of Water

Your notes

The Ion Product of Water

pH of water

- An equilibrium exists in water, where a few water molecules dissociate into proton and hydroxide ions

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

- The equilibrium constant for this reaction is:

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

$$K_c \times [H_2O] = [H^+][OH^-]$$

- Since the concentration of the H^+ and OH^- ions is very small, the concentration of water is considered to be a constant
- This means that the expression can be rewritten as:

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

  - Where K_w **(ion product of water) = $K_c \times [H_2O]$ = $1.00\ 10^{-14}$ at 298K**

- The product of the two ion concentrations is always $\mathbf{1.00 \times 10^{-14}}$
- This makes it straightforward to see the relationship between the two concentrations and the nature of the solution:

$[H^+]$ & $[OH^-]$ Table

$[H^+]$	$[OH^-]$	Type of solution
0.1	1×10^{-13}	acidic
1×10^{-3}	1×10^{-11}	acidic
1×10^{-5}	1×10^{-9}	acidic
1×10^{-7}	1×10^{-7}	neutral
1×10^{-9}	1×10^{-5}	alkaline
1×10^{-11}	1×10^{-3}	alkaline
1×10^{-13}	0.1	alkaline

Your notes

Worked example

What is the pH of a solution of potassium hydroxide, KOH (aq) of concentration 1.0×10^{-3} mol dm^{-3}?

$K_w = 1.0 \times 10^{-14}$ at 298 K

A. 3

B. 4

C. 10

D. 11

Answer:

- The correct option is **D**.
  - Since $K_w = [H^+][OH^-]$, rearranging gives $[H^+] = K_w \div [OH^-]$
  - The concentration of $[H^+]$ is $(1.0 \times 10^{-14}) \div (1.0 \times 10^{-3}) = 1.0 \times 10^{-11}$ mol dm^{-3}
  - So the **pH = 11**

How does temperature affect the ion product of water, K_w?

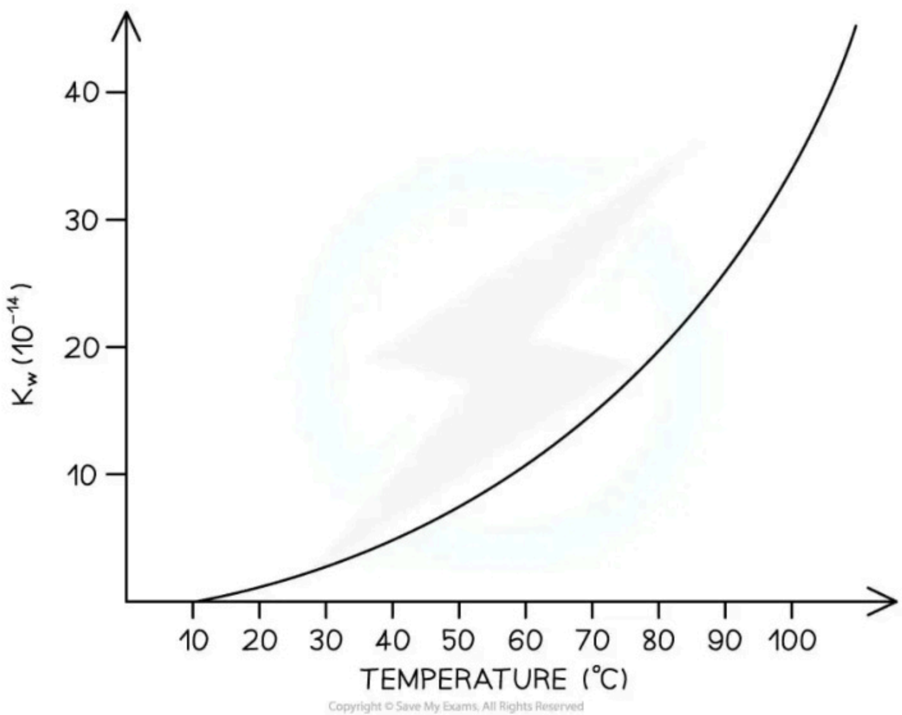
- The ionisation of water is an **endothermic** process

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

- In accordance with Le Châtelier's principle, an increase in temperature will result in the forward reaction being favoured
  - This causes an increase in the concentration of the hydrogen and hydroxide ions
  - This leads to the **magnitude of K_w increasing**
  - Therefore, the **pH will decrease**
- Increasing the temperature decreases the pH of water (becomes more acidic)
- Decreasing the temperature increases the pH of water (becomes more basic)

Graph to show how K_w changes with temperature

Your notes



As temperature increases, K_w increases so pH decreases

Strong & Weak Acids

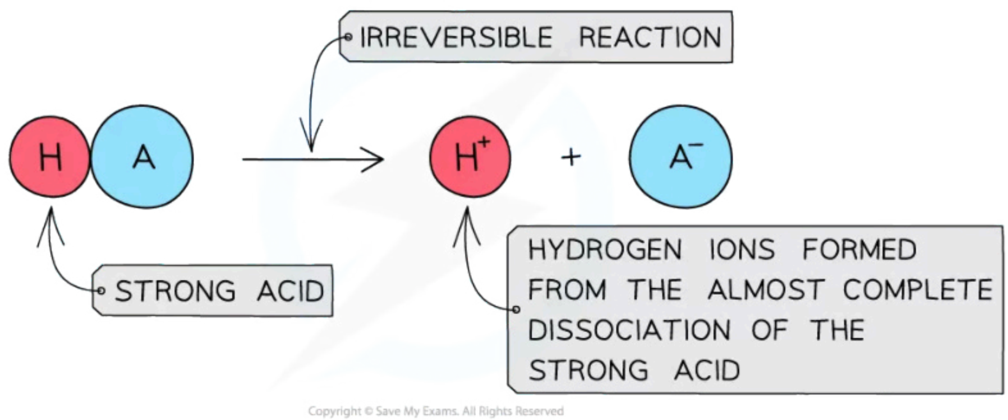
Your notes

Strong & Weak Acids

Strong acids

- A **strong acid** is an acid that **dissociates** almost **completely** in aqueous solutions
  - Examples include HCl (hydrochloric acid), HNO_3 (nitric acid) and H_2SO_4 (sulfuric acid)
  - The position of the equilibrium is so far over to the **right** that you can represent the reaction as an irreversible reaction

Diagram to show the dissociation of a strong acid



The diagram shows the complete dissociation of a strong acid in aqueous solution

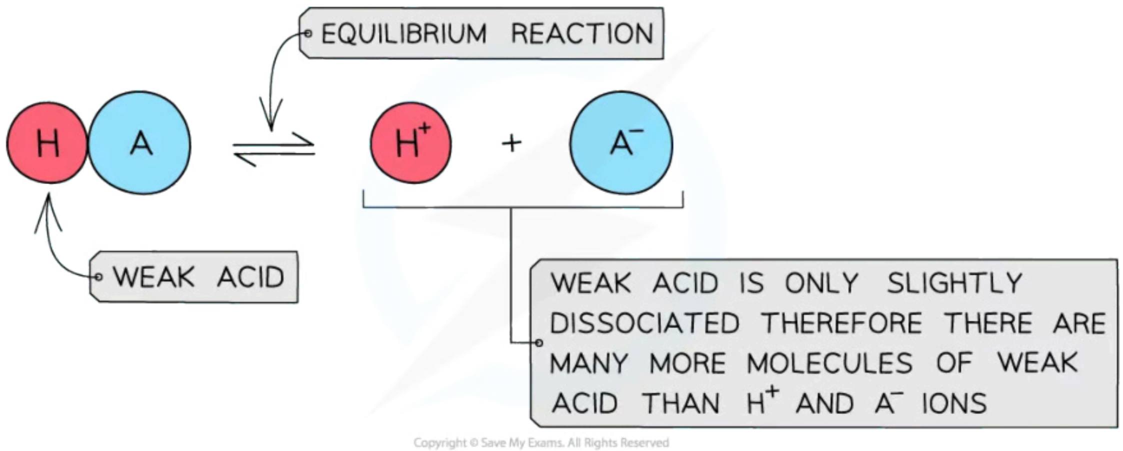
- The solution formed is **highly acidic** due to the high concentration of the H^+/H_3O^+ ions
- Since the **pH** depends on the concentration of H^+/H_3O^+ ions, the pH can be calculated if the concentration of the strong acid is known
  - $pH = -log_{10}[H^+ (aq)]$
  - [H+ (aq)] = concentration of H^+ / H_3O^+ ions
  - pH is the negative log of the concentration of H^+ / H_3O^+ ions and can be calculated if the concentration of the strong acid is known using the stoichiometry of the reaction

Weak acids

- A **weak acid** is an acid that **partially** (or incompletely) **dissociates** in aqueous solutions
  - E.g. most organic acids (ethanoic acid), HCN (hydrocyanic acid), H_2S (hydrogen sulfide) and H_2CO_3 (carbonic acid)
  - The position of the equilibrium is more towards the **left** and an equilibrium is established

Diagram to show the dissociation of a weak acid

Your notes



The diagram shows the partial dissociation of a weak acid in aqueous solution

- The solution is **less acidic** due to the lower concentration of H^+ / H_3O^+ ions

Acid & Equilibrium Position Table

	Strong Acids	Weak Acid
Position of equilibrium	Right	Left
Dissociation	Completely (→)	Partially (⇌)
H^+ concentration	High	Low
pH	Use [strong acid] to calculate pH	Use K_a to find $[H^+]$
Examples	HCl HNO_3 H_2SO_4 (first ionisation)	Organic acids (ethanoic acid) HCN H_2S H_2CO_3

- The strength of a Brønsted-Lowry acid depends on the ease with which it dissociates to release H^+ ions
  - This depends upon the strength of the bond that has to be broken to release H+

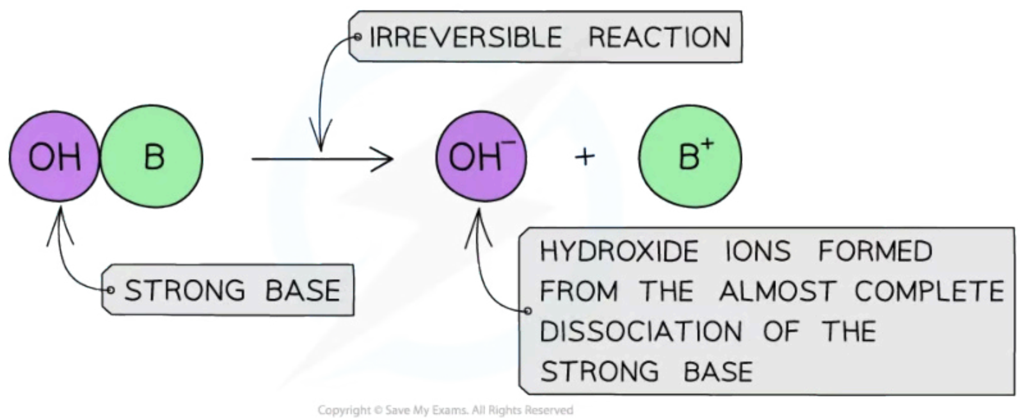
Your notes

- For example, for hydrogen halides, the size of the halogen atom increases in size going down Group 17 which increases the length of the H–X bond
- As longer bonds are weaker they need less energy to break
- The acid strength of the hydrogen halides increases down Group 17
  - HF < HCl < HBr < HI

Strong bases

- A **strong base** is a base that dissociates almost completely in aqueous solutions
  - E.g. group 1 metal hydroxides such as NaOH (sodium hydroxide)
  - The position of the equilibrium is so far over to the right that you can represent the reaction as an irreversible reaction

Diagram to show the dissociation of a strong base



The diagram shows the complete dissociation of a strong base in aqueous solution

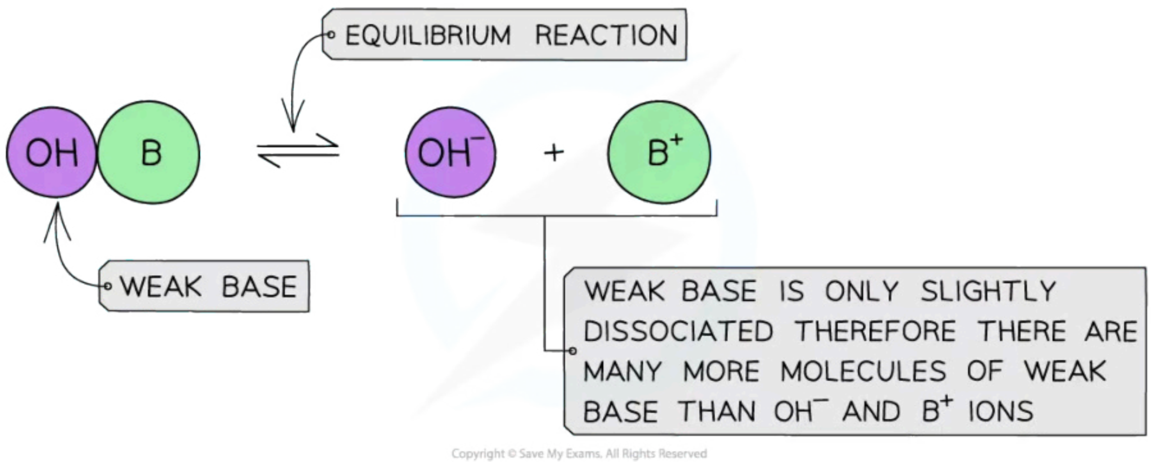
- The solution formed is highly basic due to the high concentration of the OH^- ions

Weak bases

- A **weak base** is a base that **partially** (or incompletely) **dissociates** in aqueous solutions
  - NH_3 (ammonia), amines and some hydroxides of transition metals
  - The position of the equilibrium is more to the **left** and an equilibrium is established

Diagram to show the dissociation of a weak base

Your notes



The diagram shows the partial dissociation of a weak base in aqueous solution

- The solution is **less basic** due to the lower concentration of OH^- ions

Base & Equilibrium Position Table

	Strong Base	Weak Base
Position of equilibrium	Right	Left
Dissociation	Completely (→)	Partially (⇌)
OH^- concentration	High	Low
Examples	Group 1 metal hydroxides	NH_3 Amines Some transition metal hydroxides

Strength of conjugate acids and bases

Your notes

- The conjugate base of HCl is the chloride ion, Cl^-,
- However, since the reverse reaction is virtually non-existent the chloride ion must be a very weak conjugate base

$$HCl\ (g) \rightarrow H^+\ (aq) + Cl^-\ (aq)$$

acid **conjugate base**

- In general, **strong acids** produce **weak conjugate bases** and **weak acids** produce **strong conjugate bases**
- A strong base is also fully ionised and is a good proton acceptor
- For example, the hydroxide ion is a strong base and readily accepts protons:

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

- The conjugate acid of the hydroxide ion is water, which is a weak conjugate acid
- In general **strong bases** produce **weak conjugate acids**

Examiner Tip

- Hydrogen ions in aqueous solutions can be written as either as H_3O^+ or as H^+
  - However, if H_3O^+ is used, H_2O should be included in the chemical equation:

$$HCl\ (g) \rightarrow H^+\ (aq) + Cl^-\ (aq) \text{ OR } HCl\ (g) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

- Some acids contain two replaceable protons (called '**dibasic**')
  - For example, H_2SO_4 (sulfuric acid) has two ionisations
    - H_2SO_4 acts as a strong acid: $H_2SO_4 \rightarrow H^+ + SO_4^-$
    - HSO_4^- acts as a weak acid: $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$
    - The second ionisation is only partial which is why the concentration of 1 mol dm^{-3} sulfuric acid is not 2 mol dm^{-3} in H^+ ions
- Also, don't forget that the terms **strong** and **weak** acids and bases are related to the **degree of dissociation** and not the **concentration**
  - The appropriate terms to use when describing **concentration** are **dilute** and **concentrated**

How to distinguish between strong and weak acid

- Strong and weak acids can be distinguished from each other by their:
  - **pH value** (using a pH meter or universal indicator)
  - **Electrical conductivity**
  - **Reactivity**

pH value

- An acid **dissociates** into H^+ in solution according to

$$HA \rightarrow H^+ + A^-$$

pH value of a Strong Acid & Weak Acid Table

Acid	pH of 0.1 mol dm^{-3} solution

Your notes

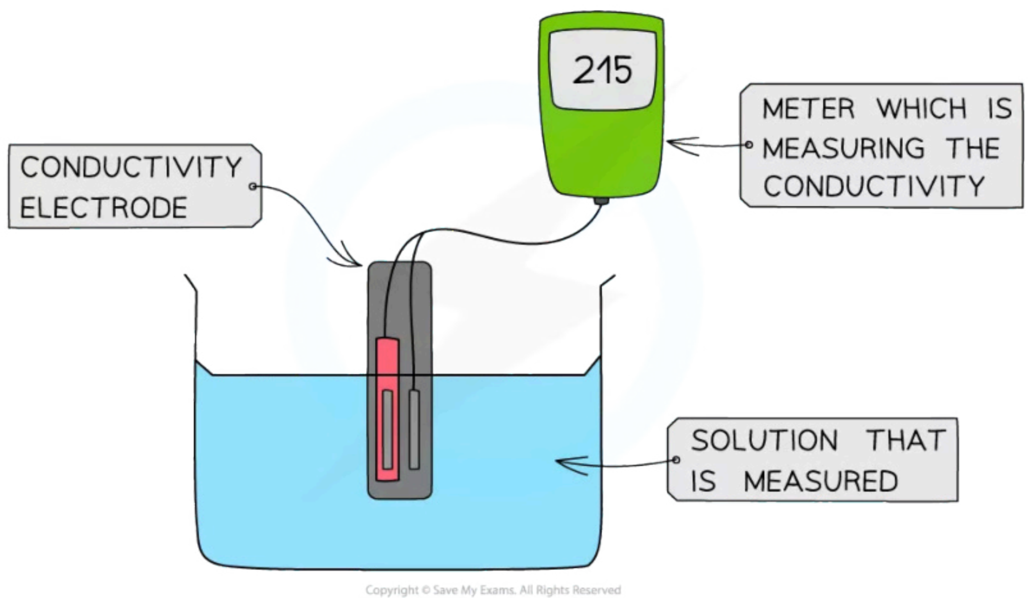
HCl (strong)	1
CH_3COOH (weak)	2.9

- The **stronger** the acid, the **greater** the **concentration of H^+** and therefore the **lower the pH**

Electrical conductivity

- Since a **stronger acid** has a **higher concentration of H^+** it **conducts electricity** better
- Stronger acids therefore have a greater **electrical conductivity**
- The electrical conductivity can be determined by using a **conductivity meter**
- Like the pH meter, the conductivity meter is connected to an electrode
- The conductivity of the solution can be read off the meter

Diagram to show how to measure the electrical conductivity of an acid



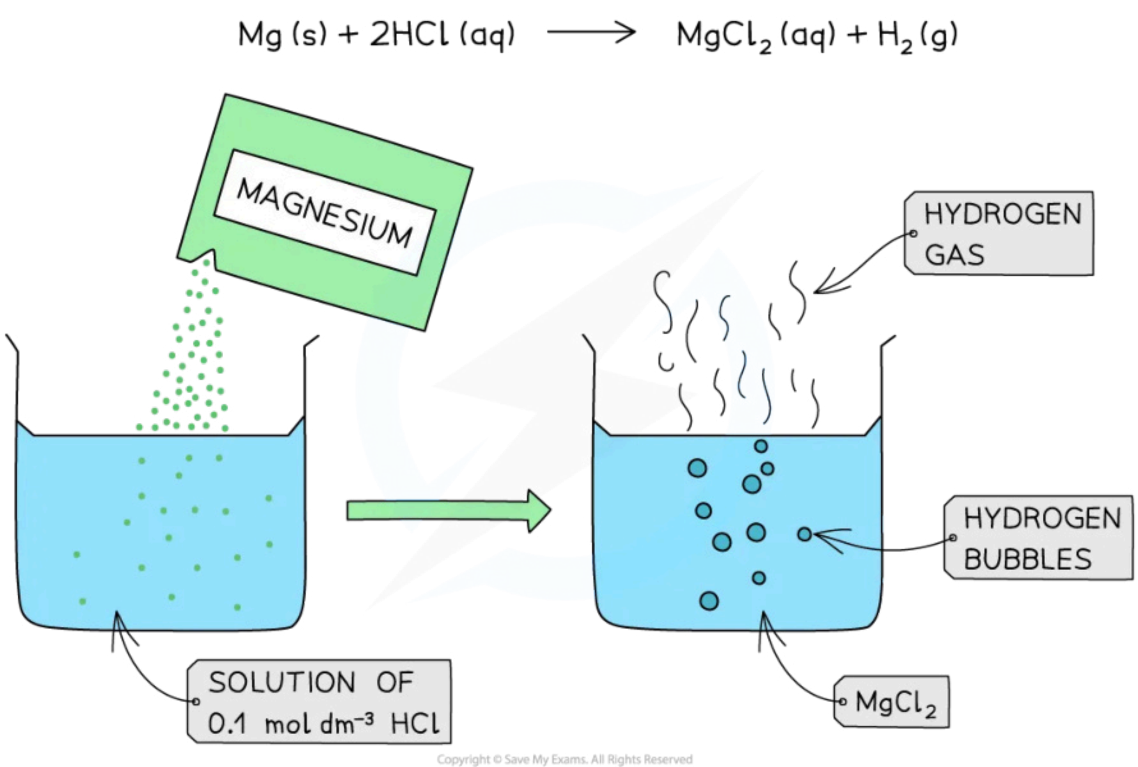
A digital conductivity meter measures the electrical conductivity of a solution using an electrode

Reactivity

- Strong and weak acids of the **same concentrations** react differently with reactive metals
- This is because the concentration of H^+ is greater in strong acids compared to weak acids
- The greater H^+ concentration means that more H_2 gas is produced in a shorter time

Diagram to show how a strong acid reacts with magnesium

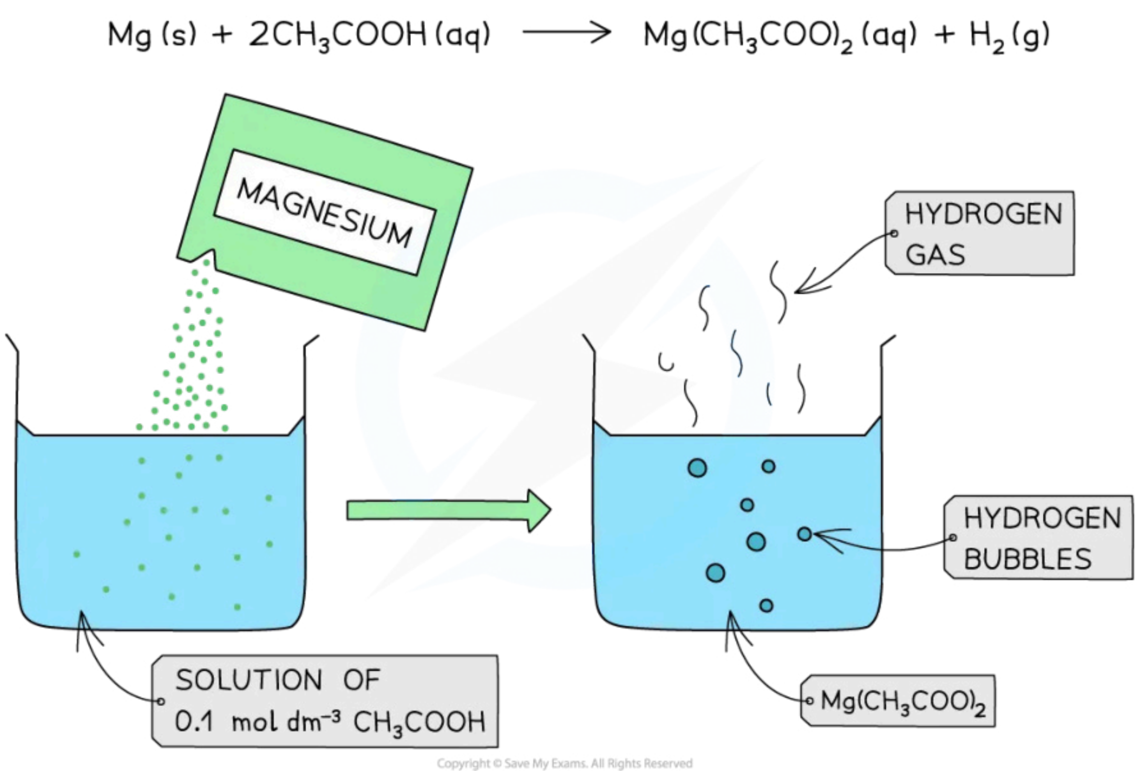
Your notes



The diagram shows the reaction of 0.1 mol dm^{-3} of a strong acid (HCl) with Mg. The reaction produces a lot of bubbles and hydrogen gas due to the high concentration of H$^+$ present in solution

Diagram to show how a weak acid reacts with magnesium

Your notes



The diagram shows the reaction of 0.1 mol dm^{-3} of a weak acid (CH_3COOH) with Mg. The reaction produces fewer bubbles of hydrogen gas due to the lower concentration of H^+ present in solution

- Similar observations would be made in the reaction between strong and weak acids with **carbonates** and **hydrogencarbonates**, although the gas given off this time is carbon dioxide
- With **oxides** and **hydroxides**, there may not be a lot of visible changes although it is likely that they would **dissolve faster** in a strong acid than in a weak acid
- These reactions are also likely to produce **larger enthalpy changes** which could be seen in **higher temperature rises**

Examiner Tip

- The above-mentioned properties of strong and weak acids depend on their ability to dissociate and form H^+ ions
- Stronger acids dissociate more
  - This means that they produce a greater concentration of H^+ ions resulting in:
    - Lower pH values
    - Greater electrical conductivity
    - More vigorous reactions with reactive metals.

Your notes

Neutralisation Reactions

Neutralisation Reactions

- A neutralization reaction is one in which an acid (pH <7) and a base/alkali (pH >7) react together to form water (pH = 7) and a salt:

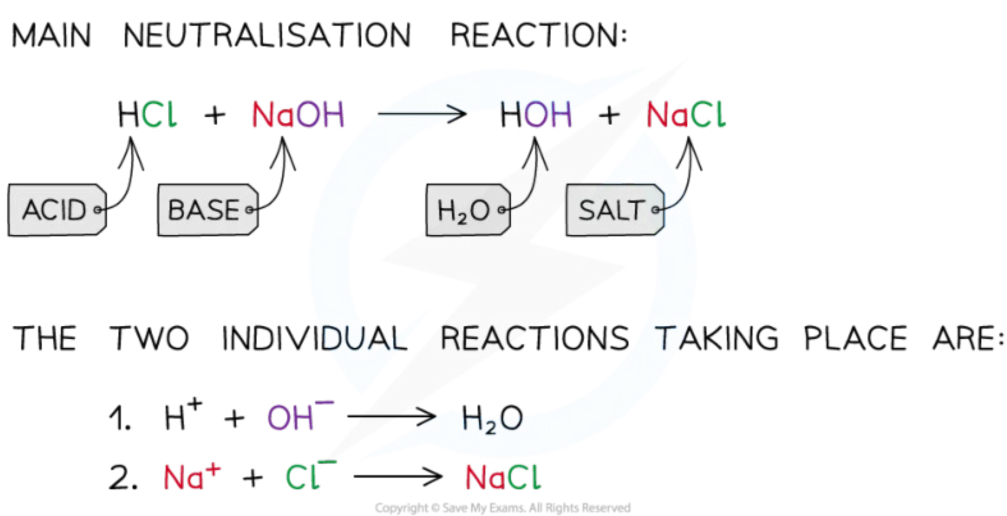
acid + base (alkali) → salt + water

- The proton of the acid reacts with the hydroxide of the base to form water:

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

- The spectator ions which are not involved in the formation of water, form the salt

Diagram to show neutralisation between an acid and a base



The diagram shows a neutralisation reaction of HCl and NaOH and the two individual reactions that take place to form the water and salt

- The name of the salt produced can be predicted from the acid that has reacted

Acid Reacted & Salt Table

Acid reacted	Salt produced
Hydrochloric acid	A chloride
Nitric acid	A nitrate
Sulfuric acid	A sulfate

Your notes

Examiner Tip

- The enthalpy of neutralisation is the enthalpy change that occurs when an acid reacts with a base to form one mole of water
- Since the reaction between strong acids and strong bases is the same regardless of the acid or base, it should be no surprise the enthalpy change is the same and is approximately -57 kJ mol^{-1}

Metals and acids

- The typical reaction of a metal and an acid can be summarised as

acid + metal → salt + hydrogen

- For example:

$$2HCl\,(aq) + Zn\,(s) \rightarrow ZnCl_2\,(aq) + H_2\,(g)$$

hydrochloric acid + zinc → zinc chloride + hydrogen

- Clearly, the extent of the reaction depends on the **reactivity** of the metal and the **strength** of the acid
- Very reactive metals would react dangerously with acids and these reactions are not usually carried out
- Metals low in **reactivity** do not react at all
  - For instance, copper does not react with dilute acids
- **Stronger acids** will react **more vigorously** with metals than weak acid
- What signs of reaction would be expected to be different between the two?
  - Faster reaction, seen as:
    - More effervescence
    - The metal dissolves faster
    - More exothermic

Metals and oxides

- The reaction of an acid with a metal oxide forms two products:

acid + metal oxide → salt + water

- For example:

$$2HCl\,(aq) + CaO\,(s) \rightarrow CaCl_2\,(aq) + H_2O\,(l)$$

hydrochloric acid + calcium oxide → calcium chloride + water

Metals and hydroxides

- The reaction with a metal hydroxide and an acid follows the same pattern as an oxide:

acid + metal hydroxide → salt + water

- A suitable example might be:

$$H_2SO_4\,(aq) + Mg(OH)_2\,(s) \rightarrow MgSO_4\,(aq) + 2H_2O\,(l)$$

Your notes

sulfuric acid + magnesium hydroxide → magnesium sulfate + water

Metals and carbonates

- The reaction between a metal carbonate and an acid produces three products:

acid + metal carbonate → salt + water + carbon dioxide

- For example:

$$2HNO_3\,(aq) + CuCO_3\,(s) \rightarrow Cu(NO_3)_2\,(aq) + H_2O\,(l) + CO_2\,(g)$$

nitric acid + copper carbonate → copper nitrate + water + carbon dioxide

Metals and hydrogencarbonates

- The reaction between a metal hydrogencarbonate and an acid is the same as the carbonate reaction with a slight difference in stoichiometry:

acid + metal hydrogencarbonate → salt + water + carbon dioxide

- An example of this would be:

$$HCl\,(aq) + NaHCO_3\,(s) \rightarrow NaCl\,(aq) + H_2O\,(l) + CO_2\,(g)$$

hydrochloric acid + sodium hydrogencarbonate → sodium chloride + water + carbon dioxide

Examiner Tip

Make sure you learn the formulae of the common acids and bases and that you can write examples of balanced equations of their characteristic reactions

- The acids and bases needed to make different salts can be deduced using the principles covered in the previous section
- The table below summarises these reactions

Making Salts Table

Type of salt	Ion	Acid needed	Formula	Base needed
Sulfates	SO_4^{2-}	sulfuric	H_2SO_4	metal oxide, hydroxide, carbonate or hydrogen carbonate
Nitrates	NO_3^-	nitric	HNO_3	
Chlorides	Cl^-	hydrochloric	HCl	
Ethanoates	CH_3COO^-	ethanoic	CH_3COOH	
Ammonium	NH_4^+	any	-	aqueous ammonia

Note that although some metals can be used to make salts, they are not classified as bases as water is not a product of the reaction

Your notes

Worked example

Which are the products of the reaction between zinc oxide and hydrochloric acid?

A. zinc chloride and carbon dioxide

B. zinc chloride, hydrogen gas and water

C. zinc, hydrogen gas and water

D. zinc chloride and water

Answer:

- The correct option is **D**.
  - Metal oxides react with acids to produce a salt and water as the only products

Your notes

pH Curves

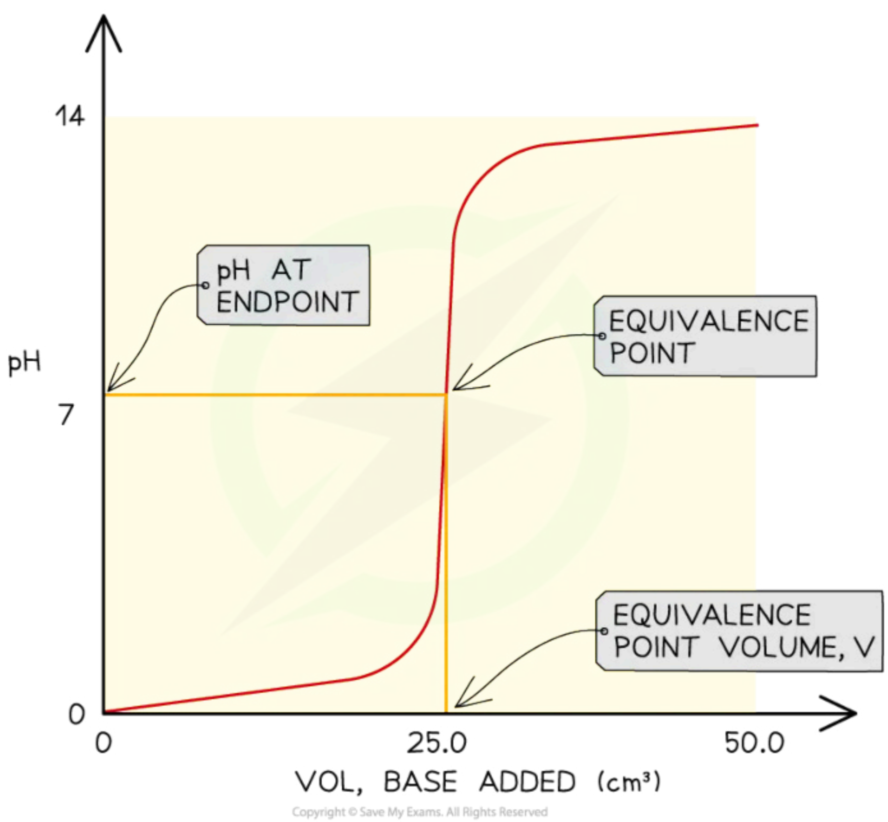
pH Curves

Strong acid - strong base pH curve

- 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 in a strong acid - strong base titration, e.g.

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

Diagram to show the general characteristics of a strong acid-strong base pH curve



The characteristics 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**

Your notes

- 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

How to calculate the pH depending on the volume of base added

- If base is added to the conical flask then the pH of the solution will rise during the titration
- Let's look at the reaction between 50 cm^3 of 0.10 mol dm^{-3} HCl (aq) and 50 cm^3 of 0.10 mol dm^{-3} of NaOH (aq)

HCl (aq) + NaOH (aq) → NaCl (aq) + H_2O (l)

- At the **start:**
  - At the start of the titration, the conical flask will only contain a strong acid so the pH can be calculated by
    - pH = $-\log_{10}[H^+]$
    - pH = $-\log_{10}[0.10]$ = 1.0

- After **25.00 cm^3** of **NaOH** has been added
  - Now, we must consider what is in excess
  - There is more acid in the flask than base in terms of volume, some of the acid has been neutralised, so we must calculate the excess moles of one of the reactants using n = c (mol dm^{-3}) x v (dm^3)
    - n(HCl) = 0.10 x 0.050 = 0.0050 mol
    - n(NaOH) = 0.10 x 0.025 = 0.0025 mol
    - n(Excess HCl) = 0.0050 - 0.0025 = 0.00250 mol
      - New volume = 0.0750 dm^3
    - $[H^+] = \frac{0.0025}{0.0750}$ = 0.0333 mol dm^{-3}
    - so pH = 1.5

- After **49.00 cm^3** of **NaOH** has been added
  - n(HCl) = 0.10 x 0.050 = 0.0050 mol
  - n(NaOH) = 0.10 x 0.049 = 0.0049 mol
  - n(Excess HCl) = 0.0050 - 0.0049 = 0.0001 mol
    - New volume = 0.0990 dm^3
  - $[H^+] = \frac{0.0001}{0.0990}$ = 0.00101 mol dm^{-3}
  - so pH = 3.0

- After **50.00 cm^3** of **NaOH** has been added the acid has been completely neutralised by the base, so the solution only contains NaCl and H_2O, therefore the pH = 7.0
- After **51.00 cm^3** of **NaOH** has been added
  - n(Added NaOH) = 0.10 x 0.051 = 0.0051 mol
  - n(Excess NaOH) = 0.0051 - 0.0050 = 0.0001 mol

- New volume = 0.101 dm^3
- $[OH^-] = \frac{0.0001}{0.101} = 0.00099$ mol dm^{-3}
- p**OH** = 3.0
- so pH = 11.0

Your notes

Interpreting pH Curves (HL)

Your notes

Interpreting pH Curves

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

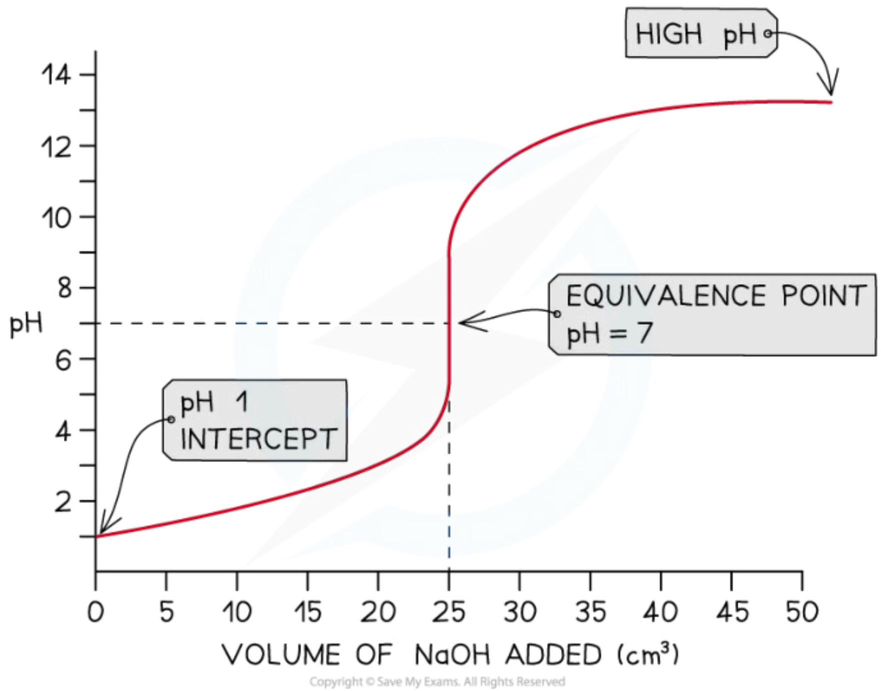
- In this example, sodium hydroxide, NaOH (aq), is being added to hydrochloric acid, HCl (aq)

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

- 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

Diagram to show a strong acid – strong base pH curve

Your notes



Strong acid – strong base pH curve. The equivalence point is at pH 7

Weak Acid + Strong Base

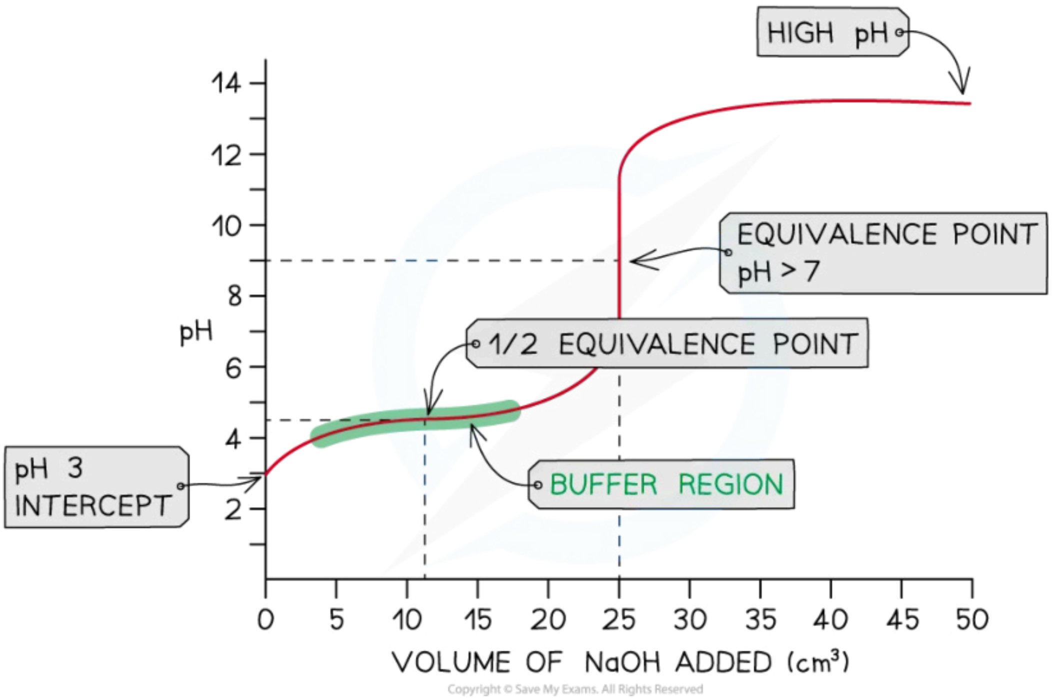
- In this example, strong sodium hydroxide, NaOH (aq), is being added to weak ethanoic acid, CH_3COOH (aq)

NaOH (aq) + CH_3COOH (aq) → 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**

Diagram to show a strong acid – strong base pH curve

Your notes



Weak acid - strong base pH curve. The equivalence point is above pH 7

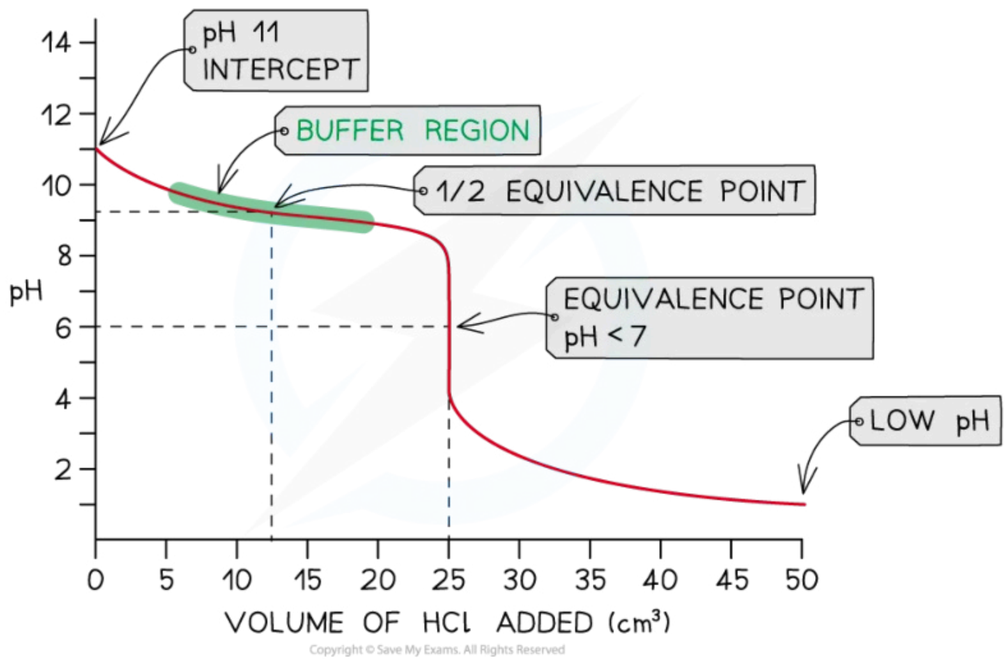
Weak Base + Strong Acid

- In this example, strong hydrochloric acid, HCl (aq), is being added to weak ammonia, NH_3 (aq)

NH_3 (aq) + HCl (aq) → 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
  - **[NH_3 (aq)] = [NH_4^+ (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**

Diagram to show a strong acid - weak base pH curve



Weak base - strong acid pH curve. The equivalence point is below pH 7

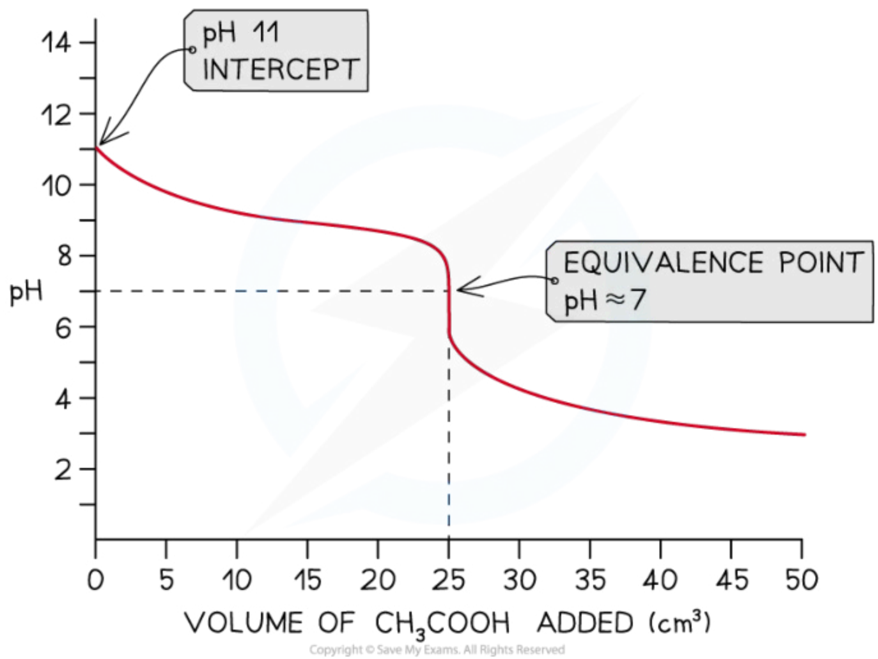
Weak Acid + Weak Base

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

NH_3 (aq) + CH_3COOH (aq) → CH_3COONH_4 (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 that the vertical section of this pH curve is not steep as with the 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 it is difficult to determine**

Diagram to show a weak acid - weak base pH curve



Weak acid - weak base pH curve. The equivalence point is difficult to determine

Your notes

The pOH Scale (HL)

The pOH Scale

pH

- The acidity of an aqueous solution depends on the number of **H^+** ions in the solution
- pH is defined as:

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

  - Where $[H^+]$ is the concentration of **H^+** ions in mol dm^{-3}
- Similarly, the **concentration of H^+** of a solution can be calculated if the pH is known by rearranging the above equation to:

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

- The pH scale is a logarithmic scale with base 10
  - For example, pH 5 is 10 times more acidic than pH 6
  - This means that each value is 10 times the value below it
- pH values are usually given to 2 decimal places

pOH

- The basicity of an aqueous solution depends on the number of hydroxide ions, OH^-, in the solution
- pOH is defined as:

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

  - Where $[OH^-]$ is the concentration of hydroxide ions in mol dm^{-3}
- Similarly, the **concentration of OH^-** of a solution can be calculated if the pH is known by rearranging the above equation to:

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

- If you are given the concentration of a basic solution and need to find the pH, this can be done by:

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

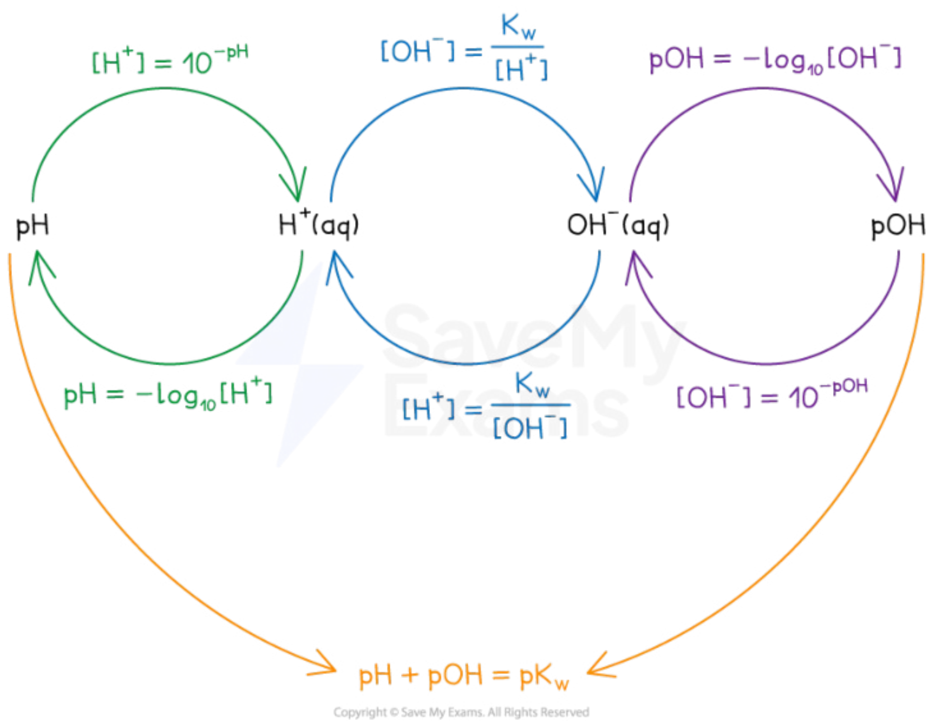
- Alternatively, if you are given the $[OH^-]$ and calculate the pOH, the pH can be found by:

$$pH = 14 - pOH$$

- As we can see, pH and pOH are interlinked and at all temperatures, pH + pOH = pK_w

Relationship between H^+, OH^-, pH and pOH

Your notes



To make a conversion, follow the arrow and equation given, so to convert OH^- (aq) to pOH use pOH = $-\log_{10}[OH^-]$

Worked example

pH and H^+ calculations

1. Find the pH when the hydrogen ion concentration is 1.60×10^{-4} mol dm^{-3}
2. Find the hydrogen ion concentration when the pH is 3.10

Answers:

1. The pH of the solution is:
   - pH = -log $[H^+]$
   - pH = -log 1.6×10^{-4}
   - pH = **3.80**

2. The hydrogen concentration can be calculated by rearranging the equation for pH
   - pH = -log $[H^+]$
   - $[H^+] = 10^{-pH}$
   - $[H^+] = 10^{-3.10}$
   - $[H^+]$ = **7.94×10^{-4} mol dm^{-3}**

Your notes

Worked example

pH calculations of a strong alkali

1. Calculate the pH of 0.15 mol dm^{-3} sodium hydroxide, NaOH
2. Calculate the hydroxide concentration of a solution of sodium hydroxide when the pH is 10.50

Answers:

- Sodium hydroxide is a strong base which ionises as follows:

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

1. The pH of the solution is:
   - $[H^+] = K_w \div [OH^-]$
   - $[H^+] = (1 \times 10^{-14}) \div 0.15 = 6.66 \times 10^{-14}$
   - pH = -log 6.66×10^{-14} **= 13.17**pH = -log[H$^+$]

2. To calculate the hydroxide concentration of a solution of sodium hydroxide when the pH is 10.50:
   - **Step 1:** Calculate hydrogen concentration by rearranging the equation for pH
     - pH = -log[H$^+$]
     - $[H^+] = 10^{-10.50}$
     - $[H^+] = 3.16 \times 10^{-11}$ mol dm^{-3}$[H^+] = 10^{-pH}$
   - **Step 2:** Rearrange the **ionic product of water** to find the concentration of hydroxide ions
     - $K_w = [H^+]\,[OH^-]$
     - $[OH^-] = K_w \div [H^+]$
   - **Step 3:** Substitute the values into the expression to find the concentration of hydroxide ions
     - Since K_w is 1.00×10^{-14}
     - $[OH^-] = (1 \times 10^{-14}) \div (3.16 \times 10^{-11})$
     - $[OH^-] =$ **3.16×10^{-4} mol dm^{-3}**

Your notes

Acid & Base Dissociation Constants (HL)

Acid & Base Dissociation Constants

Weak acids

- A **weak acid** is an acid that **partially** (or incompletely) **dissociates** in aqueous solutions
  - For example, most carboxylic acids (e.g. ethanoic acid), HCN (hydrocyanic acid), H_2S (hydrogen sulfide) and H_2CO_3 (carbonic acid)
- In general, the following equilibrium is established:

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

OR

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

- At equilibrium, the majority of HA molecules remain unreacted
- The position of the equilibrium is more towards the **left** and an equilibrium is established
- As this is an equilibrium, we can write an equilibrium constant expression for the reaction
- This constant is called the **acid dissociation constant**, K_a

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

- Carboxylic acids are weak acids
  - For example, propanoic acid, CH_3CH_2COOH (aq), dissociates according to the following equation which leads to the K_a expression for propanoic acid:

$CH_3CH_2COOH (aq) + H_2O (l) \rightleftharpoons CH_3CH_2COO^- (aq) + H_3O^+ (aq)$

OR

$CH_3CH_2COOH (aq) \rightleftharpoons CH_3CH_2COO^- (aq) + H^+ (aq)$

  - The acid dissociation constant expressions for propanoic acid:
    - $K_a = \frac{[CH_3CH_2COO^-][H^+]}{[CH_3CH_2COOH]}$
- Values of K_a are very small
  - For example, K_a for propanoic acid = 1.34×10^{-5}
  - When writing the equilibrium expression for weak acids, we assume that the concentration of **H^+ (aq)** due to the ionisation of water is negligible

Weak bases

- A weak base will also ionise in water and we can represent this with the **base dissociation constant, K_b**
- In general, the equilibrium established is:

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

- The base dissociation constant expression is:

Your notes

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

- Amines are weak bases
  - For example, 1-phenylmethanamine, $C_6H_5CH_2NH_2$ (aq), dissociates according to the following equation which leads to the K_a expression for 1-phenylmethanamine:

$C_6H_5CH_2NH_2$ (aq) + H_2O (l) ⇌ $C_6H_5CH_2NH_3^+$ (aq) + OH^- (aq)

  - Base dissociation constant expression for 1-phenylmethanamine
    - $K_b = \frac{[CH_5CH_2NH_3^+][OH^-]}{[C_6H_5CH_2NH_2]}$

pK_a and pK_b

- The range of values of K_a and K_b is very wide
- For weak acids, the values themselves are very small numbers

Table of K_a values

Acid	K_a	pK_a
Methanoic acid, HCOOH	1.77×10^{-4}	3.75
Ethanoic acid, CH_3COOH	1.74×10^{-5}	4.75
Benzoic acid, C_6H_5COOH	6.46×10^{-5}	4.18
Carbonic acid, H_2CO_3	4.30×10^{-5}	6.36

- For this reason, it is easier to work with another term called **pK_a** for acids or **pK_b** for bases
- In order to convert the values we need to apply the following calculations:

$$pK_a = -\log K_a \qquad K_a = 10^{-pK_a}$$

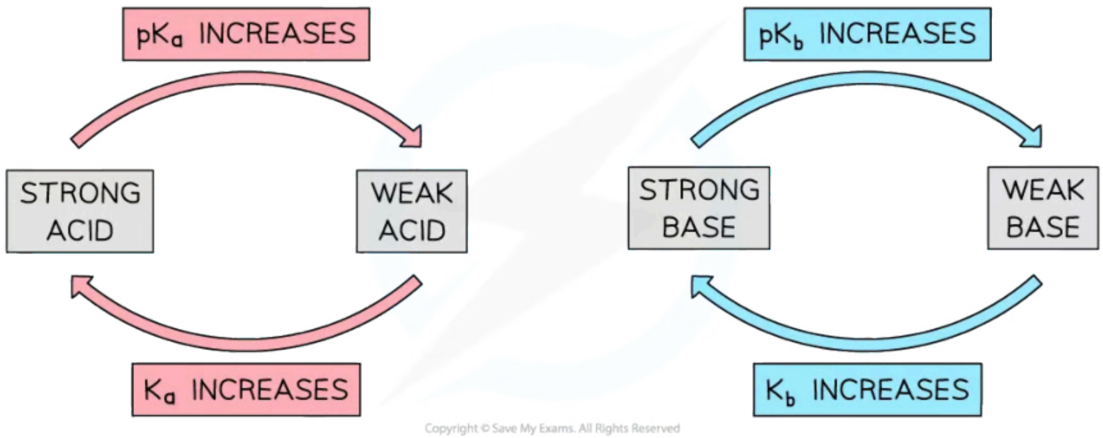
$$pK_b = -\log K_b \qquad K_b = 10^{-pK_b}$$

- The range of **pK_a** values for most weak acids lies between 3 and 7

Relative Strengths of Acids and Bases

- The larger the K_a value, the stronger the acid
- The larger the **pK_a** value, the weaker the acid
- The larger the K_b value, the stronger the base
- The larger the **pK_b** value, the weaker the base

Diagram showing the relationship between strong and weak acids / bases



pK_a and pK_b tell us the relative strengths of acids and bases

Your notes

- In all aqueous solutions, an equilibrium exists in water where a few water molecules dissociate into protons and hydroxide ions
- We can derive an equilibrium constant for the reaction:

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

- The concentration of water is constant, so the expression for K_w is:

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

- This is a specific equilibrium constant called the **ion product for water**
- The product of the two ion concentrations is **1.00 x 10^{-14}** at 298 K
- For conjugate acid-base pairs, K_a and K_b are related to K_w

$$K_a \times K_b = K_w$$

- The conjugate base of ethanoic acid is the ethanoate ion, **CH_3COO^- (aq)**

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

acid **conjugate base**

- We can then put this into the K_a expression
  - $K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$
- The ethanoate ion will react with water according to the following equation

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

- We can then put this into the K_b expression
  - $K_b = \dfrac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$
- Now, these two expressions can be combined, which corresponds to

- $K_a \times K_b = K_w$
- $K_a \times K_b = 10^{-14}$
- Or we could say that
  - $pK_a + pK_b = pK_w$
  - $pK_a + pK_b = 14$
  - This makes the numbers much more easy to deal with as using $K_a K_b = 10^{-14}$ will give very small numbers
- Combining the K_a and K_b expressions:
  - $$K_a \times K_b = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \times \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$
    $$K_a \times K_b = [H^+][OH^-] = K_w$$
- Or rearranging these:
  - $K_a = \frac{K_w}{K_b}$
  - $K_b = \frac{K_w}{K_a}$

Your notes

Solving Acid-Base Dissociation Problems (HL)

Your notes

Solving Acid-Base Dissociation Problems

K_a, pK_a, K_b and pK_b

- In reactions of weak acids and bases, we cannot make the same assumptions as for the ionisation of strong acids and bases
- For a weak acid and its conjugate base, we can use the equation:

$$K_w = K_a \times K_b$$

- By finding the -log of these, we can use:

$$pK_w = pK_a + pK_b$$

- Remember, to convert these terms you need to use:

$$pK_a = -\log K_a \qquad K_a = 10^{-pK_a}$$

$$pK_b = -\log K_b \qquad K_b = 10^{-pK_b}$$

- The assumptions we must make when calculating values for K_a, pK_a, K_b and pK_b are:
  - The initial concentration of acid ≈ the equilibrium concentration of acid
  - $[A^-] = [H^+]$
  - There is negligible ionisation of the water, so $[H^+]$ is not affected
  - The temperature is 298 K

Worked example

Calculate the acid dissociation constant, K_a, at 298 K for a 0.20 mol dm^{-3} solution of propanoic acid with a pH of 4.88.

Answer:

- **Step 1:** Calculate **$[H^+]$** using
  - $[H^+] = 10^{-pH}$
    - $[H^+] = 10^{-4.88}$
    - $[H^+] = 1.3183 \times 10^{-5}$
- **Step 2:** Substitute values into **K_a expression**
  - $K_a = \dfrac{[H^+]^2}{[CH_3CH_2COOH]}$
    - $K_a = \dfrac{(1.3182 \times 10^{-5})^2}{0.2}$
    - K_a = **8.70×10^{-10}**

Your notes

Worked example

A 0.035 mol dm^{-3} sample of methylamine (CH_3NH_2) has pK_b value of 3.35 at 298 K. Calculate the pH of methylamine.

Answer:

- **Step 1:** Calculate the value for K_b using
  - $K_b = 10^{-pK_b}$
    - $K_b = 10^{-3.35}$
    - $K_b = 4.4668 \times 10^{-4}$
- **Step 2:** Substitute values into **K_b expression** to calculate [OH⁻]
  - $K_b = \frac{[OH^-]^2}{[CH_3NH_2]}$
    - $4.4668 \times 10^{-4} = \frac{[OH^-]}{0.035}$
    - $[OH^-] = \sqrt{(4.4668 \times 10^{-4} \times 0.035)}$
    - $[OH^-] = 3.9540 \times 10^{-3}$
- **Step 3:** Calculate the pH
  - $[H^+] = \frac{K_w}{[OH^-]}$
    - $[H^+] = (1 \times 10^{-14}) \div 3.9539 \times 10^{-3}$
    - $[H^+] = 2.5291 \times 10^{-12}$
  - pH = -log [H⁺]
    - pH = -log 2.5291×10^{-12}
  - pH = **11.60 to 2 decimal places**

OR

- **Step 3**: Calculate pOH and therefore pH
  - pOH = -log [OH⁻]
    - pOH = -log 3.9540×10^{-3}
    - pOH = 2.4029
  - pH = 14 - pOH
    - pH = 14 - 2.4030
    - pH = **11.60 to 2 decimal places**

Salt Hydrolysis (HL)

Salt Hydrolysis

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

Neutralisation

Neutralisation forming an ionic salt

- 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):

$$\mathbf{HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O}$$

- 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:

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

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

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

- 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

Your notes

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:

$$\mathbf{NaOH\ (aq) + CH_3COOH\ (aq) \rightarrow CH_3COONa\ (aq) + H_2O\ (l)}$$

- In this reaction, the conjugate base of ethanoic acid is produced, **CH_3COO^- (aq)**, and this will react with water to form hydroxide ions, **OH^-** (aq)

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

- 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:

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

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

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

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

$$K_a(\text{cation}) = \frac{K_w}{K_b\ (\text{parent base})}$$

$$K_b(\text{anion}) = \frac{K_w}{K_a\ (\text{parent acid})}$$

- 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

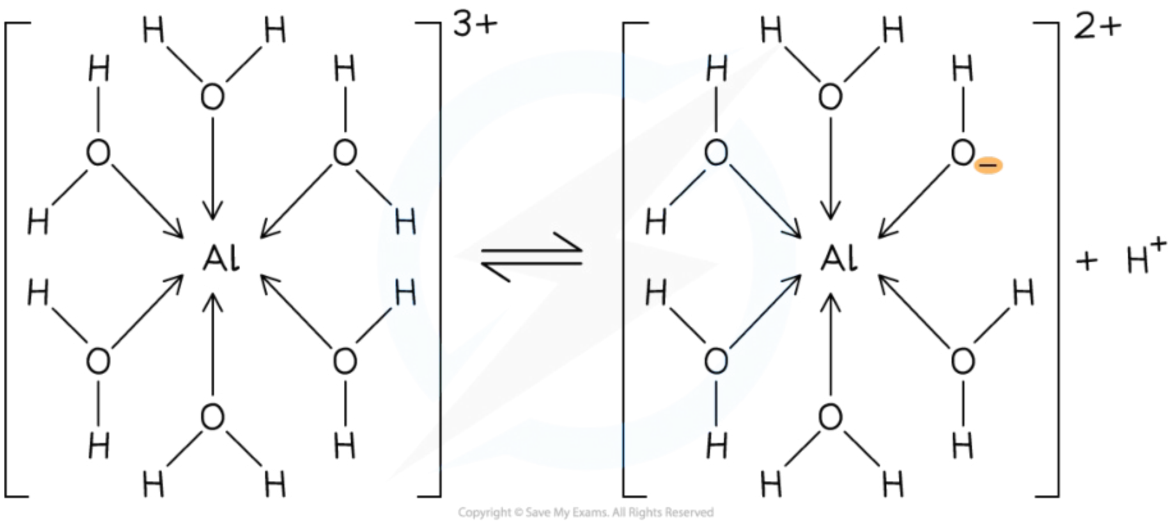
- Small metal ions that have a high charge will exhibit a high charge density
  - An example is Al^{3+}
- This makes the highly charged metal ions ideal for forming complexes as they can coordinately bond with ligands
- The complex formed can then act as a weak acid by releasing hydrogen ions when hydrolysed, 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

Your notes

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

- 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

Diagram to show how the aluminium complex forms an acidic solution



The $[Al(H_2O)_6]^{3+}$ (aq) releases an H+ ion decreasing the pH of the solution

Your notes

Acid-Base Indicators (HL)

Acid-Base Indicators

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

$$\textbf{HIn (aq)} \rightleftharpoons \textbf{H}^+\textbf{ (aq) + In}^-\textbf{ (aq)}$$

$$\textbf{colour 1} \quad \rightleftharpoons \quad \textbf{colour 2}$$

- 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 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 colour of the indicator depends on the pH of the solution
- The pH at which these transitions will occur depends on the K_a of the indicator
  - $K_\text{a} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$
- The endpoint of the reaction is where there is a balance between [HIn] and [In^-]. At this point these two concentrations are equal:
  - $K_\text{a} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} = [\text{H}^+]$
- 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 ± 1**

Weak bases as indicators

- An indicator can also be a weak base:

$$\textbf{BOH (aq)} \rightleftharpoons \textbf{B}^+\textbf{ (aq) + OH}^-\textbf{ (aq)}$$

$$\textbf{colour 1} \quad \rightleftharpoons \quad \textbf{colour 2}$$

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

Choosing an Acid-Base Indicator (HL)

Your notes

Choosing an Acid-Base Indicator (HL)

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
- Section 18 of the data booklet contains information about acid-base indicators

Common Indicators and their colours table

Indicator	Colour in acid	Colour in alkali	pK_a	pH range of colour change
Methyl orange	red	yellow	3.7	3.1 – 4.4
Bromophenol blue	yellow	blue	4.2	3.0 – 4.6
Methyl red	red	yellow	5.1	4.4 – 6.2
Phenolphthalein	colourless	pink	9.6	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 endpoint so is widely used

Weak acid – strong base

- In weak acid – strong base titrations, the pH changes from 7 to 10 at the endpoint 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

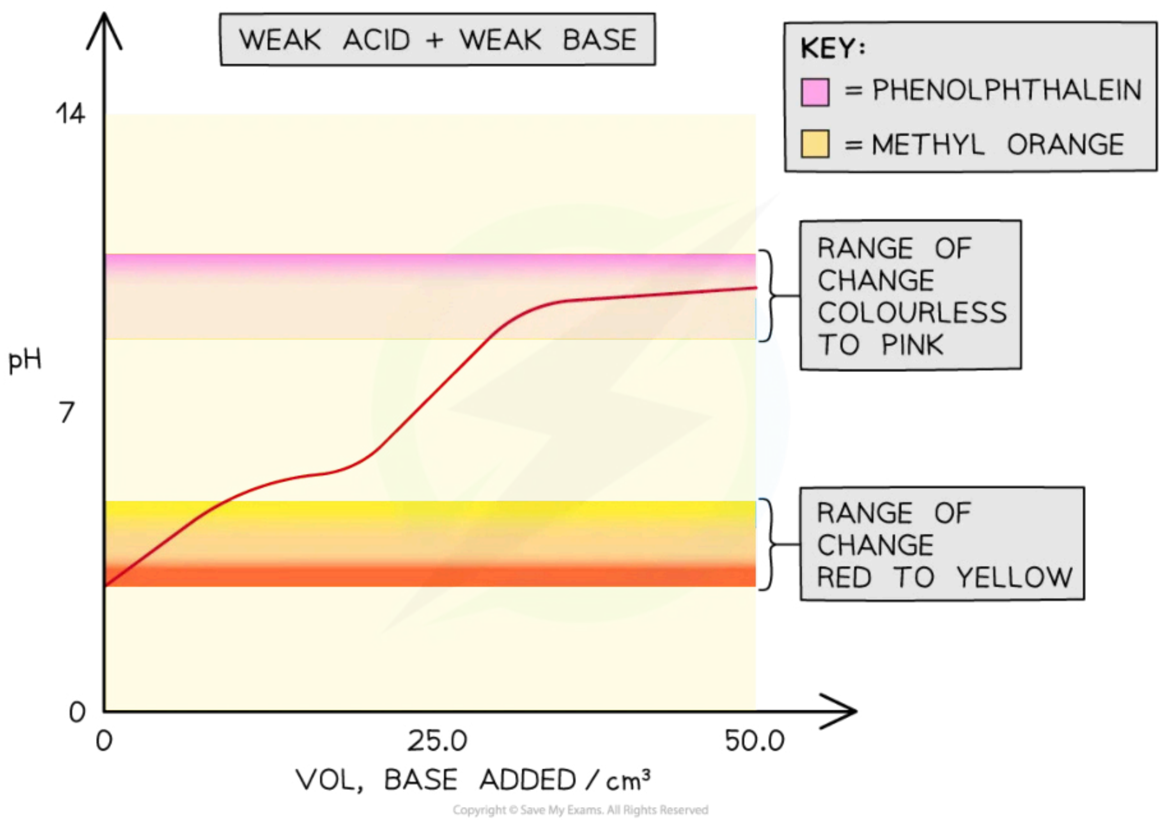
Your notes

- 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 endpoint 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 endpoints of these titrations cannot be easily determined

Weak acid – weak base titration curve including indicators



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

Your notes

Buffer Solutions (HL)

Buffer Solutions

- 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**

Acidic Buffers

- A common acidic 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 ⇌ ethanoate

high conc ⇌ low conc

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

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

sodium ethanoate → ethanoate ion

low conc. → 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

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

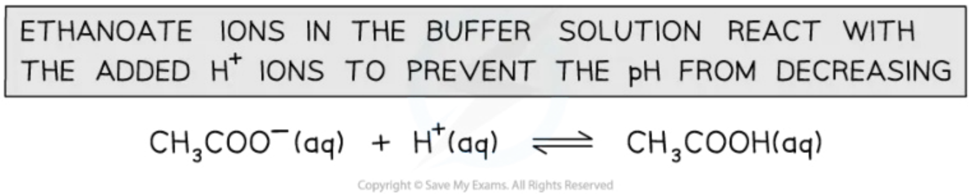
high conc. high conc.

Adding H^+ ions to an acidic 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 reacting with hydrogen ions

Your notes



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 an acidic buffer solution

- The OH^- reacts with H^+ to form water

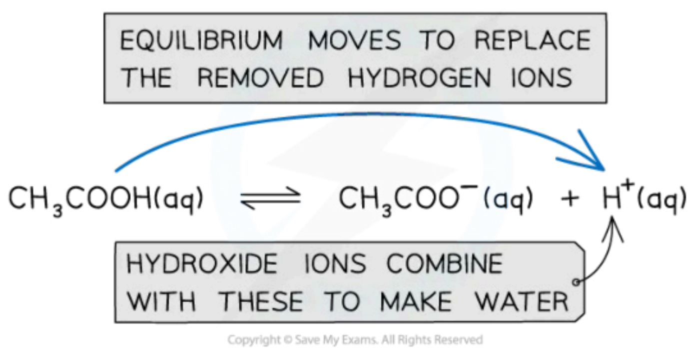
$$OH^- (aq) + H^+ (aq) \rightarrow H_2O (l)$$

- 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

Ethanoic acid dissociating into hydrogen ions and ethanoate ions



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

Basic buffers

- A basic buffer is made by mixing a solution of a weak base with its salt

- E.g. NH_3 (aq) and NH_4Cl (aq)
- In solution
  - NH_3 (aq) + H_2O (l) $\rightleftharpoons$ NH_4^+ (aq) + OH^- (aq)
  - The equilibrium lies to the left as NH_3 is a weak base
- And
  - NH_4Cl (aq) → NH_4^+ (aq) + Cl^- (aq)
  - NH_4Cl is a soluble salt so fully dissociated in solution
- Therefore the mixture contains high concentrations of NH_3 (aq) and NH_4^+ (aq) which will be able to react with any H^+ and OH^- added

Adding acid to an basic buffer

- If H^+ is added
  - NH_3 (aq) + H^+ (aq) $\rightleftharpoons$ NH_4^+ (aq)
  - H^+ will combine with NH_3 to form NH_4^+ so removing any added H^+

Adding base to a basic buffer

- If OH^- is added
  - NH_4^+ (aq) + OH^- (aq) $\rightleftharpoons$ NH_3 (aq) + H_2O (l)
  - OH^- will combine with the acid NH_4^+ and form NH_3 and H_2O so removing any added OH^-
- Therefore there is no overall change is pH if there are small amounts of acid or base are added

Examiner 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

Your notes

Your notes

Buffer Calculations (HL)

Buffer Calculations

- The pH of a **buffer solution** can be calculated using:
  - The K_a of the **weak acid**
  - The **equilibrium concentration** of the **weak acid** and its **conjugate base** (salt)

- To determine the pH, the concentration of **hydrogen ions** is needed which can be found using the equilibrium expression:
  - $K_a = \frac{[\text{salt}][H^+]}{[\text{acid}]}$ which can be rearranged to $[H^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$

- To simplify the calculations, **logarithms** are used such that the expression becomes:
  - $-\log_{10}[H^+] = -\log_{10} K_a \times -\log \frac{[\text{acid}]}{[\text{salt}]}$
- Since -$\log_{10}$ $[H^+]$ = pH, the expression can also be rewritten as:
  - $\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}$
- This is known as the Hendersen-Hasselbalch equation

Basic buffers

- $[OH^-] = K_b \frac{[\text{base}]}{[\text{salt}]}$ and $\text{pOH} = \text{p}K_b + \log_{10} \frac{[\text{salt}]}{[\text{base}]}$

The pH of a buffer can be determined from:

- The $\text{p}K_a$ or $\text{p}K_b$ values of its component acid or base
- The ratio of initial concentrations of acid and salt used to prepare the buffer

Your notes

Worked example

Calculate the pH of a buffer solution containing 0.305 mol dm^{-3} of ethanoic acid and 0.520 mol dm^{-3} sodium ethanoate.

The K_a of ethanoic acid = 1.74 x 10^{-5} at 298 K

Answer:

- Ethanoic acid is a weak acid that ionises as follows:

  CH_3COOH (aq) ⇌ H^+ (aq) + CH_3COO^- (aq)

- **Step 1:** Write down the equilibrium expression to find K_a
  - $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$
- **Step 2:** Rearrange the equation to find [H^+]
  - $[H^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$
- **Step 3:** Substitute the values into the expression
  - $[H^+] = 1.74 \times 10^{-5} \times \frac{0.305}{0.520}$ = **1.02 x 10^{-5}** mol dm^{-3}
- **Step 4:** Calculate the pH
  - pH = - log [H^+]
  - pH = -log 1.02 x 10^{-5} = **4.99**

Factors that can influence buffers

Dilution

- K_a and K_b are equilibrium constants so are not changed by dilution
- Dilution does not change the ratio of acid or base to the salt concentration as both components will be decreased by the same amount
- The overall pH change of the buffer does not change

Temperature

- A constant temperature must be maintained when using buffers as temperature will influence the pH of the solution
- Temperature affects the values of K_a and K_b
- In medical procedures, temperature fluctuations should be avoided due to the effect on the buffers in the blood