# OCR A Chemistry A-level

## Module 2.1: Atoms and Reactions

### Detailed Notes

# 2.1.1 Atomic Structure and Isotopes

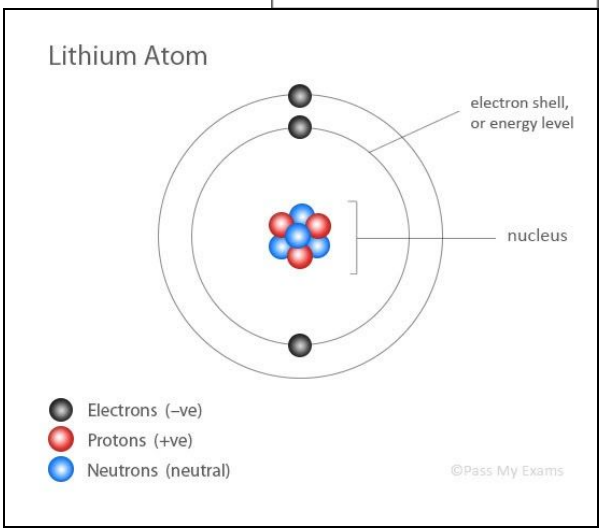
## Fundamental Particles

The model for atomic structure has evolved over time as knowledge and scientific understanding changes.

The current, accepted model of the atom consists of a **small, dense central nucleus** surrounded by **orbiting electrons** in electron **shells**. This was discovered in the Rutherford scattering experiment in 1911.

The nucleus consists of **protons and neutrons** giving it an overall **positive** charge. The mass of the atom is concentrated at the nucleus. In a **neutral** atom, the number of electrons is equal to the number of protons due to the relative charges.

Image courtesy of passmyexam.co.uk




| Particle | Proton | Neutron | Electron |
|---|---|---|---|
| **Relative Charge** | +1 | 0 | -1 |
| **Relative Mass** | 1 | 1 | 1/1840 |

The **maximum** number of **orbiting** electrons that can be held by any single shell, depends on the number of the shell. This can be calculated using $2n^2$ where **n** is the number of the shell.

*Example:*

**Electrons in shell 2 = $2(2^2)$ = 8 electrons**

Each electron shell **must fill** before the next one can hold any electrons.

## Atomic Number and Mass Number

**Mass number** is represented using ***A*** and can be calculated as the **sum of protons and neutrons** in an atom.

**Atomic number** is represented using ***Z*** and is **equal to the number of protons** in an atom. It is often referred to as the **proton number**.

Using these numbers, the quantity of each fundamental particle in an atom can be calculated.

*Example: Calculating the number of neutrons in a nitrogen atom*


**Atomic number = 7**
**Mass number = 14**

**Proton number = 7**

**Neutron number = 14 - 7**
**= 7**

Ions are formed when an atom **loses or gains electrons** meaning it is no longer neutral and will have an **overall charge**. In an ion, the number of electrons is equal to the number of protons minus the ionic charge.

*Example: Calculating the number of electrons in a lithium atom and a lithium ion*


Li = **3 electrons**

$Li^+$ = (3 - 1) electrons = **2 electrons**

## Isotopes

Isotopes are atoms of the same element with the **same atomic number**, but with a **different number of neutrons**, resulting in a **different mass number**.

Neutral atoms of isotopes will **react chemically in the same way** as their proton number and electron configuration is the same. The sharing and transfer of electrons is unaffected. However, the different mass numbers means they have **different physical properties**.

*Example:*

| | |
|---|---|
| **Hydrogen** | **= 1 proton and 1 neutron** |
| **Deuterium** | **= 1 proton and 2 neutrons** |
| **Tritium** | **= 1 proton and 3 neutrons** |

**Deuterium is used in heavy water ($D_2O$) to control nuclear processes.**

# Relative Mass

**Relative atomic mass (*Ar*)** is defined as:

**The weighted mean mass of an atom of an element, relative to one twelfth of the mean mass of an atom of the carbon-12 isotope.**

Relative atomic mass takes the **relative abundances** of the different **isotopes** of an element into account:

$$Ar = \frac{\text{mean mass of an atom of an element}}{\text{1/12 x mean mass of C-12 isotope}}$$

**Relative isotopic mass** is defined as:

**The isotopic mass of an isotope relative to one twelfth of the mean mass of an atom of the carbon-12 isotope.**

**Relative molecular mass (*Mr*)** is defined as:

**The weighted mean mass of a molecule of a compound, relative to one twelfth of the mean mass of an atom of the carbon-12 isotope.**

Relative molecular mass can be calculated for a molecule by adding together the separate Ar values of the component elements.

*Example:*

$$\text{Mr of } H_2O = 2 \times 1.0 + 1 \times 16.0 = 18.0$$

**Relative formula mass** is similar to Mr but is used for compounds with giant structures.

## Mass Spectrometry

Mass spectrometry is used to identify different isotopes and find the overall relative atomic mass of an element. Ions are very useful in the **analytical technique** of **mass spectrometry**.

**Time of Flight** (TOF) mass spectrometry records the time it takes for ions of each isotope to reach a detector. Using this, **spectra** can be produced showing **each isotope present**. The signals reflect the abundances of the isotopes present.

From a spectra, the ***Ar* can be calculated** by multiplying each **m/z** value by its **abundance** and adding each of these together, before dividing by the total abundance of all species present:

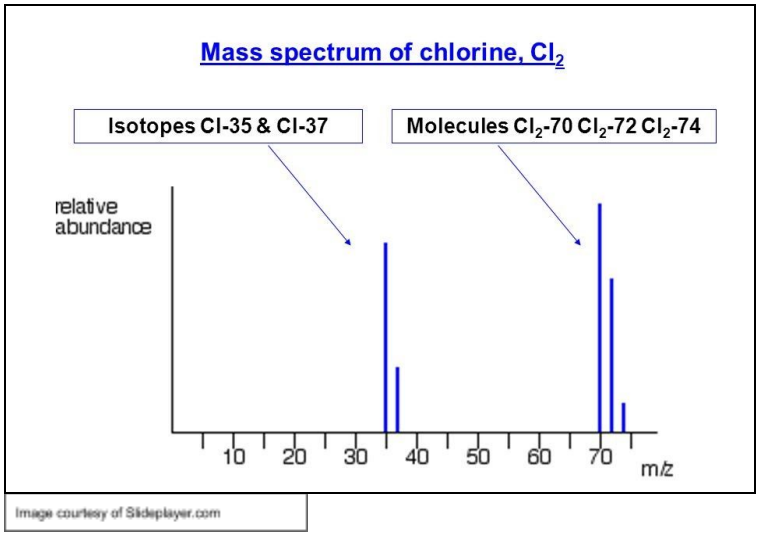
$$\text{Ar} = \frac{\text{Sum of (m/z x abundance)}}{\text{Total abundance}}$$

Using this calculated Ar, the element can be identified by referring to the Periodic Table.

## Chlorine Spectra

Spectra produced by the mass spectrometry of chlorine display a **characteristic pattern** in a **3:1 ratio for $Cl^+$ ions** and a **9:6:1 ratio for $Cl_2^+$ ions**. This is because one isotope is more common than the other and the chlorine molecule can form in different combinations. There is a **chlorine-35** isotope and a **chlorine-37** isotope which both have different abundances:

*Example:*




**$^{70}Cl_2^+$ = 35 + 35**
**$^{72}Cl_2^+$ = 35 + 37 OR = 37 + 35**
**$^{74}Cl_2^+$ = 37 + 37**

# 2.1.2 Compounds, Formulae and Equations

## Formulae and Equations

Ionic bonding occurs between a **metal and a nonmetal**. Electrons are **transferred** from the metal to the non-metal to achieve full outer shells.

When the electrons are transferred, it creates **charged particles** called **ions**.

**Binary compounds** contain only 2 elements. To name these:

- Put the metal first.
- Change the ending of the second element to -ide.
- The ionic lattice should be neutral, so the charges must balance.

*Example:*

*Calcium chloride contains calcium $Ca^{2+}$ ions and chloride $Cl^-$ ions.*
*To balance charges, 2 x $Cl^-$ are needed for every $Ca^{2+}$.*
*So, the ionic formula is $CaCl_2$.*

A **polyatomic** ion contains more than one atom. There are some key polyatomic ions that you should be aware of:

**$NO_3^-$** = nitrate ion
**$SO_4^{2-}$** = sulfate ion
**$CO_3^{2-}$** = carbonate ion
**$OH^-$** = hydroxide ion
**$NH_4^+$** = ammonium ion

It is also possible to predict an element's ionic charge from its position in the **periodic table**:

- Group 1 metals lose an electron to **form 1+ ions.**
- Group 2 metals lose two electrons to **form 2+ ions.**
- Group 7 elements need to gain an electron to form a **1- ion.**
  Group 7 elements are known as the **halogens** and their negative ions are known as **halide ions**.

### Chemical Equations

All chemical equations **must** be balanced. There should be the same total number of atoms of each element on each side of the equation. The charges must balance too.
Remember that **state symbols** should also be included for reactions.

# 2.1.3 Amount of Substance

## The Mole

**Amount of substance** defines the number of particles in a substance. It is measured in **moles**.

The mole is a **unit of measurement** for substances. It always contains the **same number of particles**.

$$N_A = 6.02 \times 10^{23} \text{ particles}$$

This number is the **Avogadro Constant** ($N_A$) and is the number of particles per mole. It allows the number of particles present in a sample of a substance with known mass to be found:

$$\text{Number of particles} = n \times N_A$$

(n = moles) ($N_A$ = Avogadro constant)

The mole is a **very important unit of measurement** in many calculations:

$$\text{Moles} = \frac{\text{mass}}{\text{Mr}} = \frac{\text{concentration} \times \text{volume}}{1000}$$

(where concentration is in mol $dm^{-3}$ and volume is in $cm^3$)

**Molar mass** is the mass per mole and has units g $mol^{-1}$.

**Molar gas volume** is the gas volume per mole and has units $dm^3$ $mol^{-1}$.

## Definition of Formulae

**Empirical formula** is the simplest whole number ratio of atoms of each element present in a compound.

The empirical formula can be found by using the composition by mass or percentage composition by mass and the relative atomic masses of the elements present.

**Molecular formula** is the number and type of atoms of each element in a molecule. It is the true number of each atom in the molecule.

The molecular formula can be determined using the Mr of the empirical formula and the true Mr of the molecule. This gives a multiplier value which can be used to scale up the empirical formula.

$$\frac{\text{Mr of molecule}}{\text{empirical Mr}} = \text{multiplier}$$

**Water of crystallisation** is water that is part of the crystalline structure. The molecules are stoichiometrically chemically bonded into the crystal structure.

An **anhydrous** substance contains no water of crystallisation.

A **hydrated** substance contains water of crystallisation.

The formula of a hydrated salt can be calculated from experimental results or from a given percentage or mass composition.

## Equations and Calculations

Chemical equations must be **balanced** before they can be used in calculations. This is because the **reacting ratios** must be correct. It can be useful to also include **state symbols** so it is clear what might be observed during the reaction, for example, bubbles of gas or a precipitate forming.

These balanced equations can then be used to calculate **reacting masses**, **percentage yield** and **atom economy**.

**Concentration** can be expressed in g $dm^{-3}$ or mol $dm^{-3}$. A 1 mol $dm^{-3}$ solution contains 1 mol of solute dissolved in every 1 $dm^{-3}$ of solution.

A **standard solution** is a solution of known concentration. This can be prepared by dissolving a known mass of solid in solvent and making it up to an exact volume.

The **limiting reagent** in a reaction is the reactant that is not in excess. It will be used up first, causing the reaction to stop. In calculations, you must use the moles of the limiting reagent along with the stoichiometric ratios of reactant to product to calculate the moles of product formed.

## The Ideal Gas Equation

When under **standard conditions**, gases and volatile liquids follow certain trends:

**Pressure is proportional to Temperature**
**Volume is proportional to Temperature**
**Pressure and Volume are inversely proportional**

These relationships can be combined to give the **ideal gas equation**:

$$pV = nRT = \frac{mRT}{Mr}$$

In order to use this equation, the variables must be in the correct **standard units**:

**p = pressure in Pascals, Pa**
**V = volume in $m^3$**
**T = temperature in Kelvin, K**
**n = moles, mol**
**m = mass in grams, g**

**R** is the **ideal gas constant**, equal to **8.31 $JK^{-1}mol^{-1}$**.

# Percentage Yields and Atom Economy

## Percentage Yield

$$\% \text{ yield} = \frac{\text{Experimental mass}}{\text{Theoretical mass}} \times 100$$

Experiments usually have a percentage yield **less than 100%**. This could be due to the reaction being **incomplete**, **loss** of products on equipment, or unwanted **side reactions**.

## Atom Economy

$$\% \text{ atom economy} = \frac{\text{Mr of desired product}}{\text{Mr of reactants}} \times 100$$

In industrial chemical processes, it is desirable to have a **high atom economy** for a reaction. This means there is **little or no waste product**, only the desired product. Therefore, it means the process is more **economically viable** for industrial scale manufacture. It also helps to **preserve raw materials**.

## Experimental techniques

Use a **digital mass balance** to measure mass. It is important to use a balance with a suitable **resolution** for your experiment.

Use a **measuring cylinder** to measure the volume of a solution. If you are making up a standard solution, you should use a **volumetric flask** of the required volume.

Use a **gas syringe** to measure the volume of gas produced in an experiment. Alternatively, measure the mass lost on a balance and use this value to calculate the moles of gas produced during the reaction.

# 2.1.4 Acids

## Acids, Bases, Alkalis and Neutralisation

An **acid** releases $H^+$ ions in aqueous solution.

An **alkali** releases $OH^-$ ions in aqueous solution. An alkali is a water-soluble base.

Common acids:

**HCl** - hydrochloric acid
**$H_2SO_4$** - sulfuric acid
**$HNO_3$** - nitric acid
**$CH_3COOH$** - ethanoic acid

Common bases:

**NaOH** - sodium hydroxide
**KOH** - potassium hydroxide
**$NH_3$** - ammonia

A **strong** acid fully dissociates in aqueous solution.

A **weak** acid partially dissociates in aqueous solution.

**Neutralisation** is the reaction of an acid with a base. In aqueous solution the ionic equation for the reaction is:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

Reactions with bases also form a **salt**:

**acid + carbonate → salt + water + carbon dioxide**
**acid + metal oxide → salt + water**

## Acid-Base Titrations

A titration is a practical method where a **standard solution** of known concentration is reacted with a solution of **unknown concentration** in order to determine the concentration of this solution. For this, there is a standard method to make up the standard solution and carry out the titration.

## Standard Solution - simple method

1. Weigh the sample bottle containing the solid on a (2 dp) balance.
2. Transfer solid to beaker and reweigh sample bottle.
3. Record the difference in mass.
4. Add distilled water and stir with a glass rod until all the solid has dissolved.
5. Transfer to a volumetric flask with washings.
6. Make up to the 250 $cm^3$ mark with distilled water.
7. Shake flask.

Common errors in this method include **systematic errors** on the balance, **lost substance** in transfer and **overfilling** of the volumetric flask. These can be reduced using **washing** methods and by reading volumes from the **bottom of the meniscus**.

## Titration - simple method

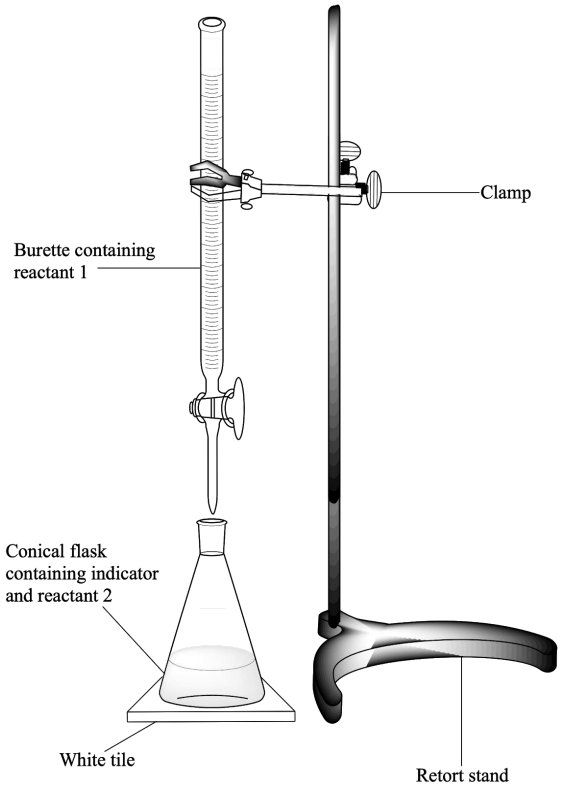
1. Fill the burette with the standard solution of known concentration, ensuring the jet space in the burette is filled and doesn't contain air bubbles.
2. Use a pipette filler and pipette to transfer 25 $cm^3$ of the solution with unknown concentration into a conical flask.
3. Add two to three drops of indicator.
4. Record the initial burette reading.
5. Titrate the contents of the conical flask by adding the solution to it from the burette until the indicator undergoes a definite, permanent colour change.
6. Record the final burette reading and calculate the titre volume.
7. Repeat until at least two concordant results are obtained (within 0.1 $cm^3$ of each other).

The equipment used in a titration all comes with their own **uncertainty values**. These must be combined to find the overall uncertainty in the final answer.

The best way of reducing uncertainties in a titration is to **increase the titre volume needed** for the reaction. This can be done by increasing the volume and concentration of the substance in the conical flask or by decreasing the concentration of the substance in the burette.

It is also important to carry out a **risk assessment** before undertaking any practical work. This should analyse the **equipment,** the **lab environment** and the **chemicals** being used, and suggest methods for **reducing the risk** and what should be done if an accident occurs.

**Diagram** - Titration setup




## 2.1.5 Redox

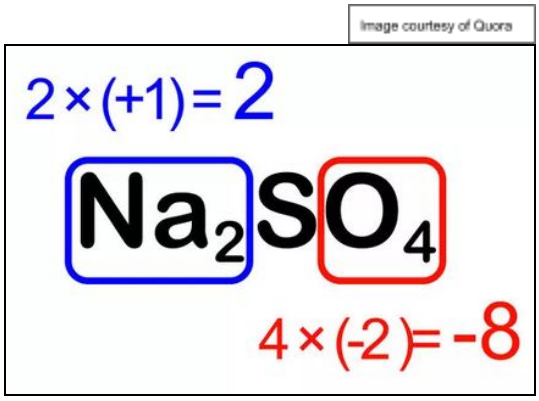
## Oxidation Number

Oxidation number gives the **oxidation state** of an element or ionic substance. Allocation of oxidation number to a species follows a number of rules:

- Oxidation number of an **element is zero**.
- Oxidation numbers in a **neutral** compound add up to **zero**.
- Oxidation numbers in a charged compound add up to **the total charge**.
- **Hydrogen** has an oxidation number of **+1**.
- **Oxygen** has an oxidation number of **-2**.
- All **halogens** have an oxidation number of **-1**.
- **Group 1** metals have an oxidation number of **+1**.
- In **metal hydrides**, the oxidation number of hydrogen is **-1**.
- In **peroxides**, the oxidation number of oxygen is **-1**.

These rules can be used to work out the oxidation number of species or elements in a reaction.

*Example:*




***This compound is neutral, so the oxidation numbers must total zero. Therefore, using the rules above, the oxidation number of sulfur can be found.***

$$2 - 8 + x = 0$$
$$-6 + x = 0$$
$$x = 6$$

**Roman numerals** are used to indicate the magnitude of an oxidation number. For example, iron has two common oxidation states, iron(II) and iron(III).

## Redox Reactions

**Oxidation** involves the **loss of electrons. Reduction** involves the **gain of electrons.**

**Oxidation** results in the oxidation number becoming more **positive** whereas **reduction** results in the oxidation number becoming more **negative**.

Oxidation and reduction occur **simultaneously** in a reaction because one species loses electrons which are then donated and gained by the other species. Therefore, they are known as **redox** reactions (reduction - oxidation).

This redox rule is remembered using the acronym **OILRIG** (oxidation is loss, reduction is gain).

## Oxidising and Reducing Agents

An oxidising agent **accepts electrons** from the species that is being oxidised. Therefore, it **gains electrons** and is **reduced**. This is seen as a **reduction** in oxidation number for the oxidising agent (gets less positive).

A reducing agent **donates electrons** to the species being reduced. Therefore, it **loses electrons** and is **oxidised**. This is seen as an **increase** in oxidation number for the reducing agent (gets more positive).

## Disproportionation Reactions

In a **disproportionation reaction**, a species is both oxidised and reduced, seen as both an increase and a decrease in oxidation number for that species.

An example is seen when chlorine reacts with cold water to produce **chlorate(I) ions ($ClO^-$)** and **chloride ions**. The oxidation state goes from zero to both **+1 and -1**.

*Example:*

$$Cl_2 + H_2O \longrightarrow ClO^- + Cl^- + 2H^+$$

## Redox Reactions with Metals

**Metals** react with **acids** to form **salts** in MASH reactions:

**metal + acid → salt + hydrogen**

You should use known oxidation numbers of species to work out the change in oxidation number for the metal.

# OCR A Chemistry A-level

## Module 2.2: Electrons, Bonding and Structure

### Detailed Notes

## 2.2.1 Electron Structure

# Energy Levels, Shells, Sub-Shells, Atomic Orbitals, Electron Configuration

### Shells

Electrons orbit the nucleus at different **energy levels**, which are an increasing distance from the nucleus. These are called **shells**. A shell is a **group of atomic orbitals** which have the same value of the principal quantum number, n. They can be split up into separate sub-shells, labelled s, p, d, and f.

The maximum numbers of electrons that can fill the first four shells are: 2, 8, 18, and 32. Given the atomic number of an element, you can deduce its **electron configuration**.

### Electron Orbitals

Electrons are held in **clouds of negative charge** called **orbitals**. An atomic orbital is a region around the nucleus that can hold up to two electrons with opposite spins. There are different types of orbital: ***s, p, d,* and *f***. Each one has a different shape:

s-orbital (spherical)



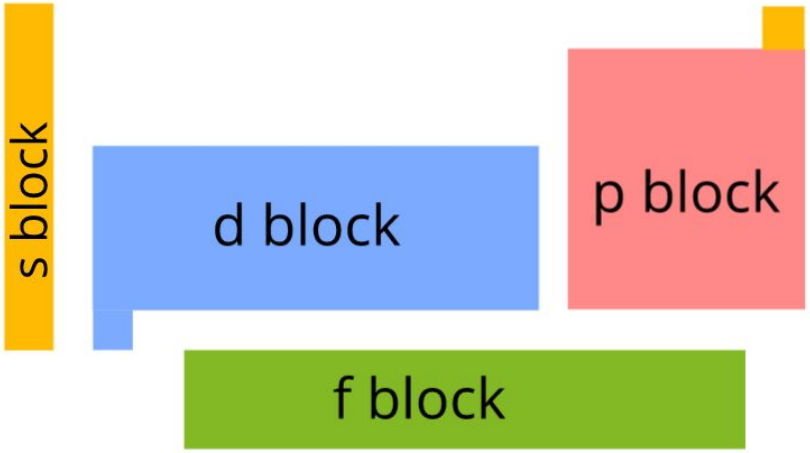
p-orbital (dumbbell)

Each subshell has a different number of orbitals and therefore can hold a different number of electrons before the next one is filled:

**s-subshell = 2 electrons**
**p-subshell = 6 electrons**
**d-subshell = 10 electrons**

These orbitals correspond with **blocks** on the Periodic Table. Each element in the block has **outer electrons in that orbital**.

*Example: The blocks of the periodic table*




The **energy** of the orbitals **increases from s to p to d** meaning the orbitals are **filled in this order**. There is one exception to this rule. The **4s orbital** has a lower energy than the **3d** orbital, and so the 4s orbital is filled first. Each orbital is filled before the next one is used to hold electrons.

*Example:*

*Sodium has 11 electrons. This gives sodium the following configuration:*

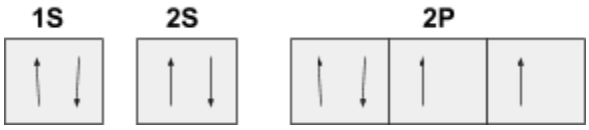
$$Na = 1s^2 2s^2 2p^6 3s^1$$

*It has 3 energy levels and 4 orbitals holding the 11 electrons.*

## Spin

Within an orbital, electrons **pair up with opposite spin** so that the atom is as **stable** as possible. Electrons in the **same orbital must have opposite spins**. Spin is represented by opposite **arrows**.

*Example: Electron orbital diagram for oxygen*




Overall there are **three rules** for writing out electron configurations:

1. The lowest energy orbital is filled first.
2. For orbitals with the same energy, electrons occupy orbitals singly with the same spin before pairing begins.
3. No single orbital holds more than 2 electrons.

# 2.2.2 Bonding and Structure

## Ionic Bonding

Ionic bonding is an **electrostatic attraction** between positive and negative ions.

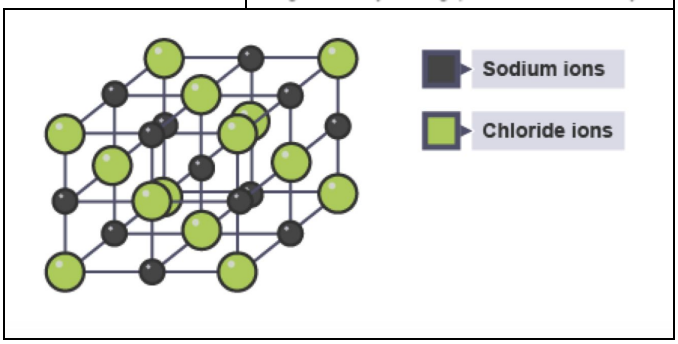
It occurs between a **metal and a nonmetal**. Electrons are **transferred** from the metal to the non-metal so that both elements achieve full outer shells.

When the electrons are transferred, it creates **charged particles** called **ions**. Oppositely charged ions **attract** each other through **electrostatic forces** to form a **giant ionic lattice**.

*Example:*

*Sodium chloride is an ionic compound formed from $Na^+$ and $Cl^-$ ions. Sodium loses an electron and chlorine gains an electron to produce ions with a full outer electron shell. These then form a giant ionic lattice.*

Image courtesy of Blogspot IGCSE Chemistry

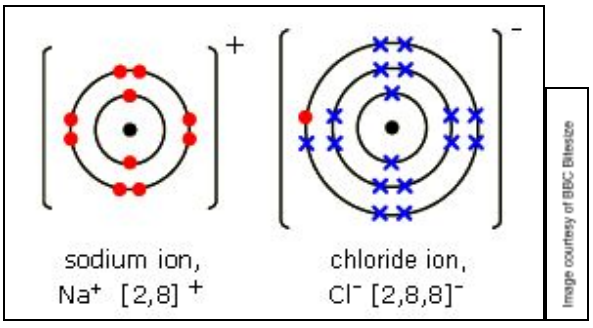



The **charge** of an ion is related to the strength of the ionic bond that forms. Ions with a **greater charge** will have a **greater attraction** to the other ions resulting in stronger forces of attraction, and therefore **stronger ionic bonding**.

Larger ions that have a **greater ionic radius** will have a **weaker attraction** to the oppositely charged ion because the attractive forces have to act over a **greater distance**.

**Cations** (+ve) and **anions** (-ve) involved in ionic bonding can be represented using **dot and cross diagrams**. The electrons being transferred from the cation are seen on the outer shell of the anion.

*The red dot clearly shows how the electron transfer has produced two ions with full outer electron shells.*



### Physical Properties

**Physical properties** of a substance include the boiling point, melting point, solubility and conductivity. These properties are different depending on the **type of bonding** and the **crystal structure** of the compound.

Substances with an **ionic crystal structure** have a **high melting and boiling point**. This is because the electrostatic forces holding the ionic lattice together are strong and require a lot of energy to overcome.

When **molten or aqueous** (in solution), ionic substances can **conduct electricity**. In this state, the ions separate and are no longer held in a lattice. Therefore, they are free to move and **carry a flow of charge**.

In the **solid** state, ions are in **fixed positions** with no mobile charge carriers, so the substance can't conduct electricity.

Ionic substances are often **brittle** materials. When the layers of alternating charges are distorted, like charges repel, breaking apart the lattice into fragments.

*Example: Diagram showing the brittle property of ionic substances*

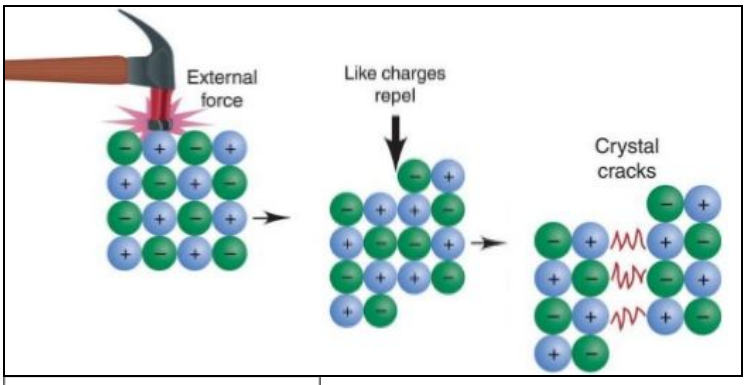



Image courtesy of Saints Chemistry

## Covalent Bonding

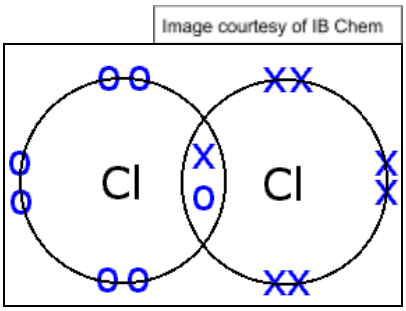
A covalent bond is the strong **electrostatic attraction** between a **shared pair of electrons** and the **nuclei** of the bonded atoms.

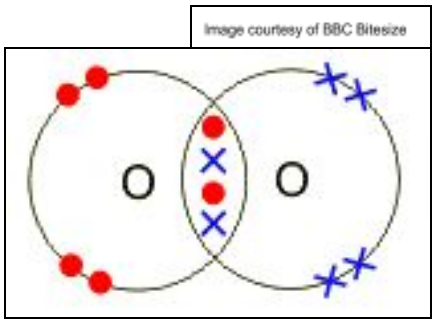
Covalent bonds form between **two nonmetals**. Electrons are **shared** between the two outer shells in order to achieve a **full outer shell**. **Multiple electron pairs** can be shared to produce **multiple covalent bonds**.

The shared electron pairs can be represented using **dot and cross diagrams.**

**Double** and **triple** bonds can also be shown on dot and cross diagrams with the multiple electron pairs being displayed in the shared segment between the two atoms.

*Example: Dot and cross diagrams, chlorine molecule (left) and oxygen molecule (right)*



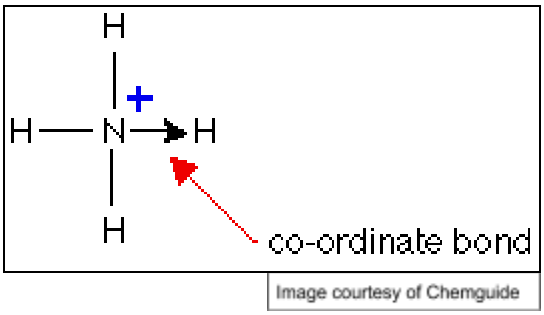

The **length** of a covalent bond is strongly linked to its **strength**. **Shorter bonds** tend to be **stronger** as the atoms are **held closer together** so the forces of attraction are greater, requiring more energy to be overcome. Double and triple bonds are shorter than single covalent bonds, explaining why they are so much stronger. **Average bond enthalpy** is used as a measure of covalent bond strength.

### Dative Bonding

Dative or coordinate bonds form when both of the **electrons in the shared pair** are supplied from a **single atom**. It is indicated using an **arrow** from the lone electron pair.

*Example:*

**Ammonia ($NH_3$) has a lone electron pair that can form a dative bond with a hydrogen ion ($H^+$) to produce an ammonium ion ($NH_4^+$).**




Once a dative bond has formed, it is treated as a **standard covalent bond** as it **reacts in exactly the same way** and has the same properties regarding length and strength.

# The Shapes of Simple Molecules and Ions

The shape of a simple molecule or ion is determined by the number of **electron pairs around the central atom** and the **repulsion** between them. Each electron pair **naturally repels** each other so that the **largest bond angle possible** exists between the covalent bonds.

In **diagrams**, a **solid line** indicates a bond that is in the plane of the paper, a **wedged line** indicates a bond that comes out of the plane of the paper and a **dotted line** indicates a bond that goes into the plane of the paper.

## Lone Pair Repulsion

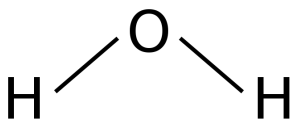
Any lone pairs present around the central atom provide **additional repulsive forces**, which changes the bond angle. For every lone pair present, the bond angle between covalent bonds is **reduced by 2.5°**. This can be seen by looking at methane, ammonia and water in the table below. All molecules have 4 electron pairs, but the bond angle decreases by 2.5° with each lone pair of electrons.

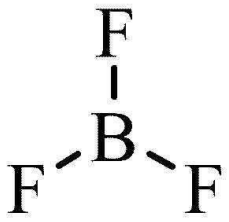
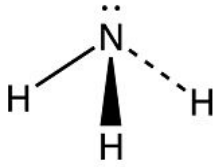
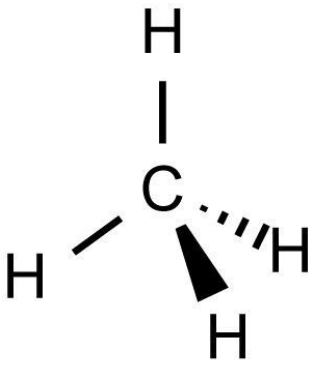
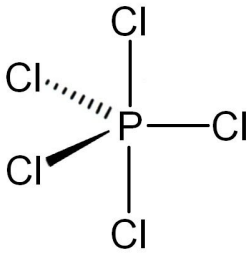
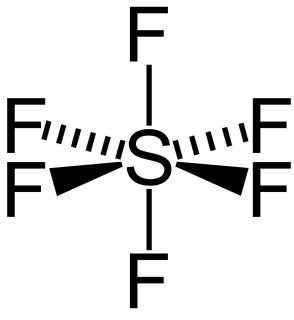
## Molecule Shapes

The shape of a molecule can be determined by considering the **type and quantity of electron pairs**:

1. Find the number of electron pairs.
2. Determine how many of the pairs are bonding pairs and how many are lone pairs.
3. Bonding pairs indicate the basic shape and lone pairs indicate any additional repulsion.

This table shows some common molecule shapes:

| Name | Bonding $e^-$ Pairs | Lone $e^-$ Pairs | Bond Angle (°) | Example |
|---|---|---|---|---|
| Linear | 2 | 0 | 180 | Cl - Be - Cl |
| Bent | 2 | 2 | 104.5 |  |

| | | | | |
|---|---|---|---|---|
| Trigonal Planar | 3 | 0 | 120 |  |
| Triangular Pyramid | 3 | 1 | 107 |  |
| Tetrahedral | 4 | 0 | 109.5 |  |
| Trigonal Bipyramid | 5 | 0 | 180 and 120 |  |
| Octahedral | 6 | 0 | 90 |  |

Images courtesy of World of Chemicals, Socratic, Quora, and Alchetron

# Electronegativity and Bond Polarity

The negative charge around a covalent bond is **not evenly distributed** around the orbitals of the bonded atoms.

## Electronegativity

Every atom has electronegativity, which is defined as:

**The ability of an atom to attract the bonding electrons in a covalent bond towards itself.**

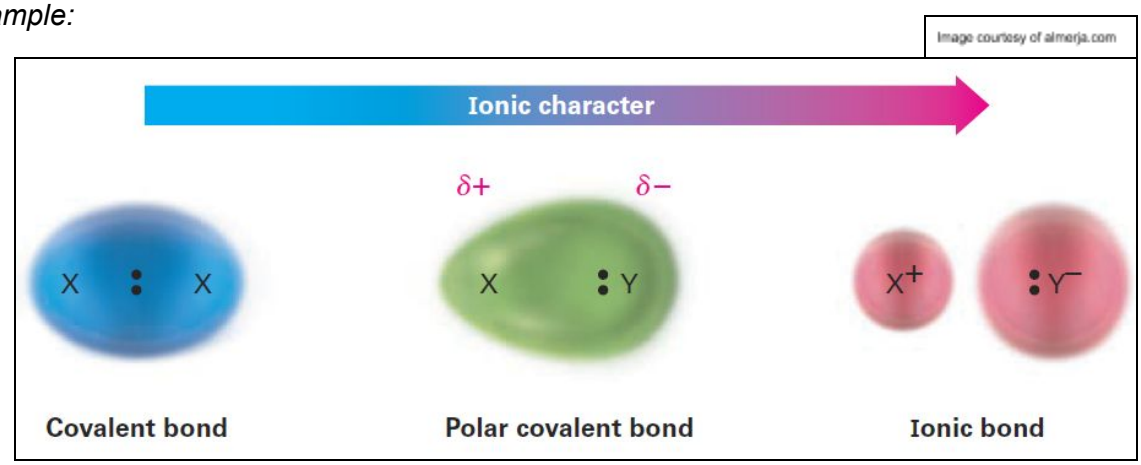
This 'power' is different for every atom depending on its **size and nuclear charge**.

- Electronegativity **increases along a period** as atomic radius decreases and charge density increases.
- Electronegativity **decreases down a group** as shielding increases and atomic radius increases so charge density decreases.

**Pauling electronegativity values** can be used to compare the electronegativity of atoms. A **higher value** on the pauling scale indicates a **greater electronegativity**. Fluorine is the most electronegative atom and has a value of 4.0.

The pauling values can be used to calculate **electronegativity differences** in a covalent bond. The greater the electronegativity difference, the greater the bond polarity. This leads to a greater degree of **ionic character**. Ionic and covalent bonding are the extremes in a continuous scale of bonding as shown below.

*Example:*

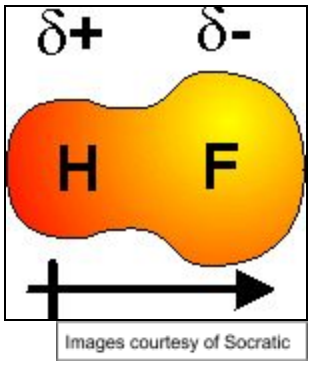



This bond polarity can be **permanent** or **induced**, depending on the molecule and how it interacts with things around it.

## Permanent Dipole

If the two atoms that are bonded have different electronegativities, a **polar bond** forms. The more electronegative atom **draws more of the negative charge towards itself** and away from other atom, producing a **∂-** region and a **∂+** region. This is a **permanent dipole**.

*Example:*



Images courtesy of Socratic

**Hydrogen fluoride is a polar molecule as fluorine is a lot more electronegative than hydrogen. This means electrons are drawn towards the fluorine atom.**

A **polar molecule** requires **polar bonds** with dipoles that do not cancel due to their direction. $CO_2$ contains two polar bonds since oxygen is more electronegative than carbon. However, these dipoles cancel due to the linear shape. Hence, $CO_2$ is **non-polar**.

Polar molecules with a permanent dipole can align to form a **lattice of molecules** similar to an ionic lattice.

## Induced Dipole

An induced dipole can form when the electron orbitals around a molecule are **influenced by the distributions of electrons on another particle**.

*Example:*

# Intermolecular Forces

There are **three main types of intermolecular force**. Each one differs in strength and in what they act between.

## Van der Waals Forces

Van der Waals forces are the **weakest** type of intermolecular force. They act as an **induced dipole** between molecules.

The strength of van der Waals forces varies depending on the Mr of the molecule and its shape. The **larger the Mr** of the molecule, the **stronger the intermolecular forces**. Straight chain molecules experience stronger van der Waals forces than branched chain molecules as they can **pack closer together**. This **reduces the distance** over which the force acts, making it stronger.

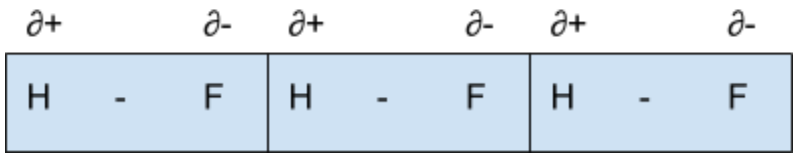
Van der Waals forces act between organic **alkane chains** and are affected by the **chain length** and the presence of **branching**. As the chain length of the alkane increases, so does the **Mr** of the molecule. This results in **stronger** intermolecular forces between the chains and the compound has a **higher boiling point** as a result.

**Branching** of alkane chains weakens van der Waal forces between the chains as they are less able to **pack tightly** together. Therefore, the distance over which the intermolecular forces act is increased and the **attractive forces** are **weakened**. This means branched chain alkanes have **lower boiling points** than straight chain alkanes.

## Permanent Dipole

Permanent dipoles are a type of intermolecular force which acts between molecules with a **polar bond**. The **∂+** and **∂-** regions on adjacent molecules attract each other and hold the molecules together in a **lattice-like structure**. These interactions are stronger than induced dipole-dipole interactions, so more energy is needed to overcome them, so melting and boiling points will be higher.

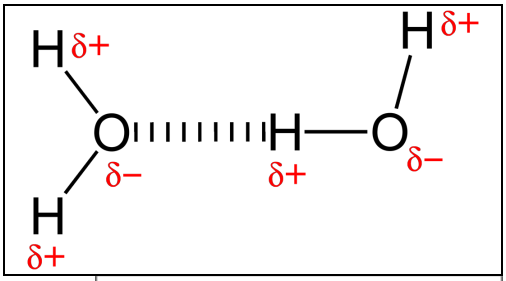
*Example:*



## Hydrogen Bonding

Hydrogen bonds are the **strongest** type of intermolecular forces. Hydrogen bonds only act between hydrogen and the three most electronegative atoms: **nitrogen, oxygen and fluorine**. The **lone pair** of electrons on these electronegative atoms forms a bond with the **∂+** hydrogen atom from another molecule. As seen in the diagram below, the hydrogen bond is often shown by a **dotted line**.

*Example:*



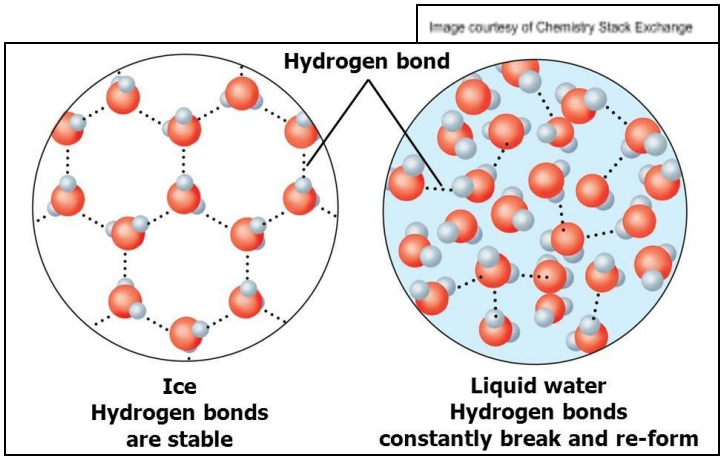

Images courtesy of The Curious Wavefunction

Molecules held together with hydrogen bonds have **much higher melting and boiling points** compared to similar sized molecules without hydrogen bonding. This shows how the type of intermolecular force heavily influences the **physical properties** of a substance.

Water has a simple molecular structure but has **unusually high melting and boiling points** for the size of the molecule due to the presence of hydrogen bonds.

The hydrogen bonds in water also result in **ice** having a much **lower density** than liquid water, as they hold the molecules in a **rigid structure** with a lot of **air gaps**.

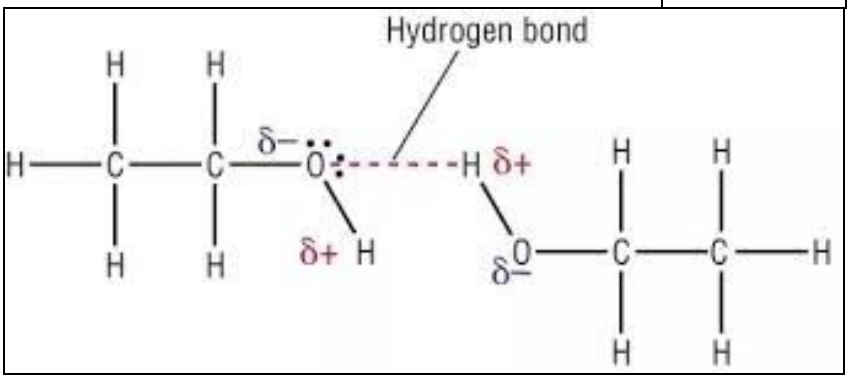
*Example: Diagram indicating how the hydrogen bonds affect the density of ice*



Hydrogen bonding is also responsible for the fact that **alcohols** have **much higher boiling points** than alkanes with a similar Mr value. This is because the lone electron pair on the oxygen atom is able to form **hydrogen bonds** with a hydrogen bonded to an oxygen on a neighbouring alcohol molecule.

*Example: Hydrogen bonds between ethanol molecules*

Image courtesy of Quora




This same property makes alcohols and water **good solvents** for compounds that are able to form hydrogen bonds in solution. However, alcohols and water can be poor for the dissolving of some **polar molecules** such as halogenoalkanes which cannot form hydrogen bonds.

Hydrogen bonds are also present in **DNA**. The **AT base pair** is held together by two hydrogen bonds and the **GC base pair** is held together by three hydrogen bonds.

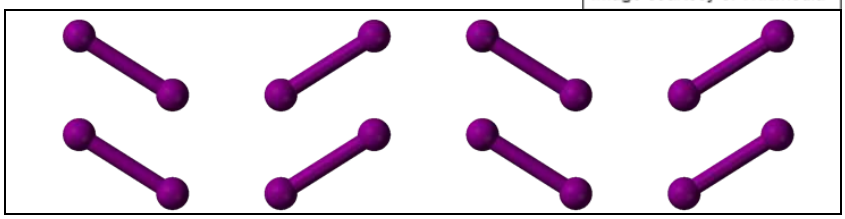
## Covalent Structures

### Simple Molecular

Substances with a simple molecular structure consist of **covalently bonded molecules** held together with weak **van der Waals** forces. These are a type of intermolecular force that act between the molecules and hold their structure.

*Example:*

Image courtesy of Wikimedia



Van der Waals forces are **very weak** and not much energy is required to overcome them, meaning simple molecular substances have **low melting and boiling points**. Simple molecular substances are **very poor conductors** as their structure contains no charged particles.

## Macromolecular - Diamond

Substances that have a macromolecular structure are **covalently bonded** into a **giant lattice** structure. Each atom has **multiple covalent bonds** which are very strong, giving the substance a **very high melting point**.

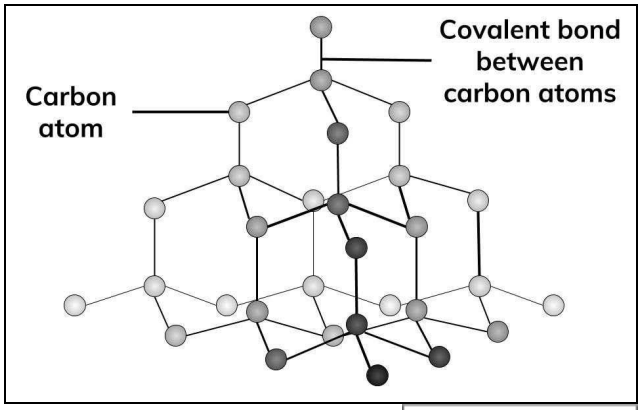


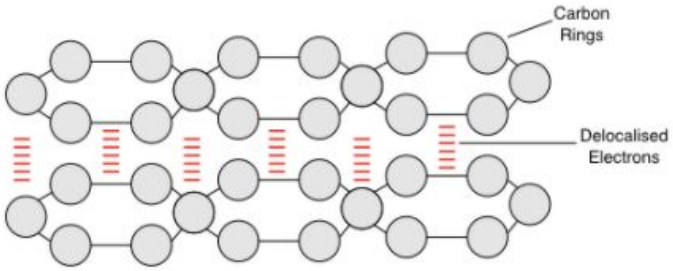
Image courtesy of Seneca

The strength of the covalent lattice makes **macromolecular** substances **rigid**. **Diamond** is a macromolecular structure made up of carbon atoms each bonded to four further carbon atoms. This makes diamond one of the **hardest**, strongest materials known.

## Macromolecular - Graphite

Graphite is a macromolecular structure made up of carbon atoms. However, in graphite, each carbon atom is bonded to three others in **flat sheets**. The electrons not used in bonding are released as **free electrons** which move between layers, meaning it can **conduct electricity**. There are **strong covalent bonds** between carbon atoms within a layer and **weak van der Waals** forces between such layers. These weak intermolecular forces allow layers to slide over each other easily. This property makes graphite a good lubricant.

*Example:*




### Graphene

Graphene is a relatively recent material consisting of single, **2D sheets of graphite** that are just **one atom thick**.

These sheets are formed of **hexagonal carbon rings** that create a very strong, rigid material that is extremely **lightweight**. Delocalised electrons move through each layer allowing graphene to **conduct** electricity.

# OCR A Chemistry A-level

## Module 3.1: The Periodic Table

### Detailed Notes

# 3.1.1 Periodicity

## The Structure of the Periodic Table

The Periodic Table arranges the known elements in order of **increasing proton number**. All the elements along a **period** (row) have the same number of **electron shells**. All the elements down a **group** (column) have the same number of **outer electrons** which is indicated by the group number. Elements in the same group have similar chemical properties.

## Periodic Trend in Electron Configuration and Ionisation Energy

Elements are classified into **blocks** within the Periodic Table, and elements in the same block have their outer electrons in the same type of **orbital**.

**s-block = Groups 1 and 2**
**p-block = Groups 3 to 0**
**d-block = Transition metals**
**f-block = Lanthanides & actinides**

Different electron configurations are often **linked to other trends** within the Periodic Table. Periodicity is the study of these trends.

The **energy** of the orbitals **increases from s to f,** meaning the orbitals are **filled in this order**. Each orbital is filled before the next one is used to hold electrons. For Period 2, first the s orbitals are filled, followed by the p orbitals. The same applies to Period 3.

*Example:*

*Nitrogen has the atomic number 7 so has 7 electrons and has the configuration:* **$1s^2 2s^2 2p^3$**

### Atomic Radius

Along a **period**, atomic radius **decreases**. This is due to an **increased nuclear charge** for the same number of electron shells. The outer electrons are pulled in closer to the nucleus as the increased charge produces a **greater attraction**. As a result, the atomic radius for that element is reduced.

Down a **group**, atomic radius **increases**. With each increment down a group, an electron shell is added. This increases the distance between the outer electrons and the nucleus, **reducing the power of attraction**. More shells also increases electron **shielding** where the inner shells create a 'barrier' that blocks the attractive forces. Therefore, the **nuclear attraction is reduced** further and atomic radius increases.

## Ionisation Energy

First ionisation energy is defined as:

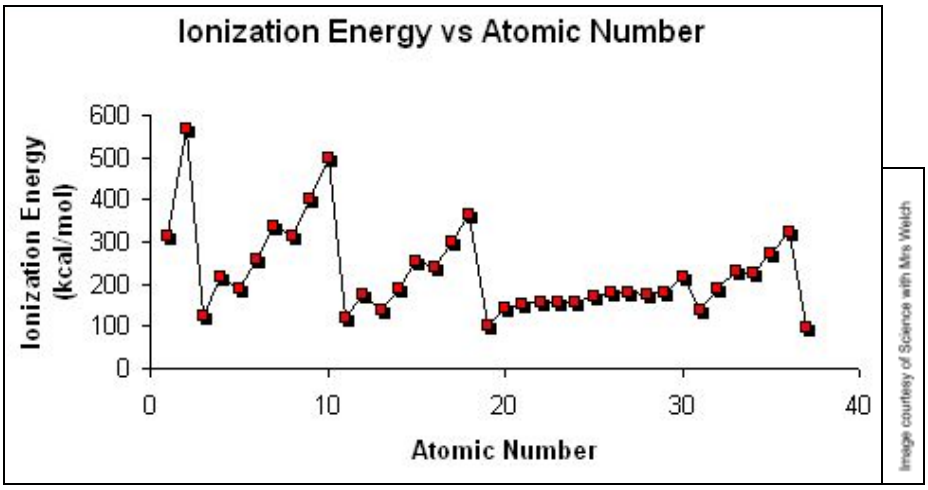
**The minimum energy required to remove one mole of electrons from one mole of atoms in a gaseous state. It is measured in $kJmol^{-1}$.**

$$Na_{(g)} \rightarrow Na^{+}_{(g)} + e^{-}$$

**Successive ionisation energies** occur when further electrons are removed. This usually requires **more energy** because as electrons are removed, the **electrostatic force of attraction** between the positive nucleus and the negative outer electron **increases**. More energy is therefore needed to **overcome this attraction,** so ionisation energy increases.

First ionisation energy follows **trends** within the Periodic Table as they are influenced by proton-electron forces of attraction and electron shielding.

- **Along a Period** - first ionisation energy **increases** due to a **decreasing atomic radius** and greater electrostatic **forces of attraction**.
- **Down a Group** - first ionisation energy **decreases** due to an **increasing atomic radius** and **electron shielding** which reduces the effect of the electrostatic forces of attraction.




**Successive ionisation energies** involve removing one mole of electrons from **one mole of gaseous ions**. For example, the third ionisation energy of potassium would involve removing one electron from $K^{2+}(g)$ to form $K^{3+}(g)$.

**Successive ionisation energies increase** because atomic radius decreases and there is greater attraction between outer shell electrons and the nucleus.

A large **jump** between successive ionisation energies indicates which **group** an element is in. The successive ionisation energies for an element are shown below:

| 1st | 2nd | 3rd | 4th | 5th |
|---|---|---|---|---|
| 801 | 2427 | 3660 | 25026 | 32827 |

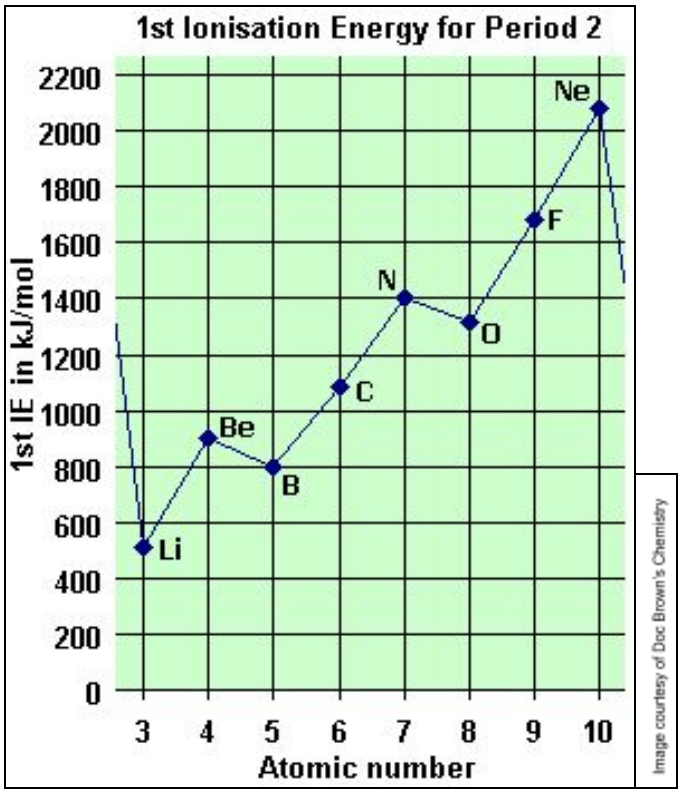
The **large jump between the third and fourth ionisation energy** shows there are 3 electrons that are relatively easy to remove then a fourth one which requires a lot more **energy to remove**. This shows that there are 3 electrons in an outer shell. This means the element is in **Group 3**. There are 5 ionisation energies for this element so it has **5 electrons**. An element with 5 electrons in Group 3 is boron.

## Period 2

First ionisation energies follow a general increasing trend along Period 2. This is due to the decreasing atomic radius and increasing nuclear charge meaning outer electrons are **held more strongly**.

Boron and oxygen are **exceptions** to this trend. **Boron** has a **lower first ionisation energy** than expected by the general trend as a result of the energy difference between the 2s and 2p sub-shells. The electron is being removed from a **higher energy level** that is further from the nucleus, so the electron is held less strongly.

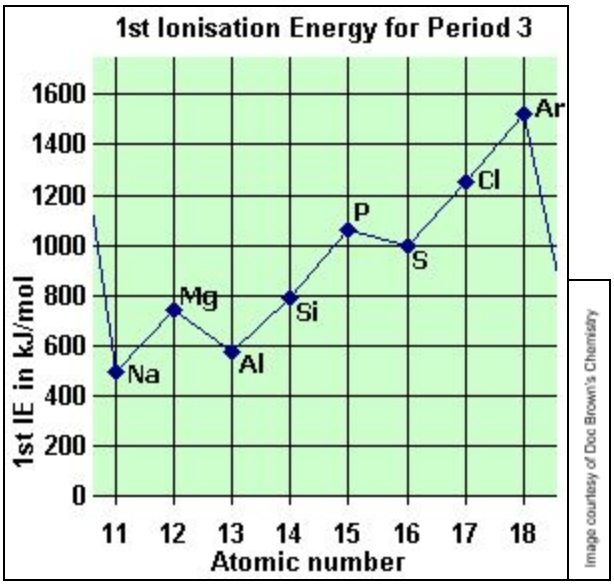
**Oxygen** has a lower first ionisation energy than would be otherwise expected due to **repulsion** within the 2p orbital when two electrons with opposite spins are placed in the same orbital. This repulsion is **destabilising** in comparison to the configuration of nitrogen and allows the electron to be removed from oxygen more easily.



### Period 3

**First ionisation energies** follow a **general increasing trend** along Period 3. This is due to the decreasing atomic radius and increasing nuclear charge meaning outer electrons are **held more strongly**.

Aluminium and sulfur are **exceptions** to this trend. **Aluminium** has a **lower first ionisation energy** than expected by the general trend as a result of the energy difference between the 3s and 3p sub-shells. The electron is being removed from a **higher energy level** that is further from the nucleus, so it is held less strongly.

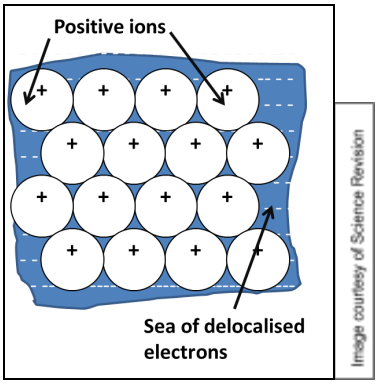



**Sulfur** has a lower first ionisation energy than would be otherwise expected due to **repulsion** within the 3p orbital when two electrons with opposite spins are placed in the same orbital. This repulsion is **destabilising** in comparison to the configuration of phosphorus and allows the electron to be removed from sulfur more easily.

## Periodic Trend in Structure and Melting Point

### Metallic Bonding

Metallic bonding consists of a **lattice of positively charged ions** surrounded by a **'sea' of delocalised electrons**. There are very strong **electrostatic forces of attraction** between the oppositely charged particles.



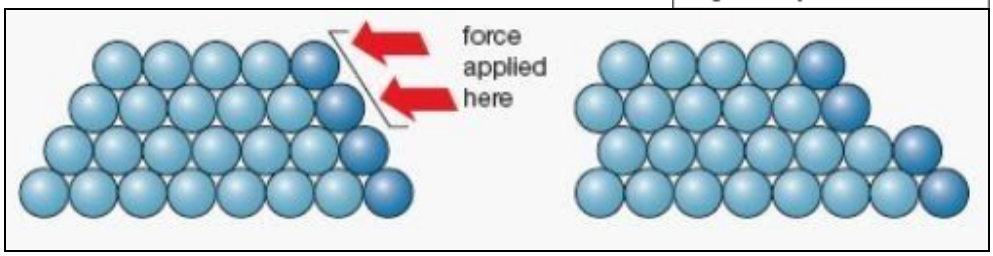

The **greater the charge** on the positive ion, the **stronger the attractive force** as more electrons are released into the 'sea'. Ions that are **larger in size**, such as barium, produce a **weaker attraction** due to their **greater atomic radius** decreasing the charge density.

## Metallic Properties

Substances with metallic structure are often **good conductors**. The 'sea' of delocalised electrons is able to move and **carry a flow of charge**.

Metals are also **malleable** as the **uniform layers** of positive ions are able to slide over one another. The delocalised electrons prevent fragmentation as they can move around the lattice.

Image courtesy of Pintrest Teachers

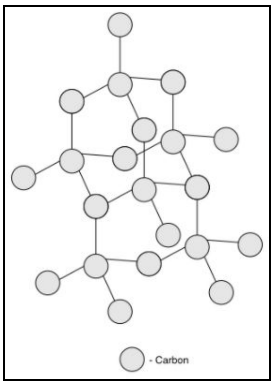



The electrostatic forces of attraction between the positive ions and delocalised electrons are very strong and therefore require a lot of energy to overcome. This means metallic substances have **high melting points** and are nearly always **solid at room temperature**. Mercury is the only metal which is a liquid at room temperature.

## Giant Covalent Lattices

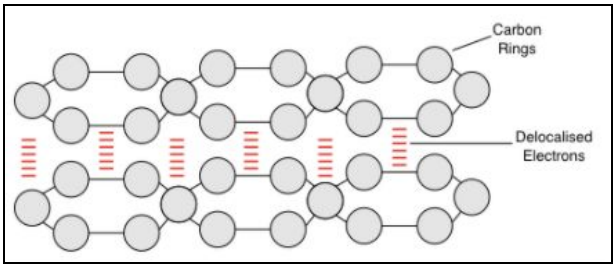
A solid giant covalent lattice is a network of atoms bonded by many **strong covalent bonds**.

Substances that have a macromolecular structure are **covalently bonded** into a **giant lattice** structure. Each atom has **multiple covalent bonds** which are very strong, giving the substance a **very high melting point**.



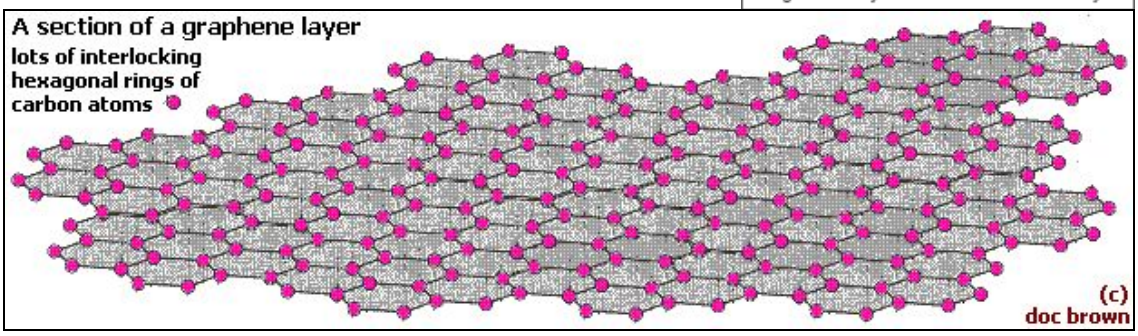

**Diamond** is a macromolecular structure made up of carbon atoms, each of which are bonded to four further carbon atoms. This provides a very **rigid** structure, making diamond one of the **hardest materials**.

**Graphite** is another **macromolecular** structure made up of carbon atoms. However, in graphite, each carbon atom is bonded to three other carbon atoms in **flat sheets**. This means there is one **delocalised electron** per carbon atom which can move between layers, meaning graphite can **conduct electricity**. There are strong covalent bonds between carbon atoms but weak van der Waals forces between the layers. These **weak intermolecular forces** allow layers to slide over each other easily, making graphite a good **lubricant**.



**Graphene** is a relatively new material consisting of single, **2D sheets of graphite** that are just **one atom thick**. These sheets are formed of **hexagonal carbon rings** that create a very strong, rigid material that is extremely **lightweight**. Delocalised electrons move through each layer allowing it to **conduct** electricity.

Image courtesy of Doc Brown's Chemistry




## Variation in Melting Points across Periods 2 and 3

The melting points of the Period 2 elements peaks towards the middle of the period due to the different **bond strength and structures**:

- Lithium and beryllium have **metallic bonding**. Their melting points increase due to a greater **positive charge of the ions** (Li = +1, Be = +2). There are **more electrons released** as free electrons in the beryllium lattice so the attractive electrostatic forces are greater than for lithium.
- **Boron** and **carbon** form giant covalent lattices with **very strong covalent bonds.** Covalent bonds require a lot of energy to break, giving them very high melting points.
- Nitrogen, oxygen, fluorine and neon are all **small**, **simple covalent molecules** with weak **van der Waals** intermolecular forces. These intermolecular forces don't require much energy to overcome so these molecules have relatively low, similar melting points.

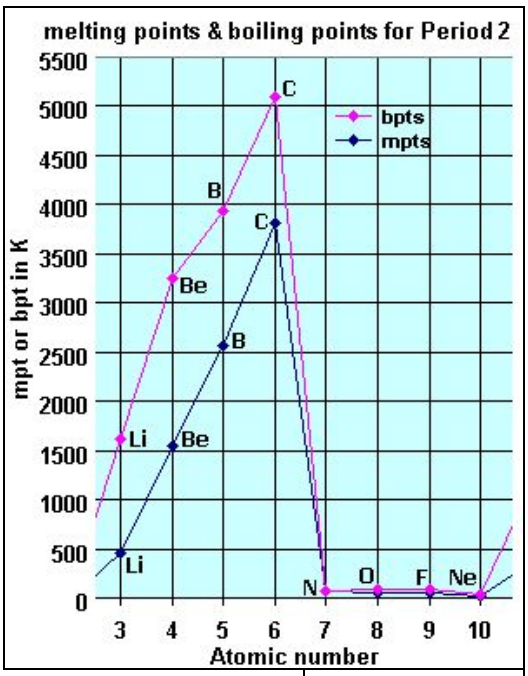



Image courtesy of Doc Brown's Chemistry

The melting points of the Period 3 elements are also linked to the **bond strength and structure**:

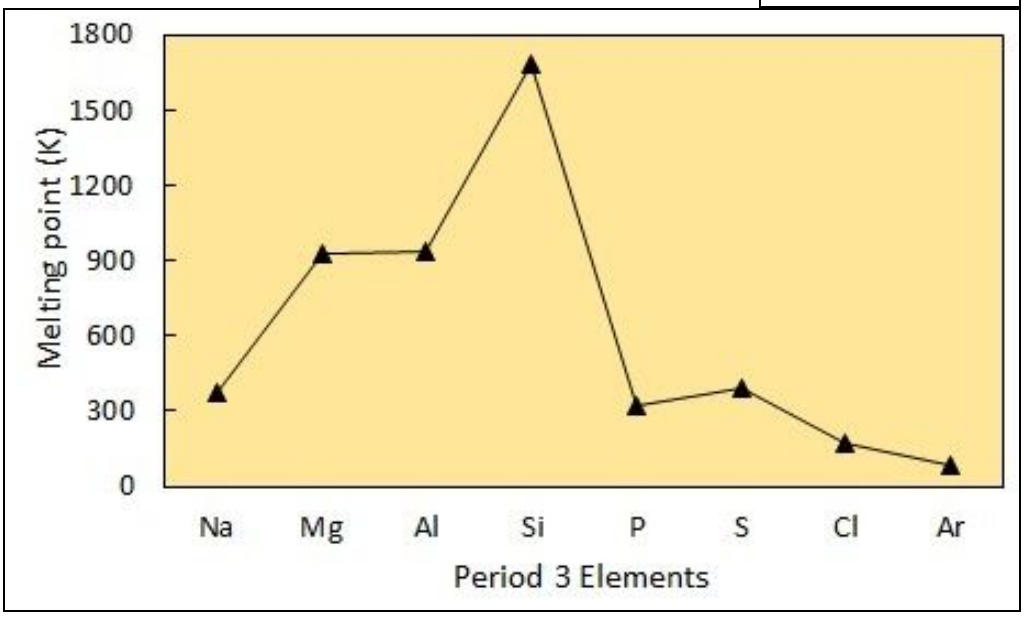
- Sodium, magnesium and aluminium are all metals with **metallic bonding**. Their melting points increase due to greater **positive charged ions** (Na = +1, Mg = +2, Al = +3). This also means **more electrons are released** as free electrons so the attractive electrostatic forces increase from Na to Al.

- Silicon is macromolecular meaning it has a **very strong covalent structure**. These covalent bonds require a lot of energy to break, giving it a very high melting point.

- Phosphorus, sulphur and chlorine are all **simple covalent molecules** with weak **van der waals** forces. These intermolecular forces don't require much energy to overcome so these molecules have relatively low, similar melting points.

- Argon is a noble gas that exists as **individual atoms** with a **full outer shell of electrons**. This makes the atom **very stable** and the van der waals forces between them very weak. As a result, the melting point of Argon is very low and it exists as a gas at room temperature.

Image courtesy of CapeChemistry



# 3.1.2 Group 2

## Redox Reactions and Reactivity of Group 2 Metals

**Group 2** metals have an $ns^2$ valence shell configuration. When Group 2 metals react, they lose two electrons to **form 2+ ions**.This allows them to achieve a full outer shell. All Group 2 elements tarnish in air and form a coating of the metal oxide. The various **physical properties** of these elements follow trends down the group:

### Atomic Radius

The atomic radius of Group 2 metals **increases** down the group due to additional electron shells.

### Reactivity

Increased electron **shielding** and increased atomic radius down the group makes the outer electrons **easier to lose**. Therefore, reactivity of the Group 2 metals **increases** down the group. The increase in reactivity down the group is demonstrated by the reactions below.

### Ionisation Energy

The first and second ionisation energies of Group 2 metals **decrease** down the group due to a greater atomic radius and increased amounts of shielding. This makes it easier for an electron to be removed.

## Reactions of Group 2 Compounds

### Reactions with Water

The Group 2 metals react with water in a redox reaction to produce a **metal hydroxide and hydrogen**. The metal hydroxide forms as an **alkaline solution**, hence why the Group 2 metals are known as the alkaline earth metals.

*Example:*

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

***The Magnesium is oxidised from an oxidation state of 0 to +2.***
***(Oxidation is loss of $e^-$)***

Magnesium reacts very slowly in this way with liquid water, however, the reaction can be much **faster with steam** as it provides the reaction with **extra energy**. When steam is used, the magnesium burns with a **bright white flame** to form hydrogen and magnesium oxide, a **white powder**.

*Example:*

$$Mg + H_2O \longrightarrow MgO + H_2$$

Down the group, the **reactivity** of the Group 2 metals with water **increases**. Calcium, strontium, and barium all react with cold water with **increasingly vigorous** reactions. These reactions all form the metal hydroxide and hydrogen gas.

The **metal oxides** of the Group 2 elements react with water to form basic metal hydroxides. The alkalinity of these increases down the group as the solubility of the metal hydroxides increases.

### Reactions with Chlorine

Group 2 metals all react with chlorine gas to form **metal chlorides,** which are all **white precipitates.** As you move down the group the reactions become **more vigorous** because the elements are **more reactive.**

*Example:*

$$Mg + Cl_2 \rightarrow MgCl_2$$

### Reactions with Oxygen

Group 2 metals react with oxygen to form **oxides**. Once the reaction has been initiated it is **vigorous**. **Strontium** and **barium** can react with excess oxygen and heat energy to form **metal peroxides**.

The general equation of Group 2 metals with oxygen is:

$$2M + O_2 \rightarrow 2MO$$

Strontium or barium may react with oxygen and form the peroxide:

$$M + O_2 \rightarrow MO_2$$

### Reactions with Dilute Acids

The Group 2 metals react with dilute acids to produce **bubbles of hydrogen gas** and solutions of **metal compounds**.

*Example:*

Hydrochloric Acid:

$$X + 2HCl \longrightarrow XCl_2 + H_2$$

Sulfuric Acid:

$$X + H_2SO_4 \longrightarrow XSO_4 + H_2$$

Nitric Acid:

$$X + 2HNO_3 \longrightarrow H_2 + X(NO_3)_2$$

### Reactions of Group 2 Hydroxides with Dilute Acid

Group 2 hydroxides react with dilute acid to form **a salt** and **water.** This is a type of **neutralisation** reaction. The salt formed depends on the acid used:

- **Hydrochloric** acid forms **chloride** salts.
- **Sulfuric** acid forms **sulfate** salts.
- **Nitric** acid forms **nitrate** salts.

*Example: Calcium hydroxide with hydrochloric acid*

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$$

## Solubility of Group 2 Compounds

### Solubility of Group 2 Hydroxides

The **solubility** of Group 2 hydroxides varies, allowing the compounds to have different uses. Solubility **increases down the group** meaning magnesium hydroxide, $Mg(OH)_2$, is the least soluble and barium hydroxide, $Ba(OH)_2$, is the most soluble.

As a result, **magnesium hydroxide** is used in medicine as an **antacid** to treat indigestion as it is alkaline and can neutralise acids. **Calcium carbonate** can also be used as an **antacid**. **Calcium hydroxide** is also used in **agriculture** to neutralise acidic soils.

### Solubility of Group 2 Sulfates

Group 2 sulfates **decrease in solubility down the group** meaning magnesium sulfate, $MgSO_4$, is the most soluble and barium sulfate, $BaSO_4$, is the least soluble.

The insolubility of **barium sulfate** means it is very useful in medicine as **barium meals**. These are a form of medical tracer that allow internal tissues and organs to be imaged. Barium sulfate is toxic if it enters the bloodstream, however because it is insoluble, it **cannot be absorbed** into the blood. Therefore, it is **safe** to use in this way.

Barium chloride is used as a **test for sulfate ions** as it reacts to form barium sulfate which forms as a **white precipitate** when sulfate ions are present.

*Example:*

$$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow BaSO_{4(s)}$$

## 3.1.3 The Halogens

## Characteristic Physical Properties

The Group 7 elements are **highly reactive non-metals.** The halogens exist as **diatomic** molecules with single covalent bonds. In reactions, in order to achieve a full outer shell, the halogens gain an electron and form a **1- ion.**

### Atomic Radius

Atomic radius of Group 7 elements **increases down the group** due to additional electron shells.

### Electronegativity

As you go down Group 7, **atomic radius and electron shielding increases**. This means electrons in the outer shells are less strongly attracted to the nucleus, and so are more easily removed. Therefore, electronegativity decreases down Group 7.

### Melting and Boiling Point

The Group 7 elements are **simple covalent molecules,** with weak **van der waals** forces. The strength of these intermolecular forces increases as the relative atomic mass of the molecule increases, so the strength of the van der waals forces **increases down the group**. This means **more energy** is required to overcome them, resulting in higher melting and boiling points. This is why **fluorine** is a **gas** at room temperature, whereas **iodine** is a **solid**.

### Reactivity

Halogens have $s^2p^5$ outer shell **electron configuration**. They need to **gain an electron** in order to react. As atomic radius increases, this becomes harder as the positive attraction of the nucleus is weakened by additional **shielding**. Therefore, down Group 7 it is harder to attract an electron so **reactivity decreases**.

### Appearance

The colour and state of the halogens at room temperature and pressure are listed below:

**Fluorine** - pale yellow gas
**Chlorine** - pale green gas
**Bromine** - red/brown liquid
**Iodine** - dark grey solid which sublimes to a purple vapour

## Redox Reactions and Reactivity of Halogens and their Compounds

### Oxidising Power of the Halogens

The halogens act as good **oxidising agents** as they accept electrons from the species being oxidised and are themselves reduced. This oxidising power **decreases down the group** as their ability to attract electrons decreases due to shielding and a greater atomic radius.
The relative oxidising strengths mean a halogen will **displace any halide beneath it** in the Periodic Table.

$Cl_2$ will displace $Br^-$ and $I^-$ ions.

$Br_2$ will displace $I^-$ ions

$I_2$ won't displace any halide ions.

### Halide Ions

The negative ions of halogens are known as **halide ions**. These ions are **good reducing agents** as they donate electrons to the species being reduced and are themselves oxidised.
This reducing power **increases down the group** as electrons are easier to lose from larger ions due to shielding and a larger atomic radius meaning there is a **weaker attraction** between the nucleus and the outer electrons.

# Reactions of Group 7 Elements and Ions

## Redox Reactions

The redox reactions between Group 1 and Group 2 halides and $H_2SO_4$ vary depending on the **reducing ability** of the halide:

*Example:*

1. Fluoride and Chloride ions

$$NaF + H_2SO_4 \longrightarrow NaHSO_4 + HF$$

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

***No further reactions*** *take place since HF and HCl are not strong enough reducing agents to reduce* $H_2SO_4$*. HF and HCl will both be observed as* ***misty fumes****.*

2. Bromide ions

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$

*HBr will be observed as* ***misty fumes*** *from the first reaction.* ***Orange fumes*** *of* $Br_2$ *and* ***choking fumes*** *of* $SO_2$ *will be observed in the second reaction, where HBr reduces* $H_2SO_4$*.*

3. Iodide ions

$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$$

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

$$6HI + SO_2 \longrightarrow H_2S + 3I_2 + 2H_2O$$

*HI will be observed as* ***misty fumes*** *from the first reaction. HI then reduces* $H_2SO_4$ *to* ***solid iodine*** *and* ***choking fumes*** *of* $SO_2$*. The HI will then further reduce the* $SO_2$ *to* ***toxic gas*** $H_2S$ *(which smells of bad eggs).*

The **greater** the reducing power of the halide, the **further** the reaction will proceed as the halide is powerful enough to reduce more species. These reactions therefore represent the trend in reducing power in halide ions. Clearly, **reducing power increases** down Group 7.

### Disproportionation Reactions

A **disproportionation** reaction is a reaction in which a species is both **oxidised** and **reduced**. Chlorine reacts with cold water to produce **chlorate(I) ions ($ClO^-$)** and **chloride ions** via a **disproportionation reaction** as the chlorine is both oxidised and reduced. The oxidation state goes from zero to both **+1 and -1**.

*Example:*

$$Cl_2 + H_2O \longrightarrow ClO^- + Cl^- + 2H^+$$

$$0 \qquad\qquad +1 \qquad -1$$

This reaction is used in **water treatment systems** where chlorine is used in small quantities to kill bacteria. This poses some risks as chlorine can be **toxic** - however the benefits of clean, treated water outweigh the risks.

A similar reaction of chlorine with cold dilute sodium hydroxide is used in bleach production. **Sodium chlorate(I)**, a key ingredient in the production of bleach, is produced via this **disproportionation** reaction.

*Example:*

$$2NaOH + Cl_2 \longrightarrow NaClO + NaCl + H_2O$$

If chlorine is reacted with **hot, concentrated alkali,** chlorine is disproportionated even further to form one species with an oxidation number of **-1** and another with an oxidation number of **+5**.

*Example:*

$$3Cl_2 + 6NaOH \rightarrow NaClO_3 + 5NaCl + 3H_2O$$

$$\mathbf{0} \qquad\qquad \mathbf{+5} \qquad \mathbf{-1}$$

### Oxidation Reactions with Group 1 and Group 2 Metals

Group 1 and Group 2 metals react with chlorine gas to form **metal chlorides,** which are all **white precipitates**. During these reactions **chlorine is reduced** and the **metal is oxidised.**

$$\underset{0}{Mg} + \underset{0}{Cl_2} \rightarrow \underset{+2\ -1}{MgCl_2}$$

## Characteristic Reactions of Halides

When combined with acidified **silver nitrate**, halide ions react to form different **coloured precipitates,** depending on the ion present. The precipitates formed can be used to identify which halide is present in a solution. It may not always be clear to distinguish the colour of the precipitate so they can be tested further using **ammonia**.

| Halide ion | $Cl^-$ | $Br^-$ | $I^-$ |
|---|---|---|---|
| **+ $AgNO_3$** | White precipitate ($AgCl$) | Cream precipitate ($AgBr$) | Yellow Precipitate ($AgI$) |
| **+ dilute $NH_3$** | Precipitate dissolves | No Change | No Change |
| **+ conc. $NH_3$** | Precipitate dissolves | Precipitate dissolves | No Change |

### Reactions of Hydrogen Halides

Hydrogen halides react with ammonia gas to form **ammonium salts**. The hydrogen halides (hydrogen chloride, hydrogen bromide and hydrogen iodide) are strong acids in solution and react with ammonia in an **acid-base reaction** to form a salt.

$$HCl + NH_3 \rightarrow NH_4Cl$$
$$HBr + NH_3 \rightarrow NH_4Br$$
$$HI + NH_3 \rightarrow NH_4I$$

Hydrogen halides react with water to form **dilute acids**. In solution, these strong acids **dissociate** to release their halide ions and hydrogen ions. The hydrogen ions form a **hydroxonium ion** with water molecules in solution. The resulting solution is **acidic**.

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$
$$HBr + H_2O \rightarrow Br^- + H_3O^+$$
$$HI + H_2O \rightarrow I^- + H_3O^+$$

# 3.1.4 Qualitative Analysis

## Tests for Ions

The following tests can be used to **determine** if any of these **ions are present**. They should be performed in the order carbonate, sulfate, then halide if a mixture of ions is present.

### Carbonate ($CO_3^{2-}$) and Hydrogencarbonate ($HCO_3^-$)

When an acid such as HCl is added, the substance containing the carbonate ions will **fizz and $CO_2$ gas is given off**. This gas can be collected and bubbled through **limewater** which will turn **cloudy**, confirming its identity as carbon dioxide.

$$XCO_3 + 2HCl \longrightarrow CO_2 + H_2O + XCl_2$$

### Sulfate ($SO_4^{2-}$)

These are tested for using **acidified $BaCl_2$** which reacts to form a **white precipitate** of barium sulfate.

$$BaCl_2 + XSO_4 \longrightarrow BaSO_4 + XCl_2$$

### Halide ions ($Cl^-$,$Br^-$,$I^-$)

When combined with **acidified silver nitrate**, halide ions react to form different **coloured precipitates** depending on the ion present. The halide can be tested further with **ammonia**.

| Halide Ion | $Cl^-$ | $Br^-$ | $I^-$ |
|---|---|---|---|
| **+ $AgNO_3$** | White precipitate (AgCl) | Cream precipitate (AgBr) | Yellow Precipitate (AgI) |
| **+ dilute $NH_3$** | Precipitate dissolves | No Change | No Change |
| **+ conc. $NH_3$** | Precipitate dissolves | Precipitate dissolves | No Change |

### Ammonium ($NH_4^+$)

If ammonium ions are present, adding NaOH and gently warming results in the formation of **ammonia gas**, which is **basic**. Therefore, the presence of ammonium ions can be tested by holding **damp red litmus paper** over a petri dish of the substance being tested. It will **turn blue** if ammonium ions are present.

# OCR A Chemistry A-level

## Module 3.2: Physical Chemistry

### Detailed Notes

# 3.2.1 Enthalpy Changes

## Enthalpy Change

Enthalpy change is heat energy change and is represented by the symbol $\Delta H^{\ominus}$. Enthalpy is measured under standard conditions of **100 kPa pressure** and a specified temperature, generally **298 K**. Standard states are the physical states of reactants under standard conditions.

In a reaction, bonds are broken and then bonds are made. For bonds to be **broken**, energy is **taken in** from the surroundings and when bonds are **formed**, energy is **given out**. The overall energy change of the reaction depends on how much energy is transferred in these processes.

When energy is taken in from the surroundings, the **enthalpy change is positive**. This is an **endothermic** reaction. When energy is released to the surroundings, the **enthalpy change is negative**. This is an **exothermic** reaction.

Overall enthalpy change ($\Delta H$) can be calculated as follows:

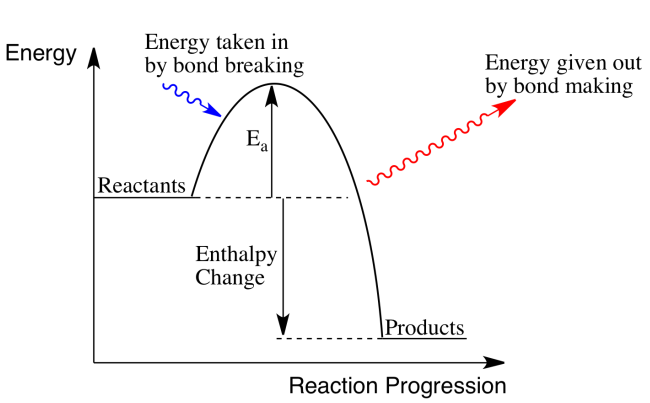
*$\Delta H$ = energy to break bonds (+ve) + energy released by making bonds (-ve)*

### Activation Energy

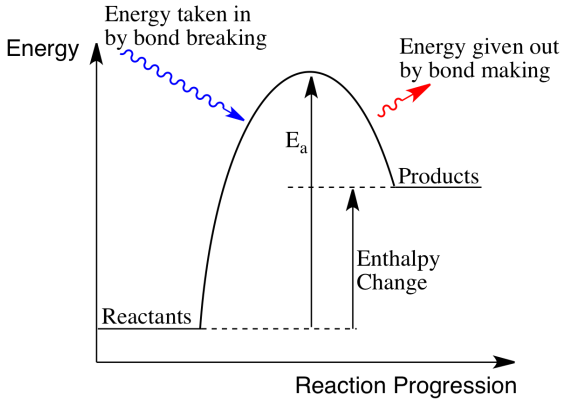
Activation energy is the **minimum energy** required for a reaction to take place between two colliding reactant particles.

Enthalpy changes are shown on an **enthalpy profile diagram**. **Activation energy** is the difference between the reactants and the top of the hump on an enthalpy profile diagram and is represented by the symbol $\mathbf{E_a}$.

*Example:*




**Exothermic Reaction**




**Endothermic Reaction**

In **endothermic** reactions, more energy is needed to break bonds than to make new ones. Therefore, the overall **$\Delta H$ is positive** and **heat is taken in** from the surroundings.

In **exothermic** reactions, the opposite is true, with more energy being needed to make new bonds than break existing ones. Therefore, **heat is given out** and **$\Delta H$ is negative.**

### Enthalpy Change of Reaction ($\Delta_r H^{\ominus}$)

This is defined as:

**The enthalpy change associated with a stated reaction. Quantities of substances in standard states react completely under standard conditions.**

### Enthalpy Change of Formation ($\Delta_f H^{\ominus}$)

This is defined as:

**The enthalpy change when one mole of a substance is produced from its elements in their standard states under standard conditions.**

### Enthalpy Change of Combustion ($\Delta_c H^{\ominus}$)

This is defined as:

**The enthalpy change when one mole of a substance is burned completely in oxygen under standard conditions.**

### Enthalpy Change of Neutralisation ($\Delta_n H^{\ominus}$)

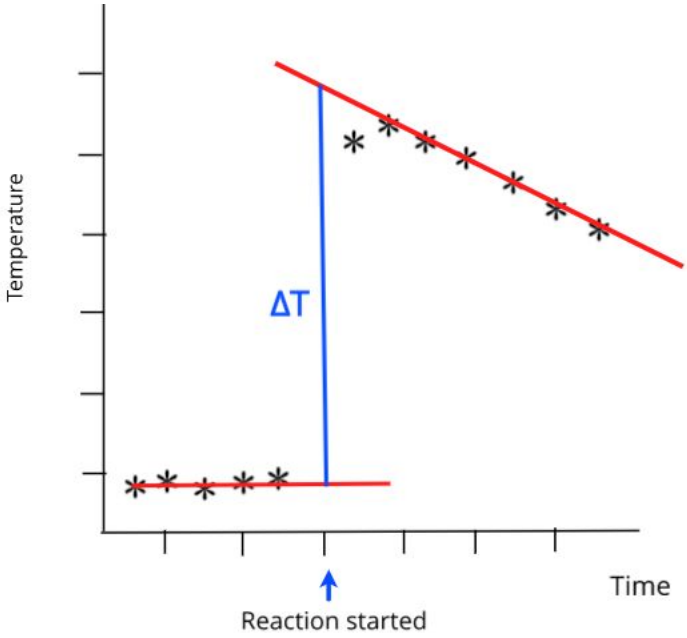
This is defined as:

**The enthalpy change when solutions of acid and alkali react together under standard conditions to produce one mole of water.**

### Calorimetry

Calorimetry is an **experimental method** for finding enthalpy change, which works by measuring **temperature change over time**. When recorded and plotted on a graph, data can be **extrapolated** to the exact point at which the reaction starts, giving a more accurate value for the change in temperature.

*Example: Graph showing the extrapolated line of best fit*




This measured change in temperature, ΔT, is **proportional** to the energy change:

$$q = mc\Delta T$$

where q = energy change (J), m = mass (g), c = specific heat capacity (J $g^{-1}K^{-1}$), ΔT = temperature change (K).

This equation allows the energy change of a substance of known mass to be calculated. It depends on its **specific heat capacity**, defined as:

**The energy required to raise 1 g of substance by 1 K without a change of state.**

Using this energy value (q), **enthalpy change per mole** (kJ $mol^{-1}$) of substance can be calculated. **ΔH** represents the enthalpy change per mole of substance.

$$\Delta H = \frac{q \times 10^{-3}}{\text{moles}}$$

### Sources of Error

ΔH values found using calorimetry are **never completely accurate,** since energy is easily lost from the system. Heat loss can occur due to **conduction**, **convection** or inaccuracies in measuring temperatures. The heat loss to the surroundings can be reduced by putting a **lid** on the calorimeter and **insulating** the outsides of the calorimeter, using an insulator like polystyrene.

Also, the **specific heat capacity** of the solution is generally taken to be 4.18 J $g^{-1}$ $K^{-1}$, which is the value for water and so might not be accurate for the **actual solution** being used. The **specific heat capacity** of the **calorimeter** is not taken into account so this leads to inaccuracies in the calculation.

## Bond Enthalpies

Bond enthalpy data is an **averaged** value representing:

**The energy required to break one mole of the stated bond in a gaseous state, under standard conditions.**

Different covalent bonds require different amounts of energy to be broken. Values can be found experimentally using **calorimetry** methods. The bond enthalpy values calculated in this way often differ from the **databook values** as they are **not exact** and they **vary in each situation**. This means the databook values are **averaged values**.

**Mean bond enthalpy** values tell you how much energy is required to break a particular bond, averaged out across the range of compounds containing that bond. These values relate to how **strong** a bond is, so they can be used to infer which bonds might **break first** in a chemical reaction. Bonds with **lower** bond enthalpy values would be expected to break first.

If a reaction requires the breaking of many strong bonds or the reaction is endothermic overall, then it is likely that the reaction will occur **slowly** at **room temperature.**

### Bond Enthalpy Calculations

Mean bond enthalpy values can be used to calculate the **overall enthalpy change** for a reaction.

$$\Delta_r H = \Sigma \Delta H(bond\ breaking) - \Sigma \Delta H(bond\ making)$$

This means that the enthalpy change for a reaction is equal to the **sum** of the bond enthalpies for the bonds **broken** in the reaction (reactants), minus the **sum** of the bond enthalpies for the bonds **made** in the reaction (products).

Mean bond enthalpy values are often **tabulated.** You need to identify the bonds broken and formed during the reaction in order to calculate the overall enthalpy change.

*Example*:

Calculate the enthalpy change when methane undergoes complete combustion in oxygen using the bond enthalpies given.

| **Bond** | **Bond enthalpy (kJ $mol^{-1}$)** |
|---|---|
| C-H | 413 |
| O=O | 498 |
| O-H | 464 |
| C=O | 799 |

**Chemical equation: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$**

**Bonds formed**

C=O x 2 = 799 x 2 = 1598

H-O x 4 = 464 x 4 = 1856

**Bonds broken**

C-H x 4 = 413 x 4 = 1652

O=O x 2 = 498 x 2 = 996

Enthalpy change = (1652+996) - (1856+1598)

= 2648 - 3454

= -806 kJ $mol^{-1}$

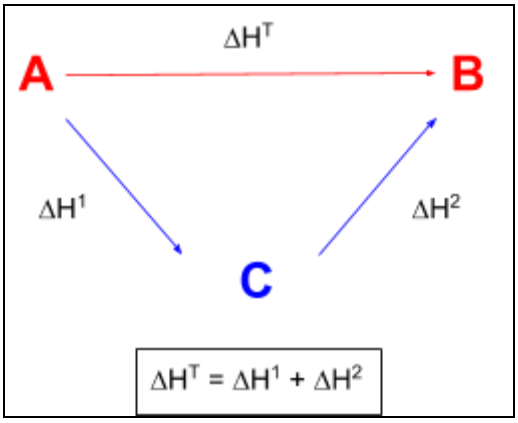
This is a negative value. This means that the reaction is **exothermic**.

# Hess's Law and Enthalpy Cycles

Energy in a reaction system must be **conserved**, as energy cannot be created or destroyed. Therefore, the **overall enthalpy change** for a reaction is **the same**, regardless of the **route taken**.

This idea is **Hess's Law** and it is used to determine the enthalpy changes for reactions where the enthalpy change **cannot be found directly** using an experimental method.

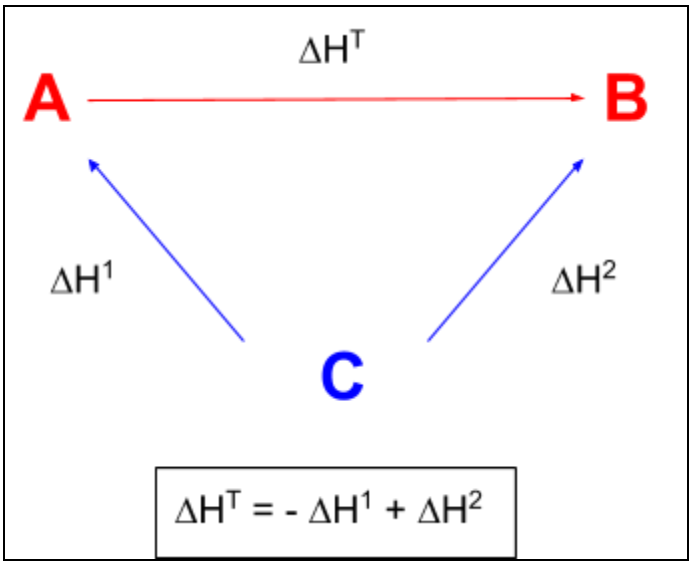
To do this, a **triangular cycle method** is used with an intermediate product. The direction of the arrows indicates whether the values should be added or taken away. They can be treated like vectors:




## Enthalpies of Formation

Hess's law can be used to calculate an enthalpy change using given enthalpies of formation. When setting up the triangular diagram, the **arrows point out from the central elements at C** as both A and B are formed from these elements.

*Example:*

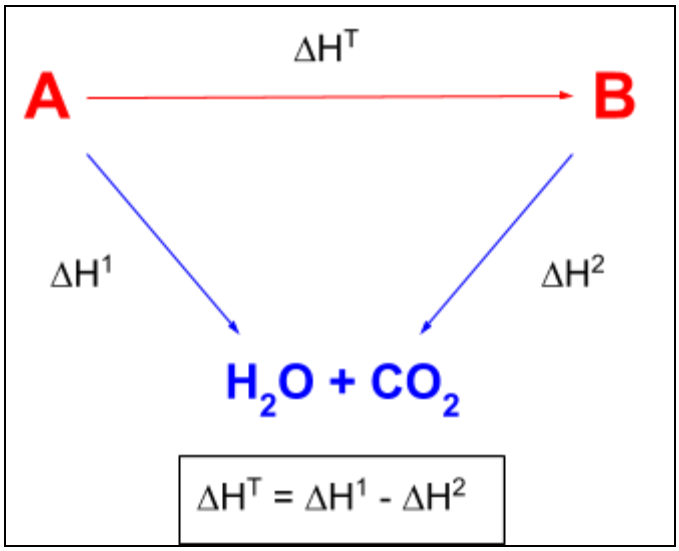



***Note:* $\Delta H^1$ *is subtracted as the reaction goes in the opposite direction to the arrow.***

### Enthalpies of Combustion

Hess's law can also be used to calculate an enthalpy change using given enthalpies of combustion. When setting up the triangular diagram, the **arrows point towards the central products (which always include $H_2O$ and $CO_2$)** as both A and B burn (combust) to form the products at C.

*Example:*




***Note: $\Delta H^2$ is subtracted as the reaction goes in the opposite direction to the arrow.***

The same principles can be **applied** to any given enthalpy values to then calculate the enthalpy change of a reaction. Just create an **alternate path of known enthalpies** to calculate the unknown value.

## 3.2.2 Reaction Rates

## Simple Collision Theory

Chemical reactions occur when reactant particles **collide**. For a reaction to occur successfully, these collisions must have energy greater than or equal to the **activation energy** of the reaction, and the **particle orientation** must be correct. The activation energy is the minimum amount of energy required for two particles to react.

### Reaction Conditions

The conditions of a reaction impact the collisions of the particles and can be altered to give the particles **more energy**. Therefore, the conditions can be changed to increase the likelihood of a collision occurring with **sufficient energy** to react. This will lead to a greater **rate of reaction**.

## Rate of Reaction

Rate of reaction considers how fast **reactants** are being **used up** or **products** are being **formed**. It can be calculated from empirical data that has been plotted on graphs.

On a **concentration-time graph**, the rate of reaction is equal to the gradient of the curve at a given point. Therefore, the graph can be used to find the **rate** at a certain time by drawing a **tangent** to the curve at this given time and calculating the **gradient** of the tangent.

*Gradient = (change in y) ÷ (change in x)*

Drawing a **tangent** to the curve when **time = 0** finds the **initial rate** of reaction. The tangent at any other position finds the rate of reaction at that moment in time. The units of rate calculated in this way are generally **mol $dm^{-3}s^{-1}$**.

*Example:*

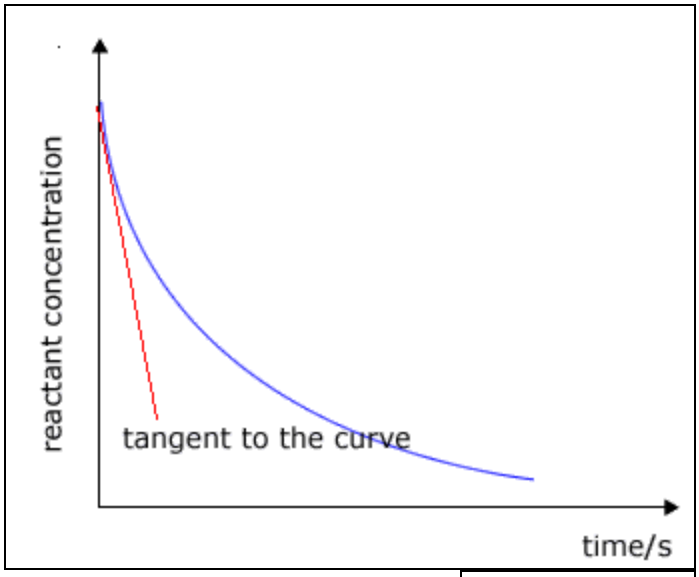


Image courtesy of IBChem

Suitable **physical quantities** to **monitor** which affect the rate of reaction include concentration, gas volume, and mass.

## Effect of Temperature

When a substance is heated, **thermal energy** is transferred to it. This energy is converted to **kinetic energy** and the molecules of the substance move **faster and further**. Increased movement of the molecules means **collisions occur more often** and with **greater energy**. As a result, more collisions have energy greater than the activation energy and result in a reaction.

Therefore, **increasing the reaction temperature will increase the rate of reaction** as there are more frequent successful collisions.

### Effect of Concentration and Pressure

When the concentration of a sample is increased, there are more molecules of substance in the same volume, meaning they are **packed closer together**. Therefore, collisions between molecules become **more likely** and the probability of a collision occurring with energy greater than or equal to the activation energy increases. As a result, the rate of reaction increases.

Increasing the **pressure** of a gas has a similar effect as molecules are **packed closer together** into a smaller volume.

### Effect of Surface Area

Increasing the surface area of a reactant, for example by crushing it into a powder, increases the **number of exposed reactant particles**. This means there are more frequent, successful collisions, so the rate of reaction **increases**.

## Catalysts

A catalyst is a substance that **increases the rate of reaction without being used up** in the reaction. It works by providing an **alternative reaction path** with a **lower activation energy.**

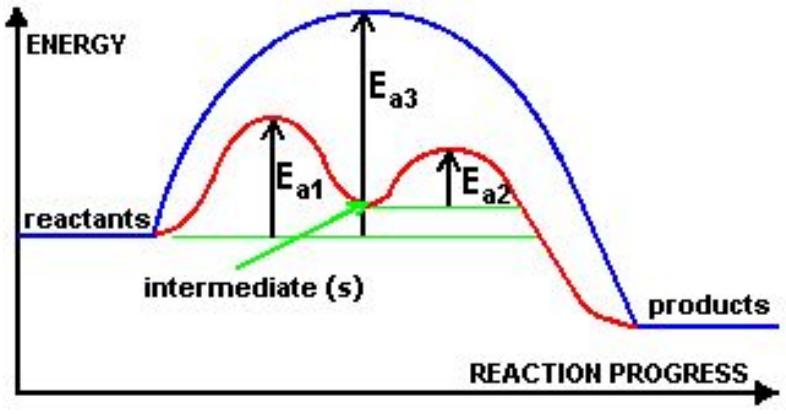
Catalysts are used in industry because they **lower the energy costs** of the reaction process. They allow lower temperatures and pressures to be used, whilst still achieving the same rate of reaction. They can also give a **higher atom economy**. Hence, they are economically important.

They also increase **sustainability** of a reaction by lowering temperatures and reducing energy demand from combustion of fossil fuels. This results in a **reduction of $CO_2$ emissions**. These benefits to the environment of improved sustainability must be weighed against the negative effect of the toxicity of some catalysts.

### The Reaction Profile of a Catalysed Reaction

***The red line shows the pathway for a catalysed reaction, while the blue line shows the pathway for when the reaction occurs without a catalyst.***

Image courtesy of docbrown.info



There is a **dip** in the **energy profile** for the catalysed reaction. This represents the **intermediate** formed during the reaction. The intermediate is **less stable** (and therefore higher in energy) than the reactants and products.

### Homogeneous Catalysts

Homogeneous catalysts are catalysts that are in the **same phase** as the reactants.

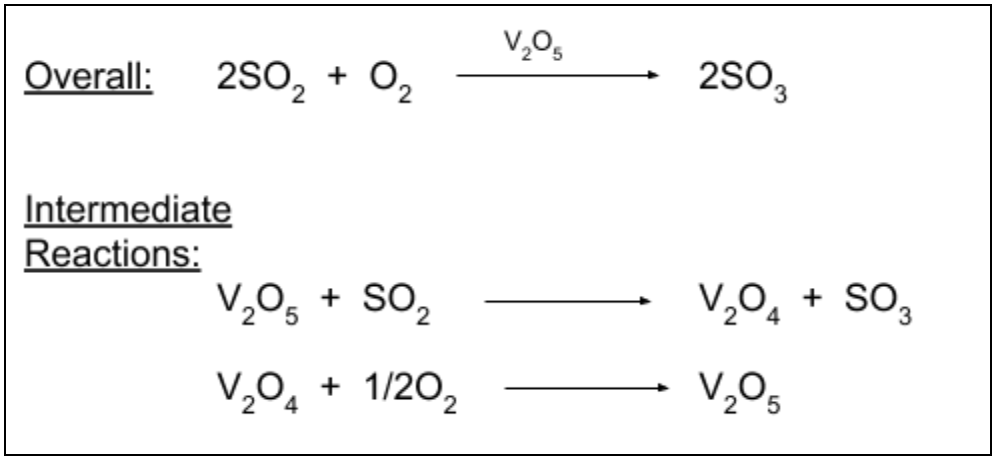
### Heterogeneous Catalysts

Heterogeneous catalysts are catalysts that are in a **different phase** to the species in the reaction. An example of this is in the Haber Process, where a **solid iron catalyst** is used to speed up the reaction between hydrogen and nitrogen **gases**.

### Transition Metal Catalysts

Transition metals make good catalysts as they have variable oxidation states. **Electrons are transferred** to produce a **reactive intermediate** and speed up the reaction rate. An example of this is the **contact process** which uses a vanadium oxide catalyst to speed up the conversion of sulfur dioxide to sulfur trioxide.

*Example:*

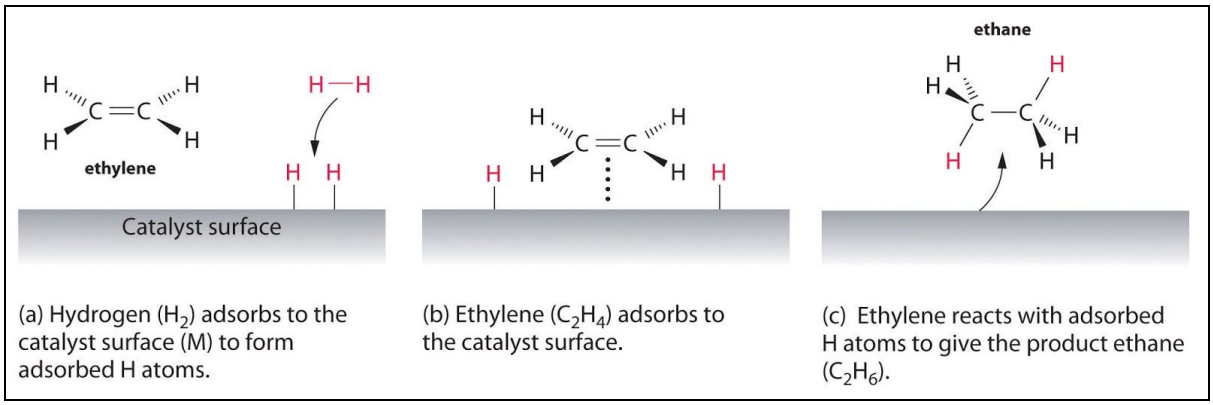



Vanadium is **reduced** from an oxidation state of +5 to +4. It is then **oxidised** back to its original oxidation state, showing it has acted as a catalyst for the reaction.

### Adsorption

A solid catalyst works by **adsorbing** molecules onto an **active site** on the surface of the catalyst. These active sites **increase the proximity** of molecules and **weaken the covalent bonds** in the molecules so that reactions occur more easily and the rate is increased. These catalysts are used in **industry** to give a **surface** for the reaction to occur on.

*Example:* Adsorption




(a) Hydrogen ($H_2$) adsorbs to the catalyst surface (M) to form adsorbed H atoms.

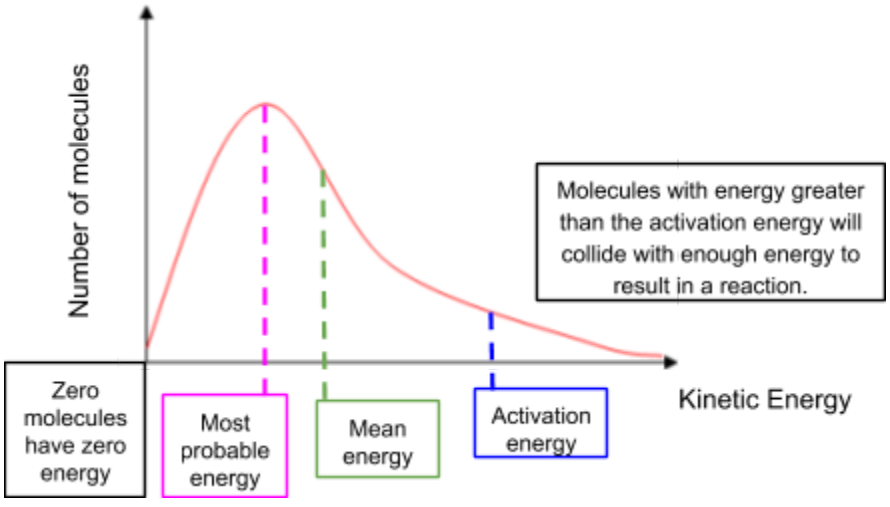
(b) Ethylene ($C_2H_4$) adsorbs to the catalyst surface.

(c) Ethylene reacts with adsorbed H atoms to give the product ethane ($C_2H_6$).

## The Boltzmann Distribution

Not all molecules in a substance have the same amount of energy. Their energies are **distributed** in a pattern called the **Maxwell-Boltzmann distribution**. This is a plot of the number of molecules against kinetic energy.

The **peak** is the **most probable energy** of a molecule. The **mean** energy is just to the right of this and divides the area below the graph into two equal halves. The curve is **asymptotic** - it doesn't quite reach the x axis. This is because there can be no maximum value for the kinetic energy of a molecule.



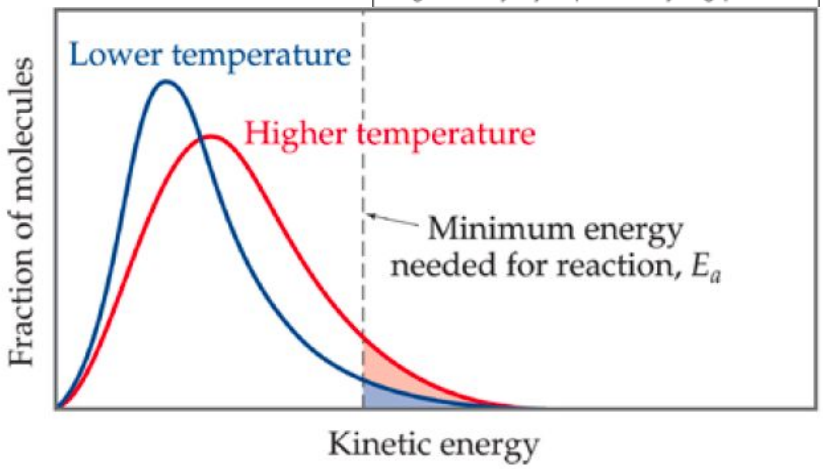

Changing the reaction conditions will **alter the shape of the curve,** so that the number of particles with energy greater than the activation energy is different. The total **area under the curve** represents the **total number of molecules** in the sample, and so this area **must remain constant**.

## Effect of Temperature

The Maxwell-Boltzmann distribution at an increased temperature **shifts to the right** because a **greater proportion** of molecules have greater kinetic energy. As a result, a greater proportion of molecules will have energy greater than or equal to the activation energy.

*Example:*

Image courtesy of johelpschemistry.blogspot.com




## Effect of Concentration, Pressure and Surface Area

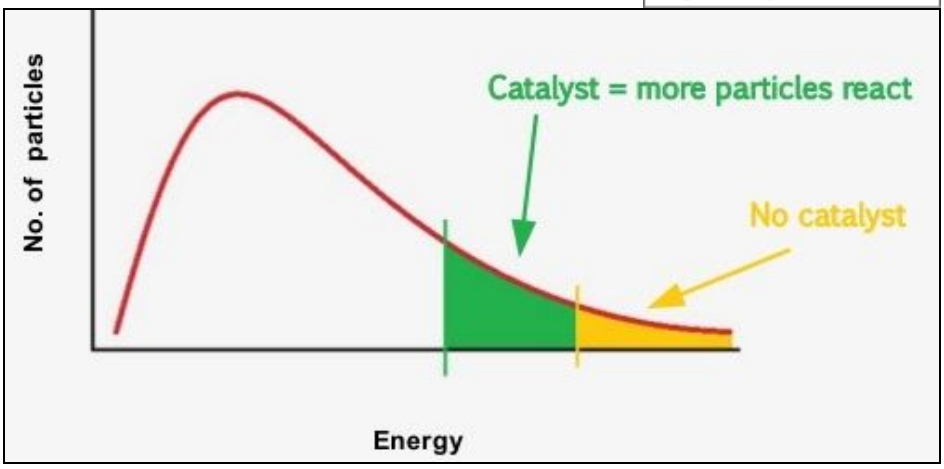
**Increasing** the **concentration**, **pressure** or **surface area** of reactants make successful collisions occur more frequently, however, they don't change the **energy** of the **individual particles**. Therefore, the shape of the Maxwell-Boltzmann distribution **does not change**.

## Effect of Catalysts

On the addition of a catalyst, the Maxwell-Boltzmann distribution curve is **unchanged in shape** but the **position of the activation energy is shifted to the left** so that a greater proportion of molecules have sufficient energy to react.

*Example:*

Image courtesy of slideshare.net



# 3.2.3 Chemical Equilibrium

## Dynamic Equilibrium and Le Chatelier's Principle

### Dynamic Equilibrium

**Reversible reactions** are reactions in which the products of a reaction can react together to reform the original reactants. They are represented using a **double arrow**. In each reaction system, one reaction direction will be **endothermic** and the opposite reaction direction will be **exothermic**.

*Example:*

$$N_2 + 3H_2 \rightleftharpoons NH_3$$

Reversible reactions will eventually reach a state of **dynamic equilibrium**. Dynamic equilibrium exists in a closed system when the **rate** of the forward reaction is **equal** to the rate of the reverse reaction. At this point, the **concentrations** of the reactants and products remain **constant.**

Dynamic equilibrium can only occur in **closed systems** where no substances can get in or out.

### Le Chatelier's Principle

Le Chatelier's principle is used to predict how an equilibrium mixture will change if the **reaction conditions are altered**. It states:

**When a system is subject to a change in conditions, the position of equilibrium will shift to lessen the effect of that change.**

It is a useful principle to consider in industry, since the reaction conditions can be altered to **maximise the yield** of a desired product.

### Changing Temperature

If you **increase** the temperature, the position of equilibrium will shift to favour the **endothermic reaction** (+ve $\Delta H$) as the excess heat needs to be removed from the system to lessen the effect of the initial increase. It will increase the yield of the endothermic products.

Likewise, if you **decrease** the temperature, the position of equilibrium will shift to favour the **exothermic reaction** (-ve $\Delta H$) as heat needs to be gained and the yield of the exothermic products will be increased.

In exam questions, the **$\Delta H$ of the forward reaction will be given** so it is clear which direction is endothermic and which is exothermic.

### Changing Pressure

**Increasing** pressure favours the side of the reaction with **fewer moles** of gas, as this helps to release the buildup in pressure. It will increase the yield of the products on the side of the reaction with the fewest moles of gas.

Likewise, **decreasing** pressure favours the side of the reaction with **more moles,** as pressure has been lost. The yield of the products on this side of the reaction will be increased.

### Changing Concentration

**Increasing** the concentration of the reactants will favour the **forward** reaction that **produces the products** as more molecules are available to react. It will increase the yield of the products on the right hand side of the reaction.

Likewise, **decreasing** the concentration of reactants will favour the **backwards** reaction that **reforms the reactants**.

### Catalysts

Catalysts do not affect the equilibrium position as they **increase the rate of the forward and backward reactions equally**. This means they allow equilibrium to be reached **faster** but have no effect on the position of equilibrium.

### Compromise between Rate of Reaction and Product Yield

Changing the conditions of reaction can shift the position of the equilibrium to favour the production of either the products or the reactants, as described above. However, a condition change which produces a **higher proportion of the product** may also **reduce the rate of the reaction**. The rate of reaction is increased by increases in temperature, pressure or concentration.

For example, **decreasing the temperature** of a reaction with a **forward endothermic reaction** would **increase** the product **yield**, but **decrease** the **rate** of reaction.

In the industry, when a factor increases the product yield but decreases the rate of a reaction, a **compromise** must be made. If the product yield was the only thing taken into account, the rate of reaction would occur **so slowly** that the product is not actually made at a useful rate. Therefore, reaction conditions are selected to give both a **relatively good product yield** and a **relatively fast rate of reaction**. You must also consider safety and economics when determining the conditions used in industrial reactions.

# The Equilibrium Constant, (Kc)

For reversible reactions, there is an equilibrium constant, **Kc**, that indicates the **position of equilibrium** for a reaction at a certain temperature. Kc for a reaction always has the **same value** unless the reaction conditions are changed, which in turn changes the position of equilibrium and hence Kc.

In order to find the value of Kc, the **concentrations** of the reactants and products at equilibrium must be known. Kc is equal to the **concentration of the products divided by the concentration of the reactants**. Any variation in the number of moles **raises the concentration of that substance to a power** with the same value as the number of moles.

*Example:*

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Image courtesy of ScienceAid.net

The equilibrium constant has **varying units** depending on the chemical reaction. The units can be found by **subbing the concentration units into the Kc expression**. Some of these then cancel to give the overall units of Kc for that reaction.

*Example:*

Image courtesy of ScienceAid.net

$$2A + B \rightleftharpoons C$$

$$\frac{\text{moldm}^{-3}}{(\text{moldm}^{-3})^2(\text{moldm}^{-3})} = \frac{1}{(\text{moldm}^{-3})^2}$$

$$= \text{mol}^{-2}\text{dm}^6$$

The value of Kc is **not affected by concentration change or use of a catalyst**, however it is affected by changing the reaction **temperature,** as the equilibrium position change results in different concentrations of reactants and products.

**Concentration** changes and the addition of a **catalyst** affect the **rate** of the reaction (the kinetics) but not the **position** of the equilibrium. They only affect how fast the system reaches equilibrium, hence they have **no impact** on the equilibrium constant.

The **position of equilibrium** can be estimated by the **magnitude** of the value of **Kc**. A large value for Kc indicates that product formation is favourable and the position of equilibrium will be far to the right. A small value for Kc indicates the opposite.

# OCR A Chemistry A-level

## Module 5.1: Rates, Equilibrium and pH

Detailed Notes

# 5.1.1 How Fast?

## Orders, Rate Equations and Rate Constants

### Rates and Rate Equations

The rate of a reaction shows how fast reactants are converted into products. It depends on the **concentrations** of the reactants and the **rate constant**. The rate of reaction is given by the rate equation:

$$A + B \rightarrow C + D$$

$$\text{Rate} = k[A]^m[B]^n$$

The constants ***m*** and ***n*** show the **order of the reaction** with respect to that species. This means that different species can have more of an effect on the rate of reaction than others. The values ***m*** and ***n*** can be 0, 1 or 2 - corresponding to **zero** order, **first** order or **second** order.

The **total order** of reaction for this chemical reaction can be found as the **sum** of the separate orders.

$$\text{Total order} = m + n$$

The **units** for rate of reaction are **mol $dm^{-3}s^{-1}$**.

### Rate Constant (k)

The rate constant for a reaction is constant when the reaction **temperature is constant**. The rate constant relates the concentrations of the species that affect the rate of a reaction to the overall rate of reaction.

The rate constant, k, can be calculated by **rearranging the rate equation** for that reaction. It has **varying units** depending on the number of species and their orders of reaction. The units of k can be found by **substituting the relevant units** into the rearranged equation and performing **cancellations**.

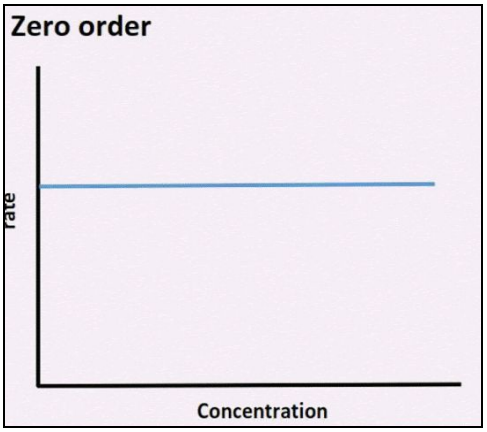
$$k = \frac{\text{Rate}}{[A]^m[B]^n}$$

# Rate Graphs and Orders

The orders of reaction (that you need to know about at A-level) range from **zero to second order**. This means that changing the concentration of reactants can have different effects on the whole reaction:

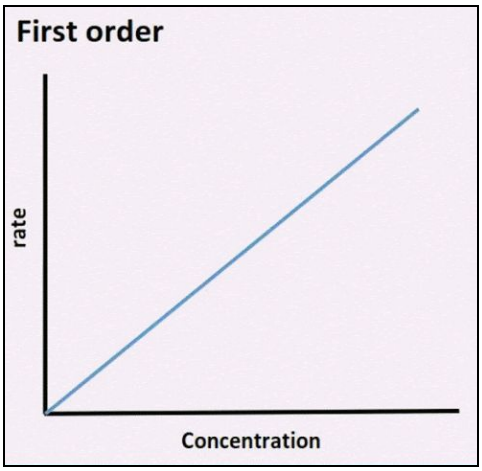
### Zero Order

- The concentration of this species has **no impact** on rate.
- Shown on a rate-concentration graph as a **horizontal** line.
- Rate = k



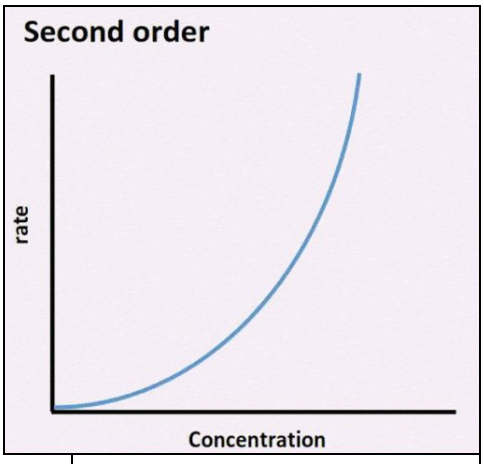

### First Order

- The concentration of the species and the rate are **directly proportional**.
- Doubling the concentration doubles the rate.
- Rate = k[A]




### Second Order

- The rate is proportional to the concentration of the species **squared**.
- Doubling the concentration will increase the rate by **four times**.
- Rate = $k[A]^2$




Images courtesy of derekcarrsavvy-chemist.blogspot.com

## Concentration-Time Graphs

Reaction orders can be worked out by using **rate-concentration** graphs as shown above, but they can also be determined from the shapes of **concentration-time** graphs. These graphs can be generated by **continuously monitoring** the concentration of reactants during an experiment. Calculating the gradient of these graphs gives the rate.

The concentration-time graph for a **zero order** reaction is **linear**:

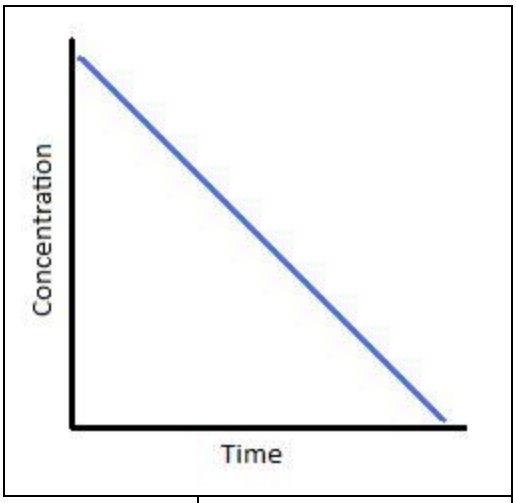



Image courtesy of chem.libretexts.org

The concentration-time graphs for first order and second order reactions are **curved**:

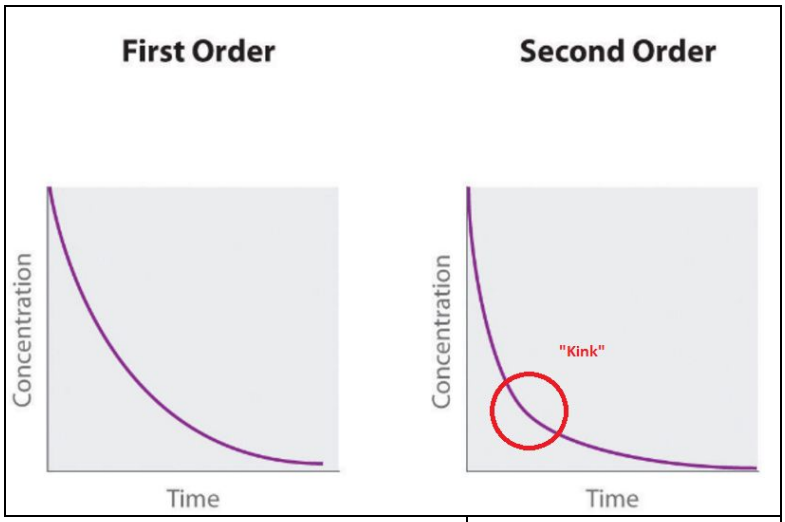



Image courtesy of stackexchange

## Initial Rates

Using the initial rate of reactions is one way the order of a reaction can be determined. This involves **varying the concentrations** of reactants and measuring the **initial rate** of the reaction.

**Doubling** the concentrations of zero, first and second order reactants would have the following effects:

- **Zero order** - **No change** to the initial rate.
- **First order** - Initial rate **doubles**.
- **Second order** - Initial rate **quadruples** ($2^2$).

*Example:*

| Trial | Initial [A] (mol $dm^{-3}$) | Initial [B] (mol $dm^{-3}$) | Initial [C] (mol $dm^{-3}$) | Initial rate (mol $dm^{-3}$ $s^{-1}$) |
|---|---|---|---|---|
| **1** | 10 | 10 | 10 | 40 |
| **2** | 20 | 10 | 10 | 80 |
| **3** | 10 | 20 | 10 | 40 |
| **4** | 10 | 10 | 20 | 160 |

From this data, you can deduce that:

- A is a **first** order reactant
- B is a **zero** order reactant
- C is a **second** order reactant

This would give the rate equation: $\mathbf{Rate = k[A][C]^2}$

## Half-life

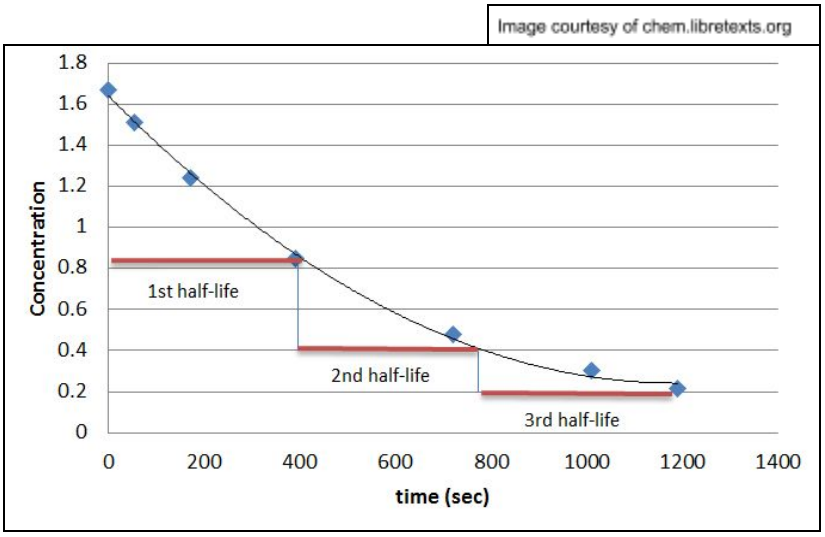
**Half-life ($t_{1/2}$): The time taken for the initial concentration of the reactants to decrease by half.**

The half-life can be found from a **concentration-time graph**. The overall order of a reaction affects how the length of the half-life changes over the course of a reaction.

### First Order Reaction

In a first order reaction, the half-life of a reaction is **constant** throughout the reaction. So the time taken for the reactant concentration to go from 100% to 50% is the same as the time taken for the reactant concentration to go from 50% to 25%, and so on.

*Example: Half life of a first order reactant*




## Experimental Techniques

There are various experimental techniques that can be used to obtain **rate data** for reactions. This allows for the calculation of the **overall order** of reaction and the rate of reaction at **given times**.

The two general ways this can be investigated is by:

- Measuring the change in a **reactant** mass or concentration over time.
- Measuring the change in a **product** mass or concentration over time.

Collecting this raw data allows you to generate a **concentration-time graph**, **mass-time graph** or **volume-time graph**, which can then be used to calculate the **rate of reaction**. To find reactant orders and the overall order of reaction the concentration of reactants can be varied and their effects on the rate of reaction can be analysed.

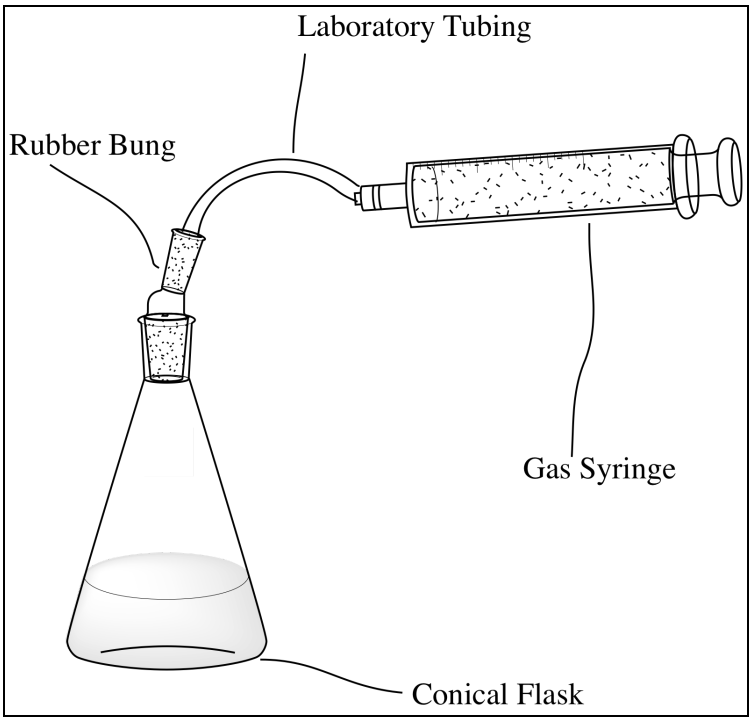
## Mass Change

If a **gas is produced** by a reaction, then the mass of the reaction mixture will **decrease** as the reaction proceeds. Plotting a mass-time graph and drawing a **tangent** to the curve can be used to find the rate of reaction.

## Volume of Gas Evolved

If a **gas is produced** by a reaction, the rate of reaction can be found by **measuring the volume of gas** produced over the course of the reaction, and plotting a graph of volume evolved against time. A **gas syringe** or an **underwater** upside down measuring cylinder can be used to collect the gas.

Experiment setup:




## Titration

Small samples of a reaction mixture can be **removed** at **regular intervals** throughout a reaction. These samples can then be **titrated** to determine the **concentration** of a given reactant or product at that time. A concentration-time graph can then be plotted.

## Colorimetry

Colorimetry can be used to determine the rate of reaction for a reaction that involves the **formation or depletion** of a **coloured species**. A colorimeter is a device that measures the amount of light that is **absorbed** by a solution. The amount of light absorbed by the solution is proportional to the **concentration** of the coloured species.

In a colorimetry experiment, a **calibration curve** is often generated. This involves using a **colorimeter** to measure the absorbance of solutions of **known concentrations**, from which a calibration curve is plotted.

Then, throughout the experiment, the absorbance of samples from the reaction mixture can be measured and the **calibration curve** used to convert the absorbance readings into concentration values. A **concentration-time** graph can then be plotted.

***Example*: Iodination of propanone**

The acid catalysed reaction of propanone and iodine can be monitored using colorimetry.

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$$

The initial solution is **brown** in colour due to the **iodine** present. As the iodine is used up in the reaction, the colour of the solution changes from **brown** to **orange**, to **yellow** and finally to **colourless**. The concentration of iodine can be found by continually taking samples of the reaction mixture and measuring the absorbance using a **colorimeter**.

## Rate Determining Step

Not all stages of a reaction occur at the same rate, but the overall rate is **determined by the slowest step** of the reaction, also known as the **rate determining step**. Therefore, the rate equation contains all the species involved in the stages **up to and including the rate determining step**.

The rate determining step can be identified from a reaction sequence by looking at which steps include the species in the rate equation. The rate determining step can also be used to **predict the mechanism** for the reaction.

*Example:*

Image courtesy of The Student Room

rate = $k[NO]^2[O_2]$

(iii) Using the rate equation, a scientist suggested a mechanism for the reaction which consisted of the two steps shown below.

| | |
|---|---|
| Step 1 | $NO + NO \rightarrow N_2O_2$ |
| Step 2 | $N_2O_2 + O_2 \rightarrow 2NO_2$ |

***In this question, step 2 would be the rate determining step as all the reactants of this step are in the rate equation given at the start.***

When constructing a reaction mechanism, the **powers in the rate equation** indicate the number of molecules of each substance involved in the slowest step and any steps before this. Any **intermediates** generated in the slowest step must be reactants in another step as they are **not present** in the balanced overall equation.

*Example mechanism:*

Nitrogen dioxide and carbon monoxide react to form nitrogen monoxide and carbon dioxide:
$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$
The rate equation for this reaction is: rate = $k[NO_2]^2$

- From the rate equation, the reaction is zero order with respect to CO(g) and second order with respect to $NO_2(g)$.
- 2 molecules of $NO_2$ are in the rate-determining step

| | | |
|---|---|---|
| 1st step | $2NO_2(g) \rightarrow NO(g) + NO_3(g)$ | (slow) |
| 2nd step | $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ | (fast) |
| Overall | $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ | |

# Effect of Temperature on Rate Constants

As the temperature increases, the rate constant increases and the rate of reaction increases.

## The Arrhenius Equation

The Arrhenius equation shows how the rate constant, *k,* and temperature, T, are related **exponentially**:

$$k = Ae^{-\frac{E_a}{RT}} \quad or \quad ln\ k = -\frac{E_a}{RT} + ln\ A$$

Where:

| | |
|---|---|
| k = | Chemical Reaction Rate |
| A = | Pre-exponential Factor |
| $E_a$ = | Activation Energy |
| R = | Gas Constant |
| T = | Temperature in Kelvin |

Image courtesy of SlidePlayer

It is a very useful equation and the **logged form** can be used in the form **'y = mx + c'** to show the relationship graphically. On a graph of ln(k) against 1/T, the gradient is $-E_a/R$ which is **negative and constant,** and the y-intercept is ln(A):

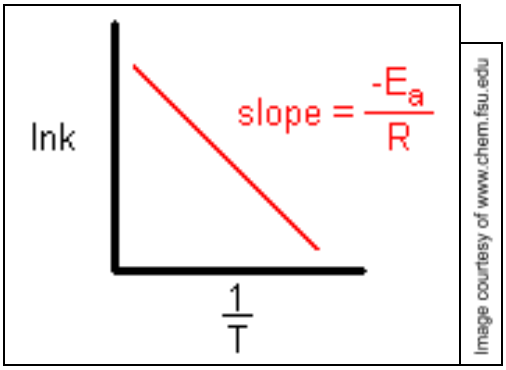



Image courtesy of www.chem.fsu.edu

The above relationship shows how the **activation energy** for a reaction (the minimum energy required for two particles to react) can be found **graphically** using experimental methods and data.

# 5.1.2 How Far?

## Equilibrium

### Mole Fractions and Partial Pressure

A **mole fraction** shows the proportion that a molecule accounts for of the total moles present. It is calculated by dividing moles of substance A by the total moles present.

Within a gaseous system, each gas has a **partial pressure**. The partial pressures add up to give the total system pressure. The partial pressure of a substance is found using the **mole fraction** of that substance and the **total pressure of the system**.

$$\text{Partial Pressure of A} = \frac{\text{Moles of A}}{\text{Total Moles}} \times \text{Total Pressure}$$

Partial pressure of A would be shown as **($P_A$).**

*Example:*

Image courtesy of SlidePlayer

A mixture of gases contains 0.51 mol $N_2$, 0.28 mol $H_2$, and 0.52 mol $NH_3$. If the total pressure of the mixture is 2.35 atm, what is the partial pressure of $H_2$?

***Total moles in the system = 0.51 + 0.28 + 0.52***
***= 1.31 moles***

***Mole fraction of $H_2$ = 0.28 / 1.31***
***= 0.21***

***($P_{H_2}$) = 0.21 x 2.35***
***= 0.50 atm***

Partial pressures are commonly measured in **Pascals** but are occasionally measured in atmospheres.

## Calculating Kc

Kc is the equilibrium constant of a reversible reaction. Kc is equal to the **concentration of the products divided by the concentration of the reactants** at equilibrium. The concentration terms are **raised to a power** of the same value as the number of moles of that substance.

*Example: The Kc expression*

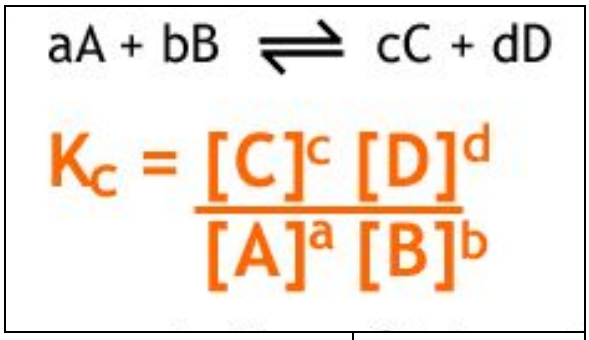



Image courtesy of ScienceAid.net

The equilibrium constant has **varying units,** depending on the chemical reaction. The units can be calculated by **substituting the concentration units into the Kc expression**. Some of these units will then cancel, giving the overall units of Kc for that reaction.

*Example: Finding the units of Kc*

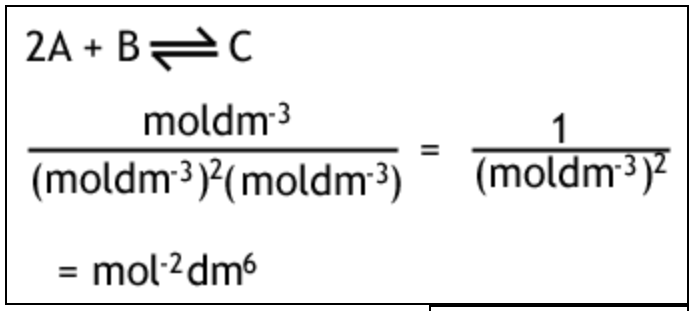



Image courtesy of ScienceAid.net

## Homogeneous and Heterogeneous

The equilibrium constant, Kc, can be found for both **homogeneous** and **heterogeneous** reactions. Homogeneous reactions are reactions in which the reactants and products are in the same **phase**, whereas heterogeneous reactions are reactions in which some of the reactants and/or products are in different phases to each other.

For **homogeneous** reactions, Kc is calculated as shown **above**.

The **difference** when calculating Kc for **heterogeneous** reactions is that any terms representing a **solid** are **not included** in the calculation.

*Example:* $H_2O_{(g)} + C_{(s)} \rightarrow H_{2(g)} + CO_{(g)}$

The solid carbon is not included in the equation for Kc: $Kc = \frac{[H_2]\,[CO]}{[H_2O]}$

## Gaseous Equilibrium Constant (Kp)

Kp is the equilibrium constant used for **gaseous equilibria**. Kp is calculated from gaseous reactants and products. If all reactants and products are in the **gaseous state**, the system is said to be **homogeneous**.

## Calculating Kp

Partial pressures allow the value of Kp for a gaseous equilibrium to be found. Kp is equal to the product of the **partial pressures of products** over the product of the **partial pressure of reactants**. It is similar to Kc in that any variation in moles **raises the partial pressure to a power** of equal quantity to the number of moles.

$$2A_{(g)} + 3B_{(g)} \rightleftharpoons Y_{(g)} + 2Z_{(g)}$$

$$Kp = \frac{(P_Y)(P_Z)^2}{(P_A)^2(P_B)^3}$$

The gaseous equilibrium constant has **varying units,** depending on the chemical reaction. The units can be calculated by **substituting the partial pressure units into the Kp expression**. Some of these units will then cancel, giving the overall units of Kp for that reaction.

*Example: Finding the units for Kp*

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$Kp = \frac{(kPa)^2}{(kPa)^2 \times kPa}$$

$$= kPa^{-1}$$

## Homogeneous and Heterogeneous

Similarly to Kc, the gaseous equilibrium constant, Kp, can be found for both **homogeneous** and **heterogeneous** reactions.

For **homogeneous** reactions, Kp is calculated as shown **above**.

The **difference** when calculating Kp for **heterogeneous** reactions is that any terms representing a **solid** are **not included** in the calculation.

Example: $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

The solid $CaCO_3$ and CaO are not included in the equation for Kp: $Kp = (\mathbf{P}CO_2)$

## Factors Affecting Kc and Kp

The values of Kc and Kp are **not affected by concentration or pressure change** or by the use of a **catalyst**. However, they are affected by changing the reaction **temperature**.

**Concentration** and **pressure** changes and the addition of a **catalyst** affect the **rate** of the reaction (the kinetics) but not the **position** of the equilibrium. They only affect how fast the system reaches equilibrium, hence they have **no impact** on the equilibrium constant.

**Temperature**, on the other hand, does change the **position** of the equilibrium, resulting in different concentrations of reactants and products.

If the forward reaction is **exothermic**, an increase in temperature will decrease the rate of the forward reaction because the equilibrium shifts to the **left** to oppose the change and favour the reverse endothermic reaction. This will decrease the concentrations of products and increase the concentrations of reactants, and therefore the equilibrium constant (Kc or Kp) **decreases**.

If the forward reaction is **endothermic**, an increase in temperature will increase the rate of the forward reaction because the equilibrium shifts to the **right** to oppose the change. This will increase the concentrations of products and decrease the concentrations of reactants, and therefore the equilibrium constant (Kc or Kp) **increases**.

Similar arguments can be made for the effect of **decreasing** the temperature.

# 5.1.3 Acids, Bases and Buffers

## Brønsted–Lowry Acids and Bases

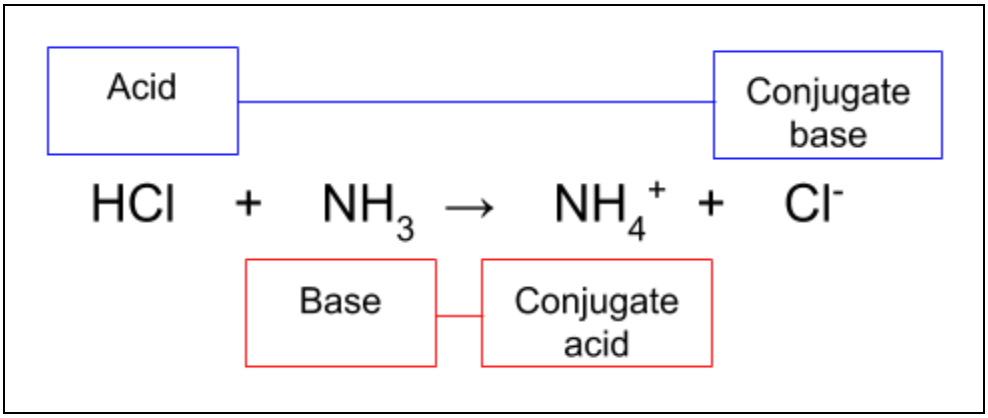
Acid-base equilibria involve the **transfer of protons** between substances. Therefore, substances can be classified as acids or bases depending on their interaction with protons.

A Brønsted-Lowry **acid** is a **proton donor**. For example, ammonium ions ($NH_4^+$).
A Brønsted-Lowry **base** is a **proton acceptor**. For example, hydroxide ions ($OH^-$).

### Brønsted–Lowry conjugate acid-base pairs

A **conjugate acid** is the species formed when a **base accepts a proton**. A **conjugate base** is the species formed when an **acid donates a proton**. Conjugate acids and conjugate bases form conjugate acid-base pairs.

*Example:*




### Ionic Equations

An ionic equation shows the **reacting ions** in a chemical equation. **Spectator ions** are ions that do not change in the reaction and are left out of the ionic equation. It is important to **balance** elements and charge in ionic equations.

In the reactions of acids with carbonates, metal oxides, and alkalis, $H^+$ is the reacting ion.

*Example:*

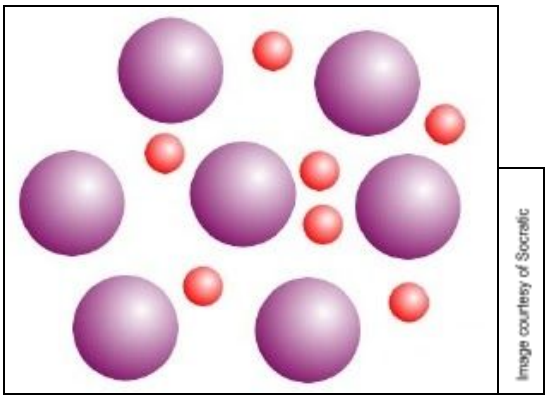
$$2H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)}$$

## Acid and Base Strength

Acid strength doesn't refer to the concentration of a solution. A **strong acid** is defined as being:

**An acid that completely dissociates into its ions when in solution.**

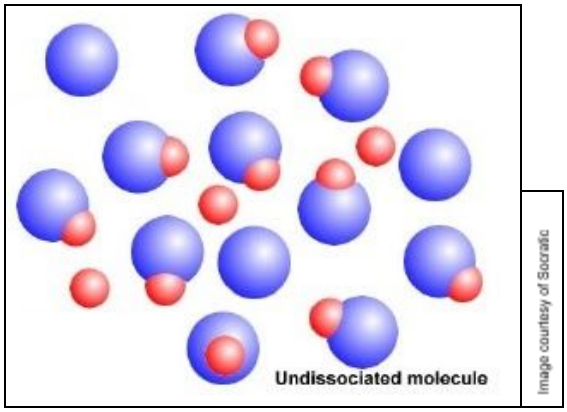
*Example:*




In comparison, a **weak acid** is defined as being:

**An acid that only slightly dissociates into its ions when in solution.**

*Example:*

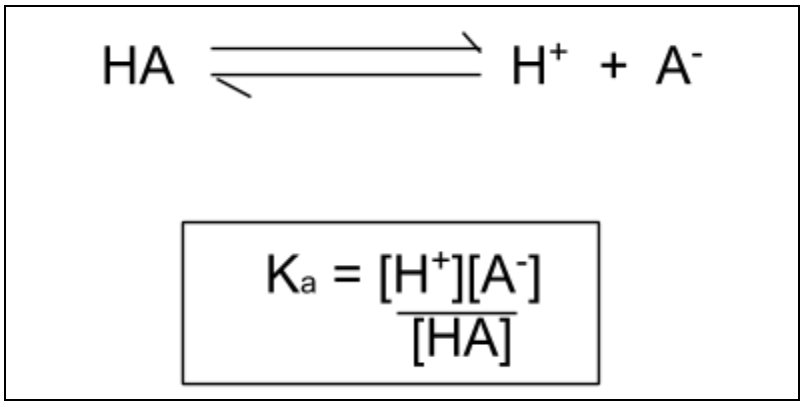



The same definitions are true for **strong** and **weak bases**.

Strong acids have pH between 0-1 and weak acids have pH between 3-7. Strong bases have pH between 12-14 and weak bases have pH between 7-11.

## The Acid Dissociation Constant

Weak acids and bases only **slightly dissociate** in solution to form an **equilibrium** mixture. Therefore, the reaction has an acid dissociation constant, $K_a$.




The constant Ka can be found using **pKa**:

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

$$K_a = 10^{-pK_a}$$

The value pKa is a logarithmic acid dissociation constant, representing how acidic something is. A **low value** of $pK_a$, or equivalently a large $K_a$, indicates a **strong acid**.

## pH and $[H^+_{(aq)}]$

### Determining pH

pH is a measure of **acidity and alkalinity**. It is a **logarithmic** scale from 0 to 14 that gives the concentration of **$H^+$ ions** in a solution. 0 is an **acidic** solution with a high concentration of $H^+$ ions whereas 14 is a **basic** solution with a low concentration of $H^+$ ions.

pH is a specific example of $pK_a$ for when $H^+$ ions are present. It can be calculated using the **concentration of hydrogen ions**, $[H^+]$, as follows:

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

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

This equation also allows the concentration of $H^+$ ions to be determined if the pH is known. When using these equations above, the concentration of $H^+$ ions is given in **mol $dm^{-3}$**.

This concentration of $H^+$ ions is equivalent to the **concentration of a strong acid** as it **completely dissociates** to ions in solution.

## Diluting Acids

If you dilute a strong acid **10 times** its pH will increase by **one unit**, because pH is a **logarithmic scale**. Diluting it **100 times** and **1000 times** would, therefore, increase the pH by **two units** and **three units,** respectively.

Weak acids do not behave in the same way. Weak acids are **not fully dissociated in solution**, so diluting them causes the **equilibrium** to **shift** to oppose the change. This means a **10x dilution** of a weak acid would increase the pH by **less than one unit**.

## Ionic Product of Water

Water **slightly dissociates** to form hydroxide and hydrogen ions in an equilibrium with its own equilibrium constant, **Kw**.

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

At **25°C**, room temperature, Kw has a constant value of **$1.0 \times 10^{-14}$**. However, as temperature changes, **this value changes**.

The **forward** reaction in the equilibrium of water is **endothermic** and is therefore favoured when the temperature of the water is increased. As a result, as temperature increases, **more $H^+$ ions** are produced meaning the water becomes **more acidic.**

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

In the same way that pKa can be calculated from Ka, **pKw** can be calculated from **Kw**.

$$pK_w = -\log_{10} K_w \qquad K_w = 10^{-pK_w}$$

The pH of a **strong base** can be calculated using pKw or Kw. For a **strong base**, the concentration of $OH^-$ will be the **same** as the concentration of the base.

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

*Rearrange Kw to find $[H^+]$:* $[H^+] = \frac{K_w}{[OH^-]}$

*Use $K_w = 10^{-14}$ and the concentration of the base to find $[H^+]$.*

*Finally, calculate pH using*: $pH = -\log_{10}[H^+]$

## Calculations

The relationships of Ka, pKa and $[H^+]$ can be used to find the **pH of weak acids and bases**. Depending on the reaction and the relative concentrations, a different method may have to be used:

HA in excess - Use [HA] and $[A^-]$ along with Ka to find $[H^+]$, then pH.

$A^-$ in excess - Use Kw to find $[H^+]$, then pH.

HA = $A^-$ - In this case, pKa is equal to pH, therefore find pKa.

## Calculating the Ka of Weak Acids

Weak acids only **partially dissociate** in solution. Therefore, the **equilibrium** of a weak acid has to be taken into account.

1. The initial concentrations, change in concentrations and equilibrium concentrations of the reactants and products have to be found.
2. The concentration of $H^+$ ions can then be found using the pH given.
3. This value can be used to find the actual equilibrium concentrations.
4. Finally, these values can be substituted into the expression for Ka.

*Example:*

A weak acid, HA, with a concentration of 0.25 M has a pH of 3.5. What is its Ka?

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

We assume that 'x' mol of HA dissociates to $A^-$ and $H_3O^+$.

| | **HA** | **$A^-$** | **$H_3O^+$** |
|---|---|---|---|
| **Initial** | 0.25 | 0 | 0 |
| **Change** | -x | +x | +x |
| **End** | 0.25 - x | x | x |

Using the pH value give, the $[H^+]$ (= x) can be calculated:

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

$$[H^+] = 10^{-3.5} = 3.16 \times 10^{-4}\ M$$

$$x = 3.16 \times 10^{-4}\ M$$

Substituting into the expression for Ka and using the equilibrium concentrations:

$$Ka = \frac{[H^+]\,[A^-]}{[HA]} = \frac{(x)\,(x)}{(0.25-x)}$$

We can now substitute in the value of x calculated earlier: x = $3.16 \times 10^{-4}$ M

$$Ka = \frac{(3.16 \times 10^{-4})^2}{(0.25 - (3.16 \times 10^{-4}))}$$

$$Ka = 3.99 \times 10^{-7}$$

### Approximations

For weak acid calculations, the following approximations are made:

| | |
|---|---|
| $[HA]_{equilibrium} \sim [HA]_{undissociated}$ | i.e. $[HA] \gg [H^+]$ |
| $[HA]_{equilibrium} \sim [A^-]_{equilibrium}$ | i.e. negligible dissociation of $H_2O$ |

These approximations are limited to calculations for weak acids. For stronger weak acids, the approximations breakdown because the first assumption may no longer be valid.

## Buffers: Action, Uses and Calculations

### Buffer Action

A buffer solution is a system that **minimises pH changes** on addition of small amounts of an acid or a base. It is formed from a **weak acid and its salt** or an excess of a **weak acid and a strong alkali**. This produces a mixture containing **$H^+$ ions** and a large **reservoir of $OH^-$** ions which helps to resist any change in pH. Therefore, a buffer solution is defined as:

**A solution which is able to resist changes in pH when small volumes of acid or base are added.**

The large reservoir of OH- ions allows the **ratio of acid to base** in the mixture to be kept almost **constant**.

Consider the following buffer solution: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

The **$OH^-$ concentration** will **increase** if a small amount of base is added, making the solution more basic. The extra $OH^-$ ions will react with the $NH_4^+$ ions, to form the **original reactants**. Therefore, the equilibrium will shift to the left to remove the $OH^-$ ions and stop the pH from changing largely.

## Buffer Calculations

Buffer calculations are long calculations that use acid-base calculations. There are two types:

**Acid + Base** - Find the number of moles of each species.
- Calculate their concentration when at equilibrium using the total volume.
- Use Ka to find $[H^+]$ and therefore pH.

**Acid + Salt** - Find the moles of the salt.
- Use Ka to find pH.

*Example:*
A buffer solution contains 0.35 mol $dm^{-3}$ methanoic acid and 0.67 mol $dm^{-3}$ sodium methanoate. For methanoic acid, Ka = $1.6 \times 10^{-4}$ mol $dm^{-3}$. Find the pH of this buffer.

We **assume** that the **sodium methanoate completely dissociates** so that the equilibrium concentration of $HCOO^-$ is the same as the initial concentration of $HCOO^-Na^+$. Similarly, HCOOH only slightly dissociates so we assume that the **equilibrium concentration** is equal to the **initial concentration**.

1. First, find the expression for Ka for methanoic acid

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

$$Ka = \frac{[H^+] \times [HCOO^-]}{[HCOOH]}$$

2. Rearrange the expression to find $[H^+]$

$$[H^+] = \frac{Ka \times [HCOOH]}{[HCOO^-]}$$

$$[H^+] = 1.6 \times 10^{-4} \times (0.35/0.67) = 8.4 \times 10^{-5}$$

3. Convert $[H^+]$ to pH

$$pH = -\log_{10}(8.4 \times 10^{-5}) = 4.08$$

### Adding Small Volumes

The pH of a buffer solution doesn't change much but will change in the **order of 0.1 or 0.01 units of pH** when a **small volume** of acid or base is added.

Adding small amounts of **acid ($H^+$) increases the concentration** of the acid in the buffer solution, meaning the overall solution will get slightly **more acidic**.

Adding small amounts of **base ($OH^-$) decreases the concentration** of acid in the buffer solution, meaning the overall solution will get slightly more **basic**.

### Uses of Buffers

Buffer solutions are common in **nature** in order to keep systems regulated. This is important as **enzymes** or reactions in living organisms often require a **specific pH**, which can be maintained using a buffer solution.

Another important buffer in nature is found in the human circulatory system. The **pH of human blood** is maintained in a buffer between **carbonic acid and hydrogencarbonate ions**. These ions **neutralise any acidic substances** that enter the bloodstream, converting them to carbonic acid and water. This buffer is present in blood plasma, maintaining a pH between 7.35 and 7.45.

## Neutralisation

### Enthalpy Change of Neutralisation

When **strong** acids and bases react together they will produce **very similar enthalpies of neutralisation**. This is because the solutions completely dissociate, so the same, simple acid-base reaction occurs between **$H^+$ and $OH^-$ ions** to produce water in each case. The other dissociated ions present are simply **spectator ions** and do not affect the reaction.

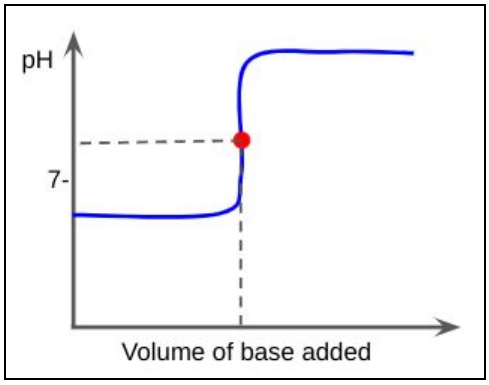
However, in reactions of **weak** acids and bases, the ions only slightly dissociate so **other enthalpy changes** also occur within the solution. As a result, the enthalpies of neutralisation can **vary** quite a lot.

### Titration Curves

A pH titration curve shows how the pH of a solution **changes** during an **acid-base reaction**. When an acid and base react, a **neutralisation point** is reached, identified as a large **vertical section** of the pH curve, through the neutralisation/equivalence point.

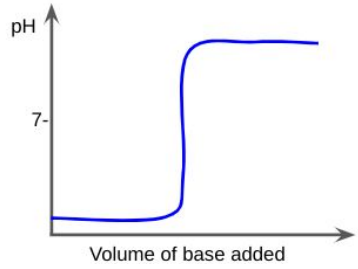
To obtain a pH titration curve, alkali is slowly added to an acid (or vice versa) and the pH is regularly measured with a **pH probe.** The **smaller** the added volumes, the **more accurate** the curve produced.

*Example: The red dot indicates the equivalence point*

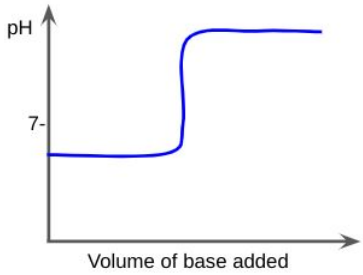



For a strong acid - strong base reaction, the neutralisation point occurs around **pH 7**. Other combinations of strong and weak acids and bases results in a **different neutralisation point**:

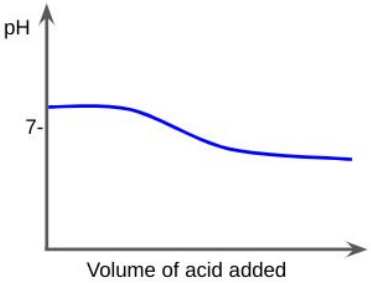
- Strong Acid + Strong Base = pH 7




- Strong Acid + Weak Base = < pH 7 (more acidic)
- Weak Acid + Strong Base = > pH 7 (more basic)

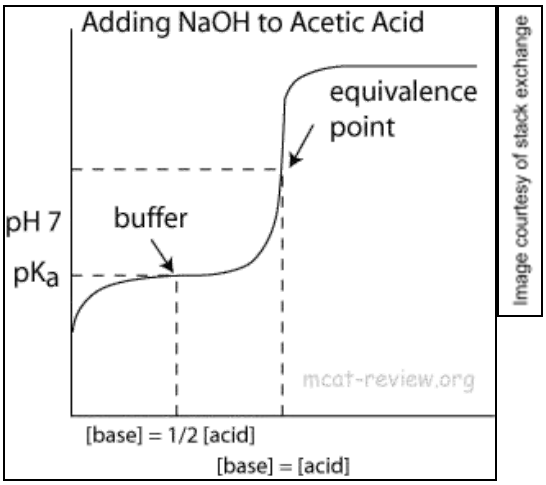



- Weak Acid + Weak Base = normally pH 7 but hard to determine



## Calculating Ka from Titration Curves

The vertical region of a titration curve is the **equivalence point**. At **half the equivalence point** the **pH is equal to pKa**, by definition.




***Therefore, by reading the pH at half the equivalence point, Ka can be easily calculated from pKa.***

## Indicators

Specific chemical indicators have to be used for specific reactions as they can **only indicate a pH change within a certain range**.

The two most common indicators used at A-level are **methyl orange** and **phenolphthalein**:

Methyl Orange - used for reactions with a **more acidic** neutralisation point.
- red in acids and turns **yellow** at the neutralisation point.

Phenolphthalein - used for reaction with a **more basic** neutralisation point.
- pink in alkalis and turns **colourless** at the neutralisation point.

| Indicator | pH at colour change | Colour in acid | Colour in base |
|---|---|---|---|
| **Methyl orange** | 3-5 | **Red** | **Yellow** |
| **Phenolphthalein** | 8-10 | **Colourless** | **Pink** |
| **Litmus** | 5-8 | **Red** | **Blue** |

It is important that, depending on the strength of the titration reactants, the **correct indicator is selected** so that the colour change occurs at neutralisation. The pH at colour change must fall within the vertical section on the titration curve.
Indicators are **weak acids** themselves, so only a few drops are used otherwise they could affect the overall pH. They should be considered as HA. The colour change occurs due to an equilibrium **shift between the HA and $A^-$ forms** of the indicator.

# OCR A Chemistry A-level

## Module 5.2: Energy

### Detailed Notes

# 5.2.1 Lattice Enthalpy

## Lattice Enthalpy

### Lattice Enthalpy ($\Delta_{LE}H$)

Lattice enthalpies are used for **ionic substances**. Lattice enthalpy is a measure of the strength of ionic bonding in a giant ionic lattice.

Lattice **dissociation** enthalpy is defined as:

**The enthalpy change when one mole of a solid ionic compound is completely dissociated into its gaseous constituent ions under standard conditions.**

This is an **endothermic process.**

Lattice **formation** enthalpy is defined as:

**The enthalpy change when one mole of a solid ionic compound is formed from its gaseous constituent ions under standard conditions.**

This is an **exothermic process.**

Lattice enthalpy cannot be measured directly. It is calculated using experimental values for other enthalpy changes in a cycle called a **Born-Haber cycle**.

### Atomisation Enthalpy ($\Delta_{at}H$)

This is defined as:

**The energy required for the formation of one mole of gaseous atoms from an element under standard conditions.**

### Enthalpy of Electron Affinity ($\Delta_{ea}H$)

This is defined as:

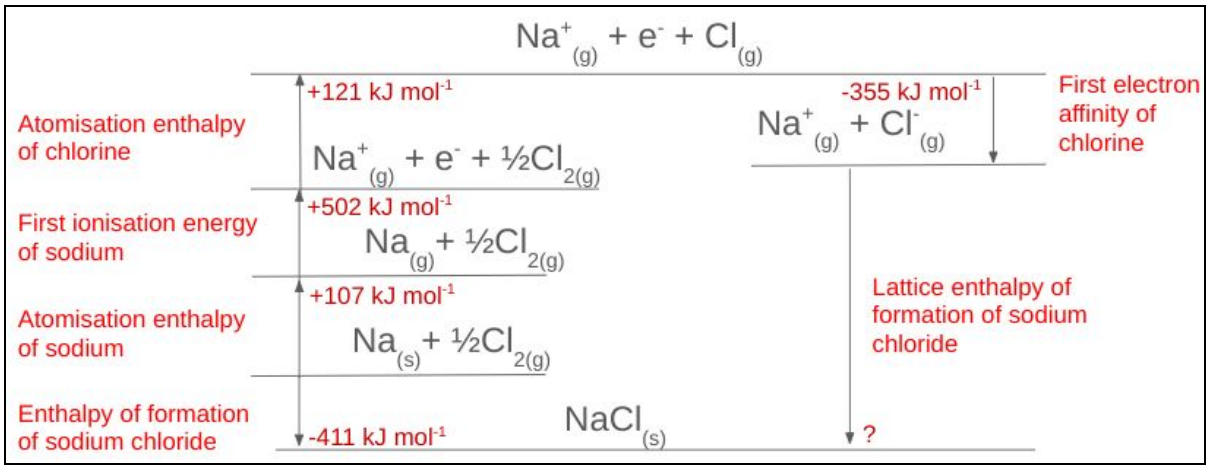
**The enthalpy change when one mole of electrons is added to a mole of gaseous atoms to form one mole of gaseous 1- ions under standard conditions.**

# Born-Haber and Related Enthalpy Cycles

Born-Haber cycles are similar to the cycles used with **Hess's Law**. Note, Hess's law states that the **enthalpy change** of a reaction is **independent** of the **route** taken. Born-Haber cycles allow **enthalpy changes** to be determined when they cannot be measured directly.

The different enthalpy changes can be **combined** to produce a **Born-Haber cycle**. In a similar way to Hess's Law, the arrows represent a reaction and they are treated like vectors. If the cycle **counters the direction** of the arrow, the sign of the enthalpy change represented by that arrow is **reversed**.

*Example:*




*In this example, lattice enthalpy of formation ($\Delta_{le}H$) is calculated by following anticlockwise rotation around the cycle: $\Delta_{le}H$ = [-(-355)-(121)-(502)-(107)+(-411)] = -786 kJ mol$^{-1}$*

This cycle, derived from **empirical** data, will produce a different value for lattice enthalpy compared with the theoretical value predicted using **electrostatic theory**. This theory assumes a **'perfect ionic model'**. Therefore, experimentally derived lattice enthalpies can be used as indicators of **the degree of covalent bonding** in a lattice.

## Perfect Ionic Model

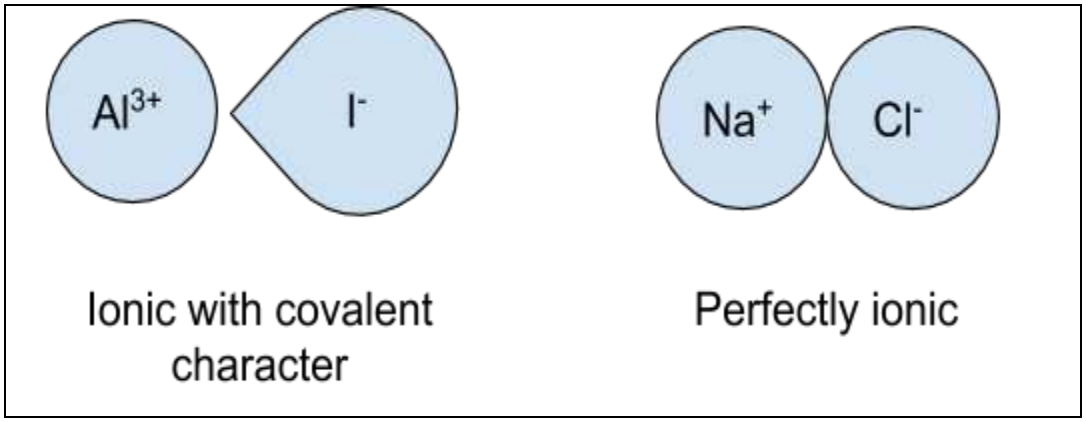
It is often assumed that the ions are **'perfectly ionic'**.

The perfect ionic model assumes that:

- All the ions are **perfectly spherical**.
- **Charge** is distributed **evenly** throughout the ion.
- The ions display **no covalent character**.

Covalent character occurs in ions when two bonded ions have **varying sizes or charges,** meaning the distribution of charge is **not even**. This **polarisation** of anions by cations creates **covalent character.**

*Example:*




**Enthalpies of Solution ($\Delta_{sol}H$) and Hydration ($\Delta_{hyd}H$)**

Enthalpies of solution and hydration can be used as another way of measuring lattice enthalpies **indirectly**. They are combined using a similar idea to Hess's Law.

Enthalpy of **solution** is defined as:

**The enthalpy change when one mole of ionic solid is dissolved in water to infinite dilution so that the ions no longer interact under standard conditions.**

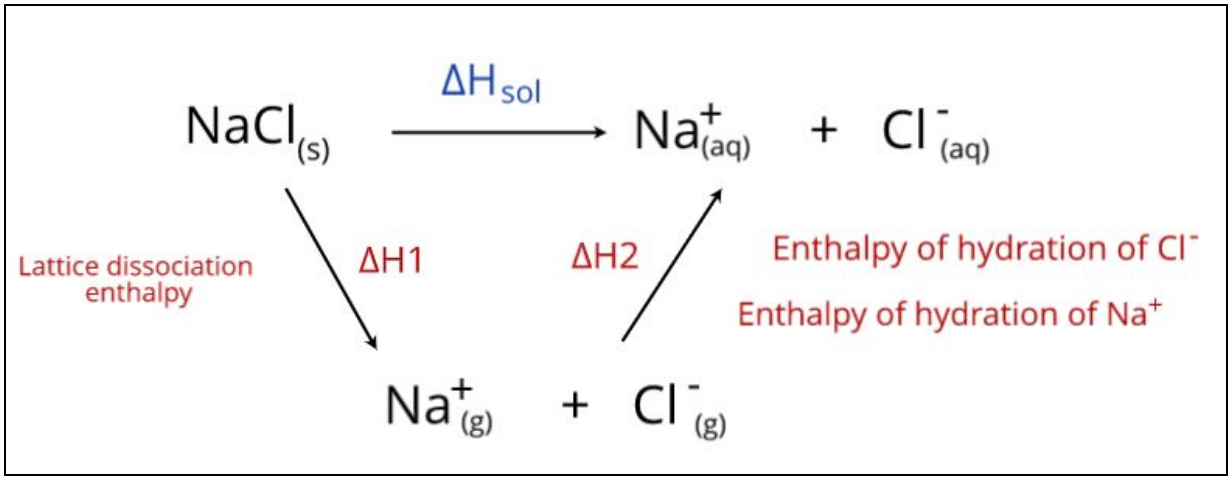
Enthalpy of **hydration** is defined as:

**The enthalpy change when one mole of gaseous ions is dissolved in water to form one mole of aqueous ions under standard conditions.**

Enthalpy of hydration is nearly always **negative** as water molecules have ***∂+ regions*** that naturally **attract** negative ions.

The enthalpy of solution and the enthalpy of hydration are combined in the following way to form an **energy cycle**.

*Example: Calculating the lattice dissociation enthalpy of sodium chloride*




$$\Delta H1 = \Delta H_{sol} - \Delta H2$$

**Factors Affecting Enthalpy of Hydration and Lattice Enthalpy**

Enthalpy of hydration is a measure of the attraction between ions (that were in a lattice) and water molecules in solution. **Positive ions** will be attracted to the **δ- oxygen atoms**, and **negative ions** will be attracted to the **δ+ hydrogen atoms.**

Attractions are stronger with **smaller ions** and with ions of a **greater charge**. This explains why hydration enthalpies **decrease** as you move **down a group** and why $Na^+$ ions have a lower enthalpy of hydration than $Mg^{2+}$ ions.

Lattice dissociation enthalpy also **increases** in magnitude with **decreasing ionic radius** and **increasing charge**. This is because the ions form **stronger attractions** and so the energy required for dissociation is greater.

## 5.2.2 Enthalpy and Entropy

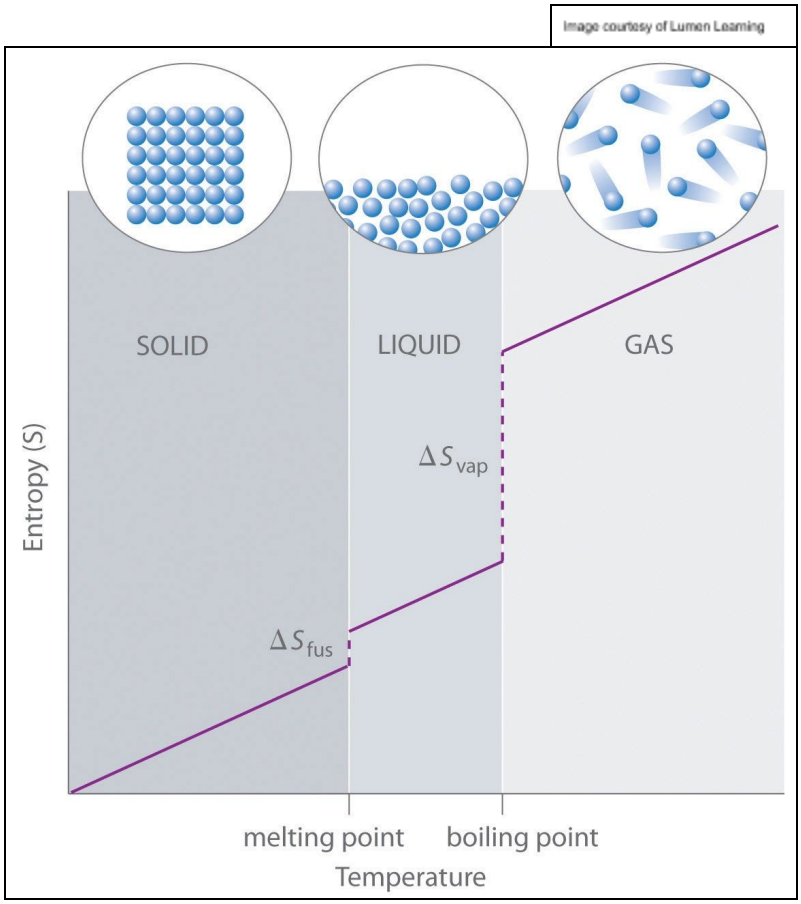
## Entropy

In chemistry, things tend towards a state of **disorder**. Entropy, **ΔS**, is a **measure of disorder**. It is a measure of the dispersal of energy in a system, which is greater the more disordered a system is.

Some **endothermic reactions** are able to occur **spontaneously** at room temperature. This shows how enthalpy is not the only driver of chemical reactions. **Entropy** is also key.

**Entropy increases as temperature increases** because the particles **gain energy** and move **faster and further apart**. In other words, the particles become less ordered.

**Gases** have the **greatest entropy** compared to solids and liquids.




When a substance melts or evaporates, there is a **sudden increase** in entropy. The entropy change of vaporisation is much greater than that of fusion as a **gas is much more disordered** than a liquid or a solid.

Another case where there is a sudden increase in entropy is in a reaction when there are **more moles of gaseous product** than reactants. In this case there is an **increase in disorder**.

When a **lattice** is **dissolved** in solution, there is an increase in entropy. This is because the ions that make up the lattice are **dissociated** and can **move** in the solution, as opposed to being held in their position by strong bonds. This freedom of movement causes an **increase in disorder.**

The overall entropy change for a reaction can be calculated. It is measured in **J $K^{-1}$ $mol^{-1}$**:

The entropy change for a reaction within a system can be calculated by finding the difference between the standard entropies of the **products** and the **reactants**:

$$\Delta S_{total} = \Sigma \Delta S_{products} - \Sigma \Delta S_{reactants}$$

If the entropy change for a reaction is **positive**, the products are **more disordered** than the reactants.

If the entropy change for a reaction is **negative**, the products are **less disordered** than the reactants.

Generally, you will only calculate the entropy change within a system. However, it is important to understand that the **natural direction of change** is towards a more disorderly state overall, which is a **positive change** in entropy. An example of this is the natural and spontaneous spreading of gas throughout a room, or the expansion of the universe.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

## Free Energy

Gibbs free-energy quantifies the balance between entropy and enthalpy in a system, acting as an **indicator of reaction feasibility**. It also allows $\Delta S$ to be found without needing to measure the effects on the surroundings:

$$\Delta G = \Delta H - T\Delta S$$

Gibbs free-energy is measured in **kJ $mol^{-1}$** so it is important that $\Delta H$ and $T\Delta S$ are used in the same, **standard units**.

This equation also takes the form **'y = mx + c',** meaning it can be represented graphically as a straight line graph of $\Delta G$ (y-axis) against T (x-axis).

$\Delta G$ is **less than or equal to zero for all spontaneous reactions**. The minimum temperature at which a reaction is spontaneous can be found by putting **$\Delta G$ equal to zero**.

A reaction becomes feasible when $\Delta G = 0$.

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

*Rearranging gives* $T\Delta S = \Delta H$

*Therefore, the temperature at which the reaction becomes feasible:*

$$T = \frac{\Delta H}{\Delta S}$$

Changing the temperature or the type of reaction occurring will **change the feasibility** of the reaction happening.

Since $\Delta G$ is dependent on both the enthalpy and the entropy, if the entropy change for a reaction is positive and large enough, a reaction with a positive $\Delta H$ (**endothermic reaction**) could still have an overall **negative $\Delta G$** and occur **spontaneously**.

### Kinetics vs. Thermodynamics

Although a reaction may be thermodynamically feasible, it still may not be able to occur due to **kinetic factors**. A reaction may be thermodynamically feasible but kinetic factors may lead it to occur at **such a slow rate** that, in practice, it does not appear to occur at all.

Another example of this is **activation energy**. A reaction may require a large activation energy that is not provided by the reaction conditions. Therefore, it will not occur spontaneously.

## 5.2.3 Redox and Electrode Potentials

## Redox

**Oxidation is the loss** of electrons and **reduction is the gain** of electrons. This can be remembered by the acronym **OILRIG** - Oxidation Is Loss, Reduction Is Gain.

Oxidation results in the **oxidation number** becoming more positive, whereas reduction results in the oxidation number becoming more negative.

Blocks of the periodic table, such as the s-block and d-block, indicate the orbital of the **outer electron**. During reactions, s-block, d-block and some p-block species tend to undergo **oxidation** whereas most p-block elements (further to the right of the periodic table) tend to undergo **reduction**.

The **oxidation number** of a species tells you the oxidation state that it is in. This is indicated by roman numerals. *Example:*

**Fe(II) = $Fe^{2+}$**
**Fe(III) = $Fe^{3+}$**

## Redox Titration Calculations

### Method for balancing half equations:

1. Balance all atoms except for oxygen and hydrogen.
2. Add **$H_2O$** to balance **oxygens** (if needed).
3. Add **$H^+$ ions** to balance **hydrogens** (if needed).
4. Add **$e^-$** to balance **charges** (if needed).

*Example:*

*Write the full half equations for $Fe^{2+} \rightarrow Fe^{3+}$ and $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ and then combine the half equations.*

**Step 1: Write the full half equation for iron.**

$Fe^{2+} \rightarrow Fe^{3+}$

[The only thing that isn't balanced are the **charges**.]

$\Rightarrow Fe^{2+} \rightarrow Fe^{3+} + e^-$

**Step 2: Write the full half equation for chromium.**

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$

[Balance **chromium**]

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

[Balance **oxygen**]

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

[Balance **hydrogen**]

$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

[Balance **charges**]

$\Rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

**Step 3: Combine the two half equations.**

$\Rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$\Rightarrow Fe^{2+} \rightarrow Fe^{3+} + e^-$

[Balance **electrons**]

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (x6) $\Rightarrow 6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

[**Cancel** the **electrons**]

$\Rightarrow 6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

# Redox Titrations

### Reaction between Iron ions and Potassium Manganate

In the redox titration between iron ions and manganate ions, the **iron ions are oxidised** while the **manganate ions are reduced**. Their half equations can be found using the method described above.

$$Fe^{2+} \rightarrow Fe^{3+} \quad \Rightarrow Fe^{2+} \rightarrow Fe^{3+} + e^-$$
$$MnO_4^- \rightarrow Mn^{2+} \Rightarrow MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

These **half equations** can be combined to give the overall **redox** equation:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

The iron solution is measured into a conical flask using a pipette and pipette filler. The endpoint of the titration is indicated when the solution in the conical flask has a permanent **pale pink colour.** At this point there is an excess of manganate ions.

### Reaction between Iodine and Sodium Thiosulphate

In the redox titration between iodine and thiosulphate ions, the **thiosulphate ions are oxidised,** while the **iodine is reduced**. Their half equations can be found using the method described above.

$$I_2 \rightarrow I^- \quad \Rightarrow I_2 + 2e^- \rightarrow 2I^-$$
$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} \quad \Rightarrow 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$$

These **half equations** can be combined to give the overall **redox** equation:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

The same principles can be applied to any redox system.

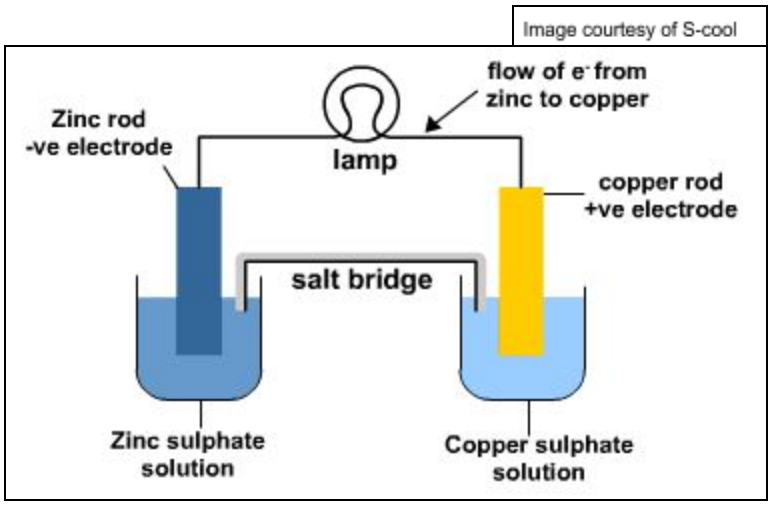
# Electrode Potentials

### Electrochemical Cells

Electrochemical cells use **redox reactions** since the **electron transfer** between products creates a flow of electrons. This flow of charged particles is an **electrical current** that flows between **electrodes** in the cell. A **potential difference** is produced between the two electrodes which can be measured using a voltmeter.

Most electrochemical cells consist of **two solutions, two metal electrodes** and a **salt bridge**. A salt bridge is a tube of **unreactive ions** that can move between the solutions to carry the flow of charge, whilst not interfering with the reaction. The salt bridge is crucial as it creates a closed loop for the circuit.

*Example*: Electrochemical cell setup - the position of the lamp is where the voltmeter can be placed to measure the potential difference.




Each electrochemical cell contains two **half-cells** which make up the full chemical cell. These half-cells each have a **cell potential** which indicates how it will react, either in an oxidation or reduction reaction.

### Cell Potentials ($E^o$)

If measured under **standard conditions**, cell potentials are measured compared to the **Standard Hydrogen Electrode (SHE)** to give a numerical value for the half-cell potential. SHE is an electrode used for **reference** on all half-cell potentials, so, by definition it has a standard electrode potential of **zero**.

**Positive** potentials mean the substances are more easily **reduced** and will **gain electrons**. **Negative** potentials mean the substances are more easily **oxidised** and will **lose electrons** to become more stable.

### Standard Hydrogen Electrode (SHE)

The standard hydrogen electrode is the **measuring standard** for half-cell potentials. It has a cell potential of **0.00V**, measured under **standard conditions**. These conditions are:

- Solutions of **1.0 mol $dm^{-3}$** concentration
- A temperature of **298K**
- **100 kPa** pressure

The cell consists of **hydrochloric acid solution, hydrogen gas** and **platinum electrodes**. Platinum electrodes are chosen as they are **metallic**, so will conduct electricity, but **inert**, so will not interfere with the reaction.

*Example:*

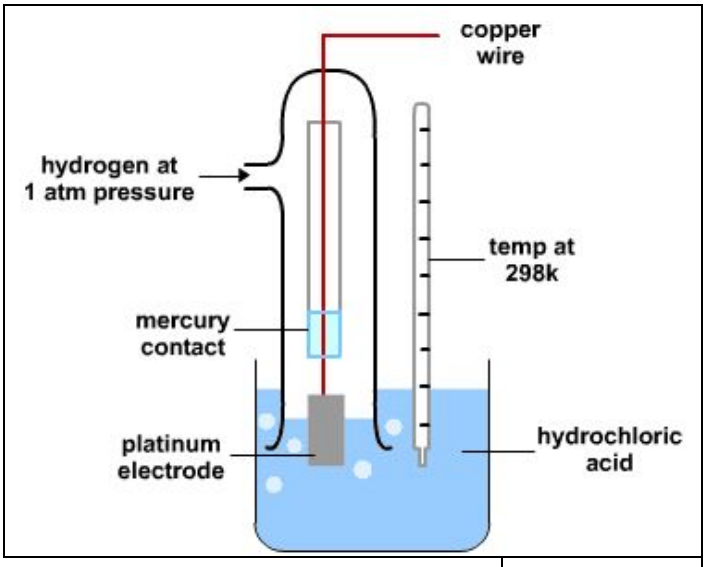



Image courtesy of S-cool

## Conventional Cell Representation

Cells are represented in a simplified way so that they don't have to be drawn out each time. This representation has **specific rules** to help show the reactions that occur:

- The half-cell with the **most negative** potential goes on the **left**.
- The **most oxidised** species from each half-cell goes **next to the salt bridge**.
- A salt bridge is shown using a **double line**.
- **State symbols** are always included.

*Example:* Compared to copper, zinc has the most negative potential so is placed on the left and undergoes oxidation.

$$Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$$

## Calculating Cell Emf

Standard cell potential values are used to calculate the **overall cell emf**. This is always calculated as the **potential of the right of the cell minus the potential of the left** of the cell, when looking at the conventional cell representation.

$$Emf_{(cell)} = E^{o}_{(right)} - E^{o}_{(left)}$$

It can also be remembered as the **most positive potential minus the most negative potential**.

If the overall cell potential is a **positive** value, the reaction taking place is **spontaneous and favourable**. The more positive the potential, the more favourable the reaction.

The cell emf can be calculated for electrochemical cells containing **different metals or non-metals** in contact with their ions, or alternatively, for electrochemical cells involving two half cells containing **the same element but in different oxidation states**.
For example, a $Fe^{2+}$ half cell and a $Fe^{3+}$ half cell could be combined to make up an electrochemical cell.

## $E^{e}_{cell}$ and Entropy

The standard emf of a cell is **directly proportional** to both **ln(K),** where K is the equilibrium constant of the reaction, and the **total entropy change, ($\Delta S_{total}$)**. This means that a positive $E^{e}_{cell}$ value will have an overall positive entropy change.

## Limitations

There are **limitations** to both calculating a standard cell potential using the SHE and using the calculated value to determine reaction **feasibility**.

Although the cell emf value will tell you if a reaction is thermodynamically feasible or not, it does not take into account the **kinetics** of the reaction. Even if a reaction is feasible, it may occur at such a **slow rate** that, in practice, it does not actually occur.

The standard cell potential relies on conditions being **standard** throughout the experiment, when in reality, the system may **deviate** from standard conditions.

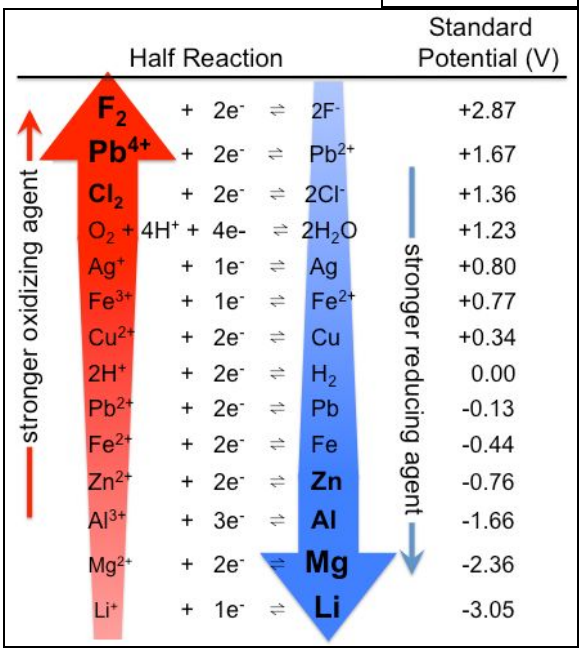
## Oxidising and Reducing Agents

Standard electrode potentials can also be referred to as **standard reduction potentials** and can be ordered into a series known as the **electrochemical series**. In this series, all half reactions are written in the reduction direction.

Electrode potentials that are very **positive** are better **oxidising agents** and will oxidise those species more negative than themselves.

Species that are very **negative** are better **reducing agents** and will reduce those species less negative than themselves.

Image courtesy of Quora




## Disproportionation

In a **disproportionation reaction**, a species is both oxidised ***and*** reduced. This is indicated by both an increase and decrease in the oxidation number for that species.

Electrode potentials can be used to assess whether a species will undergo disproportionation. If the overall $E^{\ominus}_{cell}$ value is **positive**, then the disproportionation reaction is **feasible**.

*Example:*
Will $Cu^{+}$ ions undergo disproportionation into $Cu^{2+}$ ions and copper?

| **Reaction** | **$E^{\ominus}_{cell}$** |
|---|---|
| $Cu^{2+} + 2e^{-} \rightleftharpoons Cu$ | +0.34 |
| $Cu^{2+} + e^{-} \rightleftharpoons Cu^{+}$ | +0.15 |
| $Cu^{+} + e^{-} \rightleftharpoons Cu$ | +0.52 |

The disproportionation of $Cu^{+}$ ions involves the second and third half reactions.
$E^{\theta}_{cell}$ = +0.52 - (+0.15) = +0.37V

This value is positive, therefore the reaction is **thermodynamically feasible**.

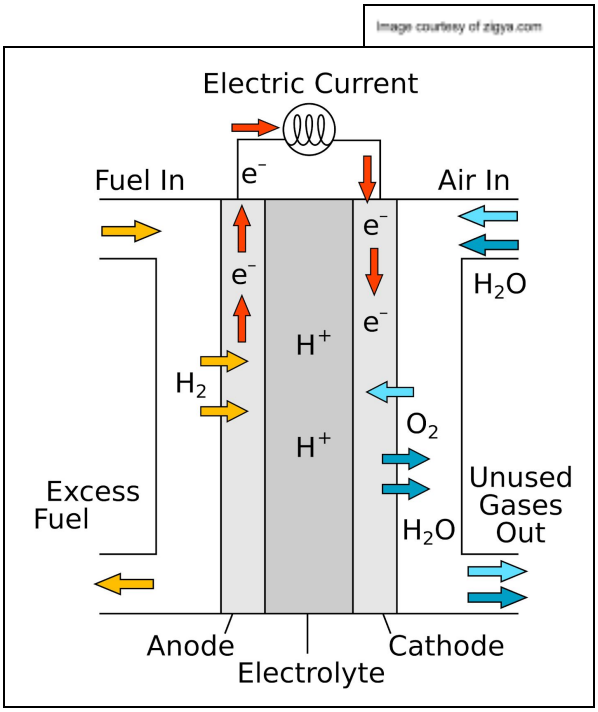
# Storage and Fuel Cells

## Commercial Cells

Electrochemical cells can be a useful **source of energy for commercial use**. They can be produced to be **non-rechargeable, rechargeable or fuel cells**.

## Fuel Cells

Fuel cells are a type of **electrochemical cell** which continuously produces a voltage when supplied with a fuel and oxygen. The fuel donates electrons at one electrode and oxygen gains electrons at the other electrode. The energy released is used to **generate a voltage**.




The most common type of fuel cell is the **hydrogen fuel cell**, which uses a **continuous supply** of hydrogen and oxygen from the air to generate a **continuous current**. Other common fuels include **hydrogen-rich compounds** like methane.

The reaction that takes place in a hydrogen fuel cell produces **water** as the only waste product, so the hydrogen fuel cell is seen as being relatively **environmentally friendly**.
The downsides to hydrogen fuel cells include the **high flammability of hydrogen** and that they are **expensive to produce,** meaning they are not yet commonly used.

The hydrogen fuel cell can be carried out with either an **acidic** or an **alkaline electrolyte**. The overall equation in both systems is the same:

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O$$

In an acidic electrolyte, such as $H_2SO_4$, there are **$H^+$ ions in solution**. The half equations are as follows:

| | |
|---|---|
| Anode | $H_2 \rightleftharpoons 2H^+ + 2e^-$ |
| Cathode | $\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$ |
| Overall | $H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O$ |

In an alkaline electrolyte, there are **$OH^-$ ions in solution**. The half equations are as follows:

| | |
|---|---|
| Anode | $H_2 + 2OH^- \rightleftharpoons 2H_2O + 2e^-$ |
| Cathode | $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ |
| Overall | $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ |

**Lithium ion batteries** are a commonly used example of an electrochemical cell. They are rechargeable, however, their benefits are counteracted by risks of toxicity and fire.

# OCR A Chemistry A-level

## Module 5.3: Transition Elements

### Detailed Notes

# 5.3.1 Transition Elements

## Properties

The transition metals are elements in the **d-block** of the periodic table that form one or more **stable ions** with a **partially filled d-orbital**. Transition metals lose electrons to form positive ions, with the s-orbital electrons being removed first.

All transition metals have **similar physical properties** including similar atomic radius, high densities and high melting points. In addition, they all have **special chemical properties**:

- Form complexes
- Form coloured ions in solution
- Variable oxidation states
- Good catalysts

Transition metals have **variable oxidation states** because the 4s and 3d orbitals are very **close** in energy levels. This not only makes it possible for electrons to be lost from both orbitals relatively easily, but also means the remaining electrons can form **stable configurations.**

*Examples:*

**Scandium** - atomic number 21 - [Ar] $4s^2$ $3d^1$

**Nickel** - atomic number 28 - [Ar] $4s^2$ $3d^8$

**Iron** - atomic number 26 - [Ar] $4s^2$ $3d^6$
**$Fe^{2+}$** - atomic number 26 (=24 electrons) - [Ar] $4s^0$ $3d^6$ or [Ar] $3d^6$

**Vanadium** - atomic number 23 - [Ar] $4s^2$ $3d^3$
**$V^{2+}$** - atomic number 23 (=21 electrons) - [Ar] $4s^0$ $3d^3$ or [Ar] $3d^3$

### Exceptions

**Copper** and **chromium** are exceptions to the rule that the 4s subshell is filled before the 3d subshell.

- Chromium has 24 electrons. According to the above rule, its electron configuration should be [Ar] $4s^2$ $3d^4$. However, it is more stable if one of the electrons from the 4s orbital is instead in the 3d orbital, **so that each 3d orbital contains one unpaired electron**. Therefore, the actual electron configuration of chromium is [Ar] $4s^1$ $3d^5$.
- Similarly with copper, instead of the electron configuration [Ar] $4s^2$ $3d^9$, it is more stable if the 3d subshell is **completely filled**. Therefore, one of the 4s electrons is moved to a 3d orbital to give the electron configuration [Ar] $4s^1$ $3d^{10}$.

### Catalysts

Some of the transition metal elements and compounds display **catalytic behaviour**. This can make transition metals and their compounds very useful in the industrial manufacture of chemicals. **$Cu^{2+}$** is used as a catalyst for the reaction of Zn with acids and **$MnO_2$** is used as a catalyst for decomposition of $H_2O_2$. It is beneficial to use catalysts in industry to reduce energy usage, however, there is also an increased risk from toxicity of many transition metals.

## Ligands and Complex Ions

### Complexes

Transition metals form **complexes**, consisting of a **central metal ion** surrounded by **ligands**.

*Example*:

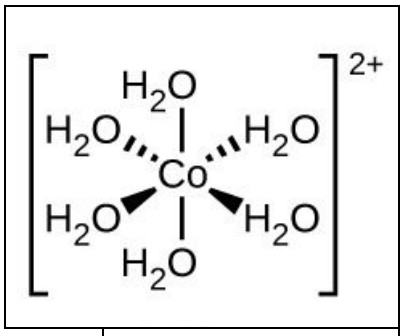



Image courtesy of BC Open Textbooks

Complexes can also be represented by formulas using square brackets.

*Example:*

$[Co(H_2O)_6]^{2+}$

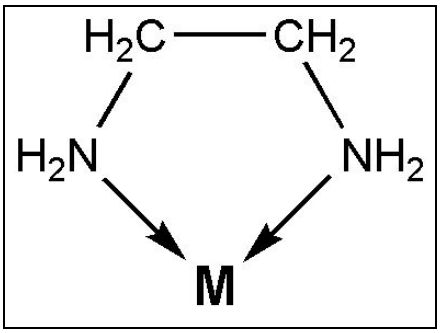
### Ligands

A ligand is a molecule or ion with a **lone electron pair** that is able to form a **dative (coordinate) bond** to the central metal ion by donation of this electron pair. Common ligands include:

- $Cl^-$
- $H_2O$
- $NH_3$

**Monodentate** ligands each form **one** coordinate bond. Examples: $H_2O$, $Cl^-$, $NH_3$.

**Bidentate** ligands each form **two** coordinate bonds. Example: $NH_2CH_2CH_2NH_2$.




**Hexadentate** ligands each form six coordinate bonds. Example: $EDTA^{4-}$.

**'Polydentate'** and **'multidentate' ligands** are general terms for any ligands that form **more than one** coordinate bond.

## Coordination Number

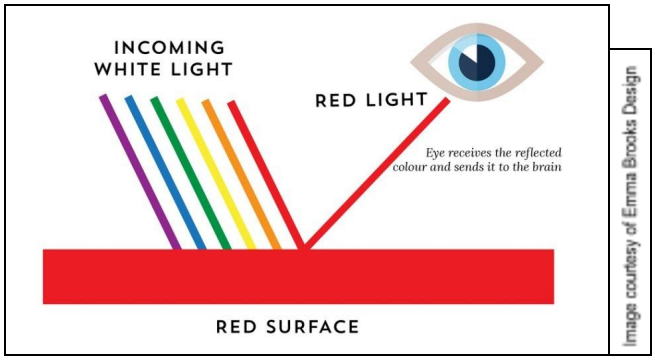
The **coordination number** of a transition metal complex is the total number of **coordinate bonds** formed with the central metal ion. Silver complexes have a coordination number of 2 and platinum complexes commonly have a coordination number of 4. The coordination number determines the **shape** of the complex ion.

## Coloured Ions

Transition metal ions can be identified by their **colour**, which changes depending on the **coordination number** of the complex, the type of **ligand** bonded to the ion and the **oxidation state**. Aqueous solutions of transition metal ions tend to be coloured.

Colour arises because of how substances **absorb and reflect** light. When white light shines on a substance, some of the wavelengths of light are absorbed, but the remaining wavelengths are **reflected and transmitted** to the human eye.

*Example:*



In transition metal complexes, ligands cause the d-orbital to split, meaning some electrons exist in a slightly higher energy level (in an **'excited state'**).

The change in energy (**∆E**) between these states corresponds to a specific **wavelength and frequency** of light. If this wavelength of light is within the visible region of the electromagnetic spectrum then a coloured compound will be seen.

## Colourless Ions

Some metal ions and complexes are colourless. Colour arises when some wavelengths of light are absorbed while others are reflected. This involves the **excitation of electrons.** Ions and complexes where there are **no available electrons to excite** cannot absorb light and are therefore **colourless**.

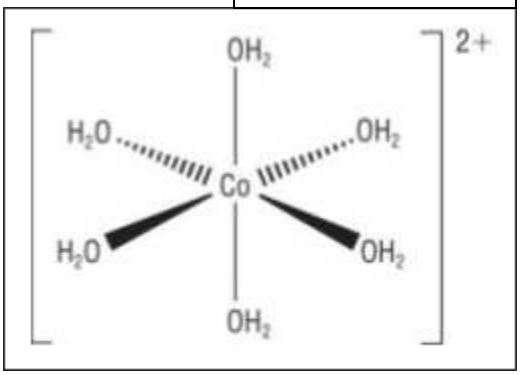
For example, zinc is in the d-block of the periodic table and has completely filled d-orbitals. Therefore, there are **no unfilled or partially filled d orbitals** into which an electron can be promoted. Therefore, zinc is colourless.

## Shapes of Complex Ions

### Octahedral Complexes

Transition metal complexes with $H_2O$ and $NH_3$ ligands commonly form **octahedral** complexes with a **bond angle of 90°**. Octahedral complexes are formed when there is six-fold coordination.

Image courtesy of chemhume.co.uk




### Tetrahedral Complexes

When complexes form with **larger ligands** such as $Cl^-$, they form **tetrahedral** complexes with a **bond angle of 109.5°** and 4 ligands coordinated. Tetrahedral complexes can show optical isomerism.

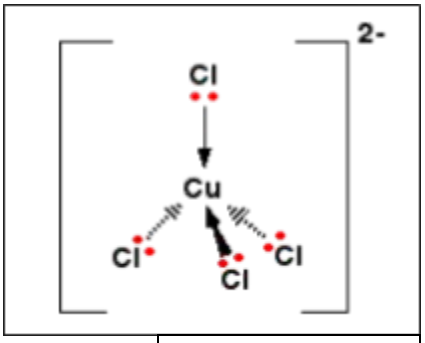



Image courtesy of Chemguide

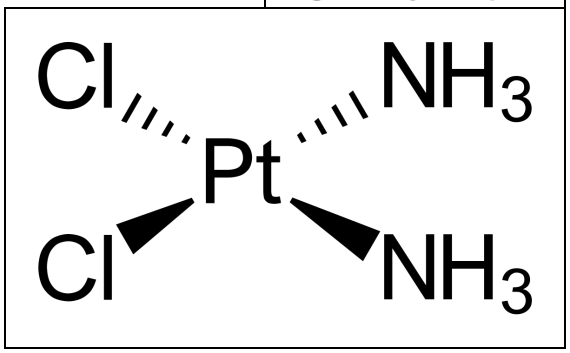
**Square Planar Complexes**

**Platinum and nickel** complexes form in a **square planar** shape. This consists of four coordinate bonds with a **bond angle of 90°**.

**Cisplatin**

This is the ***cis* isomer** of a square planar complex of **platinum**. It has both chlorine atoms on the **same side**. It is commonly used as a **cancer therapy drug**. Drugs like cisplatin target components of cells that are **chiral,** so only one isomer of the drug will be the correct orientation to 'fit' the cells. Therefore, only this **single isomer will work** and cure the disease.

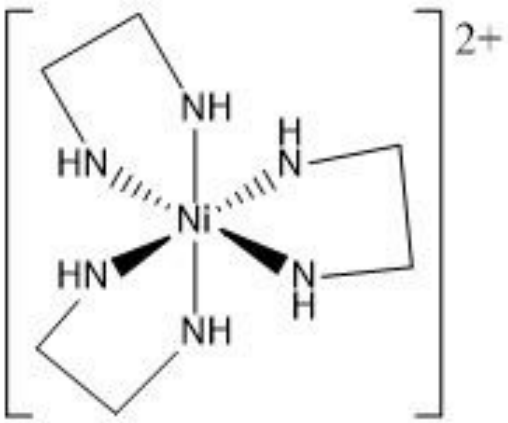
Image courtesy of Wikipedia




Cisplatin can cause serious **side effects** such as hair loss, meaning it has to be administered in **small amounts** to try and reduce these effects whilst still targeting the cancerous cells.

**Optical Isomerism**

Optical isomerism is seen in some octahedral complexes with **bidentate** ligands. These complexes have **non-superimposable** mirror images.



# Ligand Substitution

Ligands in a transition metal complex can be **exchanged** for other ligands.

Copper and cobalt aqua ions can undergo substitution with chloride ions.
The $Cl^-$ ligand is much **larger** than the $NH_3$ and $H_2O$ ligands meaning substitution with this ligand results in a **change in coordination number** for that complex.

$[Cu(H_2O)_6]^{2+}$ + $4Cl^-$ ⟶ $[CuCl_4]^{2-}$ + $6H_2O$

Blue solution — Yellow solution

$[Cu(H_2O)_6]^{2+}$ + $4NH_3$ ⟶ $[Cu(NH_3)_4(H_2O)_2]^{2+}$ + $4H_2O$

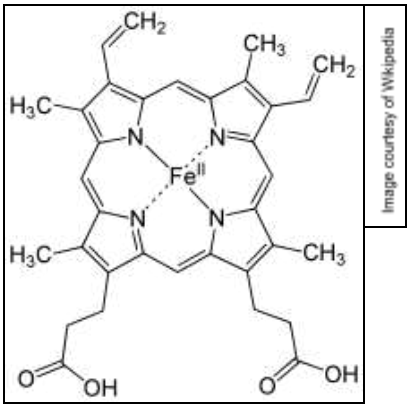
Blue solution — Deep blue solution

Complexes with just Cl- ligands always have a coordination number of **four**, producing a **tetrahedral** shaped complex.

## Haem

**Haem**, a component of haemoglobin, is another common example involving multidentate ligands. It consists of a central $Fe^{2+}$ ion and a tetradentate porphyrin ring. The central $Fe^{2+}$ ion can also form coordinate bonds with one or two additional axial ligands. This gives haemoglobin an overall **octahedral** structure. The shape and structure allow it to **transport oxygen** around the body.

*Example*:




A **ligand substitution reaction** occurs when the oxygen usually bound to haem is replaced with **carbon monoxide**. The carbon monoxide binds more strongly than oxygen so can not be removed. Therefore, carbon monoxide is **toxic** to humans as it prevents oxygen from being transported around the body.

### The Chelate Effect

In ligand substitution reactions, a **positive entropy change is favourable** as it means a more stable complex is being formed. Therefore, it is favourable to have more moles on the right of the reaction than on the left. This is achieved by substituting monodentate ligands with bidentate or polydentate ligands. This is known as the **chelate effect**.

The greater the entropy change, the **more negative** the free energy change (**$\Delta G$**) will be, meaning the reaction is **more favourable**.

### Enthalpy Change

The enthalpy change (**$\Delta H$**) for ligand substitution reactions is **very small** as the bonds being formed are very similar to the bonds that were broken. Therefore, overall enthalpy change is **near to zero**.

## Precipitation Reactions

### Reactions of Transition Metal Ions with Sodium Hydroxide and Ammonia

Metal ions become **hydrated** in water when **$H_2O$ ligands** form around the central metal ion. The reactions of five major metal aqua ions have to be known for this A-level specification: **chromium(III), iron(II), iron(III), manganese(II) and copper(II)**. These metal aqua ions react with sodium hydroxide and ammonia to form **coloured precipitates**.

Solutions of metal aqua ions react as **acids** with aqueous sodium hydroxide. Some react further with **excess sodium hydroxide.**

**Reactions with NaOH:**

| Transition Metal Ion | Metal-aqua ion | With $OH^-$ | With excess $OH^-$ |
|---|---|---|---|
| $Cr^{3+}$ | Violet solution $[Cr(H_2O)_6]^{3+}$ | Green precipitate $Cr(OH)_3(H_2O)_3$ | Green solution $[Cr(OH)_6]^{3-}$ |
| $Fe^{2+}$ | Green solution $[Fe(H_2O)_6]^{2+}$ | Green precipitate $Fe(OH)_2(H_2O)_4$ | No change |
| $Fe^{3+}$ | Yellow solution $[Fe(H_2O)_6]^{3+}$ | Brown precipitate $Fe(OH)_3(H_2O)_3$ | No change |
| $Mn^{2+}$ | Pale pink solution $[Mn(H_2O)_6]^{2+}$ | Pale brown precipitate $Mn(OH)_2(H_2O)_4$ | No change |
| $Cu^{2+}$ | Blue solution $[Cu(H_2O)_6]^{2+}$ | Blue precipitate $Cu(OH)_2(H_2O)_4$ | No change |

***It is easiest to remember the formulas of the precipitates by remembering that the number of OH- substituted is the same as the value of the charge on the initial ion.***

*Example equations:*

$[Fe(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$

$[Cu(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$

$[Fe(H_2O)_6]^{3+} + 3OH^- \longrightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O$

Solutions of metal aqua ions react as **acids** with aqueous ammonia. Some react further with **excess ammonia**. Initially, ammonia acts as a **base** to remove one $H^+$ ion per ammonia molecule used. With excess ammonia, some metal ions undergo **ligand substitution** with $NH_3$.

**Reactions with $NH_3$:**

| Transition Metal Ion | Metal-aqua ion | With $NH_3$ | With excess $NH_3$ |
|---|---|---|---|
| $Cr^{3+}$ | Violet solution $[Cr(H_2O)_6]^{3+}$ | Green precipitate $Cr(OH)_3(H_2O)_3$ | Purple solution $[Cr(NH_3)_6]^{3+}$ |
| $Fe^{2+}$ | Green solution $[Fe(H_2O)_6]^{2+}$ | Green precipitate $Fe(OH)_2(H_2O)_4$ | No change |
| $Fe^{3+}$ | Yellow solution $[Fe(H_2O)_6]^{3+}$ | Brown precipitate $Fe(OH)_3(H_2O)_3$ | No change |
| $Mn^{2+}$ | Pale pink solution $[Mn(H_2O)_6]^{2+}$ | Pale brown precipitate $Mn(OH)_2(H_2O)_4$ | No change |
| $Cu^{2+}$ | Blue solution $[Cu(H_2O)_6]^{2+}$ | Blue precipitate $Cu(OH)_2(H_2O)_4$ | Dark blue solution $[Cu(NH_3)_4(H_2O)_2]^{2+}$ |

***It is easiest to remember the formulas of the precipitates by remembering that the number of OH- substituted is the same as the value of the charge on the initial ion.***

*Example equations:*

$[Fe(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$

$[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$

$[Fe(H_2O)_6]^{3+} + 3NH_3 \longrightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$

$[Cu(H_2O)_4(OH)_2] + 4NH_3 \longrightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 2H_2O + 2OH^-$

# Redox Reactions

One of the key chemical properties of transition metals is their **variable oxidation states**. Redox reactions are used to change the oxidation state of a transition metal. These changes are often accompanied by a **colour change**.

## Iron

The most stable oxidation states of iron are **$Fe^{2+}$ and $Fe^{3+}$**.

Compounds containing $Fe^{2+}$ ions are **pale green** in colour. $Fe^{2+}$ can be oxidised with $MnO_4^-$ in acidic conditions.

Compounds containing $Fe^{3+}$ ions are **orange/brown** in colour. $Fe^{3+}$ can be reduced with $I^-$.

## Chromium

The most stable oxidation states of chromium are +6, +3, and +2, found in the species **$Cr_2O_7^{2-}$, $Cr^{3+}$, and $Cr^{2+}$** respectively. These can be interconverted by oxidation and reduction reactions.

$Cr_2O_7^{2-}$ can be reduced to $Cr^{3+}$ and $Cr^{2+}$ ions by **reduction** with **zinc** in **acidic conditions**.

$Cr^{3+}$ can be **oxidised** to $Cr_2O_7^{2-}$ by **hydrogen peroxide** in **alkaline conditions**. The reaction first forms $CrO_4^{2-}$ which is then converted to $Cr_2O_7^{2-}$ by **acidification**.

This occurs because there is an **equilibrium** between the two chromium(VI)-containing species:

$$\mathbf{2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O}$$

**Acidification** of a solution containing $CrO_4^{2-}$ will, therefore, cause the equilibrium to **shift** to the right (to use up the additional $H^+$ ions), so the concentration of $Cr_2O_7^{2-}$ will **increase**.

## Copper

The most stable oxidation states of copper are **$Cu^+$ and $Cu^{2+}$**.

$Cu^{2+}$ can be reduced to Cu by zinc.

$Cu^+$ readily **disproportionates** to Cu and $Cu^{2+}$.

# 5.3.2 Qualitative Analysis

## Tests for Ions

Qualitative analysis can be performed to **identify ions** in an unknown compound.

### Tests for Anions

The following tests can be used to determine if any of these **anions** are present. They should be performed in the order carbonate, sulfate, then halide, if a mixture of ions is present.

**Carbonate ($CO_3^{2-}$) and Hydrogencarbonate ($HCO_3^-$)**

When an acid such as HCl is added, the substance containing the carbonate ions will **fizz and $CO_2$ gas is given off**. This gas can be collected and bubbled through **limewater** which will turn **cloudy**, confirming its identity as carbon dioxide.

*Example:*

$$XCO_3 + 2HCl \longrightarrow CO_2 + H_2O + XCl_2$$

**Sulfate ($SO_4^{2-}$)**

Sulfate ions are tested for using **acidified $BaCl_2$** which reacts to form a **white precipitate** of barium sulfate.

*Example:*

$$BaCl_2 + XSO_4 \longrightarrow BaSO_4 + XCl_2$$

**Halide ions ($Cl^-$,$Br^-$,$I^-$)**

When combined with acidified silver nitrate, halide ions react to form different **coloured precipitates** depending on the ion present. The precipitates can then be tested further with ammonia.

| Halide Ion | $Cl^-$ | $Br^-$ | $I^-$ |
|---|---|---|---|
| **+ $AgNO_3$** | White precipitate (AgCl) | Cream precipitate (AgBr) | Yellow Precipitate (AgI) |
| **+ dilute $NH_3$** | Precipitate dissolves | No Change | No Change |
| **+ conc. $NH_3$** | Precipitate dissolves | Precipitate dissolves | No Change |

## Tests for Cations

The following tests can be used to determine if any of these **cations** are present.

### Ammonium ($NH_4^+$)

If ammonium ions are present, adding NaOH and gently warming results in the formation of **ammonia gas**, which is **basic**. Therefore, the presence of ammonium ions can be tested by holding **damp red litmus paper** over a petri dish of the substance being tested. It will **turn blue** if ammonium ions are present.

### Transition Metal Ions

Transition metals form coloured compounds. This property can be used to determine which transition metal ions are present in a compound. The previous section explores the colours of **chromium(III), iron(II), iron(III), manganese(II) and copper(II)** metal-aqua ions and their precipitation reactions with sodium hydroxide and ammonia.