



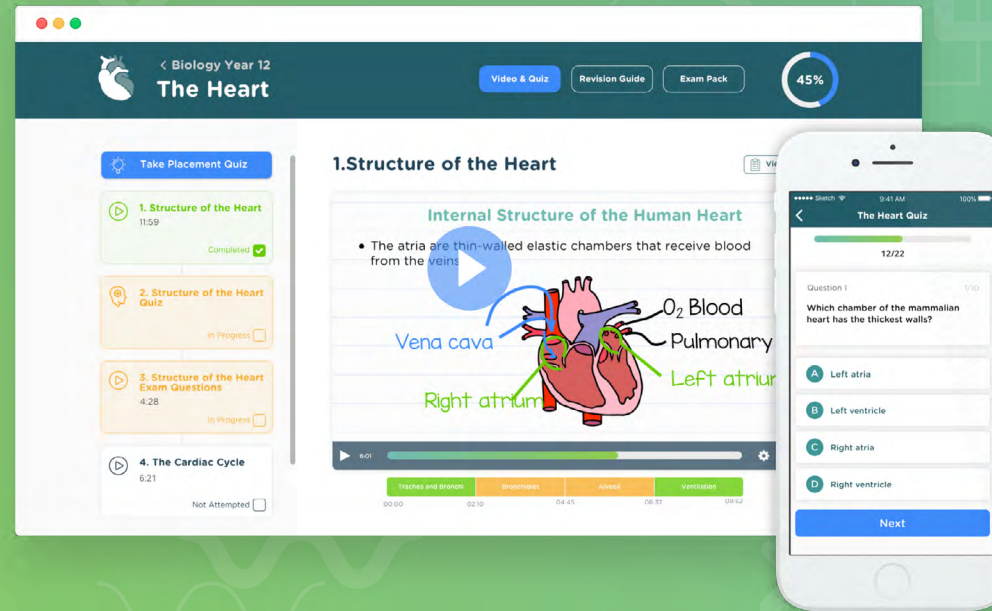
# THE ULTIMATE A-LEVEL OCR CHEMISTRY CHEATSHEET PACK





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# How to Use

The aim of this pack is simple – we wanted to condense the A-level Chemistry course into a few super condensed pages. Now you have a concise summary of the entire course that focuses on the most important definitions, key terms, diagrams and concepts.

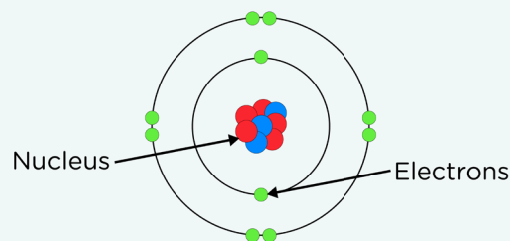
We've spent weeks working with top designers, academic writers and illustrators to ensure this is the best cheatsheet out there. Our promise to you is you won't find anything better. The cheatsheet pack has been built off the OCR specification to ensure no important information is missed – below is a table which summarises how our cheatsheets map to the OCR specification.

Specification Points	Cheatsheet
2.1.1	Atomic Structure & Isotopes
2.1.1 - 2.1.2	Compounds, Formulae, Equations & Moles
2.1.4 - 2.1.5	Acids, Bases & Redox
2.2.2	Electron Configuration & Bonding
3.1.1	Periodicity
3.1.2 - 3.1.3	Group 2 & Group 7
3.2.1	Enthalpy
3.2.2	Reaction Rates
3.2.3	Equilibrium, The Haber Process & Partial Pressure
4.1.1	Introduction to Organic Chemistry
4.1.2 - 4.1.3	Alkanes & Alkenes
4.2.1 - 4.2.2	Alcohols & Haloalkanes
4.2.3 - 4.2.4	Synthesis & Analysis
5.1.1	Rate Equations & Rate Determination
5.1.2 - 5.1.3	Acids, Bases & Buffers
5.2.1	Lattice Enthalpy & Born-Haber Cycles
5.2.2 - 5.2.3	Entropy & Redox
5.3.1	Transition Elements
6.1.1	Benzene & Phenol
6.1.2 - 6.2.1	Carbonyls
6.2.2	Amines & Amino Acids
6.2.3 - 6.2.5	Condensation Polymers & Synthesis
6.3.1	Chromatography & Tests for Ions

We hope you enjoy using it and wish you the best of luck in your A-levels.

### Atomic Structure

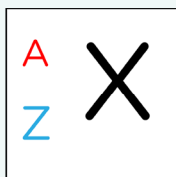
- Atoms are the components that make up all elements.
- Atoms are made up of three types of sub-atomic particles - protons, neutrons, and electrons
- Protons and neutrons make up the nucleus, where most of the mass is concentrated. Electrons orbit the nucleus in shells



Particle	Relative Mass	Relative Charge
Proton	1	+1
Neutron	1	0
Electron	1/2000	-1

### Mass Number & Isotopes

- Element, X



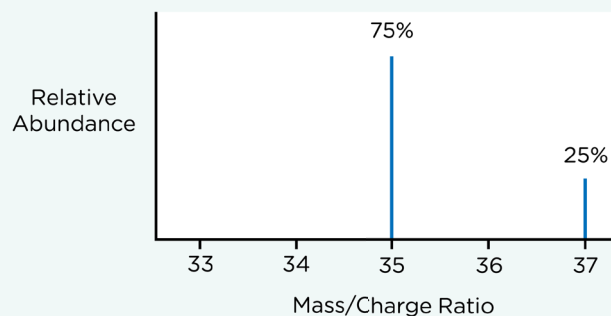
- Mass number, A, is the total number of protons and neutrons in the nucleus
- Atomic number, Z, is the number of protons. The number of positively charged protons is equal to the number of negatively charged electrons in an atom, making the atom neutrally charged
- Mass number = number of protons + number of neutrons
- Atomic number = number of protons = number of electrons
- Ions are formed by atoms losing or gaining electrons.
  - A charge of x- means that the number of electrons in the ion is the atomic number + x
  - A charge of x+ means that the number of electrons in the ion is the atomic number - x
- Isotopes are atoms with the same number of protons and different numbers of neutrons. Therefore, they have different mass numbers but the same atomic number.
- Isotopes of the same element have the same electronic configuration so react in the same way in chemical reactions but have slightly different physical properties.

### Relative Masses

- Relative isotopic mass is the mass of an atom of an isotope compared with 1/12th of the mass of an atom of carbon-12. For an isotope, the relative isotopic mass = its mass number.
- Relative atomic mass is the ratio of the average mass of an atom of an element to 1/12th of the mass of an atom of carbon-12.
- Relative molecular mass is the ratio of the average mass of a molecule of an element or compound to 1/12th of the mass of an atom of carbon-12.
- Relative formula mass is similar to relative molecular mass but applies to ionic compounds.

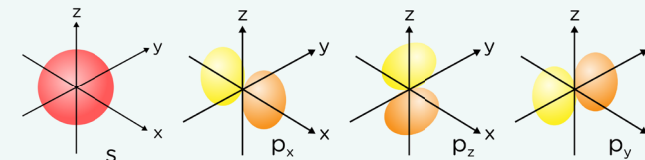
### Mass Spectrometry

- Mass spectrometry is a form of molecular chemical analysis that allows the masses of individual molecules or isotopes to be determined.
  - Mass spectrometry can be used to provide structural information, identify an unknown compound, or determine the relative abundance of each isotope of an element.
  - The mass spectrum gives information about the relative abundance of isotopes on the y axis and about the relative isotopic mass on the x axis.
  - The mass spectrum can be used to determine the relative atomic mass ( $A_r$ )
- $$A_r = \frac{\sum (\text{relative isotopic mass} \times \text{abundance})}{100}$$
- A mass spectrum for a molecular sample shows the relative molecular mass on the x axis.

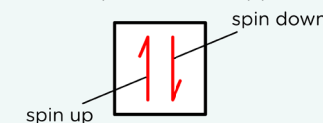


### Electronic Configuration

- Electrons orbit the central nucleus in shells. Each shell can hold  $2n^2$  electrons, where n is the principal quantum number.
- Electron shells are made up of atomic orbitals, which are regions in space where electrons may be found.
- Each shell is composed of one or more orbitals and each orbital can hold one pair of electrons.
- There are four main types of orbitals: s-, p-, d-, and f-



- There are 1 s-orbital, 3 p-orbitals, 5 d-orbitals and 7-p orbitals possible in each subshell.
- Shell/quantum number n = 1 can have the occupancy  $1s^2$
- n = 2 can have the occupancy  $2s^2 2p^6$
- n = 3 can have the occupancy  $3s^2 3p^6 3d^{10}$
- n = 4 can have the occupancy  $4s^2 4p^6 4d^{10} 4f^{14}$
- Within each shell, orbitals that are of the same energy level are grouped together in sub-shells.
- Sub-shells have different energy levels. Note that 4s is lower in energy than 3d, so 4s will fill first.
- Shells and sub-shells are filled with electrons according to a set of rules:
  - Atomic orbitals with the same energy fill individually first before pairing
  - Aufbau principle - the lowest available energy level is filled first
- Electron configuration is written with n representing principal quantum number. X is the type of orbital and y is the number of electrons in the orbitals of the subshell e.g. potassium has 19 electrons and its electron configuration is written as  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
- Electronic configurations of ions can be determined by using the same building up principle. e.g.  $K^+$  is the same as potassium but one electron has been removed, therefore it is:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$  Take care with d-block ions, as 4s fills before 3d, but it also empties before 3d when forming ions
- Electrons have an intrinsic property (spin). For two electrons in the same orbital, the spin must be opposite to minimise the repulsion.



No more than two electrons can fill an atomic orbital

### Ionic Compounds

- An ion is an atom or molecule with a net charge formed through the gain or loss of electrons
- A cation is formed from the loss of electrons
- An anion is formed from the gain of electrons
- Ionic compounds are composed of oppositely charged ions. The overall charge is zero as the ionic charges balance.  
e.g. write the formula of sodium carbonate  
Sodium is in Group 1, and so it will lose one electron, Na<sup>+</sup>  
The carbonate ion has the formula CO<sub>3</sub><sup>2-</sup>  
We need 2 x Na<sup>+</sup> to balance the -2 charge of CO<sub>3</sub><sup>2-</sup>  
The formula is Na<sub>2</sub>CO<sub>3</sub>

### Empirical & Molecular Formula

- The empirical formula is the simplest whole-number ratio of atoms of each element present in a compound.
- The empirical formula can be calculated from the composition by mass or percentage by mass.  
e.g. 6.2 g of P is combined with O<sub>2</sub> to form 14.2 g of phosphorous oxide. Calculate the empirical formula of the compound.  
mass of O<sub>2</sub>: 14.2 g - 6.2 g = 8 g  
number of moles of each element:

$$P = \frac{6.2 \text{ g}}{31 \text{ g mol}^{-1}} = 0.2 \text{ mol} \quad O = \frac{8 \text{ g}}{16 \text{ g mol}^{-1}} = 0.5 \text{ mol}$$

Divide through by the smallest number of moles to get the whole number ratio:

P	O
$\frac{0.2}{0.2}$	$\frac{0.5}{0.2}$
1	2.5
2	5

Empirical formula: P<sub>2</sub>O<sub>5</sub>

- The molecular formula gives the number and type of atoms of each element in a molecule. It is made up of a whole number of empirical units.
- The molecular formula can be determined using the empirical formula and relative molecular mass of the molecule.  
e.g. Determine the molecular formula of a compound with empirical formula CH<sub>2</sub> and a relative molecular mass of 224.  
Relative molecular mass of the empirical formula:  
C            H<sub>2</sub>  
12    +    (1 × 2) = 14  
Divide the relative molecular mass by that of the empirical formula:  
224/14=16  
Molecular formula:  
16 × CH<sub>2</sub> = C<sub>16</sub>H<sub>32</sub>

### The Mole & Concentration

- The mole is the unit used to quantify the amount of a substance. It can be applied to any amount of chemical species, including atoms, electrons, molecules and ions
- A mole is the amount of substance that contains the same number of atoms or particles as 12 g of carbon-12.
- The number of particles in 12g of <sup>12</sup>C is the Avogadro constant of 6.022 x 10<sup>23</sup> mol<sup>-1</sup>.

$$n = \frac{m}{M}$$

n is the number of moles (mol)  
m is the mass (g)  
M is the molar mass (g mol<sup>-1</sup>)

- The concentration of a solution is the amount of solute present in a known volume of solution

$$c = \frac{n}{V}$$

c is the concentration (mol dm<sup>-3</sup>)  
n is the number of moles in solution (mol)  
V is the volume (dm<sup>3</sup>)

- Remember:
  - 1 dm<sup>3</sup> = 1000 cm<sup>3</sup>
  - 1 m<sup>3</sup> = 1000 dm<sup>3</sup>

### Gas Equations

- One mole of any gas under standard conditions will occupy the same volume.
- The molar gas volume is 24 dm<sup>-3</sup> mol<sup>-1</sup> under standard conditions of 298 K and 100 kPa
- The number of moles of gas can be calculated using the equation:

$$n = \frac{V}{\text{molar gas volume}}$$

n is the number of moles of gas (mol)  
V is volume (dm<sup>-3</sup>)

- In an ideal gas the assumptions are made that:
  - Intermolecular forces between the gas particles are negligible
  - The volume of the particles themselves, relative to the volume of their container, is negligible
- The ideal gas equation is:

$$pV = nRT$$

p is pressure (Pa)  
V is volume (m<sup>3</sup>)  
n is the number of moles (mol)  
R is the gas constant (8.314 JK<sup>-1</sup>)  
T is temperature (K)

### Balanced Equations

- When a chemical reaction occurs, no atoms are created or destroyed. The atoms in the reactants rearrange to form the products.
- In a balanced equation, there is the same number of atoms of each element in both the reactants and products.
- State symbols are written after every species to indicate the physical state
  - Solid (s)
  - Liquid (l)
  - Gaseous (g)
  - Aqueous (aq) - dissolved in water
- Ionic equations can be written for any reaction involving ions in solution, where only the reacting ions and the products they form are included.
- The net ionic equation shows only the ions directly involved in the reaction (removing spectator ions).  
e.g. NaCl (aq) + AgNO<sub>3</sub> (aq) → AgCl (s) + NaNO<sub>3</sub> (aq)  
Na<sup>+</sup> (aq) + Cl<sup>-</sup> (aq) + Ag<sup>+</sup> (aq) + NO<sub>3</sub><sup>-</sup> (aq) → AgCl (s) + Na<sup>+</sup> (aq) + NO<sub>3</sub><sup>-</sup> (aq)  
Net ionic equation:  
Cl<sup>-</sup> (aq) + Ag<sup>+</sup> (aq) → AgCl (s)

### Atom Economy & Percentage Yield

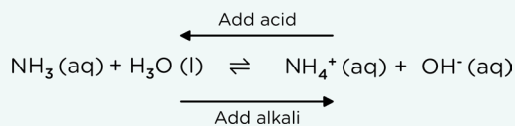
- Atom economy is a theoretical measure of the proportion of atoms from the reactants that form the desired product. In order to calculate it a balanced chemical equation is required.
- % atom economy =  $\frac{\text{molecular mass of desired products}}{\text{sum of molecular masses of all reactants}} \times 100$
- Maximising atom economy has important economic, ethical and environmental advantages:
  - More sustainable (uses fewer raw materials)
  - Minimises chemical waste
  - Maximises efficiency
  - Less money is spent on separation processes
- The limiting reagent is the reagent not in excess. It dictates the theoretical yield and the amount of product actually formed.
- Percentage yield is a measure of the percentage of reactants that have been converted into the desired product. It gives a measure of the efficiency of a reaction route.
- The percentage yield is reduced by the formation of unwanted by-products, any reactant that remains unreacted, or product that cannot be extracted from the reaction vessel.
- percentage yield =  $\frac{\text{actual yield}}{\text{theoretical yield}} \times 100$

## Acids

- Common acids include:
  - Hydrochloric acid, HCl
  - Sulphuric acid, H<sub>2</sub>SO<sub>4</sub>
  - Nitric acid, HNO<sub>3</sub>
- Acids dissociate in water: HA (aq) ⇌ A<sup>-</sup> (aq) + H<sup>+</sup> (aq)
- This process of HA separating into A<sup>-</sup> and H<sup>+</sup> ions is called dissociation.
- The strength of an acid describes how much of it dissociates when it dissolves.
- A strong acid is an acid which dissociates almost completely in water or aqueous solution. HA (aq) ⇌ A<sup>-</sup> (aq) + H<sup>+</sup> (aq)
- A weak acid is an acid which is only partially dissociated in water or aqueous solution. HA (aq) ⇌ A<sup>-</sup> (aq) + H<sup>+</sup> (aq)
- Hydrochloric acid is a strong acid:  
$$\text{HCl (aq)} \rightarrow \text{H}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$$

## Bases

- Common bases include:
  - Sodium hydroxide, NaOH
  - Potassium hydroxide, KOH
  - Ammonia, NH<sub>3</sub>
- Alkalis also dissociate in water, forming bases:
- XOH → X<sup>+</sup> + OH<sup>-</sup> e.g. NaOH → Na<sup>+</sup> + OH<sup>-</sup>



## Neutralisation

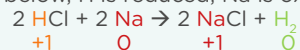
- Acids and bases react together in neutralisation reactions:  
**acid + base → salt + water**
- Acid-carbonate reactions:  
**acid + carbonate → salt + carbon dioxide + water**
- Acid-metal reactions:  
**acid + metal → salt + hydrogen gas**
- In each example H<sup>+</sup> reacts with OH<sup>-</sup> to form water.

## Oxidation Numbers

- Oxidation number is a number representing the number of electrons lost or gained by an atom in a compound.
- Oxidation is a loss of electrons during a reaction or an increase in oxidation number.
- Reduction is a gain of electrons during a reaction or a decrease in oxidation number
- The rules for assigning oxidation numbers:
  - An uncombined element has an oxidation number of 0
  - A simple ion (of a single element) has an oxidation number equal to the charge on the ion
  - The sum of oxidation numbers of the elements in a compound is equal to the overall charge of the compound
  - The charge on a complex ion, e.g. NH<sub>4</sub><sup>+</sup>, is equal to the sum of the oxidation numbers
  - The most electronegative element in a compound always has a negative oxidation number
  - Oxygen is always -2 except in peroxides where its -1
  - Hydrogen is +1 except in metal hydrides where its -1
- Oxidation numbers are represented by Roman numerals when naming compounds
- Oxidation numbers can be used to write formulae for a compound

## Redox Reactions

- Reduction: The gain of electrons and decrease in oxidation number of an element
- Oxidation: The loss of electrons and increase in oxidation number of an element
- Redox reactions involve both oxidation and reduction
- Oxidising agents cause oxidation of other species, and so are themselves reduced
- Reducing agents cause reduction of other species, and so are themselves oxidised
- In the reaction below, H is reduced, Na is oxidised.



## Redox Titrations

- Redox titrations can show how much oxidising agent is needed to react exactly with a reducing agent
- Redox reactions often involve colour changes, making it easy to see when a reaction has reached completion
- Manganate(VII) ions are readily reduced to Mn<sup>2+</sup> ions under acidic conditions. The MnO<sub>4</sub><sup>-</sup> ions are **purple**, Mn<sup>2+</sup> are **colourless**.
  - Oxidation:** Fe<sup>2+</sup> → Fe<sup>3+</sup> + e<sup>-</sup>
  - Reduction:** 8H<sup>+</sup> + MnO<sub>4</sub><sup>-</sup> + 5e<sup>-</sup> → Mn<sup>2+</sup> + 4H<sub>2</sub>O
  - Overall:** 8H<sup>+</sup> + MnO<sub>4</sub><sup>-</sup> + 5Fe<sup>2+</sup> → Mn<sup>2+</sup> + 4H<sub>2</sub>O + 5Fe<sup>3+</sup>
- In iodine-thiosulphate titrations, iodine is reduced to form iodide ions and thiosulphate ions are oxidised. Iodine is often combined with starch, which makes it dark blue. As iodine is consumed the solution turns pale yellow at the end point
  - Oxidation:** 2S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (aq) → S<sub>4</sub>O<sub>6</sub><sup>2-</sup> (aq) + 2e<sup>-</sup>
  - Reduction:** I<sub>2</sub> (aq) + 2e<sup>-</sup> → 2I<sup>-</sup> (aq)
  - Overall:** 2S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (aq) + I<sub>2</sub> (aq) → S<sub>4</sub>O<sub>6</sub><sup>2-</sup> (aq) + 2I<sup>-</sup> (aq)

## Titrations

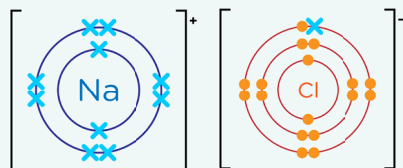
- Acid-base titrations can be used to find the concentration of a sample of either an acid or a base.
- A known concentration of an acid is gradually added to a known volume of a base of unknown concentration until the solution is neutralised i.e. the titration reaches the 'end point'
- A burette is used to gradually add the acid, a pipette is used to add a known volume of the base, and an indicator is used to cause a colour change when the reaction reaches the end point
- Calculations are used to determine the concentration of the unknown solution.
- These calculations are those you already know:  
$$n = c \times v \qquad m = n \times Mr$$

# ELECTRON CONFIGURATION & BONDING

## CHEAT SHEET

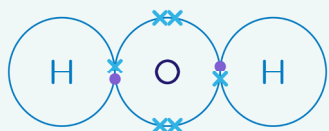
### Ionic Bonding

- An ionic bond is an electrostatic attraction between positive and negative ions, resulting in a giant lattice
- A lattice is a giant three-dimensional structure, where each ion is surrounded by oppositely charged ions
- They are often formed between ions of metals and non-metals, where each atom aims to gain a stable full outer shell.
- Electrons are represented by dots and crosses, which helps visualise the origin of the electrons clearly
- The strength of an ionic bond depends on
  - The charge on the ions - Ions with higher charges will have a greater electrostatic attraction between them and will form stronger bonds.
  - The distance between the ions - Smaller ions have a smaller internuclear distance so the electrostatic forces of attraction will be greater. Smaller ions form stronger ionic bonds in more closely packed lattices.
- Properties of ionic structures
  - High melting and boiling points
  - Soluble in polar solvents
  - Electrical conductivity when molten or dissolved in water

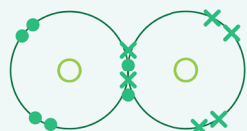


### Covalent Bonds

- Covalent bonding usually occurs between two atoms of non-metals, so that the atoms each gain a stable full outer shell
- A covalent bond is a strong electrostatic attraction between a shared pair of outer electrons and the nuclei of the bonded atoms
- Unlike ionic bonds, covalent bonds are localised
- A single covalent bond involves one shared pair of outer electrons, while a multiple covalent bond involves more than one shared pair of outer electrons



Two single covalent bonds in H<sub>2</sub>O

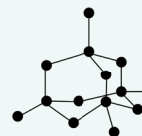


A double covalent bond in O<sub>2</sub>

- A co-ordinate (dative covalent) bond involves one atom donating both electrons in a covalent bond.
- A dative covalent bond is represented by an arrow from the atom that is donating both electrons to the atom that is accepting both electrons
  - Average bond enthalpy is a measure of the enthalpy required to break one mole of covalent bonds, hence it indicates the strength of covalent bonds.
  - Covalent compounds can have two structures, either: simple molecular structure OR giant covalent lattice.

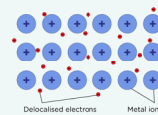
### Giant Covalent Structures

- Giant covalent lattices consist of billions of atoms held together by a network of strong covalent bonds.
- Carbon forms three types of giant covalent structures: graphite, graphene and diamond.
- In diamond, each carbon atom is bonded to four other carbon atoms
- This makes it very strong, with an incredibly high melting point, hardness, insolubility. It is an electrical insulator because all the outer shell electrons are being used in covalent bonds, so there are no mobile charge carriers



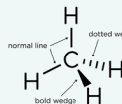
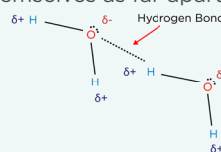
### Metallic Bonding

- Metallic bonding is the strong electrostatic attraction between positive metal ions and negative delocalised electrons in a metal lattice
- Metals have a fixed lattice structure of positive ions. The outer shell of electrons is delocalised, which can carry current.
- Metals have high melting and boiling points due to the large amounts of energy needed to overcome the metallic bonds.
- The greater the charge of a metal ion, the more electrons are delocalised. The smaller the size of the metal ions, the closer they are to the delocalised electrons. This results in stronger bonds and a higher melting point
- Metals are malleable and ductile. The ions can slide and move past each other as there are no bonds holding specific ions together



### Simple Molecules

- Simple molecular structures have low boiling points. In the solid state they are held together by weak intermolecular forces
- Covalent bonding pairs and lone pairs of electrons are charge clouds that repel each other
- Electron pairs in the outer shell arrange themselves as far apart as possible to minimise repulsion
- Bonding pairs repel each other equally. While lone pairs repel other pairs more because they are more electron dense.
- A normal line represents the bond is in plane of the paper. A dotted wedge is a bond going into the paper and a bold wedge is a bond coming out of the paper.
- The shape of a molecule is determined by electron-pair repulsion theory



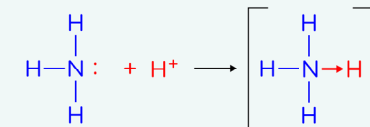
	Electron Pairs	Bonding Pairs	Lone Pairs	Bond Angles	Example
Linear	2	2	0	180°	CO <sub>2</sub>
Trigonal Planar	3	3	0	120°	BF <sub>3</sub>
Tetrahedral	4	4	0	109.5°	CH <sub>4</sub>
Pyramidal	4	3	1	107°	NH <sub>3</sub>
Non-linear	4	2	2	104.5°	H <sub>2</sub> O
Octahedral	6	6	0	90°	SF <sub>6</sub>

### Bond Polarity

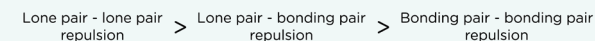
- Electronegativity is the power of an atom to attract the pair of electrons in a covalent bond. It is affected by:
  - Nuclear charge
  - Atomic radius
  - Shielding by electrons in inner shells
- A polar bond will form between two atoms with different electronegativity values where the electrons in the bond are not shared equally. This causes a permanent dipole.
- Partial negative charges (δ-), and partial positive charges (δ+) are used to show that a bond is polar.
- Molecules containing polar bonds are not always polar. The symmetry of polar bonds can cancel the effect of any permanent dipole.

### Intermolecular Forces

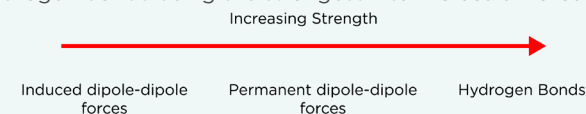
- Intermolecular interactions are the forces of attraction between molecules that do not involve the transfer of electrons. They are the result of the constant and random movements of electrons within electron shells
- The greater the strength of the bonds, the higher the melting and boiling points. E.g., down a group boiling point increases, due to greater induced dipole-dipole forces, as electron number increases



- Induced dipole-dipole (London) forces** are caused by the temporary unequal distribution of charge due to the constantly moving electrons. The temporary dipole can induce a temporary dipole in a neighbouring atom and the two dipoles will be attracted to each other. This can occur between almost all molecules.
- Permanent dipole-dipole forces** are caused by molecules with a permanent dipole being attracted to the opposite charge in other permanent dipoles, if correctly aligned.

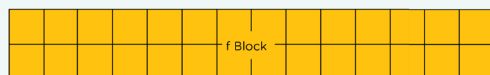
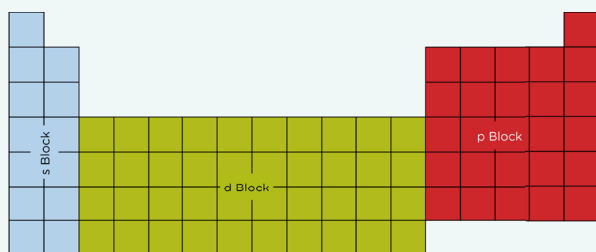


- Hydrogen bonding** requires:
  - An electron-deficient hydrogen atom and a more electronegative atom. These atoms are oxygen, fluorine and nitrogen
  - A lone pair of electrons on a highly electronegative atom on another molecule
- Hydrogen bonding in water allows ice to be less dense than water as hydrogen bonds hold the water molecules apart at a fixed position, forming an open lattice
- Water has high melting and boiling points than expected due to hydrogen bonds being the strongest intermolecular forces



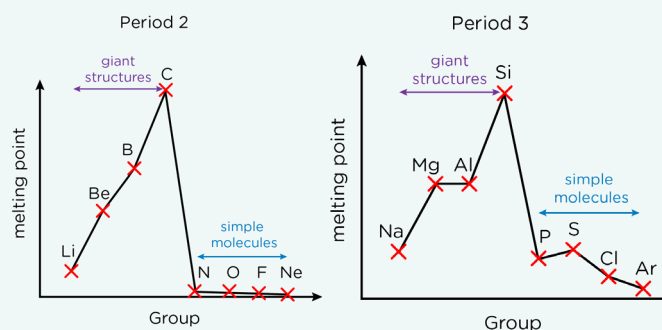
## Periodic Table

- In the Periodic Table, elements are arranged in order of increasing atomic number
- Elements can be grouped into periods (horizontal rows) and groups (vertical columns).
- Groups contain elements with similar physical and chemical properties, as they have the same number of outer shell electrons
- Periodicity is a regularly repeating pattern of atomic, physical, and chemical properties with increasing atomic number
- The Periodic Table can be split into s-, p-, d-, and f- blocks. Which is determined by which orbital the highest energy electron is in.



## Period 2 & 3

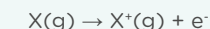
- Across Period 2, two electrons fill the 2s sub-shell before six electrons will fill the 2p sub-shell
- Across Period 3, two electrons will fill the 3s sub-shell before six electrons will fill the 3p sub-shell
- Across Period 2 and Period 3, the trend in melting point relates to the structure of the elements. The melting point increases from Group 1 to Group 14 because the elements have giant structures (metallic and then covalent). The melting points decrease from group 14 to 15 because the structure changes to simple molecular, which is only held together by weak intermolecular forces



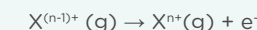
- Across the period, the atomic radius decreases as effective nuclear charge increases and there is no increase in shielding

## Ionisation Energy

- Ionisation energy is a measure of the energy required to completely remove an electron from an atom of an element to form an ion.
- First ionisation energy is the energy required to remove one electron from each atom in one mole of the gaseous element to form one mole of gaseous 1+ ions.



- Successive ionisation energies apply to the removal of electrons after the first ionisation energy. The nth ionisation energy is:



- Successive ionisation energies provide evidence for the shell structure of atoms.
  - Within each shell successive ionisation energies increase, as there is less electron repulsion
  - Between shells, there are big jumps in ionisation energies, as the electron is removed from a shell closer to the nucleus
- Factors affecting ionisation energies:
  - Atomic radii - The larger the atomic radius, the further away the outer electrons are held from the nucleus, and the smaller the nuclear attraction.
  - Nuclear charge - The greater the nuclear charge, the greater the attractive force on the outer electrons.
  - Shielding - electrons repel each other due to their negative charge. The greater the number of inner shells of electrons, the greater the repulsion of the outer shell of electrons.
- The greater the attraction, the harder it is to remove an electron. Therefore, the ionisation energy will be larger.
- Atomic radii show periodicity. Across a period, the radius decreases while down a group, the radius increases.
- Ionisation energy increases across a period, electrons are all added to the same shell resulting in greater attraction.
- Ionisation energy decreases across a group, as the number of shells increases, so does the atomic radius and shielding, reducing attraction.



### Group 2, Alkaline Earth Metals

- All Group 2 elements have 2 electrons in their outer s-subshell.
- Down the group ionisation energy decreases, as the atomic radius and shielding increases, decreasing the attraction of the electron to the nucleus
- Melting point also decrease down the group due to the increased atomic radii and shielding, so metallic bonding is weaker
- Group 2 elements undergo redox reactions:
  - with water to form hydroxides and hydrogen gas:
 
$$\text{Mg} (s) + 2\text{H}_2\text{O} (l) \rightarrow \text{Mg}(\text{OH})_2 (aq) + \text{H}_2 (g)$$

0
+1
+2
0
  - with oxygen to form oxides:
 
$$\text{Mg} (s) + \text{O}_2 (g) \rightarrow \text{MgO} (s)$$

0
0
+2-2
  - with dilute acids to form salts:
 
$$\text{Mg} (s) + \text{HCl} (aq) \rightarrow \text{MgCl}_2 (aq) + \text{H}_2 (g)$$

0
+1
+2
0
- The reactions involve the loss of electrons to form 2+ ions, which requires the input of the first two ionisation energies
- First and second ionisation energy values decrease down group 2 because of increase in atomic radius, increase in shielding, and hence a decrease in attraction between the nucleus and outer electron
- As ionisation becomes easier, reactivity increases, therefore reactivity increases down group 2

Group 2 Element	Group 2 Hydroxide	Solubility of Hydroxide
Mg	Mg(OH) <sub>2</sub>	Slightly soluble
Ca	Ca(OH) <sub>2</sub>	Sparingly soluble
Sr	Sr(OH) <sub>2</sub>	More soluble than Mg(OH) <sub>2</sub> and Ca(OH) <sub>2</sub>
Ba	Ba(OH) <sub>2</sub>	Most soluble

- Magnesium hydroxide is used in indigestion tablets to neutralise stomach acid
- Calcium hydroxide is used in increase the pH of acidic soils

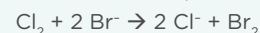
### Group 7, The Halogens

- The halogens exist as diatomic (X<sub>2</sub>) molecules
 

Halogen	Appearance
F <sub>2</sub>	Pale yellow gas
Cl <sub>2</sub>	Green gas
Br <sub>2</sub>	Red-brown liquid
I <sub>2</sub>	Black solid
- Down the group electronegativity decreases, as atomic radius and shielding increases.
- Down the group boiling point increases, as the molecules have a greater surface area and electrons for stronger London forces

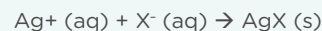
Halogen	Appearance	Boiling point	London forces
F <sub>2</sub>	Pale yellow gas	Lowest	Weakest
Cl <sub>2</sub>	Green gas	↓	↓
Br <sub>2</sub>	Red-brown liquid		
I <sub>2</sub>	Black solid	Highest	Strongest

- The halogens have seven electrons in their outer shell (s<sup>2</sup>p<sup>5</sup>), so they need to gain one electron to obtain a stable octet, forming ions with a charge of 1-, this is shown by the reduction of chlorine:
 
$$\text{Cl}_2 + 2 e^- \rightarrow 2 \text{Cl}^-$$
- A more reactive halogen will displace the halide ion of a less reactive halogen from solution
  - If a solution of chlorine (Cl<sub>2</sub>) is added to a solution of bromide (Br<sup>-</sup>), the chlorine will displace the bromine



Halogen	Colour in Water
Chlorine	Pale green
Bromine	Orange
Iodine	Brown

- Precipitation reactions with aqueous silver ions are used to test for halide ions. Silver halides are formed when AgNO<sub>3</sub> (aq) is added to a halide solution:



Silver Halide	Colour of Precipitate	Addition of Dilute Ammonia	Addition of Concentrated Ammonia
AgCl	White	Dissolves to give a colourless solution	Dissolves to give a colourless solution
AgBr	Cream	Does not dissolve	Dissolves to give a colourless solution
AgI	Yellow	Does not dissolve	Does not dissolve

### Use of Chlorine and Chlorate

- Chlorine can dissolve in water to form hydrochloric acid and chloric(I) acid in a disproportionation reaction (chlorine is both oxidised and reduced).
 
$$\text{Cl}_2 (g) + \text{H}_2\text{O} (l) \rightarrow \text{HCl} (aq) + \text{HClO} (aq)$$

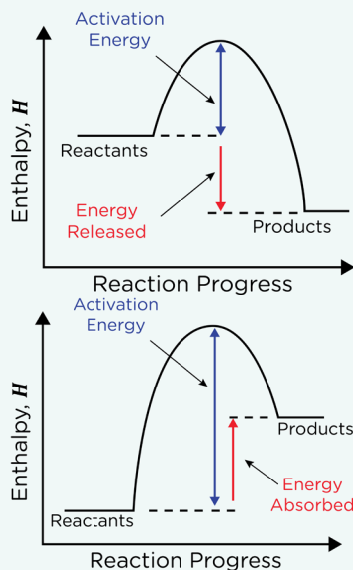
0
-1
+1
- Chloric(I) acid is an oxidising agent that kills bacteria and sanitises water
- Cl<sub>2</sub> (g) + 2NaOH (aq) → NaCl (aq) + NaClO (aq) + H<sub>2</sub>O (l)
- Sodium chlorate(I) has a bleaching action which allows it to be an active ingredient in household bleach.
- The advantages of using chlorine to treat water is that it prevents the spread of waterborne disease and sanitises water. However, it is added without direct customer consent, chlorine is a respiratory irritant and it could react to form chlorinated hydrocarbons, implicated in cancers.

## Enthalpy

- Enthalpy,  $H$ , is the thermal energy that is stored in a system
- Enthalpy change is the heat energy change measured under conditions of constant pressure.
- Enthalpy change values are usually given under standard conditions (100 kPa, 298K, 1 mol dm<sup>-3</sup> & the standard state of the substance). Standard enthalpy changes are denoted by  $\Delta H^\theta$ .
- Enthalpy change,  $\Delta H = \sum H_{\text{Products}} - \sum H_{\text{Reactants}}$**   
 $\sum H_{\text{Products}}$  total enthalpy of products (kJ mol<sup>-1</sup>)  
 $\sum H_{\text{Reactants}}$  total enthalpy of reactants (kJ mol<sup>-1</sup>)
- The standard enthalpy change of reaction ( $\Delta H_r^\theta$ ) is the enthalpy change that accompanies a reaction in molar quantities shown in a chemical equation under standard conditions
- The standard enthalpy of formation ( $\Delta_f H^\theta$ ) is the enthalpy change when one mole of a substance is formed from its constituent elements, with all reactants and products being in their standard states and under standard conditions
- The standard enthalpy of combustion ( $\Delta_c H^\theta$ ) is the enthalpy change when one mole of a substance is completely burnt in oxygen, with all reactants and products being in their standard states and under standard conditions
- The standard enthalpy change of neutralisation ( $\Delta_{\text{neut}} H^\theta$ ) is the energy change that accompanies the reaction of an acid by a base to form one mole of H<sub>2</sub>O (l) under standard conditions

## Exothermic & Endothermic Reactions

- Exothermic reactions increase the temperature of the surroundings.  $\Delta H$  is negative
- Endothermic reactions decrease the temperature of the surroundings  $\Delta H$  is positive.
- Activation energy is the minimum energy required for a reaction to occur



## Coffee Cup Calorimetry

- A coffee cup calorimeter can be used to calculate enthalpy changes of neutralisation
  - The reaction mixture is placed in a Styrofoam cup with a lid to keep it insulated, along with a stirrer and a thermometer. The Styrofoam cup can be held within another Styrofoam cup in a beaker for maximum insulation
  - A measured volume of the first reactant is added, and the temperature is recorded until stable. A measured amount of the second reactant is added, and the temperature is measured every minute whilst constantly stirring
  - A graph of temperature against time is plotted, with a line of best fit
  - $q$  can be calculated using  $\Delta T$  and converting the volumes of the solutions into masses using their densities (assumed to be 1 g cm<sup>-3</sup>)

## Bond Enthalpies

- Average bond enthalpy is the energy required to break one mole of a specified type of bond in a gaseous molecule
- The strength of a covalent bond varies according to the environment in which they are found, so an average value is taken
- The actual bond enthalpy is specific to each individual molecule
- Bond breaking is endothermic, while bond making is exothermic
- Enthalpy change can be predicted using bond enthalpies  

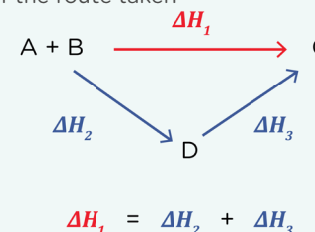
$$\Delta H = \sum (\text{bond enthalpy of reactants}) - \sum (\text{bond enthalpy of products})$$
- The enthalpy change values calculated from bond enthalpies are approximate and not as accurate as those calculated from Hess' Law cycles

## Spirit Burner Calorimetry

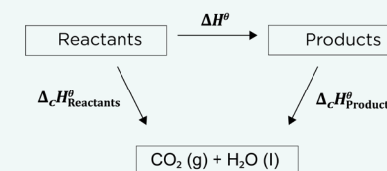
- A spirit burner calorimeter can be used to calculate enthalpy changes of combustion
  - The substance being heated or cooled, usually water, is placed in a beaker with a thermometer. A spirit burner is placed underneath the beaker to heat it
  - The spirit burner containing the fuel is weighed and a known volume of water is added to the beaker and its initial temperature measured
  - The spirit burner is burnt, and the water continuously stirred
  - After a few minutes, the flame is extinguished, and the spirit burner is reweighed. The final temperature of the water is measured
  - The measured values are used to calculate  $q$

## Hess's Law

- Hess's law is that the enthalpy change of a reaction is independent of the route taken

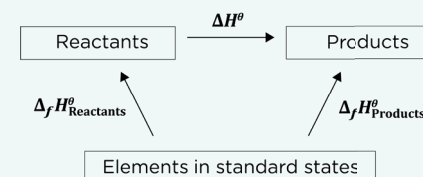


- Enthalpy changes of combustion can be used to find the enthalpy change of a reaction



$$\Delta_r H^\theta = \Delta_c H_{\text{Reactants}}^\theta - \Delta_c H_{\text{Products}}^\theta$$

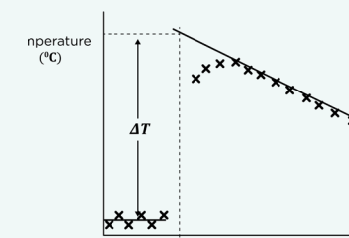
- Enthalpy changes of formation can be used to find the enthalpy change of a reaction
- The enthalpy of formation for an element is 0 kJ mol<sup>-1</sup>.



$$\Delta_r H^\theta = -\Delta_f H_{\text{Reactants}}^\theta + \Delta_f H_{\text{Products}}^\theta$$

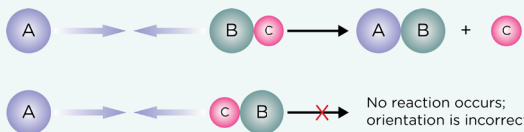
## Calorimetry

- Calorimetry is the process of measuring the amount of heat given off or taken in during a chemical reaction
- $q = mc\Delta T$   
 $q$  is the heat change (J)  
 $m$  is the mass of the substance (g)  
 $c$  is the specific heat capacity (J g<sup>-1</sup> K<sup>-1</sup>)  
 $\Delta T$  is the temperature change (K or °C)



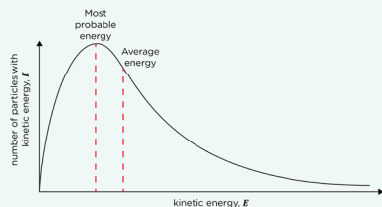
### Collision Theory

- Particles in a gas or liquid are constantly moving and colliding with each other. However, not all collisions result in a reaction.
- For a reaction to occur, two particles must collide with:
  - Sufficient energy to overcome the activation energy
  - The correct orientation



### Maxwell-Boltzmann Distribution

- The Maxwell-Boltzmann curve shows the distribution of molecular kinetic energies in a gas at a constant temperature
- In the Boltzmann distribution:
  - The area under the curve is equal to the total number of molecules in the system
  - The curve starts at the origin — no molecules have zero energy
  - Only molecules with an energy greater than the activation energy,  $E_a$ , can react
  - The curve's peak represents the most probable energy that a molecule will have
  - The average energy is to the right of, and slightly greater than, the most probable energy

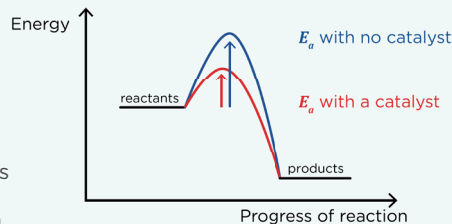


### Catalysts

- A catalyst is a substance that increases the rate of a chemical reaction without being used up in the process.
- Catalysts work by reacting with the reactants to form an intermediate. Catalysts are then regenerated later in the reaction
- Homogeneous catalysts are in the same phase as the reactants
- Heterogeneous catalysts are in a different phase to the reactants
- Heterogeneous catalysts work by:
  - Adsorption — the reactants forming weak bonds with the atoms on the surface of the catalyst, holding the reactants in the correct position for them to react.
  - Desorption — the products detach from the atoms on the surface of the catalyst
  - As the products detach more reactants can be adsorbed, and the process is repeated
- The use of catalysts has economic, environmental and social benefits
  - The demand for fossil fuels is lowered
  - Emission of pollutants are lowered
  - Reduced energy use means lower costs

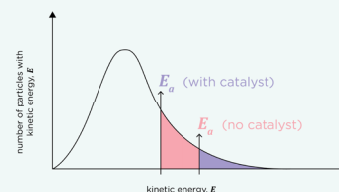
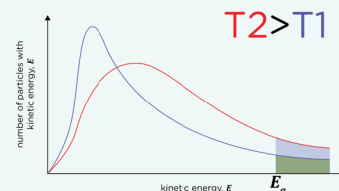
### Rate of Reaction

- The rate of reaction is the change in the concentration of a reactant or product in a given time.
- **Rate =  $\frac{\text{change in concentration}}{\text{time}}$**
- Factors affecting the rate of reaction:
  - Temperature- increasing the temperature increases the kinetic energy of the molecules, leading to more frequent successful collisions and an increase in the rate of reaction
  - Pressure — increasing the pressure of a gaseous reaction increases the number of gaseous molecules in a given volume, so molecules are closer together. This leads to more frequent successful collisions and an increase in the rate of reaction
  - Concentration — increasing the concentration of an aqueous reactant increases the number of molecules in a given volume, so molecules are closer together. This leads to more frequent successful collisions and an increase in the rate of reaction
  - Catalysts — adding a catalyst provides an alternative pathway that has a lower activation energy, leading to more frequent successful collisions and an increase in the rate of reaction



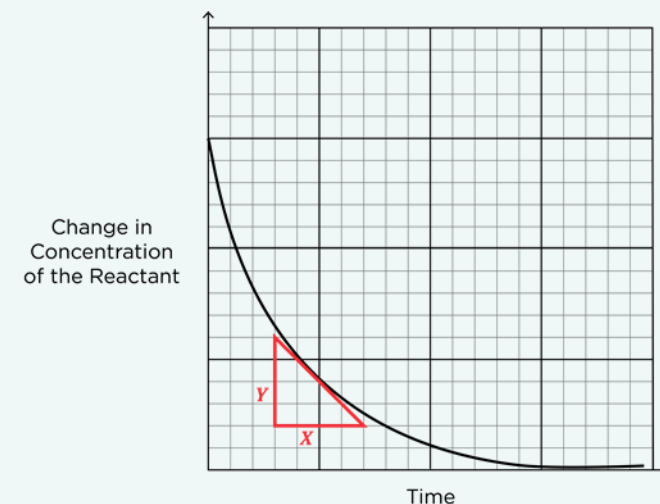
### The Effect of Temperature and Catalysts on The Maxwell-Boltzmann Distribution

- At higher temperatures, the kinetic energy of the molecules increases, so the molecules move faster
- A greater proportion of molecules have an energy greater than the activation energy, so more frequent successful collisions occur, increasing the rate of reaction.
- The area under the curve remains the same as the number of molecules in the system
- Catalysts lower the activation energy of a reaction by providing an alternative reaction route with a lower activation energy
- A greater proportion of molecules have an energy greater than the new, lower activation energy, and more frequent successful collisions occur, increasing the rate of reaction.
- The addition of the catalyst does not change the distribution of the molecular energies.



### Calculating the Rate of Reaction

- The rate of a reaction can be calculated by recording the amount of a reactant or a product at regular time intervals during a single reaction (continuous monitoring) or by determining the initial rate of several reactions and finding an average.
- There are several methods of continuous monitoring
  - Monitoring by gas collection - use a syringe to measure the volume of gas evolved
  - Mass loss - set up the system on a balance so the decrease in mass of reactants can be measured
  - Colorimetry - concentration change is monitored by measuring the amount of light absorbed by a sample
- A graph can be plotted using the variable measured against time:
  - $y/x = \text{concentration change/time} = \text{rate}$



### Chemical Equilibrium

- Reversible reactions at equilibrium are denoted by the equilibrium symbol:  $\rightleftharpoons$
- Many chemical reactions are reversible
- A chemical system is in dynamic equilibrium when all three of the following conditions are met:
  - The concentration of reactants and products is constant
  - The rate of the forwards reaction is the same as the rate of the backwards reaction
  - The reaction is in a closed system
- Le Chatelier's principle- when a system in dynamic equilibrium is subjected to change, the position of the equilibrium will shift to oppose the change
- If the conditions of a reaction are changed, the position of equilibrium will shift to favour either the forwards or backwards reaction to oppose the change.
- The effect of a change in temperature on the position of equilibrium will depend on the enthalpy change of the reaction. If the forward reaction is exothermic and the backwards reaction is endothermic:
  - Increasing the temperature will cause the position of equilibrium to shift in the endothermic direction to absorb the added heat
  - Decreasing the temperature will cause the position of equilibrium to shift in the exothermic direction to add more heat
- Changing the concentration of a reactant or product will cause the position of equilibrium to shift to oppose this change
  - Increasing the concentration of the reactants will cause the position of equilibrium to shift to make more of the product
  - Increasing the concentration of the products will cause the position of equilibrium to shift to remove the extra product, making more reactants
- Changing the pressure of a system will only change the position of the equilibrium if the reaction involves gases.
  - Increasing the pressure of the system will cause the position of equilibrium to shift to the side with the fewest moles of gas
  - Decreasing the pressure of the system will cause the position of equilibrium to shift to the side with more moles of gas
- Adding a catalyst does not change the position of equilibrium, but increases the rate at which the equilibrium is established

### Haber Process

- Nitrogen gas reacts with hydrogen gas to form ammonia in the Haber process
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H = -92 \text{ kJ mol}^{-1}$
- The optimum conditions for the Haber process are:
  - High pressure — increasing the pressure will cause the position of equilibrium to shift to the right, favouring the forwards reaction as there are fewer moles on the right (two moles) than on the left (four moles). Therefore, more ammonia is produced, and the pressure will be reduced, opposing the change
  - Low temperature — the forward reaction is exothermic, so decreasing the temperature will cause the position of equilibrium to shift to the right, favouring the forwards reaction. Therefore, more ammonia is produced and the temperature increases, opposing the change
- These optimum conditions are not favourable because:
  - Maintaining high pressures is expensive and unsafe
  - Low temperature would mean a slow rate of reaction
- In industry, conditions must be used that strike a balance between obtaining a good yield and being economically feasible
- Compromise conditions must be used in industrial processes to ensure a good yield whilst considering the following factors:
  - The rate of reaction
  - Cost and risks of equipment
  - Side reactions
- The industrial conditions used today in the Haber process are a compromise and are:
  - 400–500 °C — allows a reasonable rate of reaction and yield
  - 200 atm — allows a high yield without costing too much or posing a safety risk
  - Iron catalyst increases the rate of reaction and allows equilibrium to be established more quickly at a lower temperature, saving energy and increasing profits

### Partial Pressure

- Mole fractions indicate the fraction of a mixture occupied by a particular gas.  
**Mole fraction,  $X_A = \frac{\text{number of moles of gas A}}{\text{total number of moles of all gases}}$**
- Partial pressure is the pressure each gas in a mixture would exert on its own. The partial pressure of a gas A is denoted by  $p(\text{A})$  or  $P_A$ .
- The total pressure of a gas mixture is the sum of all partial pressures from each gas.
- The amount of pressure a gas exerts in a fixed volume depends on how many particles there are - more particles means greater pressure.
- $p(\text{A}) = \text{mole fraction of gas A} \times \text{total pressure}$**   
 $p(\text{A})$  partial pressure of gas A (kPa)  
mole fraction of gas A (mol)  
total pressure (kPa)

### Equilibrium Constant

- The equilibrium constant,  $K_c$ , indicates where the equilibrium lies - it is the ratio of the concentration of products and reactants in a reversible reaction
- The concentration, in  $\text{mol dm}^{-3}$ , of a species X involved in the expression for  $K_c$  is represented by [X]
- For the general reaction:  $a\text{A} + b\text{B} \rightleftharpoons d\text{D} + e\text{E}$   
$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{D}]^d[\text{E}]^e}{[\text{A}]^a[\text{B}]^b}$$
- The units of the equilibrium constant will vary depending on how many species take part in the reaction and the stoichiometry
- The magnitude of  $K_c$  indicates the extent of the reaction:
  - $K_c = 1$ : equilibrium lies halfway between the reactants and the products
  - $K_c > 1$ : equilibrium lies further to the right and the products are favoured
  - $K_c < 1$ : equilibrium lies further to the left and the reactants are favoured

### Equilibrium Constant, $K_p$

- $K_p$  is an equilibrium constant associated with equilibrium reactions, only involving gases. It is written in terms of partial pressures rather than concentrations.
- For the equilibrium reaction:  
 $a\text{A}(\text{g}) + b\text{B}(\text{g}) \rightleftharpoons c\text{C}(\text{g}) + d\text{D}(\text{g})$   
$$K_p = \frac{p(\text{C})^c p(\text{D})^d}{p(\text{A})^a p(\text{B})^b}$$
- The units of  $K_p$  are variable and depend on the specific reaction that is under consideration
- Temperature can affect the position of equilibrium
  - Increasing the temperature will cause the position of equilibrium to shift in the endothermic direction. Increasing  $K_p$
  - Decreasing the temperature will cause the position of equilibrium to shift in the exothermic direction. Decreasing  $K_p$
- Pressure can affect the position of equilibrium
  - Increasing the pressure will shift the position of equilibrium to the side with less moles of gas
  - Decreasing the pressure will shift the position of equilibrium to the side with more moles of gas
- Changing pressure will not affect the value of  $K_p$ ; instead, the position of equilibrium will shift to keep  $K_p$  constant.
- Catalysts do not affect the value of  $K_p$ . Instead, it affects how quickly equilibrium is reached.

### Formulae

- General formula — the simplest algebraic formula for a homologous series
- Structural formula gives the minimum detail on the arrangement of atoms in a molecule, without drawing any bonds
- Molecular formula shows the number and types of atoms of each element in a compound. However, it does not give any information on how the molecule is bonded together.
- Skeletal formula is a simplified formula used to represent organic molecules. Lines represent bonds between atoms, junctions are carbon atoms. Other labels are omitted.
- Displayed formula shows the relative positioning of atoms and the bonds between them. All atoms and bonds are shown
- Empirical formula the simplest whole-number ratio of each element present in a compound.

### Isomerism

- Isomers are compounds with the same molecular formula but a different arrangement of atoms
- Structural isomers are compounds with the same molecular formula but a different structural formula. They may contain the same functional group but on a different carbon atom, or different functional groups e.g. ketones and aldehydes with the same number of carbon atoms have the same molecular formula

### Nomenclature

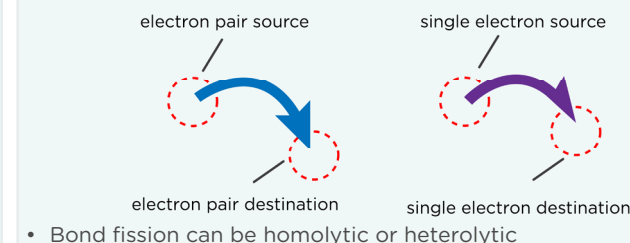
- Hydrocarbons can be:
 

Carbon Atoms in alkyl group	Prefix
1	Methyl
2	Ethyl
3	Propyl
4	Butyl
5	Pentyl
6	Hexyl

  - Aliphatic — carbon atoms form straight or branched chains
  - Alicyclic — carbon atoms form a ring
  - Aromatic — carbon atoms form a ring and have a delocalised electron system
  - Saturated — containing only single bonds
- Homologous series are compounds with the same functional group and similar chemical and physical properties. They differ by the number of repeating units they contain
- A functional group is the group of atoms responsible for the characteristic reactions of a compound.
- To name a compound:
  - The stem is the main part of the name derived from the longest carbon chain.
  - The suffix after the stem, comes from the most significant functional group
  - The prefix before the stem comes from functional groups attached to the main carbon chain
  - Numbers and hyphens indicating the position of functional groups on the carbon chain
  - Functional groups are prioritised alphabetically

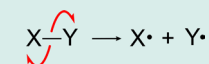
Compound	Functional Group	Prefix	Suffix
Alkanes	$\begin{array}{c}   \\ -C-C- \\   \end{array}$	-	-ane
Alkenes	$\begin{array}{c}   \quad   \\ C=C \\   \quad   \end{array}$	-	-ene
Alcohols	$-O-H$	Hydroxy-	-ol
Carboxylic Acids	$\begin{array}{c} O \\    \\ -C \\   \\ O-H \end{array}$	-	-oic acid
Haloalkanes	$\begin{array}{c} -F \\ -Cl \\ -Br \\ -I \end{array}$	Fluoro- Chloro- Bromo- Iodo-	-
Aldehydes	$\begin{array}{c} O \\    \\ -C \\   \\ H \end{array}$	-	-al
Ketones	$\begin{array}{c} O \\    \\ R-C-R' \end{array}$	-	-one

### Reaction Mechanisms



#### Homolytic Fission

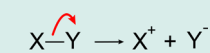
When the bond breaks, each electron in the bond goes to a different atom.



This results in the formation of highly reactive free radicals, each with an unpaired electron, represented by a dot.

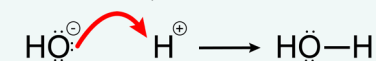
#### Heterolytic Fission

When the bond breaks, both the electrons in the bond go to the same atom.

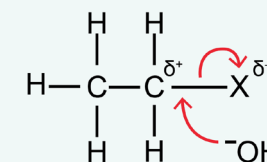


This results in the formation of a positively charged cation and a negatively charged anion.

- Bonds are formed on the collision of:
  - Two free radicals with unpaired electrons



- Oppositely charged ions
- Bonds can also be formed when ions are attracted to dipoles, e.g. nucleophilic substitution reactions

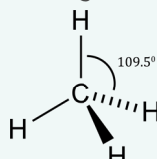


# ALKANES & ALKENES

## CHEAT SHEET

### Alkanes

- Alkanes are a homologous series made up of saturated hydrocarbons, containing only carbon and hydrogen atoms joined by sigma bonds
- Carbon atoms have four electrons in their outer shell. Therefore, each carbon atom can form four covalent bonds, resulting in tetrahedral geometry
- Alkanes are not polar and only weak London forces of attraction occur, as carbon and hydrogen have similar electronegativities.
- Boiling point of alkanes increases with chain length, as there is a greater surface area and number of electrons for stronger London forces.
- Shorter carbon chain alkanes and more branched alkanes have a smaller the surface area for contact between molecules and weaker London forces, resulting in lower boiling points
- C-C and C-H  $\sigma$  bonds are strong and non-polar therefore alkanes are not reactive. The electronegativities of C and H are so similar that the C-H bonds are considered non-polar



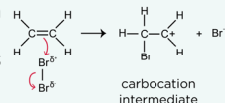
### Combustion of Alkanes

- Alkanes can be used as a fuel source
- In complete combustion, the alkane burns with a clean blue flame. Water vapour and carbon dioxide are formed (greenhouse gases). E.g.
 
$$\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$$
- In incomplete combustion, the alkane burns with a dirty yellow flame. It can produce carbon, carbon monoxide and unburned hydrocarbons as products.
 
$$\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$$

$$\text{CH}_4(\text{g}) + 1.5\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$$

### Chlorination of Alkanes

- Alkanes react with the halogens, specifically chlorine and bromine, in the presence of UV light to form haloalkanes
- Methane reacts with chlorine to form chloromethane and hydrogen chloride:  $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$
- This reaction is a free radical substitution with the steps:
  - Initiation – free radicals are formed when exposed to UV  $\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$
  - Propagation – free radicals are used up and created in a chain reaction  $\text{Cl}\cdot + \text{CH}_4 \rightarrow \cdot\text{CH}_3 + \text{HCl}$   
 $\cdot\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$
  - Termination – free radicals are removed.  
 $2\text{Cl}\cdot \rightarrow \text{Cl}_2$   
 $2\cdot\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$   
 $\cdot\text{CH}_3 + \text{Cl}\cdot \rightarrow \text{CH}_3\text{Cl}$
- Radical substitution reactions have limitations:
  - Further substitution could occur if another chloride radical collides with the product of propagation
  - If the carbon chain is longer, a mixture of products forms as substitution occurs at different positions along the chain

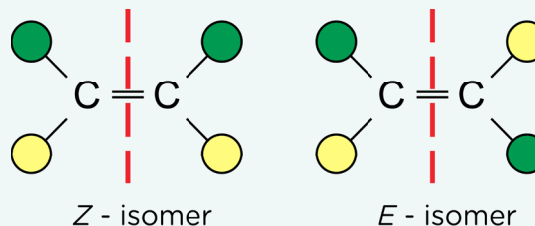


### Alkenes

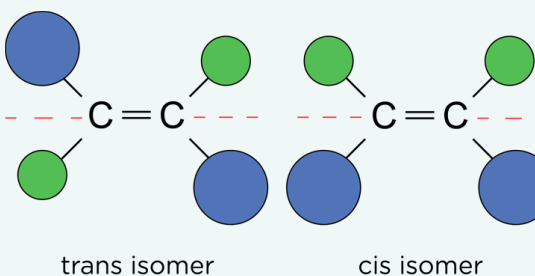
- Alkenes are a homologous series made up of unsaturated hydrocarbons containing at least one C=C double bond, with the general formula  $\text{C}_n\text{H}_{2n}$ .
- C-H – these are  $\sigma$ -bonds formed due to the direct overlap of the electron clouds belonging to each carbon atom
- C=C – these contain both a  $\sigma$ -bond and two  $\pi$ -bonds. It is an area of high electron density, so can react with electrophiles.
- $\pi$ -bonds – formed due to the overlap of adjacent p-orbitals above and below the carbon atoms. It restricts the rotation around the planar C=C double bond, leading to stereoisomerism in some alkenes
- Due to electron pair repulsion, alkenes have a trigonal planar shape with a bond angle of  $120^\circ$ .

### Stereoisomerism

- Stereoisomers are organic compounds with the same molecular and structural formulae but a different arrangement of atoms in space
- E/Z* isomerism is a type of stereoisomerism that can arise in alkenes due to the restricted rotation around the C=C bond
- If a carbon atom has two of the same substituent attached, it will not show *E/Z* isomerism
- Substituents can be assigned priorities based on atomic mass using Cahn-Ingold-Prelog rules to name *E/Z* isomers. The greater the atomic mass, the higher the priority
- When the highest priority groups are on different sides of the double bond, the isomer is an *E*-isomer.
- When the highest priority groups are on the same side of the double bond, the isomer is a *Z*-isomer

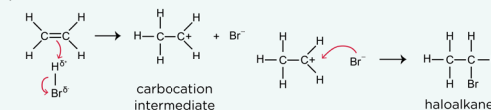


- Cis-trans* isomerism is a type of *E/Z* isomerism. It arises when the carbon atoms at each end of the double bond are attached to two different groups, but at least one of the groups attached to one carbon are identical to a group on the other carbon

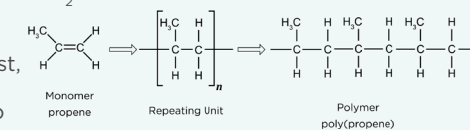
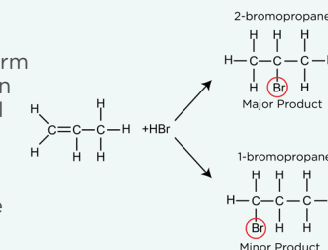


### Addition Reactions of Alkenes

- An electrophile is an electron pair acceptor attracted to areas of high electron density
- Electrophilic addition with HBr

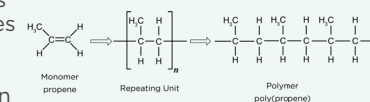


- Major and minor products form when an unsymmetrical alkene reacts. The major product will form from the most stable carbocation intermediate, with the most alkyl groups attached. Tertiary > secondary > primary carbocations. This reduces the positive charge, due to inductive electron donation.
- Electrophilic addition with  $\text{Br}_2$ . A dipole is induced in the halogen molecule by the high electron density of the C=C
- Bromine water acts as a test for unsaturation. An unsaturated compound will decolourise the bromine water, as a dihaloalkane will form, using up the bromine
- At  $150^\circ$  in the presence of a catalyst (Ni), alkenes undergo addition reactions with  $\text{H}_2$  to form alkanes
- At high pressure in the presence of a sulfuric acid catalyst, gaseous alkenes react with steam to form alcohols
- As with addition with HBr, a major and minor product forms



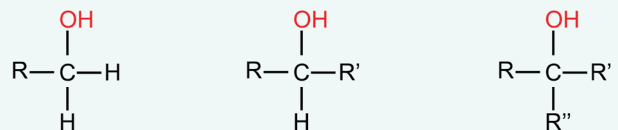
### Addition Polymers

- Addition polymers are macromolecules made from small repeating units of monomers
- They are formed from alkenes and substituted alkenes
- Addition polymers are unreactive as the main carbon chain is saturated and non-polar, with only weak London forces between the chains
- Polyalkanes are non-biodegradable therefore pose a risk to the environment. They can be disposed of by:
  - Recycling – reduces the pressure on landfill and means that fossil fuels can be conserved. The polymers can be used by manufacturers to make new products. However, PVC must be processed carefully to prevent toxic HCl (g) escaping
  - Fuels – Polymers contain lots of stored energy in their bonds, therefore they can be incinerated to produce heat which helps generate electricity
  - Feedstock Recycling – the monomers of a waste polymer are collected and reused in synthesis



### Properties of Alcohols

- Alcohols are a homologous series of saturated organic compounds with -OH groups attached



Primary alcohol

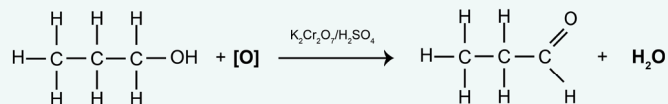
Secondary alcohol

Tertiary alcohol

- Alcohols can form hydrogen bonds in polar solvents, e.g. water, making them soluble. As chain length increases, solubility decreases
- Longer alkyl chains have a greater surface area for contact and a greater number of electrons, allowing stronger London forces of attraction. Therefore, as chain length increases, boiling point increases, and volatility decreases

### Oxidation of Alcohols

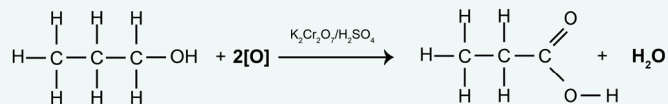
- Primary alcohols can be oxidised to aldehydes. Conditions: gentle heating. Oxidising agent and immediate distillation



Propan-1-ol

Propanal

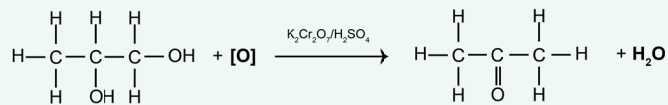
- Primary alcohols can be further oxidised to carboxylic acids. Conditions: heat under reflux, no distillation, oxidising agent.



Propan-1-ol

Propanoic Acid

- Secondary alcohols can be oxidised to ketones. Conditions: heat under reflux and oxidising agent.



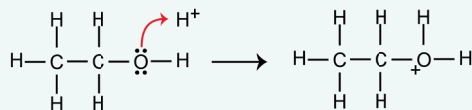
Propan-1-ol

Propanone

- Tertiary alcohols cannot be oxidised as they do not have an H atom on the carbon bonded to the -OH group
- Acidified potassium dichromate(VI) is a suitable oxidising agent

### Reactions of Alcohols

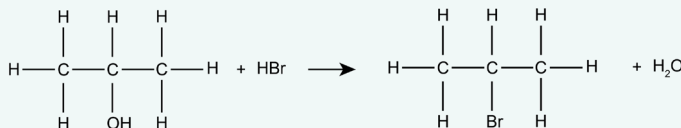
- Alcohols can be **combusted** as a fuel source, forming carbon dioxide and water e.g.  $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
- Alcohols can be **dehydrated** to form an alkene and water, using a concentrated phosphoric acid catalyst and heating under reflux e.g.



Ethanol

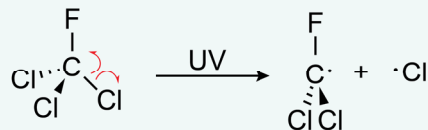
- The alkenes produced can be used to form addition polymers without using monomers derived from crude oil.
- Alcohols undergo substitution by reacting with hydrogen halides. The hydrogen halides are formed by reacting a sodium halide with sulfuric acid:  
 $\text{NaX} (\text{s}) + \text{H}_2\text{SO}_4 (\text{aq}) \rightarrow \text{NaHSO}_4 (\text{aq}) + \text{HX} (\text{aq})$

- The hydroxyl group on an alcohol is replaced with a halogen

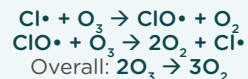


### Ozone Depletion

- In the Earth's atmosphere, there is a layer of ozone ( $\text{O}_3$ ) which protects us from the harmful UV radiation produced by the sun
- Chlorofluorocarbons (CFCs) are a type of organic compound that contain chlorine and fluorine atoms. They can diffuse through layers of the atmosphere where they are exposed to UV radiation, which causes homolytic fission, forming radicals



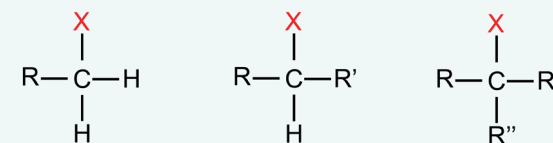
- The chlorine radicals produced catalyse the decomposition of ozone



- The chlorine radicals are regenerated and act as a catalyst in the breakdown of ozone molecules into oxygen
- Holes in the ozone layer increase the likelihood of skin cancers and sunburns
- OCR

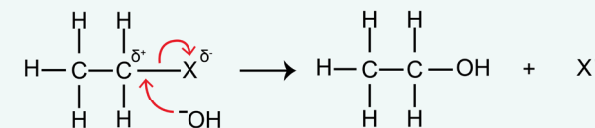
### Haloalkanes

- Haloalkanes are saturated organic compounds that contain at least one halogen atom, e.g. F, Cl, Br, or I.



Primary haloalkane    Secondary haloalkane    Tertiary haloalkane

- The C-X bond has a permanent dipole due to the large difference in electronegativity between the carbon and halogen atoms. With the electrons closer to the halogen atom.
- The  $\delta^-$  on the carbon atom makes it easily attacked by electron-rich nucleophiles (an electron pair donor that is attracted to electron deficient regions).
- Nucleophilic substitution occurs with hydroxide ions, resulting in hydrolysis of the haloalkane:

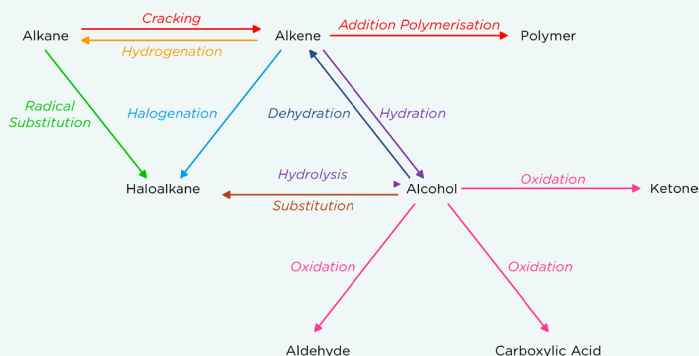


Haloalkane

Alcohol

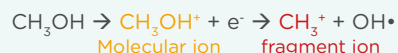
- The  $\text{OH}^-$  ions can be generated by using an aqueous metal hydroxide solution (e.g. KOH) or by using water in the presence of  $\text{AgNO}_3$  and ethanol
- Going down Group 7, the electronegativity of the halogen atoms decreases, so the polarity of the C-X bond also decreases. We would expect fluoroalkanes to be the most reactive, however iodoalkanes are the most reactive because bond enthalpy decreases down the group. C-I bond is the longest and weakest

## Synthetic Routes



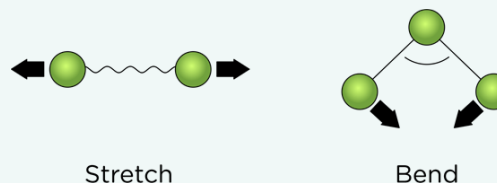
## Mass Spectrometry

- A molecular ion (M<sup>+</sup>) is formed when molecules in a sample are ionised.
- The molecular ion peak (the peak with the highest m/z ratio in the mass spectrum) can be used to determine the relative molecular mass
- Molecular ions are able to break up into fragments during ionisation. This creates a fragmentation pattern on the mass spectrum. Different compounds will produce different fragment peaks



## Infrared Spectrometry

- A pair of atoms joined by a chemical bond constantly vibrate. Heavy atoms will cause the bond to vibrate more slowly, and stronger bonds will vibrate more quickly.
- The absorption of infra-red radiation increases the vibrational energy of a bond, by either bending or stretching



- Particular bonds, and therefore functional groups, can be identified by looking at the frequencies absorbed in a infrared spectrum.
- An infra-red spectrum is produced by a spectrometer:
  - A beam of IR radiation in the range 200 - 4000 cm<sup>-1</sup> passes through a sample
  - The molecule absorbs some of the frequencies, and the emerging beam is analysed to identify the frequencies that have been absorbed
  - A computer plots a graph of transmittance against wavenumber
- Each peak in the spectrum represents the absorption by a specific bond vibration in the molecule
- The bonds present in greenhouse gases (carbon dioxide, methane & water) can absorb infrared radiation that is reflected by the Earth's surface, contributing to global warming.

## Combined Techniques

- The wide variety of analytical techniques that we have come across can be used to provide data and information to help us determine the structure of unknown compounds.
- The molecular formula of a compound can be determined using the empirical formula and relative molecular mass of the molecule.  
e.g. Determine the molecular formula of a compound with empirical formula CH<sub>2</sub> and a relative molecular mass of 224.  
Relative molecular mass of the empirical formula:

$$12 + (1 \times 2) = 14$$

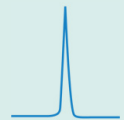
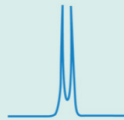
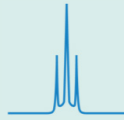
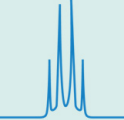
Divide the relative molecular mass by that of the empirical formula:

$$224/14=16$$

Molecular formula:  
16 × CH<sub>2</sub> = C<sub>16</sub>H<sub>32</sub>

## Nuclear Magnetic Resonance (NMR) Spectroscopy

- NMR gives information about the position of <sup>13</sup>C or <sup>1</sup>H atoms in a molecule
- Nuclei in different chemical environments in the sample molecule will resonate at different frequencies, allowing an NMR spectrum to be produced and interpreted.
- Tetramethylsilane (TMS) is used as a standard to measure an NMR spectrum peak against. The 4 methyl groups are in the same chemical environment and produce an intense signal
- A chemical shift is the scale used in NMR spectroscopy. It depends on the molecular environment, hence functional groups have different shifts.
- The number of peaks in <sup>13</sup>C NMR represents the number of carbon environments in a molecule
- Each peak in a <sup>1</sup>H NMR spectrum has an integration trace. This shows the relative number of <sup>1</sup>H in each <sup>1</sup>H environment
- High resolution <sup>1</sup>H also shows spin-spin coupling. This is useful because spin-spin coupling causes splitting patterns which give information about neighbouring hydrogen atoms. The splitting patterns are determined by the N+1 rule
- The N+1 Rule- If there are n hydrogen atoms attached to carbon atoms adjacent to a <sup>1</sup>H environment, then the peak representing that environment will be split into n+1 peaks

Number of Adjacent H	Number of Peaks	Name	Diagram
0	1	Singlet	
1	2	Doublet	
2	3	Triplet	
3	4	Quartet	

- Common solvent used in NMR is CDCl<sub>3</sub>, ie deuterated solvents.
- In deute rated solvents, any H atoms are replaced with deuterium. They do not affect the spectra



### Rate Equations

- The rates of chemical reactions are dependent on the concentrations of the species involved in the reactions.
- The rate equation is an expression which describes the dependence of the reaction rate on the concentrations of the species involved in the reaction.  
For the reaction:  $A \rightarrow \text{Products}$   
**Rate =  $k[A]^x$**   
For the reaction:  
 $A + B \rightarrow \text{Products}$   
**Rate =  $k[A]^m[B]^n$**
- $k$  rate constant
- $m$  and  $n$  orders of reaction with respect to reactants A and B
- The rate equation is experimentally determined- it cannot be determined from chemical equations.
- The order of reaction with respect to a species tells us how the concentration of the species affects the rate
  - If the order of reaction is 0, a double in concentration of the species does not affect the rate **rate =  $k[A]^0 = k$**
  - If the order of reaction is 1 a double in concentration of the species, doubles the rate **rate =  $k[A]^1 = k[A]$**
  - If the order of reaction is 2 a double in concentration of the species, quadruples the rate **rate =  $k[A]^2$**
- The sum of the orders of all the reactants will give the overall order of the reaction
- The order of reaction depends on the mechanism of a reaction and must be found experimentally
- The units of rate constants are variable — they depend on the orders of the reactants involved. Rate constants can only be compared if they have the same units.



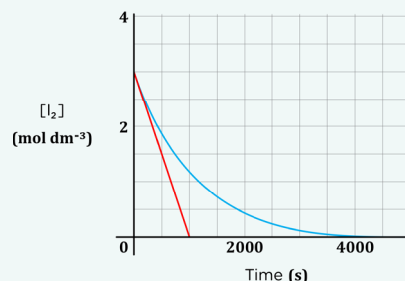
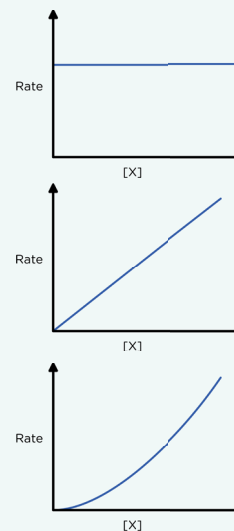
### Monitoring the Rate of a Reaction

- The rate of a reaction can be calculated by recording the amount of a reactant or a product at regular time intervals during a single reaction (continuous monitoring) or by determining the initial rate of several reactions and finding an average.
- There are several methods of continuous monitoring
  - Monitoring by gas collection - use a syringe to measure the volume of gas evolved
  - Mass loss - set up the system on a balance so the decrease in mass of reactants can be measured
  - Colorimetry - concentration change is monitored by measuring the amount of light absorbed by a sample
- Clock reactions allow determination of the rate of reaction for a specific concentration
- The time taken for a certain amount of product to form is measured for a specific concentration of one of the reactants via an easily observable endpoint, which may be:
  - A colour change, e.g. iodine clock reaction causes an orange to dark-blue colour change
  - A precipitate formation from a clear solution
- The time taken for precipitate formation can be monitored or the time taken for a distinct colour change to occur

$$\text{Rate} \propto \frac{1}{\text{time}}$$

### Determination of Rate Equations

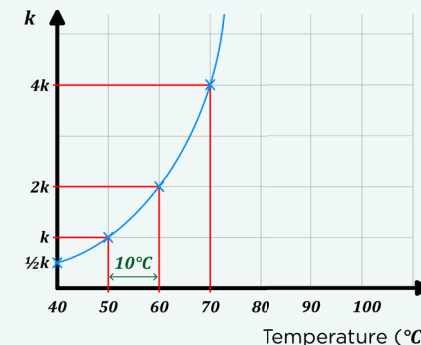
- Rate-concentration graphs allow us to easily see how the concentration of a reactant affects the rate of reaction
  - Zero order reactions
  - First order reactions. The gradient is equal to the rate constant.
  - Second order reactions
- A concentration-time graph can be used to calculate the initial rate by drawing a tangent at  $t=0$  and working out the gradient.



- The shape of a concentration-time graph will indicate the order of the reaction with respect to the reactant:
- The rate-determining step is the slowest step in the reaction mechanism of a multistep reaction.
- The slowest step in a reaction will dictate how fast the whole reaction will happen
- For any reactant in the rate equation, the order indicates how many molecules of the reactant are involved in the rate-determining step (RDS), either directly or by forming an intermediate.
- The rate constant can be determined by calculating the half-life of a reaction ( $t_{1/2}$ )
- $t_{1/2}$  is the time taken for the reactant concentration to decrease by half
- $k = \frac{\ln 2}{t_{1/2}}$

### The Effect of Temperature on Rate Constants

- Temperature is a measure of the amount of energy that molecules have on average — the higher the temperature, the more energy molecules have and the more likely they are to collide and react.
- Increasing the temperature increases the rate of reaction and therefore the rate constant increases too



- The Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

- $k$  is the rate constant
- $A$  is the Arrhenius constant
- $E_a$  is the activation energy ( $\text{J mol}^{-1}$ )
- $R$  is the gas constant ( $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ )
- $T$  is temperature (K)

- For the rate constant to increase:
  - The temperature must increase
  - The activation energy must decrease
- The Arrhenius rearrangement can be rearranged by taking the natural log of both sides of the equation:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

- This is in the format of an equation for a straight line. By plotting  $\ln(k)$  against  $1/T$

$$y = mx + c$$

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$

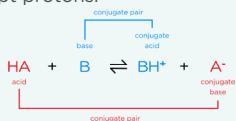
- The activation energy can be calculated by:  
 $E_a = -\text{gradient} \times R$
- The Arrhenius constant can be calculated from the y intercept

$$y\text{-intercept} = \ln A$$

$$e^{\ln A} = A$$

### Brønsted-Lowry Acid and Base

- Brønsted-Lowry Acid is a species that can donate protons.  
 $HA(aq) + H_2O(l) \rightarrow H_3O^+(aq) + A^-(aq)$
- Brønsted-Lowry Base is a species that can accept protons.  
 $B(aq) + H_2O(l) \rightarrow BH^+(aq) + OH^-(aq)$
- Conjugate acid-base pairs are a pair of species that interconvert by the gain or loss of a proton.
- Monobasic Acids — each molecule can release one proton, e.g. HCl  
 $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
- Dibasic Acids — each molecule can release two protons in two steps, e.g.  $H_2SO_4$   
 $H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$   
 $HSO_4^-(aq) \rightarrow H^+(aq) + SO_4^{2-}(aq)$
- Neutralisation reactions:
  - acid + base  $\rightarrow$  salt + water
  - acid + carbonate  $\rightarrow$  salt + carbon dioxide + water
  - acid-metal reactions: acid + metal  $\rightarrow$  salt + hydrogen gas



### Strong and Weak Acids

- A strong acid is an acid which dissociates almost completely in water or aqueous solution.  $HA(aq) \rightleftharpoons A^-(aq) + H^+(aq)$
- A weak acid is an acid which is only partially dissociated in water or aqueous solution.  $HA(aq) \rightleftharpoons A^-(aq) + H^+(aq)$
- The dissociation constant for a weak acid,  $K_a$ , is used to measure the strength of a weak acid:

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

- $[A^-]$  conjugate base concentration (mol dm<sup>-3</sup>)
- $[H^+]$  H<sup>+</sup> ion concentration (mol dm<sup>-3</sup>)
- $[HA]$  acid concentration (mol dm<sup>-3</sup>)

- The greater the strength of the weak acid, the greater its  $K_a$  value.
- The pH of a weak acid can be calculated using the concentration of the acids and  $K_a$ 
  - It is assumed  $[H^+] = [A^-]$

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

- The concentration of HA present is given by the concentration of HA before any dissociation minus the concentration of H<sup>+</sup> ions:

$$K_a = \frac{[H^+]^2}{[HA] - [H^+]}$$

- As the degree of dissociation of the weak acid is very small:

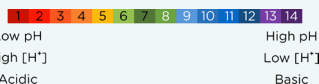
$$[HA] - [H^+] \approx [HA]$$

$$K_a = \frac{[H^+]^2}{[HA]}$$

- $[H^+] = \sqrt{K_a \times [HA]}$  the H<sup>+</sup> ion concentration can be used to find the pH
- A logarithmic scale for pH can be used  $pK_a = -\log_{10} K_a$
- $K_a = 10^{-pK_a}$
- The weaker the weak acid, the smaller the  $K_a$  value, and therefore, the higher the  $pK_a$
- The assumption that  $[H^+] = [A^-]$  fails for high pH conditions, because the dissociation of water is significant, resulting in an increased  $[H^+]$
- The calculations also assume that at equilibrium,  $[HA] \gg [H^+]$ , which may not be true for stronger weak acids

### pH

- The concentration of H<sup>+</sup> ions, often written as  $[H^+]$ , present in a solution determines how acidic it is.
- The pH scale is logarithmic to cover the wide range of hydrogen ion concentrations in aqueous solution
- $pH = -\log_{10}[H^+]$
- The greater the concentration of H<sup>+</sup> ions, the lower the pH value, and the more acidic the solution is
- $[H^+] = 10^{-pH}$
- The pH of a strong acid can be calculated from its concentration:
  - Strong acids fully dissociate:  $HA(aq) \rightarrow A^-(aq) + H^+(aq)$
  - Therefore, the concentration of H<sup>+</sup> ions is equal to the concentration of the acid before dissociation:  $[HA] = [H^+]$
  - This is only the case for monoprotic acids, such as HBr. Diprotic acids, such as  $H_2SO_4$ , will require the concentration of the acid before dissociation to be multiplied by two to get the concentration of H<sup>+</sup> ions.



### Ionic Product of Water

- Species that can act as both an acid and a base are called amphoteric, e.g. water
- Water slightly dissociates into hydroxide and hydroxonium ions.  
 $2H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq)$   
 $H_2O(l) \rightleftharpoons OH^-(aq) + H^+(aq)$
- The equilibrium constant for the dissociation of water is:

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

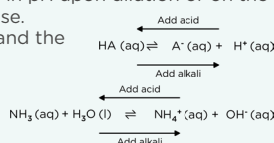
The concentration of H<sub>2</sub>O is constant for a given temperature

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

- Ionic product of water,  $K_w = [OH^-][H^+]$
- $K_w$ , like other equilibrium constants, only changes with temperature.
- $K_w$  can be used to calculate the pH of a strong base from its concentration
  - Strong bases dissociate almost fully, meaning the concentration of OH<sup>-</sup> ions is equal to the concentration of the base before dissociation:  $[base] = [OH^-]$
  - $[H^+] = \frac{K_w}{[OH^-]}$
  - $pH = -\log_{10}[H^+]$

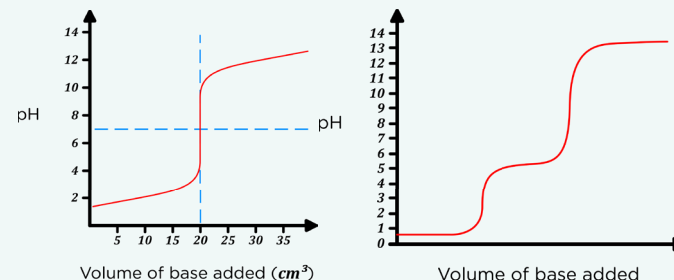
### Buffers

- A buffer is a solution that minimises changes in pH upon dilution or on the addition of a small amount of an acid or a base.
- Acidic buffers are a mixture of a weak acid and the salt of the same weak acid
- Basic buffers are a mixture of a weak acid and a strong alkali
- The pH of a buffer solution can be calculated if the concentration of H<sup>+</sup> ions is known:
  - $[H^+] = K_a \times \frac{[HA]}{[A^-]}$
  - It is assumed the concentration of the acid before dissociation is equal to the concentration of the acid at equilibrium:  $[HA]_{undissociated} = [HA]_{equilibrium}$
  - It is also assumed the salt is ionic so will fully dissociate:  $[Salt] = [A^-]_{equilibrium}$
- The carbonic acid-hydrogencarbonate ion buffer is an important buffer that regulates the pH of blood



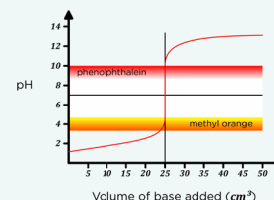
### Titrations

- Acid-base titrations can be used to find the concentration of a sample of either an acid or a base.
- A known concentration of an acid is gradually added to a known volume of a base of unknown concentration until the solution is neutralised
- A pH meter or an indicator can be used to monitor the pH
- The equivalence point is the point at which all of the acid in the known volume has reacted with the base
- Titration curves: a diprotic acid indicates two equivalence points

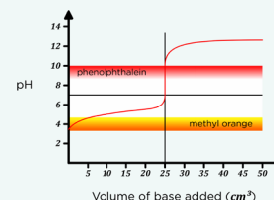


- Indicators are used to visualise the equivalence point more easily
- An acid-base indicator is a weak acid,  $HIn$ , with the equilibrium:  $HIn(aq) \rightleftharpoons In^-(aq) + H^+(aq)$
- The indicator and its conjugate base are different colours in solution. Most indicators change colour over a range of two pH units spread around their end point
- An indicator must have:
  - A sharp colour change
  - An end point close to the equivalence point
  - A clear colour change

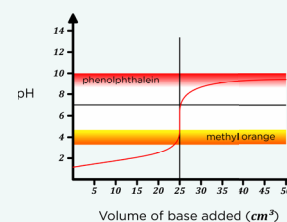
#### Strong Acid-Strong Base:



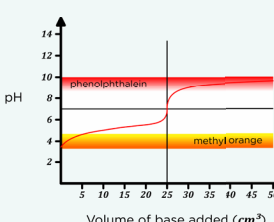
#### Weak Acid-Strong Base:



#### Strong Acid-Weak Base:

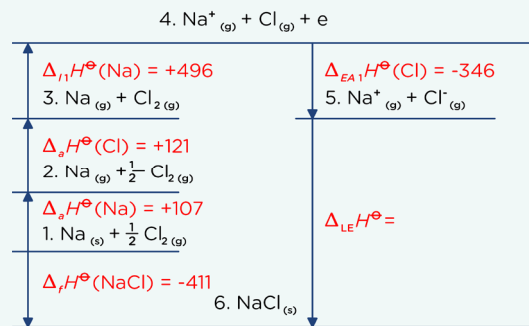


#### Weak Acid-Weak Base:



### Born-Haber Cycles

- Lattice enthalpy cannot be measured directly, so Hess's law is used (the total enthalpy change is independent of the route taken).
- A Born-Haber cycle is used to calculate lattice enthalpy e.g.

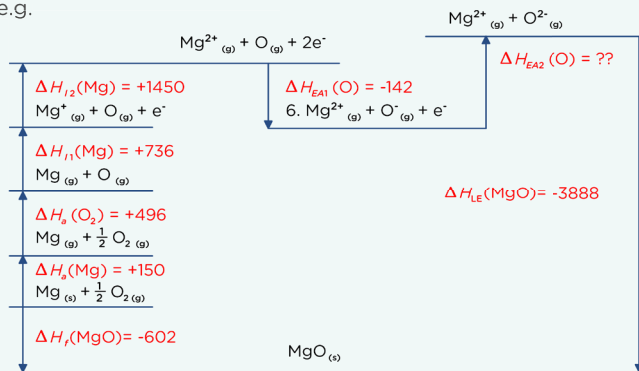


The lattice enthalpy of sodium chloride:

$$\Delta_{LE}H^\ominus = -(-346 \text{ kJ mol}^{-1}) - (+496 \text{ kJ mol}^{-1}) - (+107 \text{ kJ mol}^{-1}) - (+121 \text{ kJ mol}^{-1}) + (-411 \text{ kJ mol}^{-1})$$

$$\Delta_{LE}H^\ominus = -789 \text{ kJ mol}^{-1}$$

- Calculations involving group 2 elements require extra steps compared to sodium chloride:
  - There are two moles of chlorine ions in each mole of  $\text{MgCl}_2$ , so the atomisation enthalpy of chlorine needs to be doubled
  - Group 2 elements form 2+ ions, so the second ionisation energy of sodium must also be included
  - The first electron affinity of chlorine also needs to be doubled as two moles of  $\text{Cl}^-$  ions are being formed
- The Born-Haber cycle can also be used to calculate one of the other enthalpy changes in the same way e.g.



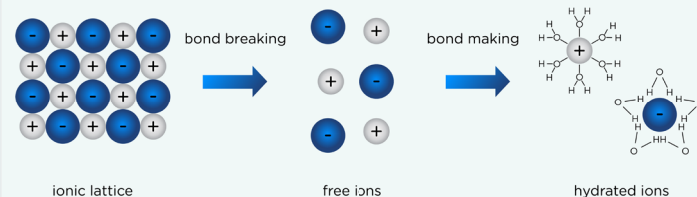
The second electron affinity of oxygen:

$$\Delta_{EA2}H^\ominus = -(-142 \text{ kJ mol}^{-1}) - (+1450 \text{ kJ mol}^{-1}) - (+736 \text{ kJ mol}^{-1}) - \frac{1}{2}(+496 \text{ kJ mol}^{-1}) + (-150 \text{ kJ mol}^{-1}) + (-602 \text{ kJ mol}^{-1}) - (-3888 \text{ kJ mol}^{-1})$$

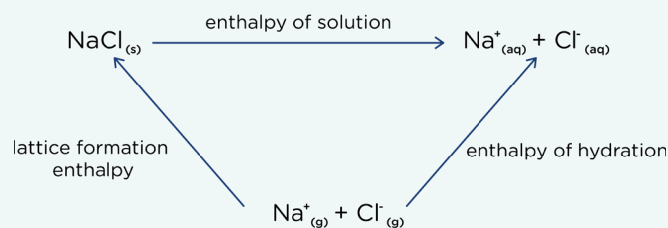
$$\Delta_{EA2}H^\ominus = +844 \text{ kJ mol}^{-1}$$

### Dissolving Ionic Compounds

- Dissolving an ionic compound has two steps
  - The bonds between the ions in the lattice break (endothermic)
  - Bonds between the ions and water is made (hydration - is exothermic)

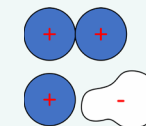


- Standard Enthalpy of Solution,  $\Delta_{sol}H^\ominus$  is the enthalpy change when one mole of solute dissolves completely in sufficient solvent under standard conditions to form a solution in which the molecules or ions are far enough apart not to interact with each other
- The hydration of ions requires the interactions between the solvent and the solute to be of similar strength to the interactions between the positively and negatively charged ions in the lattice for the ions to dissolve
- Ions dissolve well in polar solvents, like water, because of the favourable electrostatic interactions between the oppositely charged ions in the solvent and the ions
- Standard enthalpy of hydration,  $\Delta_{hyd}H$  is the enthalpy change when one mole of aqueous ions is formed from gaseous ions under standard conditions.
- The enthalpy of solution and the enthalpy of hydration provides another path to calculate the lattice enthalpy of dissociation / formation



### Theoretical Lattice Enthalpies

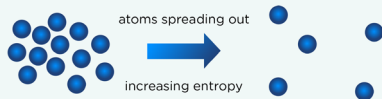
- A perfect ionic model of a lattice assumes that all of the ions are spherical, and have evenly distributed charge around them
- The experimental lattice enthalpy value may differ from the calculated value, giving evidence that some ionic compounds have partially covalent character
- Positive ions normally polarise neighbouring negative ions
- More polarisation = more covalent character
- Small, positively charged ions (like  $\text{H}^+$ ) are more polarising than large positive ions, and large negatively charged ions (like  $\text{I}^-$ ) are more polarisable than small negative ions (like  $\text{F}^-$ )



### Lattice Enthalpy

- Standard lattice enthalpy of formation,  $\Delta_{LE}H^\ominus$  is the enthalpy change when one mole of an ionic lattice is formed from its gaseous ions under standard conditions.
- Lattice enthalpy gives an indication of the strength of the ionic bonds
- Greater ionic charge and smaller ionic radius result in stronger bonding. More energy is stored in stronger bonds therefore lattice enthalpy values are more exothermic
- Lattice enthalpy cannot be measured directly, so other measurements need to be known
- Standard Enthalpy of Formation,  $\Delta_fH^\ominus$  is the enthalpy change when one mole of a compound is formed from its constituent elements in their standard states, under standard conditions
- Standard Enthalpy of Atomisation,  $\Delta_aH^\ominus$  is the enthalpy change when one mole of gaseous atoms are formed from an element in its standard state.
- First ionisation energy,  $\Delta_{I1}H^\ominus$  is the energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of gaseous  $1^+$  ions.
- First electron affinity,  $\Delta_{EA1}H^\ominus$  is the enthalpy change when one mole of gaseous  $1^-$  ions are formed from one mole of gaseous atoms
- Second electron affinity,  $\Delta_{EA2}H^\ominus$  is the enthalpy change when one mole of gaseous  $2^-$  ions are formed from one mole of gaseous  $1^-$  ions

### Entropy



- Entropy is a measure of dispersal of energy through a system, which increases as disorder increases
- The terms feasible or spontaneous are used to describe reactions that can take place on their own.
- It is a fundamental observation that in any spontaneous process, the total entropy of the universe will always increase
- $\Delta S = \sum S^{\theta}_{\text{products}} - \sum S^{\theta}_{\text{reactants}}$
- $\Delta S$  = change in the total entropy
- $\sum S^{\theta}_{\text{products}}$  = total standard entropy of the products
- $\sum S^{\theta}_{\text{reactants}}$  = total standard entropy of the reactants
- Reactions that produce gases result in an increase in entropy
- Entropy increases during changes in state that give the particle access to a greater number of configurations
- solid < liquid < gas (in order of increasing entropy)
- The sign of an entropy change can be predicted when the reactants and products have different numbers of moles of gas molecules. If the products have fewer moles, then entropy decreases
- Fewer moles of gas → Fewer particles → Fewer configurations → Lower entropy

### Gibbs Free Energy

- Whether a reaction will happen spontaneously depends on temperature, enthalpy change and entropy changes
- The Gibbs Free-Energy Equation:

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

$\Delta G$  = change in free energy of the system ( $kJ\ mol^{-1}$ )

$\Delta H$  = change in enthalpy of the system ( $kJ\ mol^{-1}$ )

$T$  = temperature of the system ( $K$ )

$\Delta S$  = change in entropy of the system ( $J\ K^{-1}\ mol^{-1}$ )

- $\Delta G$  allows us to predict whether a reaction is feasible
- Reactions are only feasible if  $\Delta G$  is zero or negative
- $\Delta G$  depends on temperature - some reactions may be feasible at one temperature and not another
- To calculate the temperature at which a reaction becomes feasible, the Gibbs Free-Energy equation has to be rearranged

		$\Delta H$	
		Negative	Positive
$\Delta S$	Positive	Feasible $\Delta G = \Delta H - T\Delta S_{\text{system}}$ $\Delta G$ will be negative	Maybe $\Delta G = \Delta H - T\Delta S_{\text{system}}$ $\Delta G$ can be negative if $T$ is high enough
	Negative	Maybe $\Delta G = \Delta H - T\Delta S_{\text{system}}$ $\Delta G$ can be negative if $T$ is low enough	Never feasible $\Delta G = \Delta H - T\Delta S_{\text{system}}$ $\Delta G$ can never be negative

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

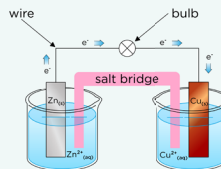
$$\Delta H = T\Delta S$$

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

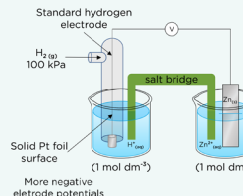
- Kinetics also influences whether a reaction can occur. If the activation energy is too high or the rate of reaction is very slow, the reaction may not happen even if the reaction is thermodynamically favourable.

### Electrode Potentials

- Redox reactions can be used in electrochemical cells to generate electricity (a flow of charge).
- Electrochemical cells consist of two half-cells. At one oxidation occurs, at the other reduction. Electrons flow between the two cells, driving the redox reaction.



- $$Zn \rightarrow Zn^{2+} + 2e^{-}$$
- $$Cu^{2+} + 2e^{-} \rightarrow Cu$$
- An equilibrium is reached:
- $$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$$
- Each one of these beakers is a half-cell. A solution in a standard half-cell will have a concentration of  $1.00\ mol\ dm^{-3}$
  - An electrode is a solid surface which allows the transfer of electrons to and from it.
  - The system above describes metal/metal ion half-cells. It is possible to make an ion/ion cell by using the same element with different oxidation states e.g. a mixture of  $Fe^{2+}$  and  $Fe^{3+}$  establishes an equilibrium:  $Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$
  - In an ion/ion half cell there is no solid metal to transport electrons out of the cell so a platinum electrode is used
  - The standard electrode potential,  $E^{\theta}$  is the voltage measured under standard conditions when the half-cell is connected to a standard hydrogen electrode.

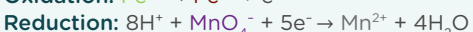


- Standard conditions includes 298K, 100 kPa and  $1.00\ mol\ dm^{-3}$ .
- The voltage measured is also known as the electromotive force of the cell (EMF).
- An electrochemical series is a list of standard electrode potentials of all the possible half-cells.
- The more negative the electrode potential, the more the oxidation (backwards) reaction is favoured.

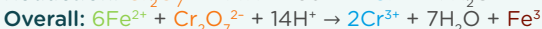
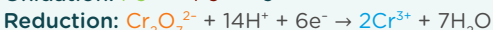
$$E^{\theta}_{\text{cell}} = E^{\theta}_{\text{positive terminal}} - E^{\theta}_{\text{negative terminal}}$$

### Redox Titrations

- Redox titrations can be carried out to show how much oxidising agent is needed to react exactly with a reducing agent.
- Transition metals have variable oxidation states, so they are often present in either the oxidising or reducing agent
- Manganate(VII) ions are readily reduced to  $Mn^{2+}$  ions under acidic conditions (purple to colourless). This can be used to find the amount of  $Fe^{2+}$  in a solution

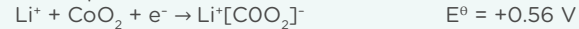
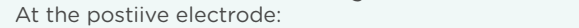


- $Fe^{2+}$  can also be oxidised by dichromate (VI) ions



### Electrochemical Cells

- Electrochemical cells can be used as a commercial source of electrical energy
- In a rechargeable battery, when the chemicals have reacted fully, a potential difference can be applied to the cell in the opposite direction, which will regenerate the original chemicals
- Lithium-ion batteries are rechargeable:



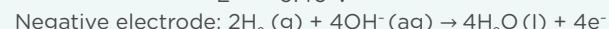
$$E^{\theta}_{\text{cell}} = +0.56\ V - (-3.04\ V) = +3.60\ V$$

- Some cells are non-rechargeable and disposed of when the chemicals have fully reacted.
- In fuel cells the chemicals are stored externally and are fed into the cell when electricity is required.

- An alkaline hydrogen fuel cell:



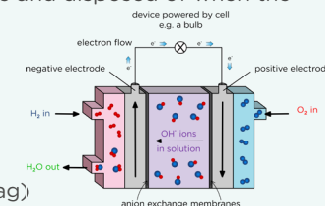
$$E^{\theta} = +0.40\ V$$



$$E^{\theta} = -0.83\ V$$



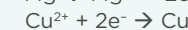
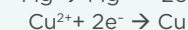
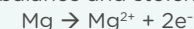
$$E^{\theta}_{\text{cell}} = +1.23\ V$$



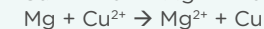
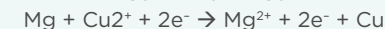
Advantages	Disadvantages
They are more efficient than burning fossil fuels.	Energy is needed to build the fuel cells and produce hydrogen - this energy comes from fossil fuels.
They release water, which isn't harmful.	Hydrogen is highly flammable so needs to be carefully handled.
They do not need to be recharged - they keep producing electricity for as long as they have fuel.	Highly toxic and can ignite - Li is a very reactive metal.

### Redox Equations

- Redox reactions involve both oxidation and reduction
- A redox reaction can be constructed from two half-equations; one representing an oxidation process, and the other a reduction process
- To construct a full equation from half equations:
  - Balance the electrons
  - Combine the equations
  - Cancel the electrons
  - Check the charge balance and stoichiometry e.g.



1)



2)

3)

## General Properties of Transition Metals

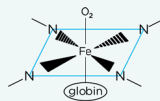
- A transition element is a d-block element which has at least one stable ion with an incomplete d-subshell
- Across the periodic table from scandium to zinc, orbitals are added to 3d orbitals
- Transition metal ions form coloured compounds because of the movement of electrons in partially filled d-orbitals. Particular wavelengths of light are absorbed, so the remaining wavelengths are the colour perceived.
- All the transition metals have more than one oxidation state.
- Transition metals and their compounds act as catalysts.
- Transition metals often form complexes. A complex is a central metal atom or ion surrounded by ligands.
- A ligand is a molecule or ion that forms a co-ordinate bond with a transition metal by donating a lone pair of electrons.
- The co-ordination number is the number of co-ordinate bonds to the central metal atom or ion.

## Substitution Reactions

- All ligands contain at least one lone pair of electrons in their outer shell
- Cu(II) ions undergo ligand substitution of H<sub>2</sub>O with NH<sub>3</sub>  

$$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$$
- The Cl<sup>-</sup> ligand is larger than the uncharged ligands NH<sub>3</sub> and H<sub>2</sub>O. Therefore, exchange of the ligand H<sub>2</sub>O by Cl<sup>-</sup> can involve a change of co-ordination number  

$$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \rightleftharpoons [\text{Cu}(\text{Cl})_4]^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$$
- The haem group in haemoglobin is a Fe(II) complex with a multidentate ligand
- Oxygen can reversibly form a coordinate bond to the Fe<sup>2+</sup> ion and travel through the bloodstream, being released where it's needed
- Carbon monoxide is toxic because it binds irreversibly to haemoglobin, forming a stronger bond than oxygen does.

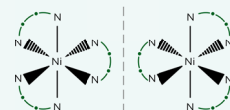
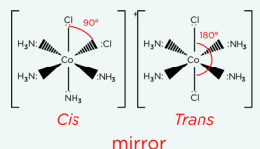


## Formation of Coloured Ions

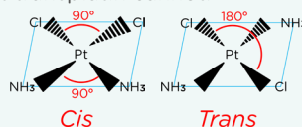
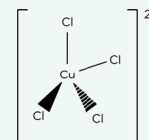
- Transition metal ions have distinctive colours which are used to identify them
- d electrons move from the ground state to an excited state when colours of light are absorbed
- The colour of a transition metal ion is the sum of the remaining colours that are not absorbed
- The colour of a complex depends on the identity of the metal, its oxidation state, and the ligands that are coordinately bonded to the metal

## Complex Ions

- A complex ion consists of a metal centre surrounded by ligands (a molecule or ion that forms a coordinate bond by donating a lone pair of electrons)
- The number of coordinate bonds in a complex gives the coordination number of the metal centre
- Complex ions most commonly form octahedral complexes with small ligands (eg H<sub>2</sub>O and NH<sub>3</sub>). Octahedral complexes can display cis-trans isomerism with monodentate ligands and optical isomerism with bidentate ligands



- Tetrahedral complexes are commonly formed with larger ligands e.g. [CuCl<sub>4</sub>]<sup>2-</sup>
- Cis and trans isomers can also exist if the complex is square planar with two pairs of identical ligands, e.g. cisplatin, which can bind to DNA to prevent replication causing death of cancer cells. But transplatin cannot.



## Catalysts

- Transition metals and their compounds can act as heterogeneous and homogeneous catalysts
- Heterogeneous catalysts are in a different state to the reactants
- Homogeneous catalysts are in the same state as the reactants
- Examples of heterogeneous catalysts are
  - in the Contact process V<sub>2</sub>O<sub>5</sub> catalyses  

$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$$
  - In the Haber Process Fe catalyses N<sub>2</sub>(g) + 3H<sub>2</sub>(g) ⇌ 2NH<sub>3</sub>(g)
  - Hydrogenation of vegetable fats to make margarine is catalysed by Ni (-CH=CH- + H<sub>2</sub> → -CH<sub>2</sub>-CH<sub>2</sub>-)
  - The decomposition of hydrogen peroxide is catalysed by manganese (IV) oxide: 2H<sub>2</sub>O<sub>2</sub> → 2H<sub>2</sub>O + O<sub>2</sub>
- Examples of homogeneous catalysts are
  - The reaction between the persulphate ion (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) and the iodide ion is catalysed by Fe<sup>2+</sup>.  

$$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$$

$$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$$

$$2\text{I}^-(\text{aq}) + 2\text{Fe}^{3+}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$$

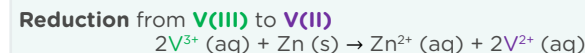
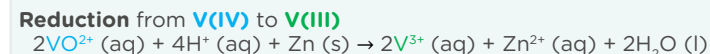
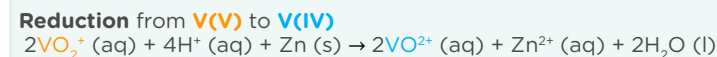
## Precipitate Reactions of Transition Metals

- A precipitate reaction is when two solutions containing soluble ions are mixed, forming an insoluble compound. They occur when sodium hydroxide or ammonia is added to transition metal solutions
- Fe<sup>2+</sup> eventually oxidised by air to Fe<sup>3+</sup> making brown Fe(OH)<sub>3</sub>(s)
- If excess ammonia is added to Cr(OH)<sub>3</sub>, purple [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> forms
- If excess ammonia is added to Cu(OH)<sub>2</sub>, deep blue [Cu(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)]<sup>2+</sup> forms

Metal-aqua ion	Excess OH <sup>-</sup>
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> (aq) Pale green solution	[Fe(OH) <sub>3</sub> ] Green ppt*
[Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> (aq) Pale blue solution	[Cu(OH) <sub>2</sub> ] Pale blue ppt
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> (aq) Purple/yellow/brown solution	[Fe(OH) <sub>3</sub> ] Brown ppt
Mn <sup>2+</sup> (aq) Pale pink solution	Mn(OH) <sub>2</sub> Light brown ppt
Cr <sup>3+</sup> (aq) Colourless solution	Cr(OH) <sub>3</sub> Grey green ppt

## Variable Oxidation States

- Vanadium has 4 oxidation states II, III, IV & V
- Vanadium species in oxidation states IV, III and II are formed by the reduction of vanadate(V) ions by zinc in acidic solution



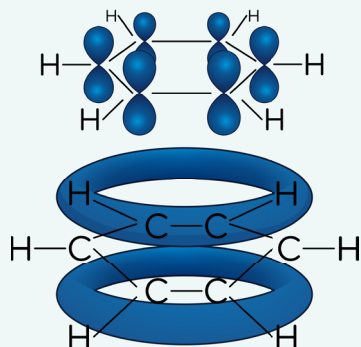
- Manganate(VII) ions are readily reduced to Mn<sup>2+</sup> ions under acidic conditions (purple to colourless). This can be used to find the amount of Fe<sup>3+</sup> in a solution



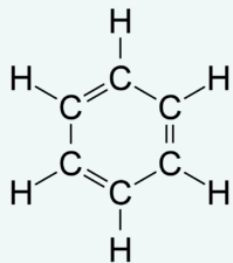
- When transition metals are oxidised, the 4s electrons are lost before the 3d electrons

### Bonding in Benzene

- Compounds that contain a benzene ring are aromatic.
- The molecular formula  $C_6H_6$  led to the belief that the structure of benzene was cyclohexa-1,3,5-triene. This is the Kekule model of benzene, which is incorrect
- Benzene is a planar cyclic structure consisting of a ring of carbon atoms, each with a single hydrogen atom attached that sticks out into a flat plane



- Benzene has a delocalised electron system, arising due to the overlap of one p-orbital from each carbon atom, above and below the plane of the ring.

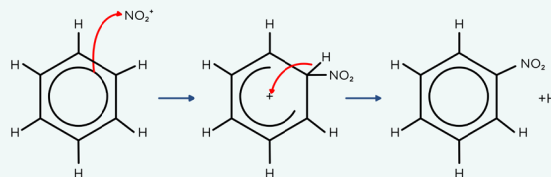


- Evidence for the delocalised structure:

- Bond length - X-ray diffraction patterns show the C-C bond lengths in benzene are all the same, being in between the length of carbon single and double bonds
- Hydrogenation - The enthalpy change of hydrogenation for benzene is less exothermic than that of theoretical cyclohexa-1,3,5-triene, showing that benzene is more stable than the Kekule model
- Resistance to reaction - benzene does not decolorise bromine water like normal alkenes do, and it does not undergo electrophilic substitution addition reactions

### Electrophilic Substitution of Benzene

- The benzene ring is a region of high electron density, which means it attracts electrophiles
- Electrophilic substitution proceeds by the general mechanism, where the identity of  $E^+$  represents an electrophile

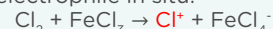


- Nitration of benzene ( $E^+ = NO^+$ )
    - A concentrated sulfuric acid catalyst is used and the reaction carried out under reflux, with concentrated nitric acid
- Overall:  $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$
- Generation of the electrophile:  
 $HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^- \rightarrow H_2O + NO_2^+ + HSO_4^-$
- Regeneration of sulphuric acid catalyst:  $H^+ + HSO_4^- \rightarrow H_2SO_4$

- Halogenation ( $E^+ = Cl^+$  or  $Br^+$ )  
 The aromatic ring in benzene is too stable to react directly with halogens, therefore a halogen carrier ( $FeCl_3/FeBr_3$ ,  $AlCl_3/FeBr_3$  or Fe) is used



Generation of the electrophile in situ:

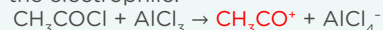


Regeneration of the halogen carrier catalyst:

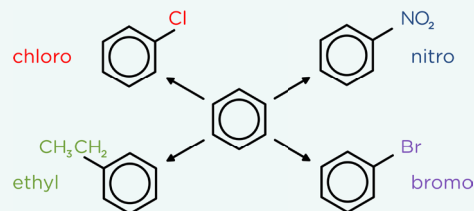


- Friedel-Crafts acylation reactions involve adding an acyl group to benzene. A strong Lewis acid, such as  $AlCl_3$ , is used as a catalyst. The reaction is carried out at  $60^\circ C$  under reflux in anhydrous conditions

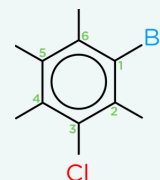
Generation of the electrophile:



- A benzene derivative is a benzene ring that has undergone substitution. Depending on the identity of the substitute a different prefix is used

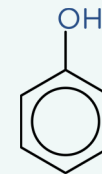


- Double-substituted benzene derivatives are named by numbering the carbon atoms and stating what carbon each group is on
- If one derivative has two different groups, the prefixes are used in alphabetical order, e.g. 1-bromo-3-chlorobenzene

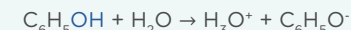


### Phenol

- Phenol has a hydroxyl group (-OH) directly attached to a benzene ring
- It can be distinguished from typical alcohols as it cannot act as a nucleophile



- Phenol is a weak acid because it partially dissociates in water



- It reacts in an acid-base reaction with KOH. Normal alcohols do not partake in acid-base reactions

- However, phenol can be distinguished from carboxylic acids as they don't react with carbonates

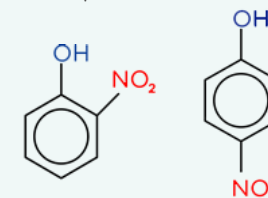
- The reactivity of phenol is greater than benzene because electrons are donated from the p-orbital of the oxygen to the delocalised aromatic ring. The increased electron density allows phenol to be more susceptible to electrophilic attack
  - Phenol can induce a dipole in  $Br_2$ , therefore it undergoes direct halogenation, unlike benzene
  - Phenol decolourises bromine water, but benzene doesn't

### Electrophilic Substitution of Phenol

- Unlike benzene, phenol undergoes nitration at room temperature with dilute nitric acid
- $$C_6H_5OH + HNO_3 \rightarrow C_6H_4(NO_2)OH + H_2O$$

- The hydroxyl group activates the carbon atoms at the 2 and 4 positions on the aromatic ring by pushing electron density into the  $\pi$ -system. Therefore substitution reactions mainly occur on the 2 and 4 position

- Nitration of phenol forms a mixture of 2-nitrophenol and 4-nitrophenol

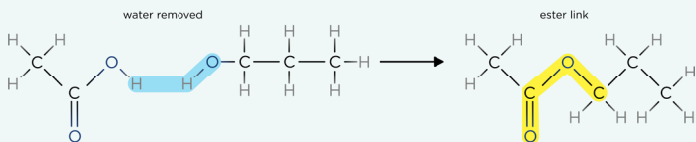


- If concentrated  $HNO_3$  is used, a triple substitution occurs, forming 2,4,5-trinitrophenol

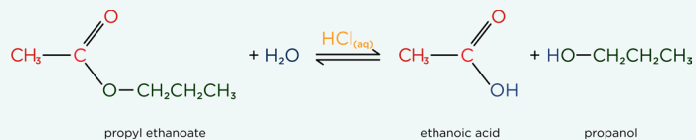
- The presence of an  $NH_2$  group on the ring makes the 2- and 4-directing effect stronger

### Carboxylic Acids & Esters

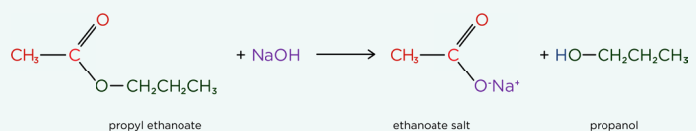
- Carboxylic acids have the functional group -COOH
- Carboxylic acids partially dissociate in water, making them weak acids
- Carboxylic acids can react with carbonates to liberate CO<sub>2</sub>.  
 $2\text{CH}_3\text{COOH}(\text{aq}) + \text{Na}_2\text{CO}_3(\text{s}) \rightarrow 2\text{CH}_3\text{COO}^-\text{Na}^+(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- They also react with alkalis and metal oxides as acids do
- Carboxylic acids with short carbon chains (up to four carbons) are soluble because they can form hydrogen bonds with water molecules
  - The C=O and O-H bond in carboxylic acids are polar bonds, allowing for the hydrogen bonds to form
  - As the chain length increases, the solubility decreases, because the size of the hydrophobic non-polar part of the molecule increases
- Esters have the general formula RCOOR'.
- Esters can be made when alcohols and carboxylic acids are reacted in the presence of a sulphuric acid catalyst



- The alcohol gives the first part of the name and the acid gives the second part of the name
- Esters are used as solvents, plasticisers, perfumes and food flavourings
- Acid catalysed hydrolysis of esters forms a carboxylic acid and an alcohol



- Base catalysed hydrolysis of ester forms a carboxylate salt and an alcohol

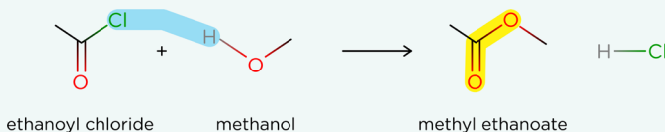


### Detecting Carbonyls

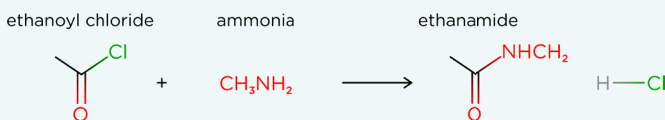
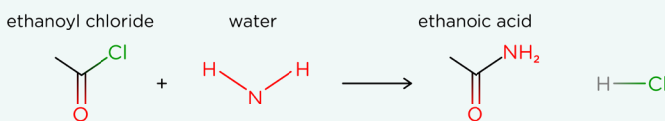
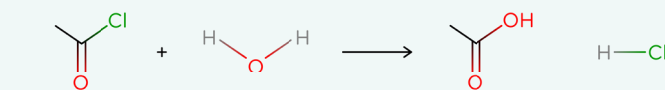
- Brady's reagent is used to test for the presence of carbonyls. It consists of a mixture of methanol, sulfuric acid and a solution of 2,4-dinitrophenylhydrazine (2,4-DNP)
  - When Brady's reagent is added to an aldehyde or a ketone, an observation is made as the orange transparent solution forms a yellow/orange precipitate of a 2,4-DNP derivative
  - The observation is not seen with carboxylic acids and esters despite these compounds also having C=O bonds
  - The specific aldehyde or ketone can be observed by comparing the melting point of the precipitate with a database
- Tollen's reagent (ammoniacal silver nitrate) is a colourless weak oxidising agent which reacts with aldehydes, but not ketones, therefore it can be used to distinguish between the two
  - When Tollen's reagent is added to an aldehyde a silver mirror is observed
  - The silver ions are reduced to silver metal and the aldehyde is oxidised to a carboxylic acid
  - No observation is made when it is added to a ketone

### Acylation

- Acyl chlorides are a derivative of carboxylic acids, where the -OH group is replaced by a -Cl group
- They are prepared by reacting a carboxylic acid with SOCl<sub>2</sub>:  
 $\text{CH}_3\text{COOH} + \text{SOCl}_2 \rightarrow \text{CH}_3\text{COCl} + \text{SO}_2 + \text{HCl}$
- Acyl chlorides react with alcohols to form esters in a nucleophilic addition-elimination reaction.



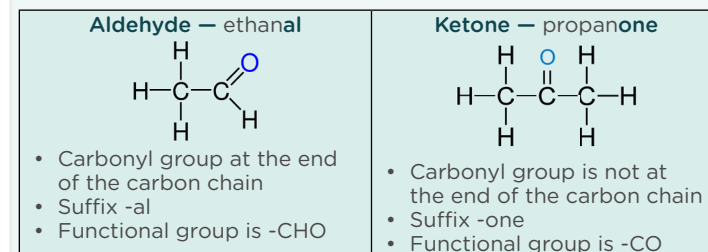
- Acyl chlorides will react with a variety of nucleophiles



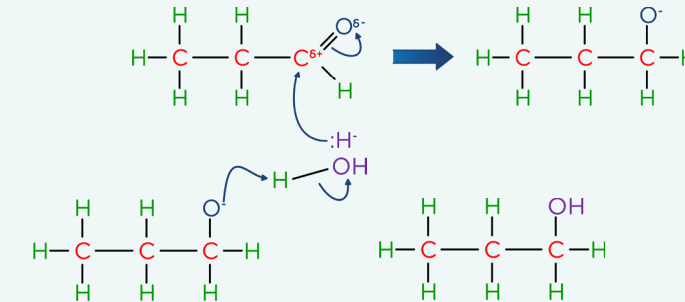
ethanoyl chloride + methylamine → N-methylethanamide + H-Cl

### Aldehyde & Ketones

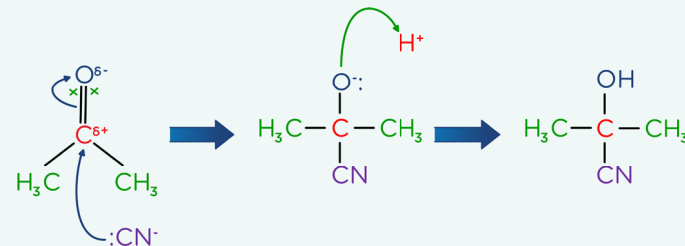
- Aldehydes and ketones are carbonyl compounds containing the C=O functional group.



- Aldehydes can be oxidised to form carboxylic acids by heating under reflux with potassium dichromate (oxidising agent) and concentrated sulphuric acid
- Carbonyls have a permanent dipole making them susceptible to nucleophilic addition reactions.
- Aldehydes can be reduced to primary alcohols and ketones to secondary alcohols using NaBH<sub>4</sub> as the reducing agent e.g. reduction of propanal CH<sub>3</sub>CH<sub>2</sub>CHO + 2[H] → CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH

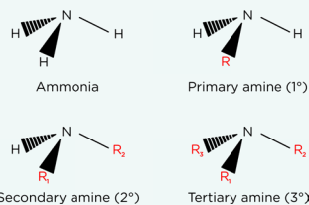


- Nucleophilic addition of cyanide ions can be used to extend the length of a carbon chain
- Reactions of carbonyls with KCN and dilute acid, produces a hydroxynitrile. Aldehydes and unsymmetrical ketones form two optical isomers, as there is an equal chance of either isomer being formed. This is a racemic mixture.

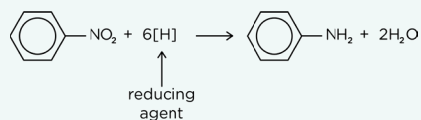
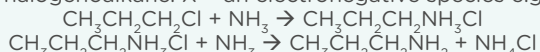


- Cyanide-containing compounds can be toxic or irritants.

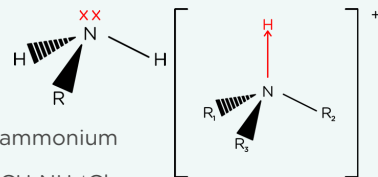
### Amines



- Aliphatic amines are those without aromatic rings present. Primary aliphatic amines can be prepared by reacting ammonia with a haloalkane. X = an electronegative species e.g. Cl, Br
- Additional substitution of the hydrogen atoms on the nitrogen can occur, resulting in secondary amines, followed by tertiary amines, followed by quaternary ammonium salts (R<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> where R = any alkyl chain)
- Aromatic amines are made by reducing nitroarenes such as nitrobenzene, refluxed at 100°C using a reducing agent of tin and concentrated HCl. The tin and concentrated HCl react to form hydrogen

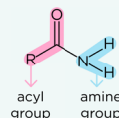


- Amines act as Lewis bases because the nitrogen atom on an amine has a lone pair of electrons which it can donate to a Lewis acid
- Amines act as Brønsted-Lowry bases because the nitrogen atom on an amine can accept a proton
- They react with dilute inorganic acids to form alkylammonium salts

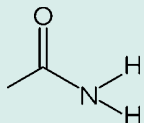


### Amides

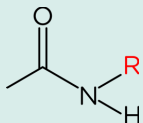
- Amides are a group of nitrogen-containing organic compounds. They contain both an amine group and an acyl group



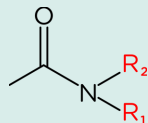
Primary (1°) amides are formed by reacting acyl chlorides with ammonia



Secondary (2°) amides are formed by mixing acyl chlorides with primary amines

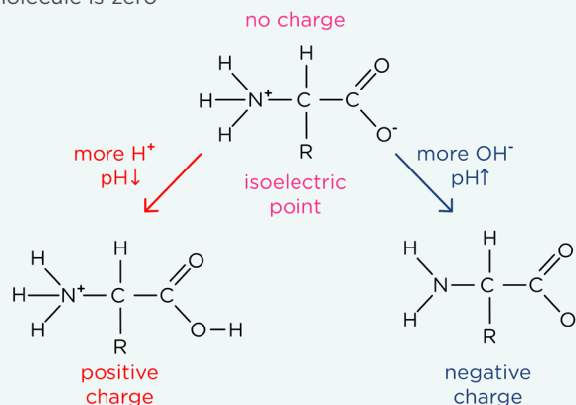


Tertiary (3°) amides are formed by mixing acyl chlorides with secondary amines.



### Amino Acids

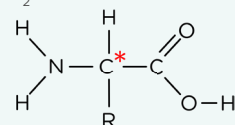
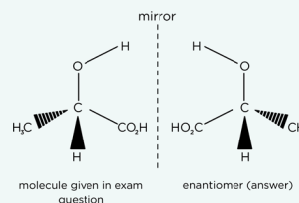
- α-amino acids contain both the amine functional group and the carboxylic acid functional group (carboxyl group) attached to the same carbon atom.
- The general formula of an amino acid is RCH(NH<sub>2</sub>)COOH
- Amino acids are amphoteric, meaning they have both acidic and basic properties and can exist as zwitterions, having no charge overall.
- The isoelectric point is the pH at which the overall charge of a molecule is zero



- Amino acids undergo reactions with their carboxylic acid group and amine group
- Carboxylic acid group reacts with: metal oxides, alkalis, carbonates, alcohols
- Amine group reacts with: inorganic acids e.g. HCl

### Optical Isomerism

- Optical isomers are species which are non-superimposable mirror images of each other. One isomer rotates plane-polarised light clockwise, and the other rotates it anticlockwise
- Optical isomerism is a form of stereoisomerism and occurs as a result of chirality in molecules
- A chiral centre is a carbon atom with 4 different groups attached (it is asymmetric). It is denoted by an asterisk
- Amino acids have a chiral centre provided the R group is not just -H, -COOH or -NH<sub>2</sub>



- A 50:50 mix of the enantiomers (a racemic mixture) will have no overall effect on plane-polarised light as the effects from the two enantiomers cancel out

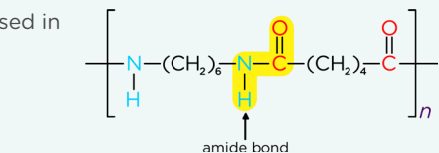
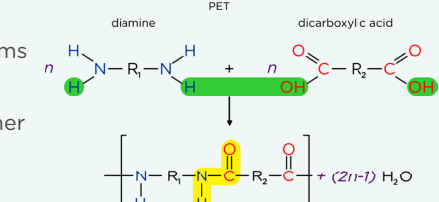
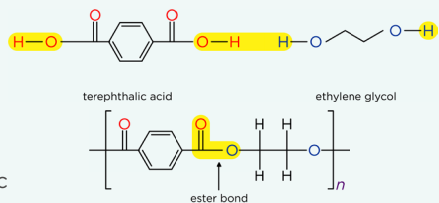
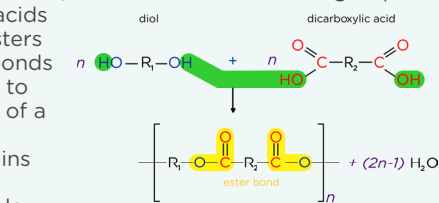
### Basic & Nucleophilic Properties of Amines

- Amines are weak bases
- In primary amines the lone pair of electrons on the N atom is readily donated due to the extra electron density from the alkyl groups. Aryl groups are electron-withdrawing so the lone pair of electrons on the nitrogen atom in an aryl amine is attracted into the benzene ring, so the electron pair is less easily donated.
- The lone pair of electrons on the nitrogen atom in amines allows them to act as nucleophiles.
- Haloalkanes undergo nucleophilic substitution with an ammonia nucleophile to form amines. This reaction can also happen with primary amines acting as the nucleophile, using the same mechanism as ammonia, to form secondary amines
- Reaction of haloalkanes with secondary amine forms tertiary amines. Reaction of haloalkanes with tertiary alkanes forms quaternary ammonium salts.
- Quaternary ammonium salts containing a large alkyl group are often used as cationic surfactants. This is because they have one long non-polar hydrocarbon chain and a charged end.
- Ammonia and primary amines can also act as nucleophiles in addition-elimination reactions with acyl chlorides and acid anhydrides
- When ammonia reacts, the product formed is a primary amide.
- Primary amines react by the same mechanism, but the product formed is an N-substituted (secondary) amide.



### Condensation Polymers

- Condensation polymerisation involves the reaction of two different types of monomers, with different functional groups.
- Reacting dicarboxylic acids with diols forms polyesters
- Square brackets with bonds through them are used to represent a repeat unit of a polymer
- Adjacent polyester chains are held together by permanent dipole-dipole attractions due to the presence of the polar carbonyl group
- The polyester terylene (PET) is formed from the monomers terephthalic acid and ethylene glycol. Typically used in plastic bottles, sails, sheets and clothing
- Reacting dicarboxylic acids and diamines forms polyamides
- Adjacent polyamide strands are held together by hydrogen bonds



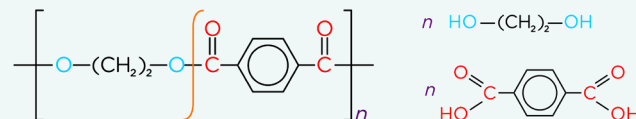
- Nylon is a polyamide used in textiles

- Kevlar is a polyamide used in bullet and stab-proof vests

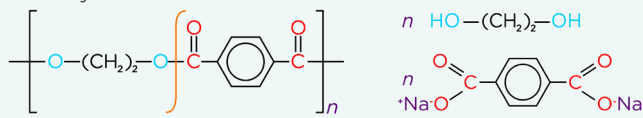
- Polypeptides are also condensation polymers made up of amino acids

### Hydrolysis of Polymers

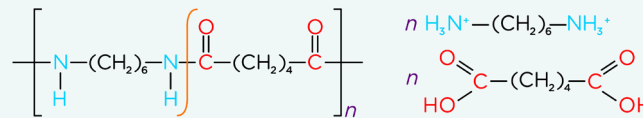
- Polyesters and polyamides undergo acid hydrolysis with a strong aqueous acid, or base hydrolysis with hot aqueous sodium hydroxide
- Acid hydrolysis of a polyester produces a diol and a dicarboxylic acid



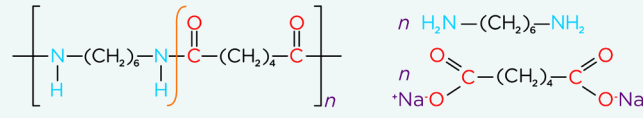
- Alkali hydrolysis of a polyester produces a diol and the salt of a dicarboxylic acid



- Acid hydrolysis of a polyamide produces a diammonium salt and a dicarboxylic acid

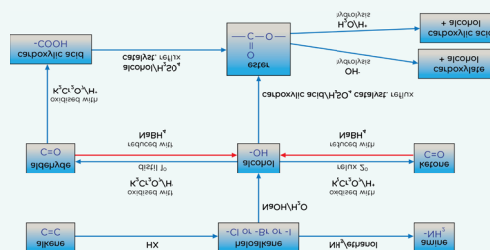


- Alkali hydrolysis of a polyamide produces a diamine and the salt of a dicarboxylic acid

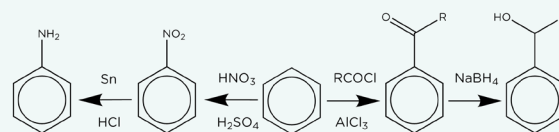


### Organic Synthesis

- Aliphatic functional groups.

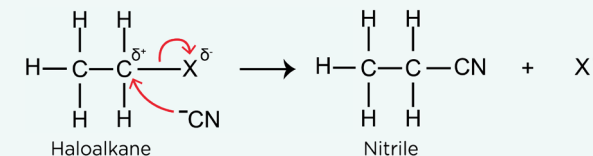


- Aromatic functional groups.

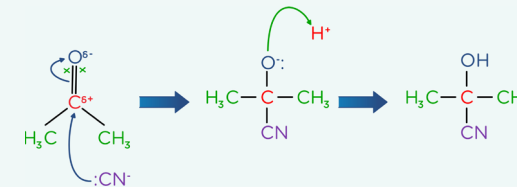


### Extending Carbon Chain Length

- Synthetic chemists design new molecules by changing functional groups and changing the length of a carbon chain
- Nucleophilic substitution with cyanide ions can achieve chain extension:



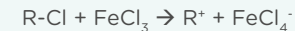
- The solvent used is ethanol, because if water was present  $\text{OH}^-$  would act as the nucleophile, preventing chain extension
- Cyanide ions can also react with carbonyls in nucleophilic addition



- Both reactions form nitriles which can undergo further reactions e.g. reduction and hydrolysis
  - Reduction:  $\text{LiAlH}_4$  is added to the nitrile and heated with a nickel catalyst at high pressure  $\text{RCN} + 2\text{H}_2 \rightarrow \text{RCH}_2\text{NH}_2$
  - Hydrolysis: Addition of water and a strong acid catalyst to the nitrile under reflux  $\text{RCN} + 2\text{H}_2\text{O} + \text{HCl} \rightarrow \text{RCOOH} + \text{NH}_4\text{Cl}$

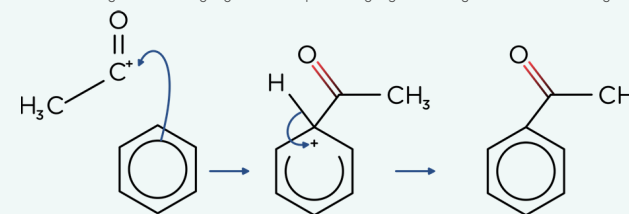
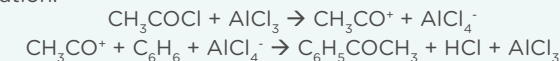
### Alkylation and Acylation of Aromatic Compounds

- Friedel-Crafts alkylation is used to add a hydrocarbon chain to an aromatic compound
- An alkyl nucleophile is generated by reacting a haloalkane with  $\text{FeCl}_3$  *in situ*



The  $\text{R}^+$  reacts with the aromatic species via electrophilic substitution

- Acylation:



### Chromatography

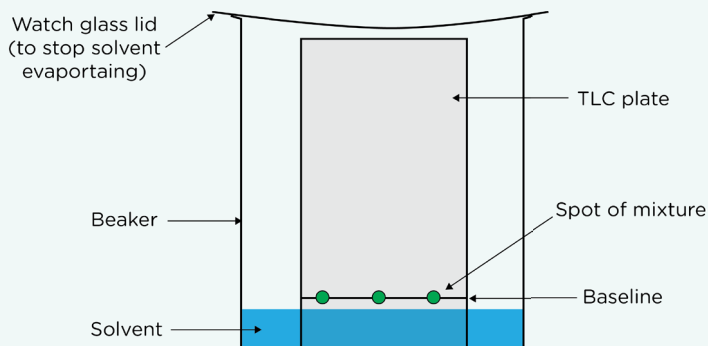
- Chromatography is a separation technique used for separating and identifying the species present in a mixture.
- The mobile phase is the substance in chromatography that carries the soluble components of the mixture
- The stationary phase is the substance in chromatography that holds back the components that are attracted to it.
- Each component in the mixture has a different level of solubility in the mobile phase and retention by the stationary phase, resulting in the separation of these components

### Thin Layer Chromatography

- In thin layer chromatography a plate is coated with a solid (stationary phase) and a solvent (mobile phase) moves up the plate
  - An organic solvent is used as the mobile phase
  - A sheet coated with a thin layer of silica gel or alumina acts as the stationary phase
- Thin layer chromatography can be used to separate and identify components of a mixture by their  $R_f$  values.

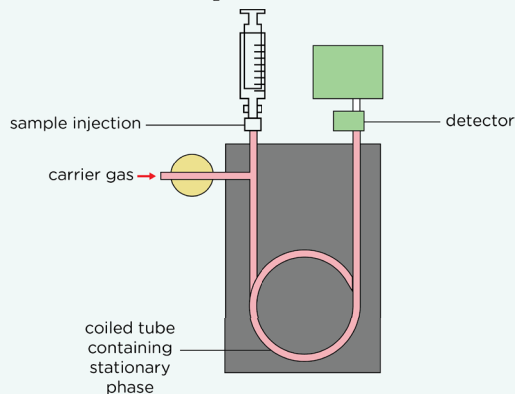
$$R_f = \frac{\text{distance moved by spot}}{\text{distance moved by solvent}}$$

- Different components have different attractions to the solvent and to the stationary phase. If a component is strongly attracted to the stationary phase it will not travel very far up the chromatogram
- TLC can be used to check the purity of a sample, or to determine the extent of a chemical reaction
- The  $R_f$  values can be compared to database values in order to identify components



### Gas Chromatography

- In gas chromatography (GC) a column is packed with a solid or with a solid coated by a liquid, and a gas is passed through the column under pressure at high temperature.
  - Stationary phase is a solid or liquid coating inside a long-coiled tube
  - An inert gas such as  $N_2$  acts as the mobile phase



- The time taken for a component to leave the coil is called the retention time. This can be compared with standards to identify different substances.
- A chromatograph shows these retention times as a series of peaks with the area under each peak being proportional to the amount of that component present
- Mass spectrometry can be used to analyse the components separated by GC
- The mass spectrum of each component can be compared to spectra in a database, allowing the components to be identified with greater certainty.

### Tests for Functional Groups

Functional Group	Test	Result
Alkene	$Br_2$ (aq)	Decolourises
Haloalkane	$AgNO_3$ (aq) and ethanol	White ppt - $Cl^-$ Cream ppt - $Br^-$ Yellow ppt - $I^-$
Carbonyl	Brady's reagent	Yellow/orange ppt
Aldehyde	Tollen's reagent	Silver mirror
Carboxylic acid	Universal indicator or metal carbonate	pH of a weak acid. Effervescence with a carbonyl
Phenol	Universal indicator, no reaction with carbonates	pH of a weak acid. No effervescence with a carbonyl
Alcohol	$H^+ / Cr_2O_7^{2-}$	Colour change from orange to green if it is a 1° or 2° alcohol

### Tests for Ions

- Qualitative tests give information on the identity of ions present in a sample
- To test for the presence of carbonate ions in a sample:
  - Add a dilute strong acid to the sample. If carbonate ions are present  $CO_2$  (g) will evolve
  - Test the gas evolved by bubbling it through limewater, if it is  $CO_2$  the limewater turns cloudy due to the formation of  $CaCO_3$
- To test for the presence of halide ions in solution, add dilute nitric acid and an aqueous solution of  $AgNO_3$

Silver Halide	Colour of Precipitate	Addition of Dilute Ammonia	Addition of Concentrated Ammonia
AgCl	White	Dissolves to give a colourless solution	Dissolves to give a colourless solution
AgBr	Cream	Remains	Dissolves to give a colourless solution
AgI	Yellow	Remains	Remains

- To test for the presence of sulfate ions in a sample, add barium ions.  $Ba^{2+}$  (aq) +  $SO_4^{2-}$  (aq)  $\rightarrow$   $BaSO_4$  (s).  $BaSO_4$  is a white precipitate
- To test for ammonium ions add sodium hydroxide solution and warm gently
 
$$NH_4^+ \text{ (aq)} + OH^- \text{ (aq)} \rightarrow NH_3 \text{ (g)} + H_2O \text{ (l)}$$
  - Test the gas evolved with damp red litmus paper. If the sample contains ammonium ions, the red litmus paper will turn blue
- To test for transition metal ions, add aqueous ammonia or sodium hydroxide dropwise
  - $Cu(II)$   $\rightarrow$  Blue precipitate
  - $Fe(II)$  or  $Cr(III)$   $\rightarrow$  Green precipitate
  - $Mn(II)$   $\rightarrow$  Brown precipitate
- To distinguish  $Fe(II)$  or  $Cr(III)$  add excess ammonia
  - $Fe(II)$   $\rightarrow$  No change
  - $Cr(III)$   $\rightarrow$  Purple solution