



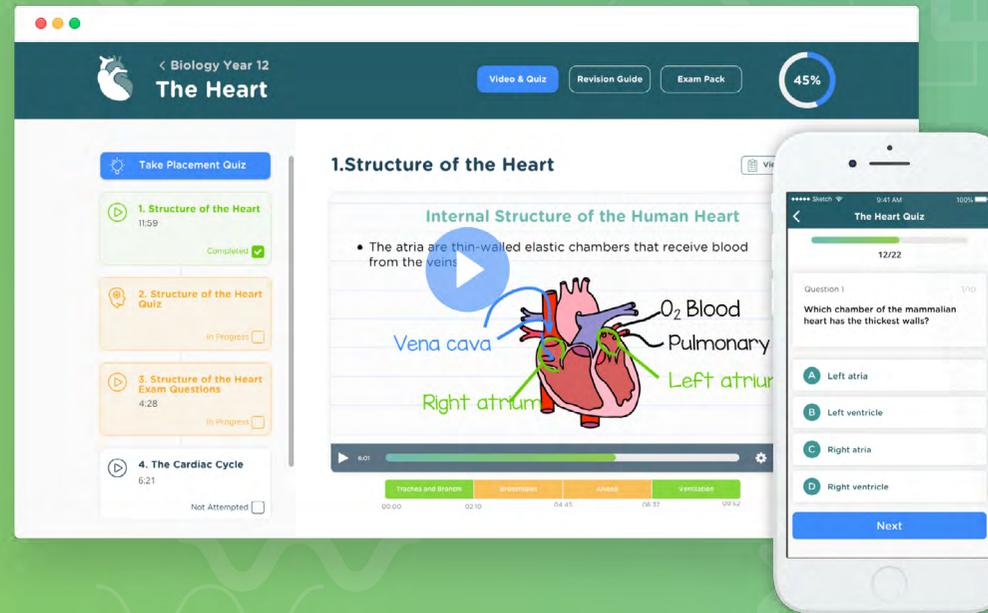
# THE ULTIMATE A-LEVEL AQA CHEMISTRY CHEATSHEET PACK





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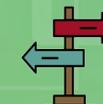
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# How to Use

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.

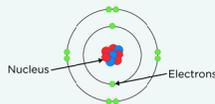
We've spent weeks working with top designers, academic writers and illustrators to ensure this is the best cheatsheet out there. Our promise to you is you won't find anything better. The cheatsheet pack has been built off the AQA specification to ensure no important information is missed – below is a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

Specification Points	Cheatsheet
3.1.1	Atomic Structure, Mass, Mass Spectrometry & Electronic Configuration
3.1.2	Ionisation Energy & Basic Equations
3.1.3	Bonds
3.1.4	Enthalpies, Calorimetry & Hess's Law
3.1.5	Collision Theory, Maxwell-Boltzmann, Rate of Reaction & Chemical Equilibrium
3.1.6 - 3.1.7	The Haber Process, Equilibrium Constant, Redox Reactions & Lattice Enthalpy
3.1.8	Born-Haber Cycles, Entropy & Gibbs Free Energy
3.1.9	Rate of Reaction & Rate Equations
3.1.10 - 3.1.11	K <sub>p</sub> , Electrode Potentials & Cells
3.1.12	Acids, Bases, Titration & Buffers
3.2.1 - 3.2.3	Periodic Table
3.2.5 - 3.2.6	Transition Metals
3.3.1	Precipitate Reactions & Introduction to Organic Chemistry
3.3.2 - 3.3.3	Alkanes & Haloalkanes
3.3.4 - 3.3.5	Alkenes & Alcohols
3.3.6 - 3.3.8	Organic Analysis, Optical Isomers, Aldehydes & Ketones
3.3.9 - 3.3.10	Carboxylic Acids, Esters & Benzene
3.3.11 - 3.3.12	Amines, Condensation Polymers & Amino Acids
3.3.13 - 3.3.14	Proteins, Enzymes, DNA & Organic Synthesis
3.3.15 - 3.3.16	NMR & Chromatography

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



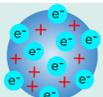
Particle	Relative Mass	Relative Charge
Proton	1	+1
Neutron	1	0
Electron	1/1840	-1

### The Evolution of Atomic Structure Over Time

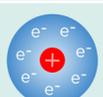
- The model of the atom has changed over time as new evidence has become available.



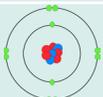
Dalton proposed that all atoms of one element are the same and are different from the atoms of another element. Atoms in his model were tiny and indivisible.



Thomson discovered the electron. He proposed the plum pudding model where negatively charged electrons move in a 'sea' of charge in a positively charged atom.



Rutherford found that most of the mass is concentrated in the positive nucleus, with negative electrons orbiting it. The positive and negative charges balance to make the atom neutral.



Bohr suggested that electrons orbit the nucleus on paths. Bohr's planetary model provided an explanation for the difference in energy of electrons at different distances from the nucleus.



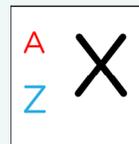
The current model is composed of protons, neutrons, and electrons. Protons and neutrons are found in the nucleus and are made up of smaller quarks, whereas electrons surround the central nucleus.

### 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.

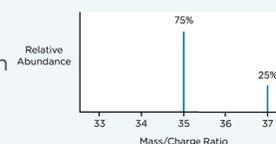
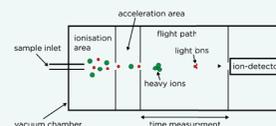
### Mass Number & Isotopes

- 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.



### 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.
- In time of flight mass spectrometry, the steps include:
  - Ionisation - the sample is dissolved in a volatile solvent and ejected through a hollow needle. The needle is connected to a positive terminal of a high voltage supply. This produces tiny positively charged droplets.
  - Acceleration - ions are accelerated towards a negatively charged plate to give all ions constant kinetic energy. So, the velocity of each ion will depend on its mass
  - Ion drift - ions pass through a hole in the negative plate, forming a beam
  - Detection - the positive ion picks up an electron which causes a current to flow. Flight times are recorded
  - Data analysis - the signal from the detector passes to a computer which generates a mass spectrum
- 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 (Ar)

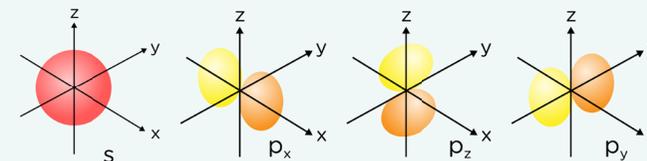


$$A_r = \frac{\sum (\text{relative isotopic mass} \times \text{abundance})}{100}$$

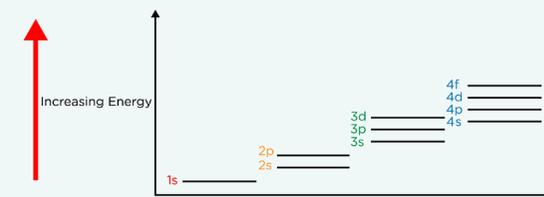
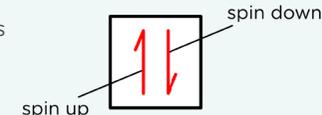
- A mass spectrum for a molecular sample shows the relative molecular mass on the x axis.

### 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-



- Electrons have an intrinsic property (spin). For two electrons in the same orbital, the spin must be opposite to minimise the repulsion.
  - Within each shell, orbitals that are of the same energy level are grouped together in sub-shells.
  - There are 1 s-orbital, 3 p-orbitals, 5 d-orbitals and 7-p orbitals possible in each subshell.
  - 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
  - No more than two electrons can fill an atomic orbital
- 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  $1s22s22p63s23p64s1$

nxy

### 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.
 
$$X(g) \rightarrow X^+(g) + e^-$$
- Successive ionisation energies apply to the removal of electrons after the first ionisation energy. The  $n$ th ionisation energy is:
 
$$X^{(n-1)+}(g) \rightarrow X^{n+}(g) + e^-$$
- 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 electric 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.

### 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  $^{12}\text{C}$  is the Avogadro constant of  $6.022 \times 10^{23} \text{ mol}^{-1}$ .
- $$n = \frac{m}{M}$$
- $n$  is the number of moles (mol)  
 $m$  is the mass (g)  
 $M$  is the molar mass ( $\text{g mol}^{-1}$ )
- 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 ( $\text{mol dm}^{-3}$ )  
 $n$  is the number of moles in solution (mol)  
 $V$  is the volume ( $\text{dm}^3$ )
- Remember:
  - $1 \text{ dm}^3 = 1000 \text{ cm}^3$
  - $1 \text{ m}^3 = 1000 \text{ dm}^3$

### Gas Equations

- One mole of any gas under standard conditions will occupy the same volume.
- The molar gas volume is  $24 \text{ dm}^3 \text{ mol}^{-1}$  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 ( $\text{dm}^3$ )

- 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 ( $\text{m}^3$ )  
 $n$  is the number of moles (mol)  
 $R$  is the gas constant ( $8.314 \text{ JK}^{-1}$ )  
 $T$  is temperature (K)

### 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:  
 $16 \times \text{CH}_2 = \text{C}_{16}\text{H}_{32}$

### 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.
- Spectator ions are ions that do not take part in the overall reaction and are found in both the reactants and products
- The net ionic equation shows only the ions directly involved in the reaction (removing spectator ions).
  - e.g.  $\text{NaCl (aq)} + \text{AgNO}_3 \text{ (aq)} \rightarrow \text{AgCl (s)} + \text{NaNO}_3 \text{ (aq)}$
  - $\text{Na}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)} + \text{Ag}^+ \text{ (aq)} + \text{NO}_3^- \text{ (aq)} \rightarrow \text{AgCl (s)} + \text{Na}^+ \text{ (aq)} + \text{NO}_3^- \text{ (aq)}$
  - Net ionic equation:  
 $\text{Cl}^- \text{ (aq)} + \text{Ag}^+ \text{ (aq)} \rightarrow \text{AgCl (s)}$
- Stoichiometry expresses the molar ratios between reactants and products in a reaction. It is used to determine the quantity of products or reactants required or produced by a known reaction.

### 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 =  $\frac{\text{actual yield}}{\text{theoretical yield}} \times 100$

### Ions

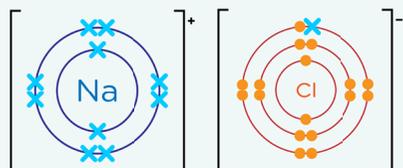
- An ion is an atom or molecule with a net charge formed through the gain or loss of electrons
- A cation is formed from the loss of electrons
- An anion is formed from the gain of electrons
- The noble gases do not form ions, as they already have a stable full outer shell of electrons, making them unreactive.
- Molecular ions are formed when groups of two or more atoms that are covalently bonded gain or lose electrons

Charge	Molecular ion
+1	Ammonium: $\text{NH}_4^+$
-1	Hydroxide: $\text{OH}^-$ Nitrate: $\text{NO}_3^-$ Hydrogencarbonate: $\text{HCO}_3^-$
-2	Carbonate: $\text{CO}_3^{2-}$ Sulphate: $\text{SO}_4^{2-}$ Sulphite: $\text{SO}_3^{2-}$

- 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,  $\text{Na}^+$ . The carbonate ion has the formula  $\text{CO}_3^{2-}$ . We need  $2 \times \text{Na}^+$  to balance the  $-2$  charge of  $\text{CO}_3^{2-}$ . The formula is  $\text{Na}_2\text{CO}_3$ .

### Ionic Bonding

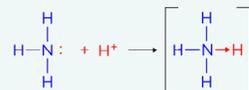
- An ionic bond is an electrostatic attraction between positive and negative ions, resulting in a lattice
- A lattice is a giant three-dimensional structure, where each ion is surrounded by oppositely charged ions
- They are often formed between ions of metals and non-metals, where each atom aims to 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
- A single covalent bond involves one shared pair of outer electrons
- A multiple covalent bond involves more than one shared pair of outer electrons
- 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

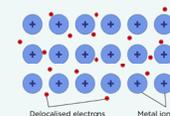


### Crystalline Structures

Crystal	Type of structure	Melting point	Conductivity	Diagram
Diamond	Giant covalent	High	None	
Graphite		High	Yes (has delocalised electrons as carbon makes only 3 bonds)	
Ice	Molecular	Low	None	
Iodine				
Magnesium	Metallic	High	In all states	
Sodium chloride	Ionic	High	Only when aqueous or molten	

### Metallic Bonding

- Metallic bonding is the bonding in metals
- 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.
- Metals are good electrical conductors, due to the delocalised electrons free to move and carry the current.
- Metals have high melting and boiling points due to the large amounts of energy needed to overcome the metallic bonds. Melting point is influenced by:
  - Charge of metal ion - Metal ions of greater charge contribute more electrons to the delocalised sea, therefore there are more electrostatic forces of attraction between the ions and electrons, resulting in a higher melting point
  - Size of metal ion - smaller cations are closer to the delocalised electrons, resulting in a stronger metallic bond, 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

- The shape of a molecule or ion is dictated by the number of electron pairs around the central atom and whether they are bonding or lone pairs.
- 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
  - Lone pair - lone pair repulsion > Lone pair - bonding pair repulsion > Bonding pair - bonding pair repulsion
- Bonding pairs repel each other equally. While lone pairs repel other pairs more because they are more electron dense.
- Each lone pair reduces the bond angle by about  $2.5^\circ$ .
- A normal line represents the bond 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.



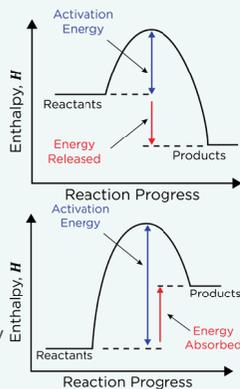
	Electron Pairs	Bonding Pairs	Lone Pairs	Bond Angles	Example
Linear	2	2	0	$180^\circ$	$\text{CO}_2$
Trigonal Planar	3	3	0	$120^\circ$	$\text{BF}_3$
Bent	3	2	1	$<120^\circ$	$\text{SO}_2$
Tetrahedral	4	4	0	$109.5^\circ$	$\text{CH}_4$
Trigonal Pyramidal	4	3	1	$107^\circ$	$\text{NH}_3$
V-Shaped	4	2	2	$104.5^\circ$	$\text{H}_2\text{O}$
Trigonal Bipyramidal	5	5	0	$90^\circ, 120^\circ$	$\text{PCl}_5$
Seesaw	5	4	1	$87^\circ, 102^\circ$	$\text{SF}_4$
T-Shaped	5	3	2	$88^\circ$	$\text{ClF}_3$
Linear	5	2	3	$180^\circ$	$\text{XeF}_2$
Octahedral	6	6	0	$90^\circ$	$\text{SF}_6$
Square Pyramidal	6	5	1	$<90^\circ$	$\text{BrF}_5$
Square Planar	6	4	2	$90^\circ$	$\text{XeF}_4$

### 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 & the standard state of the substance). Standard enthalpy changes are denoted by  $\Delta H^\ominus$ .
- Enthalpy change,  $\Delta H = \sum H_{\text{Products}} - \sum H_{\text{Reactants}}$**   
 $\sum H_{\text{Products}}$  total enthalpy of products ( $\text{kJ mol}^{-1}$ )  
 $\sum H_{\text{Reactants}}$  total enthalpy of reactants ( $\text{kJ mol}^{-1}$ )
- The standard enthalpy of formation ( $\Delta_f H^\ominus$ ) 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 ( $\Delta_c H^\ominus$ ) 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

### 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

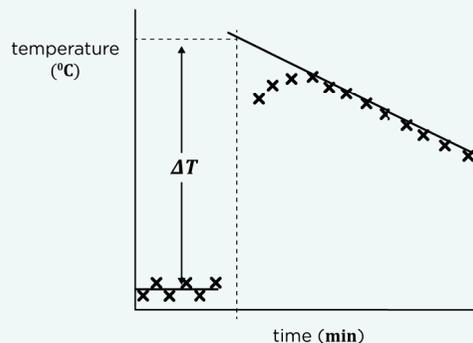


### Calorimetry

- Calorimetry is the process of measuring the amount of heat given off or taken in during a chemical reaction
- Experimental values of enthalpy changes often differ from those found in data books because: the reaction may be incomplete, incomplete combustion of the fuel may occur, the heat capacities and densities of the solutions are only approximates, heat may be lost from the water to the surroundings, the experimental conditions may not be standard and some of the fuel or water may evaporate before reweighing.
- $q = mc\Delta T$   
 $q$  is the heat change (J)  
 $m$  is the mass of the substance (g)  
 $c$  is the specific heat capacity ( $\text{J g}^{-1} \text{K}^{-1}$ )  
 $\Delta T$  is the temperature change (K or  $^\circ\text{C}$ )

### 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  $1 \text{ g cm}^{-3}$ )

### Bond Enthalpies

- Bond enthalpies provide us with information about how much energy is needed to break a bond.
- Mean bond enthalpy is the enthalpy change when one mole of covalent bonds is broken to give the free atoms, averaged over a range of compounds
- Some bonds can only occur in one environment, such as Cl-Cl and H-Cl, as Cl and H can only form one bond.
- Some bonds can occur in multiple environments, such as C-H and C=O, as C can form multiple bonds with a wide range of elements — resulting in different environments
- The strength of these bonds will vary 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  

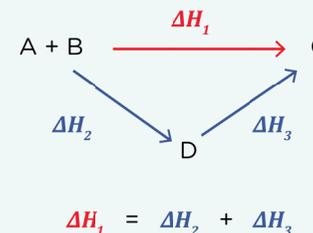
$$\Delta H = \sum (\text{bond enthalpy of reactants}) - \sum (\text{bond enthalpy of products})$$
- The enthalpy change values calculated from bond enthalpies are approximate and not as accurate as those calculated from Hess' Law cycles

### Spirit Burner Calorimetry

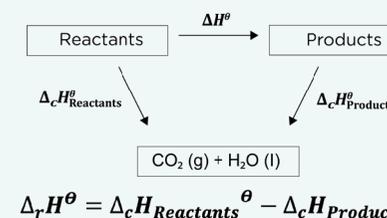
- A spirit burner calorimeter can be used to calculate enthalpy changes of combustion
  - The substance being heated or cooled, usually water, is placed in a beaker with a thermometer. A spirit burner is placed underneath the beaker to heat it
  - The spirit burner containing the fuel is weighed and 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 reweighed. The final temperature of the water is measured
  - The measured values are used to calculate  $q$

### Hess's Law

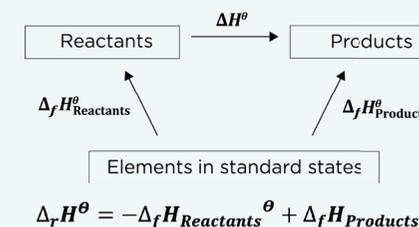
- Hess's law is that the enthalpy change of a reaction is independent of the route taken



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

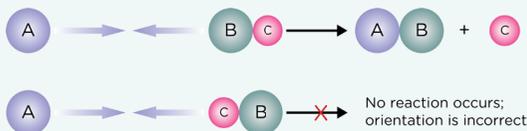


- Enthalpy changes of formation can be used to find the enthalpy change of a reaction
- The enthalpy of formation for an element is 0  $\text{kJ mol}^{-1}$ .



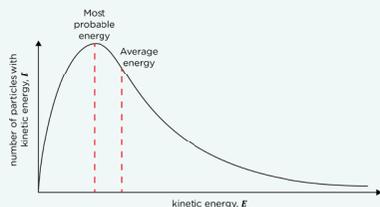
## Collision Theory

- 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

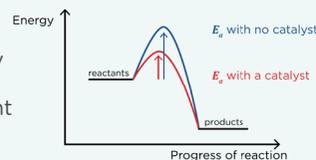


## Catalysts

- 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

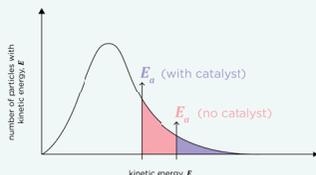
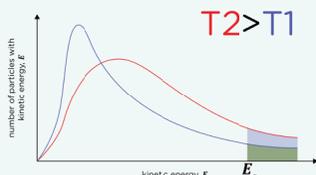
## Rate of Reaction

- 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
  - Surface area — increasing the surface area of solid reactants increases the area over which a reaction can occur, leading 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 remains the same
- 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.



## 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

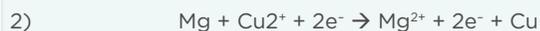
### Haber Process

- Nitrogen gas reacts with hydrogen gas to form ammonia in the Haber process
- $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$   $\Delta H = -92 \text{ kJ mol}^{-1}$
- 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

### Redox Equations

- 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.



### 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:  $aA + bB \rightleftharpoons dD + eE$ 

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$
- 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
- Factors including pressure, concentration and the addition of a catalyst does not affect the value of the equilibrium constant.
- Temperature does affect the equilibrium constant. If the forward reaction is exothermic and the reverse reaction is endothermic:
  - Increasing the temperature, will favour the endothermic reaction, forming less product and decreasing  $K_c$
  - Decreasing the temperature will favour the exothermic reaction, forming more product and increasing  $K_c$

### Oxidation Numbers

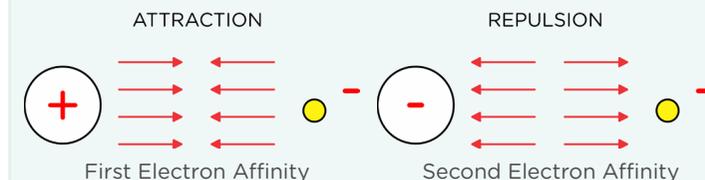
- Oxidation number is a number representing the number of electrons lost or gained by an atom in a compound.
- Oxidation is a loss of electrons during a reaction or an increase in oxidation number.
- Reduction is a gain of electrons during a reaction or a decrease in oxidation number
- The rules for 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.  $NH_4^+$ , 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

### Redox Reactions

- 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
  - Disproportionation reactions involve both oxidation and reduction of the same element
    - e.g. The decomposition of hydrogen peroxide
- $$2H_2O_2 \rightarrow 2H_2O + O_2$$
- Oxidation Number of O:  $-1 \rightarrow -2 \quad 0$
- O is both oxidised and reduced during this reaction

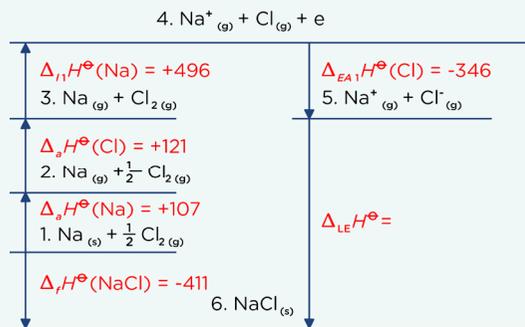
### Lattice Enthalpy

- 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.
- Standard lattice enthalpy of dissociation is the enthalpy change when one mole of an ionic lattice completely dissociates into its gaseous ions under standard conditions.
- The enthalpy of formation and the enthalpy of dissociation are opposites.
- Lattice enthalpy gives an indication of the strength of the ionic bonds
- Lattice enthalpy cannot be measured directly, so other measurements need to be known
- Standard Enthalpy of Formation,  $\Delta_f H^\ominus$  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,  $\Delta_a H^\ominus$  is the enthalpy change when one mole of gaseous atoms are formed from an element in its standard state.
- First ionisation energy,  $\Delta_1 H^\ominus$  is the energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of gaseous  $1^+$  ions.
- Second ionisation energy,  $\Delta_2 H^\ominus$  is the enthalpy change when one mole of gaseous  $2^+$  ions are formed from 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
- The first electron affinity is always exothermic because the electron is attracted to the positively charged nucleus of an atom. But the second electron affinity is endothermic because energy must be put in to overcome the repulsion between the electron and negatively charged ion



### 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.

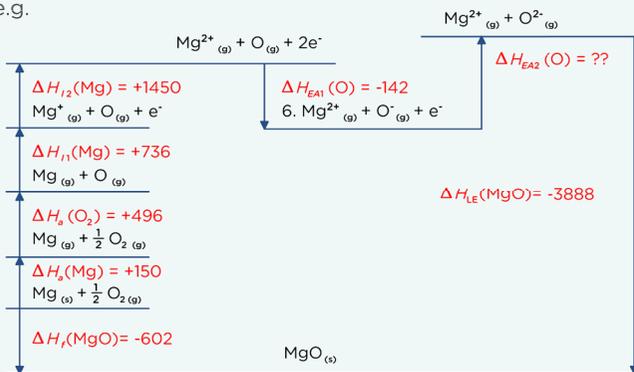


The lattice enthalpy of sodium chloride:

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

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

- 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.



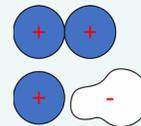
The second electron affinity of oxygen:

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

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

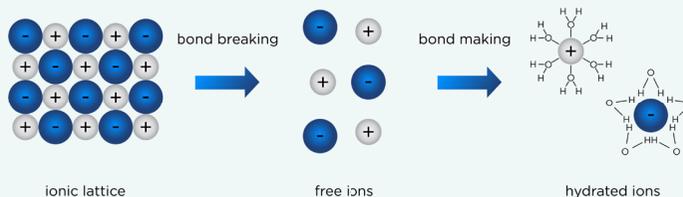
### Theoretical Lattice Enthalpies

- 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  $\text{F}^-$ )

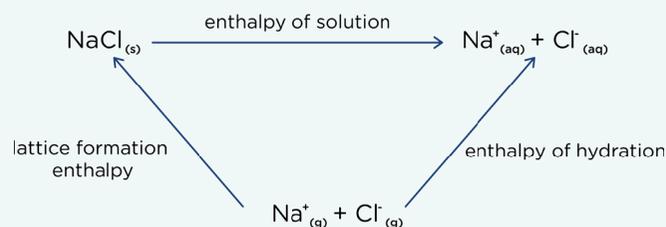


### Dissolving Ionic Compounds

- 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



### Entropy

- Entropy can be thought of as a measure of disorder
- 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
- $\Delta S = \Sigma S^\ominus_{products} - \Sigma S^\ominus_{reactants}$
- $\Delta S$  = change in the total entropy
- $\Sigma S^\ominus_{products}$  = total standard entropy of the products
- $\Sigma S^\ominus_{reactants}$  = 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 ( $\text{kJ mol}^{-1}$ )

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

$T$  = temperature of the system (K)

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

- $\Delta G$  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 $\Delta G = \Delta H - T\Delta S_{min}$ $\Delta G$ will be negative	Maybe $\Delta G = \Delta H - T\Delta S_{min}$ $\Delta G$ can be negative if T is high enough
	Negative	Maybe $\Delta G = \Delta H - T\Delta S_{min}$ $\Delta G$ can be negative if T is low enough	Never feasible $\Delta G = \Delta H - T\Delta S_{min}$ $\Delta G$ 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.

### Rate of Reaction

- The rate of reaction is the change in concentration of a reactant or product per unit time.
- Rate** =  $\frac{\text{change in concentration}}{\text{time}}$
- 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 for monitoring the rate of reaction:
  - Concentration change — take samples from a reaction at regular intervals in time and carry out a titration to measure the concentration
  - Gas evolving experiments — measure the volume of gas evolved, usually with a syringe, or set the system on a balance and measure the decrease in mass as the gas is released
  - Colour change — measure the colour change during an experiment with a colorimeter
  - pH change — use a pH meter to follow the pH change during a reaction

### 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** =  $k[A]^m[B]^n$
- Directly proportional to

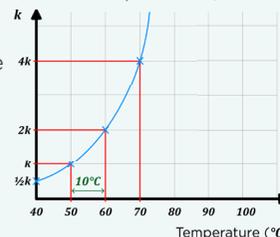
rate  $\propto [A]^x$

Concentration of A

Order of reaction with respect to A
- $k$  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.

### 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.
  - 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  $1/T$
- The activation energy can be calculated by:

$$y = mx + c$$

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

$$E_a = -\text{gradient} \times R$$

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

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

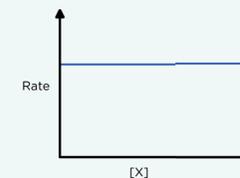
### Clock Reactions

- 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.
- To calculate the initial rate, some assumptions are made:
  - The concentration of the reactant does not change significantly over the timescale
  - The temperature is constant
  - The endpoint has not been over-estimated by observing the colour change or precipitate formed too late
- The time taken for precipitate formation can be monitored or the time taken for a distinct colour change to occur

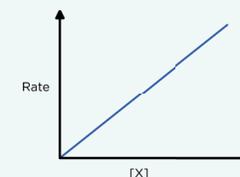
$$\text{Rate} \propto \frac{1}{\text{time}}$$

### Determination of Rate Equations

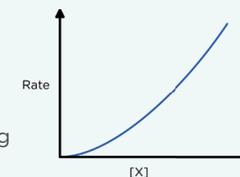
- Rate-concentration graphs allow us to easily see how the concentration of a reactant affects the rate of reaction
  - Zero order reactions



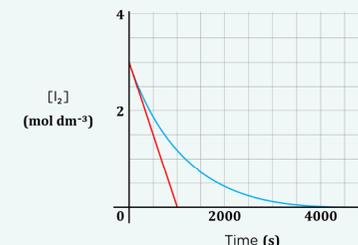
- First order reactions. The gradient is equal to the rate constant.



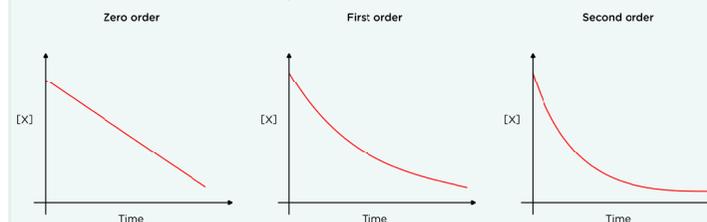
- Second order reactions



- 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.

### Partial Pressure

- Mole fractions indicate the fraction of a mixture occupied by a particular gas.

$$\text{Mole fraction, } X_A = \frac{\text{number of moles of gas A}}{\text{total number of moles of all gases}}$$

- 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  $p(A)$  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.
- $p(A) = \text{mole fraction of gas A} \times \text{total pressure}$   
 $p(A)$  partial pressure of gas A (kPa)  
 mole fraction of gas A (mol)  
 total pressure (kPa)

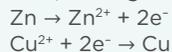
### Equilibrium Constant, $K_p$

- $K_p$  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:  
 $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$   

$$K_p = \frac{p(C)^c p(D)^d}{p(A)^a p(B)^b}$$
- 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.

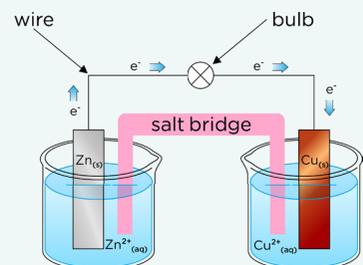
### Electrode Potentials

- Redox reactions can be used in electrochemical cells to generate electricity (a flow of charge).
- An electrochemical cell is a device capable of generating a potential difference from redox reactions
- 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.

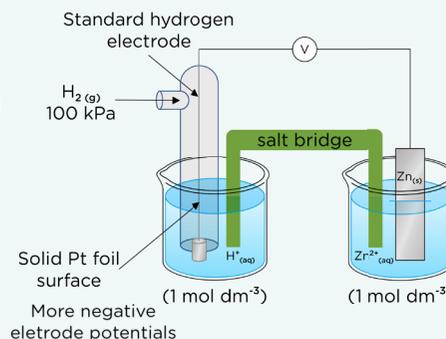


An equilibrium is reached:  
 $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$

- Each one of these beakers is a half-cell. A solution in standard half-cell will have concentration of  $1.00 \text{ mol dm}^{-3}$
- An electrode is a solid surface which allows the transfer of electrons to and from it.
- In half cells involving gases, the gas is bubbled through the liquid and an electrode provides a surface for the reaction to occur on.
- In half cells with both oxidation states present as aqueous ions, equimolar solutions of both ions are present with a platinum electrode.
- 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  $1.00 \text{ mol dm}^{-3}$ .
- $E^\theta$  gives the position of equilibrium, telling us a half-cell's tendency to accept or release electrons
- 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.



Half-Cell equation	$E^\theta/V$
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.74
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$	0.00
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\frac{1}{2}\text{I}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{I}^-(\text{aq})$	+0.54

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

### 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:

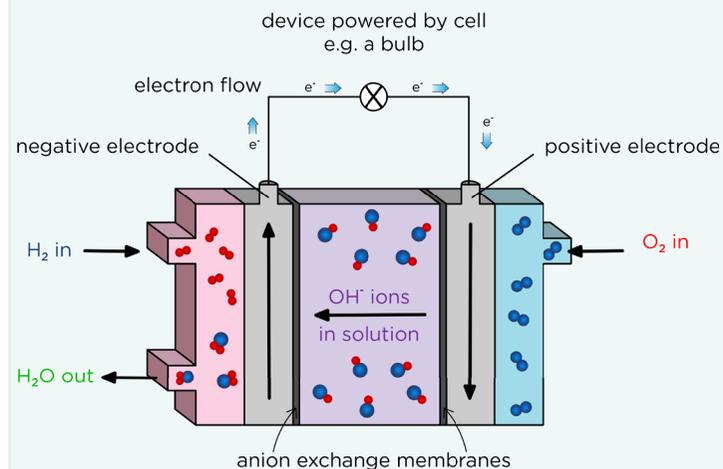
At the positive electrode:



At the negative electrode:  $\text{Li} \rightarrow \text{Li}^+ + \text{e}^- \quad E^\theta = -3.04 \text{ V}$

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

- 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:



Positive electrode:  $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$

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

Negative electrode:  $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$

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

Overall reaction:  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$

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

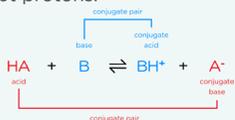
Advantages	Disadvantages
1. They are more efficient than burning fossil fuels	1. Energy is needed to build the fuel cells and produce hydrogen — this energy comes from fossil fuels
2. They release water, which isn't harmful	2. Hydrogen is highly flammable so needs to be carefully handled
3. They do not need to be recharged — they keep producing electricity for as long as they have fuel	

# ACIDS, BASES, TITRATION & BUFFERS

## CHEAT SHEET

### 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.
- Monoprotic Acids — each molecule can release one proton, e.g. HCl  
 $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
- Diprotic 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 → salt + water**
- Acid-carbonate reactions:  
**acid + carbonate → salt + carbon dioxide + water**
- Acid-metal reactions:  
**acid + metal → salt + hydrogen gas**



### Strong and Weak Acids

- When an acid is dissolved in water, an equilibrium is established:  
 $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$   
 $HA(aq) \rightleftharpoons A^-(aq) + H^+(aq)$
- This process of HA separating into  $A^-$  and  $H^+$  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.  $HA(aq) \rightleftharpoons A^-(aq) + H^+(aq)$
- 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>)  
 $[H^+]$   $H^+$  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  $H^+$  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  $H^+$  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  $pK_a$

### pH

- The concentration of  $H^+$  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  $H^+$  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  $H^+$  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  $H^+$  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:

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

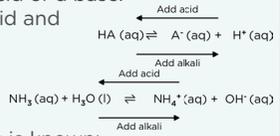
The concentration of  $H_2O$  is constant for a given temperature

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

- 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  $OH^-$  ions is equal to the concentration of the base before dissociation:  
 $[base] = [OH^-]$
  - $[H^+] = \frac{K_w}{[OH^-]}$
  - $pH = -\log_{10}[H^+]$**

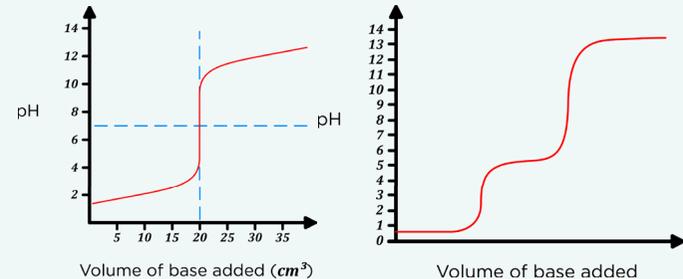
### Buffers

- 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 base and the salt of the same weak base
- The pH of a buffer solution can be calculated if the concentration of  $H^+$  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:  
 $[Salt] = [A^-]_{equilibrium}$

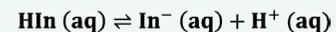


### Titrations

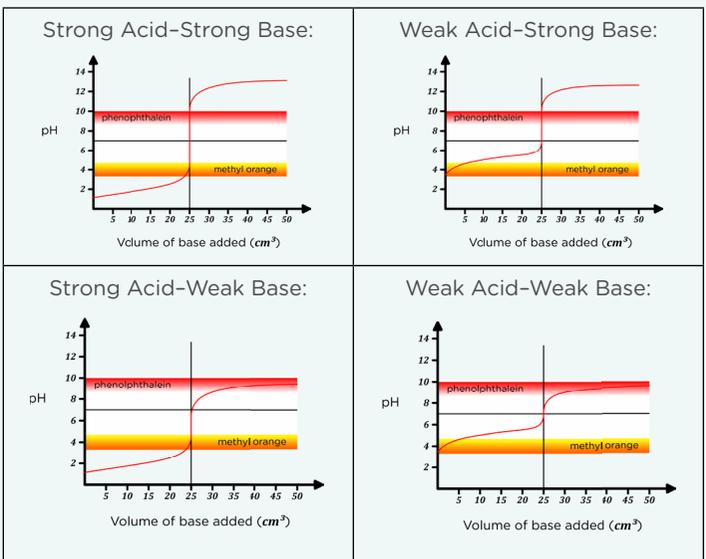
- Acid-base titrations can be used to find the concentration of a sample of either an acid or a base.
- A known concentration of an acid is gradually added to a known volume of a base of unknown concentration until the solution is neutralised
- A pH meter or an indicator can be used to monitor the pH
- 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:

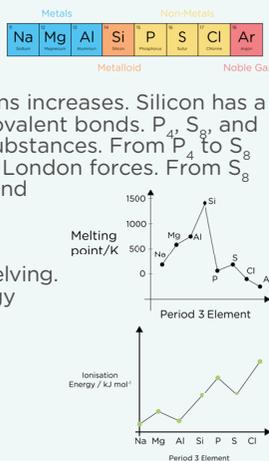


- The indicator and its conjugate base are different colours in solution. Most indicators change colour over a range of two pH units spread around their end point
- An indicator must have:
  - A sharp colour change
  - An end point close to the equivalence point
  - A clear colour change



## Period 3

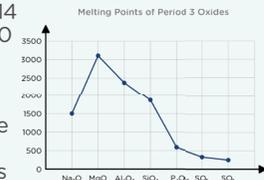
- Across period 3, the trend in melting point relates to the structure of the elements. The melting point increases from Na to Al as the ionic charge and the number of delocalised electrons increases. Silicon has a giant covalent structure with strong covalent bonds. P<sub>4</sub>, S<sub>8</sub>, and Cl<sub>2</sub> are all simple molecular covalent substances. From P<sub>4</sub> to S<sub>8</sub> there are more electrons and stronger London forces. From S<sub>8</sub> to Cl<sub>2</sub> to Ar there are fewer electrons and weaker London forces.
- Across the period, the atomic radius decreases as effective nuclear charge increases and there is no increase in shielding.
- Across the period, the ionisation energy increases as nuclear charge increases.
  - Aluminium is an exception as the 3s electrons shield the 3p electron
  - Sulfur is an exception as an electron is being removed from an p orbital containing 2 electrons, so there is electron-pair repulsion



## Properties of Period 3 Elements

- 2Na (s) + 2H<sub>2</sub>O (l) → 2NaOH (aq) + H<sub>2</sub> (g) (fast reaction)
- Mg (s) + 2H<sub>2</sub>O (l) → Mg(OH)<sub>2</sub> (aq) + H<sub>2</sub> (g) (slow reaction)
- All of the Period 3 elements can react with oxygen to form oxides to form Na<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>4</sub>O<sub>10</sub>, SO<sub>2</sub> and SO<sub>3</sub>
- Sodium burns with a yellow flame, magnesium burns with a white flame, aluminium with a brilliant white flame and sulfur with a blue flame.
- Na<sub>2</sub>O (s) + H<sub>2</sub>O (l) → 2NaOH (aq) pH 12-14
- MgO (s) + H<sub>2</sub>O (l) → Mg(OH)<sub>2</sub> (aq) pH 9-10
- These species can react in this way because they are purely ionic, so hydration can occur
- Aluminium oxide and silicon dioxide are both insoluble and do not react with water due to the strong covalent bonds
- When the non-metal oxides react with water, acidic solutions are formed.

Oxide	Bonding	Structure
Na <sub>2</sub> O	Ionic	Giant ionic
MgO	Ionic	Giant ionic
Al <sub>2</sub> O <sub>3</sub>	Ionic (with large amount of covalent character)	Giant ionic
SiO <sub>2</sub>	Covalent	Giant covalent
P <sub>4</sub> O <sub>10</sub>	Covalent	Molecular
SO <sub>2</sub>	Covalent	Molecular
SO <sub>3</sub>	Covalent	Molecular



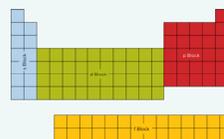
- $$P_4O_{10} (s) + 6H_2O (l) \rightarrow 4H_3PO_4 (aq)$$

$$SO_2 (g) + H_2O (l) \rightarrow H_2SO_3 (aq)$$

$$SO_3 (l) + H_2O (l) \rightarrow H_2SO_4 (aq)$$
- The basic oxides act as bases and neutralise acids:
  - Na<sub>2</sub>O (s) + 2HCl (aq) → 2NaCl (aq) + H<sub>2</sub>O (l)
  - MgO (s) + H<sub>2</sub>SO<sub>4</sub> (aq) → MgSO<sub>4</sub> (aq) + H<sub>2</sub>O (l)
- The acidic oxides act as acids and neutralise bases:
  - SiO<sub>2</sub> (s) + 2NaOH (aq) → Na<sub>2</sub>SiO<sub>3</sub> (aq) + H<sub>2</sub>O (l)
  - P<sub>4</sub>O<sub>10</sub> (s) + 12NaOH (aq) → 4Na<sub>3</sub>PO<sub>4</sub> (aq) + 6H<sub>2</sub>O (l)
  - SO<sub>2</sub> (g) + 2NaOH (aq) → Na<sub>2</sub>SO<sub>3</sub> (aq) + H<sub>2</sub>O (l)
  - SO<sub>3</sub> (l) + 2NaOH (aq) → Na<sub>2</sub>SO<sub>4</sub> (aq) + H<sub>2</sub>O (l)
- Al<sub>2</sub>O<sub>3</sub> is an amphoteric oxide and can act as either an acid or base. It neutralises both acids and bases:
  - Al<sub>2</sub>O<sub>3</sub> (s) + 3H<sub>2</sub>SO<sub>4</sub> (aq) → Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (aq) + 3H<sub>2</sub>O (l)
  - Al<sub>2</sub>O<sub>3</sub> (s) + 2NaOH (aq) + 3H<sub>2</sub>O (l) → 2NaAl(OH)<sub>4</sub> (aq)

## 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).
- 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.

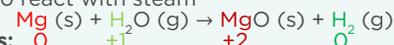


## Group 2, Alkaline Earth Metals

- 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 react with water to form hydroxides and hydrogen gas



- Oxidation numbers: Mg (+2), O (-2), H (+1)
- Magnesium can also react with steam



Oxidation numbers: Mg (+2), O (-2), H (+1)

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

- Mg(OH)<sub>2</sub> (milk of magnesia) is used to neutralise excess hydrochloric acid in the stomach, relieving indigestion
- Titanium oxide reacts with carbon and chlorine to form titanium chloride, which is purified by fractional distillation and then reduced to titanium using magnesium
- TiCl<sub>4</sub> (l) + 2Mg (s) → 2MgCl<sub>2</sub> (s) + Ti (s)
- Ca(OH)<sub>2</sub> (hydrated lime) is used to neutralise acidic soil
- CaO and CaCO<sub>3</sub> can be used to remove SO<sub>3</sub> from flue gases
- CaO (s) + 2H<sub>2</sub>O (l) + SO<sub>2</sub> (g) → CaSO<sub>3</sub> (s) + 2H<sub>2</sub>O (l)
- CaCO<sub>3</sub> (s) + 2H<sub>2</sub>O (l) + SO<sub>2</sub> (g) → CaSO<sub>3</sub> (s) + 2H<sub>2</sub>O (l) + CO<sub>2</sub> (g)

Group 2 Element	Group 2 Sulphate	Solubility of Sulphate
Mg	MgSO <sub>4</sub>	Soluble
Ca	CaSO <sub>4</sub>	Slightly soluble
Sr	SrSO <sub>4</sub>	Insoluble
Ba	BaSO <sub>4</sub>	Insoluble

- BaSO<sub>4</sub> can be ingested to visual soft tissue in imaging
- Acidified BaCl<sub>2</sub> can be used to test for the presence of sulphate ions as barium sulphate, a white precipitate, will be formed. The solution needs to be acidified to remove any sulphites or carbonates, which would result in the formation of a white precipitate
- Ba<sup>2+</sup> (aq) + SO<sub>4</sub><sup>2-</sup> (aq) → BaSO<sub>4</sub> (s)

## 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, reducing the force on electrons. So oxidising ability also decreases.
- Down the group boiling point increases, as the molecules have a greater surface area and electrons for stronger London forces
- A more reactive halogen will displace the halide ion of a less reactive halogen from solution

Halogen	Colour in Water
Chlorine	Pale green
Bromine	Orange
Iodine	Brown

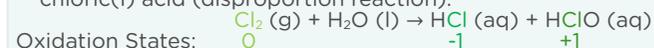
  

Halogen	Halide
F <sub>2</sub>	F <sup>-</sup>
Cl <sub>2</sub>	Cl <sup>-</sup>
Br <sub>2</sub>	Br <sup>-</sup>
I <sub>2</sub>	I <sup>-</sup>
At <sub>2</sub>	At <sup>-</sup>

- Sodium halides will react with concentrated sulphuric acid. NaX (s) + H<sub>2</sub>SO<sub>4</sub> (l) → NaHSO<sub>4</sub> (s) + HX (g)
- Halide ions react with silver nitrate solution to form a silver halide precipitate
- Dilute nitric acid removes any soluble impurities that could interfere with the test to identify halide ions

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 (disproportion reaction).



Oxidation States: Cl (0), H (+1), O (-2)

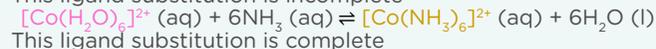
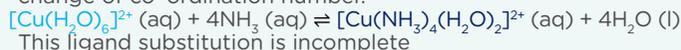
- Chloric(I) acid is an oxidising agent that kills bacteria and sanitises water
- 2Cl<sub>2</sub> (g) + 2H<sub>2</sub>O (l) → 4HCl (aq) + O<sub>2</sub> (g)
- Cl<sub>2</sub> (g) + 2NaOH (aq) → NaCl (aq) + NaClO (aq) + H<sub>2</sub>O (l)
- Sodium chlorate(I) has a bleaching action which allows it to be 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.

### General Properties of Transition Metals

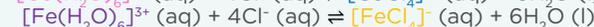
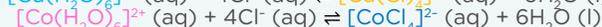
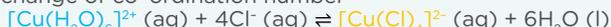
- A transition element is a d-block element which has at least one stable ion with an incomplete d-subshell
- Transition metal ions form coloured compounds because of the movement of electrons in partially filled d-orbitals. Particular wavelengths of light are absorbed, so the remaining wavelengths are the colour perceived.
- All the transition metals have more than one oxidation state.
- The highest oxidation states will readily accept electrons (be reduced), which makes them powerful oxidising agents.
- Transition metals and their compounds act as catalysts by:
  - Providing a surface for the reaction to take place
  - Binding to reactants to form intermediates
- 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
- Monodentate ligands can donate just one lone pair of electrons each and form one coordinate bond. E.g. H<sub>2</sub>O, NH<sub>3</sub> and Cl<sup>-</sup>
- The ligands NH<sub>3</sub> and H<sub>2</sub>O are similar in size and are unchanged. Therefore, exchange of a H<sub>2</sub>O ligand for a NH<sub>3</sub> occurs without change of co-ordination number.



- 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



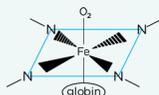
- Bidentate ligands have 2 lone pairs it can donate e.g. H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup>
- Multidentate ligands can donate multiple lone pairs of electrons from different atoms within the ligands to form multiple coordinate bonds eg EDTA<sup>4-</sup>

- Chelation is when multidentate ligands replace monodentate ligands in complexes



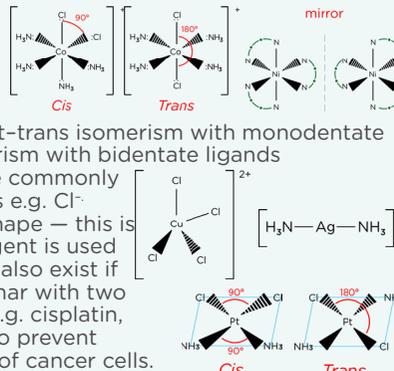
- For the reaction to be thermodynamically feasible, the Gibbs free energy change must be negative.
- The haem group in haemoglobin is a Fe(II) complex with a multidentate ligand

- 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.



### Complex Ions

- 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. Cl<sup>-</sup> [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> has a linear shape — this is formed when Tollens' reagent is used
- 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.



### 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 light is absorbed

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$\Delta E$  difference in energy (J)

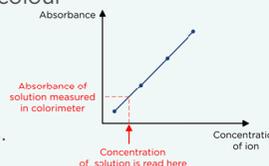
$h$  Planck's constant (Js)

$\nu$  frequency of light absorbed (s<sup>-1</sup> or Hz)

$c$  speed of light in vacuum (3.00 x 10<sup>8</sup> ms<sup>-1</sup>)

$\lambda$  wavelength of light absorbed (m)

- Changes in oxidation state, co-ordination number and ligand alter  $\Delta E$  and this leads to a change in colour
- A simple colorimeter can be used to calculate the concentration of transition metal ions in solution
- The wavelength of visible light absorbed can also be used to spectroscopy for identification of ions.



### Reactions of Ions in Aqueous Solution

- In aqueous solution, the following metal-aqua ions are formed:
  - [M(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> when M = Fe or Cu
  - [M(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> when M = Al or Fe
- The acidity of [M(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> is greater than that of [M(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. This is because M<sup>3+</sup> ions are smaller and have a higher charge, so the electrons from the oxygen atoms of the water ligands are more strongly attracted to the M<sup>3+</sup> ions. This weakens the O-H bonds in the water ligands, meaning H<sup>+</sup> ions are more easily lost
- Aluminium hydroxide shows amphoteric character by dissolving in both acids and bases
 
$$\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3(\text{s}) + 3\text{HCl}(\text{aq}) \rightarrow [\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3\text{Cl}^-(\text{aq})$$

$$\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow [\text{Al}(\text{OH})_4]^{-}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$

### 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
- Reduction from V(V) to V(IV)**  

$$2\text{VO}_2^+(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{Zn}(\text{s}) \rightarrow 2\text{VO}^{2+}(\text{aq}) + \text{Zn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$$
- Reduction from V(IV) to V(III)**  

$$2\text{VO}^{2+}(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{Zn}(\text{s}) \rightarrow 2\text{V}^{3+}(\text{aq}) + \text{Zn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$$
- Reduction from V(III) to V(II)**  

$$2\text{V}^{3+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{V}^{2+}(\text{aq})$$
- Electrode potentials for a transition metal ion changing from a higher to a lower oxidation state gives the thermodynamic feasibility of the reduction.
  - redox potentials are influenced by pH and by the ligand. Redox potentials are larger in more acidic solutions as it is easier to reduce the ion
  - redox titrations can be carried out to show how much oxidising agent is needed to react exactly with a reducing agent.
  - 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



### Catalysts

- Transition metals and their compounds can act as heterogeneous and homogeneous catalysts
- Heterogeneous catalysts are spread onto a support medium to maximise their surface area and minimise the cost
- Heterogeneous catalysts can become poisoned by impurities that block the active sites and consequently have reduced efficiency. They can be expensive to replace.
- in the Contact process V<sub>2</sub>O<sub>5</sub> acts as a heterogeneous catalyst
 
$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$$
  - Sulphur dioxide adsorbs onto vanadium(V) oxide
  - V<sub>2</sub>O<sub>5</sub>(s) + SO<sub>2</sub>(g) → V<sub>2</sub>O<sub>4</sub>(s) + SO<sub>3</sub>(g)
  - V<sub>2</sub>O<sub>4</sub>(s) + 1/2O<sub>2</sub>(g) → V<sub>2</sub>O<sub>5</sub>(s)
  - Desorption
- The reaction between the persulphate ion (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) and the iodide ion is catalysed by the homogenous catalyst Fe<sup>2+</sup>.
 
$$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$$
  - S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq) + 2Fe<sup>2+</sup>(aq) → 2SO<sub>4</sub><sup>2-</sup>(aq) + 2Fe<sup>3+</sup>(aq)
  - 2I<sup>-</sup>(aq) + 2Fe<sup>3+</sup>(aq) → I<sub>2</sub>(aq) + 2Fe<sup>2+</sup>(aq)
- The reaction between ethanedioate ions and potassium manganate(VII) which is catalysed by Mn<sup>2+</sup> (autocatalysis).
 
$$2\text{MnO}_4^-(\text{aq}) + 5\text{C}_2\text{O}_4^{2-}(\text{aq}) + 16\text{H}^+(\text{aq}) \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 10\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l})$$
  - 2MnO<sub>4</sub><sup>-</sup>(aq) + 16H<sup>+</sup>(aq) + 8Mn<sup>2+</sup>(aq) → 8H<sub>2</sub>O(l) + 10Mn<sup>3+</sup>(aq)
  - 5C<sub>2</sub>O<sub>4</sub><sup>2-</sup>(aq) + 10Mn<sup>3+</sup>(aq) → 10CO<sub>2</sub>(g) + 10Mn<sup>2+</sup>(aq)

### Precipitate Reactions of Transition Metals

- A precipitate reaction is when two solutions containing soluble ions are mixed, forming an insoluble compound
- Reaction of metal ions with carbonate:
  - With aqueous  $M^{3+}$  ions, the carbonate will behave as a base by removing protons from the water, forming a hydroxide precipitate:  $2[M(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow 2M(OH)_3(H_2O)_3(s) + 3CO_2(g) + 3H_2O(l)$
  - Aqueous  $M^{2+}$  ions aren't acidic enough, so form a solid metal (II) carbonate instead of  $H_3O^+$ .  $[M(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MCO_3(s) + 6H_2O(l)$
- Reaction of metal ions with hydroxides:

Metal-aqua ion	Reaction with $OH^-$ (aq)	Reaction with $NH_3$ (aq)
$M^{2+}$ (aq)	$[M(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow [M(OH)_2(H_2O)_4](s) + 2H_2O(l)$	$[M(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightarrow [M(OH)_2(H_2O)_4](s) + 2NH_4^+(aq)$
$M^{3+}$ (aq)	$[M(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightarrow M^{3+}(OH)_3(H_2O)_3(s) + 3H_2O(l)$	$[M(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \rightarrow [M(OH)_3(H_2O)_3](s) + 3NH_4^+(aq)$

Metal-aqua ion	Dropwise $OH^-/NH_3$	Excess $OH^-$	Excess $NH_3$	$CO_3^{2-}$
$[Fe(H_2O)_6]^{2+}$ (aq) Pale green solution	$[Fe(H_2O)_4(OH)_2]$ Green ppt*	$[Fe(H_2O)_4(OH)_2]$ Green ppt*	$[Fe(H_2O)_4(OH)_2]$ Green ppt*	$FeCO_3$ Green ppt
$[Cu(H_2O)_6]^{2+}$ (aq) Pale blue solution	$[Cu(H_2O)_4(OH)_2]$ Pale blue ppt	$[Cu(H_2O)_4(OH)_2]$ Pale blue ppt	$[Cu(H_2O)_2(NH_3)_4]^{2+}$ Deep blue solution	$CuCO_3$ Blue-green ppt
$[Fe(H_2O)_6]^{3+}$ (aq) Purple/yellow/brown solution	$[Fe(H_2O)_3(OH)_3]$ Brown ppt	$[Fe(H_2O)_3(OH)_3]$ Brown ppt	$[Fe(H_2O)_3(OH)_3]$ Brown ppt	$[Fe(H_2O)_3(OH)_3]$ Brown ppt and bubbles of $CO_2$
$[Al(H_2O)_6]^{3+}$ (aq) Colourless solution	$[Al(H_2O)_3(OH)_3]$ White ppt	$[Al(OH)_4]^-$ Colourless solution	$[Al(H_2O)_3(OH)_3]$ White ppt	$[Al(H_2O)_3(OH)_3]$ White ppt and bubbles of $CO_2$

- $Fe^{2+}$  eventually oxidised by air to  $Fe^{3+}$  making brown  $[Fe(H_2O)_3(OH)_3](s)$

### 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.

### Nomenclature

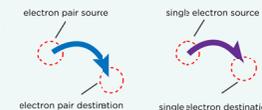
- Hydrocarbons can be:
  - Aliphatic — carbon atoms form straight or branched chains
  - Alicyclic — carbon atoms form a ring
  - Aromatic — carbon atoms form a ring and have a delocalised electron system
- Homologous series are compounds with the same functional group and similar chemical and physical 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

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

Compound	Prefix	Suffix
Alkanes	-	-ane
Alkenes	-	-ene
Alcohols	Hydroxy-	-ol
Carboxylic Acids	-	-oic acid
Haloalkanes	Fluoro- Chloro- Bromo- Iodo-	-
Aldehydes	-	-al
Ketones	-	-one

### Reaction Mechanisms

- Bond fission can be homolytic or heterolytic



#### 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.

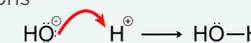
- Bonds are formed on the collision of:
  - Two free radicals with unpaired electrons
  - Oppositely charged ions

#### Heterolytic Fission

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

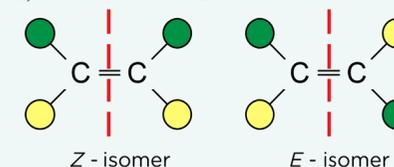


This results in the formation of a positively charged cation and a negatively charged anion.



### 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
  - Chain isomers — These are molecules with the same molecular formula but a different arrangement of the carbon chain. Chains can be straight or branched
  - Position isomers — These are molecules with the same functional group attached to a different position on the carbon chain
  - Functional group isomers — These are molecules with the same molecular formula but different functional groups
- 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

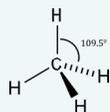


# ALKANES & HALOGENOALKANES

## CHEAT SHEET

### Alkanes

- Alkanes are a homologous series made up of saturated hydrocarbons with the general formula  $C_nH_{2n+2}$ .
- Carbon atoms have four electrons in their outer shell. Therefore, each carbon atom can form four covalent bonds
- 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.
- The more branched the molecules are, the smaller the surface area for contact between molecules and the weaker the London forces resulting in lower boiling points



### Fractional Distillation

- Crude oil is a fossil fuel formed from the breakdown of plant and animal remains that have been subjected to high pressure over millions of years. It is composed mainly of alkanes.
- Fractional distillation will separate crude oil into different fractions
- A fraction is a group of hydrocarbons that have a similar boiling point
- The crude oil is vaporised in a furnace and passed into the bottom of a fractionating column
- In the column, there is a temperature gradient where it is hotter at the bottom and cooler at the top
- The vapour passes up the column and the different fractions will condense at different heights onto trays. Longer hydrocarbons have higher boiling points, so condense lower down

### 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.
 
$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$
- In incomplete combustion, the alkane burns with a dirty yellow flame. It can produce carbon, carbon monoxide and unburned hydrocarbons as products.
 
$$CH_4(g) + O_2(g) \rightarrow C(s) + 2H_2O(g)$$

$$CH_4(g) + 1.5O_2(g) \rightarrow CO(g) + 2H_2O(g)$$
- Sulfur-containing alkenes can produce sulphur dioxide during combustion that dissolves in rainwater to cause acid rain.
- Sulfur dioxide can be removed from flue gases using calcium oxide or calcium carbonate
 
$$CaO(s) + 2H_2O(l) + SO_2(g) \rightarrow CaSO_3(s) + 2H_2O(l)$$

$$CaCO_3(s) + 2H_2O(l) + SO_2(g) \rightarrow CaSO_3(s) + 2H_2O(l) + CO_2(g)$$
- Combusting nitrogen-containing alkanes will form nitrogen oxides, which contribute to acid rain and photochemical smog.
- Catalytic converters can remove gaseous pollutants from internal combustion engines by using precious metals spread over a mesh to form less harmful products such as  $N_2$ ,  $CO_2$ , and  $H_2O$ .

### Cracking

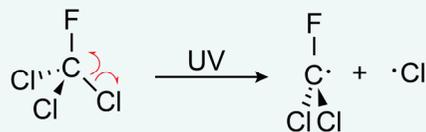
- Cracking converts longer chain hydrocarbons to more economically valuable shorter chain hydrocarbons
- Cracking involves breaking C-C bonds in alkanes
- In thermal cracking, alkanes are heated to high temperatures under high pressures. C-C bonds break homolytically and free radicals are formed. These react to form shorter chain hydrocarbons including at least one alkene. It produces a high proportion of alkenes.
- In catalytic cracking, alkanes are heated to lower temperatures under lower pressures passed over a zeolite catalyst consisting of silicon dioxide and aluminium oxide. This method is used mainly to produce motor fuels (branched & cycloalkanes) and aromatic compounds.

### Chlorination of Alkanes

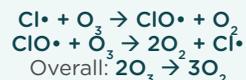
- Alkanes react with the halogens, specifically chlorine and bromine, in the presence of UV light to form haloalkanes
- Methane reacts with chlorine to form chloromethane and hydrogen chloride:  $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
- This reaction is a free radical substitution with the steps:
  - Initiation — free radicals are formed when exposed to UV  $Cl_2 \rightarrow 2Cl\cdot$
  - Propagation — free radicals are used up and created in a chain reaction  $Cl\cdot + CH_4 \rightarrow \cdot CH_3 + HCl$   
 $\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot$
  - Termination — free radicals are removed.  
 $2Cl\cdot \rightarrow Cl_2$   
 $2\cdot CH_3 \rightarrow C_2H_6$   
 $\cdot CH_3 + Cl\cdot \rightarrow CH_3Cl$

### Ozone Depletion

- In the Earth's atmosphere, there is a layer of ozone ( $O_3$ ) 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



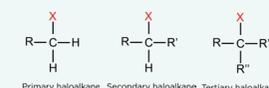
- The chlorine radicals produced catalyse the decomposition of ozone



- 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

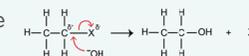
### Halogenoalkanes

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

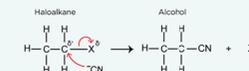


- The C-X bond has a permanent dipole due to the large difference in electronegativity between the carbon and halogen atoms. With the electrons closer to the halogen atom.
- The  $\delta^-$  on the carbon atom makes it easily attacked by electron-rich nucleophiles (an electron pair donor that is attracted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

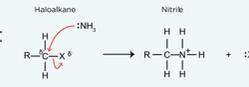
- Nucleophilic substitution with hydroxide ions:



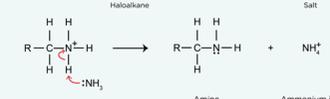
- Nucleophilic substitution with cyanide ions:



- Nucleophilic substitution with ammonia:

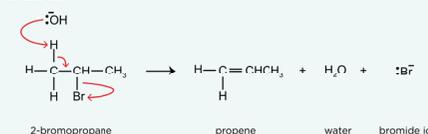


if ammonia is used in excess:



- 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
- When a haloalkane is reacted with hydroxide ions under different conditions, an elimination reaction occurs, as the hydroxide ions act as a base.

- 2-bromopropane reacts with potassium hydroxide to form propene, water, and a bromide ion:



- Major and minor products can form. The major product has more substituted double bonds



- When haloalkanes react with  $OH^-$  ions, there are two possibilities: substitution or elimination. Dependent on conditions used

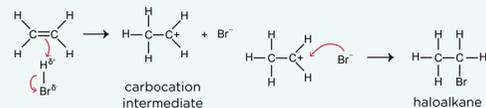
Substitution	Elimination
<ul style="list-style-type: none"> <li>Aqueous ethanol as a solvent</li> <li>Aqueous hydroxide</li> <li>Mixture must be warmed</li> </ul>	<ul style="list-style-type: none"> <li>Ethanol (anhydrous) as solvent</li> <li>Anhydrous conditions</li> <li>High temperature — heat under reflux</li> </ul>

### Alkenes

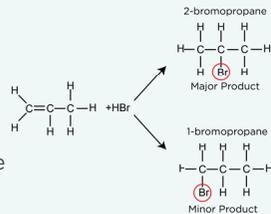
- Alkenes are a homologous series made up of unsaturated hydrocarbons containing at least one C=C double bond, with the general formula  $C_nH_{2n}$ .
- C-H — these are  $\sigma$ -bonds formed due to the direct overlap of the electron clouds belonging to each carbon atom
- C=C — these contain both a  $\sigma$ -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
- Alkenes have a trigonal planar shape with a bond angle of  $120^\circ$ .

### Addition Reactions of Alkenes

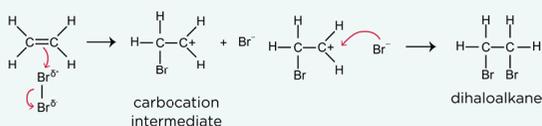
- An electrophile is an electron pair acceptor attracted to areas of high electron density
- Electrophilic addition with HBr



- 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.

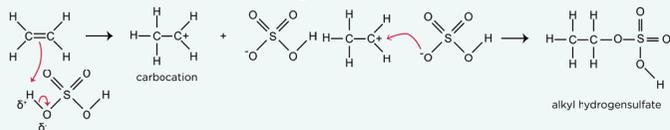


- Electrophilic addition with  $Br_2$ . A dipole is induced in the halogen molecule by the high electron density of the C=C
- Bromine water acts as a test for unsaturation. An unsaturated

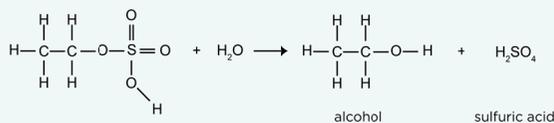


compound will decolourise the bromine water, as a dihaloalkane will form, using up the bromine

- Electrophilic addition with  $H_2SO_4$

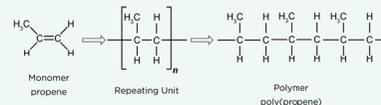


If water is added, an alcohol will reform:



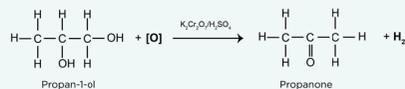
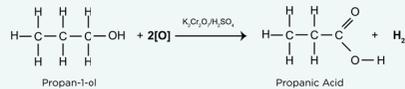
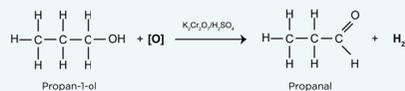
### Addition Polymers

- Addition polymers are macromolecules made from small repeating units of monomers
- They are formed from alkenes and substituted alkenes
- Addition polymers are often called poly(alkenes)
- Addition polymers are unreactive as the main carbon chain is saturated and non-polar, with only weak London forces between the chains
- Plastics can be modified using plasticisers, which force the polymer chains apart to reduce London forces and make the polymer more flexible.



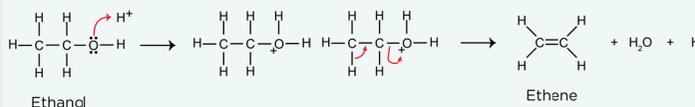
### Oxidation of Alcohols

- Alcohols are a homologous series of saturated organic compounds with the general formula  $C_nH_{2n+1}OH$ .
- Alcohols can form hydrogen bonds in water, making them soluble.
- Primary alcohols can be oxidised to aldehydes. Conditions: gentle heating. Oxidising agent and immediate distillation
- Primary alcohols can be further oxidised to carboxylic acids. Conditions: heat under reflux, no distillation, oxidising agent.
- Secondary alcohols can be oxidised to ketones. Conditions: heat under reflux and oxidising agent.
- 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.  $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
- Alcohols can be dehydrated to form an alkene and water, using a concentrated acid catalyst and heating under reflux e.g.



- The alkenes produced can be used to form addition polymers without using monomers derived from crude oil.

### Alcohol Production

- Ethanol is produced industrially by fermentation of glucose using yeast undergoing anaerobic respiration.  $C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$
- The conditions required are  $35^\circ C$ , anaerobic conditions and less than 15% ethanol solution, for optimum enzyme function.
- Ethanol can be distilled from the reaction mixture using fractional distillation to increase its purity.
- The ethanol produced can be used as a biofuel, which is a fuel produced from renewable sources.

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>Basic equipment needed</li> <li>The sugar used is renewable</li> <li>Carbon-neutral (in theory)</li> <li>Increased income for farmers</li> </ul>	<ul style="list-style-type: none"> <li>Slow rate of reaction</li> <li>Ethanol not pure</li> <li>Batch process — high production costs</li> <li>Land used to grow crops could be used to grow food</li> </ul>

- The carbon dioxide that is released upon combustion and fermentation is balanced by the carbon dioxide absorbed during the photosynthesis. (carbon neutral)

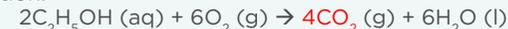
Photosynthesis:



Fermentation:

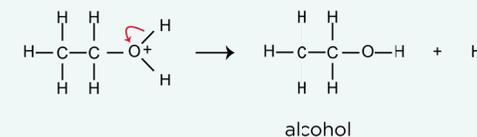
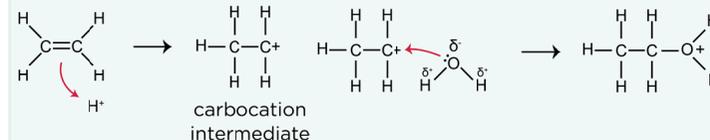


Combustion:



However, there is  $CO_2$  emission during fuel transportation.

- Ethene, derived from crude oil, can be used to produce ethanol through hydration in the presence of an acid catalyst  $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$



Advantages	Disadvantages
<ul style="list-style-type: none"> <li>Fast rate of reaction</li> <li>Ethanol produced is pure</li> <li>Continuous process — low production costs</li> </ul>	<ul style="list-style-type: none"> <li>Advanced equipment needed</li> <li>Ethene used is non-renewable</li> <li>High pressure means high energy costs</li> </ul>

### Test Tube Reactions

- The presence of alkenes can be tested by adding a few drops of bromine water and shaking. Bromine water will go from orange to colourless if alkenes are present, due to addition of bromine across the double bond.
- The presence of haloalkanes can be tested by adding dilute nitric acid and adding silver nitrate. A coloured precipitate is formed.  $\text{Ag}^+_{(\text{aq})} + \text{X}^-_{(\text{sq})} \rightarrow \text{AgX}_{(\text{s})}$

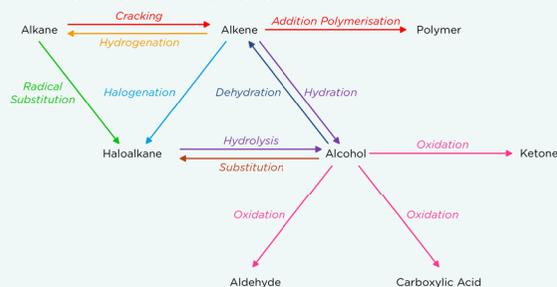
Silver Halide	Colour	Haloalkane Present
Silver Chloride	White Precipitate	Chloroalkane
Silver Bromide	<b>Cream</b> Precipitate	Bromoalkane
Silver Iodide	<b>Yellow</b> Precipitate	Iodoalkane

- Ketones and aldehydes can be distinguished by using Tollens' reagent or Fehling's solution
  - Tollens' reagent is made by dilute sodium hydroxide solution to a colourless silver nitrate solution, forming a light brown precipitate. Then dilute ammonia solution is added to dissolve the brown precipitate, forming a colourless solution. Warming the sample with Tollens' reagent will form a silver mirror if an aldehyde is present.
  - Warming the sample with Fehling's solution will turn the solution from blue to a dark red precipitate if an aldehyde is present
- The presence of carboxylic acids can be tested by adding a metal carbonate. If present,  $\text{CO}_2$  will be formed, which turns limewater cloudy.

**metal carbonate + acid  $\rightarrow$  salt + carbon dioxide + water**

- The presence of alcohols can be tested by the addition of acidified potassium dichromate(VI). If a primary or secondary alcohol is present, the orange solution will turn green.

### Synthetic Routes

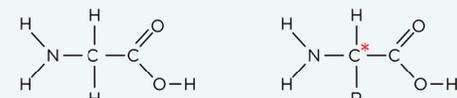
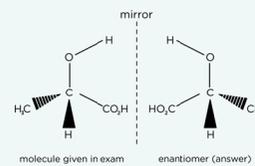


### Mass Spectrometry

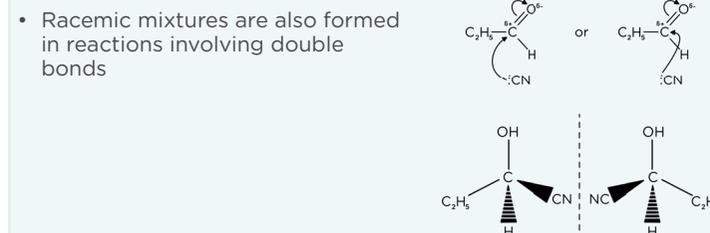
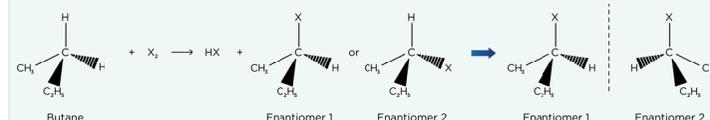
- A molecular ion ( $\text{M}^+$ ) is formed when molecules in a sample are ionised. This can be done using two methods:
  - Electron-impact ionisation — the sample is vaporised and bombarded with high energy electrons and an electron is removed
  - Electrospray ionisation
- The molecular ion peak (the 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

### Optical Isomerism

- Optical isomers/enantiomers 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).
- All amino acids except glycine have a chiral centre



- 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
- Racemic mixtures are formed when two achiral molecules react

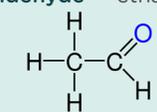
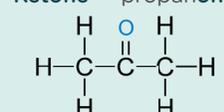


### Infrared Spectrometry

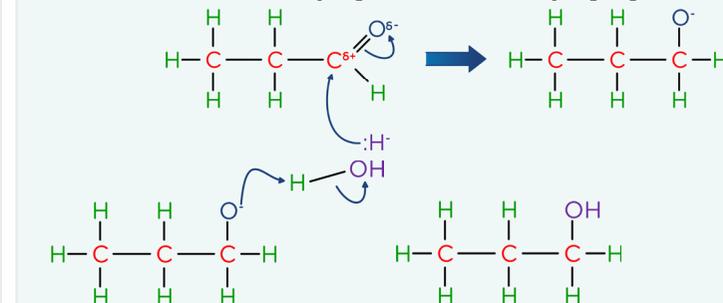
- A chemical bond constantly vibrates and can absorb infrared radiation at characteristic wavenumbers
- Particular bonds, and therefore functional groups, can be identified by looking at the frequencies absorbed in an infrared spectrum.
- The fingerprint region is the region of an infrared spectrum below  $1500 \text{ cm}^{-1}$ .
- The fingerprint region is largely unique to a specific molecule and allows identification of a molecule by comparison to a database of compounds.
- 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.
- Infrared spectroscopy can also be used to identify impurities. Extra peaks in an infrared spectrum indicate that the sample is not pure.

### Aldehyde & Ketones

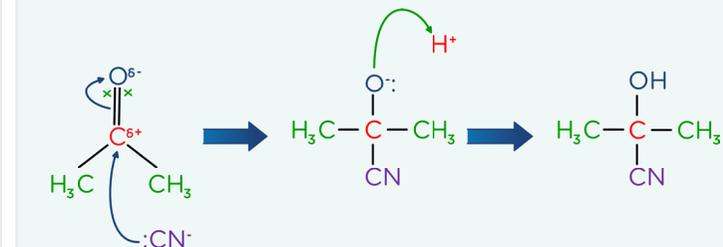
- Aldehydes and ketones are carbonyl compounds containing the  $\text{C}=\text{O}$  functional group.

Aldehyde — ethanal	Ketone — propanone
	
<ul style="list-style-type: none"> <li>Carbonyl group at the end of the carbon chain</li> <li>Suffix -al</li> <li>Functional group is -CHO</li> </ul>	<ul style="list-style-type: none"> <li>Carbonyl group is not at the end of the carbon chain</li> <li>Suffix -one</li> <li>Functional group is -CO</li> </ul>

- 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  $\text{NaBH}_4$  as the reducing agent e.g. reduction of propanal  $\text{CH}_3\text{CH}_2\text{CHO} + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$



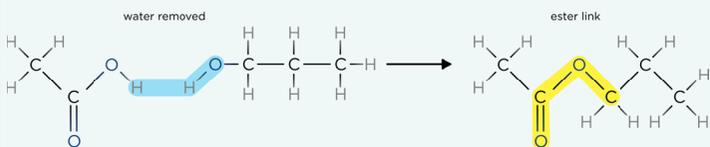
- Nucleophilic addition of cyanide ions can be used to extend the length of a carbon chain
- Reactions of carbonyls with KCN and dilute acid, produces a hydroxynitrile. Aldehydes and unsymmetrical ketones form two optical isomers, as there is an equal chance of either isomer being formed. This is a racemic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



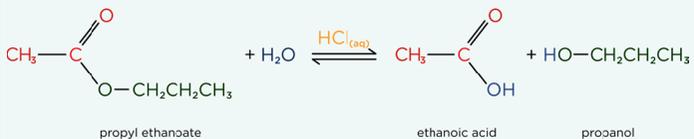
- Cyanide-containing compounds can be toxic or irritants.

## Carboxylic Acids & Esters

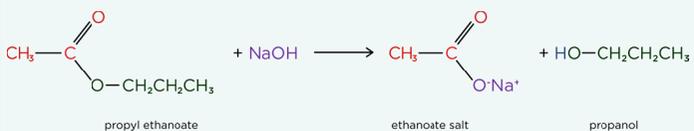
- Carboxylic acids have the functional group  $-\text{COOH}$
- Carboxylic acids partially dissociate in water, making them weak acids
- Carboxylic acids can react with carbonates to liberate  $\text{CO}_2$ .  
 $2\text{CH}_3\text{COOH}(\text{aq}) + \text{Na}_2\text{CO}_3(\text{s}) \rightarrow 2\text{CH}_3\text{COO}^-\text{Na}^+(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- Esters have the general formula  $\text{RCOOR}'$ .
- 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



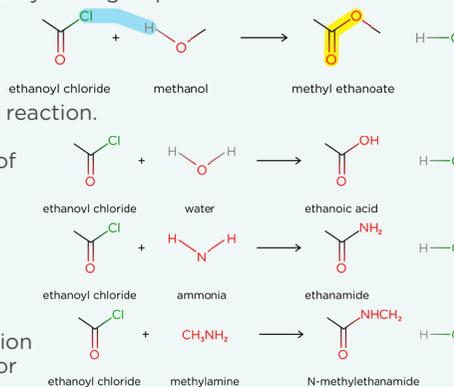
- Base catalysed hydrolysis of ester forms a carboxylate salt and an alcohol



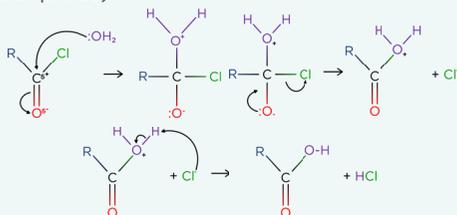
- Vegetable oils and animal fats are esters of propane-1,2,3-triol (glycerol). Animal fats are saturated while vegetable fats are unsaturated. The kink caused by the double bond reduces London forces.
- Vegetable oils and animal fats can be hydrolysed in alkaline conditions to give soap (salts of long-chain carboxylic acids) and glycerol with methanol and a strong alkaline catalyst
- Biodiesel is a mixture of methyl esters it can be made by reacting vegetable oils

## Acylation

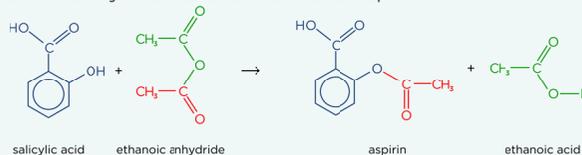
- Acyl chlorides are a derivative of carboxylic acids, where the  $-\text{OH}$  group is replaced by a  $-\text{Cl}$  group
- Acyl chlorides react with alcohols to form esters in a nucleophilic addition-elimination reaction.
- Acyl chlorides will react with a variety of nucleophiles



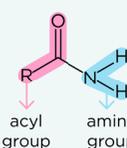
- Mechanism for reaction with water (similar for other nucleophiles):

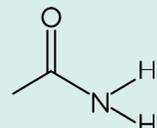
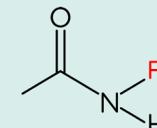
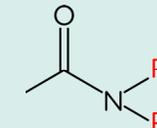


- An acid anhydride has the structure of a double ester that shares an oxygen atom
- Ethanoic anhydride is used to make aspirin.



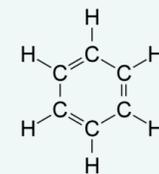
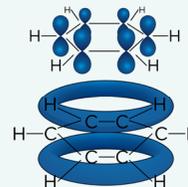
- The advantages of using ethanoic anhydride rather than ethanoyl chloride is that: it's cheaper, less corrosive, safer, produces a less toxic by-product and does not react with water readily.
- Amides structure:



Primary Amides	Secondary Amides	Tertiary Amides
		
Formed by reacting acyl chlorides with ammonia	Formed by reacting acyl chlorides with primary amines	Formed by reacting acyl chlorides with secondary amines

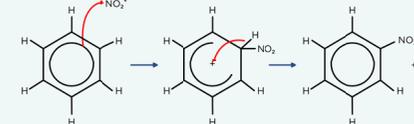
## Bonding in Benzene

- Compounds that contain a benzene ring are aromatic.
- Benzene has 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.
- Electrons are shared evenly, so all bond lengths are the same, between that of a single bond and a double bond
- The delocalisation of electrons gives benzene extra stability than the theoretical cyclohexa-1,3,5-triene molecule, which has alternating double and single bonds. This is reflected by the hydrogenation of benzene being less exothermic than predicted by cyclohexa-1,3,5-triene molecule.
- Benzene undergoes electrophilic substitution reactions rather than electrophilic additions because a lot of energy is needed to disrupt the delocalised system



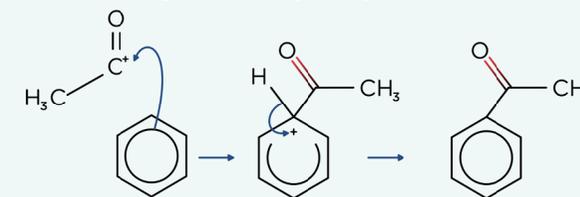
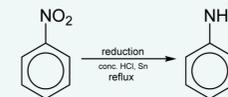
## Electrophilic Substitution of Benzene

- The benzene ring is a region of high electron density, which means it attracts electrophiles
- Nitration of benzene:  $\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$ 
  - Generation of the electrophile:  
 $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{O} + \text{NO}_2^+ + \text{HSO}_4^-$



- Regeneration of sulphuric acid catalyst:  
 $\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4$

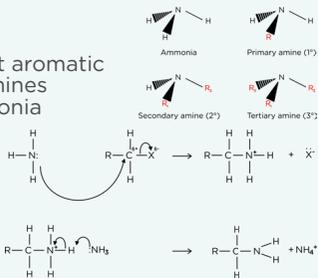
- Nitrated benzene rings can be used in the production of explosives, dyes and phenylamine.
- Friedel-Crafts acylation reactions involve adding an acyl group to benzene. e.g.  $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CO}^+ + \text{AlCl}_4^-$



A halogen carrier, such as  $\text{AlCl}_3$ , is used to convert the acyl chloride into an electrophile

### Amines

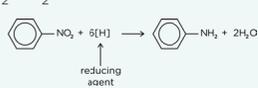
- Aliphatic amines are those without aromatic rings present. Primary aliphatic amines can be prepared by reacting ammonia with a haloalkane. X = an electronegative species e.g. Cl, Br
- Primary aliphatic amines can also be made by the reduction of nitriles using a nickel catalyst and hydrogen gas:



A reducing agent such as  $\text{LiAlH}_4$ , can be used instead of hydrogen gas:



- Aromatic amines are made by reducing nitroarenes such as nitrobenzene, refluxed at  $100^\circ\text{C}$  using a reducing agent of tin and concentrated HCl. The tin and concentrated HCl react to form hydrogen
- Aromatic amines are used in the production of dyes as they're brightly coloured

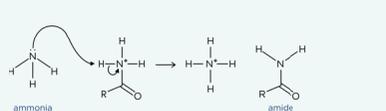
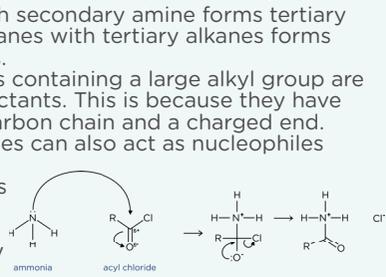
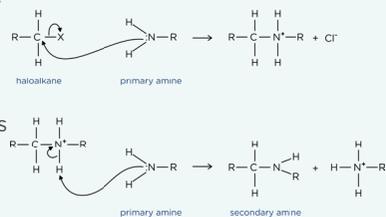


### Basic & Nucleophilic Properties of Amines

- 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.

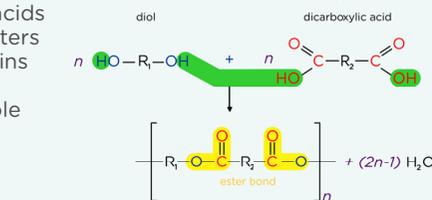


- The lone pair of electrons on the nitrogen atom in amines allows them to act as nucleophiles.
- Haloalkanes undergo nucleophilic substitution with an ammonia nucleophile to form amines. This reaction can also happen with primary amines acting as the nucleophile, using the same mechanism as ammonia, 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.

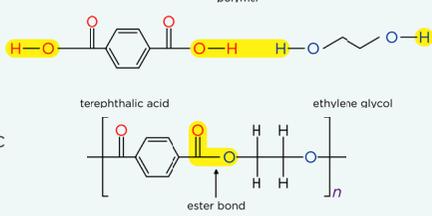


### Condensation Polymers

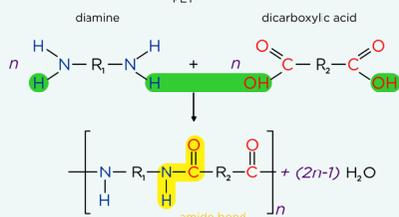
- Condensation polymerisation involves the reaction of two different types of monomers, with different functional groups.
- Reacting dicarboxylic acids with diols forms polyesters
- Adjacent polyester chains are held together by permanent dipole-dipole attractions due to the presence of the polar carbonyl group



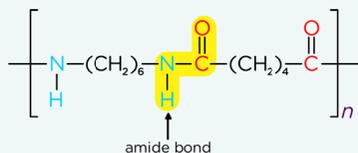
- The polyester terylene (PET) is formed from the monomers terephthalic acid and ethylene glycol. Typically used in plastic bottles, sails, sheets and clothing



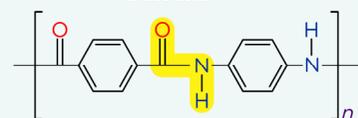
- Reacting dicarboxylic acids and diamines forms polyamides
- Adjacent polyamide strands are held together by hydrogen bonds



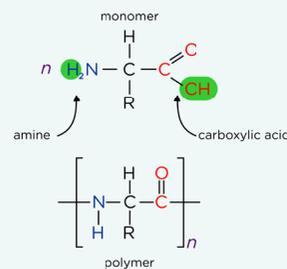
- Nylon is a polyamide used in textiles



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



- Polypeptides are also condensation polymers made up of amino acids



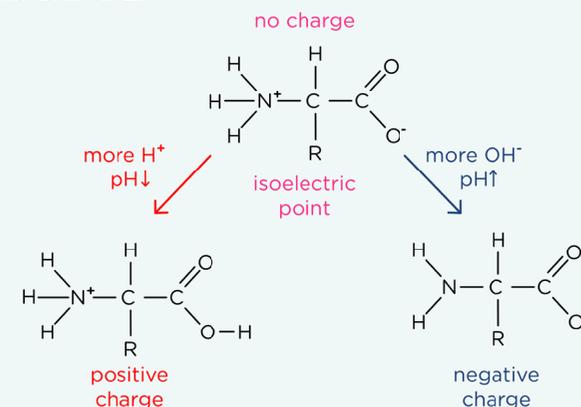
### Disposal of Polymers

- Polyalkenes are chemically inert and non-biodegradable due to the non-polar saturated C-C bonds.
- Condensation polymers can undergo hydrolysis due to the polar C=O bonds which make them susceptible to attacks by nucleophiles. This makes them biodegradable.
- Advantages and disadvantages of different methods of disposal

Advantages of Recycling	Disadvantages of Recycling
<ul style="list-style-type: none"> <li>Saves diminishing crude oil resources</li> <li>Energy input to refining oil not needed</li> <li>Plastic does not end up in landfill</li> </ul>	<ul style="list-style-type: none"> <li>Plastic must be collected, cleaned, transported and sorted which is expensive and requires energy and time</li> <li>There are concerns about the quality of the products</li> </ul>
Landfill	Incineration
<ul style="list-style-type: none"> <li>A cheap and easy method</li> <li>Damaging to wildlife</li> <li>Uses up large areas of land</li> <li>Methane is released which contributes to global warming</li> <li>Leaks from landfill sites contaminate water supplies</li> </ul>	<ul style="list-style-type: none"> <li>The heat used in incineration can be used to generate electricity</li> <li>Increases the level of carbon dioxide in the atmosphere</li> <li>Incomplete combustion can lead to toxic carbon monoxide or unburnt carbon (soot) being released</li> <li>Other toxic gases, such as styrene and HCl, can be released</li> </ul>

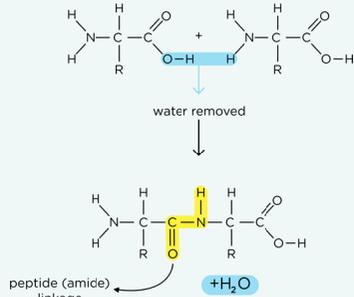
### Amino Acids

- $\alpha$ -amino acids contain both the amine functional group and the carboxylic acid functional group (carboxyl group) attached to the same carbon atom.
- 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

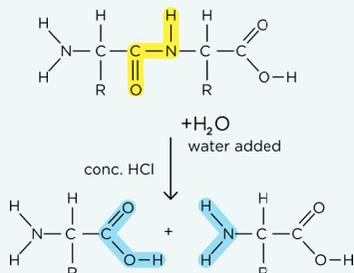


## Proteins

- Proteins are sequences of amino acids joined by peptide links
- Peptide linkages are formed from condensation reactions

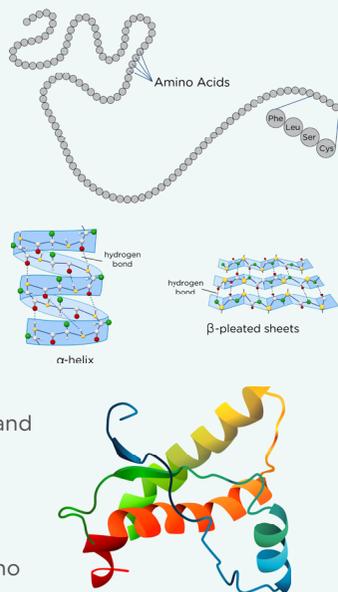


- Hydrolysis of the peptide link produces the constituent amino acids



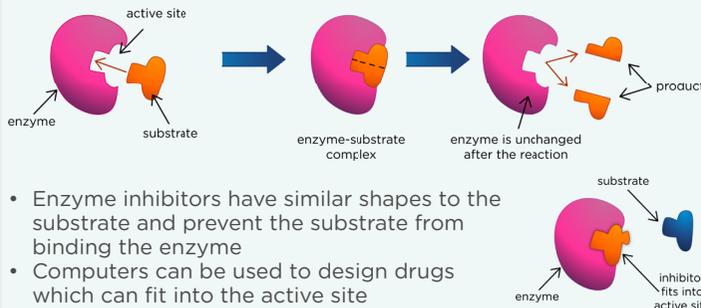
- There are three levels of protein structure: primary, secondary and tertiary

- Primary structure is the sequence of amino acids in the polypeptide chain.
- Secondary structure is the way the chains of amino acids interact with each other to form either an  $\alpha$ -helix or a  $\beta$ -pleated sheet.
- Tertiary structure is the three-dimensional shape into which the  $\alpha$ -helix or  $\beta$ -pleated sheet is folded.
- The secondary and tertiary structures are a consequence of various types of intermolecular forces
  - Hydrogen bonds — these stabilise both the secondary and tertiary structures
  - London and dipole-dipole forces — these stabilise the tertiary structure
  - Disulphide bonds — these are only important when the amino acid cysteine is part of the protein in the tertiary structure



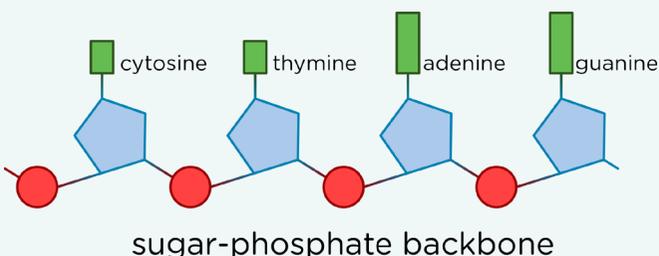
## Enzymes

- An enzyme is a protein-based biological catalyst.
- Every enzyme has an active site, which is a part of the three-dimensional tertiary protein structure of an enzyme that is responsible for its catalytic activity
- The lock and key theory of enzyme activity states that the substrate must fit exactly in the active site, with the correct orientation, in order for a reaction to happen. The wrong stereoisomer is not catalysed (stereospecific).



## Deoxyribonucleic Acid (DNA)

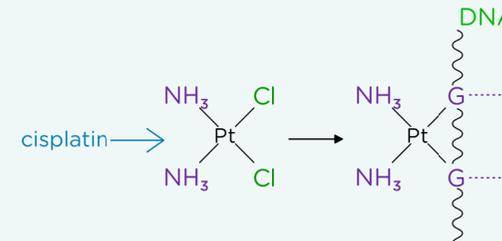
- DNA is made up of nucleotide monomers: a phosphate group, 2-deoxyribose pentose sugar and a base. The base can be adenine, cytosine, guanine or thymine.
- A strand of DNA is a polymer of nucleotides linked by phosphodiester bonds between the phosphate group of one nucleotide and the 2-deoxyribose of another nucleotide. Resulting in a sugar-phosphate backbone.



- The DNA double helix is composed of two complementary DNA strands held together by hydrogen bonds between complementary base pairs
  - Adenine and thymine form two hydrogen bonds
  - Cytosine and guanine form three hydrogen bonds

## Anticancer Drugs

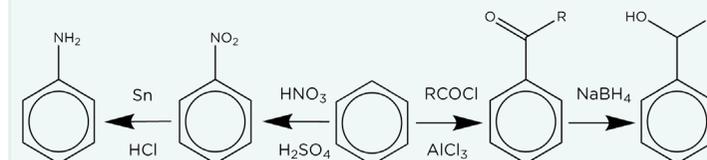
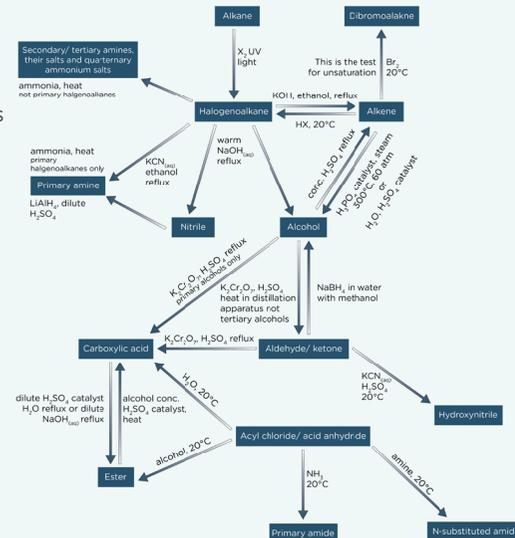
- The Pt (II) complex cisplatin is used as an anticancer drug. It prevents DNA replication in cancer cells by a ligand replacement reaction with DNA in which a bond is formed between platinum and a nitrogen atom on adjacent guanines



- The DNA strands are then kinked, so they cannot unravel properly to replicate
- Cisplatin can have adverse side effects because it also binds to healthy cells. However, it is still used as a treatment because the advantages outweigh the disadvantages

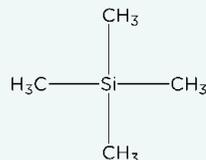
## Organic Synthesis

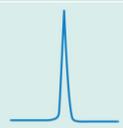
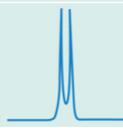
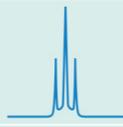
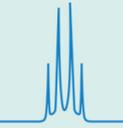
- Chemists avoid using solvents and aim to use non-hazardous starting materials to reduce the potential for accidents and environmental damage and the amount of waste.
- Chemists aim to design production methods with fewer steps that have a high percentage atom economy to reduce waste and convert more of the reactants to products.



### Nuclear Magnetic Resonance (NMR) Spectroscopy

- NMR gives information about the position of  $^{13}\text{C}$  or  $^1\text{H}$  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 which relates to the difference in frequency between a chemical environment and TMS. It depends on the molecular environment.
- The number of peaks in  $^{13}\text{C}$  NMR represents the number of carbon environments in a molecule
- Each peak in a  $^1\text{H}$  NMR spectrum has an integration trace. This shows the relative number of  $^1\text{H}$  in each  $^1\text{H}$  environment
- High resolution  $^1\text{H}$  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  $^1\text{H}$  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  $\text{CDCl}_3$  ie deuterated solvents.
- In deuterated solvents, any H atoms are replaced with deuterium. They do not affect the spectra

### Chromatography

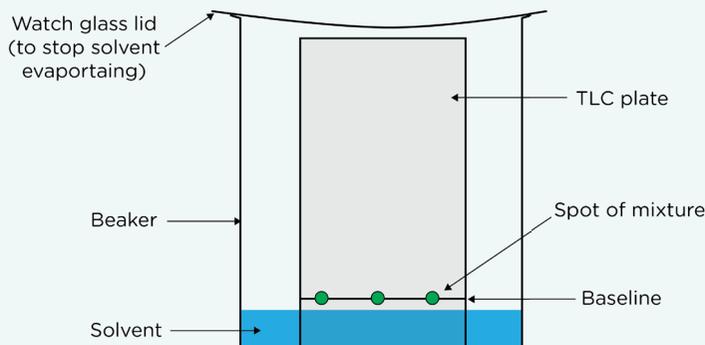
- Chromatography is a separation technique used for separating and identifying the species present in a mixture.
- The mobile phase is the substance in chromatography that carries the soluble components of the mixture
- The stationary phase is the substance in chromatography that holds back the components 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 and a solvent 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 amino acids by their  $R_f$  values.

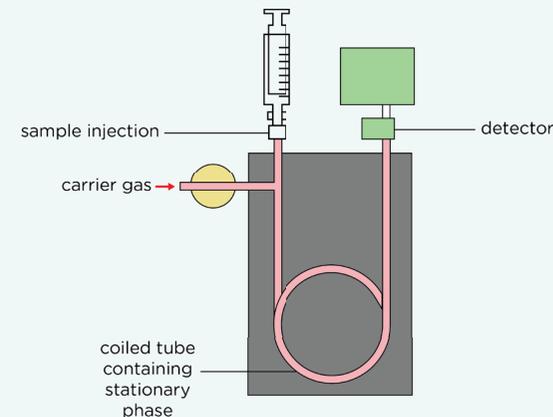
$$R_f = \frac{\text{distance moved by spot}}{\text{distance moved by solvent}}$$

- Different amino acids have different R groups, so they all have different affinities for the solvent. Therefore, moving up the plate at different rates depending on their affinity.
- Amino acids are colourless, so to make them visible a developing agent is used, such as ninhydrin or ultraviolet light
- $R_f$  values are affected by temperature, a spot of a pure substance is often added to the baseline for comparison. If the correct conditions are used the  $R_f$  values can be compared to database values



### 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  $\text{N}_2$  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.

### Column Chromatography

- In column chromatography (CC) a column is packed with a solid and a solvent moves down the column
  - Silica or aluminium oxide is packed into a narrow column and acts as the stationary phase
  - The mixture is dissolved in a solvent which is poured through the column. This acts as the mobile phase

