

HIGHER LEVEL



# FAST FACTS

PEARSON BACCALAUREATE

HIGHER LEVEL

# Chemistry

2<sup>nd</sup> Edition

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# Chapter 1: Stoichiometric relationships – fast facts

## 1.1 Introduction to the particulate nature of matter and chemical change

Physical and chemical properties depend on the ways in which different atoms combine.

- Elements are single substances, composed of atoms of the same type.
- Compounds contain a fixed ratio of atoms of different elements and have different properties from their component elements.
- Mixtures contain more than one element or compound that are not chemically combined.
- Kinetic-molecular theory describes the differences in the properties of solids, liquids, and gases on the basis of the different kinetic energies of the particles.
- Every substance changes state by melting/freezing and boiling/condensing at a defined temperature at constant pressure.
- Chemical equations summarize the change when reactants are converted to products.
- State symbols indicate the state of a substance: (s) solid, (l) liquid, (g) gas and (aq) aqueous solution (dissolved in water).
- The coefficients in a chemical equation describe the relative amounts of reactants and products.

## 1.2 The mole concept

The mole makes it possible to correlate the number of particles with a mass that can be measured.

- The amount of substance ( $n$ ) is measured in moles (mol). The mole concept applies to all species: atoms, molecules, ions, electrons, formula units.
- 1 mol contains the same number of chemical species as there are atoms in exactly 12 g of the isotope carbon-12,  $^{12}_6\text{C}$ .
- 1 mol of any substance contains  $6.02 \times 10^{23}$  species.
- $6.02 \times 10^{23} \text{ mol}^{-1}$  is called Avogadro's constant ( $L$ ). It has units as it is the number of particles per mole.
- The relative atomic mass ( $A_r$ ) of an element is the average mass of an atom according to relative abundances of its isotopes, on a scale where the mass of one atom of  $^{12}_6\text{C}$  is 12 exactly. It has no units.
- The relative molecular mass ( $M_r$ ) is the sum of the relative atomic masses of the atoms in the molecular formula.
- The relative formula mass of an ionic compound is the sum of the relative atomic masses of the ions in the formula.
- The molar mass ( $M$ ) is the relative mass expressed in g and has units of  $\text{g mol}^{-1}$ .
- The empirical formula gives the ratio of the atoms of different elements in a compound. It is the molecular formula expressed as its simplest ratio.
- The molecular formula is a whole-number multiple of the empirical formula.





- The empirical formula of a compound containing the elements X, Y and Z can be determined by completing the following table:

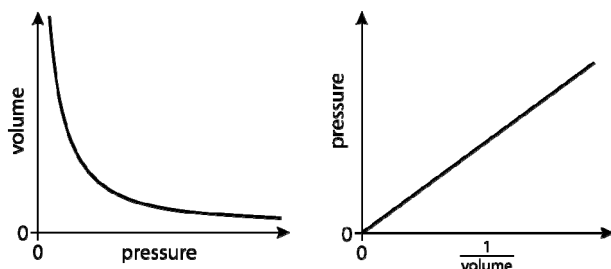
	Mass/g or % of X	Mass/g or % of Y	Mass/g or % of Z
Mass / g	$m_x$	$m_y$	$m_z$
$n$ / mol	$= m_x/M_x$	$= m_y/M_y$	$= m_z/M_z$
Simplest ratio (divide by smallest amount in previous row)			

- The molecular formula shows the number of atoms of each element present in a molecule.
- Number of mol = mass/molar mass:  $n = m/M$
- Number of particles = number of mol  $\times$  Avogadro's constant:  $N = nL$

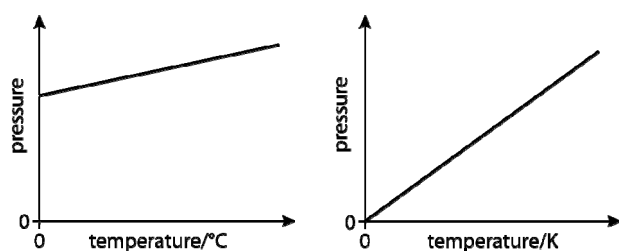
### 1.3 Reacting masses and volumes

Mole ratios in chemical equations can be used to calculate reacting ratios by mass and gas volume.

- The limiting reactant determines the theoretical yield of product. The other reactants are in excess.
- The theoretical yield is the mass or amount of product produced according to the chemical equation, assuming 100% reaction of the limiting reagent.
- Percentage yield = (experimental yield/theoretical yield)  $\times$  100%
- The kelvin is the SI unit of temperature:  $T$  (K) =  $T$  ( $^{\circ}$ C) + 273
- Units of volume:  $1 \text{ dm}^3 = 1 \times 10^{-3} \text{ m}^3 = 1 \times 10^3 \text{ cm}^3$
- For a fixed mass of an ideal gas at constant  $T$ :  $P = k_1/V$  ( $k_1$  constant)



- For a fixed mass of an ideal gas at constant  $V$ :  $P = k_2T$





# Chemistry

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- The combined gas law: for a fixed mass of gas:  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- The ideal gas equation:  $PV = nRT$
- $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T$  must be in K.
- Temperature (in K) is a measure of the average kinetic energy of the particles. Particles have minimum kinetic energy at absolute zero (0 K).
- As kinetic energy =  $\frac{1}{2}mv^2$  and all gases have the same kinetic energy at the same temperature, particles with smaller mass move faster.
- Avogadro's law states that equal volumes of different gases contain equal numbers of particles at the same temperature and pressure.
- Number of mol = volume/molar volume =  $V/V_{\text{mol}}$
- Molar volume,  $V_m$ , of any gas at STP =  $2.27 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$ .
- STP for gases is standard temperature (0 °C or 273 K) and pressure (100 kPa).
- Density = mass/volume;  $\rho = m/V$
- A solution is a homogeneous mixture of a liquid (the solvent) with another substance (the solute). The solute can be solid, liquid, or gas but the solvent is generally a liquid.
- Concentration is the amount of solute in a known volume of solution. It can be expressed either in  $\text{g dm}^{-3}$  or  $\text{mol dm}^{-3}$ . Concentration in  $\text{mol dm}^{-3}$  is often represented by square brackets around the substance:
 
$$[\text{solute}] (\text{mol dm}^{-3}) = n_{\text{solute}} (\text{mol})/V_{\text{solution}} (\text{dm}^3) \qquad n_{\text{solute}} = [\text{solute}] \times V_{\text{solution}} (\text{dm}^3)$$

$$n_{\text{solute}} = [\text{solute}] \times V_{\text{solution}} (\text{cm}^3)/1000$$
- Titration is a chemical technique in which one solution is used to analyse another solution to find its concentration or amount.





## Chapter 2: Atomic structure – fast facts

### 2.1 The nuclear atom

The mass of an atom is concentrated in its minute, positively charged nucleus.

- Protons and neutrons are known as nucleons and are present in the nucleus of an atom.
- Electrons have a negative charge, occupy space outside the nucleus and are responsible for an atom's volume.
- The relative masses and relative charges of the sub-atomic particles are:

	Relative mass	Relative charge
Proton	1	+1
Neutron	1	0
Electron	$5 \times 10^{-4}$	-1

- The mass of the electron is generally considered to be negligible.
- **Atomic number (Z)** = number of protons. It is the fundamental characteristic of an element.
- **Mass number (A)** = number of (protons + neutrons).
- **Isotopes** are atoms with the same atomic number but with different mass numbers. They have the same number of protons but different numbers of neutrons.
- For a species  ${}^A_ZX$ :  
 number of protons = Z  
 number of electrons = Z  
 number of neutrons = A – Z
- Isotopes differ in physical properties that depend on mass such as density, rate of diffusion, etc. This difference is very significant for the isotopes of hydrogen because deuterium,  ${}^2_1\text{H}$ , has twice the mass of the more abundant  ${}^1_1\text{H}$ . As isotopes have the same electron arrangement they have the same chemical properties.
- For an element, the mass spectrum gives two important pieces of information: the number of isotopes and the abundance of each isotope. This allows the relative average atomic mass,  $A_r$  to be calculated.
- **Relative atomic mass ( $A_r$ )** of an element is the average mass of an atom according to the relative abundances of its isotopes, on a scale where the mass of one atom of  ${}^{12}_6\text{C}$  is 12 exactly.  
 For example for Cl which has two isotopes  ${}^{35}_{17}\text{Cl}$  (75 %) and  ${}^{37}_{17}\text{Cl}$  (25 %):  

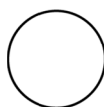
$$A_r = \frac{(35 \times 75) + (37 \times 25)}{100} = 35.50$$
- For a molecule, the peak with largest mass represents the molecular (parent) ion and its mass gives the relative molecular mass ( $M_r$ ) of the compound.



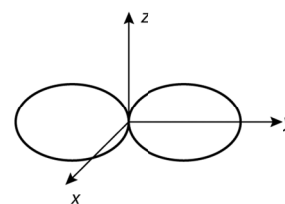
## 2.2 Electron configuration

The electron configuration of an atom can be deduced from its atomic number.

- The electromagnetic spectrum includes waves in order of decreasing frequency/energy:  $\gamma$  rays, X-rays, ultraviolet radiation, visible light, IR radiation, microwaves, and radio waves (see section 3 of the IB data booklet).
- Frequency ( $\nu$ ) and wavelength ( $\lambda$ ) are related by:  $c$  (speed of light) =  $\nu \lambda$ .
- The energy of a photon ( $E_{\text{photon}}$ ) is related to the frequency ( $\nu$ ) of the radiation by Planck's equation:  $E_{\text{photon}} = h\nu$  (the equation is given in section 1 of the IB data booklet)  
 $h$  is Planck's constant (see section 2 of the IB data booklet).
- A **continuous spectrum** contains radiation of all wavelengths within a given range (e.g. the visible spectrum).
- A **line spectrum** consists of discrete lines of different wavelengths/frequencies.
- The emission spectrum of hydrogen atom consists of different series of lines in different regions of the electromagnetic spectrum.
- The lines in an emission spectrum are produced by excited electrons falling from higher to lower energy levels:  $\Delta E_{\text{atom}} = h\nu = hc/\lambda$ .
- As the energy levels of the hydrogen atom converge at higher energy as they are further from the nucleus, the lines in the spectrum also converge at higher energy/frequency.
- The main energy levels of electrons in atoms (in order of increasing energy) are identified by integers,  $n = 1, 2, 3, 4 \dots$
- Each main energy level can hold a maximum of  $2n^2$  electrons.
- Each main energy level contains  $n$  sub-levels and  $n^2$  orbitals.
- The sub-levels in order of increasing energy are identified by letters: **s, p, d, f**, etc.
- The **electron configuration** of an atom describes the number of electrons in each energy sub-level.
- Orbitals** are regions in space in which an electron may be found in an atom. Each orbital can hold two electrons of opposite spin.
- They have characteristic shapes. s orbitals are spherical and p orbitals are dumb-bell shaped. There are three p orbitals orientated along the x, y and z axis.
- The **Pauli exclusion principle** states that only electrons with opposite spin can occupy the same orbital.



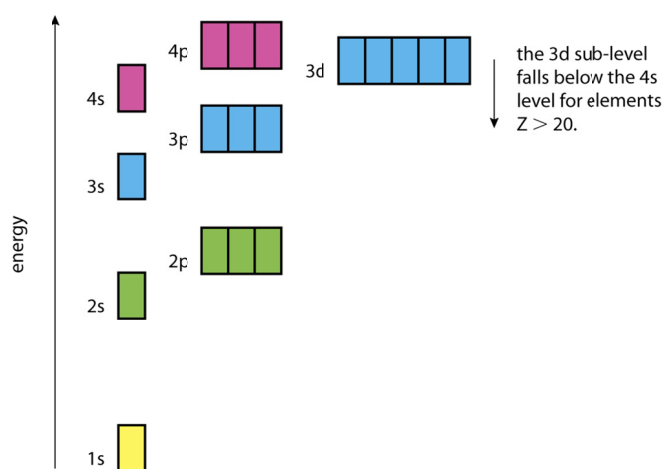
s orbital



$p_y$  orbital



- Orbital diagrams are used to describe the number of electrons in each orbital. Each orbital is represented by a box and each electron by a single-headed arrow which represents the direction of its spin.
- The relative energies of the sub-levels and their composition are summarized.



Level	Sub-level	Maximum no. of electrons in sub-level	Maximum no. of electrons in level
$n = 4$	4f	14 (seven f orbitals)	32
	4d	10 (five d orbitals)	
	4p	6 (three p orbitals)	
	4s	2 (one s orbital)	
$n = 3$	3d	10 (five d orbitals)	18
	3p	6 (three p orbitals)	
	3s	2 (one s orbital)	
$n = 2$	2p	6 (three p orbitals)	8
	2s	2 (one s orbital)	
$n = 1$	1s	2 (one s orbital)	2

Here is a useful mnemonic to the order of filling orbitals. Follow the arrows to see the order in which the sub-levels are filled.

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4f, 5d, 6p, 7s ...

- The **Aufbau principle** states that orbitals with lower energy are filled before those with higher energy.
- Hund's rule** states that every orbital in a sub-level is singly occupied with electrons of the same spin before any one orbital is doubly occupied.
- The number of electrons in a sub-level is represented by a superscript number.
- Condensed electron configurations use square brackets to show the noble gas core.

7s	7p	7d	7f	7g	7h	7h
6s	6p	6d	6f	6g	6h	
5s	5p	5d	5f	5g		
4s	4p	4d	4f			
3s	3p	3d				
2s	2p					
1s						

Element	Electron configuration	Element	Electron configuration
H	$1s^1$	Sr	$[\text{Ar}] 3d^1 4s^2$
Li	$1s^2 2s^1$	Cr	$[\text{Ar}] 3d^5 4s^1$
B	$1s^2 2s^2 2p^1$	Ni	$[\text{Ar}] 3d^8 4s^2$
Na	$1s^2 2s^2 2p^6 3s^1$	Cu	$[\text{Ar}] 3d^{10} 4s^1$





- Note the exceptional configuration of copper and chromium, which can be accounted for the stability of the half- full (d5) and full (d10) d sub-shell.
- The block nature of the Periodic Table is determined by the highest energy occupied sub-level. Elements in the s block have valence electrons in s orbitals; elements in the p block have valence electrons in the p sub-level.
- Positive ions are formed by removing electrons from the neutral atom. The electron configuration of  $\text{Na}^+$  for example is  $1s^2 2s^2 2p^6$ . Negative ions are formed by adding electrons to a neutral atom. The electron configuration of  $\text{F}^-$  is  $1s^2 2s^2 2p^6$ .

## 12.1 Electron configuration

The quantized nature of energy transitions is related to the energy states of electrons in atoms and molecules.

- The ionization energy of hydrogen corresponds to the transition  $n = 1$  to  $n = \infty$  (the convergence limit at higher energies).
- The **first ionization energy** is the minimum energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of univalent cations in the gaseous state. It is the enthalpy change for the reaction:  $\text{X}(\text{g}) \rightarrow \text{X}^+(\text{g}) + \text{e}^-$ .
- Ionization energy can be calculated from the equation  $E_{\text{photon}} = h\nu$  (the equation is given in section 1 of the IB data booklet)
- Trends in first ionization energies across periods gives evidence for the existence of main energy levels and sub-levels.
- First ionization energy:
  - decreases down a group – due to increasing distance of outer electrons from the nucleus
  - increases in general along a period – due to increasing effective nuclear charge
  - shows regular discontinuities in the increase across a period – due to the existence of sub-shells.
- Successive ionization energies of the same element give evidence for electron configurations.
- Large increases in successive ionization energies of an atom occur when an electron is removed from a different energy level. Smaller increases occur when an electron is removed from a different sub-level. For example, a very small jump occurs when there is a change from a  $p^4$  to a  $p^3$  configuration as paired electrons are easier to remove than unpaired electrons as they are strongly repelled by their partner.



## Chapter 3: Periodicity – fast facts

### 3.1 The Periodic Table

The arrangement of elements in the Periodic Table helps to predict their electron configuration.

- The Periodic Table arranges elements according to increasing atomic number / increasing number of protons.
- The horizontal rows are called **periods** and vertical columns are called **groups**.
- The period number ( $n$ ) is the outer energy level that is occupied by electrons.
- Elements in the same period have outer electrons in the same energy level.
- The groups are numbered from 1 to 18.
- Elements in the same group have the same number of outer electrons and have similar chemical properties.
- The Periodic Table is arranged in 4 blocks – s, p, d and f – which are associated with the highest sub-level occupied by electrons.
- The position of an element is related to the electron configuration of its atoms. Magnesium, for example, is in Period 3, as it has three occupied energy levels, and in Group 2, as there are two electrons in its outer energy level. It is in s block as it has outer electrons in the s sub-level.
- Metals are found on the left of the Periodic Table and non-metals on the right. Metalloids form a diagonal staircase between the metals and non-metals.
- Group 1 = alkali metals, Group 17 = halogens, Group 18 = noble gases.
- The **transition metals** are in the large section of **d-block** elements in the middle of the Periodic Table from Sc to Zn, etc. Zn is not a transition metal because it does not form ions with incomplete d sub-levels.
- Lanthanoids and actinoids are metals in the first and second row of the f block.

### 3.2 Periodic trends

Elements show trends in their physical and chemical properties across periods and down groups.

- The chemical and physical properties of elements arranged in order of increasing atomic numbers vary periodically. **Periodicity** is the regular repetition of properties of elements arising from patterns in their electron arrangement.
- Effective nuclear charge refers to the nuclear pull experienced by the outer electrons in an atom, taking into account the shielding effect of inner full shells of electrons.
- **Atomic radius:** atomic radii decrease along a period as the nuclear charge increases and electrons are added to the same outer shell. The attraction between the outer electrons and nucleus increases.
- As a group is descended and the number of occupied energy levels increases, the atomic radii increase.
- **Ionic radius:** Cations are smaller than their parent atoms, as the formation of positive ions involves the loss of the outer shell.
  - Anions are larger than their parent atoms, as their formation involves the addition of electrons into the outer shell. The increased electron repulsion between the electrons in the outer energy level increases the radius of the outer shell.
  - Cation < atom < anion



- Patterns in ionic radii across a period are more complex.
  - The ionic radii decrease from Groups 1 to 14 for the positive ions. The ions  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  are **isoelectronic** and have the same electron configuration ( $1s^2 2s^2 2p^6$ ). The decrease in ionic radius is due to the increase in nuclear charge with atomic number across the period, which increases the attraction between the nucleus and the outer electrons.
  - The ionic radii decrease from Groups 14 to 17 for the negative ions. The ions  $\text{Si}^{4-}$ ,  $\text{P}^{3-}$ ,  $\text{S}^{2-}$  and  $\text{Cl}^-$  are isoelectronic and have the same electron arrangement ( $1s^2 2s^2 2p^6 3s^2 3p^6$ ). The decrease in ionic radius is due to the increase in nuclear charge across the period.
  - The positive ions are smaller than the negative ions in the same period, as the former have one less occupied electron shell.
- The **first ionization energy (IE)** of an element is the minimum energy required to form one mole of singly charged positive ions ( $\text{M}^+$ ) by removing an electron from each atom (M) in the gaseous state:  $\text{M}(\text{g}) \rightarrow \text{M}^+(\text{g}) + \text{e}^-$  (units:  $\text{kJ mol}^{-1}$ ).
- First ionization energies decrease down a group. This is due to the increased distance between the nucleus and the outer energy level that reduces the force of attraction between the nucleus and the outer electrons.
- Ionization energies increase along a period due to the increase in effective nuclear charge, which causes the outer electrons to be held more tightly.
- There are regular discontinuities in the trend of increasing ionization energies along a period, due to the existence of sub-levels within the main energy levels.
- **Electron affinity** is the energy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous ions:  $\text{X}(\text{g}) + \text{e}^- \rightarrow \text{X}^-(\text{g})$
- First electron affinities are usually endothermic, and increase along a period due to increasing nuclear charge.
- **Electronegativity** is a measure of the attraction of a nucleus for bonding electrons.
- Electronegativity increases along a period and decreases down a group.
- The noble gases are not assigned electronegativities as they do not readily form bonds with other elements.
- The electronegativities of diagonal elements remain approximately the same as both the group and period number increase. Boron and aluminium, for example, both have electronegativities of 1.6.
- The electronegativity of H is the same as that of P.
- Metals have low ionization energies and electronegativities; non-metals have high ionization energies and electronegativities.
- The **melting points** decrease down Group 1 as there is a decrease in the strength of the **metallic bonding**. The increase in ionic radii reduces the force of the attraction between the  $\text{M}^+$  ions and the **delocalized electrons**.
- The melting points increase down Group 17, as there is an increase in the strength of London (dispersion) forces with increasing number of electrons.
- The chemical properties of elements are generally due to the number of electrons in the outer energy level of their atoms.

### Group 1

- All the metals are too reactive to be found native in nature.
- They generally donate electrons and act as **reducing agents**:  $\text{M} \rightarrow \text{M}^+ + \text{e}^-$
- Reactivity increases down the group with the decrease in ionization energies.
- Their ability to conduct electricity is also due to the mobility of their outer electron.





- The alkali metals react with water to produce hydrogen and the metal hydroxide. The resulting solution is alkaline owing to the presence of hydroxide ions:  $2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$

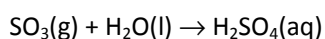
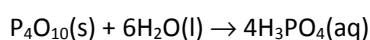
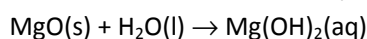
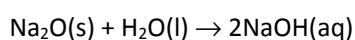
### Group 17

- The halogens are diatomic non-polar molecules.
- They generally accept electrons and act as **oxidizing agents**:  $X_2 + 2e^- \rightarrow 2X^-$
- Reactivity decreases down the group, as the atom gets larger and attraction for extra electrons decreases. The more reactive halogens,  $X_2$ , **displace** the less reactive halogens, Y, from their compounds:  
 $X_2 + 2Y^- \rightarrow Y_2 + 2X^-$   
 e.g. the more reactive Cl displaces Br:  $Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$
- The halogens react with the Group 1 metals to form ionic **halides**:  $2M + X_2 \rightarrow 2MX$   
 The most vigorous reaction occurs between the elements which are furthest apart in the Periodic Table.

### Period 3 oxides

- Oxides change from basic through amphoteric to acidic across a period.

Formula and state at room temperature	Na <sub>2</sub> O(s)	MgO(s)	Al <sub>2</sub> O <sub>3</sub> (s)	SiO <sub>2</sub> (s)	P <sub>4</sub> O <sub>10</sub> (s)/ P <sub>4</sub> O <sub>6</sub> (s)	SO <sub>3</sub> (l)/ SO <sub>2</sub> (g)	Cl <sub>2</sub> O <sub>7</sub> (l)/ Cl <sub>2</sub> O(g)
Structure	Ionic			Giant covalent	Molecular covalent		
Acid/base character	Basic		Amphoteric	Acidic			



As SiO<sub>2</sub>(s) is insoluble it does not change the pH if added to H<sub>2</sub>O.



### 13.1 First-row d-block elements

The transition elements have characteristic properties; these properties are related to their all having incomplete d sub-levels.

- Transition metals have partially filled d orbitals in their atoms or ions.
- Zn is not a transition element because it has a full d sub-level in its atoms and ions.
- Characteristic properties include: variable oxidation number, complex ion formation with ligands, existence of coloured compounds, have catalytic and magnetic properties.
- Multiple oxidation states arise because the 3d and 4s sub-levels are close in energy and both are involved in bonding.
- All d-block elements except Sc show an oxidation state of +2.
- All d-block elements except Zn show an oxidation state of +3.
- A ligand is a molecule or negative ion that donates a pair of electrons to a central metal ion to form a covalent (coordinate) bond. They are Lewis bases.
- Complex **ions** are formed when a central metal ion is bonded to a ligand with a coordinate bond. Examples include  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{CuCl}_4]^{2-}$ , and  $[\text{Ag}(\text{NH}_3)_2]^+$ .
- The charge on a complex ion is the sum of the charges of the metal ion and the ligands.
- Transition metals act as heterogeneous catalysts as they can provide a surface for reaction: they use the 3d and 4s electrons to form weak bonds to reactant molecules.
- Magnetic properties are a result of unpaired electrons in the transition metal atom or ion.

### 13.2 Coloured complexes

d orbitals have the same energy in an isolated atom, but split into two sub-levels in a complex ion. The electric field of ligands cause the d orbitals in complex ions to split so that the energy of an electron transition between them corresponds to a photon of visible light.

Transition metal ions are coloured due to **d–d electron transitions** between d orbitals which are split in the electric field due to the presence of the ligands.

- The colour observed is complementary to the colour absorbed, and can be deduced from the colour wheel.
- The colour of a complex depends on the identity of the metal ion, the oxidation state of the metal, and the identity of the ligand.
- Ions with higher charge and ligands with greater charge density produce a greater split in the d orbitals.
- The spectrochemical series arranges the ligands according to the energy separation between the two sets of d orbitals.
- Polydentate ligands form more than one coordinate bond with the metal ion.



# Chapter 4: Chemical bonding and structure fast facts

## 4.1 Ionic bonding and structure

Ionic compounds consist of ions held together in lattice structures by ionic bonds.

- An ion is a charged particle.
- The number of charges on an ion is equal to the number of electrons lost (positive ion) or gained (negative ion) by an atom.
- Metals lose electrons to form positive ions (cations); non-metals gain electrons to form negative ions (anions).
- The charge on an ion can usually be predicted from the group of the element in the Periodic Table; transition metal elements can form more than one ion.
- Common polyatomic ions include:  $\text{OH}^-$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ .
- Ionic compounds consist of ions held together by forces of electrostatic attraction.
- Ionic compounds are electrically neutral, as they consist of a lattice in which the total number of positive charges is balanced by the total number of negative charges. The formula of the compound is expressed as its simplest ratio, e.g. the ions  $\text{X}^{m+}$  and  $\text{Y}^{n-}$  will form the compound  $\text{X}_n\text{Y}_m$ .
- In the ionic lattice, each ion is surrounded by a fixed number of ions of the opposite charge, known as the coordination number.
- Ionic compounds usually have high melting and boiling points, and are more soluble in water than in non-polar solvents. They conduct electricity when molten or in aqueous solution but not when solid.

## 4.2 Covalent bonding

Covalent compounds form by the sharing of electrons.

- A covalent bond is the electrostatic attraction between a pair of electrons and positively charged nuclei.
- A molecule is a group of atoms held together by covalent bonds.
- Two pairs of shared electrons = double bond.
- Three pairs of shared electrons = triple bond.
- Increasing number of bonds  $\Rightarrow$  shorter and stronger bonds.
- Polar bonds form when the two atoms bonded together have different electronegativity values.





### 4.3 Covalent structures

Lewis (electron dot) structures show the electron domains in the valence shell and are used to predict molecular shape.

- Lewis (electron dot) structures show all the valence electrons of the atoms in the molecule or polyatomic ion.
- The octet rule refers to the fact that most atoms form a stable arrangement with eight electrons in their outer shell.
- Exceptions to the octet rule include:
  - less than an octet –  $\text{BeCl}_2$ ,  $\text{BF}_3$  (central atom very small)
  - expanded octet –  $\text{PCl}_5$ ,  $\text{SF}_6$  (central atom from third period or beyond).
- VSEPR theory: the total number of electron domains determines their geometrical arrangement by maximum repulsion; the shape of the molecule then depends on the number of bonding pairs within this arrangement.

Number of charge centres	Number of bonding pairs	Shape of molecule
2	2	linear
3	3	planar triangular
3	2	V-shaped
4	4	tetrahedral
4	3	triangular pyramidal
4	2	V-shaped
5	5	triangular bipyramidal
5	4	see-saw
5	3	T-shaped
5	2	linear
6	6	octahedral
6	5	square pyramidal
6	4	square planar

- Resonance structures occur when there is more than one possible position for a double bond.
- Carbon, silicon, and silicon dioxide form giant covalent molecules.
- Carbon occurs as allotropes with different bonding within giant molecules – diamond, graphite, fullerene, and graphene.



- The polarity of a molecule depends on:
  - i the polarities of its bonds
  - ii its molecular shape – whether cancellation occurs between the polar bonds.
- Coordinate bonds form when both the shared electrons originate from the same atom.

## 4.4 Intermolecular forces

The physical properties of molecular substances result from different types of forces between their molecules.

- The forces between molecules are largely determined by the charge separation within the molecule:
  - non-polar molecules  $\Rightarrow$  London (dispersion) forces
  - polar molecules  $\Rightarrow$  dipole–dipole attraction
  - polar molecules in which H is bonded to O, N, or F  $\Rightarrow$  hydrogen bonding.
- van der Waals forces refer to London (dispersion) and dipole–dipole attractions.
- In order of strength:  
London (dispersion) < dipole–dipole < hydrogen bonding
- The stronger the intermolecular force, the lower the volatility (higher boiling point).
- Polar substances are more soluble in water and less soluble in non-polar solvents.
- Covalent compounds are generally not good electrical conductors, unless they are able to ionize in solution, e.g. HCl(aq).

	Covalent substances	Ionic compounds
Volatility	low	high
Electrical conductivity	low	high
Solubility in polar solvents	low	high
Solubility in non-polar solvents	high	low

## 4.5 Metallic bonding

Metallic bonds involve a lattice of cations with delocalized electrons.

- Metal atoms are held together by the electrostatic attraction between a lattice of positive ions and delocalized electrons.
- The strength of the metallic bond increases with the charge on the cation and decreases with the radius of the ion.
- The properties of metals – electrical and thermal conductivity, malleability, ductility – are a result of the delocalized electrons.
- Alloys form as a result of the non-directional bonding in metals and often have enhanced properties.



## 14.1 Further aspects of covalent bonding and structure

Larger structures and more in-depth explanations of bonding systems often require more sophisticated concepts and theories of bonding.

- Sigma ( $\sigma$ ) bonds form when atomic orbitals (s, p, or hybridized) overlap along the bond axis; all single bonds are  $\sigma$  bonds.
- Pi ( $\pi$ ) bonds form when p atomic orbitals overlap laterally; the electron density is concentrated above and below the bond axis.
- Double bond = one  $\sigma$  bond and one  $\pi$  bond.
- Triple bond = one  $\sigma$  bond and two  $\pi$  bonds.
- Atoms in Period 3 and below can expand their octet using unoccupied d orbitals. This gives rise to molecules with 5 or 6 electron domains around the central atom.
- The number of resonance structures that can be drawn for a molecule is the same as the number of possible positions for a double bond.
- Delocalization of  $\pi$  electrons leads to greater stability and bonds of intermediate length and strength.
- Formal charge (FC) can be used to determine which of some possible structures is the preferred structure. The most stable structure is the one with the lowest values for formal charge for the atoms.
- $FC = (\text{number of valence electrons}) - [\frac{1}{2}(\text{number of bonding electrons}) - (\text{number of non-bonding electrons})]$
- Ozone is a resonance hybrid with a bond order of 1.5. Oxygen is a diatomic molecule with a bond order of 2. Ozone is therefore dissociated by light of longer wavelength.
- The catalytic breakdown of ozone by CFCs and  $\text{NO}_x$  has contributed to significant depletion of the ozone layer.

## 14.2 Hybridization

Hybridization results from the mixing of atomic orbitals to form the same number of new equivalent hybrid orbitals that can have the same mean energy as the contributing atomic orbitals.

- Hybridization occurs when different atomic orbitals mix to form new atomic orbitals for bonding.
- The shape of hybridized orbitals:
  - $sp^3 \Rightarrow$  tetrahedral
  - $sp^2 \Rightarrow$  planar triangular
  - $sp \Rightarrow$  linear





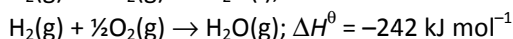
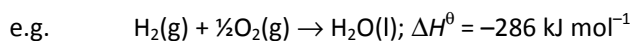
# Chapter 5: Energetics/thermochemistry

## – fast facts

### 5.1 Measuring energy changes

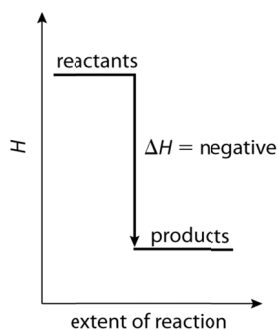
The enthalpy changes from chemical reactions can be calculated from their effect on the temperature of their surroundings.

- **Energetics** deals with heat changes in chemical reactions. Heat is a form of energy.
- Temperature is a measure of the average kinetic energy of the particles.
- Total energy is conserved in chemical reactions.
- Enthalpy is the amount of heat energy contained in a substance. It is stored in the chemical bonds as potential energy. When substances react, the difference in the enthalpy between the reactants and products (at constant pressure) results in a heat change which can be measured.
- The reaction mixture is called the **system** and anything around the system is called the **surroundings**.
- **Thermochemical equations** give the balanced equation with the enthalpy change.

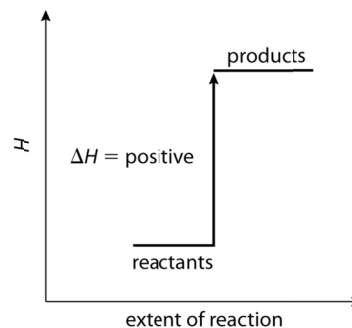


State symbols must be shown, as  $\Delta H^\ominus$  depends on the state of the reactants or products.

- Chemical reactions that involve transfer of heat between the system and the surroundings are described as endothermic or exothermic.
- In **exothermic reactions** heat is released to the surroundings.
- In **endothermic reactions** heat is absorbed from the surroundings.
- The enthalpy change ( $\Delta H$ ) for chemical reactions is indicated in  $\text{kJ mol}^{-1}$ .
- Exothermic reactions have negative  $\Delta H$  values. The temperature of the reaction mixture rises as the chemicals give out heat.
- Endothermic reactions have positive  $\Delta H$  values. The temperature of the reaction mixture falls as the chemicals absorb heat.



An exothermic reaction: the products are more **stable** than the reactants as they have a lower enthalpy.



An endothermic reaction: the products are less stable than the reactants as they have a higher enthalpy.



- The **standard state** of an element or compound is its most stable state under the standard conditions (pressure 101.3 kPa, temperature 298 K).
- The **standard enthalpy change** ( $\Delta H^\theta$ ) is the heat energy transferred under **standard conditions** (pressure 100 kPa, concentration 1 mol dm<sup>-3</sup> and all substances in their standard states.) Only  $\Delta H^\theta$  can be measured, not  $H$  for the initial or final state of a system.
- The **standard enthalpy change of combustion** ( $\Delta H_c^\theta$ ) is the enthalpy change for the complete combustion of one mole of a substance in its standard state in excess oxygen under standard conditions. All combustion reactions are exothermic.
- The **standard enthalpy change of formation** ( $\Delta H_f^\theta$ ) is the enthalpy change when one mole of a substance is formed from its elements in their standard states under standard conditions.
- Calorimetry** is the technique of measuring heat changes in physical processes and chemical reactions.
- Heat changes can be calculated from the temperature changes:
  - heat change ( $q$ ) = mass ( $m$ )  $\times$  specific heat capacity ( $c$ )  $\times$  temperature change ( $\Delta T$ )
- The **specific heat capacity** is the amount of heat energy required to raise the temperature of unit mass (e.g. 1 kg or 1 g) of a substance, by 1 °C or 1 K.
- $\Delta H_c^\theta$  for reactions in aqueous solutions can be calculated if it is assumed that all the heat goes into the water.

$$\Delta H_c^\theta = \frac{-m_{\text{H}_2\text{O}} \times c_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}}{n_{\text{fuel}}}$$

The experiment is performed with a calorimeter which is a good conductor. This allows heat from the flame to pass to the water.

$$\Delta H_{\text{reaction}}^\theta = \frac{-m_{\text{H}_2\text{O}} \times c_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}}{n_{\text{limiting reagent}}}$$

The experiment is performed with a calorimeter which is an insulator of heat, which reduces heat losses from the system.

- If a calorimeter absorbs heat:  $Q = (m_{\text{H}_2\text{O}} \times c_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}) + (m_{\text{calor}} \times c_{\text{calor}} \times \Delta T_{\text{calor}})$
- Heat loss and incomplete combustion can lead to **systematic** errors in experimental results.

## 5.2 Hess's law

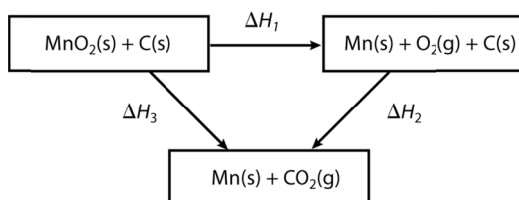
In chemical transformations energy can neither be created nor destroyed (the first law of thermodynamics).

- Hess's law states that the total enthalpy change for a reaction is independent of the route taken. It is a special case of the law of conservation of energy.

e.g.

Hess's law:

$$\Delta H_3 = \Delta H_1 + \Delta H_2$$



- $\Delta H_{\text{reaction}} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$



## 5.3 Bond enthalpies

Energy is absorbed when bonds are broken and is released when bonds are formed.

- **Average bond energy** is the energy required to break one mole of the same type of bond in the gaseous state averaged over a variety of similar compounds.
- Bond breaking absorbs energy and is endothermic. Bond making releases energy and is exothermic.

$$\Delta H_{\text{reaction}}^{\ominus} = \sum E_{\text{bonds broken}} - \sum E_{\text{bonds formed}}$$

when  $\sum E_{\text{bonds broken}} > \sum E_{\text{bonds formed}}$ : the reaction is endothermic

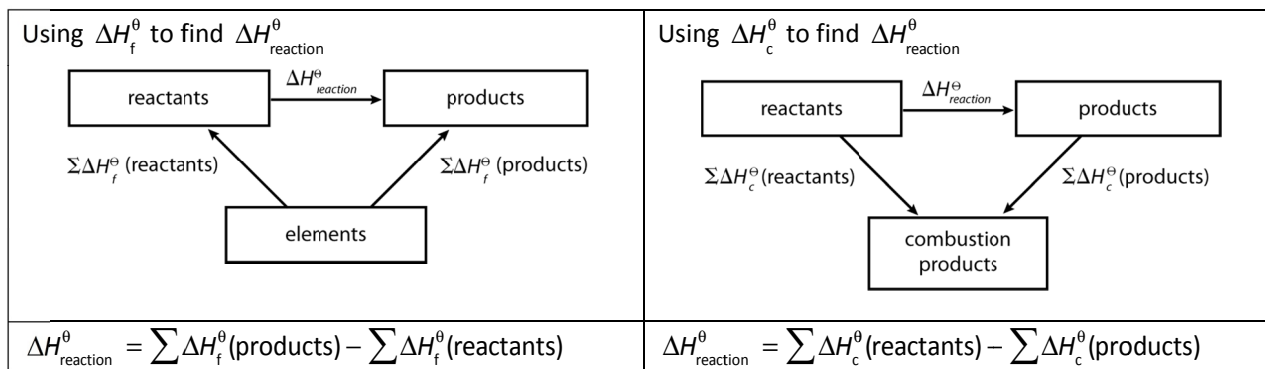
when  $\sum E_{\text{bonds formed}} > \sum E_{\text{bonds broken}}$ : the reaction is exothermic

- The bonds in oxygen,  $\text{O}_2$ , are stronger than those in ozone,  $\text{O}_3$  and are broken by UV light of different wavelengths.
- The ozone cycle describes how ozone is both formed and depleted by natural processes in the atmosphere.

## 15.1 Energy cycles

The concept of the energy change in a single step reaction being equivalent to the summation of smaller steps can be applied to changes involving ionic compounds.

- The enthalpy of formation of any element in its stable state is zero, as there is no enthalpy change when an element is formed from itself.



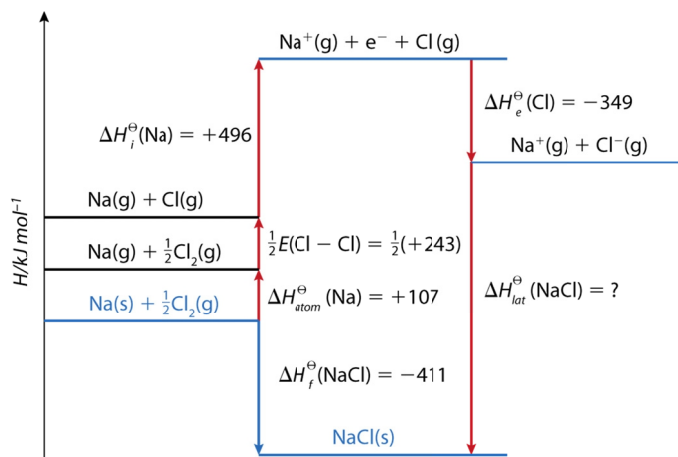
$\Delta H_{\text{reaction}}^{\ominus}$  calculated from  $\Delta H_f^{\ominus}$  or  $\Delta H_c^{\ominus}$  is more accurate than  $\Delta H_{\text{reaction}}^{\ominus}$  values based on bond enthalpies, which refer only to the gaseous state and are average values.

- The first **electron affinity** is the enthalpy change when one mole of gaseous atoms attracts one mole of electrons:  $\text{X}(\text{g}) + \text{e}^{-}(\text{g}) \rightarrow \text{X}^{-}(\text{g})$   $\Delta H_e^{\ominus}$
- The **lattice enthalpy** is the enthalpy change that occurs when one mole of a solid ionic compound is separated into gaseous ions under standard conditions. For example, for alkali metal halides:  $\text{MX}(\text{s}) \rightarrow \text{M}^{+}(\text{g}) + \text{X}^{-}(\text{g})$   $\Delta H_{\text{lat}}^{\ominus}$
- $\Delta H_{\text{lat}}^{\ominus}$  depends on the attraction between the ions:
  - an increase in the **ionic radius** of the ions decreases  $\Delta H_{\text{lat}}^{\ominus}$
  - an increase in **ionic charge** increases  $\Delta H_{\text{lat}}^{\ominus}$ .
- The **Born–Haber cycle** is a special case of Hess's law for the formation of ionic compounds. It allows the **experimental lattice enthalpy** to be calculated from other enthalpy changes.



- **Theoretical lattice enthalpies** can be calculated using a (purely) **ionic model** from the ionic charges and radii.
- The hydration enthalpy of an ion depends on the attraction between the ions and the polar water molecules.

### Born–Haber cycle for NaCl



$$\Delta H_{\text{lat}}^{\ominus} = 411 + 107 + \frac{1}{2}(+243) + 496 - 349 = +786.5 \text{ kJ mol}^{-1}$$

## 15.2 Entropy and spontaneity

A reaction is spontaneous if the overall transformation leads to an increase in total entropy (system plus surroundings). The direction of spontaneous change always increases the total entropy of the universe at the expense of energy available to do useful work. This is known as the second law of thermodynamics.

- **Entropy** ( $S$ ) is a property which quantifies the degree of disorder or randomness in a system.
- Ordered states have low  $S$ , disordered states have high  $S$ :  $S(s) < S(l) < S(g)$
- Generally matter and energy become more disordered, and  $S_{\text{universe}}$  increases.
- $\Delta S_{\text{reaction}}^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$
- **Gibbs' free energy** ( $G$ ) is the criterion for predicting the spontaneity of a reaction or process: it is related to  $\Delta S_{\text{total}}^{\ominus}$ . It gives the energy available to do useful work and is related to the enthalpy and entropy changes of the system:  $\Delta G_{\text{system}}^{\ominus} = \Delta H_{\text{system}}^{\ominus} - T\Delta S_{\text{system}}^{\ominus}$
- $\Delta G_{\text{sys}} < 0$  for a spontaneous process,  $\Delta G_{\text{sys}} = 0$  at equilibrium.
 

Calculating $\Delta G_{\text{reaction}}^{\ominus}$ (when $T = 298 \text{ K}$ )	Calculating $\Delta G_{\text{reaction}}^{\ominus}$ (for all $T$ )
$\Delta G_{\text{reaction}}^{\ominus} = \sum \Delta G_{\text{(products)}}^{\ominus} - \sum \Delta G_{\text{(reactants)}}^{\ominus}$	$\Delta G_{\text{reaction}}^{\ominus} = \Delta H_{\text{reaction}}^{\ominus} - T\Delta S_{\text{reaction}}^{\ominus}$

$T$  must be in K. As the units of  $S$  are  $\text{J mol}^{-1} \text{K}^{-1}$  and  $H$  are  $\text{kJ mol}^{-1}$  they need to be changed to be consistent.
- $\Delta G_{\text{sys}}$  and thus the direction of change varies with temperature.
 

At low temperature:  
 $\Delta G_{\text{system}}^{\ominus} \approx H_{\text{system}}^{\ominus}$ : exothermic reactions are spontaneous.

At high temperature:  
 $\Delta G_{\text{system}}^{\ominus} = -T\Delta S_{\text{system}}^{\ominus}$ : this allows some endothermic reactions to occur if  $\Delta S_{\text{system}}^{\ominus} > 0$





## Chapter 6: Kinetics – fast facts

### 6.1 Collision theory and rates of reaction

The greater the probability that molecules will collide with sufficient energy and proper orientation, the higher the rate of reaction.

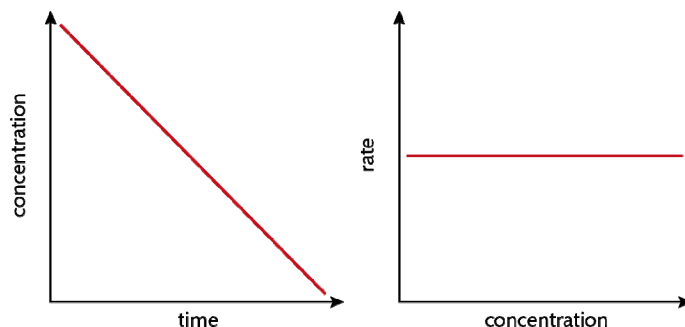
- Rate of reaction = decrease in concentration of reactants or increase in concentration of products per unit time
- Units of rate of reaction =  $\text{mol dm}^{-3} \text{s}^{-1}$ .
- Concentration changes in a reaction can be followed indirectly by measuring changes in mass, volume, or absorbance.
- Rate of reaction at time  $t$  = gradient of tangent to curve of [R] or [P] vs time, at time  $t$ .
- Absolute temperature is a measure of average kinetic energy.
- Activation energy,  $E_a$ , is the minimum KE particles must have in order to react.
- Collision theory: collisions between reactant particles will lead to reaction when:
  - the particles have  $\text{KE} > E_a$  and
  - the particles have the correct collision geometry.
- The Maxwell–Boltzmann distribution shows the number of particles in a sample with a particular value of kinetic energy. The area under the curve represents the number of particles. It can be used to illustrate the effects of different factors on the rate of reaction.
- The effects of temperature, concentration, pressure, particle size, and catalysts on the rate of reaction can all be interpreted in terms of the collision theory.
- Catalysts speed up reactions by providing an alternate reaction route with a lower activation energy, but are not themselves chemically changed by the reaction. Catalysed reactions form a transition state of lower energy than the uncatalysed reaction.
- Enzymes are biological catalysts.

### 16.1 Rate expression and reaction mechanism

- Rate expressions can only be determined empirically and these limit possible reaction mechanisms. In particular cases, such as a linear chain of elementary reactions, no equilibria, and only one significant activation barrier, the rate equation is equivalent to the slowest step of the reaction.
- For a reaction with reactants A and B:
 
$$\text{rate} = k [\text{A}]^m [\text{B}]^n$$
 where  $k$  = rate constant  
 $m$  and  $n$  are the orders of reaction with respect to A and B respectively  
 $m + n$  = overall order of reaction.
- The value of  $k$ , the rate constant, depends on the particular reaction and on the temperature.
- The units of  $k$  depend on the order of the reaction.
- Constant half-life  $\Rightarrow$  first-order reaction.
- Many reactions proceed in a series of small steps known as elementary steps.
- Molecularity = the number of reactant particles taking part in an elementary step.



- The rate-determining step = the slowest step in the reaction. It is the step with the highest activation energy.
- The order of the reaction is determined by the molecularity of the rate-determining step.
- Rate equations can *only* be derived from empirical data. The order of reaction with respect to a particular reactant can be determined by following the change in rate of reaction as the concentration of that reactant is changed.
- Concentration–time and rate–concentration graphs can be used to represent zero-, first-, and second-order reactions.



- A proposed mechanism for a reaction must be consistent with:
  - i the overall reaction's stoichiometry
  - ii kinetic data derived from experiment

## 16.2 Activation energy

The activation energy of a reaction can be determined from the effect of temperature on reaction rate.

- The Arrhenius equation (given in section 1 of the IB data booklet) shows the temperature dependence of the rate constant.
- The Arrhenius plot,  $\ln k$  versus  $1/T$ , can be used to calculate the activation energy  $E_a$ . The gradient of the line in the Arrhenius plot =  $-E_a/R$
- The Arrhenius equation shows that increasing the temperature increases the value of the rate constant  $k$ . But the extent of this increase depends on the value of  $E_a$  for the reaction. Reactions with higher values for  $E_a$  have a higher temperature dependency of  $k$  than reactions with lower values for  $E_a$ .

### Get it straight

- All substances at the same temperature have the same average kinetic energy.
- The rate equation *cannot* be predicted from the overall stoichiometry of the reaction.
- The units of the rate constant  $k$  vary – they depend on the order of the reaction.
- Activation energy is not temperature dependent.



## Chapter 7: Equilibrium – fast facts

### 7.1 Equilibrium

Many reactions are reversible. These reactions will reach a state of equilibria when the rates of the forward reaction and reverse reaction are equal. The position of equilibrium can be controlled by changing the conditions.

- Equilibrium state is when rate of forward reaction = rate of backward reaction in a closed system.
- The equilibrium mixture contains a fixed concentration of reactants and products.
- For a reaction  $aA + bB \rightarrow cC + dD$ 

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$
- $K_c$ , the equilibrium constant, is a constant for a given reaction at a specified temperature.
- The higher the value of  $K_c$  the further to the right the equilibrium mixture lies.
- $Q$ , the reaction quotient, is a measure of the relative amounts of reactants and products in a reaction mixture at a particular time. It is calculated by substituting non-equilibrium values for reactant and product concentration into the equilibrium expression:
  - if  $Q = K_c$ , then the reaction is at equilibrium
  - if  $Q < K_c$ , reaction is not at equilibrium; reaction proceeds to right in favour of products
  - if  $Q > K_c$ , reaction is not at equilibrium; reaction proceeds to left in favour of reactants.
- Manipulations of the same reaction at the same temperature are expressed by corresponding changes to the value of  $K_c$ :
  - inverting the reaction  $\Rightarrow K_c^{-1}$
  - doubling the reaction coefficients  $\Rightarrow K_c^2$
  - halving the reaction coefficients  $\Rightarrow \sqrt{K_c}$
  - adding together two reactions  $\Rightarrow K_{c1} \times K_{c2}$
- When a change is applied to an equilibrium mixture, the composition will change to minimize the effect of the change. The new equilibrium mixture will have different concentrations of reactant and product, but the value of  $K_c$  will be unchanged at the same temperature.
- Catalysts do not change the yield or the equilibrium mixture because they have an equal effect on the forward and backward reactions.
- Optimum conditions for an industrial process are based on equilibrium, kinetic, and economic considerations.
- When  $K_c$  is very small,  $[R]_{\text{equilibrium}} \approx [R]_{\text{initial}}$
- The equilibrium law is used in calculations of reacting concentrations and equilibrium mixtures.
- Equilibrium occurs at a maximum value of entropy and a minimum value of Gibbs free energy.
- Gibbs free energy,  $\Delta G$ , and the equilibrium constant,  $K_c$ , can both be used to measure the position of an equilibrium reaction. They are related by the expression  $\Delta G = -RT \ln K$



## 17.1 The equilibrium law

The position of equilibrium can be quantified by the equilibrium law. The equilibrium constant for a particular reaction only depends on the temperature.

- When  $K_c$  is very small,  $[R]_{\text{equilibrium}} \sim [R]_{\text{initial}}$ .
- The equilibrium law is used in calculations of reacting concentrations and equilibrium mixtures.
- Equilibrium occurs at a maximum value of entropy and a minimum value of Gibbs free energy.
- Gibbs free energy,  $\Delta G$ , and the equilibrium constant,  $K_c$  can both be used to measure the position of an equilibrium reaction. They are related by the expression  $\Delta G = -RT \ln K$

### Get it straight

- The *only* thing that changes the value of  $K_c$  for a reaction is the temperature.



## Chapter 8: Acids and bases – fast facts

### 8.1 Theories of acids and bases

Many reactions involve the transfer of a proton from an acid to a base.

- Brønsted–Lowry acid = proton donor.
- Brønsted–Lowry base = proton acceptor.
- A conjugate acid–base pair differ by a single proton: conjugate base +  $\text{H}^+$   $\rightleftharpoons$  conjugate acid
- Amphoteric species can act as both Brønsted–Lowry acids and bases.

### 8.2 Properties of acids and bases

The characterization of an acid depends on empirical evidence such as the production of gases in reactions with metals, the colour changes of indicators, or the release of heat in reactions with metal oxides and hydroxides.

- acid + metal  $\rightarrow$  salt + hydrogen
- acid + base  $\rightarrow$  salt + water + carbon dioxide
- acid + carbonate  $\rightarrow$  salt + water + carbon dioxide
- Soluble bases are called alkalis.
- The reaction between an acid and a base to produce a salt is known as neutralization.
- Neutralization reactions are exothermic.
- Titration is a technique used to deliver precise volumes of acid and base in a neutralization reaction. It is often used to determine the concentration of a solution.

### 8.3 The pH scale

The pH scale is an artificial scale used to distinguish between acid, neutral, and basic/alkaline solutions.

- The pH scale is a convenient measure of the  $[\text{H}^+]$  in a solution, which enables different solutions to be compared.
- $\text{pH} = -\log_{10} [\text{H}^+]$ ;  $[\text{H}^+] = 10^{-\text{pH}}$
- At 25 °C:
  - $\text{pH} < 7 \Rightarrow [\text{H}^+] > [\text{OH}^-] = \text{acidic}$
  - $\text{pH} = 7 \Rightarrow [\text{H}^+] = [\text{OH}^-] = \text{neutral}$
  - $\text{pH} > 7 \Rightarrow [\text{H}^+] < [\text{OH}^-] = \text{basic}$
- A change of one pH unit = a ten-fold change in  $[\text{H}^+]$ .
- pH can be determined using universal indicator and pH meters.
- The ionic product constant of water,  $K_w$ , has a fixed value at a fixed temperature.
- $K_w = [\text{H}^+] [\text{OH}^-]$
- The concentrations of  $\text{H}^+$  and  $\text{OH}^-$  are inverse in an aqueous solution.





## 8.4 Strong and weak acids and bases

The pH depends on the concentration of the solution. The strength of acids or bases depends on the extent to which they dissociate in aqueous solution.

- Strong acids and bases dissociate almost completely in solution.
- Weak acids and bases dissociate only partially in solution.
- Strong acids are good proton donors and form weak conjugate bases.
- Strong bases are good proton acceptors and form weak conjugate acids.
- Strong acids: HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>
- Strong bases: LiOH, NaOH, KOH, Ba(OH)<sub>2</sub>
- Weak acids: CH<sub>3</sub>COOH, H<sub>2</sub>CO<sub>3</sub>
- Weak bases: NH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>
- Comparisons of the strength of acids and bases must use solutions of equal concentration.
- Strong and weak acids and bases can be distinguished by:
  - i pH measurement/indicator
  - ii conductivity
  - iii rate of reaction with metals, metal oxides, metal hydroxides, metal hydrogencarbonates and metal carbonates.

### 18.1 Lewis acids and bases

The acid–base concept can be extended to reactions that do not involve proton transfer.

- Lewis acid = lone pair acceptor.
- Lewis base = lone pair donor.
- Lewis acid/base reactions lead to coordinate bonds.
- A nucleophile is an electron-rich species that donates an electron pair – it is a Lewis base.
- An electrophile is an electron-deficient species that accepts an electron pair – it is a Lewis acid.

### 18.2 Calculations involving acids and bases

The equilibrium law can be applied to acid–base reactions. Numerical problems can be simplified by making assumptions about the relative concentrations of the species involved.

The use of logarithms is also significant here.

- $\text{pH} = -\log_{10} [\text{H}^+]$ ;  $[\text{H}^+] = 10^{-\text{pH}}$
- $\text{pOH} = -\log_{10} [\text{OH}^-]$ ;  $[\text{OH}^-] = 10^{-\text{pOH}}$
- $K_w = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14}$  at 25 °C
- $10^{-\text{pH}} \times 10^{-\text{pOH}} = 1.00 \times 10^{-14}$  at 25 °C
- $\text{pH} + \text{pOH} = 14.00$  at 25 °C
- $\text{p}K_w = -\log_{10} (K_w)$ ;  $K_w = 10^{-\text{p}K_w}$



- $\text{pH} + \text{pOH} = \text{p}K_w$
- The value of  $K_w$ , and therefore of pH, is temperature dependent.
- For strong acids and strong bases, pH can be calculated from the concentration because full dissociation is assumed.
- Weak acids and weak bases, pH cannot be calculated from the concentration because full dissociation is not assumed.
- For weak acids and weak bases, the acid and base dissociation constants,  $K_a$  and  $K_b$ , give a measure of the relative strengths of the acid and base. Higher values for  $K_a$  and  $K_b$  represent stronger acids and bases.
- $$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$
- $$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{HA}]}$$
- The relationship between the values of  $K_a$  and  $K_b$  for a conjugate acid/base pair is inverse.
- $K_a \times K_b = K_w$
- $\text{p}K_a = -\log_{10} [K_a]$ ;  $[K_a] = 10^{-\text{p}K_a}$
- $\text{p}K_b = -\log_{10} [K_b]$ ;  $[K_b] = 10^{-\text{p}K_b}$
- $\text{p}K_a + \text{p}K_b = \text{p}K_w$
- Lower values for  $\text{p}K_a$  and  $\text{p}K_b$  represent stronger acids and bases.

### 18.3 pH curves

pH curves can be investigated experimentally but are mathematically determined by the dissociation constants of the acid and base. An indicator with an appropriate end point can be used to determine the equivalence point of the reaction.

- A buffer solution is resistant to changes in pH on the addition of a small amount of acid or base.
- Buffer solutions consist of a weak acid and its conjugate base or a weak base and its conjugate acid.
- Buffers respond to added acid by reacting with the base in the buffer, and to added base by reacting with the acid in the buffer. These reactions cause a shift in the equilibria positions and by removing added  $\text{H}^+$  or  $\text{OH}^-$  keep the pH approximately constant.
- The pH of a buffer solution depends on:
  - the  $K_a$  or  $K_b$  of the acid/base
  - the ratio of the concentration of acid/base to salt.
- The pH of a buffer does not change with dilution.
- The pH of a buffer is temperature dependent.
- The buffer capacity refers to the amount of acid or base that can be added before the pH changes dramatically. This is reduced with dilution of the buffer.
- The pH of a salt solution depends on the hydrolysis of its ions in aqueous solution. This is determined by the parent acid and base.
- Cation hydrolysis, the conjugate from weak bases, causes the pH of the solution to decrease.
- Anion hydrolysis, the conjugate from weak acids, causes the pH of the solution to increase.



- pH of salt solutions are:

	Strong acid	Weak acid
Strong base	neutral pH 7	basic pH >7
Weak base	acidic pH <7	difficult to generalize

- Equivalence occurs when stoichiometrically equal amounts of acid and base have reacted together, so the solution contains a salt and water only. The pH of the salt formed depends on the relative strength of acid and base that reacted together, as shown in the table above.
- pH curves show the change in pH as a base is added to an acid, or vice versa, in a titration reaction.
- The intercept with the pH axis shows the initial pH of the acid or base.
- The buffer region on the pH curve represents the region where small additions of acid or base result in little or no change in pH.
- There is a jump in the pH at equivalence point, known as the point of inflection.
- The pH at equivalence (half-way up the jump) depends on the relative strengths of the acid and base reacted together. This is due to the different pH values of the salt solutions formed.
- pH at half-equivalence point =  $pK_a$  of acid
- An indicator is a weak acid or a weak base, in which the acid or base and its conjugate have different colours.
- The pH at which an indicator changes colour is known as its end-point. This occurs when the concentration of dissociated and undissociated forms are equal:  $[HIn] = [In^-]$
- The end-point of an indicator is when  $pH = pK_a$  or  $pK_b$ .
- An indicator is appropriate for use in a titration when its end-point ( $pK_a/pK_b$  value) falls within the range of the pH of the equivalence point.
- As different titrations have different pH at the equivalence point, different indicators must be chosen to signal the equivalence point effectively.

## 8.5 Acid deposition

Increased industrialization has led to greater production of nitrogen and sulfur oxides leading to acid rain, which is damaging our environment. These problems can be reduced through collaboration with national and intergovernmental organizations.

- Normal rainwater is acidic due to dissolved  $CO_2$ .
- Acid deposition includes all forms of precipitation from the atmosphere as gas or solid that have a pH <5.6.
- Acid deposition results from oxides of nitrogen and sulfur:  $HNO_3$ ,  $HNO_2$ ,  $H_2SO_4$ , and  $H_2SO_3$  dissolved in water.
- Sulfur oxides are produced mostly from the burning of fossil fuels, especially coal. The reactions produce  $SO_2$  that is oxidized further to  $SO_3$ . Reactions with water form  $H_2SO_4$  and  $H_2SO_3$ . Photo-oxidation involving free radicals may occur.
- Nitrogen oxides are produced mostly from internal combustion engines. NO is the primary pollutant which is oxidized to  $NO_2$ , which then dissolves in water to form  $HNO_3$  and  $HNO_2$ .
- Acid deposition has impacts on structures, especially limestone and metals, due to erosion and corrosion. The reactions are the same as those covered in section 8.2.
- Acid deposition has negative effects on plant and animal life and on bodies of water.



- Responses to acid deposition include removing sulfur from fuels (hydrodesulfurization) and/or from flue gases. Nitrogen oxides are reduced by catalytic converters in vehicles and by carrying out combustion at lower temperatures.

### Get it straight

- *Strong* acids dissociate fully; *concentrated* acids have a high ratio of acid to water. Both of these will increase the  $[H^+]$  and so decrease the pH.
- *Weak* acids do not dissociate fully; *dilute* acids have a low ratio of acid to water. Both of these will decrease the  $[H^+]$  and so increase the pH.
- Acids and bases can be strong and dilute, e.g.  $0.0001 \text{ mol dm}^{-3}$  HCl, or weak and concentrated, e.g.  $10.0 \text{ mol dm}^{-3}$   $\text{CH}_3\text{COOH}$ , as well as strong and concentrated, or weak and dilute.
- Strong/conc. acid  $\Rightarrow$  high  $[H^+]$   $\Rightarrow$  low pH  $\Rightarrow$  high pOH
- Strong/conc. base  $\Rightarrow$  high  $[OH^-]$   $\Rightarrow$  low pOH  $\Rightarrow$  high pH
- The stronger the acid  $\Rightarrow$  higher  $K_a$   $\Rightarrow$  lower  $pK_a$
- The stronger the base  $\Rightarrow$  higher  $K_b$   $\Rightarrow$  lower  $pK_b$



## Chapter 9: Oxidation and reduction – fast facts

### 9.1 Oxidation and reduction

Redox (reduction–oxidation) reactions play a key role in many chemical and biochemical processes.

- Oxidation = gain of oxygen; reduction = loss of oxygen
- Oxidation = loss of hydrogen; reduction = gain of hydrogen
- Oxidation = loss of electrons; reduction = gain of electrons
- Oxidation = increase in oxidation state; reduction = decrease in oxidation state
- Oxidizing agents oxidize other species and themselves get reduced.
- Reducing agents reduce other species and themselves get oxidized.
- Transition metals and most main-group non-metals have variable oxidation states.
- Oxidation numbers are used to represent the oxidation states of elements in names of compounds, using Roman numerals.
- The activity series ranks metals according to the ease with which they undergo oxidation.
- The more reactive a metal, the stronger it is as a reducing agent.
- The more reactive a non-metal, the stronger it is as an oxidizing agent.
- More reactive metals are able to reduce the ions of less reactive metals in displacement reactions.
- More reactive non-metals are able to oxidize the ions of less reactive non-metals.
- Half-equations show the electrons lost/gained in oxidation/reduction reactions and can be used as a step in balancing a redox equation.
- Redox titrations are used to determine concentrations of solutions by finding the equivalence point when two reactants have reacted stoichiometrically, by transferring electrons from the reducing agent to the oxidizing agent.
- The Winkler method uses redox titration to measure the dissolved oxygen content of water.

### 9.2 and 19.1 Electrochemical cells

Voltaic cells convert chemical energy to electrical energy and electrolytic cells convert electrical energy to chemical energy. Energy conversions between electrical and chemical energy lie at the core of electrochemical cells.

#### Voltaic cells

- Voltaic cells convert energy from spontaneous exothermic chemical processes to electrical energy. They are formed by connecting together two half-cells by a salt bridge and an external circuit.
- The anode is the electrode where oxidation occurs. It has a negative charge in a voltaic cell.
- The cathode is the electrode where reduction occurs. It has a positive charge in a voltaic cell.
- Electrons flow through the external circuit of a voltaic cell from anode to cathode. Voltaic cells generate an EMF known as the electrode potential,  $E$ .
- The higher the  $E^\ominus$  value of a cell the greater its tendency to be reduced.
- The lower the  $E^\ominus$  value of a cell the greater its tendency to be oxidized.



- The standard hydrogen electrode is used as the reference standard for voltaic cells, and is assigned a value of 0.00 V.
- The standard electrode potential of a half-cell is measured with reference to the standard hydrogen electrode, operating under standard conditions.
- Using reduction potentials (with the signs as given):

$$E_{\text{cell}}^{\ominus} = E_{\text{half-cell where reduction occurs}}^{\ominus} - E_{\text{half-cell where oxidation occurs}}^{\ominus}$$

- $E_{\text{cell}}^{\ominus}$  must be positive for a spontaneous reaction.
- The equation  $\Delta G^{\ominus} = -nFE^{\ominus}$
- Spontaneous reactions have negative  $\Delta G^{\ominus}$  and positive  $E^{\ominus}$ .
- Non-spontaneous reactions have positive  $\Delta G^{\ominus}$  and negative  $E^{\ominus}$ .
- Reactions at equilibrium have  $\Delta G^{\ominus}$  and  $E^{\ominus} = 0$

### Electrolytic cells

- Electrolytic cells use electrical energy to drive non-spontaneous chemical change.
- The anode is the electrode where oxidation of anions occurs. It has a positive charge in an electrolytic cell.
- The cathode is the electrode where reduction of cations occurs. It has a negative charge in an electrolytic cell.
- The electrolyte is a molten salt or aqueous solution that undergoes chemical change.
- In an electrolytic cell, current is supplied through a power source, and enters and leaves the electrolyte at the electrodes. It is carried through the electrolyte by mobile ions.
- Neutral products are discharged from each electrode.
- In aqueous solution water can be oxidized to oxygen at the anode and reduced to hydrogen at the cathode.
- The products of electrolysis in aqueous solution depend on:
  - the  $E^{\ominus}$  values
  - the concentration of electrolyte
  - the nature of the electrode.
- The amount of product in electrolysis depends on:
  - the ion charge
  - the current
  - the time.
- charge (C) = current (A)  $\times$  time (s)
- The equation for the discharge of an ion shows the moles of electrons required.
 

e.g.  $2\text{Cl}^{-} \rightarrow \text{Cl}_2 + 2\text{e}^{-}$   $\therefore$  1 mole  $\text{Cl}_2$  discharged requires 2 moles of electrons.
- Electroplating involves the electrolytic coating of an object with a thin layer of metal.

### Get it straight

- In voltaic cells the anode is negative and the cathode is positive.
- In electrolytic cells the anode is positive and the cathode is negative.
- In all cells, oxidation occurs at the anode and reduction occurs at the cathode.
- In all cells, electrons flow from the anode to the cathode.





# Chapter 10: Organic chemistry – fast facts

## 10.1 Fundamentals of organic chemistry

Organic chemistry focuses on the chemistry of compounds containing carbon.

- A homologous series is a series of compounds with the same general formula, where each member differs from the successive member by  $-\text{CH}_2-$ . Members of the same homologous series show a trend in their physical properties and have similar chemical properties.
- Different formulas are used to describe an organic compound:
  - empirical formula is the simplest ratio of atoms present in a molecule
  - molecular formula is the actual number of atoms present in a molecule
  - condensed structural formula gives the minimum information to describe the molecule non-ambiguously
  - full structural formula shows all the bonds in a molecule
  - stereochemical formula shows the 3-dimensional arrangement of the atoms.(Note: skeletal formula is not a structural formula as it does not include all the hydrogen atoms.)
- Saturated compounds contain single bonds only, and unsaturated compounds contain double or triple bonds.
- IUPAC nomenclature is used to describe organic compounds.
- Stem: named for the longest carbon chain where:  
C1 = meth-, C2 = eth-, C3 = prop-, C4 = but-, C5 = pent-, C6 = hex-, C7 = hept-, C8 = oct-
- Suffix used for the functional group ending:  
-ene, -anol, -anal, -anone, -anoic acid, -anoate, -amide, -amine, -anenitrile, -benzene
- Prefix used for substituent groups, using the smallest number to denote the main-chain C atom.  
methyl-, ethyl-, propyl-, fluoro-, chloro-, bromo-, iodo-, amino-
- The functional group is the reactive part of a molecule. It defines the class of compound e.g. the hydroxyl group defines the class, the alcohols.
- Structural isomers are molecules with the same molecular formula but different structural formulas. They contain atoms attached in a different order, and have distinct physical and chemical properties. Structural isomers can be straight/branched chains or differ in the position or nature of the functional group.
- Primary, secondary, and tertiary carbon atoms are attached to a functional group, and differ in the number of hydrogen atoms to which they are also attached. Primary, secondary, and tertiary compounds e.g. alcohols and haloalkanes, show some different chemical properties.
- Arenes contain the benzene ring. They are known as aromatic compounds. Organic compounds without the benzene ring are known as aliphatic compounds.
- Benzene has distinct properties due to its delocalized pi electrons, which give it an extra stability. It is a planar, non-polar molecule, which does not readily undergo addition reactions despite being highly unsaturated.
- The volatility of organic compounds depends on:
  - i the size of the molecule/length of the hydrocarbon chain and
  - ii the functional group.
- The larger members of a homologous series are less volatile due to stronger London (dispersion) forces.

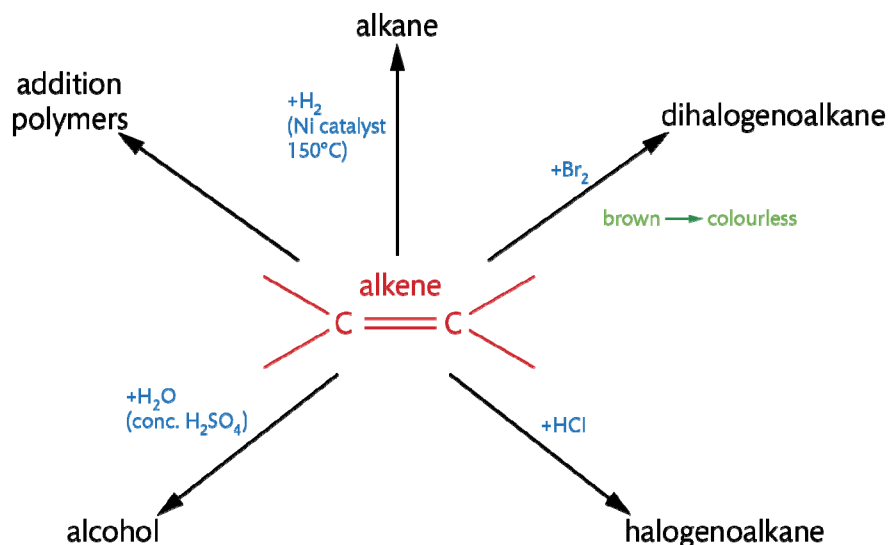


- More polar functional groups decrease the volatility of the compound.

## 10.2 Functional group chemistry

Structure, bonding and chemical reactions involving functional group interconversions are key strands in organic chemistry.

- Hydrocarbons contain carbon and hydrogen only. Alkanes, alkenes, alkynes, and benzene are hydrocarbons.
- Hydrocarbons undergo combustion and release significant energy. These reactions have high activation energy.
- In excess  $O_2$ , hydrocarbons burn to produce  $CO_2$  and  $H_2O$ . In limited  $O_2$ , they undergo incomplete combustion and produce  $CO$  or  $C$ .
- The products of burning hydrocarbons have harmful effects on the environment and health.
- Alkanes are saturated hydrocarbons. They have low reactivity as the  $C-C$  and  $C-H$  bonds are strong.
- Alkanes undergo substitution reactions with halogens in UV light. The halogen undergoes photochemical homolytic fission to produce free radicals in the initiation step. The radicals substitute for  $H$  in the alkanes in propagation reactions that also produce free radicals. The reaction produces a mixture of substituted products. Termination steps involve two free radicals joining together.
- Alkenes are unsaturated hydrocarbons containing a carbon-carbon double bond. The double bond is the site of reactivity as the pi bond breaks relatively easily, and so alkenes are more reactive than alkanes.
- Alkenes undergo addition reactions, by breaking their double bond.
- Addition reactions of alkenes include:
  - addition of  $H_2$  (hydrogenation)  $\Rightarrow$  alkanes
  - addition of halogens  $\Rightarrow$  dihalogenoalkane
  - addition of hydrogen halide (hydrohalogenation)  $\Rightarrow$  halogenoalkane
  - addition of  $H_2O$  (hydration)  $\Rightarrow$  alcohol
- Alkenes decolorize bromine water in the dark or light, and this colour change can be used to distinguish between alkanes and alkenes.
- Alkenes undergo addition reactions to form addition polymers by breaking their double bonds. The repeat unit shows the structure of the monomer with open bonds on each side.





- Alcohols are fuels and, like hydrocarbons, yield products that depend on the amount of oxygen available.
- Alcohols differ in their ability to be oxidized. Oxidizing agents include acidified potassium dichromate(VI) or potassium manganate(VII) and the reaction is heated.
  - Primary alcohols are oxidized first to aldehyde, and with prolonged oxidation to carboxylic acid. The aldehyde product can be separated by distillation as it has the lowest boiling point in the mixture. For prolonged oxidation to carboxylic acid, reflux is used. The oxidizing agent changes colour as it is reduced.
  - Secondary alcohols are oxidized to the ketone. The oxidizing agent changes colour as it is reduced.
  - Tertiary alcohols are not oxidized under these conditions. The oxidizing agent does not change colour.
- Alcohols react with carboxylic acids to produce an ester and water. Concentrated sulfuric acid is used as a catalyst in the reaction. It is a condensation/esterification reaction.
 
$$\text{acid} + \text{alcohol} \rightarrow \text{ester} + \text{water}$$

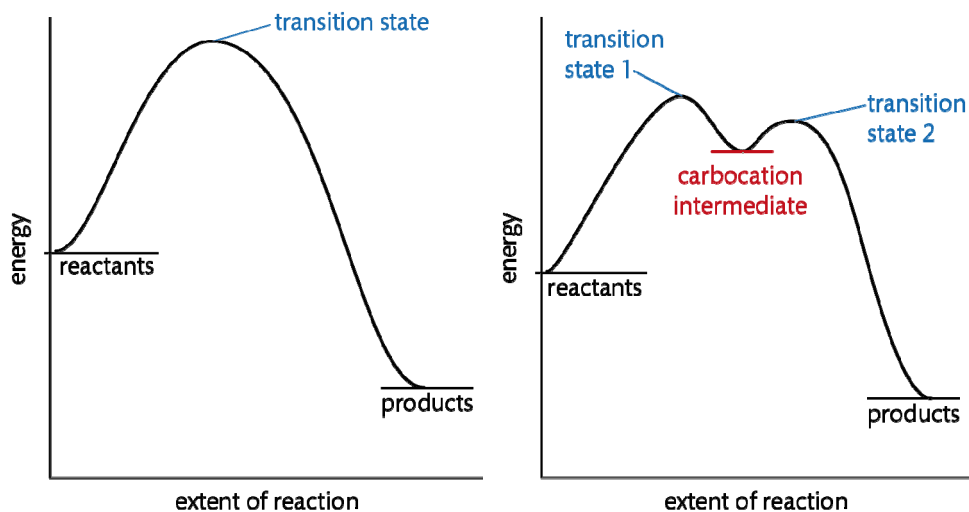
$$\text{RCOOH} + \text{R}'\text{OH} \rightarrow \text{RCOOR}' + \text{H}_2\text{O}$$
- Halogenoalkanes contain the polar bond C–halogen, and so are more reactive than alkanes.
- Halogenoalkanes are susceptible to attack by nucleophiles at the electron-deficient carbon of the C–halogen bond. Nucleophiles are species that possess a lone pair of electrons, and can also possess a negative charge.
- Halogenoalkanes undergo substitution reactions where the halogen is replaced by a nucleophile.
- Halogenoalkanes react with NaOH(aq) to form an alcohol.
 
$$\text{e.g. RCl} + \text{NaOH} \rightarrow \text{ROH} + \text{NaCl}$$
- Benzene does not readily undergo addition reactions, but instead undergoes substitution reactions that preserve the stable ring structure. These reactions are carried out by electrophiles, electron-deficient species that are attracted to the electron-dense benzene ring. They are known as electrophilic substitution reactions.

## 20.1 Types of organic reactions

Key organic reaction types include nucleophilic substitution, electrophilic addition, electrophilic substitution, and redox reactions. Reaction mechanisms vary and help in understanding the different types of reaction taking place.

### Nucleophilic substitution reactions

- Between halogenoalkanes and NaOH.
- S<sub>N</sub>1 mechanism = substitution reaction, nucleophilic, unimolecular. Proceeds via a carbocation intermediate formed by heterolytic fission of the C–halogen bond. Favoured by tertiary halogenoalkanes due to stability of the tertiary carbocation. Carried out in protic polar solvents.
- S<sub>N</sub>2 mechanism = substitution reaction, nucleophilic, bimolecular. Proceeds in one concerted step via a transition state. The reaction is stereospecific. Carried out in aprotic, polar solvents.
- OH<sup>−</sup> is a stronger nucleophile than H<sub>2</sub>O as it has a negative charge, in addition to lone pairs.



### Electrophilic addition reactions

- Alkene + Br<sub>2</sub> / interhalogens / hydrogen halides
- The pi bond in alkenes is an electron-dense area, to which electrophiles are attracted. Electrophiles are electron-deficient species, generated by heterolytic fission, e.g. Br<sup>+</sup> from Br<sub>2</sub>.
- The reaction involves breaking the pi bond of the double bond, creating two new bonding positions for the addition product.
- The major product of the reaction of addition of unsymmetrical reagents to unsymmetrical alkenes can be predicted from Markovnikov's rule. This prediction is based on the favoured mechanism proceeding via the more stable carbocation.

tertiary carbocation > secondary carbocation > primary carbocation in stability

### Electrophilic substitution reactions

- Benzene + HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>
- The delocalized ring of pi electrons in benzene is an electron-dense area, to which electrophiles are attracted.
- Substitution reactions in benzene substitute a hydrogen atom of the ring for the electrophile, which preserves the stability of the benzene ring structure.
- Nitration of benzene uses a nitrating mixture of the concentrated acids HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. This generates the electrophile NO<sub>2</sub><sup>+</sup> that substitutes in benzene.

### Reduction reactions

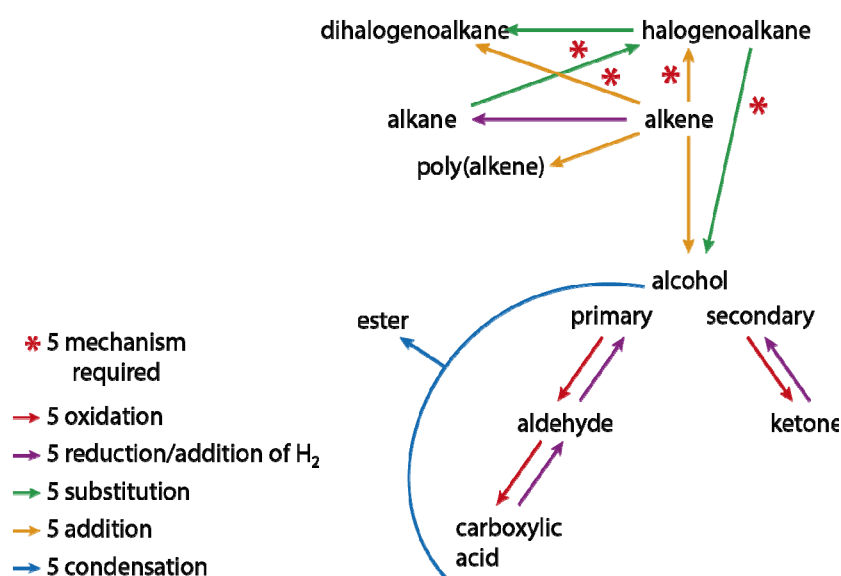
- These are often defined in terms of gain of H/loss of O in organic chemistry.
- Reducing agents for carbonyl compounds are NaBH<sub>4</sub> or LiAlH<sub>4</sub>, which both produce H<sup>-</sup>:
  - carboxylic acid is reduced to aldehyde
  - aldehyde is reduced to primary alcohol
  - ketone is reduced to secondary alcohol
- Reducing agents for nitrobenzene are Sn/conc. HCl. Nitrobenzene is reduced to phenylammonium ions, and then to phenylamine.



## 20.2 Synthetic routes

Organic synthesis is the systematic preparation of a compound from a widely available starting material or the synthesis of a compound via a synthetic route that often can involve a series of different steps.

- Organic chemistry often involves converting an available starting material into a required product in a multi-step process.
- Retro-synthesis involves working backwards from a desired product, and deducing the precursor molecules that can react to form the target molecule.
- Functional group chemistry determines reaction conversions in synthetic routes.



## 20.3 Stereoisomerism

Stereoisomerism involves isomers which have different arrangements of atoms in space but do not differ in connectivity or bond multiplicity (i.e. whether single, double, or triple) between the isomers themselves.

- Stereoisomers differ in the spatial/three-dimensional arrangement of the atoms in a molecule.
- Configurational isomerism refers to stereoisomers that cannot be interconverted without breaking sigma bonds and so have a permanent difference in their geometry.
- cis-trans* isomers and *E/Z* isomers occur where there is a restriction on rotation around substituted groups. This occurs in (i) cyclic and (ii) double-bonded molecules, as here there is no free rotation.
- Where there are only two types of substituents the isomers are called *cis* and *trans* – *cis* has the same groups on the same side, and *trans* has them on opposite sides of the reference plane.
- Where there are more than two different substituents, the *E/Z* nomenclature must be used, which has broader application. Using priority rules, each group attached to each C atom of the ring or double bond is assigned a priority based on atomic number. The *E* isomer has the two groups of highest priority on the same side of the double bond or ring, and the *Z* group has them on the opposite sides.
- Optical isomers occur when a molecule contains a chiral/asymmetric carbon atom. This is attached to four different groups, and gives rise to enantiomers that are non-superimposable mirror images of each other.



- Optical isomers differ in the direction in which they rotate plane-polarized light. This can be measured using a polarimeter.
- A racemic mixture contains equal amounts of the two enantiomers and is optically inactive.
- Diastereoisomers arise when a molecule has more than one chiral centre, and has different configurations in some but not all of these positions. Diastereoisomers are not mirror images of each other.
- Enantiomers differ from each other in their direction of rotation of plane-polarized light, and in their reactivity with other chiral molecules. This is important in living cells, as all biochemical reactions are stereospecific.

### Get it straight

- Free radicals have an unpaired electron but do not carry a charge; ions carry a charge.
- Homolytic fission generates free radicals; heterolytic fission generates ions.
- Combustion refers to complete oxidation of the molecule and involves destruction of the carbon chain. Oxidation of an organic compound refers to a chemical change at a functional group, which leaves the carbon structure of the molecule intact.



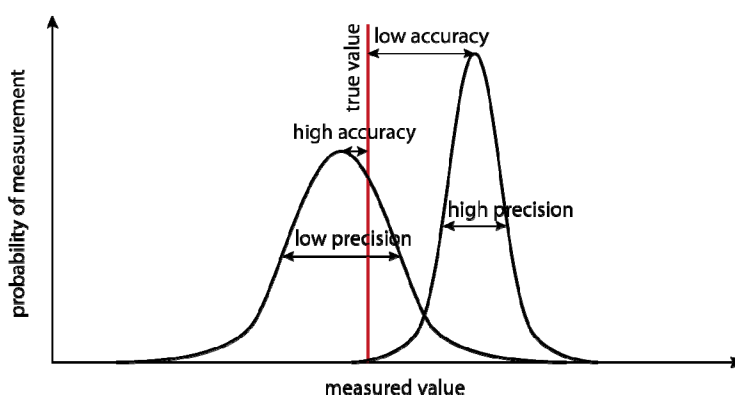


# Chapter 11: Measurement and data processing and analysis – fast facts

## 11.1 Uncertainty and error in measurement and results

All measurement has a limit of precision and accuracy, and this must be taken into account when evaluating experimental results.

- Qualitative data includes all non-numerical information obtained from observations, not from measurement.
- Quantitative data are obtained from measurements and are always associated with random errors/uncertainties determined by the apparatus and by human limitations such as reaction times.
- **Random** errors are caused by:
  - the readability of the measuring instrument
  - the effects of changes in the surroundings, such as temperature variations and air currents
  - insufficient data
  - the observer misinterpreting the reading.
- Random errors make a measurement less precise, but not in any particular direction. They are expressed as an uncertainty range, such as  $25.05 \pm 0.05$  °C.
- The uncertainty of an **analogue** scale is  $\pm$  (half the smallest division).
- The uncertainty of a **digital** scale is  $\pm$  (the smallest scale division).
- **Systematic** errors occur when there is an error in the experimental procedure. Measuring the volume of water from the top of the meniscus rather than the bottom, or overshooting the volume of a liquid delivered in a titration will lead to readings which are too high. Heat losses in an exothermic reaction will lead to smaller observed temperatures changes.
- Experiments are **repeatable** if the same person duplicates the experiment with the same results.
- Experiments are **reproducible** if several experimentalists duplicate the results.
- The **precision** or reliability of an experiment is a measure of the random error. If the precision is high then the random error is small.
- The **accuracy** of a result is a measure of how close the result is to some accepted or literature value. If an experiment is accurate then the systematic error is very small.
- Random uncertainties can be reduced by repeating readings; systematic errors cannot be reduced by repeating measurements.
- Precise measurements have small random errors and are reproducible in repeated trials. Accurate measurements have small systematic errors and give a result close to the accepted value.





- The number of **significant figures** in any answer should reflect the number of significant figures in the given data.
- When data are multiplied or divided the answer should be quoted to the same number of significant figures as the least precise.
- When data are added or subtracted the answer should be quoted to the same number of **decimal places** as the least precise value.
- When adding or subtracting measurements, the total absolute uncertainty is the sum of the absolute uncertainties.
- When multiplying or dividing measurements, the total percentage uncertainty is the sum of the individual percentage uncertainties. The absolute uncertainty can then be calculated from the percentage uncertainty.
- To find the absolute uncertainty in a calculated value for  $ab$  or  $a/b$ :
  - 1 Find the percentage uncertainty in  $a$  and  $b$ .
  - 2 Add the percentage uncertainties of  $a$  and  $b$  to find the percentage uncertainty in the calculated value.
  - 3 Convert this percentage uncertainty to an absolute value.If one uncertainty is much larger than others, the approximate uncertainty in the calculated result can be taken as due to that quantity alone.
- The **experimental error** in a result is the difference between the recorded value and the generally accepted or literature value.
- **Percentage uncertainty** = (absolute uncertainty/measured value)  $\times$  100%
- **Percentage error** = (accepted value – experimental value)/accepted value  $\times$  100%

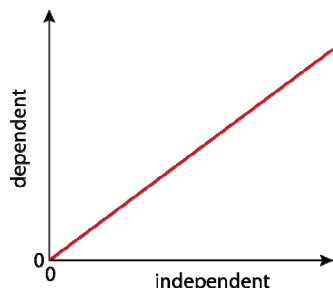
## 11.2 Graphical techniques

Graphs are a visual representation of trends in data.

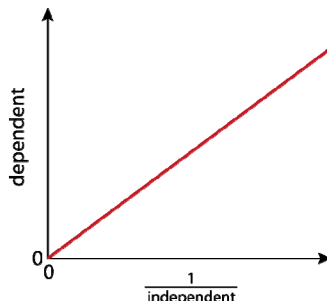
- Graphical techniques are an effective means of communicating the effect of an independent variable on a dependent variable, and can lead to determination of physical quantities.
- The independent variable is the *cause* and is plotted on the horizontal axis. The dependent variable is the *effect* and is plotted on the vertical axis.
- Sketched graphs have labelled but unscaled axes, and are used to show qualitative trends, such as variables that are proportional or inversely proportional.
- Drawn graphs have labelled and scaled axes, and are used in quantitative measurements.
- **When drawing graphs:**
  - give the graph a title and label the axis with both quantities and units.
  - use the available space as effectively as possible and use sensible scales – there should be no uneven jumps.
  - plot all the points correctly.
  - identify any points which do not agree with the general trend.
  - think carefully about the inclusion of the origin. The point (0, 0) can be the most accurate data point or it can be irrelevant.
- You should be able to give a qualitative physical interpretation of a particular graph. See the next page for examples.



- The variables are **proportional**.



- The variables are **inversely proportional**.



- A best-fit straight line does not have to go through all the points but should show the overall trend.

- The equation for a straight line is:

$$y = mx + c$$

$x$  is the independent variable

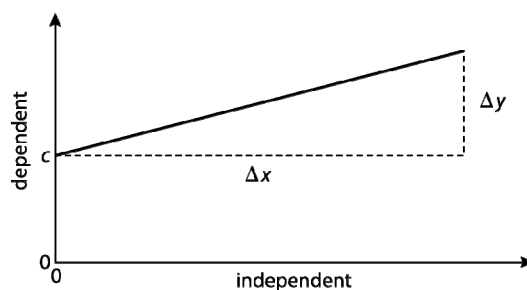
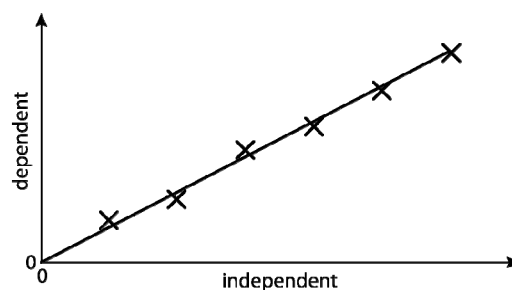
$y$  is the dependent variable

$m$  is the gradient

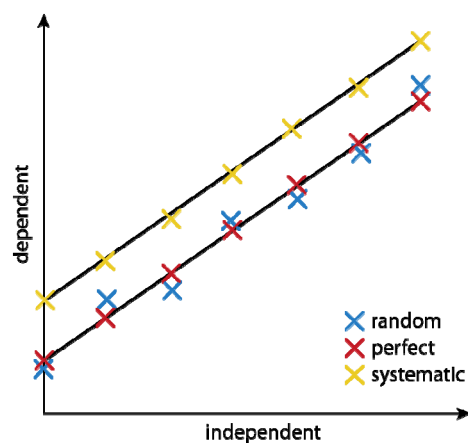
$$m = \frac{\Delta y}{\Delta x}$$

$m$  has units

$c$  is the intercept on the vertical axis

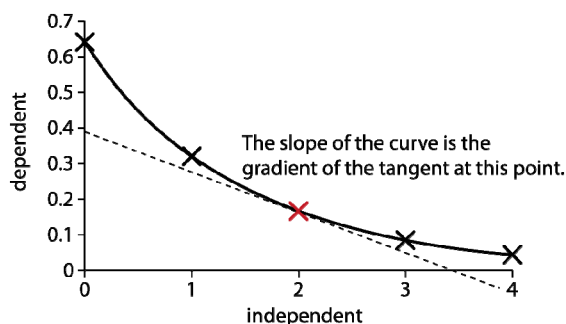


- A systematic error produces a displaced line.
- Random uncertainties lead to points on both sides of the perfect line.





- The gradient of a curve is given by the gradient of the tangent at that point.
- The process of assuming that the trend line applies between two points is called **interpolation**.
- A line is **extrapolated** when it is extended beyond the range of measurement.



### 11.3 Spectroscopic identification of organic compounds

Analytical techniques can be used to determine the structure of a compound, analyse the composition of a substance, or determine the purity of a compound. Spectroscopic techniques are used in the structural identification of organic and inorganic compounds.

- The **degree of unsaturation** (or **index of hydrogen deficiency**) provides a measure as to the degree of unsaturation of an organic molecule. It relates to how many molecules of hydrogen would in theory be needed to convert an unsaturated molecule to a saturated molecule.
- Mass spectrometry (MS), proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) and infrared spectroscopy (IR) are techniques that can be used to help identify and to determine the structure of compounds.
- The data booklet contains characteristic ranges for IR absorptions (section 26),  $^1\text{H}$  NMR data (section 27), specific MS fragments (section 28) and the formula to determine IHD.

#### Mass spectrometry

- Molecules are hit by fast-moving electrons, forming a positive ion. The ion can fragment. The largest fragment is the **parent ion**.
- A **fragmentation pattern** can provide evidence for the structure of the compound.

#### Infrared spectroscopy

- Energy needed to excite molecules to make them vibrate more occurs in the infrared region of the spectrum.
- IR radiation can cause a bond to stretch or bend. Stretching a bond requires more energy than bending a bond and generally occurs at higher wavenumbers.
- Absorption of particular wavenumbers of IR radiation correspond to particular bonds. Bonds with atoms of small mass absorb at higher wavenumbers than atoms with larger mass. Double bonds occur at higher wavenumbers than single bonds. Characteristic absorption bands can be found in section 26 of the IB data booklet.
- Hydrogen bonding broadens the absorptions.
- The intensity of the absorption depends on the polarity of the bond.
- In a polyatomic molecule such as carbon dioxide it is more correct to consider the molecule stretching and bending as a whole, rather than considering the individual bonds.
- In carbon dioxide, for example, there are four modes of vibration. The symmetric stretch is IR inactive as it produces no change in dipole moment.



symmetric stretch inactive As the molecule remains symmetrical, it has no change in dipole.	asymmetric stretch $\approx 2350 \text{ cm}^{-1}$ The molecule has a temporary dipole moment when the C=O bond lengths are of unequal length.	two symmetric bends $\approx 670 \text{ cm}^{-1}$ The molecule has a temporary dipole moment as it bends away from its linear geometry. The two vibrations are identical, except that one is in the plane of the page and the other is out of the plane of the page.	

- Molecules with several bonds can vibrate in many different ways and with many different frequencies. The complex pattern can be used as a fingerprint to be matched against the recorded spectra of known compounds in a database. A comparison of the spectrum of a sample with that of a pure compound can also be used as a test of purity.

### Nuclear magnetic resonance spectroscopy

- Studies the alignment of protons (or  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  atoms) in magnetic fields.
- The position of the NMR signal relative to the standard tetramethylsilane is called the **chemical shift** of the proton. Hydrogen nuclei in particular environments have characteristic chemical shifts.
- Tetramethylsilane has 12 hydrogen atoms bonded in the same atypical environment close to a silicon atom. It gives one strong signal away from signals produced in most organic compounds.
- The integrated trace indicates the relative number of hydrogen atoms in the different environments.

## 21.1 Spectroscopic identification of organic compounds

Although spectroscopic characterization techniques form the backbone of structural identification of compounds, typically no one technique results in a full structural identification of a molecule.

### Nuclear magnetic resonance spectroscopy

- Under high resolution individual peaks may split into further peaks due to **spin-spin coupling**. If a proton has  $n$  protons as nearest neighbours its NMR peak is split into  $(n + 1)$  peaks.
- The splitting patterns can be deduced from Pascal's triangle and are summarized below:

Number of chemically equivalent protons causing splitting	Splitting patterns with relative intensities
0	1
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1



- When analysing high-resolution NMR spectra, the following additional points should be noted:
  - Protons bonded to the same atom do not interact with one another as they are equivalent and behave as a group.
  - Protons on non-adjacent carbon atoms do not generally interact with one another.
  - The O—H single peak in ethanol does not split unless the sample is pure, as rapid exchange of the protons between ethanol molecules averages out the different possible spins.

### *X-ray diffraction*

- Used to produce an electron density map of a crystalline solid. This can be related to the atoms which make up the molecule.
- The identity of the atoms can be determined from the pattern in electron densities which are related to an element's electron configuration. Hydrogen atoms are not generally detected as they have only one electron.





## Chapter 12: Materials – fast facts

### A.1 Materials science Introduction

Materials science involves understanding the properties of a material, and then applying those properties to desired structures.

- Properties of a material depend on the degree of covalent, ionic, or metallic character that substance has and can be deduced from its position on a **bonding triangle**.
- The bonding is based on the magnitude and difference in the electronegativities of the constituent elements:
  - high average electronegativity with large difference in the electronegativities = ionic
  - low average electronegativity with zero difference in electronegativity = metallic
  - high average electronegativity and small difference in electronegativity = covalent
- **Ceramics** are made by baking metal oxides and other minerals to high temperature. They form giant ionic or giant covalent structures, and are hard but brittle.
- **Glasses** are a form of ceramic made by the rapid cooling of a molten mixture of silicon dioxide and a metal oxide, in which some of the disorder of the liquid is trapped in the solid structure.
- **Composite materials** are formed when fibres of one material are trapped in a matrix of another material. It allows the tailoring of the properties of the material.

### A.2 Metals and inductively coupled plasma (ICP) spectroscopy

Metals can be extracted from their ores and alloyed for desired characteristics. ICP-MS/OES spectroscopy ionizes metals and uses mass and emission spectra for analysis.

- The extraction of a metal from its ore depends on its position in the reactivity series:
  - high = electrolysis
  - intermediate = reduction with hydrogen, carbon or carbon monoxide
  - low = found native, or produced by heating the ore
- Displacement of one metal by a more reactive metal can also be used to produce a metal  
e.g.  $\text{Zn} + \text{CuSO}_4 \rightarrow \text{Cu} + \text{ZnSO}_4$
- Reduction of hematite in a blast furnace with carbon monoxide produces iron  
 $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$
- Aluminium is extracted from its molten ore ( $\text{Al}_2\text{O}_3$ ) by electrolysis in molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) which reduces the operating temperature and increases the conductivity.
- The amount of metal produced depends on the number of electrons supplied.
- **Faraday's law** states that the amount of product formed during electrolysis is equivalent to the amount of electrons supplied ( $1 \text{ Faraday} = 96500 \text{ C mol}^{-1}$ ).
- Alloys are **homogeneous mixtures** of metals with other metals or non-metals formed by mixing the liquid metals and allowing them to solidify. Alloys are stronger than the metals from which they were made.
- In a magnetic field materials can be **diamagnetic** (repelled by the field), or **paramagnetic** (attracted to the field). Some are **ferromagnetic** – they retain the magnetic field once the external field is removed.



- Trace amounts of metals can be identified and quantified by ionising them with argon gas plasma in **Inductively Coupled Plasma (ICP) Spectroscopy** using **Mass Spectroscopy ICP-MS** and **Optical Emission Spectroscopy ICP-OES**.
- **Plasma** is a high energy state composed of isolated atoms, ions, and electrons.
- In ICP spectroscopy plasma is used to collide with sample atoms. Ions are produced and electrons from the sample are promoted to excited states. When they fall to lower states the radiation emitted is characteristic of a particular element. The number of photons emitted is also proportional to the concentration of the element in the sample.

### A.3 Catalysts

Catalysts work by providing an alternate reaction pathway for the reaction. Catalysts always increase the rate of the reaction and are left unchanged at the end of the reaction.

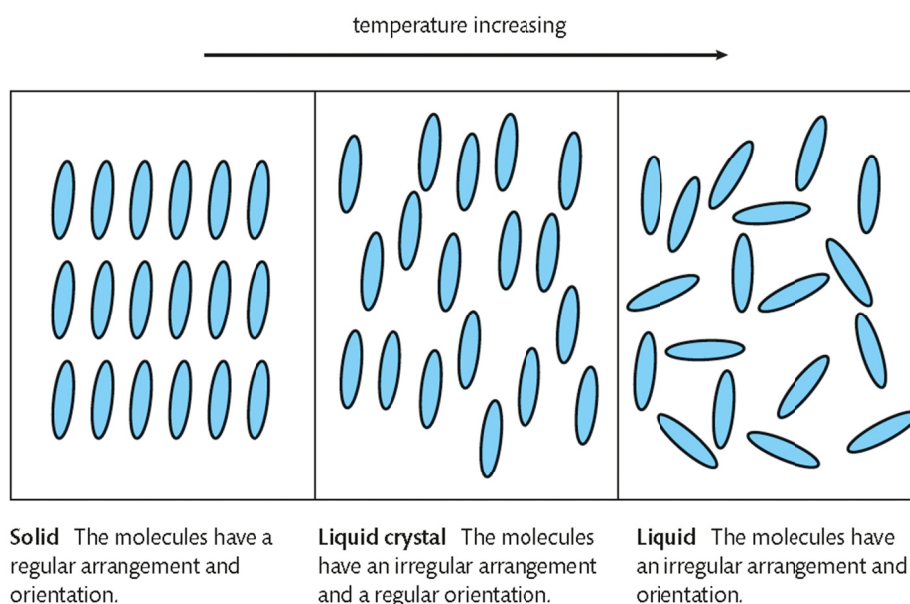
- Catalysts provide reactions with an alternative pathway of lower energy.
- Catalysts increase the rate of some reactions but they do not change the position of equilibrium. They are not chemically changed at the end of the reaction.
- A substance is adsorbed when it is weakly attached to a surface. It is absorbed when it enters pores in the material.
- **Homogeneous catalysts** are in the same state as the reactants, **heterogeneous catalysts** are in a different state from the reactants and are more widely used in industry due to ease of separation of the catalyst from the products.
- An **activated complex** is an unstable combination of reactant molecules that can go on to form products or fall apart to form reactants
- A **reaction intermediate** is a species that is produced and consumed during a reaction but does not occur in the overall equation.
- Many catalysts are transition metals or their compounds as they have variable oxidation states and can adsorb small reactant molecules onto their surface. An unstable activated complex is formed which can then form a reaction intermediate in the process.
- **Zeolites (aluminium silicates)** are widely used as catalysts as they have large surface areas on which reactions can take place. Zeolites act as selective catalysts because of their cage structures
- **Nanoparticles** can also be used as they have a large surface area in proportion to their mass.
- Catalysts can be modified with **promoters** to increase the catalytic activity, or with inhibitors to decrease the activity.
- The choice of catalyst will depend on a number of factors:
  - Selectivity: does the catalyst give a high yield of the desired product?
  - Efficiency: how much faster is the reaction with the catalyst?
  - Life expectancy: for how long does it work before it is poisoned?
  - Environmental impact: the ability to work under a range of conditions of temperature and pressure. A heterogeneous catalyst may melt and or become less effective if its operating temperatures are too high or its surface becomes coated with unwanted products.



## A.4 Liquid crystals

Liquid crystals are fluids that have physical properties which are dependent on molecular orientation relative to some fixed axis in the material.

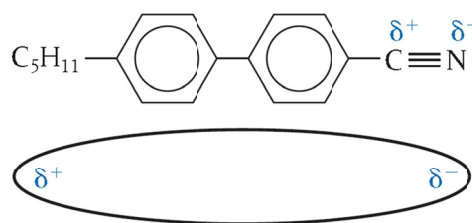
- Liquid crystals are fluids that have physical properties (electrical, optical and elasticity) that are dependent on molecular orientation to some fixed axis in the material.
- **Nematic** liquid crystals have the long molecules arranged irregularly but orientated in the same direction.
- **Thermotropic** liquid crystals are pure substances that show liquid crystal behaviour in a temperature range between the solid and liquid state.



- **Lyotropic** liquid crystals have regions of oriented molecules which may be oriented differently from other regions of molecules.
- The phase transitions of thermotropic liquid crystals depend on temperature, while those of lyotropic liquid crystals depend on both temperature and concentration.
- The elasticity and electrical and optical properties of the liquid crystal depend on the orientation of the molecule relative to some fixed axis in the material. Biphenyl nitriles can be oriented differently if a small electric field is applied across the liquid crystal. This can affect how light passes between polarized filters.
- **Twisted nematic liquid crystal devices** align the molecules to be parallel to the direction of polarization in a polarizing filter. A small electric charge disrupts the alignment of the molecules preventing light from being transmitted.



- **Biphenyl nitriles** show liquid crystal behaviour.
- These molecules have three key features:
  - Long alkyl chain: this limits the ability of the molecules to pack together and so lowers the melting point and helps maintain the liquid crystal state.
  - Biphenyl groups: the two planar benzene rings make the molecule rigid and rod shaped.
  - Nitrile group: the high electronegativity of nitrogen makes the functional group polar. This increases the intermolecular interactions between the molecules and allows the orientation of the molecule to be controlled by an electric field.



The molecule is polar as nitrogen has a greater electronegativity than carbon.

## A.5 Polymers

Polymers are made up of repeating monomer units which can be manipulated in various ways to give structures with desired properties.

- The properties of polymers can be altered by changing the nature of the **monomers** used to make the polymer.
- **Addition polymers** are formed when the double bonds of many monomer molecules open up to form a long continuous chain. The properties of the addition polymer can be changed by altering its chain length and the degree of branching of the polymer.
- **Isotactic** addition polymers have substituents on the same side. **Atactic** addition polymers have the substituents randomly placed.
- Areas of regular arrangement between polymer molecules lead to a **crystalline** structure. Areas of irregular arrangement lead to **amorphous** forms.
- **Low density poly(ethene)** is formed from branched molecules, they cannot pack closely so the forces between the chains are relatively weak.
- **High density poly(ethene)** is more rigid as the polymer chains are unbranched and so can pack more closely together.
- Properties of a polymer can also be altered by adding **plasticizers**. These are bulky molecules that prevent the chains from lying close to each other – and so making the polymer more flexible. They increase the flexibility by weakening the intermolecular forces between the polymer chains.
- Some polymers can be ‘expanded’ by adding a small amount of a volatile hydrocarbon which expands on processing, forming bubbles that force the polymer into the shape of the mould.
- **Thermoplastics** can be softened by heating whereas **thermosetting** polymers (which usually have cross-linking between the polymer chains) can only be moulded once. Heating a thermosetting polymer tends to break it down (char) rather than softening it.
- **Elastomers** are flexible and can be deformed under force but will return to nearly their original shape once the stress is released.
- **Atom economy** is a measure of efficiency applied in green chemistry.

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



## A.6 Nanotechnology

Chemical techniques position atoms in molecules using chemical reactions whilst physical techniques allow atoms/molecules to be manipulated and positioned to specific requirements.

- Nanotechnology is based on small clusters of atoms (usually between 10 and a few hundred), having a size between 1 and 100 nm. It creates and uses structures that have novel properties because of their small size and builds on the ability to control or manipulate on the atomic scale.
- Individual atoms can be 'imaged' and manipulated using a scanning tunnelling microscope or an atomic force microscope.
- Molecular self assembly is the bottom up assembly of nanoparticles and can occur by selectively attaching molecules to specific surfaces. Self-assembly can also occur spontaneously in solution due to intermolecular interactions such as **hydrogen bonding** and **van der Waals'** forces.
- Carbon can form buckminsterfullerene ( $C_{60}$ ), or nano-tubes (with a diameter of about 1 nm). A single layer of graphite (graphene) is one of the thinnest and one of the strongest materials known.
- **Carbon nanotubes** are made from pentagons and hexagons of carbon atoms. The inclusion of pentagons into the hexagonal structure of graphite allows the carbon atoms to form a closed spherical cage.
- Possible methods of producing nanotubes are arc discharge, **chemical vapour deposition (CVD)** and **high pressure carbon monoxide (HPCO)**.
- **Arc discharge** involves either vaporizing the surface of one of the carbon electrodes, or discharging an arc through metal electrodes submerged in a hydrocarbon solvent, which forms a small rod-shaped deposit on the anode.
- Carbon nanotubes are strong due to the strong covalent bonding within the walls of the nanotube.
- Carbon nanotubes can conduct electricity due to the presence of delocalised electrons. Different tubes have different electrical properties because the behaviour of electrons is very sensitive to the dimensions of the tube. Some tubes are conductors and some are semi-conductors.
- As tubes have large surface areas and specific dimensions, they have the potential to be very efficient and size-selective heterogeneous catalysts.
- Possible implications of nanotechnology include uncertainty as to toxicity levels on a nanoscale, unknown health risks with new materials, concern that human defence systems aren't effective against particles on the nanoscale, and responsibilities of the industries and governments involved in this research.

## A.7 Environmental impact: plastics

Although materials science generates many useful new products, there are challenges associated with recycling and high levels of toxicity of some of these materials.

- Plastics do not degrade easily because of the strong covalent bonds between the atoms in the polymer.
- Volatile plasticizer molecules (e.g. **phthalates**) are thought to have health implications, particularly for small children.
- Incineration of plastics produces pollution. Incineration of PVC forms HCl and also **polychlorinated dioxins**.
- **Dioxins** contain unsaturated six-member heterocyclic rings with two oxygen atoms, usually in position 1 and 4. Dioxins do not decompose in the environment and can be passed on in the food chain.
- Chlorinated dioxins are hormone disrupting leading to cellular and genetic damage.
- Plastics require more processing to be recycled than other materials.



- Plastics have a resin identification code which can aid their recycling. Their IR spectrum may also help with their identification.
- Polymers can be depolymerized to split them up into their monomers, using heat in the absence of air.
- House fires can release many toxins due to plastics (shower curtains, etc.). Low smoke zero halogen cabling is often used in wiring to prevent these hazards.

## A.8 Superconducting metals and X-ray crystallography

Superconductivity is zero electrical resistance and expulsion of magnetic fields.  
X-ray crystallography can be used to analyse structures.

- Resistance in metals is caused by collisions between electrons and the positive ions in the lattice.
- **Superconductors** are materials that offer no resistance to electric currents below a critical temperature.
- Current in a superconductor is carried by a **Cooper pair** of electrons which move freely through the superconductor.
- The lattice becomes distorted by the presence of one electron and the positive ions are more closely packed. This increase in positive charge density attracts another electron into the same region to pair up with the original electron.
- Superconductors exhibit the **Meissner effect** – when in a magnetic field they can produce a magnetic field equal and opposite to the field in which they are placed.
- **Type 1 semiconductors** (usually metals and metalloids) have a sharp transition to superconductivity on cooling, whereas **type 2 semiconductors** (usually metallic compounds and alloys) have a gradual transition to superconductivity on cooling.
- Atoms within a solid can pack in a **cubic close-packed** arrangement where each atom is surrounded by 12 other nearest neighbours. In a **body-centred cubic** arrangement each atom is surrounded by 8 other nearest neighbours.
- **X-ray diffraction** can be used to determine the arrangement of atoms in a crystal. X-rays are beamed at layers of atoms within a crystal, and are reflected off the layers. When constructive interference occurs the distance between the layers of atoms can be calculated using the **Bragg equation**:  $n\lambda = 2d \sin \theta$

## A.9 Condensation polymers

Condensation polymers are formed by the loss of small molecules as functional groups from monomers join.

- **Condensation polymers** are formed when monomers with two functional groups combine to produce a polymer and a small molecule (usually  $\text{H}_2\text{O}$  but may be  $\text{HCl}$  or  $\text{NH}_3$ ).
- **Polyesters** are formed when an alcohol group on one monomer joins to an acid group on another monomer. PET is an example of a polyester.
- **Polyamides** are formed when an amine group on one monomer joins to an acid group on another monomer. Nylon and Kevlar are examples.
- **Kevlar** is a polyamide with a strong and ordered structure. The hydrogen bonds between O and N can be broken with the use of concentrated sulfuric acid.
- **Green Chemistry** aims to reduce the demand for resources and energy, decrease waste, and reduce environmental pollution. Many green chemistry polymers are biopolymers.





## A.10 Environmental impact: heavy metals

Toxicity and carcinogenic properties of heavy metals are the result of their ability to form coordinated compounds, have various oxidation states, and act as catalysts in the human body.

- Heavy metals (e.g. mercury, lead, cadmium) are toxic. Toxic doses of transition metals can disturb the normal oxidation/reduction balance in cells through various mechanisms.
- Some methods of removing heavy metals are precipitation, adsorption, and chelation.
- A **chelate** is a complex containing at least one polydentate ligand. **Polydentate ligands** form more stable complexes than similar monodentate ligands due to the **chelate** effect, which can be explained by considering entropy changes.
- The **solubility product ( $K_{sp}$ )** can be used as an indication of the solubility of a heavy metal compound. For example, mercury sulfide has a  $K_{sp} = [\text{Hg}^{2+}(\text{aq})][\text{S}^{2-}(\text{aq})]$ .
- For a heavy metal compound in solution, adding one of its ions from another source causes the heavy metal compound to precipitate from solution. This is the **common ion effect**.
- Some transition metal ions (e.g.  $\text{Fe}^{2+}$ ) can react with hydrogen peroxide in the body to produce hydroxyl free radicals (Fenton reaction). These free radicals can cause damage in biological systems.
- The Haber–Weiss reaction generates free radicals by the reaction between hydrogen peroxide and the superoxide ion ( $\text{O}_2^{\cdot-}$ ), which is a normal cellular metabolite.



## Chapter 13: Biochemistry – fast facts

### B.1 Introduction to biochemistry

Metabolic reactions involve a complex interplay between many different components in highly controlled environments.

- The sum of all chemical reactions occurring in an organism is known as metabolism. These reactions occur in aqueous solution in controlled environments.
- Anabolism refers to metabolic pathways of synthesis, catabolism refers to metabolic pathways of breakdown.
- Condensation reactions occur during synthesis, and hydrolysis reactions occur during breakdown.
- Photosynthesis synthesizes energy-rich molecules from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  using light energy.
- Respiration is the controlled breakdown of energy-rich molecules in cells to release energy.
- The functions of biomolecules depend on their structures and shapes.

### B.2 and B.7 Proteins and enzymes

Proteins are the most diverse of the biopolymers responsible for metabolism and structural integrity of living organisms. Analyses of protein activity and concentration are key areas of biochemical research.

- 2-amino acids are amphoteric and can exist as zwitterions or as cations or anions in solution. Their charge depends on the pH and their isoelectric point. They can act as pH buffers.
- There are 20 different amino acids that differ in their R group.
- Amino acids join by condensation reactions forming peptide bonds, which are amide links. There is an enormous variety of protein structures possible due to the variety of amino acids.

Protein structure	Nature of interactions
primary	covalent (amide / peptide) bonds between amino acids
secondary	hydrogen bonds within the polypeptide chain involving groups in the peptide bonds
tertiary	interactions between side chains including hydrophobic interactions, hydrogen bonds, ionic bonds, disulfide bridges
quaternary	interactions between polypeptide chains, including the same interactions as in the tertiary structure

- Fibrous proteins are insoluble and have a dominant secondary structure. They are used in structural components. Globular proteins are soluble and have a dominant tertiary structure. They are the molecular tools in cells.
- The specific three-dimensional shape of a globular protein is known as its conformation and is essential for its function.
- Enzymes are biological catalysts that are made of protein and control every biochemical reaction.



- Enzymes bind specifically to their substrate (reactant) at a region called the active site. The formation of enzyme–substrate complex provides an alternate reaction route that has a lower activation energy.
- Enzyme studies show saturation kinetics as  $[S]$  increases.
  - $V_{\max}$  refers to the maximum rate of the reaction under the specified conditions.
  - $K_m$  refers to the substrate concentration required for the rate to be  $V_{\max}/2$ .
  - The lower the value for  $K_m$  the greater the affinity of the enzyme for its substrate.
- Enzyme activity depends on its conformation, and so is sensitive to changes in temperature, pH, and heavy metal ions.
- Chemical inhibitors can regulate enzymes. There are two main types:

	Competitive inhibition	Non-competitive inhibition
binding site on enzyme	binds at active site	binds at allosteric site
effect on $V_{\max}$	not affected	decreased
effect on $K_m$	increased	not affected

- Product inhibition generates a feedback loop that can be used to regulate the concentration of enzymes according to the needs of the cell.
- The amino acid composition of a protein can be analysed by paper chromatography and by gel electrophoresis.
- The pH of a buffer solution can be determined from knowledge of the  $pK_a$  or  $pK_b$  of its acid/base and by the ratio of its acid/base to salt.

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}$$

- The protein concentration in a solution can be determined using UV-vis spectroscopy and a calibration curve based on known standard concentrations. The Beer–Lambert law shows that the absorbance of a compound at fixed wavelength is directly proportional to its concentration.

### B.3 Lipids

Lipids are a broad group of biomolecules that are largely non-polar and are therefore insoluble in water.

- Lipids are a broad group of non-polar biomolecules.
- Lipids are more reduced than carbohydrates and so release more energy when oxidized.
- Fatty acids can be saturated or unsaturated. Unsaturated fats have lower melting points than saturated fats; they are often liquids at room temperature and are known as oils.
- Triglycerides form by condensation of three fatty acids with one glycerol molecule, and contain ester links.
- The degree of unsaturation in a fat is known as its iodine number.
- Lipids are essential components of cells, especially in membranes, but excess dietary fats can cause negative health effects such as circulatory problems. Saturated fat and trans fats cause the greatest problems.
- Phospholipids contain two fatty acids and a phosphate group condensed to glycerol. They form a bilayer in cell membranes.



- Cholesterol is a steroid.
- Hydrolysis of a fat produces fatty acids and glycerol. It is carried out by enzymes called lipases, and acidic or alkaline conditions.
- Rancidity of fats occurs either at the ester linkages in triglycerides or at the carbon-carbon double bonds in unsaturated triglycerides. Saturated fats are more stable than unsaturated fats.

## B.4 Carbohydrates

Carbohydrates are oxygen-rich biomolecules that play a central role in metabolic reactions of energy transfer.

- Carbohydrates contain C and H:O in the same ratio as in water.
- Monosaccharides contain -OH groups and either an aldehyde or ketone group. They cyclize in solution to form ring structures, which are represented by Haworth projections.
- Monosaccharides condense to form disaccharides and polysaccharides with glycosidic (ether) linkages.
- Monosaccharides are soluble and are used in transport and as energy sources; polysaccharides are insoluble and are used for storage and structural components.

## B.5 Vitamins

Vitamins are organic micronutrients with diverse functions and which must be obtained from the diet.

- Vitamins are organic micronutrients; they are synthesized in the body. Vitamin D can be made by the action of sunlight on the skin.
- Vitamins are sensitive to heat. Their solubility in water depends on their ability to form hydrogen bonds with the water.
- Vitamin deficiency diseases are caused by lack of a balanced diet. Over-processing of food, poor education, and nutrient depletion can all contribute to this. Solutions include fortification of staple foods, supplementation, and education.

## B.8 Nucleic acids

DNA is the genetic material that expresses itself by controlling the synthesis of proteins by the cell.

- The monomers of nucleic acids are nucleotides, composed of a pentose sugar, phosphoric acid, and nitrogenous base. The bases are purines (A and G) and pyrimidines (C, T, and U).
- DNA is a double helix of two polynucleotide strands. The two strands are held together by two or three H bonds between the stacked bases: A=T, C≡G
- The complementary base pairing ensures that the sequence of bases in one strand uniquely determines the sequence in the complementary strand. This provides the basis of DNA replication.
- DNA has a negative charge due to the phosphate groups. It associates with basic histones in chromosomes.
- RNA is a single polynucleotide chain. It contains the base U in place of T in DNA and ribose in place of deoxyribose.
- The genetic code is the means by which the sequence of bases in DNA is used to determine the sequence of amino acids in a protein. It is a triplet code and is universal.



- Genetically modified food refers to food produced from organisms that have had their DNA altered by genetic engineering.

## B.9 Pigments

Biological pigments include a variety of chemical structures with diverse functions and which absorb specific wavelengths of light.

- Pigments are coloured compounds produced by metabolism. Their colour is due to highly conjugated systems with delocalized electrons, which absorb in the visible region of the spectrum.
- Porphyrim compounds are chelates of metals with nitrogen-containing cyclic ligands.
- Chlorophyll is the primary pigment involved in trapping light energy in photosynthesis. Its porphyrin ring contains magnesium. It undergoes a redox change and is reduced back to its original form by electrons from water. Chlorophyll is more sensitive to changes in temperature in acidic conditions.
- Hemoglobin and myoglobin contain heme groups with iron(II) ion, and act to transport and store oxygen. Hemoglobin is a tetrameric protein, which binds four oxygen molecules cooperatively. Its oxygen dissociation curve is shifted to the right (releases oxygen more easily) at warmer temperatures and lower pH/higher concentration of CO<sub>2</sub>. CO acts as a competitive inhibitor for O<sub>2</sub>. Fetal hemoglobin has a higher affinity for oxygen than adult haemoglobin; its oxygen dissociation curve is shifted to the left.
- Myoglobin has a higher affinity for oxygen and stores oxygen. It is monomeric so does not show cooperative binding.
- Cytochromes contain iron which undergoes redox change from iron(II) to iron(III). They form the electron transport chain in aerobic respiration and photosynthesis.
- Carotenoids and anthocyanins act as accessory pigments in photosynthesis.
- Carotenoids are lipid soluble and can be oxidized in light-catalysed reactions.
- Anthocyanins are water soluble and can act as pH indicators.
- Pigments can be analysed by thin-layer chromatography (TLC), a form of adsorption chromatography. TLC works on smaller samples than paper chromatography and is more sensitive.

## B.10 Stereochemistry in biomolecules

Most biochemical processes are stereospecific and involve only molecules with a certain configuration of chiral carbon atoms.

- Proteins: amino acids are chiral (except glycine) and exist in the L form.
- Lipids: unsaturated fats occur mostly in the *cis* form, with relatively low melting points. Partial hydrogenation of fats converts some of these groups into the *trans* position, which is associated with health problems, such as cardiovascular disease.
- Carbohydrates: sugars exist as D or L stereoisomers; the D form is the most abundant in nature. Alpha and beta sugars differ in the positions of the –OH groups in C<sub>1</sub> for glucose and C<sub>2</sub> for fructose. Starch and glycogen are polymers of alpha glucose, and cellulose is a polymer of beta glucose.
- Vitamins: vitamin A, retinal, undergoes an isomeric conversion from 11-*cis*-retinal to all-*trans*-retinal in the visual cycle.



## B.6 Biochemistry and the environment

Our increasing knowledge of biochemistry has led to several environmental problems, while also helping to solve others.

- Xenobiotics are chemicals found in the environment that are not normally present there. They include antibiotics and other pharmaceutically active compounds, pesticides, plastics, etc.
- Bioaccumulation refers to the build-up of a toxin in an organism.
- Biomagnification refers to the increasing concentration of xenobiotics at increasing trophic level in food webs.
- Host-guest chemistry involves specifically synthesized molecules that bind to toxins in the environment, forming a supermolecule with bonds other than covalent.
- Biodegradable substances can be decomposed in the natural environment.
- Bioremediation includes the use of enzymes that break down pollutants in the environment.
- Green Chemistry seeks to reduce the release into the environment of hazardous substances.





## Chapter 14: Energy – fast facts

### C.1 Energy sources

Societies are completely dependent on energy resources. The quantity of energy is conserved in any conversion but the quality is degraded.

- Energy is the ability to do work. The law of **conservation of energy** says that energy cannot be created or destroyed, only changed from one form to another.
- A useful energy source releases energy at a reasonable rate and produces minimal pollution.
- A **fuel** can release useable energy by changing its chemical or nuclear structure.
- In any cyclical process designed to convert heat to work, some energy is always degraded. **Degraded energy** is energy that is no longer available for the performance of useful work.
- The quality of energy is degraded as heat is transferred to the surroundings. Energy and materials go from a concentrated into a dispersed form. The quantity of the energy available for doing work decreases.
- **Renewable resources** can be replenished at a rate faster than they are used (e.g. wood).
  - energy density =  $\frac{\text{energy release from fuel}}{\text{volume of fuel consumed}}$
  - specific energy =  $\frac{\text{energy release from fuel}}{\text{mass of fuel consumed}}$
  - efficiency of energy transfer =  $\frac{\text{useful output energy}}{\text{total input energy}} \times 100\%$
- Nuclear fuels have a higher energy density and specific energy than fossil fuels.

### C.2 Fossil fuels

The energy of fossil fuels originates from solar energy that has been stored by chemical processes over time. These abundant resources are non-renewable but provide large amounts of energy due to the nature of chemical bonds in hydrocarbons.

- **Fossil fuels** were formed by the reduction of biological compounds that contain carbon, hydrogen, nitrogen, sulfur and oxygen at high temperature and pressure in the absence of air.
- **Crude oil** is valuable as a source of chemicals and as a fuel; however, it is a limited resource.
- Crude oil needs to be refined before use as it is a mixture of organic compounds and inorganic impurities (e.g. sulfur). Fractional distillation separates the mixture into useful **fractions**, these can be further distilled to produce useful hydrocarbons.
- **Cracking** breaks down large alkanes into smaller alkanes and alkenes. **Thermal cracking** uses heat, **catalytic cracking** uses lower temperatures and a catalyst (e.g.  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ ). **Hydrocracking** with hydrogen and a Pt catalyst produces branched chains, cyclic hydrocarbons, and aromatic compounds.
- In a petrol engine the fuel may ignite due to heat and pressure alone – auto-ignition – this gives rise to **knocking** which can damage the engine. The tendency to auto-ignite is based on the fuel's **octane number**. The higher the number the less likely it is to auto-ignite.
- **Catalytic reforming** reduces the tendency of a fuel to auto-ignite by making it more branched. This can also be achieved by reacting alkanes with low mass alkenes.



- Natural gas is mostly methane. Supplies of methane can be increased by cracking hydrocarbons or by coal gasification.
- **Coal gasification** and **liquefaction** are chemical processes that convert coal to gaseous and liquid hydrocarbons.
- All fossil fuels are non-renewable and produce the greenhouse gas carbon dioxide.
- A **carbon footprint** is the total amount of greenhouse gases produced during human activities. It is generally expressed in equivalent tons of carbon dioxide.

### C.3 Nuclear fusion and fission

The fusion of hydrogen nuclei in the Sun is the source of much of the energy needed for life on Earth. There are many technological challenges in replicating this process on Earth but it would offer a rich source of energy.

Fission involves the splitting of a large unstable nucleus into smaller stable nuclei.

- Nuclear reactions involve the protons and neutrons in the nucleus, and the atoms may be converted to other elements. In chemical reactions only valence electrons are involved and atoms do not change their identity.
- **Alpha particles** ( $2p$  and  $2n$ ) are emitted by nuclei with too many protons; **beta particles** (electrons) are emitted when a neutron decays in a nucleus with too many neutrons; **gamma rays** are emitted when the nucleons rearrange themselves.
- The **mass defect** is the difference between the mass of the nucleus and the sum of the masses of the individual nucleons. The **binding energy** is the energy released when a nucleus is made from protons and neutrons.
- **Nuclear fusion** is the joining of light nuclei (occurs for elements with atomic number less than 26, Fe); **nuclear fission** is the splitting of heavy nuclei (occurs for isotopes with atomic number greater than 56).
- The **electron volt** is the energy given to an electron when it is accelerated through a potential difference of 1 V.  $1 \text{ eV} = 1.602189 \times 10^{-19} \text{ J}$ . It is a convenient unit of energy in nuclear reactions.

#### Nuclear fusion

- Nuclear fusion is a possible source of energy, but the high temperatures needed and the formation of a confined plasma cause practical problems. However, the fuel is abundant, radioactive products have a short half-life, and little waste needs to be transported or stored.
- **Absorption spectra** are used to analyze the composition of stars

#### Nuclear fission

- Nuclear fission produces large amounts of energy. **Chain reactions** can trigger fission in other atoms. In a nuclear reactor this is controlled using moderators (e.g. boron) to stop the reaction going out of control.
- The **critical mass** is the minimum amount of fissionable material needed to sustain a chain reaction.
- Uncontrolled nuclear reactions are used in nuclear weapons.
- **Fast breeder reactors** can convert U-238 into the more fissionable Pu-239; however, plutonium is toxic, breeder reactors are not very efficient, and require liquid metals as coolants.
- Radioactive waste may contain isotopes with long and short half-lives. The half-life is the time it takes for half the number of atoms to decay.
- Most nuclear waste has very long half-lives causing problems with transport and storage.
- Safety and risk issues include: health, problems associated with nuclear waste and core meltdown and the possibility that nuclear fuels may be used in nuclear weapons.



## C.4 Solar energy

Visible light can be absorbed by molecules that have a conjugated structure with an extended system of alternating single and multiple bonds. Solar energy can be converted to chemical energy in photosynthesis.

- Light can be absorbed by chlorophyll and other pigments containing a conjugated electronic structure, and begin the process of **photosynthesis**.
- A **conjugated system** contains alternate double and single bonds. The benzene ring is a conjugated system. The wavelength of the light absorbed by an organic molecule increases with the length of the conjugated system.
- **Chromophores** within organic molecules absorb light. Chromophores contain unsaturated groups such as C=C, C=O, -N=N-, etc.
- Photosynthesis converts light energy into chemical energy.  $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$
- The products of photosynthesis can be converted into ethanol, which can be used as a biofuel, by **fermentation**:  $\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$
- Energy content of vegetable oils is similar to that of diesel fuel but they are not used in internal combustion engines as they are too viscous. **Transesterification** of vegetable oils produces a mixture of oils with low viscosity that can be used as a replacement for diesel.

## C.5 Environmental impact: global warming

Gases in the atmosphere that are produced by human activities are changing the climate as they are upsetting the balance between radiation entering and leaving the atmosphere.

- Greenhouse gases allow the passage of incoming solar short-wavelength radiation but absorb the longer-wavelength radiation from the Earth. Some of the absorbed radiation is re-radiated back to Earth.
- Greenhouse molecules such as  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  absorb IR radiation that is radiated from the earth, as there is a change in dipole moment as the bonds in the molecule stretch and bend which increases their vibrational energy. This natural process is called the greenhouse effect. Human activities can increase the amount of these gases present in the atmosphere and lead to increased global warming.
- The ability of a gas to absorb IR radiation is known as its greenhouse factor.  $\text{CO}_2$  has a value of 1.
- Increasing the amount of  $\text{CO}_2$  in the atmosphere can increase the acidity of oceans as there is an equilibrium between the gas in the atmosphere and dissolved  $\text{CO}_2$ . This affects shell-forming animals.
- Global dimming caused by particulates in the atmosphere can reduce global temperatures by preventing radiation from reaching the earth.
- There are essentially three strategies for reducing carbon dioxide levels:
  - increased energy efficiency and conservation
  - reduced dependence on carbon-based energy resources
  - capture and storage of carbon from fossil fuels or from the atmosphere.

## C.6 Electrochemistry, rechargeable batteries, and fuel cells

Chemical energy from redox reactions can be used as a portable source of electrical energy.

- An electrochemical cell has **internal resistance** due to the finite time it takes for ions to diffuse. The maximum current of a cell is limited by its internal resistance.



- The **voltage** of a battery depends on the nature of the electrodes and on the electrolytes.
- In a **primary cell** the electrochemical reaction is not reversible. **Rechargeable cells** (e.g. lead–acid batteries, nickel–cadmium batteries, lithium-ion batteries) involve redox reactions that can be reversed using electricity.
- **Fuel cells** convert chemical energy from a fuel into electricity through a redox reaction with oxygen or other oxidizing agents. Hydrogen or methanol may be used. They need a constant supply of fuel and oxygen to sustain the chemical reaction.
- The **thermodynamic efficiency** of a fuel cell  $= \Delta G / \Delta H$
- **Microbial fuel cells (MFCs)** are a possible sustainable energy source using different carbohydrates or substrates present in wastewaters as the fuel.
- Under non-standard conditions the potential of a half-cell can be calculated using the **Nernst equation**:

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{RT}{nF} \times \log_{10} Q \text{ (where } Q \text{ is the reaction quotient)}$$

- $Q$  is the equilibrium expression with non-equilibrium concentrations.
- A **concentration cell** is a voltaic cell where the two half-cells are made of the same material but differ in the concentration of the electrolyte.
- The total work produced by a cell depends on the quantity of materials used; large batteries deliver more power as they produce more charge per unit time.

## C.7 Nuclear fusion and fission

Large quantities of energy can be obtained from small quantities of matter.

- The **mass defect** is the difference between the mass of the nucleus and the sum of the masses of the individual nucleons. The **binding energy** is the energy released when a nucleus is made from protons and neutrons.
- The energy produced in a nuclear reaction can be calculated from the mass difference between the products and reactants using Einstein mass–energy equivalence relationship  $E = mc^2$
- The **critical mass** is the minimum amount of fissionable material needed to sustain a chain reaction.
- The different isotopes of uranium in uranium hexafluoride can be separated, using diffusion or centrifugation causing **fuel enrichment**.
- The effusion rate of a gas is inversely proportional to the square root of the molar mass (Graham's Law).

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \sqrt{\frac{M_2}{M_1}}$$

- Radioactive decay is kinetically a **first order** process with the **half-life** ( $t_{1/2}$ ) related to the **decay constant** ( $\lambda$ ) by the equation  $\lambda = \frac{\ln 2}{t_{1/2}}$ .
- The number of atoms at a given time is given by  $N = N_0 e^{-\lambda t}$  where  $t$  is the time and  $N_0$  the number of atoms when  $t = 0$ .
- Nuclear decay produces **ionizing** radiation which can damage DNA, oxidize polyunsaturated fatty acids in lipids, and oxidize amino acids in proteins.



## C.8 Photovoltaic and dye-sensitized solar cells (DSSC)

When solar energy is converted to electrical energy the light must be absorbed and charges must be separated. In a photovoltaic cell both of these processes occur in the silicon semiconductor, whereas these processes occur in separate locations in a dye-sensitized solar cell (DSSC).

- Molecules with longer conjugated systems absorb light of longer wavelength.
- The electrical conductivity of a **semiconductor** increases with an increase in temperature whereas the conductivity of metals decreases.
- Semiconductors (such as silicon) can act as a semiconductor when they are given more energy or exposed to light. Some electrons may be removed from the outer shell of the silicon atom leaving a hole where electrons from adjacent silicon atoms can move into, thus increasing its conductivity.
- Semiconductors can be **doped** with Group 15 elements (e.g. As), giving the lattice more electrons (n-type semiconductor), or with Group 13 elements (e.g. Ga), giving the lattice fewer electrons, i.e. more holes (p-type semiconductor).
- **Photovoltaic cells** include sheets of n-type and p-type silicon. Light of the correct energy can create more electrons and positive holes. These electrons may have enough energy to pass through an external circuit from the n-type semiconductor to the p-type semiconductor.
- In a photovoltaic cell the light is absorbed and the charges separated in the silicon semi-conductor. The processes of absorption and charge separation are separated in a dye-sensitised solar cell.
- **Dye-sensitized solar cells** have an anode made up of titanium dioxide nanoparticles coated in a molecular dye that absorbs sunlight. The dye contains a large conjugated system of overlapping p-orbitals. The cathode is a transition metal wire.
- The dye absorbs a photon of light and becomes excited, the excited electron moves to the titanium dioxide, and then through the external circuit to the transition metal electrode.
- An electrolyte prevents the electron from re-combining with the charged dye molecule.
- In a **Gratzel dye-sensitized solar** cell the anode is made from a  $\text{TiO}_2$  semiconductor covered in an organic dye. The electrolyte is made from an  $\text{I}_3^-/\text{I}_2$  mixture.
- The use of nanoparticles coated with light-absorbing dye increases the effective surface area and allows more light over a wider range of the visible spectrum to be absorbed.



## Chapter 15: Medicinal chemistry – fast facts

### D.1 Pharmaceutical products and drug action

Medicines and drugs have a variety of different effects on the functioning of the body.

- Drugs can be administered in different ways : orally, inhalation, absorption through skin, suppositories, eye or ear drops, or by injection.
- Bioavailability refers to the fraction of an administered drug that reaches its target in the body. Intravenous administration gives a bioavailability of 100%. Drugs taken orally have a lower bioavailability due to the first-pass effect. Bioavailability is influenced by the solubility of the drug in water and in lipid, and by functional groups in the drug which influence polarity and so solubility.
- Side-effects refer to unintended physiological effects of drugs in the body. They can be beneficial, harmless, or adverse – so must be monitored.
- Tolerance occurs when repeated doses of a drug result in smaller physiological effects.
- Addiction occurs when the dependency on a drug leads to withdrawal symptoms if it is withheld.
- Dosage refers to the amount of a drug taken over an interval of time.
- The therapeutic window is the range of concentrations of a drug in the blood between its therapeutic and toxic levels.
- The therapeutic window is quantified as the therapeutic index. This is the ratio of the lethal dose (in animals, LD50) or toxic dose (in humans, TD50), divided by the minimum effective dose (ED50).
- Drugs with a low therapeutic index have a low margin of safety, so dosage here is crucial. Animal and human tests of drug dosages should be kept to a minimum.
- Understanding drug–receptor interactions has contributed largely to rational drug design. Drug development depends on identifying the need and identifying a suitable target in the body. The process is slow and costly, though optimized by combinatorial chemistry and the synthesis of analogues.
- Drug trials for potential drugs involve animals and humans in three phases. Each phase involves larger numbers of patients. Phase III uses double-blind trials to test the effectiveness of the drug against a placebo.

### D.2 Aspirin and penicillin

Natural products with useful medicinal properties can be chemically altered to produce more potent and safe medicines.

- Aspirin is a mild analgesic that acts to block the pain stimulus at source. It also acts as an anticoagulant in the blood. It has a synergistic effect with alcohol, which can cause stomach bleeding.
- Aspirin can be synthesized from salicylic acid in an esterification reaction. The reaction uses ethanoyl chloride and concentrated sulfuric acid or phosphoric acid.
- Purification of aspirin involves recrystallization, which causes it to crystallize from a hot saturated solution of ethanol during cooling, while the impurities stay in the solution.
- The aspirin product can be characterized by melting point determination and by IR spectroscopy. Aspirin gives distinct peaks due to its  $-\text{COOH}$  and ester groups.
- Modification of aspirin to soluble form involves reacting it with an alkali to form an ionic salt.





- Penicillin is an antibiotic that was first extracted from the mould *Penicillium* and characterized using X-ray crystallography.
- Penicillin contains a beta-lactam ring in which the carbon atoms are under bond strain. Breakage of these bonds allows the antibiotic to inhibit the bacterial enzyme transpeptidase that is essential in the synthesis of bacterial cell walls. This kills the bacteria.
- The side-chains in penicillin have been modified to allow the drug to be administered orally, as this modification prevents its breakdown in the stomach.
- Many bacteria have become resistant by developing beta-lactamase enzymes which break the beta-lactam ring. Different forms of penicillin, methicillin and oxacillin, have modified side-chains which prevent the binding of the beta-lactamase enzyme.
- Response to antibiotic resistance must include monitoring of over-prescription by medical practitioners and greater patient compliance in completing a dose.

### D.3 Opiates

Potent medical drugs prepared by chemical modification of natural products can be addictive and become substances of abuse.

- Opiates are strong analgesics, derived from poppy seeds, which act to reduce the perception of pain in the brain. They bind to specific opioid receptors in the brain.
- The blood–brain barrier is largely lipid and so is crossed more easily by non-polar drug molecules.
- The opiates cause side-effects such as constipation, which are not serious, but they also have narcotic effects and are highly addictive. Addiction to diamorphine (heroin) is a very serious condition and is often linked to other social problems due to the dependence.
- Morphine is converted into codeine by methylation and into diamorphine by esterification. Diamorphine is able to cross the blood–brain barrier more quickly and so is the fastest acting opioid. In terms of their analgesic properties, side-effects and narcotic effects:  
codeine < morphine < diamorphine

### D.4 pH regulation of the stomach

Excess stomach acid is a common problem that can be alleviated by compounds that increase the stomach pH by neutralizing or reducing its secretion.

- HCl is produced by parietal cells in the gastric glands of the stomach.
- Excess acid from the stomach causes dyspepsia and can lead to ulceration.
- There are two types of drugs that prevent the production of excess acid.
  - i Drugs that block the histamine- $H_2$  interaction in the gastric glands: these drugs compete with histamine for binding at the receptors. They include ranitidine.
  - ii Drugs that inhibit the proton pump that parietal cells use to pump  $H^+$  ions into the stomach lumen. They include omeprazole and esomeprazole.
- Antacids are weak bases that act to neutralize excess stomach acid. They include calcium, magnesium, and aluminium hydroxides and sodium carbonate and hydrogencarbonate. The stoichiometry of these reactions determines the amount of HCl that can be neutralized by each antacid.



- Cells contain buffer solutions that keep the pH relatively constant on the addition of small amounts of acid or base.
- The pH of a buffer solution can be determined from the  $pK_a$  or  $pK_b$  of the parent acid/base and by the relative concentrations of acid/base and salt.
- The Henderson–Hasselbalch equation is: 
$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{base}]}$$

## D.5 Antiviral medications

Antiviral medications have recently been developed for some viral infections while others are still being researched.

- Viruses lack a cell structure and so are more difficult to treat in the body than bacteria. Viruses consist only of genetic material (DNA or RNA) and protein. They synthesize other components inside the host cell.
- Antiviral drugs target specific viral infections. They work by causing changes to the cell membrane which prevent the entry of viruses, altering the cell's DNA so it cannot be used by the virus, or blocking enzyme activity to prevent viral multiplication.
- Oseltamivir and zanamivir are antivirals for flu that inhibit the enzyme neuraminidase, which allows new viral particles to escape from the host cell and cause infection. They must be taken immediately as symptoms appear or the viral infection will already have spread too far.
- Oseltamivir and zanamivir have similar structures, and act as competitive inhibitors with neuraminidase as their structures are similar to sialic acid, its normal substrate.
- HIV infection, which can lead to AIDS, is particularly difficult to treat. The virus destroys cells in the immune system, mutates very rapidly, and can often lie dormant within cells for years. Anti-retrovirals target interactions between the virus and host cells, the enzyme reverse transcriptase, and the release of new viral particles.

## D.7 Taxol: a chiral auxiliary case study

Chiral auxiliaries allow the production of individual enantiomers of chiral molecules.

- Taxol is derived from the bark of Pacific yew trees and is used to treat cancer.
- Taxol acts as a chemotherapeutic agent by binding to tubulin in microtubules, which prevents spindle formation during cell division. This prevents growth of the tumour.
- Taxol is a chiral molecule with 11 chiral carbon centres. Many diastereoisomers are therefore possible.
- Taxol is now produced in semi-synthetic synthesis starting with extracts from yew needles. The reactions involve the use of a chiral auxiliary. This binds to the reactant in such a way that it determines the stereochemistry of the next step.
- Enantiomer selectivity is common in the drug industry as different enantiomers often have different effects in the body.
- A polarimeter can be used to identify enantiomers.



## D.8 Nuclear medicine

Nuclear radiation, whilst dangerous owing to its ability to damage cells and cause mutations, can also be used to both diagnose and cure diseases.

- Medical treatment uses radioisotopes that are alpha, beta, gamma, proton, neutron, or positron emitters.
- Radioactive emissions have ionizing effects in cells.
- The half-life of a radioactive isotope is the time taken for an initial amount of substance to fall to one half of its initial value. Radioactive decay reactions have a constant half-life; they are first-order reactions. The shorter the half-life the greater the activity of the radionuclide.
- Diagnostic approaches use MRI, an application of NMR, and PET scanners.
- The tracers used in diagnosis include technetium-99m, which is a gamma emitter. It has a convenient half-life (6 hours), and binds well to a range of biologically active substances.
- Radionuclide therapy can be internal or external. External therapy generally uses cobalt-60.
- Internal radionuclide therapy includes target alpha therapy using lead-212, and boron neutron capture therapy.
- Side-effects of radiotherapy include nausea, sterility, skin damage, and fatigue.

## D.9 Drug detection and analysis

A variety of analytical techniques is used for detection, identification, isolation, and analysis of medicines and drugs.

- Drug preparation usually involves techniques of separation and purification, exploiting differences in solubility and volatility.
- Solvent extraction separates components of a mixture on the basis of their partition between different solvents.
- Recrystallization involves crystallizing a product out from a hot solvent, in which impurities are more soluble.
- Fractional distillation separates mixtures into fractions on the basis of their different boiling points. The vapour above a mixture of liquids is always enriched in the more volatile component. Successive cycles of boiling and condensation cause greater separation of the components.
- Raoult's law states that the vapour pressure of a volatile substance in a solution is equal to the vapour pressure of the pure substance multiplied by its mole fraction.
- Drug detection relies on accurate analytical instrumentation.
  - Steroid detection uses gas chromatography and mass spectrometry.
  - Alcohol detection uses breathalysers based on redox reactions or fuel cells.
- Characterization of drugs uses mass spectrometry, IR spectroscopy, and NMR spectroscopy.

## D.6 Environmental impact of some medications

The synthesis, isolation, and administration of medications can have an effect on the environment.

- Solvent waste is a major emission of the pharmaceutical industry. Environmental issues include by-products of incineration and the direct consequences on soil and water of dumping toxic compounds.



# Chemistry

## Fast Facts

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- Medical nuclear waste includes low-level waste and high-level waste. Some radioisotopes from medical diagnosis generate high-level waste, and secure means are needed to preventing this from entering the soil and water supply.
- Antibiotic resistance is an increasing problem that demands global measures for the controlled use of antibiotics.
- The antiviral drug tamiflu can be prepared using Green Chemistry principles, including the isolation of the precursor from fermentation reactions.
- Green Chemistry principles are helping to reduce waste and reduce the environmental impact of many aspects of the pharmaceutical industry.