CHEMISTRY

CHAPTER SUMMARIES

Student CD included inside

John Green

Sadru Damji

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CHAPTER 1 QUANTITATIVE CHEMISTRY
(IB TOPIC 1) SUMMARY

Introduction

- $1 dm^3 = 1$ litre $= 1 \times 10^{-3} m^3 = 1 \times 10^3 cm^3 = 1000$ ml

- Amount of substance, n, is measured in moles (mol).

- 1 mol of a chemical species contains the same number of particles as there are atoms in exactly 12 g of C-12 ($^{12}_{6}C$) isotope.

- 1 mol of any substance contains 6.02×10^{23} particles; 6.02×10^{23} mol^{-1} is called Avogadro's Constant (L or N_A)

- A_r, the relative atomic mass of an element is the ratio of the mass of an atom of the element to the mass of one atom of C-12; A_r has no units.

- M_r, the relative molecular mass also has no units.

- M, the molar mass is the mass of one mole of any chemical species and has the units g mol^{-1}.

The amount of substance, n in moles $= \dfrac{mass\,(g)}{molar\,mass\,(g\,mol^{-1})}$;

$$n = \dfrac{V\,(dm^3)}{V_m\,(dm^3\,mol^{-1})}.$$

Number of Particles	$\Leftrightarrow$ Avogadro Constant (6.02×10^{23} mol^{-1})	Amount in moles	$\Leftrightarrow$ Molar mass	Mass in grams
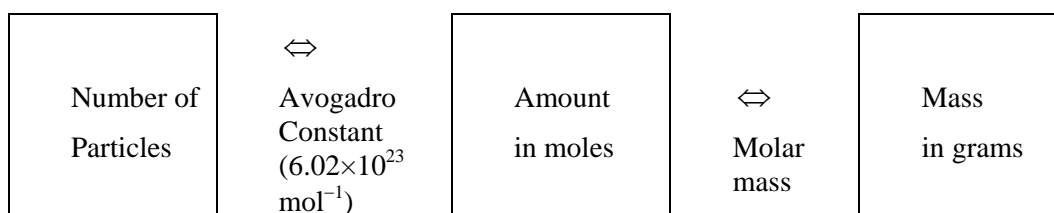
- Use Avogadro Constant to convert between amount and number of particles.

- Use molar mass of substance to convert between amount in moles and mass in grams.

- Empirical formula gives the simplest whole number ratio of atoms in a compound.

- Molecular formula gives the actual number of atoms of each element in the molecule of a compound.

If a molecular formula is given, percentage composition can be calculated.

If the percentage composition is given:

- Consider 100 g of sample, the % of each element becomes its mass.

- Convert the mass of each element to its amount in moles.

- Determine simplest whole number ratio – this is its empirical formula.

- Molecular formula is a whole-number multiple of the empirical formula.

- Substances react by amounts based on a balanced chemical equation.

If masses are given, convert these to amounts of substances.

- In stoichiometric problems, apply mole ratios as specified in the balanced chemical equation.

- The % yield indicates how efficient a reaction is (given by: $\dfrac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$).

- STP for gases is standard temperature (0°C or 273 K) and pressure (1 atmosphere or 101.325 kPa).

- Molar volume, V_m, of any gas at STP = 22.4 dm^3.

In a balanced chemical equation, coefficients stand for the amount of substance. For gases, these also refer to volumes of gases.

Concentration, $c = \dfrac{\text{amount n (mol)}}{\text{Vol solution (dm}^3)} = \dfrac{n}{V}\ \text{mol dm}^{-3}$.

$n = cV$; volume must be in dm^3.

On dilution, the amount of solute does not change but the volume increases and the concentration decreases

Amount $n = \dfrac{m\,(g)}{M\,(g\,mol^{-1})}$.

For a reaction $aA + bB \rightarrow$ products, where a and b are coefficients, then $\frac{1}{a}n_A = \frac{1}{b}n_B$.

Percentage yield $= \dfrac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$.

(There are many worked examples given in the chapter)

CHAPTER 2   ATOMIC STRUCTURE
(IB TOPICS 2 AND 12) SUMMARY

Introduction

- **Relative masses**: p = 1, n = 1, e = 1/1840; *charges*: p = +1, n = 0, $e^- = -1$.

- Protons and neutrons are present in the nucleus of an atom, electrons are in orbits or shells around the nucleus.

- **Atomic number, Z** = number of protons; the fundamental characteristic of an element.

- **Mass number, A** = number of (protons + neutrons).

- **Isotopes:** same atomic number, different mass number OR same number of protons, different number of neutrons OR atoms of the same element with different masses.

- **Isotopes** differ in physical properties that depend on mass such as density, rate of diffusion etc. Chemical properties are the same because of the same electronic configuration or arrangement.

- **Atomic mass** of an element is the average of the atomic masses of its isotopes; depends on isotopes relative abundance; leads to non-integer atomic masses.

Mass Spectrometer

- Stages of Operation: Vaporization of sample, ionization to produce M^+ ions, acceleration of ions by electric field, deflection of ions by magnetic field, vacuum, detection of ions.

- Degree of deflection:

- Lower the mass, higher the deflection.

- Higher the charge, higher the deflection.

- Deflection reflects mass/charge ratio; for charge of +1, deflection depends on mass.

- For an element, the mass spectrum gives **two** important pieces of information: the number of isotopes, and the abundance of each isotope; thus the relative average atomic mass, A_r can be calculated.

- For a molecule, the highest peak represents the molecular (parent) ion and its mass gives the relative molecular mass, M_r of the compound (and the fragmentation pattern can help determine its structure).

  o A continuous spectrum contains light of all wavelengths in the visible range.

  o A line spectrum consists of a few lines of different wavelengths.

  o When electrons are excited, they jump to higher energy levels.

  o Electrons fall back to lower energy levels, and the energy equivalent to the difference in energy level is emitted in the form of photons.

  o Energy levels come together in terms of energy the farther away they are from the nucleus; this explains the convergence of lines in a line spectrum.

  o The maximum number of electrons in a main energy level n is $2n^2$:

    1st energy level, n = 1; maximum 2 e^-;

    n = 2, maximum 8 e^-;

    n = 3, maximum 18 e^-.

The electron arrangement (or configuration) indicates the number of electrons and their energy distribution. This determines an element's physical and chemical properties.

- **Main (or principal) energy levels, sub-levels and orbitals:** The main energy levels, n are assigned whole number integers, $n = 1, 2, 3, 4…$. $n = 1$ represents the lowest energy level. Each main energy level contains n sub-levels and a total of n^2 orbitals.

  o s, p, d, f etc. is the common notation for sub-levels and orbitals within sub-levels. An orbital is an area of space around the nucleus in which an electron moves.

  o Orbitals have characteristic shapes. There is one *s* orbital which is *spherical* in shape, three *p* orbitals which are *dumbbell* shaped, called p_x, p_y p_z, and arranged in the x, y, and z directions respectively, five *d* orbitals and seven *f* orbitals (both with complex shapes). The relative energies of s, p, d, and f orbitals with in a sub-level are: $s < p < d < f$.

  o Each orbital can have a maximum of 2 electrons. $n = 1$ has one sub-level which is called an s sub-level and which contains one s orbital. $n = 2$ has two sub-levels: 2s and 2p; $n = 3$ has 3 sub-levels: 3s, 3p and 3d; $n = 4$ has 4 sub-levels:4s, 4p, 4d and 4f, etc.

- **The Aufbau ('building-up') Principle:** Electrons are placed in orbitals in order of increasing energy, starting with the lowest energy level, and in general, filling each sub-level completely before beginning the next. This is due to the fact that systems in nature prefer minimum energy in order to achieve maximum stability.

- **Hund's Rule:** Occupation of sub-levels takes place singly as far as possible before pairing starts.

- **Pauli exclusion principle:** No two electrons in an atom can be in exactly the same state; no two electrons in a given atom can have the same four quantum numbers (that is, these can not be in the same place at the same time)

- nl^x notation is used to describe the electron configuration of an element: n is the main energy level, l the sub-level, and x is the number of electrons in the sub-level.

- The **ionisation energy** of an atom is the minimum amount of energy required to remove a mole of electrons from a mole of gaseous atoms to form a mole of gaseous ions.
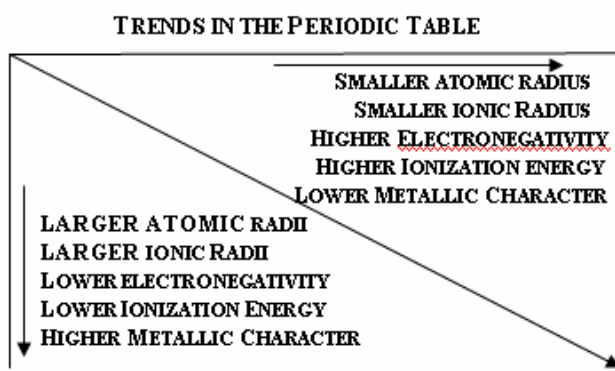
(N.B. Shading indicates Topic 12 (AHL) material.)

CHAPTER 3   PERIODICITY
(IB TOPICS 3 AND 13) SUMMARY

Basic concepts

- Periodic Table is arranged according to increasing atomic number and consists of horizontal rows called periods, and vertical columns called groups (or families). The arrangement is such that elements with similar chemical properties fall directly beneath each other in the same group.

- A period is a series of elements arranged according to increasing atomic number, which begins with the first element having one electron in a new main energy level.

- A group is a vertical column consisting of elements with the same electron arrangement in their outer energy levels, which gives the group similar chemical properties.

- Modern Periodic Law states that chemical and physical properties of elements vary periodically if elements are arranged in order of increasing atomic numbers.

- Periodicity is the regular repeating of properties according to arrangement of elements in the periodic table (i.e., after regular intervals) such as atomic radius, ionisation energy, etc. arising from the systematic filling of successive energy level.

- Valence electrons are electrons in the outermost energy level (the highest energy level) of an atom and are usually the electrons that take part in a chemical reaction.

- Properties of elements are chiefly due to the number and arrangement of electrons in the outer energy level of atoms.

- The number of valence electrons is the same for a group, but increases across a period.

- The transition metals are the large d-block elements in the middle of the Periodic Table from Sc to Zn etc. (includes three transition series).

- Ionization Energy (IE) is the minimum energy required to form a mole of 1+ ions (by removing an electron from each atom) in the gaseous state: $M (g) \rightarrow M^+ (g) + e^-$ (units: $kJ\ mol^{-1}$)

- Electronegativity is a measure of how strongly the atom attracts the electrons in a covalent bond.

TRENDS IN THE PERIODIC TABLE

SMALLER ATOMIC RADIUS
SMALLER IONIC RADIUS
HIGHER ELECTRONEGATIVITY
HIGHER IONIZATION ENERGY
LOWER METALLIC CHARACTER

LARGER ATOMIC RADII
LARGER IONIC RADII
LOWER ELECTRONEGATIVITY
LOWER IONIZATION ENERGY
HIGHER METALLIC CHARACTER

NOTE that the properties are nearly constant along the diagonal (however, the transition elements have great similarities)

Alkali metals

- are extremely reactive, electropositive metals. They react vigorously with O_2 in the air and oxidize fast to form ionic oxides.

- contain one valence electron that is very easily lost due to low ionization energy; thus they are very good reducing agents: Na (s) $\rightarrow$ Na$^+$ (aq) + e$^-$.

- In compounds, these exist as +1 cations with noble gas electron configuration.

- Since a valence e$^-$ further away from the nucleus down a group is more easily removed, reactivity increases from Li to Cs.

- Reaction with Water: Reactivity increases down the group:

$$2 \text{ Li (s)} + 2 \text{ H}_2\text{O (l)} \rightarrow 2 \text{ LiOH (aq)} + \text{H}_2 \text{ (g)} + \text{heat}$$

- Reaction with Halogens: form ionic salts (e.g. Na$^+$Cl$^-$); the reaction is highly exothermic. The alkali halides are ionic, neutral, water-soluble, white crystalline compounds.

$$2 \text{ Na (s)} + \text{Cl}_2 \text{ (g)} \rightarrow 2 \text{ NaCl (s)} + \text{heat}$$
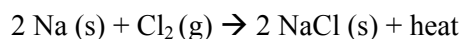
Halogens

- Are non-metallic; metallic character increases down the group (I_2 is a shiny solid).

- Higher ionization energies indicate little tendency to lose electrons.

- Have 7 valence electrons and achieve noble gas configuration by gaining an electron to form an anion (e.g. Cl$^-$), or by sharing an e$^-$ pair with another atom (e.g., Cl_2).

- Are diatomic (F_2, Cl_2, Br_2, I_2), non-polar molecules. They are simple molecular substances with only weak van der Waal's between molecules (Bonding, Ch. 4).

- Higher electronegativities mean that halogens have a tendency to accept an electron, and act as oxidizing agents: $X_2 + 2$ e$^- \rightarrow 2$ X$^-$.

- Oxidizing strength decreases down the group, since the atom gets larger and attraction for the electrons decreases.

- Reactions of halogens X_2 with halide ions X$^-$: Halogen *Displacement* Reactions: Weaker halogens are displaced from their salts by more powerful oxidizing agents. Thus Cl_2 can displace Br_2 from Br$^-$ and I_2 from I$^-$ (as it is a stronger oxidizing agent than both Br and I), but it cannot displace F_2 from F$^-$.

- Identification of Halide Ions – Reaction with silver ions, Ag$^+$: Silver halides, with different colored precipiates can be used to identify a halide ion:

    1. AgNO$_3$ (aq) + NaF (aq) $\rightarrow$ No precipitate formed.

    2. AgNO$_3$ (aq) + NaCl (aq) $\rightarrow$ AgCl (s) + NaNO$_3$ (aq), a white precipitate.

    3. Ag$^+$ (aq) + Br$^-$ (aq) $\rightarrow$ AgBr (s), a cream precipitate.

    4. Ag$^+$ (aq) + I$^-$ (aq) $\rightarrow$ AgI (s), a yellow precipitate.

Period 3 elements

- Ionization energy and electronegativity increase across the period; thus elements do not lose electrons as easily and metallic character decreases across the period. Bonding changes from metallic to covalent.

- Na, Mg and Al are metallic, good conductors of heat and electricity, with low to medium melting points, and lower electronegativities.

- Si is a semi-conductor / metalloid. It forms a network covalent solid of very high melting point.

- P, S and Cl are elements of higher electronegativity and are non-metallic. These form simple molecular substances (see bonding) with lower boiling points; the bonding between atoms is covalent and the bonding between molecules is weak van der Waal's forces.

Period 3 oxides and chlorides

Period 3 oxides and chlorides	Bonding in oxides and chlorides	Electrical conductivity of molten oxides and chlorides	Acid/base properties of oxides	Acid/base properties of chlorides	pH of chlorides in water
s block elements: Na and Mg	Ionic solids with high melting points; bonding between active metals of low IE and active non-metals of high electronegativity	Ions present, e.g. $Na^+ + Cl^-$ $Mg^{2+} + O^{2-}$; conduct electricity in the molten state (and in aqueous sol)	Oxides form basic solutions $Na_2O + H_2O$ $\rightarrow 2NaOH$; $MgO + H_2O$ $\rightarrow Mg(OH)_2$	Chlorides (NaCl, $MgCl_2$) form neutral solutions. $MgCl_2$ is actually very slightly acidic.	NaCl : pH =7 $MgCl_2$: pH ~ 7
p block elements Al, Si; P, S, Cl	Al_2O_3 is ionic; SiO_2 is a giant covalent structure (with very high melting point). Others: covalent bonding; form simple molecular substances	No mobile ions present; non-conductors	Oxides are acidic except Al_2O_3 which is amphoteric (can act as an acid or a base)	Chlorides are acidic; undergo hydrolysis reaction to produce HCl vapor	Al_2Cl_6: pH ~ 3 $SiCl_4$, PCl_5, S_2Cl_2 : pH ~ 2

d-block elements

- d-block elements with characteristic properties form at least one ion with a partially filled d sub-level (with 1 to 9 electrons); Sc and Zn are not typical of d-block elements.

- Characteristic properties are: presence of variable oxidation states, formation of complex ions, colored complexes, and catalytic activity.

- 4s is lower in energy (but further from the nucleus) than 3d sub-level; 4s electrons are lost before 3d; both 4s and 3d can behave as valence electrons because these are close in energy.

- Multiple oxidation states are due to 4s and 3d being close in energy. All d-block elements (except Sc) show an oxidation state of +2. All d-block elements except Zn show an oxidation state of +3.

- Complexes are formed when a central metal ion is bonded to ligands; ligands contain (at least one) lone e^- pair that form coordinate bonds with the central transition metal ion.

- Color is due to d-d electron transitions between split d orbitals.

- Transition metals behave as surface catalysts and their compounds more often as intermediate catalysts, which are important for industrial and biological reactions.

(N.B. Shading indicates Topic 13 (AHL) material.)

CHAPTER 4   BONDING

(IB TOPICS 4 AND 14) SUMMARY

A chemical bond is the interaction between atoms within a molecule, between molecules or between ions of opposite charges. Bond formation is an exothermic process; it gives out energy and leads to a more energetically stable state.

Bonding in liquids and solids

1. **Covalent bonding** results from electron sharing between non-metals or a non-metal and a metal of higher electronegativity. The electron pair is attracted by both nuclei leading to a bond that is directional in nature.

    (i) *van der Waals' Forces*: For a non-polar molecule, only weak, temporary, instantaneous dipole-dipole interaction called van der Waals' forces exist between molecules. These molecules are low melting point solids and low boiling point liquids and gases. Larger the molecule, stronger the van der Waals' forces, higher its boiling and melting points.

    (ii) *Dipole-dipole Interaction*: In a polar molecule, besides weak van der Waals' forces, the molecules experience stronger permanent dipole-dipole interaction.

    (iii) *Hydrogen Bonding*: Elements of high electronegativity (F, O, N), bonded to a (tiny) hydrogen atom give rise to a special case of dipole-dipole interaction called H-bonding. This is important in determining solubility, melting and boiling points, and stability of crystal structures. Hydrogen bonding also plays an important role in biological systems. Hydrogen bonded molecules experience stronger hydrogen bonding in addition to van der Waals' forces and dipole-dipole interaction.

    Strength of bonding: van der Waals' < dipole-dipole < H-bond << covalent bond $\approx$ ionic bond. However, van der Waals' forces can become extensive depending on the size of the molecules, e.g., in polymers and long chain hydrocarbon molecules.

2. **Ionic bonding** occurs as a result of electron transfer from active metals of Groups 1, 2, 3 to active non-metals of Groups 6, 7, leading to electrostatic attraction between ions of opposite charges. Ionic crystals are regular repeating arrays of positive and negative ions, packed so that each positive ion is surrounded by negative ions and vice versa in a 3 dimensional lattice structure. Ionic crystals have high melting and boiling points, are water soluble (water solubility varies considerably) and conduct electricity when molten or in aqueous solution, but not in the solid state, as ions are not free to move about in a solid ionic crystal.

3. **Metals** are good conductors of electricity and heat, ductile and malleable. Metals have low ionization energies and vacant valence orbitals. Metals consist of regular, repeating arrangements of metal ions (cations) in which the bonding electrons are mobile or delocalized and can move rapidly through the metal, since an electron is much smaller than the spaces between the cations. This explains high conductivity of elements. Electrons can acquire large amounts of kinetic energy and rapidly transfer it to cooler parts of the metal: this explains thermal conductivity. The movement of cations between layers can take place with no change in metallic bonding. This explains ductility and malleability.

4. **Allotropes of carbon**: Diamond, Graphite and C_{60} Fullerene form covalent bonds and network solids. In diamond, each carbon is covalently bonded to four other carbon atoms in a three dimensional tetrahedral arrangement. Diamond is very hard, stable with a very high melting point and does not conduct electricity as all its valence electrons are involved in covalent bonding (sp^3 hybridized). Graphite has a layered structure; each layer has carbon atoms covalently bonded to three other carbon atoms (sp^2 hybridized) in a hexagonal arrangement but with only weak van der Waals' forces between layers. Graphite is easy to break, and soft with lubricating qualities. Graphite is a good conductor due to mobility of electrons in pi orbitals that are delocalized. C_{60} fullerene contains 60 carbon atoms (20 hexagons and 12 pentagons). It is a highly symmetrical, closed-carbon-caged molecule. Within each molecule, each carbon atom is covalently bonded to three other carbon atoms (sp^2 hybridized). C_{60} molecules contain two bond lengths –

the hexagons can be considered "double bonds" and are shorter; the longer bonds in the pentagonal rings suggest that electron delocalization is poor.

• **Lewis Electron-Dot Structures**: Structures showing covalent bonds by using symbols of element(s) involved, and indicating *all* the valence electrons by using dots, crosses, a combination of dots and crosses or by using a line to represent a pair of electrons.

• **Valence Shell Electron Pair Repulsion (VSEPR) Theory**: Electron pairs in the valence shell of the central atom are arranged as far apart as possible due to mutual repulsion. This minimizes the forces of repulsion between the electron pairs. The species therefore has minimum energy and maximum stability.

SHAPES WITH ONLY BONDED ELECTRON PAIRS ON THE CENTRAL ATOM:

#of Bonded e^- Pairs	Structure	Angle	Examples
2 (and no lone e- pairs)	Linear	180°	$BeCl_2$, CO_2, C_2H_2
3 (and no lone e- pairs)	Trigonal planar	120°	BCl_3, CO_3^{2-}, NO_3^-
4 (and no lone e- pairs)	Regular Tetrahedral	109.5^o	CH_4, BF_4^-, NH_4^+
5 (and no lone e- pairs)	Trigonal bipyramidal	$90^o, 120^o, 180^o$	PCl_5
6 (and no lone e- pairs)	Octahedral or square bipyramidal	90° and 180°	SF_6

SHAPES WITH 3 ELECTRON PAIRS (BONDED + LONE PAIRS) ON CENTRAL ATOM

Number of bonded e^- pairs	Number of lone e^- pairs	Structure	Angle	Examples
3	0	Trigonal planar	120°	BCl_3, CO_3^{2-}, NO_3^-
2	1	Bent, V-Shaped, or angular	less than 120° (or $\approx 120^o$)	O_3, SO_2, NO_2^-

SHAPES WITH 4 ELECTRON PAIRS (BONDED + LONE PAIRS) ON CENTRAL ATOM

Number of bonded e^- pairs	Number of lone e^- pairs	Structure	Angle	Examples
4	0	Regular Tetrahedral	Regular Tetrahedral $109\frac{1}{2}^o$	CH_4, BF_4^-, NH_4^+
3	1	Trigonal pyramidal	$\angle \approx 107^o$ or less than 109°	NH_3, PCl_3, SO_3^{2-}
2	2	Bent, V-shaped or Angular	$\angle \approx 105^o$ or less than 109°	H_2O

SHAPES WITH 5 ELECTRON PAIRS (BONDED + LONE PAIRS) ON CENTRAL ATOM

Number of bonded e⁻ pairs	Number of lone e⁻ pairs	Structure	Angle	Examples
5	0	Trigonal bipyramidal	$90^o, 120^o, 180^o$	PCl_5
4	1	Unsymmetrical tetrahedral	$\approx 90^o, 120^o, 180^o$	SF_4
3	2	T-shaped	$90^o, 180^o$	ClF_3
2	3	Linear	180°	I_3^-

SHAPES WITH 6 ELECTRON PAIRS (BONDED + LONE PAIRS) ON CENTRAL ATOM

Number of bonded e⁻ pairs	Number of lone e⁻ pairs	Structure	Angle	Examples
6	0	Octahedral or square bipyramidal	90° and 180°	SF_6
5	1	Square pyramidal	$\approx 90^o$ and 180°	BrF_5
4	2	Square planar	90°	XeF_4

- Note that it is important to specify the angle as both O_3 and H_2O are bent molecules, but with different angles around the central atoms.

- A lone e⁻ pair is spread out over a larger volume than a shared e⁻ pair, causing a distortion from regular geometry, and causing the angle to be slightly reduced.

- A Resonance structure is one of two or more Lewis structures for a species that cannot be described adequately by a single structure. Resonance structures have the same sigma bonds but differ in the arrangement of the pi bonds. The actual bonding is a mixture of the various possible arrangements, and will have a lower energy than any of the individual forms. The phenomenon is called delocalization because the valence electrons provided by individual atoms are no longer held in the vicinity of that atom, but are mobile and shared by a number of atoms. It is this spreading out of the electrons that gives the structure its lower potential energy than it would have if double and single bonds were arranged in such a way that orbital overlap could not take place. Thus, delocalization stabilizes a structure.

- Bonds have electron distribution with axial symmetry around the axis joining the two nuclei (from combination of two s orbitals or an s and a p or hybridized orbitals); π bonds result from the sideways overlap of parallel p orbitals with electron distribution above and below the nuclei.

- Hybridization involves mixing of atomic orbitals to give new hybrid orbitals of equivalent energy, i.e., it is the redistribution of energy in different orbitals (in the valence shell) of an atom.

Type of Hybridization	Examples	Bonds	Shape	Angle
sp^3 (combination of: one s and three p orbtals)	CH_4 NH_3 H_2O	4 σ bonds 3 σ; 1 lone e⁻ pair 2 σ; 2 lone e⁻ pairs	Tetrahedral Trigonal pyramidal Bent/angular/"V"	= 109.5° <109.5° (≈107°) <109.5° (≈105°)
sp^2 (combination of: one s and two p orbtals)	C_2H_4 BCl_3 C_6H_6	Each C has 3 σ; 1 π C=C has 1 σ; 1 π B has 3 σ bonds Each C has 3 σ; 1 π	Planar Planar Planar	120° 120° 120°
sp (combination of: one s and one p orbtal)	C_2H_2 $BeCl_2$	Each C has 2 σ; 2 π C≡C has 1 σ; 2 π Be has 2 σ bonds	Linear Linear	180° 180°

(N.B. Shading indicates Topic 14 (AHL) material.)

Basic concepts

Energetics deals with heat changes in chemical reactions. It is measured in joules, J. Units of energy: joule; 1 cal = 4.184 J. In an exothermic reaction, heat is given out to the environment and the temperature of the system increases. Endothermic reaction is one in which heat is taken in from environment and the temperature of the system decreases. The reaction mixture is called the system and anything around the system is called the surrounding or environment.

ΔH°, **Standard enthalpy** change is heat change (given out or evolved) under standard conditions of 101.3 kPa pressure and a temperature of 298 K. Only ΔH can be measured, not H for the initial or final state of a system. $\Delta H^\circ_{reaction}$ is the sum of the change in enthalpies of products minus sum of the change in enthalpies of reactants.

$$\Delta H^\circ_{reaction} = \Sigma \Delta H^\circ_{products} - \Sigma \Delta H^\circ_{Reactants}$$

Thermochemical equations include a balanced equation and an indication of the heat flow: e.g.,

$$H_2 (g) + \tfrac{1}{2}O_2 (g) \rightarrow H_2O (l); \qquad \Delta H^o = -285.8 \text{ kJ mol}^{-1}$$
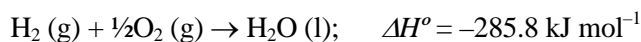
1. Coefficients refer to number of moles.

2. States of substances must be specified.

3. $\Delta H \propto$ amount of substance that reacts or is produced in a reaction.

Standard Enthalpy Change of Formation, ΔH^o_f is the enthalpy change when one mole of a compound is formed from its elements in their stable states under standard conditions of 298 K and 101.3 kPa pressure. By definition the enthalpy of formation of any element in its stable form at 298 K and 101.3 kPa pressure equals zero. This is because no energy change is required to form an element from itself. Enthalpy change of a reaction is the sum of the ΔH^o_f of products minus sum of ΔH^o_f of the reactants.

$$\Delta H^o_{rxn} = \Sigma \Delta H^o_{f, Products} - \Sigma \Delta H^o_{f, Reactants}$$

ΔH_{neut}: **Enthalpy of neutralization** is the heat evolved when one mol of H_3O^+ reacts with 1 mol OH^- ions. Heat is evolved because bond formation takes place: $H_3O^+ + OH^- \rightarrow 2H_2O$.

ΔH_{latt}: **Lattice enthalpy** is the energy required for the conversion of one mol of an ionic solid into gaseous ions or energy given out when one mole of ionic solid is formed from ions in gaseous state.

For NaCl it is: $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$; $\Delta H_{latt} = +$

OR $Na^+(g) + Cl^-(g) \rightarrow NaCl (s)$; $\Delta H_{latt} = -$

Calorimetry is the technique of measuring heat changes in physical processes (such as melting or heat gained by a solid) and chemical reactions. In order to calculate heat change, we need:

Specific heat, c: the energy required to change the temperature of 1 g of the substance by 1°C. Note: in case of aqueous solutions, we assume solutions are dilute enough, and use the specific heat of water. Units of specific heat: $J \text{ g}^{-1}°C^{-1}$ (=$J \text{ g}^{-1} K^{-1}$ since change in 1°C = change in 1 K).

Mass of the substance (in aqueous solutions, the mass of solution, not of solute), and ΔT, the change in temperature. Thus: the heat change, $Q = mc\Delta T$.

The equation $Q = mc\Delta T$ can be used to calculate:

1. Heat change of a substance, given its mass, specific heat and temperature change.

2. $\Delta H^\circ_{reaction}$ in aqueous solution using experimental data on temperature changes, quantities of reactants and mass of solution (where it is assumed that that the solution is dilute enough so that specific heat of solution = specific heat of water = 4.18 J g^{-1} C^{-1}).

Note that if a calorimeter is used that also absorbs energy, then its mass, m and specific heat, c (or heat capacity, m x c) must also be known:

$$\Delta H_{sol} = \text{heat absorbed by solution + heat absorbed by calorimeter}$$

$$= (m_{solution} \times c_{sol} \times \Delta T_{sol}) + (m_{flask} \times c_{flask} \times \Delta T_{flask})$$

According to **Hess's Law,** *ΔH* of a reaction is independent of any intermediate steps. Hess's law is a special case of the law of conservation of energy.

Bond Enthalpy is the energy required when one mole of bonds is broken in the gaseous state (bond enthalpies are valid only in the gaseous state). Bond breaking needs energy and is an endothermic process. Bond making releases energy and it is an exothermic process. Average bond energy is the average energy required to break a mole of the same type of bonds in the gaseous state in a variety of similar compounds.

If bond enthalpies are given then: $\Delta H^o_{rxn} = \Sigma BE_{bonds\ broken} - \Sigma BE_{bonds\ made}$ (*not p*roducts – reactants)

Born-Haber cycle, a special case of Hess's law for the formation of ionic compounds involves three key steps:

1. ΔH°_f, standard change in enthalpy of formation of the ionic crystal, i.e., starting from the elements in their stable states under standard conditions, e.g., Na (s) + ½ Cl$_2$ (g) to form the ionic solid, NaCl (s).

2. Starting from the same elements, produce *gaseous* ions, e.g., Na$^+$ (g) and Cl$^-$ (g). This involves a series of processes: convert Na (s) to Na (g) (sublimation) and then to Na$^+$ (g) (ionization energy). Similarly, convert ½ Cl$_2$ (g) to Cl (g) (½ the BE), then form Cl$^-$ (g) (Electron affinity).

3. Lattice Enthalpy: Na$^+$ (g) + Cl$^-$ (g) $\rightarrow$ NaCl (s)

Lattice enthalpy value from Born-Haber cycle is called experimental lattice energy value, as experimental values of the other processes involved are used to arrive at it. On the other hand, a theoretical value can be calculated using a (purely) ionic model and distance between the ions using laws of electrostatics. Comparison between the theoretical and experimental lattice enthalpies gives an indication of whether the substance is ionic (if there is good agreement) or has covalent character.

Entropy, *S* is a property that relates to the degree of disorder or randomness in a system. In general, systems in nature prefer greater disorder. The change in entropy, $\Delta S = S_p - S_R$. For a reaction, $\Delta S^o = \Sigma S^o_{product} - \Sigma S^o_{reactants}$. By definition, *ΔS*, the entropy change is positive for increasing disorder.

Free energy, *G* is the criterion for predicting the spontaneity of a reaction. Change in free energy, *ΔG* accounts for both *ΔH* and *ΔS* and is determined by the Gibbs-Helmholtz equation: $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$; *ΔG°* is the standard free energy change at 298 K and 101.3 kPa pressure, *ΔH°* is the standard enthalpy change, *ΔS°* the standard entropy change and T is temperature in Kelvin.

ΔG is a measure of the driving force of a reaction, i.e., its tendency to proceed spontaneously. A reaction or physical process can occur spontaneously if *ΔG* is negative. A spontaneous reaction or process may be used to do work (*ΔG* it is the amount of energy available to do useful work) on another system. For minimum energy *ΔH* = –, for maximum entropy *ΔS* = + Thus, *ΔG* is negative for any spontaneous reaction. For a non-spontaneous reaction (or spontaneous in the reverse direction) *ΔG* is positive and for an equilibrium process *ΔG* = 0.

(N.B. Shading indicates Topic 15 (AHL) material.)

CHAPTER 6 KINETICS
(IB TOPICS 6 AND 16) SUMMARY

Reaction rate

Rate of a reaction is the decrease in the concentration of a reactant or the increase of the concentration of a product with unit time. For a A $\rightarrow$ b B, $rate = -\dfrac{1}{a}\dfrac{\Delta[A]}{\Delta t} = \dfrac{1}{b}\dfrac{\Delta[B]}{\Delta t}$; rate is a positive quantity.

Rates can be determined by measuring the change in the concentration of a reactant or product with time. Possible methods are pressure measurements for gases using a manometer or pressure gauge, volume measurement for gases using a gas syringe, color changes using a colorimeter or spectrophotometer, heat changes using a thermometer, mass changes using a balance, pH changes using a pH meter, titrations, etc.

Collision Theory

- The reactant particles must collide together.

- Particles must have the correct geometrical alignment.

- Particles must have a minimum energy of $E \geq E_a$, the activation energy.

- Activation energy is the minimum energy required for reactants to react in order to convert into products (via a transition state or activated complex).

- Transition state is an unstable arrangement in which the bonds are in the process of being broken and formed and presents the maximum point on a potential energy diagram; it can not be isolated.

Factors that Influence Rates of Reactions

- Increase in concentration: Greater number of particles per unit volume per time means greater frequency of collisions and faster rate.

- Increase in temperature: This causes an increase in average kinetic energy; particles collide more frequently and more forcefully. Thus number of particles with $E \geq E_a$ increases greatly and rate increases (more forceful collisions is a more important factor than more frequent collisions).

- Increasing the surface area of solids reactants: This increases the number of particles that can collide, i.e., increases the frequency of successful collisions.

- Catalysts: Lower the activation energy of reaction by providing an alternate pathway and thus increase the rate of reaction. Catalysts are specific to reactions and are used in industry.

  o Homogeneous catalysis: Where the catalyst is in the same phase as the reactants, e.g., esterification reaction to produce sweet smelling compounds for perfumes, and in the food industry.

  o Heterogeneous catalysis: Where the catalyst and reactants are in different phases e.g., in the manufacture of ammonia, sulfuric acid, hydrogenation of alkenes etc.

  o A catalyst does not change the position of equilibrium; rather it increases the rate of both the forward and reverse reactions to the same extent; does not change ΔH of a reaction.

- Rate expression (law) is the dependence of rate on concentration expressed mathematically.

- For the reaction: A + B + C $\rightarrow$ products, rate $= k[A]^m[B]^n[C]^p$, where m, n, and p are the orders of the reaction with respect to each reactant A, B, C. The overall order $= (m + n + p)$.

Orders of reaction are obtained experimentally, not from Stoichiometry; however any mechanism must be consistent with overall Stoichiometry of the reaction.

- Rate constant, k, is the constant in the rate expression. It is temperature dependent. Units of rate constant depend on the rate expression; units of zero order rate constant, k_o = units of rate = mol dm^{-3} s^{-1}. Units of 1st order rate constant, k_1 = s^{-1}. Units of 2nd order rate constant, k_2 = dm^3 mol^{-1} s^{-1}; units of 3rd order rate constant, k_3 = dm^6 mol^{-2} s^{-1} (units must not be memorized, but easily derived from the appropriate rate expression).

- The rate expression, determined only experimentally, need not be a simple one, i.e., it need not contain whole numbers, or positive numbers for that matter although this is often the case.

- In general, given the rate as a function of concentration, reaction order can be determined as follows:

- If only one reactant is involved, since rate = k [conc.]n, find the ratio of the rates at two different concentrations and apply the relation:

$$\frac{rate_2}{rate_1} = \left(\frac{[conc_2]}{[conc_1]} \right)^n ; n \text{ is the reaction order.}$$

- If two reactants, A and B, are involved, rate = k [A]^m [B]^n:

- Find the ratio of the rates when [B] is constant but [A] changes. Using the equation above, find the order with respect to A.

- Repeat the process when [A] is constant but [B] changes to determine the order with respect to B.

Orders of reaction

o   Zero-order reaction is when the rate of a reaction is independent of the concentration of a reactant: rate=k [A]0 = k. Graph of [A] vs time is a straight line, with a negative slope = rate. [A]t = [A]0 – kt.

o   First-order reaction is where the rate doubles when concentration doubles: rate =k [A]1. Graph of [A] against time is an exponential curve; graph of ln [A] vs. t is a straight line with a negative slope where slope = k the rate constant. Half-life of a first order reaction is a constant; t1/2=0.693/k. Integrated form of first order equation:

ln [A]t = − kt + ln [A]0 OR ln [A]0 – ln[A]t = kt OR $\quad \ln \frac{[A]_0}{[A]_t} = kt$;

o   [A]t = [A]0e-kt (the last two equations are given in the Data Book).

o   irst-order reaction is where the rate doubles when concentration doubles: rate =k [A]1. Graph of [A] against time is an exponential curve; graph of ln [A] vs. t is a straight line with a negative slope where slope = k the rate constant. Half-life of a first order reaction is a constant; t1/2=0.693/k. Integrated form of first order equation: ln [A]t

= − kt + ln [A]0 OR ln [A]0 – ln[A]t = kt OR $\quad \ln \frac{[A]_0}{[A]_t} = kt$; [A]t = [A]0e-kt (the last two equations are given in the Data Book).

o   If the rate quadruples when concentration doubles: rate = k [A]2. Graph of 1/[A] against time is a straight line for a second order reaction with a positive slope = k.

o   For a third-order reaction, if rate = k[A]3, then as [A] doubles, rate increases 8 times.

o   Rate increases with temperature when concentrations are constant, k increases rapidly with T and is temperature dependent, producing a straight line graph of ln k vs 1/T with a negative slope. Slope of the line = - Ea/R. Thus Ea can be determined; T must be in Kelvin, not °C.

o   Arrhenius Equation gives the dependence of k on T (equation given in the Data booklet): $k = A\,e^{-\frac{E_a}{RT}}$:

o $$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$ **OR** $\log_{10} k = \log_{10} A - \frac{E_a}{2.303\,R}\left(\frac{1}{T}\right)$ *where:* A, the

Arrhenius constant is the collision factor that represents the frequency of successful collisions with the favourable geometry, R is the Ideal Gas Constant (= 8.314 J mol^{-1} K^{-1}), E$_a$ is the activation energy (the minimum energy required for a reaction to occur), and T must be in Kelvin scale.

- Molecularity is based on proposed mechanism and refers to the number of particles in the slow, rate-determining step (i.e., the number of species involved in making the transition state or the activated complex of the slow step).

- Mechanism is a model of how a reaction occurs.

  o   The slowest step of a mechanism is called the rate-determining step.

  o   Intermediates are species produced in earlier steps that are consumed in later steps.

  o   Transition state is an unstable arrangement in which the bonds are in the process of being broken and formed and presents the maximum point on a potential energy diagram; it can not be isolated.

  o   Mechanism must account for overall Stoichiometry, rate expression, etc.

  o   Rate of overall reaction is the rate of the slowest step.

  o   Stoichiometry of an equation gives no information about the rate expression or about the mechanism of a reaction. However any mechanism must be consistent with overall Stoichiometry, rate expression, etc. For a 3rd order reaction, the first step (containing a maximum of two particles) cannot be the slow, rate determining step.

A Unimolecular step	A Bimolecular step
- A unimolecular step involves a single species as a reactant.	- A bimolecular steps involves collision of two species (that form a transition state or an activated complex that can not be isolated).
- Its rate law is therefore 1st order with respect that reactant.	- Its rate law is 1st order with respect to each of the colliding species and is therefore 2nd order overall.

(N.B. Shading indicates Topic 16 (AHL) material.)

Equilibrium

Dynamic Equilibrium is recognized by a constant macroscopic property in a closed system due to the concentration of all the reactants and products remaining constant at the same temperature. It is explained in terms of the rate of the forward reaction *equal* to the rate of the reverse reaction.

For the equilibrium $aA + bB \rightleftarrows cC + dD$ where a, b, c, and d are coefficients in the balanced equation, the **equilibrium expression** at a particular temperature (where square brackets $[\ ]_{eq}$ represent equilibrium concentration in mol dm^{-3}) is:

$$K_c = \frac{[C\ ]^{c}_{eq}\ [D\ ]^{d}_{eq}}{[A\ ]^{a}_{eq}\ [B\ ]^{b}_{eq}}\ ;\ \ K_c \text{ is the equilibrium constant at a particular temperature.}$$

In the K_c expression, the right side of the chemical equation is written as the numerator, the left side of the chemical equation is written as the denominator, and the coefficients become *exponents*. Square brackets represent equilibrium concentrations.

Units of K_c depend on the powers to the concentration in the equilibrium expression.

Significance of K_c

- When $K_C > 1$, concentration of *products* generally exceeds that of reactants at equilibrium.
- When $K_C \gg 1$, reaction goes *almost* to completion.
- When $K_C < 1$, concentration of *reactants* generally exceeds that of products at equilibrium.
- When $K_C \ll 1$, reaction *hardly* proceeds.

Law of Multiple Equilibria

- When equations are added, multiply K_C values.
- When equations are subtracted, divide K_C values.
- When an equation is doubled, square K_C value.
- When an equation is halved, take square root of K_C value (a new equilibrium constant value).
- When an equation is reversed, inverse K_C value.

Le Chatelier's Principle

This principle helps predict the direction of the effect: If a stress or change is applied to a system at equilibrium, the processes that take place counteract (minimize) the effect of that change and establish a new equilibrium. Thus, concentrations of the species change in such a way as to *minimize* the effect of the stress (the stress can not be totally eliminated).

Conditions that alter the position of equilibrium: Change in concentration changes the position of equilibrium (favors forward or reverse reaction), but does not change the value of K_c. A change in temperature changes both the position of equilibrium and the value of K_c.

Effect of adding a Catalyst: Catalysts increase rates of reactions. Any catalyst has the same effect on the rates of the forward and reverse reactions. The addition of a catalyst to a system at equilibrium does not alter the position of equilibrium. The system reaches the same equilibrium more quickly but with no net change in equilibrium concentrations; thus K_c does not change.

Concentration Change and Le Chatelier's Principle: If the concentration of one of the reactants or products in a system at equilibrium is increased, the effect of the change may be minimized by the establishment of a new equilibrium so that the concentration of the added substance is reduced. K_C does not change.

CHAPTER 7 EQUILIBRIUM
(IB TOPICS 7 AND 17) SUMMARY

A + B ⇌ C + D ⟵	A + B ⇌ C + D ⟶
1. Remove any reactant: K_C remains constant.	1. Remove any product: K_C remains constant.
2. Equilibrium shifts to the left, to replace some of the reactant removed, to minimize change.	2. Equilibrium shifts to the right, to replace some of the product removed, to minimize change.

Pressure Change and Le Chatelier's Principle: If pressure of the system is increased, concentration increases, and the effect of this change may be counteracted by the establishment of a new equilibrium so that the volume is decreased. The equilibrium constant, K_C, does not change as only concentration is changed:

(1) If $\Delta V_{gases} = V_P - V_R = +$, for example: $H_2O\,(g) \rightleftharpoons H_2\,(g) + \frac{1}{2}\,O_2\,(g)$. If pressure is increased, the system now occupies less volume, i.e., the increase in pressure is counteracted if hydrogen and oxygen combine to form gaseous water which occupies less volume. Thus the reverse reaction is favoured until a new equilibrium is established. K_c does not change.

(2) If $\Delta V_{gases} = -$, for example: $3\,H_2\,(g) + N_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$. There is a decrease in volume of gases. So increase in pressure will favour formation of more ammonia, i.e., the forward reaction is favoured to relieve the stress of pressure until a new equilibrium is established. K_C doesn't change.

(3) If $\Delta V_{gases} = V_P - V_R = 0$, for example : $CO\,(g) + NO_2\,(g) \rightleftharpoons CO_2\,(g) + NO\,(g)$. There is no change in volume of gases ($\Delta V = 0$). Thus, no change in equilibrium position when the pressure is altered in such cases. The rates of the forward and reverse reactions will increase equally as concentrations of reactants and products increase. K_c remains constant.

Temperature Change and Le Chatelier's Principle: Changing the temperature of a system results in the establishment of a new equilibrium constant. Increase in temperature favours the change that takes place with absorption of thermal energy:

	Endothermic reactions: e.g.: A + B + heat ⇌ C + D	Exothermic reactions: e.g.: E + F ⇌ G + H + heat
Increase in temperature	Favors forward reaction to use up some of the heat supplied	Favors reverse reaction to use up some of the heat supplied
• Effect on Concentration	[C] and [D] increase and [A] and [B] decrease	[G] and [H] decrease and [E] and [F] increase
• Effect on K_C	K_C increases	K_C decreases
Decrease in temperature	Favours the reverse reaction to produce some of the heat taken away.	Favours the forward reaction to produce some of the heat taken way.
• Effect on Concentration	[C] and [D] decrease and [A] and [B] increase	[G] and [H] increase and [E] and [F] decrease
• Effect on K_C	K_C decreases	K_C increases.

Thus, the equilibrium shifts in such a way as to absorb heat when the temperature is increased and to evolve heat when the temperature is decreased. Do not confuse effect of change in temperature on equilibrium with effect on rate of reaction. It helps if you think of the change in heat as part of the reactants or products. Recall that K_C varies only with temperature.

CHAPTER 7 EQUILIBRIUM

(IB TOPICS 7 AND 17) SUMMARY

Solving Equilibrium Problems

- Write the balanced equation and the K_c expression for the reaction
- List the initial concentrations of all reactants and products
- Determine the concentration changes to reach equilibrium, and the equilibrium concentrations
- Substitute into the equilibrium expression to solve for the unknown concentration, or determine K_c value.

The Haber Process: Summary: $N_2(g) + 3H_2 (g) \leftrightarrows 2NH_3(g); \Delta H = -$

- All the species are gases
- There are 4 moles (volumes) of gases in the reactants and only 2 in the product
- The forward reaction is exothermic.

Change in **concentration**: Increased concentration of H_2 (g) and/or N_2 (g) increases the number of collisions of reactants per unit time and the rate of the forward reaction *increases*. This also increases the pressure on the system; in order to relieve the pressure, the forward reaction is favored with more ammonia produced; K_c remains constant.

Change in **pressure**: Since there are 4 mol gases on the reactant side, and 2 in the product side, an increase in pressure forces the system to occupy less volume so as to relieve some of the pressure applied. Thus the forward reaction is favored. Rate also increases as concentration of gases increases. K_c remains constant.

Change in **temperature**: An increase in temperature increases the number of particles with $E \geq E_a$, and reaction rate increases. Since the forward reaction is exothermic, increased temperature favors the reverse reaction in order to use up some of the heat supplied to relieve the stress. K_c decreases with increase in temperature (K_c is temperature dependent).

Addition of **iron** as a catalyst speeds up both the forward and reverse reactions equally; the same equilibrium is reached faster; there is no change in equilibrium concentrations and the value of K_c remains the same.

The Contact Process Summary: $2 SO_2 (g) + O_2 (g) \leftrightarrows 2 SO_3 (g); \Delta H = -$

- All the species are gases
- There are 3 moles (volumes) of gases in the reactants and only 2 in the product
- The forward reaction is exothermic.

Change in **concentration**: Increased concentration of SO_2 (g) and O_2 (g) increases the number of collisions of reactants per unit time and the rate of the forward reaction increases. This also increases the pressure on the system; in order to relieve the pressure, the forward reaction is favored with more sulfur trioxide produced; K_c remains a constant.

Change in **pressure**: Since there are 3 mol gases on the reactant side, and 2 on the product side, an increase in pressure forces the system to occupy less volume so as to relieve some of the pressure applied. Thus the forward reaction is favored. Rate also increases as concentration increases. K_c remains constant.

Change in **temperature**: An increase in temperature increases the number of particles with $E \geq E_a$ and the reaction rate increases. Since the forward reaction is exothermic, a temperature increase favors the reverse reaction in order to to use up some of the heat supplied to relieve the stress. K_c decreases with increase in temperature (K_c is temperature dependent).

Addition of **V_2O_5** or Pt as a catalyst speeds up both the forward and reverse reactions equally; the same equilibrium is reached faster; there is no change in equilibrium concentrations and the value of K_c remains the same.

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Phase Equilibrium (Between Liquid and Its Own Vapor)

When the rate of condensation equals the rate of evaporation, saturated vapor pressure is present and a dynamic equilibrium is established:

The saturated vapor pressure of a liquid at a given temperature is independent of the amount of liquid or vapor present and of the volume of the container.

Enthalpy of Vaporization, Boiling Point & Intermolecular Forces: The molar enthalpy of vaporization, ΔH_{vap}, is the heat required to convert one mole of a substance *at its boiling point* from a liquid to a gas

If intermolecular attraction is strong (as in H_2O), then molecules in a liquid cannot easily escape into the vapor phase. Thus higher the ΔH_{vap}, the lower the volatility of the liquid. Consequently, the liquid will have a low vapor pressure (and high molar enthalpy of vaporization) because more energy is needed to overcome inter-particle forces to form the vapor.

- Weaker the inter-particle forces, higher the vapor pressure, lower the boiling point, lower the ΔH_{vap}.

- Stronger the inter-particle forces, lower the vapor pressure, higher the boiling point, higher the ΔH_{vap}.

(N.B. shading indicates Topic 17 (AHL) material)

General properties

Characteristic Properties of Acids corrosive, taste sour, and turn blue litmus red.

Aqueous solutions of acids have pH < 7. Acids react with hydroxides and oxides to form salt and water; Acids react with "active"* metals to form hydrogen gas; Acids react with carbonates to produce carbon dioxide; Similarly acids react with hydrogen carbonates.

Characteristic Properties of bases: Bases feel slippery, taste bitter, and turn red litmus blue.

Aqueous solutions of bases have pH > 7. React with acids to form salt (and water if a hydroxide):

Alkalis are bases that dissolve in water, e.g., NaOH. Substances such as ammonia, NH_3, soluble carbonates (e.g., Na_2CO_3) and hydrogen carbonates (e.g., $NaHCO_3$) are called bases; undergo base hydrolysis to form OH^-; With ethylamine, ethyl ammonium ion is formed:

Neutralization is the reaction of an acid and a base to give salt and water; in the salt, cations (e.g., Na^+) come from the base and anions (e.g., Cl^-) come from the acid:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
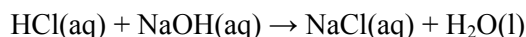
Brønsted-Lowry and Lewis theories

- A Brønsted-Lowry acid is a proton donor.

- A Brønsted-Lowry base is a proton acceptor.

- A Brønsted-Lowry acid-base reaction is characterised by proton transfer.

- When an acid transfers a proton, it produces a conjugate base.

- When a base accepts a proton, a conjugate acid is produced.

- The 2 related species in a proton transfer reaction, known as a conjugate acid-base pair, differ by a proton.

$$HCl\ (aq) + CO_3{}^{2-}\ (aq) \leftrightharpoons HCO_3{}^-\ (aq) + Cl^-\ (aq)$$

$\quad$ Acid$_1$ $\qquad$ Base$_2$ $\qquad$ Acid$_2$ $\qquad$ Base$_1$
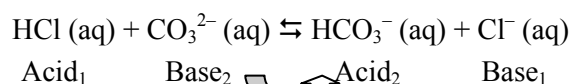
- Lewis acid: a species that can accept an electron pair. Lewis acids are cations or neutral molecules with available empty orbitals, e.g., H^+, Cl^+, $NO_2{}^+$, $CH_3{}^+$, $AlCl_3$, BF_3. These are called electrophiles.

- Lewis base: a species that can donate an electron pair. Lewis bases are anions or neutral molecules with lone e^- pair(s), e.g., OH^-, Cl^-, H_2O:, :NH_3. These are called nucleophiles (or nucleophilic reagents).

Electrolytes are substances that dissolve in water to give solutions containing ions.
Strong Electrolyte is a substance that dissolves and completely dissociates into ions (ionises completely). This is shown by a single arrow.

Weak Electrolyte is a substance that dissolves and dissociates into ions partially (to a limited extent)

A strong acid ionizes or dissociates essentially completely in water, and K_a, the acid dissociation constant for strong acids is large e.g., HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$.

"Strong" refers to complete dissociation, and "weak" refers to partial dissociation into ions. Acid strength relates to the extent of dissociation, not concentration. Concentrated solution contains larger amount of solute per dm^3 volume solution; dilute contains lower amount of solute per dm^3 volume solution (in Chemistry, strong is not the same as concentrated; weak is not the same as dilute).

A weak acid or a weak base ionizes only partially in water. HF ($\approx 90\%$ undissociated at 25°C) and organic acids such as ethanoic acid are examples of weak acids. Ammonia and aminoethane are examples of weak bases:

CHAPTER 8 ACIDS AND BASES

(TOPICS 8 AND 18) SUMMARY

Experimental Data to Distinguish Between Strong and Weak Acids and Bases

1. Since HCl is a strong acid, in solution the concentration of H^+ = 0.10 mol dm^{-3} and thus its pH is 1.0. Since CH_3COOH (aq) is a weak acid, $[H^+]$ will be much less than 0.10 mol dm^{-3} with a higher pH ($\approx$ 3). Thus, can be distinguished by differences in the pH value of equimolar aqueous solutions.

2. Can also be distinguished by measuring the conductivities of equimolar aqueous solutions. Because the strong acid is completely ionized, there are more ions in solution and as a result it will show greater conductivity, whereas the weak acid is only partially ionised, with fewer ions and lesser conductivity.

3. Rate of reaction of acids with Mg or carbonate: The strong acid reacts faster to produce H_2 or CO_2 gas more quickly as there are more H^+ ions present whereas the weak acid reacts slowly as there are fewer H^+ ions present.

Water Dissociation: H_2O (l) $\leftrightarrows$ H^+ (aq) + OH^- (aq); $K_w = [H^+][OH^-] = 1.0$ x 10^{-14} mol^2 dm^{-6} at 25°C.

K_a x $K_b = K_w$ for any combination of a weak acid and its own conjugate base (or weak base and its own conjugate acid).

pH is a measure of acidity; pOH is a measure of basicity. One way to measure H^+ concentration is to measure the pH of a solution. The relationship between pH of a solution and hydrogen ion concentration (or $[H^+]$) is:

$$pH = \log_{10} \frac{1}{[H^+]} = -\log_{10}[H^+] \ . \ \therefore [H^+] = 1.0 \, x \, 10^{-pH} \ . \ \text{Similarly,}$$

$$pOH = -\log_{10}[OH^-] = \log_{10} \frac{1}{[OH^-]}$$

Salt Hydrolysis

A salt, an ionic compound, contains cations (e.g., Na^+) from a base and anions (e.g., Cl^-) from an acid. Equal amounts of monoprotic acids react with equal amounts of monohydroxy bases, but the aqueous solutions formed will have different pH values depending on the strength of the acid and the base. Thus, in aqueous solutions, properties of salts, which are completely dissociated into ions, are those of their ions.

*   Strong acids (HCl, HBr, HI, HNO_3, H_2SO_4) produce neutral anions (Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-})
*   Stronger the acid, weaker the conjugate base; weaker the acid, stronger the conjugate base.
*   Strong bases (NaOH, KOH...) produce neutral cations (Na^+, K^+, ...).
*   Stronger the base, weaker the conjugate acid; weaker the base, stronger the conjugate acid.
*   Neutral ions, called spectator ions, do not affect acid-base behaviour of salts.
*   Salt formation (note: Cation of salt comes from the base, anion from the acid):
    o   Strong acid + Strong base $\rightarrow$ Salt will be neutral; pH = 7.0
    o   Weak acid + Strong base $\rightarrow$ Salt will be basic; pH > 7
    o   Strong acid + Weak base $\rightarrow$ Salt will be acidic; pH < 7
    o   For weak acid + weak base $\rightarrow$ Salt will be approximately neutral (pH $\approx$7) depending on the relative strength of the weak acid and the weak base.
*   An amphoteric substance can behave either as an acid or as a base: e.g., $Al(OH)_3$.

    As a base, it reacts with H^+: $Al(OH)_3$ (aq) + 3 H^+ (aq) $\rightarrow$ Al^{3+} (aq) + 3 H_2O (l) (note: cations come from base)

    As an acid, it reacts with OH^-: $Al(OH)_3$ (aq) + OH^- (aq) $\rightarrow$ $Al(OH)_4^-$ (aq) (note: anions come from acid)

To determine acid-base property of a salt solution:

- Identify the cation and anion present.
- Deduce whether each is acidic, basic, or neutral. (1) If both are neutral, salt is neutral; (2) if one is neutral and the other acidic, the salt is acidic; (3) if one is neutral and the other basic, the salt is basic.
- If one ion is acidic and the other basic, the salt may be approximately neutral depending on the relative strengths of the acid and the base.
-

A **buffer** is a solution that resists change in pH when a small amount of a strong acid or a strong base is added to it. A buffer consists of a weak acid and its conjugate base or a weak base and its conjugate acid in equilibrium with each other. A buffer is therefore made up of a salt of a weak acid plus the weak acid e.g. sodium ethanoate + ethanoic acid: $Na^+CH_3COO^-$ + CH_3COOH is an example of an acidic buffer. Or a salt of a weak base plus the weak base e.g., $NH_4^+Cl^-$ + NH_3 (a basic buffer). It is necessary to have both components.

(i) If now OH^- ions from a strong base are added to the buffer solution, these react with the acid of buffer; effectively, the strong base OH^- has been replaced by the weaker base, and its effect on pH minimized.

(ii) If H^+ ions from a strong acid are added to the buffer, these will react with the base of buffer; ehe strong acid H^+ has been replaced by the weaker acid and its effect on pH minimized. Thus effect of adding any strong base, OH^- or strong acid, H^+ to a buffer is minimized.

When [acid] = [conjugate base], an optimum buffer is present and has equal ability to minimize the effect of added $[H^+]$ or $[OH^-]$. Also, when [acid] = [conjugate base], then $[H^+]$ = K_a or $pH = pK_a$.

On dilution of a buffer, the ratio of [acid] to [conjugate base] does not change as the two concentrations are affected equally. Thus the pH of a buffer does not change on dilution, but the pH of a 0.10 mol dm^{-3} HCl or CH_3COOH does change on dilution, e.g., 0.10 mol dm^{-3} HCl: pH = 1.0; 0.050 mol dm^{-3} HCl: pH = 1.3.

The pH of a buffer depends on:

(a) K_a of the weak acid, and (b) The relative concentrations of acid and conjugate base.

Experimental Determination of K_a (or K_b) value for a weak acid (or a weak base):

There are two ways in which to create the condition [acid] = [conj. base]:

(1) Take equal concentration of the weak acid and conjugate base and mix these to produce the buffer.

(2) By the half-neutralisation method: e.g., dissolve a known sample of weak acid HX in a fixed volume of solution. Neutralize half the amount (in moles) of HX with a strong base. At half-neutralization, $pH = pK_a$ for an acidic buffer, and $pOH = pK_b$ for a basic buffer

Acid – Base Titrations

An indicator signals the endpoint of a titration by changing colour. End point of titration is the experimentally determined point when the same amount (in moles) of acid and base have been added. Equivalence point is the theoretical value when quantities of substances specified in a chemical equation have reacted together.
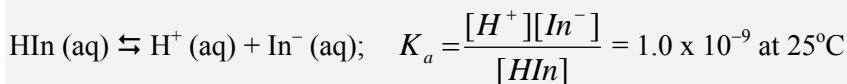
Back Titration

If an unknown base is present, to this is added a known amount of excess acid. The excess acid can be determined by titration with a standard base. Thus the amount of acid required to neutralize the unknown base and therefore, the amount of unknown base can be calculated – this procedure is called back titration.

Indicators signal the endpoint of a titration by changing colour. Indicators used in acid-base titrations are usually organic dyes and are mostly weak acids (or weak bases) where the acid and the conjugate base of the indicator are different colours. Consider phenolphthalein, HIn, as an example a weak organic acid, $K_a = 1.0 \times 10^{-9}$, in which HIn is colourless and its conjugate base, In^- is pink:

$$\text{HIn (aq)} \leftrightarrows \text{H}^+ \text{(aq)} + \text{In}^- \text{(aq)}; \quad K_a = \frac{[H^+][In^-]}{[HIn]} = 1.0 \times 10^{-9} \text{ at } 25^{\circ}\text{C}$$

An indicator changes colour over ≈ 2 pH unit range. Phenolphthalein, is colourless below pH ≈ 8, pink above 10 and end point colour change occurs at pH = 9. The end point for any indicator depends on its K_a value − the pH at the end point equals the pK_a of the indicator.

In carrying out an acid-base titration, select an indicator that changes colour at or near the equivalence point of the reaction at which equal quantities of the acid and base have been added i.e. pK_a of (weak acid) indicator should be close to pH of solution at equivalence point.
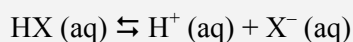
Titration curves

Acid-base Titration Summary:

(a) Strong acid + strong base: solution at equivalence point, pH = 7.0; large pH change; can use phenolphthalein (pH range 8.3 – 10); or methyl red: (4.2 – 6.3); or methyl orange (pH range: 3.1 – 4.4).

(b) Weak acid + strong base: solution at equivalence point, pH > 7; use phenolphthalein (pH range 8 – 10)

(c) Strong acid + weak base: solution at equivalence point, pH < 7; use methyl orange (pH range: 3.1 – 4.4)

(d) Weak acid + weak base: solution at equivalence point, pH about 7; gradual change in pH; no suitable color indicator; record change in pH using a pH meter and obtain point of inflection for equivalence point.

Methods of Determining K_a of a Weak Acid or a Weak Base

1. Determine pH of a solution of known concentration of the weak acid. Knowing pH, calculate $[H^+]$ = x.

$$\text{HX (aq)} \leftrightarrows \text{H}^+ \text{(aq)} + \text{X}^- \text{(aq)}$$

[initial]: 0.10	—	—
[eq.]: 0.10 – x	x	x

> Assume x is negligible; i.e., x << 0.10

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{x^2}{0.10-x} = \frac{x^2}{0.10} \text{ ; if x} = 1.0 \times 10^{-pH}, \text{ then } K_a \text{ can be calculated.}$$

2. Can obtain K_a or K_b from titration curve by the half-neutralization method:

(N.B. Shading indicates Ch 18 (AHL) material.)

Basic concepts

Oxidation: Loss of Electrons (*LEO*); Increase in oxidation number (historically: gain of O or loss of H)

Reduction: Gain of Electrons; Decrease in oxidation number (*GER*) (historically: gain of H (or loss of O)

Oxidation Number: Represents a charge on a mono-atomic ion or the apparent charge on an element if the more electronegative element is assigned the bonding electrons. Quantitatively, it reflects the oxidation state of an element; an increase in oxidation number by 1 implies a transfer of one e^-: $Na(s) \rightarrow Na^+(aq) + e^-$.

An **element** has an oxidation number = 0. For a mono-atomic ion, oxidation number of element = charge on ion. For a multi-atomic ion, sum of oxidation numbers = charge on ion. Some elements have the same oxidation number in all their compounds (e.g., Na^+). Multiple oxidation states are common for d-block elements; the oxidation number is then written in Roman numerals to indicate the oxidation state of the element, e.g.: Fe^{2+}: Fe(II); Fe^{3+}: Fe(III).

An oxidizing agent oxidizes another substance; it is reduced in the process (gains electrons); it experiences a decrease in oxidation number; thus, found in its higher/highest oxidation state: e.g.: $Cr_2O_7^{2-}$; MnO_4^-; F_2.

A reducing agent reduces another substance; it is oxidized in the process (loses electrons); it experiences an increase in oxidation number; thus found in its lower/lowest oxidation state: e.g., Na, Ti^{3+}, I^-.

Reactivity series: A list of elements in order of decreasing reducing ability: An element higher in the series displaces a lower one from its ions: $Cu(s) + 2 Ag^+(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$. For oxidizing agents, a stronger oxidizing agent displaces a weaker one from its ions: $Cl_2(g) + 2 Br^-(aq) \rightarrow Br_2(aq) + 2 Cl^-(aq)$.

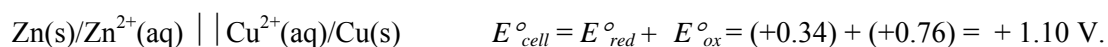**Electrodes**: conductors at which reactions occur in electrochemical and electrolytic cells.

Anode: Anions, negative ions, go to anode; electrode at which oxidation occurs (anodic oxidation).

Cathode: Cations, positive ions go to cathode; electrode at which reduction occurs (cathodic reduction).

A **cell** contains electrodes placed in an electrolyte solution; the electrodes are connected to an external circuit.

An **Electrochemical (Galvanic or Voltaic) Cell** uses a spontaneous redox reaction to convert chemical energy to electrical energy. It consists of two half-cells: Oxidation occurs at the more negative half-cell. This contains the reducing agent that is oxidized at the (−) electrode, the anode and gives up electrons to the external circuit. Reduction occurs at the more positive half-cell (and thus contains the oxidizing agent that is reduced). The salt bridge maintains electrical neutrality: anions go to the anode, cations go to the cathode. For a current to flow, a potential difference between the two half-cells must exist – this is called the cell potential or e.m.f. of the cell.

Cell Diagram: The more negative electrode is written first, to the left, followed by the more positive electrode:

$Zn(s)/Zn^{2+}(aq) \parallel Cu^{2+}(aq)/Cu(s)$ $\qquad E^{\circ}_{cell} = E^{\circ}_{red} + E^{\circ}_{ox} = (+0.34) + (+0.76) = +1.10 \text{ V}$.

Electrode potentials

The **Standard Hydrogen Electrode** (SHE) is assigned a value of 0 V under standard conditions of 25°C, solution concentrations of 1.0 mol dm^{-3} and 1 atmosphere pressure for gases. Positive $E°_{cell}$ indicates a spontaneous reaction $(-\Delta G°)$; negative $E°_{cell}$ means a non-spontaneous in the forward direction, or a spontaneous reverse reaction.

Standard electrode/reduction potential is the e.m.f. of a half-cell connected to the standard hydrogen potential (at 25°C, 1.0 mol dm^{-3} solution concentrations and gas at 1 atmosphere pressure). If reduction occurs at the standard half-cell, its sign is +; its sign is negative if reduction occurs at the standard hydrogen electrode (see Table 15).

By convention, a cell diagram is written so that the oxidation half-reaction metal/metal ions are placed first, on the left and the reduction half reaction metal ions/metal placed next on the right of the cell diagram; a "$|$" (or "/") is placed between the metal and its ions and the two aqueous solutions are then separated by a salt bridge represented by two complete or dashed lines:

Cell Diagram: $Zn(s)/Zn^{2+}(aq) \mid\mid Cu^{2+}(aq)/Cu(s)$ $E°_{cell} = +1.10V$

$E°_{cell}$ is the difference between the two standard electrode potentials. It is common to list: $E°_{cell}$ = $E°_{red\ (right\ hand\ side)} - E°_{red\ (left\ hand\ side)}$ = + 0.34 V – (– 0.76) = +1.10V**.** It is also possible to determine the cell voltage from the two half oxidation and reduction reactions by using the equation:

$$E°_{cell} = E°_{red} + E°_{ox}.$$

For the above cell, the two half reactions are:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\ e^{-}; E°_{ox} = +0.76V \text{ (note: for an electrode, } E°_{ox} = -E°_{red})$$

$$Cu^{2+}_{(aq)} + 2\ e^{-} \rightarrow Cu_{(s)}; E°_{red} = +0.34V$$
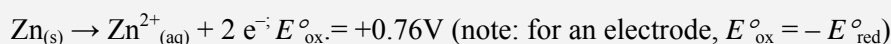
$$E°_{cell} = E°_{red} + E°_{ox}. = +0.76 + 0.34 = +1.10V$$

Electrolysis

Electrolysis involves use of electrical energy to carry out a non-spontaneous redox reaction.

The **electrolyte** contains ions that are free to move about (and carry the current: in solution, current involves the movement of charged particles). Cations go to the (–) electrode, the cathode where reduction takes place. Anions go to the (+) electrode, the anode where oxidation takes place.

Factors that affect discharge of ions in electrolysis

- Position in the electrochemical series: The lower the metal ion is in the electrochemical series, the stronger the oxidizing agent, the more readily it gains electrons (is reduced) at the cathode to form the metal: e.g.: H_2 (g) is formed at the cathode instead of Na from NaCl (aq) or NaOH (aq); however, in electrolysis of $CuSO_4$ (aq), Cu is formed, not H_2 at (–) electrode (cathode), since Cu is below H in the activity series.

- Concentration: Sometimes the rule does not match the observed result, e.g., chloride ions in aqueous solution. For dilute solutions, mainly O_2 gas is produced at the (+) electrode (anode) from the oxidation of water. For concentrated NaCl solution, mainly Cl_2 gas is produced from the oxidation of Cl^- at the (+) electrode.

- Nature of the electrode: If an inert electrode is used such as graphite or Pt, it does not take part in the reactions, e.g., in electrolysis of $CuSO_4$ (aq): H_2O is oxidized at the (+) electrode to produce O_2. But if Cu is used as the (+) electrode, the anode, it is oxidized to Cu^{2+} ions while Cu^{2+} ions are reduced to Cu at the (–) electrode and thus $[Cu^{2+}]$ remains the same.

Electrolysis uses direct current from a battery as a source of electrical energy to carry out a non-spontaneous redox reaction. The (+) and (−) terminals of the battery are connected to the electrolytic cell consisting of two electrodes, the (+) electrode, the anode and the (−) electrode, the cathode, in a solution containing cations (M^+) and anions (X^-). The battery, a source of electrons, supplies electrons to the cathode and removes them from the anode. Cations go to the (−)cathode where reduction takes place to use up the electrons coming in. Anions go to the (+) anode where oxidation occurs to supply the electrons.

Applications of Electrolysis

Many important metals e.g., Na and Al are prepared by electrolysis of their molten salts; other chemicals, e.g., NaOH are prepared by electrolysis of aqueous solutions e.g. NaCl (aq).

Electroplating is a process in which a thin layer of metal is deposited on an electrically conducting surface using electrical energy; it is an important application of electrolytic cells. In copper plating, for example, reduction occurs at (−) cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; oxidation occurs at (+) anode: $H_2O(l) \rightarrow \frac{1}{2}O_2 (g)+2H^+(aq)+2e^-$. The overall reaction: $Cu^{2+} + H_2O \rightarrow Cu + \frac{1}{2} O_2 + 2H^+$. Thus, as the reaction progresses, pH of solution and color intensity (due to Cu^{2+} (aq)) both decrease.

Factors affecting amount of product formed during electrolysis

- Charge on the ion: $Na^+ (l) + 1 e^- \rightarrow Na (l)$ compared to: $Al^{3+} (l) + 3 e^- \rightarrow Al (l)$: Thus one mole of Al requires three times the amount of electrons (and thus the charge) compared to 1 mol Na.

- Amount of electrons, i.e., the charge passed through the system: Charge (coulombs) = current (amperes) x time (seconds). More current used or charge passed for longer time periods produces more product.

(N.B. Shading indicates Ch 19 (AHL) material.)

CHAPTER 10 ORGANIC CHEMISTRY
(IB TOPICS 10 AND 20) SUMMARY

Organic chemistry is the study of carbon compounds (with some exceptions). Carbon, electronic configuration 2.4 ($1s^2 2s^2 2p^2$), is an element of Group IV/4, period 2and forms four covalent bonds by sharing electrons. C atoms combine with each other and with other nonmetal atoms and form bonds (C-C, C-H bonds) of high stability. This explains catenation, the occurrence of chains of carbon atoms to form a large number of stable compounds. Carbon also forms stable multiple bonds with itself, and with N and O atoms.

Organic compounds can be classified into families of compounds called a homologous series with the same functional groups with similar chemistry. A functional group (such as C=C alkene, -OH in alcohols, $-NH_2$ in amines, -CHO in aldehydes, -C=O carbonyl group in ketones) consists of an atom or group of atoms.

Characteristics of any homologous series:

- Molecular formula of any member differs from its predecessor by CH_2 (methylene group).

- Represented by a general formula: C_nH_{2n+2} for alkanes (if n=3, then C_3H_8).

- Similar chemical properties (due to the same functional group).

- Gradual change in the physical properties e.g., the boiling increase gradually.

Nomenclature
The modern system for naming compounds is based on the names of the alkanes, and uses the IUPAC rules (although trivial/historical names are still often used).
- Select the longest continuous carbon-chain and name it according to the parent alkane, alkene or alkyne.
- Any group that is not a part of the longest continuous chain becomes a branch or substituent in the chain. The C atoms on the longest chain are numbered in order to identify the branches. The end of the chain from which the numbering starts is chosen so as to give the branches the lowest numbers
- Branches are located by the number of the C atom on the chain
- If two or more of the same branch are present, use *di* for two, *tri* for three etc. in the naming If several different branches are present, these are written in alphabetical order (ethyl before methyl), and the name is written as one word with commas between numbers and a dash between a number and the name, eg: 1,1-dichloro-2-iodoethane.

Isomers: Isomers are different compounds with the same molecular formula (having different physical and/or chemical properties; at least one property must be different). Structural isomers: Same molecular formula but different structural formula. Chain isomers differ in the carbon chain, e.g.: butane and 2-methylpropane. Position isomers have the same functional group but in a different position on the carbon chain, e.g.: propan-1-ol and propan-2-ol. Functional group isomers contain different functional groups, e.g.: propanal and propanone.

Stereoisomerism

Geometric Isomerism: Requires (i) no rotation around at least one bond and (ii) 2 bulky groups. Gives rise to cis and trans isomers, e.g.: trans-1,2-dichloroethene (non-polar) and cis-1,2-dichloroethene (polar). Similarly, trans-1,3-dichlorocyclobutane (non-polar) and cis-1,3-dichlorocyclobutane (polar).

Optical Isomers: Non-superimposable mirror images called enantiomers that rotate the plane of polarized light in opposite directions, i.e., differ in their optical activity, the ability to rotate the plane of polarized light. An asymmetric molecule (C atom with 4 different groups represented as C*) containing a chiral center has optical isomers. Living systems have a strong preference for one form of the optical isomers, e.g., L-aspartame is sweet (Nutrasweet) but the D-enantiomer is bitter. All amino acids, except aminoethanoic acid can show optical activity, e.g., 2-aminopropanoic acid.

- Plane polarized light is light vibrating in only one plane.

- An optically active compound is one that is capable of rotating plane-polarized light.

- An asymmetric molecule containing a chiral center can exist as two different isomers, called enantiomers, that are non-superimposable mirror images, and exhibit optical activity.

- A carbon atom with four different groups rotates the plane of polarized light; thus such molecules are chiral (asymmetric), and the carbon atom is identified as C^*. The molecule is asymmetric because of tetrahedral geometry around the carbon atom.

- The rotation by a pair of enantiomers is equal but of opposite sign.

- An equi-molar (meaning same concentration) mixture of a pair of enantiomers is optically inactive (does not rotate plane of polarised light) and is called a racemic mixture.

- Physical properties of enantiomers are identical except rotation of plane polarized light.

- Chemical properties of enantiomers are identical with non-optically active compounds.

Combustion of Hydrocarbons: In the presence of oxygen, hydrocarbons are oxidized when the necessary activation energy, E_a is supplied; that is, when hydrocarbons are ignited, combustion takes place. In the presence of excess O_2, the combustion tends to be complete, producing CO_2 (g) and H_2O (l) – combustion reactions are exothermic. CO_2 is a greenhouse gas that absorbs infrared radiation reflected from the Earth's surface and causes global warming. Incomplete combustion in the presence of O_2 as a limiting reagent leads to the formation of poisonous carbon monoxide, CO as well as carbon, C (soot particles). CO is an odorless gas that readily reacts with the red pigment, hemoglobin, in the blood to form carboxyhemoglobin, a stable complex.

Reactivity of alkenes: Alkenes are **more** reactive than alkanes. Alkenes contain a **double** bond consisting of a strong σ bond and a weaker π bond that is broken; this requires energy. However **two** strong σ bonds are formed in its place releasing energy; hence alkenes are energetically unstable with respect to their products in addition reactions (or products are more stable). A double bond has a much higher e^- density (serves as a source of electrons), attracting **e^- deficient groups** called **electrophiles** in addition reactions. The excess e^- density in alkenes (and alkynes) implies **nucleophilic** behavior.

Typical Reactions of Alkenes: Addition

Characterized by addition reactions in which the C=C double bond is converted into a single bond and atoms (or groups of atoms) are **added** to **each** of the 2 carbon atoms across the double bond.

$$CH_2=CH_2 + X—Y \rightarrow CH_2X—CH_2Y.$$
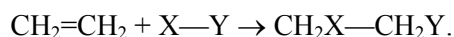
1. With $H_{2\,(g)}$ passed over nickel as catalyst at 150°C: **Hydrogenation:**

$$CH_2=CH_2 + H_2 \xrightarrow{Ni(s);150C} CH_3\text{-}CH_3 \;(C_2H_6\text{: ethane produced})$$

2. With Cl_2 and Br_2, reaction can take place in the dark; no u.v. light, heat or catalyst is required:

$$CH_2=CH_2 + Br_2 \rightarrow CH_2Br—CH_2Br; \text{ 1,2-dibromoethane (\textbf{not} 1,1-dibromoethane)}$$
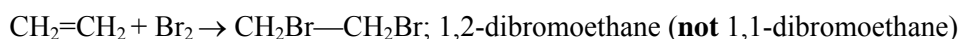
S_N2 mechanism is for primary halides – a one step mechanism: nucleophile approaches from side opposite to X (inversion of configuration takes place); two species involved in slow step $\therefore$ bimolecular. The predominant mechanism for tertiary halogenoalkanes is S_N1 and for primary halogenoalkanes is S_N2. Both mechanisms occur for secondary halogenoalkanes. Regardless of the mechanism, the overall change in all nucleophilic substitution reactions is that the nucleophile, the attacking group reacts with the alkyl halide, R–X and substitutes for the halide ion, X^-, the leaving group: $Nu^- + R–X \rightarrow R–Nu + X^-$.

Regardless of the mechanism, the overall change in all nucleophilic substitution reactions is that the nucleophile, the attacking group reacts with the alkyl halide, R–X and substitutes for the halide ion, $\tilde{X}$, the leaving group: $N\tilde{u} + R–X \quad R–Nu + \tilde{X}$.

Effect of Attacking Nucleophiles and Different Leaving Halides on Nucleophilic Substitution Mechanism:

1. The Nucleophile: For S_N1 reactions, rates depend only on the concentration of the tertiary halide, and not on the nucleophile (unimolecular). Thus changing the nucleophilic agent will not change the rate of an S_N1 reaction as it is not involved in the slow, rate determining step. However, for an S_N2 mechanism where rate = k [R–X]1[Nu–]1, the more strongly nucleophilic the reagent, the faster the rate of reaction. Thus, the strong base OH– is a more strongly nucleophilic agent than H2O (polarity difference) and undergoes a faster rate of substitution in the S_N2 mechanism.

2. The Halogen: In both S_N1 and S_N2 mechanisms, the weaker the C-halide (C-X) bond, the faster the reaction, since the leaving group will break off more easily. Thus for the C-X bonds, the rate of reaction is: C–I > C–Br > C–Cl > C–F, because as the size increases down the halogen group, the bonding electrons in C–I are the furthest apart. It is therefore the longest and weakest bond whereas C–F would be the shortest and strongest bond. Thus the halide leaves the fastest in the order $I^- > Br^- > Cl^- > F^-$ and the rate of reactivity decreases from alkyl iodide to alkyl fluoride.

3. Nature of the halogenoalkane Influences Rate of Reactivity:

    (i) Tertiary > secondary > primary. This is because a tertiary carbocation is more stable than a secondary which is more stable than a primary carbocation.

    (ii) $S_N1 > S_N2$: This is because S_N1 mechanism involves tertiary halides and the spontaneous formation of the tertiary carbocation, whereas S_N2 mechanism involves a transition state of relatively high activation energy, *E*a.

N.B. Aromatic halides are much less reactive than the halogenoalkanes. The lone electron pair on the halogen atom delocalizes with the π electron cloud of the benzene ring. Thus the C–X has greater electron density, is stronger and more difficult to break. Also, the electron rich aromatic ring repels a nucleophile (also electron rich).

(N.B. Shading indicates Ch 20 (AHL) material.)

Uncertainties and errors

Random uncertainties (or errors) arise mostly from inadequacy or limitation in the instrument or the way a measurement is made. Random errors make a measurement less precise, but not in any particular direction. These are written as an uncertainty range, such as 44.20 ± 0.05 cm^3.

Systematic errors are due to identifiable causes, and arise from flow in the instrument or errors made in taking a measurement such as an incorrect calibration of a pH meter or reading the top rather than the bottom of the meniscus. Systematic errors always affect a result in a particular direction (always smaller or larger) unlike random errors. Random uncertainties can be reduced by repeating readings; systematic errors can not reduced by repeating readings.

Precision

If an experiment is repeated many times, the precision is a measure of how close the repetitions will be to each other. 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.

Accuracy

The accuracy of a result is a measure of how close the result is to some accepted or literature value Accuracy is a measure of the systematic error. If an experiment is accurate then the systematic error is very small.

A measurement can have a great degree of precision, yet be inaccurate such as if the top of a meniscus is read in volume readings using a pipette or a measuring cylinder instead of he bottom of the meniscus.

Significant figures

The number of significant figures in any calculation should be based on the number of decimal places/significant figures in the data based on the following simple treatment:

- In addition and subtraction: Add absolute uncertainties

- In multiplication, division and powers: Add percentage uncertainties

- If one uncertainty is much larger than the others, ignore the other uncertainties and estimate the uncertainty based on the larger one using the rules above.

CHAPTER 12 MODERN ANALYTICAL CHEMISTRY
(IB OPTION A) SUMMARY

Analytical chemistry involves qualitative and quantitative analysis of a sample to determine its chemical composition and structure and to determine purity. Analytical methods are usually faster, more precise and easier to automate than 'wet' methods, and a combination of analytical techniques is often used to obtain complete structural information.

Spectroscopy

Many analytical techniques involve spectroscopy - the way in which the absorption or emission of electromagnetic radiation by substances varies with frequency involving radiation such as UV, IR and microwave.

The energy of a quantum of radiation is directly proportional to its frequency and the energy is inversely proportional to its wavelength. Thus high frequency (and hence short wavelength) radiation carry a great deal of energy and those of low frequency radiation carry much less.

A particle (atom, molecule or ion) can absorb a quantum of light and this will affect its state depending on the amount of energy that the quantum carries: γ-rays can bring about changes in the nucleus.

X-rays cannot cause changes in the nucleus, but have enough energy to remove electrons in inner filled shells of atoms. Ultraviolet and visible light have enough energy to affect the valence electrons. UV radiation causes sunburn with too much exposure to sunlight. Microwaves affect the rotational state of molecules. Radio waves can alter the spin state of some nuclei when they are exposed to magnetic fields and are used in NMR spectroscopy.

In emission spectroscopy the frequency of the radiation emitted by excited particles dropping to a lower energy state is studied. In absorption spectroscopy radiation of a wide range of frequencies is passed through the sample and the way in which the absorption of radiation varies with its frequency is studied. Energy of particular frequencies is absorbed and used to enable a particle to move from a lower to a higher energy state.

A double-beam **spectrometer** allows radiation from a source that is split into two equal beams, one passed through the sample and the other through a reference containing the same solvent but without the substance being studied. The two beams are then recombined at the detector. The signals from the sample and reference beams are then compared electronically to see if the sample absorbs radiation of any frequency. As the spectrum of the sample is scanned, the frequency of the radiation is varied and a graph of absorption against frequency, wavelength or wavenumber is drawn. Comparison of the spectrum of the unknown compound with a data bank enables its identification.

IR: A quantum of infrared radiation has sufficient energy to excite a molecule to a higher vibrational level. In order to absorb infrared light a vibrational motion must result in a change in the dipole moment of the molecule. The information from an IR spectrum can be used to identify bonds present, but not always the functional groups present.

In a **mass spectrometer**, fragmentation of a molecule occurs at the weakest bonds and where branches occur. For a molecule, a plot of relative intensities of signals of various *m/z* values from the fragmentation pattern is called a mass spectrum and is highly characteristic of a particular compound, like its fingerprint. Mass spectra are used to prove the identity of a compound and to help establish its structure. Some simple fragments detected in a mass spectrometer include: $(M_r - 15)^+$ loss of CH_3, $(M_r - 17)^+$ loss of OH, $(M_r - 18)^+$ loss of H_2O, $(M_r - 29)^+$ loss of C_2H_5 or CHO, $(M_r - 31)^+$ loss of CH_3O, $(M_r - 45)^+$ loss of COOH.

NMR is an extremely diagnostic tool for the determination of structure as an NMR spectrum provides information of the chemical environment of the protons in a molecule. Electrons in a magnetic field orbit in such a way as to set up a magnetic field that opposes the applied field. Thus the magnetic field experienced by the nucleus, and hence the precise frequency at which it absorbs radiation, depends on the electron density near to the nucleus and therefore on the chemical environment of the nucleus.

CHAPTER 12 MODERN ANALYTICAL CHEMISTRY
(IB OPTION A) SUMMARY

The body scanner operates on the principle of NMR spectroscopy. The main constituents of the body that contain hydrogen atoms, and hence produce signals, are water and lipids. Different parts of the body have different water-lipid ratios in the tissue and therefore absorb radio frequency radiation in different ways. The patient is placed in a strong magnetic field and as the scanner is moved around the body, data about the absorption at various angles can be accumulated to allow a three-dimensional image of the various organs in the body to be built up. The advantage of this technique called Magnetic Resonance Imaging (MRI) in body scanning is obvious as radio waves are harmless. MRI is used to diagnose cancer, Multiple Sclerosis (MS) and other conditions.

Tetramethylsilane (TMS), $(CH3)_4Si$ is used as a reference in NMR spectroscopy and all absorptions measured against it. TMS has the advantage of being chemically inert, producing a single strong signal, as it has 12 hydrogens in identical chemical environments, it absorbs radiation at lower frequency and different from most organic compounds, so it does not interfere with other absorption signals. Also, it has a low boiling point and the pure compound can be obtained by easy removal of TMS.

Interpretation of an NMR spectrum involves:

- Number of peaks: Since each peak represents hydrogen atoms in the same chemical environment, then the number of peaks gives the number of different chemical environments hydrogen atoms are present in.

- chemical shift: TMS is used as a reference at $\delta = 0$ ppm. Different chemical environments produce different chemical shifts that can be identified using a data of chemical shifts (such as the IB Data Booklet).

- Area under each peak is proportional to the number of hydrogen atoms present in that particular chemical environment.

- Spin-spin splitting takes place since the spins of adjacent protons interact with each other; the splitting pattern depends on the number of protons it interacts with. Splitting patterns in high resolution spectra provide (n+1) peaks if there are n number of adjacent hydrogen atoms in the same chemical environment.

Atomic spectroscopy is mainly used for the determination of trace metals in organic and inorganic samples such as aluminum in blood serum, calcium in blood serum, plants, soil samples, in water (for water hardness), mercury and lead in food samples amongst others.

The non-excited vaporized metal atoms absorb its characteristic radiation from an external source and become excited, that is, it causes transition from the ground state to the excited state. Each metal absorbs light of characteristic wavelength or frequency. The ratio of the intensity of the transmitted light to that of the incident light energy is proportional to the concentration of the metal atoms present and excited. Thus, a calibration curve can be obtained by using standard solutions of known concentrations. The concentration of the unknown can then be determined from the calibration curve

The components of **AA spectrophotometer** consist of a monochromatic light source of the same wavelength as that absorbed by the metal being detected. The application of high voltage across the electrodes excites the atoms on the cathode producing a constant, intense light source characteristic of the metal. The light source is focused into the flame in an atomizer unit. A flame or graphite furnace is used to atomize the sample into gaseous metal atoms. This involves three steps: desolvation (removing the solvent), vaporization of the solid sample to a gas and dissociation of the compound to free atoms (atomization). The choice of fuels includes the gases ethyne (acetylene, C_2H_2), hydrogen (H_2) and propane (C_3H_8) all of which are explosive.

The monochromatic light detector is set to the specific wavelength characteristic of the metal atoms being detected. Once the sample is introduced in the flame, it absorbs some of the monochromatic light from the hollow cathode lamp. There is a decrease in the intensity due to the atomic absorption which depends on the concentration of the metal atoms present. The monochromatic detector signal appears as the absorption in a computer read-out.

Chromatography

Chromatography is a method of analysis that is used for the separation of components of a mixture (for example the separation of chlorophylls in plant extracts), as well as qualitative analysis, that is identification of components present (such as the detection of amino acids in a mixture) and quantitative analysis, that is how much of a component is present (such as detection of levels of alcohol in blood).

Chromatography operates on the principle of partition or adsorption. Partition involves the way in which components of a mixture distribute themselves between two immiscible liquid phases, depending on their solubility in each phase.

- **Adsorption** involves the way a substance bonds to the surface of a solid stationary phase, made of polar solid. Thus, solubility of a component in the liquid phase and how strongly it is adsorbed to the solid stationary phase determines the rate at which it elutes. Depending on the polarity of the components, different strength of interaction will take place between each component in the mixture and the polar solid stationary phase. Thus, the more polar a component, stronger the interaction to the solid phase, slower the rate of elution. The greater the solubility in the mobile phase, the faster the rate of elution. The difference lies only in the nature of the two phases and hence the type of bonding that operates between the components of the mixture and these phases. Adsorption is the case in Column chromatography, High Performance Liquid Chromatography (HPLC) and sometimes TLC.

- In **paper** chromatography, water bonded to the cellulose in paper is the stationary phase and the organic liquid moving past it is the mobile phase. A spot of the mixture is applied to absorbent paper, rather like filter paper. The end of this is then dipped in the solvent used to 'develop' the chromatogram. The solvent soaks through the paper by capillary action, moving past the spot where the mixture was applied and onwards. The components that bond strongly to the solvent will be carried along in the direction that the solvent is moving, whereas those that do not bond to it will remain almost stationary. R_f is the ratio of the distance traveled by the component to the distance traveled by the solvent.

- **Thin layer** chromatography (TLC) is very similar to paper chromatography and the physical arrangement being almost identical. The difference is that the stationary phase is a thin layer, usually of silica (silicon dioxide, SiO_2) or alumina (aluminum oxide, Al_2O_3) on a glass or plastic support. When dry, the separation of the components depends on the extent to which the components bond to the surface, i.e. are adsorbed by the stationary layer of silica or alumina, which in turn mainly depends on the polarity of the substance. SiO_2 and Al_2O_3 both contain highly polar oxygen atom and thus have a high attraction for polar water. Thus in the presence of water, it becomes the stationary phase adsorbed to the silica or alumina and separation takes place more by partition. Because the particles in TLC are much finer than the pores in paper it usually gives better and faster separation and works with fairly small samples.

- The principle of **column** chromatography is very similar to adsorption in thin layer chromatography, as the stationary phase is usually silica or alumina and separation depends on whether a component is strongly adsorbed onto the surface of this or remains dissolved in the mobile solvent phase used to elute the column. The oxide powder is packed into a column with the solvent and the mixture applied at the top of the packing. The solvent is allowed to slowly drip out of the bottom of the column, controlled by a tap, and fresh solvent added at the top so that the packing never becomes dry. As the mixture moves down it separates out into its components. If the components are colorless, then separate fractions of the solution leaving the column in liquid chromatography must be collected and tested for the presence of the components of the mixture.

Where the mobile phase is an inert gas, the rate at which the components move through the liquid phase is dependent on its volatility, for example in Gas Liquid Chromatography (GLC). Thus, when components are being partitioned between two phases, the more volatile a component in the mobile phase, the faster it will be carried. In GLC the mobile phase is a gas and the stationary phase is packed into a very long (often a number of metres) thin column, that is coiled into a helix packed with an oxide (usually SiO_2 or Al_2O_3), or more frequently (in HRGC, high resolution gas chromatography) a very thin column is coated on the inside with an oxide layer in which separation occurs because molecules of the mixture are adsorbed onto the surface of the oxide. Sometimes, the oxide acts as a support for a high boiling point oil or wax. In this case separation depends on the partition of the components between the gas phase and solution in the oil.

In GLC, the mixture is injected into a steady gas flow at the start of the column and it vaporizes at the temperature used. The column is housed in an oven which controls the rate at which the sample passes through the column. The components of the mixture are detected as they reach the end of the column, either by the effect they have on the thermal conductivity of the gas, or by the current that results from the ions formed when they are burnt in a flame. The results are shown as a graph of the detector signal against the time, the retention time, since the mixture was injected into the gas flow and the area under the peak is proportional to the amount of the component in the mixture. GLC is used to identify components that can vaporize without decomposition such as analysis of vegetable oil mixtures, analysis of gas mixtures from underground mines or from petrochemicals, analysis of components of fruit odors, detection of drugs in urine samples from athletes, detection of steroids, and blood alcohol levels.

Gas Chromatography-Mass Spectrometry, GC-MS is a powerful technique that involves coupling the output of the gas chromatography column to the input of the mass spectrometer that identifies each component as it elutes by means of its mass spectrum. This is particularly useful in food and drug testing as well as in forensic science.

The principle of High Performance Liquid Chromatography (HPLC) is similar to gas chromatography except that the mobile phase is a liquid, forced under high pressure (up to 10^7 Pa) through a rather shorter column (usually $10 - 30$ centimetres long), rather than a gas. Its advantage over gas chromatography lies in the fact that it can be used for non-volatile and ionic substances. One of the major weaknesses of this technique is that the detector systems are less sensitive than those usually used in gas chromatography.

For a volatile sample, generally gas chromatography on a suitable column will offer the best solution. For a non-volatile sample HPLC will often provide the solution. Column chromatography is most suitable for preparative purposes, whilst paper and thin layer techniques involve the minimum amount of apparatus, if all that is required is a simple qualitative check.

The energy carried by a quantum of light in the UV and visible regions of the spectrum corresponds to the difference in energy between filled and unfilled electron orbitals in many ions and molecules. In solution, the ions of many metals are colorless. In some such ions (for example, sodium ions) the difference in energy between the highest filled orbital and the lowest unfilled orbital is quite large and so they only absorb very short wavelength UV light. In the transition metals, the difference in energy between filled and unfilled split d-orbitals is much smaller so that these ions in solution absorb energy in the far UV and visible regions, the latter being responsible for the fact that many of these ions are colored, and are of different colors. The color of these ions is the complementary color of the colors absorbed. UV-visible spectroscopy is used in assaying of metal ions, organic structure determination and detection of drug metabolites.

Orbitals in a sub-level are all at the same energy. However, in the presence of ligands, Lewis bases with lone electron pair(s), the d orbitals are split into two sets at different energy levels.

The difference in energy, ΔE corresponds to wavelength in the visible light. The transitions between split d orbitals are only possible if there are partially filled d orbitals containing 1 to 9 electrons. The number of d electrons present, the oxidation number of the metal, the different ligands and the transition metal present produce different degrees of splitting, giving rise to different colors.

In the same way that atoms and ions have atomic orbitals, molecules have molecular orbitals, some of which are filled, others are unfilled. In molecules, such as water, and in simple ions, the difference in energy between the highest filled orbital and the lowest unfilled orbital is quite large, they only absorb very short wavelength UV light and the solution appears colorless.

Carotene which has extensive conjugation and is an orange color because it absorbs blue and green light.

Completely saturated compounds show no absorption in the visible and the far UV region. A double-bonded compound absorbs in the far UV region. Presence of two or more chromophores, unsaturated organic groups that absorb radiation mostly in the UV and visible regions specially if conjugated, lower the energy difference between orbitals and increases the wavelength of radiation absorbed. When there is an extended system of delocalised bonds and conjugated double bonds the absorption moves into the visible region to produce a colored compound such as carotene which is an orange because it absorbs blue and green light.

The amount of light of a particular frequency which a solution absorbs depends on the nature of the compound which determines the molar extinction (or absorption) coefficient, ε; (units of ε: $dm^3\ mol^{-1}\ cm^{-1}$.), its concentration (c in $mol\ dm^{-3}$) and the distance the light passes through the solution (l, in cm). $A = \varepsilon cl$. This is known as the Beer-Lambert law, and A (which is unit-less) is the absorbance of the solution, the reading given directly by most UV/visible spectrophotometers.

Iron content in blood serum and the copper content of bronze (by converting Cu to Cu^{2+}) can be determined using a standardization or calibration curve.

(Shaded areas indicate AHL material)

The energy value of a food can be calculated by carrying out a calorimetric experiment involving combustion of a known mass of the foodstuff and then applying the formula $\Delta H = m \times c \times \Delta T$.

Proteins

Proteins comprise long chains of 2-amino-acids joined to each other through peptide (-NH-CO-) linkages. 2-amino acids have the general formula, where the side-chain (Q) varies between amino acids.

Because of their ability to hydrogen bond amino acids are water soluble. They have both acid and base groups so in neutral solution these groups exchange a hydrogen ion so the amino acid exists as a "zwitterion" ($^{+}H_3N$-CH(Q)-CO-O^{-}). This has two opposite charges so is electronically neutral, but if the solution becomes more acidic the carboxylate group becomes protonated ($^{+}H_3N$-CH(Q)-CO-OH) so it becomes positively charged; similarly in alkaline solution the amino group will lose a hydrogen ion (H_2N-CH(Q)-CO-O^{-}) so it becomes negatively charged. The exact pH at which this occurs varies from acid to acid and the pH at which there is no net charge is known as the "isoelectronic point" of the acid. Because of these acid-base reactions, solutions of amino acids act as buffers, that is they keep a fairly constant pH when small amount of strong acid or alkali are added.

Amino acids can join together to form proteins and polyeptide, (similar to proteins but shorter). The reaction is a condensation reaction.

Note that there are two possible products depending on the order of the amino acids. If there were 3 different amino acids there would be 6 possible combinations.

The structure of proteins is vital to their correct functioning. There are four levels of structure:

- Primary structure – the order of the amino acids in the protein chain

- Secondary structure – the initial folding of the structure into hydrogen bonded α-helix or β-pleated sheet conformations.

- Tertiary structure – the folding of the secondary structure, generally dictated by the hydrophobic/hydrophilic nature of the side chain and S-S bridges.

- Quaternary structure – the grouping together of a number of protein chains to give the protein

The amino acids present in a protein can be deduced by hydrolysing the protein (enzymes or 6M HCl) and then carrying out chromatography (perhaps two-dimensional) and electrophoresis (at different pHs) to identify the amino acids present. Usually this is done by comparison with the behaviour of known samples under identical conditions.

Proteins play many roles in living organisms:

- Structural – collagen

- Enzymes – for example amylases which break down starch.

- Hormones – insulin

- Immunoproteins – forming antibodies

- Transport – for example haemoglobin in carrying oxygen

- Energy – in starvation conditions protein can be used for energy rather than carbohydrates or fats

Carbohydrates

The major function of carbohydrates in humans is as an energy source, though they can also store energy and act as precursors for biologically active molecules, such as nucleic acids.

The simplest carbohydrates are the monosaccharides, which have the formula $(CH_2O)_n$ and contain, in the case of reducing sugars (like glucose) a aldehyde group, and in the case of non-reducing sugars (like fructose) a ketone group.

Those that have five (pentoses, like ribose) or six (hexoses, like glucose and fructose) carbon atoms can form a ring structure that results from a hydroxyl group further down the chain bonding to the carbon of the carbonyl group. Two forms (α- and β-) are possible depending on which side of the carbonyl group the oxygen of the hydroxide joins on (see text).

Monosaccharides in their ring form, can join together by condensation reactions to form disaccharides (containing two sugars; like lactose, maltose and sucrose) and polysaccharides (containing many sugars; like starch, glycogen and cellulose).

Starch and cellulose are both formed from glucose. Starch, which has two forms, one comprising relatively short straight chains (amylose) and a second (amylopectin) which has a much higher molar mass and branched chains, has α-linkages between the glucose rings whereas cellulose has β-linkages.

Humans, like most mammals, cannot digest cellulose, nevertheless this and other indigestible plant matter (known as dietary fibre) is a vital component of our diet because it prevents many problems of the digestive system, such as diverticulosis and Crohn's disease.

Lipids

There are three types of lipids found in the human body; triglycerides (such as fats and oils), phospholipids (like lecithin) and steroids (for example cholesterol).

The major functions of lipids in the include:

- energy storage
- insulation and protection of organs
- acting as precursors of steroid hormones
- forming structural components of cell membrane
- omega-3 poly-unsaturated fatty acids reduce the risk of heart disease
- poly-unsaturated fats may lower levels of LDL cholesterol.

Lipids are the most concentrated type of energy storage because, unlike carbohydrates, they contain no oxygen hence they can undergo greater oxidation.

Lipids, if eaten to excess, have negative health effects through causing obesity and increasing the risk of cardiovascular disease (especially saturated fats and trans-fatty acids), though a few (especially polyunsaturated and omega-3 ones) have beneficial effects.

Cholesterol occurs in two different forms in the human body; HDL (high-density lipoprotein) which has only about 50% cholesterol and hence removes cholesterol from the walls of blood vessels, has a positive effect on cardiovascular health, and LDL (low-density lipoprotein) which contains over 70% cholesterol and deposits cholesterol on the walls of blood vessels, narrowing them and having a negative effect on cardiovascular health,

Triglycerides are esters of glycerol and long chain fatty acids.

The chains of the fatty acids can be either saturated (no double bonds), mono-unsaturated (one double bond) or poly-unsaturated (more than one double bond). This reaction is reversed when triglycerides are digested, a reaction which is catalysed by the enzyme lipase

The number of double bonds can be found by reacting the triglyceride with iodine (which adds to the double bonds). The "iodine number" is the number of grams of iodine that adds to 100 g of the triglyceride; the greater the iodine number, the more unsaturated, as the number of moles of iodine molecules reacting with one mole of the triglyceride will equal the number of C=C bonds present.

Essential fatty acids are those that the body cannot synthesise and therefore are essential components of our diet. Two important examples are linoleic acid (an omega-6 fatty acid) and linolenic (an omega-3 fatty acid). Both contain 18-carbon atoms, but linoleic acid contains two C=C double bonds with the first 6 carbon atoms away from the end (omega) carbon of the chain, whereas linolenic acid contains three C=C double bonds with the closest 3 carbon atoms away from the end carbon. Omega-3 acids are particularly important in brain development.

Nutrients

The food we eat can be divided into macronutrients (needed in relatively large quantities – proteins, carbohydrates, fats and mineral salts) and micronutrients (necessary but only in small quantities – vitamins, essential oils and many trace elements such as Fe, Cu, Co, Zn etc.).

Shortage of particular nutrients can lead to specific diseases:

- protein—marasmus and kwashiorkor
- iron—anemia
- iodine—goitre
- retinol (vitamin A)—xerophthalmia (night blindness)
- niacin (vitamin B3)—pellagra
- thiamin (vitamin B1)—beriberi
- ascorbic acid (vitamin C)—scurvy
- calciferol (vitamin D)—rickets.

Action that can be taken to combat such deficiency diseases include:

- providing food rations that are composed of fresh and vitamin- and mineral-rich foods
- adding nutrients missing in commonly consumed foods
- genetic modification of food
- providing nutritional supplements
- providing selenium supplements to people eating foods grown in selenium-poor soil.

Some **vitamins** are fat soluble (A, D, E & K) and others water soluble (notably B & C). This is because of their molecular structure; the water soluble ones have a number of hydroxyl groups allowing them to hydrogen bond to water.

Hormones, such as (ADH, aldosterone, estrogen, progesterone, testosterone, insulin, adrenaline and thyroxine) are chemical messengers secreted directly into the blood by endocrine glands.

Many hormones are steroids and have a similar carbon structure to cholesterol, but with different functional groups attached to it.

The oral contraceptive is based on hormones such as estrogen and progesterone, which mimic changes that occur normally in pregnancy to prevent ovulation.

Anabolic steroids are related to testosterone and can lead to an increase in muscle bulk, hence many athletes are tempted to use these illegally in spite of many negative side effects, such as aggressive behaviour, impotence and increased risk of cardiovascular problems.

Enzymes

Enzymes are biological catalysts that are involved in almost all biochemical processes. They are generally proteins and compared to inorganic catalysts they are:

- far more effective
- much more specific
- easily "denatured" (made ineffective) by changes of temperature, pH etc

Denaturing occurs because the shape of the protein has been altered by changes in the tertiary, and sometimes the secondary, structure of the protein. Such changes can be brought about by heating the enzyme (causing hydrogen-bonds to break), altering the pH (and hence the charges on acidic and basic side chains), or adding heavy metal ions (which form complex ions with groups on the protein).

Catalysts provide an active site that the substrate bonds to (lock and key model). Whilst bonded the substrate is changed and then released free up the enzyme to bond to more substrate molecules.

The shape of the active site is very specific to the substrate, so that reactions of even very closely related molecules are unaffected. For example urease will catalyse the hydrolysis of urea, but not other amides,

At low substrate concentrations the reaction rate is proportional to [substrate] because the formation of the enzyme-substrate complex is rate determining, but at high substrate concentration the rate will tend to a limiting value, independent of [substrate] because the change occurring to the substrate become rate determining.
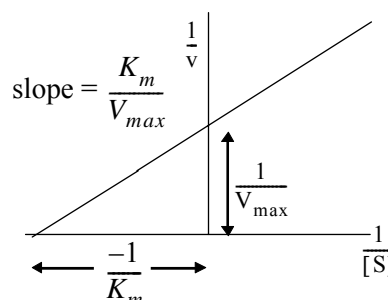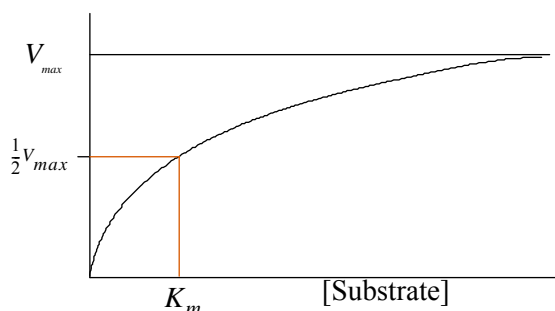
If the rate constant for formation of the enzyme-substrate complex is k_1, the rate constant for it splitting up to reform the enzyme and substrate is k_2 and the rate at which it is converted to the products is k_3, then it can be shown that the maximum rate (V_{max}) is related to the substrate concentration, [S], by the Michaelis-Menten equation:

$$\text{rate} = v = \frac{V_{max}[S]}{K_m + [S]}$$ where the Michaelis constant, $K_m = \frac{k_2 + k_3}{k_1}$

Km is equal to the substrate concentration required to give a rate equal to half the maximum rate and it will vary with temperature and pH, but not concentration. The equation above can be rearranged to give a linear function:

$$\frac{1}{\text{Rate}} = \left[\frac{K_m}{V_{max}} \times \frac{1}{[S]} \right] + \frac{1}{V_{max}}$$

From which the Michaelis constant and the maximum rate (V_{max}) may be found by plotting $^1/_{Rate}$ against $^1/_{[S]}$ (see plot above).

Enzyme activity can be inhibited (made less effective). There are two types of inhibition, competitive and non-competitive. In competitive inhibition the inhibitor can bond to the active site and hence competes with the substrate, so that the a larger concentration of substrate is required to reach the maximum rate (V_{max}), which is however unchanged. A non-competitive inhibitor will bond to some other part of the enzyme with the effect of reducing its activity. In this case the maximum rate (V_{max}) is reduced.

Nucleic Acids

Nucleic acids are polymers made up of nucleotides, joined by a covalent bond between the phosphate of one nucleotide and the sugar of the next. A nucleotide contains a phosphate group, a pentose sugar and a side chain of one of five organic nitrogenous bases {adenine (A), cytosine (C), guanine (G), thymine (T) and uracil (U)} attached to the sugar of the phosphate-sugar backbone.

DNA (deoxyribonucleic acid) differs from RNA (ribonucleic acid) in three important ways:

- DNA contains deoxyribose, containing one less –OH group than the ribose found in RNA

- DNA has the base thymine, whereas RNA has uracil, the other bases are found in both

- DNA exists as a double strand, joined by the bases, whereas RNA has a single strand

DNA comprises two strands of the deoxyribose-phosphate backbone joined by hydrogen bonds between the bases attached to the backbone.

Because of their shapes each base can only effectively hydrogen bond to one of the other bases, hence thymine will always bond to adenine and guanine to cytosine, known as complementary base pairs. This means that one strand is a "negative image" of the other.

When DNA replicates the two strands untwist and bond on to the complementary nucleotides. That means that where there is a cytosine on the chain, a guanine will attach itself. These new nucleotides then polymerise so that the final result are two double helices, identical to the originals.

The order of the bases on the DNA, present in the nucleus of all cells, acts as a code to provide the instructions about how to construct a new organism. For example to synthesise a particular protein the code on the DNA is transcribed in forming a molecule of messenger RNA (mRNA) with the complementary code. This code is then translated during protein synthesis to give the correct protein primary structure. A particular group of three bases corresponds to a particular amino-acid (the triplet code, or codon). For example the triplet G-C-U corresponds to alanine.

Because DNA contains the instructions for making a particular organism and all human beings are unique, each of us has slightly different DNA. This means that the DNA from samples of cells can be identified as belonging to a particular individual and it will be closely related to the DNA of blood relatives. This has many uses, for example in forensics and in establishing paternity.

Respiration

Cellular respiration, which entails the exothermic oxidation of glucose, normally takes place under either aerobic conditions, though it can also occur under anaerobic conditions. In both glucose is initially converted into the pyruvate ion, in the presence of nicotinamide adenine dinucleotide (NAD^+), which is reduced in the first stage and then oxidised in the second:

$$C_6H_{12}O_6 + 2\ NAD^+ \rightarrow 2\ C_3H_3O_3^- + 2\ NADH + 4\ H^+ + energy$$
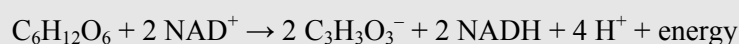
In the presence of oxygen (aerobic respiration), this changes to carbon dioxide and water.

$$2CH_3COCOO^- + 2NADH + 4H^+ + 6O_2 \rightarrow 6CO_2 + 6H_2O + 2NAD^+$$
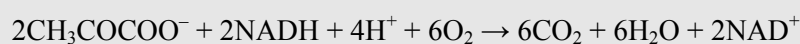
In anaerobic respiration, the pyruvate is converted to lactate in human beings (though in yeast it is converted to ethanol and carbon dioxide):

$$CH_3COCOO^- + NADH + H^+ \rightarrow CH_3CHOHCOO^- + NAD^+ + energy$$

The presence of lactic acid in muscle cells, resulting from oxygen depletion is responsible for the pain resulting from muscle fatigue.

Metal ions play a vital role in the oxygen transport process. Firstly iron is a component of haemoglobin. Oxygen molecules bond on to the iron atom and are then transported away from the lungs to cells that have in sufficient of oxygen, in which the low pH, caused by the presence of lactic acid (the product of anaerobic oxidation) causes changes which result in the release of the oxygen. Secondly copper is a vital component of the cytochromes, which are essential enzymes in the processes through which glucose is oxidised.
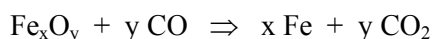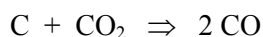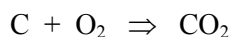
(N.B. Shading indicates AHL material.)

Iron and steel

The principal ores of iron are Haematite (Fe_2O_3) and Magnetite (Fe_3O_4)

In the blast furnace the solid ore, coke (C) and limestone ($CaCO_3$) are fed in at the top and air blown in at the bottom. Starting at the bottom the reactions producing the iron are:

$$C + O_2 \Rightarrow CO_2$$

$$C + CO_2 \Rightarrow 2\,CO$$

$$Fe_xO_y + y\,CO \Rightarrow x\,Fe + y\,CO_2$$

The limestone is added is to react with sand (SiO_2), inevitably a major impurity:

$$CaCO_3 \Rightarrow CaO + CO_2$$

$$CaO + SiO_2 \Rightarrow CaSiO_3$$
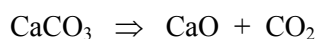
The iron produced in this way contains a great deal of dissolved carbon (~4%), as well as other impurities, which make it very brittle. To remove these pure oxygen is blown through the molten liquid to convert these to the oxides. The volatile ones (such as CO_2) escape as gases, the non-volatile ones (such as SiO_2) react with the calcium oxide which is also added.

The properties of the steel may be modified either by adding other metals or non-metals to form alloys with the iron, or by heat treating it, which affects the crystal structure of the iron.

Three common heat treatment processes are:

- Annealing, in which the metal is allowed to cool slowly to produce a soft malleable steel

- Quenching, in which very hot metal is rapidly cooled so that the high-temperature crystal structure is retained, giving a hard, brittle steel

- Tempering, in which the quenched steel is reheated to achieve a hardness intermediate between that achieved by annealing and quenching.

Some common steels, along with their composition and uses are:

Aluminium

Aluminium is obtained from Bauxite – impure, hydrated aluminium oxide. The aluminium oxide is separated from Fe_2O_3, the main impurity, by dissolving the amphoteric Al_2O_3 in concentrated sodium hydroxide, filtering off the Fe_2O_3, then acidifying the mixture to precipitate out pure alumina, Al_2O_3.

Because it is too high in the reactivity series for chemical reduction, aluminium is obtained from alumina by electrolysis:

- The Al_2O_3 is dissolved in molten cryolite (Na_3AlF_6) which reduces the melting point and improves the conductivity, at about 900°C

- Aluminium is formed at the steel lining cathode and the molten metal sinks to the bottom of the cell.

- $Al^{3+}(l) + 3\,e^- \rightarrow Al(l)$

- At the carbon anode, oxygen, from the oxidation of the oxide ions, reacts with the carbon:

  o $2\,O^{2-}(l) \rightarrow O_2(g) + 4\,e^-$

  o $C(s) + O_2(g) \rightarrow CO_2(g)$

- The carbon anodes therefore burn away and require periodic replacement.

Aluminium has a very low density and, owing to a thin impervious layer of its oxide, it is corrosion resistant. Though quite soft it can be made harder by alloying with other metals such as magnesium.

The production of both steel and aluminium consume large amounts of energy and use great volumes of water. They both generate CO_2, a greenhouse gas, and produce solid waste (slag and Fe_2O_3 respectively) which requires disposal. In both cases recycling waste metal can greatly reduce the environmental impact.

Petrochemicals

Currently about 90% of oil is used as a fuel and about 10% for petrochemicals. It is probably easier and, because of the production of greenhouse gases, such as CO_2, better for the environment to search for new energy sources to conserve more oil for petrochemical production.

Owing to the low reactivity of alkanes, cracking to form alkenes is an important first step in petrochemical production. They all involve heating fractions from the fractional distillation of oil, in the absence of air, for a brief period then rapidly cooling. There are three important types of cracking:
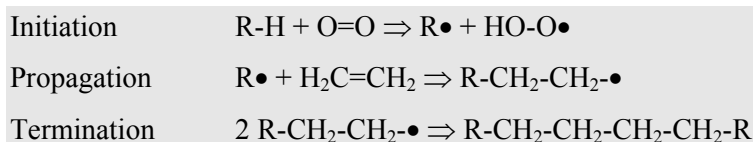
- Thermal cracking; in which the gaseous alkane is heated to a very high temperature giving ethene as the major product.

- Catalytic cracking; in which the alkane vapour is passed over a zeolite catalyst at a lower temperature to give less ethene and more branch-chained hydrocarbons, which are excellent fuels.

- Steam cracking; in which the alkane vapour is mixed with steam before cracking which produces more aromatic hydrocarbons.

There are two distinct processes by which ethene polymerises to form polyethene, giving two distinctly different products:
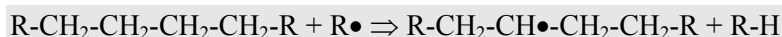
LDP (Low Density Polyethene) - carried out at high temperature and very high pressure in the presence of a free-radical initiator (trace of O_2 or peroxides). Produces branch chain polymers which cannot form a regular lattice - hence lower density, weaker intermolecular forces and lower melting point.

HDP (High Density Polyethene) - carried out at much lower P and T in presence of complex catalysts ($Al(C_2H_5)_3$ & $TiCl_4$). Produces a polymer with very little branching that can form a regular lattice - hence higher density, stronger intermolecular forces and higher melting point.
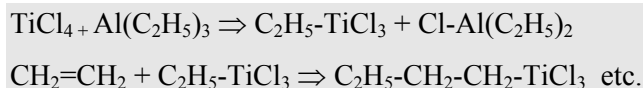
Production of LDP involves a free radical mechanism:

Initiation	$R\text{-}H + O=O \Rightarrow R\bullet + HO\text{-}O\bullet$
Propagation	$R\bullet + H_2C=CH_2 \Rightarrow R\text{-}CH_2\text{-}CH_2\text{-}\bullet$
Termination	$2\ R\text{-}CH_2\text{-}CH_2\text{-}\bullet \Rightarrow R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R$

The radicals ($R\bullet$) can however remove hydrogen atoms in the middle of a chain, giving rise to branching of the chains:

$R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R + R\bullet \Rightarrow R\text{-}CH_2\text{-}CH\bullet\text{-}CH_2\text{-}CH_2\text{-}R + R\text{-}H$

Production of HDP involves the formation of a complex with the catalyst. Ethene molecules then insert themselves into this very polar ("ionic", $C^{\delta-}\text{-}Ti^{\delta+}$) bond resulting in polymer chains without any branching. The following equation is an oversimplification of this:

$TiCl_{4} + Al(C_2H_5)_3 \Rightarrow C_2H_5\text{-}TiCl_3 + Cl\text{-}Al(C_2H_5)_2$

$CH_2=CH_2 + C_2H_5\text{-}TiCl_3 \Rightarrow C_2H_5\text{-}CH_2\text{-}CH_2\text{-}TiCl_3$ etc.

CHAPTER 14 CHEMISTRY IN INDUSTRY AND TECHNOLOGY
(IB OPTION C) SUMMARY

When propene polymerises to form polypropene, there are again two distinct products:

Isotactic - the methyl groups are on alternate carbons and are on the same side of the hydrocarbon chain. This allows a regular lattice structure, so stronger intermolecular forces and a higher melting point.

Atactic - there is a random distribution of methyl groups and they are on different sides of the hydrocarbon chain. This interferes with regular lattice structure, so weaker intermolecular forces and a lower melting point.

Condensation polymers result from the joining of monomers that have two functional groups on each monomer and a small molecule (often water) is formed for each bond between the monomers. Usually two monomers are involved, each having two identical functional groups. Common examples are give in the text.

The properties of polymers are very dependent on their structure and hence may be altered by modifications to the structure. Some examples are:

- Because of the polar nature of chlorine, PVC has strong forces between the polymer chains hence it is quite rigid. Adding plasticisers (smaller molecules that come between the polymer chains) reduces the intermolecular forces giving a much more flexible product.

- If volatile hydrocarbons are present when styrene (phenylethene) polymerises then they vapourise to leave large gaps between the polymer chains. This produces a very low density polymer (expanded polystyrene) with excellent thermal insulation properties.

- If water is added during the polymerisation of polyurethane it reacts with the isocyanate to produce carbon dioxide gas ($-NCO + H_2O \Rightarrow -NH_2 + CO_2$) which results in a foam suitable for soft furnishings.

- Polyacetylene contains conjugated double bonds (that is alternate single and double bonds), but in spite of the possible extensive delocalisation it is only a poor conductor unless doped with iodine.

The structure of the polymer determines its properties, hence phenol-methanal polymers are very rigid owing to the extensive cross-linking between the chains and in Kevlar, used for bullet-proof vests, there is strong hydrogen bonding between the polymer chains.

Kevlar molecules (see structure above) has rigid rod-shaped molecules with strong intermolecular hydrogen bonds between the chains. As a result it can give rise to a lyotropic liquid crystal with a very strong, ordered structure.

If concentrated sulfuric acid is added to Kevlar, then the O and N atoms are protonated, destroying the hydrogen bonded structure.

The feel of fibres made from some polyesters can be rather harsh and they are not easy to dye. Blending with other fibres, either natural (like cotton) or synthetic (like polyamides) can improve these properties.

Some specific examples of desirable properties are phenol-methanal polymers which are rigid and are excellent electrical insulators making them ideal for power sockets etc. Polyurethane foams have a low density and high elasticity making them excellent for use as padding in mattresses and soft furnishings. PET has a high tensile strength and low gas permeability making it ideal for "fizzy" drink bottles, plus it is easily recycled.

Homogeneous catalysts (such as an acid in esterification, or Fe^{2+} in the reaction of H_2O_2 & I^-) are in the same phase as the reactants. They react with one of the reactants to produce an intermediate, which is consumed at a later stage to regenerate the catalyst. These stages have lower activation energies than the uncatalysed process. Homogeneous catalysts can however be difficult to separate from the final product.
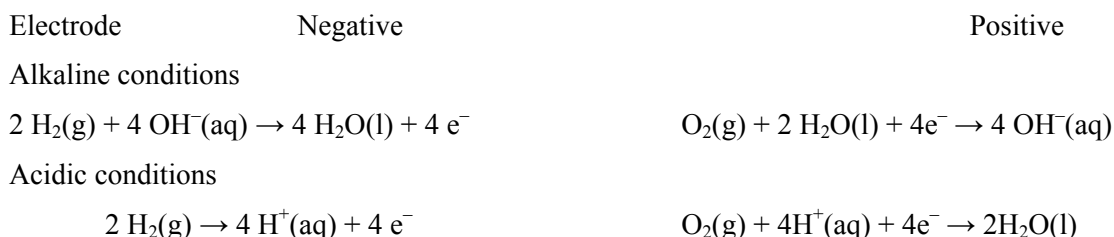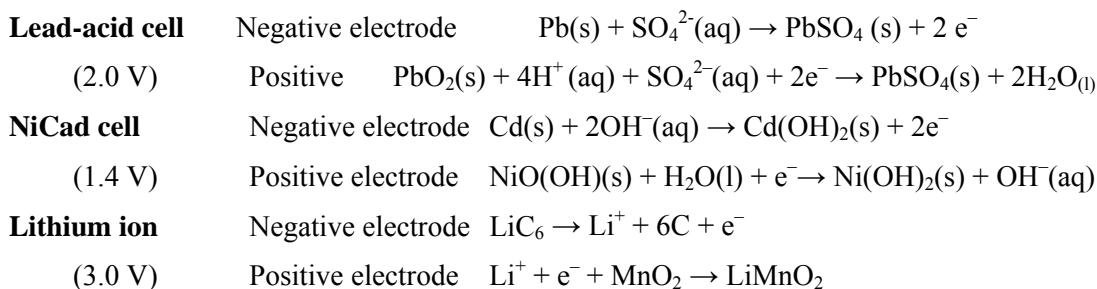
Heterogeneous catalysts are in a different phase to the reactants and hence are easy to separate. They provide an active surface on which the reaction can take place with a reduced activation energy. It is important that the product does not bond to the surface so the surface is freed for other reactants. As it is a surface phenomenon heterogeneous catalysts must have high surface areas.

Most industrial processes involve catalysts because they speed up the reaction (greater efficiency) and can also increase the yield of the desired product rather than by-products (greater selectivity). Some disadvantages are the way conditions can reduce the activity of catalysts (denaturing of enzymes, surfaces deactivated by "poisons") and the environmental impact of the escape of toxic catalysts.

The highly exothermic reaction between hydrogen and oxygen can be harnessed to produce electricity, and hence the production of hydrogen used to store energy, in a fuel cell:

Electrode   Negative   Positive

Alkaline conditions

$2\,H_2(g) + 4\,OH^-(aq) \rightarrow 4\,H_2O(l) + 4\,e^-$ $O_2(g) + 2\,H_2O(l) + 4e^- \rightarrow 4\,OH^-(aq)$

Acidic conditions

$2\,H_2(g) \rightarrow 4\,H^+(aq) + 4\,e^-$ $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Energy can also be stored through rechargeable batteries the reactions below are those that take place when they are delivering a current:

Lead-acid cell   Negative electrode $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2\,e^-$

    (2.0 V)   Positive $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O_{(l)}$

NiCad cell   Negative electrode $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

    (1.4 V)   Positive electrode $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$

Lithium ion   Negative electrode $LiC_6 \rightarrow Li^+ + 6C + e^-$

    (3.0 V)   Positive electrode $Li^+ + e^- + MnO_2 \rightarrow LiMnO_2$

Fuel cells and rechargeable batteries are both ways of converting the chemical energy of an exothermic reaction into electrical energy. The major difference is that the reactions in rechargeable batteries have to be reversible.

Liquid crystals are fluids that have anisotropic physical properties (electrical, optical and elasticity), if the molecules of the fluid all have the same orientation. Many natural materials, such as cellulose, DNA and spider silk display this.

There are two types of **liquid crystal**:

Thermotropic liquid-crystals - are pure substances, such as biphenyl nitriles, that show liquid-crystal behaviour over a temperature range between the solid and liquid states.

Lyotropic liquid crystals - are solutions, such as soap and water, that show the liquid crystal state at certain concentrations.

In the nematic phase rod-shaped molecules are distributed randomly but tend to align themselves giving rise to anisotropic properties. If the temperature is raised, the increased thermal agitation disrupts this directional order until it is lost at the temperature at which the normal liquid phase is formed.

CHAPTER 14 CHEMISTRY IN INDUSTRY AND TECHNOLOGY (IB OPTION C) SUMMARY

Liquid-crystal displays (LCDs) are used in digital watches, calculators and laptops In these the orientation of the polar molecules can be controlled by the application of a small voltage across a thin film of the material. The ordered areas of the display have anisotropic optical properties, hence the light and dark areas can be controlled by the applied voltage to a grid of electrodes.

In order to be useful, a liquid crystal must be stable, maintain the liquid crystal state over a large temperature range, be polar so the orientation can be controlled by an electrical field and be capable of rapidly changing orientation.

Biphenyl nitriles (R-◎-◎-CN)produce an effective liquid crystal state because the biphenyl group makes the molecule more rigid and rod-shaped, whilst the nitrile group makes the molecule polar, so that the intermolecular forces are strong enough to make the molecules align.

Nanotechnology involves research and technology development at the 1 nm to 100 nm range. It creates and uses structures that have novel properties because of their small size and builds on the ability to control or manipulate at atomic scale.

Scanning probe microscopes are able to move individual atoms on a surface one atom at a time, whereas chemical reactions allow atoms to be positioned at a particular site in a molecule.

Nanotubes are cylinders made only from carbon hexagons (like a looped round graphite sheet). The closed ends of the tube also involve pentagons to produce the curvature (as in fullerenes). Nanotubes can be either single or multiple, comprising a series of concentric single nanotubes.

Nanotubes have anisotropic properties with high tensile strength along their axes. As the surface of nanotubes allows the flow of electrons (like graphite), the electrical conductivity of nanotubes increases with their length.

The threat to health of nanoscale particles is largely unknown, hence there are people who have significant concerns in this regard. It is an issue that requires industrial responsibility and strong political leadership.

Silicon, a semiconductor, has four electrons in its valence shell, meaning that the lowest electron band in the lattice structure is totally filled. It therefore cannot conduct except when electrons gain enough energy to jump into the next unfilled band (hence conductivity increases with temperature).

If traces of atoms with one more electron (e.g. As, Sb) are added to the structure (doping) then the extra electrons have to go in the unfilled band, increasing conductivity (n-type semiconductors). Similarly if traces of atoms with one less electron (e.g. Ga, In) are added to the structure then this creates a space ("hole") in the filled band, again increasing conductivity (p-type semiconductors).

If p-type and n-type conductors are placed next to each other electrons flow from the surface of the n-type conductor to the p-type conductor, producing an electric field. This allows a p→n flow, but not a n→p flow, because the extra electrons just inside the p-type repel other electrons. If solar energy excites electrons in silicon into the conducting band then they can move p→n, but not the other way, hence the n-type semiconductor becomes the negative terminal of as solar cell. Electrons can flow through the external circuit back to the p-type (which acts as the positive terminal because it has lost electrons).
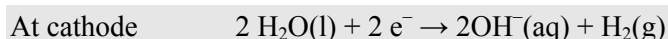
In a LCD display each pixel contains a liquid crystal sandwiched between two scratched glass plates, which have a polarising film aligned with the direction of the scratches. The liquid crystal molecules in contact with the glass line up with the scratches, and because the scratches in the two plates are at 90° to each other, the molecules form a twisted arrangement

between the plates, stabilised by intermolecular forces between the chains. These molecules rotate the plane of polarisation of plane-polarized light so that light will pass through the film and the pixel will appear bright. If a voltage is applied across the film, the polar molecules will align with the field, rather than the scratches, so the twisted structure is lost and the plane of the plane-polarized light is no longer rotated. As a result, the crossed polarising films cause the pixel to appear dark.

The electrolysis of brine (aqueous NaCl) produces chlorine, hydrogen and sodium hydroxide:

At cathode $2 H_2O(l) + 2 e^- \rightarrow 2OH^-(aq) + H_2(g)$

At anode $2 Cl^- \rightarrow Cl_2(aq) + 2e^-$ (but at low [Cl-]) $4 OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4 e^-$)

As a result Na^+ and OH^- remain in the solution, hence sodium hydroxide.

It is important to keep the products apart, otherwise they react to form bleach:

$Cl_2(aq) + 2 OH^-(aq) \rightarrow 2 Cl^-(aq) + ClO^-(aq) + H_2O(l)$

In the membrane and diaphragm cells this is done by physically separating the two electrode compartments with. In the diaphragm cell the flow from anode to cathode is ensured by a pressure differential. In the membrane cell the compartments are separated by a membrane that allows cations (Na^+) to pass through, but not anions (Cl^- and OH^-), hence no OH^- can travel back to the anode compartment.

An alternative is the mercury-cell in which mercury is used as the cathode, which results in the formation of a sodium amalgam rather than hydrogen. This amalgam is then pumped to a separate vessel where it is allowed to react with water to give the sodium hydroxide:

$Na^+(aq) + e^- \rightarrow Na_{(Hg)}$

$2 Na_{(Hg)} + 2 H_2O(l) \rightarrow 2 Na^+(aq) + 2 OH^-(aq) + H_2(g)$
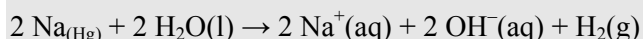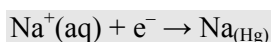
Though it produces purer products than the diaphragm cell, the mercury-cell is being phased out in favour of the membrane cell because of concerns of brain damage that can result from the escape of mercury and its concentration in the food chain.

Chlorine is used in the production of plastics (Polychloroethene - PVC), treating drinking water to kill bacteria, bleaching paper, producing chlorinated solvents, antiseptics and insecticides.

Sodium hydroxide is used in the production of wood pulp for paper, the purification of bauxite, soap manufacture and as a general alkali in the chemical industry.

(Shaded areas indicate AHL material)

CHAPTER 15 MEDICINES AND DRUGS
(IB OPTION D) SUMMARY

Introduction

The body has its own natural healing processes that usually overcome tissue damage and infections by microbes, though sometimes medicine or drugs may be required. A medicine or drug is any chemical that does one or more of the following:

• Alters the physiological state, including consciousness, activity level or coordination

• Alters incoming sensory sensations

• Alters mood or emotions

The placebo effect is the well established fact that administration of inactive substances, instead of active drugs, still leads to a reported improvement in the condition.

Drugs can be administered orally, parenteral (that is by injection, which can be intravenous, intramuscular or subcutaneous), inhalation or rectally.

The testing of new drugs is a lengthy process. The stages involved usually include:

- Tests on microbes or tissue cultures

- Animal tests to establish the LD_{50} (the dose lethal to half the population)

- Double-blind clinical trials

The **therapeutic window** is a measure of the relative margin of safety of a drug. It is the ratio of the lethal dose (LD_{50}) to the therapeutic dose of the drug (ED_{50} - the dose required for the drug to have a noticeable effect on half the population).

The stomach naturally contains HCl, giving it a pH~2. Sometimes excess acidity can cause discomfort, which can be relieved by antacids such as $Al(OH)_3$, $Mg(OH)_2$, $CaCO_3$, and $NaHCO_3$, which neutralise the acid.

Analgesics counteract pain. Mild analgesics function by intercepting the pain stimulus at the source, for example by interfering with the production of substances (such as prostaglandins) that cause pain, swelling or fever. Strong analgesics work by temporarily bonding to receptor sites in the brain, preventing the transmission of pain impulses without depressing the central nervous system.

- Aspirin and Paracetamol are common mild analgesics. In addition to its analgesic effect, aspirin has been found to be useful in preventing the recurrence of heart attacks and strokes, though it can lead to ulceration and stomach bleeding, as well as allergic reactions and Reye's syndrome (a potentially fatal liver and brain disorder in children). Paracetamol is very safe in the correct dose (though overdoses can lead to serious liver damage, brain damage and even death).

- Morphine, codeine and diamorphine (heroin) are strong analgesics. These have similar carbon structures, but differ in the side chain attached to it. Though very potent, highly effective and lead to a sense of euphoria, these drugs have many negative effects:

  o they can cause constipation

  o they cause drowsiness

  o they are addictive

  o patients develop a tolerance to the drug so it becomes less effective

  o long term use can result in sterility

The effect of **depressants** (though are often described as anti-depressants because they are prescribed to relieve depression) is dose dependent:

- at low doses they may exert little or no effect

- at moderate doses they induce sedation (soothing, reduction of anxiety)

- at higher doses it may induce sleep

- at extremely high doses they may cause death.

Common examples are diazepam (Valium), nitrazepam (Mogadon) and fluoxetine hydrochloride (Prozac). Valium and Mogadon have very similar structures with a benzene ring fused to a seven-membered heterocyclic ring to which a phenyl group is attached

Ethanol, a depressant, is one of the most commonly used drugs. Whilst in the short term it provokes positive feelings through reducing stress and lowering inhibitions, there are serious short and long term negative effects of overindulgence:

- Alcohol has even more severe negative effects when combined with other drugs, Alcohol and aspirin together leads to an increased risk of stomach bleeding. Cocaine can react with alcohol to produce cocaethylene which is far more toxic than cocaine. Taking alcohol along with sedatives with alcohol is particularly dangerous as it can easily lead to coma and death.

- Detection of alcohol levels is important, especially with regard to drink driving prosecution. One of the simplest is the potassium dichromate(VI) breathalyzer, which turns from orange to green (Cr^{3+}). More sophisticated techniques involve the analysis of blood or urine by chromatography, the absorption of infrared radiation or the intoximeter which uses a fuel cell.

Stimulants are the opposite of depressants, which have the effect of making people feel more alert through an increase the heart rate, blood pressure, respiration and wakefulness. Because they override the natural controls on the consumption of energy reserves, excessive use can lead to exhaustion.

- Amphetamines and epinephrine (adrenaline) are chemically similar in that both derive from the phenylethylamine structure, hence amphetamines mimic the effects of epinephrine and so are known as sympathomimetic drugs.

- Nicotine, in the form of tobacco (for example in cigarettes), is a widely used drug. In the short-term there is a stimulating effect coupled with increased heart rate and blood pressure, as well as a reduction in urine output. In the long term it is addictive and there are significant negative long-term effects including increased risk of heart disease, coronary thrombosis and peptic ulcers.

- Caffeine is a respiratory stimulant found in drinks such as tea and coffee. It is a weak diuretic, which when consumed in large amounts can cause anxiety, irritability and sleeplessness. Whilst their structures are not closely related, both caffeine and nicotine contain a tertiary amine group.

Antibiotics

- Penicillins, initially discovered by Fleming, but developed by Florey and Chain to make large scale production possible, were the first widely used antibacterials (antibiotics).

- Penicillins all have a similar structure with a four-membered heterocyclic ring fused to a five-membered one. The side chains attached to these can be altered to enhance their resistance to hydrolysis both in the stomach and by enzymes produced by penicillin-resistant bacteria.

- Penicillins interfere with the cross-linking of the cell walls of bacteria, so weakening them, causing them to easily burst. Because they do not have a cell wall, penicillins have no effect on animal cells

- If antibacterials are widely used in low concentrations (for example in animal feed), or a course of antibacterials is not fully completed, then bacteria that show some resistance to the antibacterial will survive, which results in the development of drug-resistant bacteria. This has resulted in the resurgence of a number of diseases such as tuberculosis (TB).

Antivirals

Bacteria are single cell microorganisms, measuring about 1 μm, that are capable of independent existence whereas viruses, which basically comprise only genetic material in a protective protein coat, are about a tenth of this size and cannot exist separate from other living organisms, because they rely on invading cells to reproduce.

Because viruses are so different to bacteria, antibacterial drugs have no effect on viruses. One class of antiviral drugs depends on altering the cell's ribosomes (protein production organelles) so that the virus cannot use them to produce its own proteins. Some other antiviral drugs block specific enzymes that only the virus produces.

AIDS has been found to be closely associated with the HIV virus. The HIV virus can bind to T cells (a type of white blood cell) rendering it ineffective. This greatly weakens the immune response system that protects the body from infections, rendering the individual much more susceptible to many diseases.

The HIV virus has the ability to mutate rapidly, making it difficult to develop a drug or vaccine that will remain effective against it. As with other viruses, the fact that their metabolism is linked closely to that of the cell, makes it difficult to destroy viruses without affecting healthy cells.

Drugs that have been developed to combat AIDS are expensive, whilst the disease is very prevalent in developing countries where the cost of this treatment is prohibitive. The stigma associated with AIDS also often prevents people infected seeking diagnosis and treatment.

Enzymes are very stereospecific, that is they will usually only act on one stereoisomer and not the other. Therefore in order to be effective drugs need to be similarly stereo specific, that is usually only one isomer will be biochemically active.

Transition metal **complex ion**s, like organic molecules containing a double bond or a ring, can exhibit geometrical (*cis-* / *trans-*) isomerism. For example the square planar diamminedichloroplatinum(II) can exist in either a *cis-* or *trans-* form. The *cis-*isomer is found to be a highly effective anti-cancer drug (cisplatin), whereas the *trans-*isomer inactive.

The same is also true of **optical isomers**, which contain a chiral centre. One example is the drug thalidomide. One enantiomer alleviates morning sickness in pregnant women, while the other can leads to deformities in the limbs of the fetus the woman is carrying. The use of a racemic mixture to treat morning sickness therefore led to the birth of many tragically deformed children in the 1950s.

The stereochemistry of **penicillins** is also vital to their action. The four-membered beta-lactam ring structure has a lot of steric strain owing to its small bond angles. This enhances the reactivity of the amide group within it, allowing it to bond to the enzyme transpeptidase, responsible for the construction of the cell wall of bacteria, inhibiting its action.

Diamorphine (**heroin**) is much more active than morphine. This is because in diamorphine the polar hydroxyl groups in morphine are replaced by the far less polar ester group, increasing its solubility in the lipids of the central nervous system.

Traditionally compounds are synthesised individually and then tested for pharmacological activity – an expensive, time consuming process. **Combinatorial chemistry** simultaneously produces a large number of related compounds (a "combinatorial library"), which can then be tested in parallel. In the case of polymeric compounds often one end of the chain is anchored to a solid support, allowing it to be readily removed from the liquid phase reactants.

An alternative approach is to link the biological activity of a molecule to its 3D shape and the polarity of specific regions. Other compounds that produce a similar environment can then be investigated by computer modeling. If they appear to be promising *in silico* then the compound can be synthesized and tested.

Some regions of the body are essentially aqueous and others non-aqueous. Often the efficacy of a drug may be affected by altering its solubility though changing the polarity. Introducing polar groups (e.g. -OH), or those that can form ions (-COOH $\Rightarrow$ -COO$^-$ or –NH$_2$ $\Rightarrow$ –NH$_3^+$) will increase the aqueous solubility, whereas hydrocarbon side-chains will reduce it. Soluble aspirin (where the weak acid is converted to its ionic salt) and fluoxetine hydrochloride are examples of water soluble ionic derivatives.

Usually if a molecule has a chiral centre on of the optical isomers will be far more physiological activity than the other. Normal synthesis produces a racemic mixture which is very difficult to separate into the separate isomers. Chiral auxiliaries hold the non-chiral precursor in such a way that the reaction producing the chiral centre can occur in only one manner, producing just on of the enantiomers. Taxol, an anti-cancer drug, is produced by such a stereospecific synthesis.

There are a number of drugs, such as lysergic acid diethylamide (LSD), mescaline, psilocybin and **tetrahydrocannabinol** (THC), are described as mind-altering, or hallucinogens because they create an altered state of conscious. in which normally impossible things seem to occur. LSD, mescaline and psilocybin all have quite similar structures, involving an indole ring, or in the case of mescaline a side chain that can take on a similar conformation to such a ring.

Tetrahydrocannabinol (THC), found in cannabis, is significantly less potent than the other mind-altering drugs and in some parts of the world its use is legal. Ther are arguments for and against its legalization.   *(Shaded area indicates AHL material)*

Air Pollution

The major substances responsible for air pollution are carbon monoxide (CO), oxides of nitrogen (NO_x), oxides of sulfur (SO_x), particulates and volatile organic compounds (VOCs).

The major source of **carbon monoxide** is from the natural atmospheric oxidation of methane ($2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$); the greatest anthropogenic source is the incomplete combustion of organic compounds, for example in car engines (e.g. $C_8H_{18} + 11O_2 \rightarrow 5CO_2 + 3CO + 9H_2O$).

The major source of **oxides of nitrogen** (NO_x) is the combination of nitrogen and oxygen at high temperatures either naturally (lightning) or anthropogenically (high temperature flames, e.g. car engines), initially giving nitrogen monoxide ($N_2 + O_2 \rightarrow 2NO$), which on cooling is rapidly oxidised to nitrogen dioxide ($N_2 + 2O_2 \rightarrow 2NO_2$). Bacterial decomposition of organic matter also forms large quantities of dinitrogen monoxide (N_2O).

Most **oxides of sulfu**r come from the atmospheric oxidation of hydrogen sulfide, produced in volcanic areas and from the anaerobic decomposition of organic matter ($2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$). The major anthropogenic source of oxides of sulfur (SO_x) is the combustion of coal. In this process sulphur and containing compounds form sulfur dioxide (e.g. $C_5H_{11}SH + 9O_2 \rightarrow 5CO_2 + SO_2 + 6H_2O$). This is slowly oxidise in the air to sulfur trioxide ($2SO_2 + O_2 \rightarrow 2SO_3$).

Natural sources of particulates include sandstorms and volcanic activity. The two major anthropogenic particulates are soot and fly-ash. Soot (carbon particles) is formed during combustion when the supply of air is very limited formed (e.g. $C_8H_{18} + 6O_2 \rightarrow 5C + 3CO + 9H_2O$). Fly-ash results from burning fuel containing a high proportion of non-combustible matter, for example cheap coal.

Anaerobic decomposition of organic matter and animal digestion are both major sources of volatile organic compounds (VOCs). Anthropogenically produced VOCs come mainly from liquid fuels used in transport (e.g. gasoline) either released from storage tanks of in the exhaust as a result of poor combustion.

Vehicles are a major source of pollution (CO, NO_x, particulates, VOCs). Catalytic converters can cause oxides of nitrogen to oxidise carbon monoxide ($2CO + 2NO \rightarrow 2CO_2 + N_2$) and also result in the combustion of VOCs. Also adjusting the fuel:air ratio can control soot formation and control the oxides of nitrogen.

Coal fired power plants are also a major source of pollution (SO_x, particulates). Washing the coal removes some sulphur and injecting lime into the fluidised-bed combustion chamber converts a lot of sulfur dioxide into calcium sulfite ($CaO + SO_2 \rightarrow CaSO_3$), finally wet alkaline scrubbing can remove sulfur dioxide from the waste gases ($SO_2 + OH^- \rightarrow HSO_3^-$). Fly-ash may be significantly reduced by fitting electrostatic precipitators.

Acid rain

In acid deposition acidic particles, gases and precipitation leave the atmosphere. This can be wet deposition (removal by rain, fog or snow) or dry deposition (removal of acidic gases or settling of solid acid particles).

Dissolved CO_2 ($CO_2 + H_2O \rightarrow H^+ + HCO_3^-$) makes rain is naturally acidic (pH~5.6) so acid rain is that with a pH <5.6, usually because oxides of sulfur and oxides of nitrogen dissolve to form H_2SO_3, H_2SO_4, HNO_2 and HNO_3.

The effects of acid rain include:

- Enhanced erosion of stone and metal objects ($CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2$)

- Damage to aquatic life either directly or through enhanced Al^{3+} levels

- Damage to plant life

- Human health consequences (irritating respiratory system

Ways to minimise the damage from acid rain depend on the methods mentioned above to reduce atmospheric levels of oxides of sulfur and oxides of nitrogen.
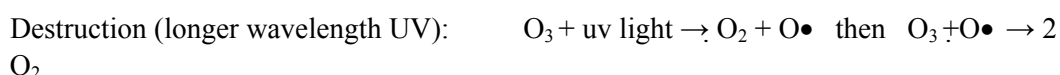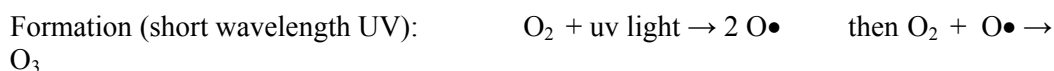
Greenhouse effect

The sun is at a much higher temperature than the earth, therefore the radiation it emits (sunlight) is a lot shorter wavelength. Some gases in the atmosphere do not absorb sunlight but do absorb the longer wavelength (infrared) radiation emitted by the earth. Some of this is radiated back towards the earth and hence trapped, hence the term "greenhouse effect".

The major gases that give rise to this effect are CH_4, H_2O, CO_2, N_2O and chlorofluorocarbons (CFCs). Their contribution to the "greenhouse effect" depends on both the concentration of the gas and its effectiveness at absorbing infrared radiation. Naturally occurring water vapour is by far the most important, but of those of anthropogenic origin CO_2 dominates with an effect equal to the sum of CH_4, CFCs and N_2O.

The temperature of the earth therefore depends on the concentration of such gases and both at present seem to be increasing an effect which is generally attributed to increased anthropogenic emissions. Effects of an increase in global temperatures are reduction in the size of glaciers and polar ice-caps, resulting in a rise in sea-level, as well as significant changes in weather patterns which lead to drought, crop loss and famine.

Ozone layer

In the stratosphere an equilibrium level of ozone exists as a result of its formation and destruction by ultraviolet light. These reactions prevent harmful UV light reaching the earth's surface.

Formation (short wavelength UV): O_2 + uv light $\rightarrow$ 2 O• then O_2 + O• $\rightarrow$ O_3

Destruction (longer wavelength UV): O_3 + uv light $\rightarrow$ O_2 + O• then O_3 + O• $\rightarrow$ 2 O_2

Some pollutants increase the destruction rate, hence reducing the equilibrium ozone concentration. The major ones are chlorofluorocarbons (CFCs), used as a refrigerant and a propellant in aerosol sprays, and oxides of nitrogen (NO_x), from high temperature combustion with engines or high flying aircraft being particularly important in this context,

A number of alternatives to CFCs have been proposed, such as hydrocarbons, fluorocarbons and hydrofluorocarbons (HFCs), none of which have the weak C-Cl bond responsible for effect on ozone levels. They all have low toxicity, though hydrocarbons have the disadvantage of being highly flammable. Unfortunately, like CFCs, they all absorb infrared radiation and hence contribute to the "greenhouse effect".

When organic matter decomposes it consumes oxygen, hence the extent to which the oxygen concentration of water is reduced (over a fixed period at a given temperature) is a measure of how much of these pollutants is present. This is known as the biochemical oxygen demand (BOD). Aerobic bacterial decomposition of organic matter results in the formation of CO_2, NO_3^- and SO_4^{2-}. If no oxygen is present, anaerobic bacterial decomposition occurs instead and the products are CH_4, NH_3 and H_2S.

Sometimes an increase in nutrient levels in water can lead to excessive plant growth. When these plants die, as a result of seasonal changes or depletion of the nutrients, then the dead organic matterstarts to decompose and consume oxygen. This can consume all the oxygen so that anaerobic decomposition sets in. This process is known as eutrophication.

Power stations, and many other industrial plants, use water for cooling or to condense steam. When this warm water is returned to the environment, it results in thermal pollution. Thuis affects the balance of the natural environment owing to changes in metabolic rates and oxygen solubility.

Water

Waste water can contain a wide variety of toxic chemicals:

- heavy metals - from mining and indutrial processes, like electroplating

- pesticides - from agricultural pest control

- dioxins -an impurity in weed-killers and pesticides

- polychlorinated biphenyls (PCBs) - from capacitors and transformers used in power supply

- organic matter - from food processing

- nitrates and phosphates - from excessive fertiliser application

Three levels of water treatment are used depending on the nature of pollution in the waste water and what is to be done with the treated water:

- **Primary** treatment comprises filtration and sedimentation to remove suspended solids

- **Secondary** treatment comprises aerobic bacterial oxidation of organic matter, often involving bubbling oxygen through a suspension of activated sludge

- **Tertiary** treatment removes ionic pollutants, such as heavy metals, nitrates and phosphates. Heavy metals may be removed by ion exchange resins or precipitated as their sulfides. Nitrates can be reduced to nitrogen gas by denitrifying bacteria under anaerobic conditions and phosphates may be precipitated as calcium phosphate.

After any stage the water may be treated with chlorine/ozone to kill off pathogens.

Desalination of sea water is becoming increasingly important. It may be achieved by multi-stage distillation (in which hot water from the condenser heat the incoming water) or by reverse osmosis (in which water, under high pressure, is forced through a membrane that does not permit ions or large molecules to pass).

Continual irrigation can lead to salinization because when the water evaporates salts dissolved in the irrigation water, concentrate in the topsoil and affect plant growth. This is particularly a problem in hot, dry climates and when soils are poorly drained.

If the same crop is continually grown on a particular piece of land, then harvested and removed, the soil becomes depleted in the particular nutrients and minerals required by that crop. Application of fertilisers is often not specific enough and may lead to over-application, hence crop rotation may be a better long term solution to nutrient depletion.

As well as creating pollution of groundwater through over-application and run-off, repeated use of herbicides, pesticides and fertilizers can result in soil pollution. This results from the way these chemicals interfere with the natural ecological cycles involving animals, plants and micro-organisms in the soil, reducing biodiversity.

Soil

Soil organic matter (SOM) comes from the decomposition of dead plants and animals and comprises high-molecular-weight organic materials (such as polysaccharides and proteins), the simpler molecules that result from their breakdown (such as monosaccharides and amino acids) and humic substances.

As well as acting as a reservoir of essential nutrients (P, N, S), soil organic matter (SOM) improves the water retention and thermal properties of soil. It also improves its buffering capacity and reduces the effect of toxic cations by complex formation.

Common organic pollutants found in soils include:

- petroleum hydrocarbons - from lubricants, such as engine oil
- agrichemicals - fertilizers, pesticides and herbicides from over-application
- volatile organic compounds (VOCs) - from spilt fuels, such as diesel oil
- solvents - used in many industrial products and present in paints, adhesives etc.
- polyaromatic hydrocarbons (PAHs) - from the incomplete combustion of fossil fuels
- polychlorinated biphenyls (PCBs) - from capacitors and transformers used in power supply
- organotin compounds - in marine sludges as a result of use in anti-fouling marine paints
- semi-volatile organic compounds (SVOCs) - industrial solvents, hydraulic fluids etc.

Waste

Waste disposal is an increasing problem; most is currently dealt with by landfill or incineration:

- Landfill is simple but the problems are identifying suitable sites, the problem of the build up of potentially explosive flammable gases from anaerobic decomposition and the pollution of ground water supplies by the leaching of toxic substances, such as heavy metals.

- Incineration greatly reduces the volume of waste matter, but the plant and fuel can be costly also some materials can produce toxic combustion products.

Recycling has many benefits, provided waste is efficiently separated. Commonly recycled materials are :

- Steel - scrap steel is added to molten iron from the blast furnace, so that energy is saved in the reduction of the ore and alloying materials are re-used.

- Aluminium - the smelting of aluminium consumes vast quantities of electricity so that recycling saves 95% of the energy consumed in aluminium manufacture.

- Glass - broken glass, preferably colour sorted, is added to the raw materials in glass manufacture. It is then melted and moulded into new containers. This saves raw materials and energy.

- Plastic - plastic waste has to be sorted accoring to the polymer present; not an easy task. The plastic can then be melted and moulded. Some plastics, such as thermosetting ones, cannot be recycled.

- Paper - the waste paper is pulped, de-inked, bleached and then reformed into paper. Though it conserves raw materials, theere is inevitably some degradation of quality during this processing.

Radioactive waste can be classified as low-level waste or high level-waste according to the intensity and half-life of the radiation produced:
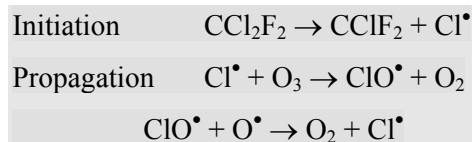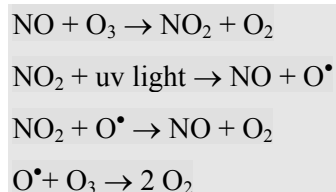
- Low-level - mainly materials that have been exposed to radiation around a nuclear reactor producing low levels of short-lived radioactivity. These materials are stored securely until the radioactivity has fallen to a low enough level for disposal by incineration, or dilution and releasing into the sea.

- High-level - mainly from spent fuel rods that are highly radioactive, often with half-lives of thousands of years. Initially these wastes, in secure containers, have to be stored in cooling ponds because of the heat the decay generates. Then they are either converted into a glass (vitrification) or sealed in strong corrosion resistant containers and stored deep underground in stable geological strata

The bond in molecular oxygen (O=O) is stronger than the bond in ozone (a σ-bond plus a delocalised π-bond, giving a bond order of 1½) so that the dissociation of ozone can absorb UV light that has too long a wavelength to dissociate oxygen molecules.

UV light causes the weak C-Cl; bond in CFCs to dissociate generating chlorine atoms, which initiate a free radical chain reaction breaking down ozone to diatomic oxygen:

Initiation $\qquad CCl_2F_2 \rightarrow CClF_2 + Cl^\bullet$

Propagation $\qquad Cl^\bullet + O_3 \rightarrow ClO^\bullet + O_2$

$\qquad\qquad ClO^\bullet + O^\bullet \rightarrow O_2 + Cl^\bullet$

Nitrogen monoxide acts as a homogeneous catalyst in the conversion of ozone to diatomic oxygen:

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + uv\ light \rightarrow NO + O^\bullet$

$NO_2 + O^\bullet \rightarrow NO + O_2$

$O^\bullet + O_3 \rightarrow 2\ O_2$

Ozone depletion is greatest in the antarctic during early spring because in the winter that region is isolated from global atmosperic circulation and very low temperatures result in the formation of many ice crystals. Reactions that take place on the surface of these crystals allow for the conversion of chlorine containing molecules into more reactive species. In spring the sun returns and UV light causes bond fission in these reactive species forming free radicals that cause rapid ozone depletion. Later in spring global atmosperic circulation is restored, so ozone arrives from other latitudes.

Photochemical smog occurs in cities that experience strong sunlight and have heavy traffic, which produces volatile organic compounds (VOCs) and nitrogen oxides (NO$_x$). Geographical conditions such as surrounding high mountains, that help to create a temperature inversion trapping air close to the ground, and a lack of wind exacerbate this.
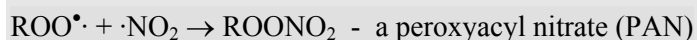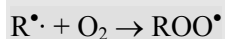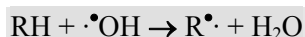
The effect of UV light on nitrogen dioxide produces very reactive species such as ozone and hydroxyl radicals:

$NO_2 + uv\ light \rightarrow NO + O^\bullet$

$O\cdot + O_2 \rightarrow O_3$

$O + H_2O \rightarrow 2 \cdot^\bullet OH$

$O_3 + H_2O \rightarrow 2\ ^\bullet OH + O_2$
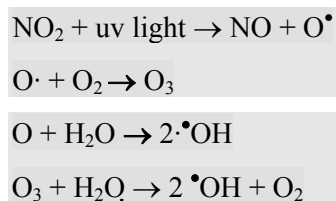
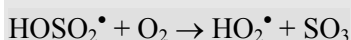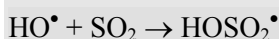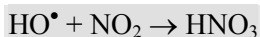These can then react with other species present to produce a complex mixture of products, many of which are repiratory irritants. Some examples of these reactions are:

$^\bullet OH + NO_2 \rightarrow HNO_3$

$RH + \cdot^{\bullet}OH \rightarrow R^{\bullet}\cdot + H_2O$

$R^{\bullet}\cdot + O_2 \rightarrow ROO^{\bullet}$

$ROO^{\bullet}\cdot + \cdot NO_2 \rightarrow ROONO_2$ - a peroxyacyl nitrate (PAN)

Hydroxyl radicals, produced in the reactions above can also rapidly oxidise oxides of sulfur and nitrogen to form their corresponding acids:

$HO^{\bullet} + NO_2 \rightarrow HNO_3$

$HO^{\bullet} + NO \rightarrow HNO_2$

$HO^{\bullet} + SO_2 \rightarrow HOSO_2^{\bullet}$

$HOSO_2^{\bullet} + O_2 \rightarrow HO_2^{\bullet} + SO_3$

$SO_3 + H_2O \rightarrow H_2SO_4$

These are readily soluble in water and are major contributors to **acid rain**.

Ammonia can react with these acids to form the ammonium salts:

$2\ NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

$NH_3 + HNO_3 \rightarrow NH_4NO_3$
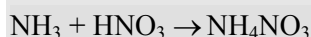
which are then deposited either as solids or dissolved in rainwater. The ammonium ion dissociates in water to produce an acidic solution:

$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$
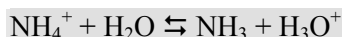
The ammonium ion can be oxidised by bacterial action in the soil to produce more nitric acid:

$NH_4^+ + 2O_2 \rightarrow 2H^+ + NO_3^- + H_2O$

A sparingly soluble salt is in equilibrium with its ions according to the equation

$MX(s) \leftrightarrows M^+(aq) + X^-(aq)$.
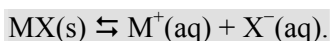
The equilibrium constant for this, called the solubility product, is given by the expression:

$K_{sp} = [M^+][X^-]$

hence the molar solubility can be calculated from the solubility product and vice versa.

If we try to dissolve a sparingly soluble salt in a solution already containing one of its ions (for example dissolving AgCl in 1 mol dm^{-3} HCl), then to keep K$_{sp}$ constant the solubility will be less than in water (K$_{sp}$ for AgCl = 1 x 10^{-10} mol^2 dm^{-6}, so in water the solubility would be 1 x 10^{-5} mol dm^{-3}, but in the HCl it would only be 1 x 10^{-10} mol dm^{-3}). This is known as the common ion effect.

Clays, present in soils, contain anionic groups and are therefore capable of binding cations to their surface. Their capacity to do this is know as their cation-exchange capacity.

The cations attached to the clay can be exchanged depending on the relative concentrations and bonding powers of the cations present in the surrounding solution. In general the smaller and more highly charged a cation is the more strongly it will bind to the surface, therefore, for example magnesium ions would replace potassium ions:

$Clay(K)_2\ (s) + Mg^{2+}(aq) \rightarrow Clay(Mg)(s) + 2\ K^+(aq)$
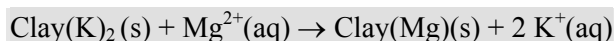
Hydrogen ions can also replace the cations and hence the availability of these ions can be affected by pH. The more strongly the cation bonds, then the lower the pH required to release it, so that ions such as Al^{3+} and Fe^{3+} are only released under quite acidic conditions.

Other pH sensitive equilibria also affect the availability of nutrients. For example many metals form insoluble hydroxides so their ions may not be available in alkaline solution:

$$M^{2+}(aq) + 2OH^-(aq) \rightarrow M(OH)_2(s)$$
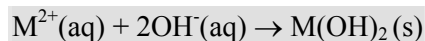
Phosphates can react with calcium ions to form insoluble calcium phosphate, making the phosphorus unavailable to plants:

$$Ca^{2+}(aq) + HPO_4^{2-}(aq) \rightarrow CaHPO_4(s)$$
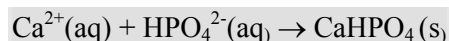
but in acidic solution the phosphate is converted to the dihydrogen phosphate ion, which forms a soluble salt with calcium making the phosphorus available:

$$H^+(aq) + HPO_4^{2-}(aq) \rightarrow H_2PO_4^-(aq)$$
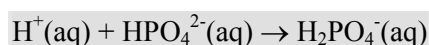
Soil organic matter (SOM) plays a vital role in soil chemistry. Amongst its functions it:

- contributes to cation-exchange capacity

- enhances the ability of soil to buffer changes in pH

- binds to organic and inorganic compounds in soil

- reduces the negative environmental effects of pesticides, heavy metals and other pollutants by binding contaminants

- forms stable complexes with cations

(Shaded areas indicate AHL material

A **food** may be considered any substance that we deliberately take into our mouths and swallow, that is any natural or artificial materials intended for human consumption. Ideally, a food must contain one or more nutrient.

The six major nutrients are lipids, carbohydrates, proteins, vitamins, minerals, as well as water. A nutrient is a component of food that is used by the body to provide energy, or for the growth and repair of tissue.

Fats and oils are lipids; these are trimesters (also called triglycerides) made from a propan-1,2,3-triol (glycerol) and three long-chain carboxylic acids (called fatty acids). The nature of the R group determines the physical and chemical properties of the lipid.

Carbohydrates have the empirical formula CH_2O. Monosaccharides with the general formula $(CH_2O)_n$ (n>2) are the simplest carbohydrates. Each monosaccharide contains one carbonyl group (C=O) and at least two hydroxyl groups (-OH). Condensation of two monosaccharide forms a disaccharide. Carbohydrates comprise sugars and polymers such as starch and cellulose derived from monosaccharides.

Proteins are polymers of 2-amino acids. All proteins contain C, H, O and N and some also have P and S in their chemical composition.

Chemically oils and fats are similar, the main difference being in their melting point with fats being solid at room temperature and oils being liquid. Longer the carbon chain, greater the molar mass, stronger the van der Waals' forces and higher the melting point. Greater the degree of unsaturation, lower the melting point. *Cis*-unsaturated oils (the sort most commonly found naturally) have lower melting points than the equivalent *trans*-unsaturated oils.

Lipids that are crystalline solids and relatively hard at room temperature tend to have saturated hydrocarbon chains. Oils, liquid at room temperature, give less crystalline, softer solids when solidified, are unsaturated. Poly-unsaturated oils have lower melting points and form softer solids than mono-unsaturated oils.

Unsaturated oils are less stable due to reaction of carbon-carbon double bond with oxygen (and hydrogen, water or microbes) and therefore keep less well than saturated fats. Unsaturated oils are often hydrogenated at high pressure and a temperature in the presence of nickel catalyst to produce more saturated lipids. Although this offers some practical advantages (such as the product is more convenient for some cooking techniques, it is more stable because the rate of oxidation is decreased and the texture can the controlled), it comes at a health cost because mono- and poly-unsaturated fats are healthier than saturated fats. Also partial hydrogenation can lead to the formation of *trans*-fats which do not occur naturally and are difficult to metabolise and hence accumulate in the fatty tissues of the body. *Trans*-fats also cause an increase in the levels of LDL cholesterol, which can lead to atherosclerosis and a resultant increase in the probability of strokes and heart problems.

Shelf life

Shelf life is the length of time a product can be stored with out it degrading so that it changes in flavour, smell, texture and appearance, or because of the growth of undesirable organisms which makes it unfit for consumption.

Exposure to air can result in degradation from a change in water content (making it dry and changing its texture) as well as an increase in the rate of oxidation leading to a decrease in nutrient value, discolouration of the surface and rancidity. Conversely if dry foods absorb water vapour from the air they become moist and more vulnerable to microbial degradation. Chemical changes occurring within the food can result in a pH change (e.g. becoming sour), develop undesirable flavours, change colour and/or decrease its nutritional value.

Light provides energy for photochemical reactions to occur leading to rancidity, the fading of the colour and the oxidation of nutrients, especially vitamins. As with all chemical changes, an increase in temperature leads to an increase in the rate of degradation of foods.

Rancidity is the development of unpleasant smells in fats and oils. In hydrolytic rancidity the ester bond is broken down in the presence of lipase, heat and moisture to yield free fatty acids. For example, butanoic acid gives a rancid smell and taste to milk and butter that have been stored too long. Oxidative rancidity which involves the reaction of the carbon-carbon double bond in unsaturated lipids with oxygen from the air. This results in complex free radical reactions to produce a wide variety of products, many of which have unpleasant odours or tastes. The presence of light and of enzymes accelerates the rate at which oxidative rancidity occurs. In highly unsaturated lipids, such as fish oils, oxidative rancidity can be a major problem.
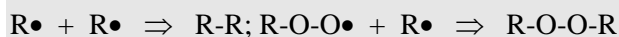
Auto-oxidation is a free radical process chain reaction that involves the reaction of oxygen molecules with the double bonds of unsaturated lipids and the mechanism involves three steps:

Initiation – formation of free radicals by exposure to light (photo-oxidation) which causes homolytic fission of a carbon-hydrogen bond: $R\text{-}H \Rightarrow R\bullet + \bullet H$.

Propagation – the free radicals react rapidly with oxygen molecules to form peroxide radicals, which then abstract hydrogen from other substrate molecules reforming the hydrocarbon radicals:

$R\bullet + O_2 \Rightarrow R\text{-}O\text{-}O\bullet; R\text{-}O\text{-}O\bullet + H\text{-}R \Rightarrow R\text{-}O\text{-}O\text{-}H + R\bullet$

Termination – This involves the removal of free radicals from the system by reactions between radicals with three possible combinations:

$R\bullet + R\bullet \Rightarrow R\text{-}R; R\text{-}O\text{-}O\bullet + R\bullet \Rightarrow R\text{-}O\text{-}O\text{-}R$

$R\text{-}O\text{-}O\bullet + R\text{-}O\text{-}O\bullet \Rightarrow [R\text{-}O\text{-}O\text{-}O\text{-}O\text{-}R] \Rightarrow R\text{-}O\text{-}O\text{-}R + O_2$

R-O-O-H formed in the propagation step are very reactive molecules and are gradually converted to aldehydes and ketones. These, and the long chain fatty acids that the aldehydes are further oxidised to, have unpleasant smells and tastes responsible for spoiling of the food.

Ways of minimizing rate of rancidity and prolonging shelf life of foods include: keeping moisture levels low during processing, using an inert gas or hermetic sealing or minimizing amount of air in packaging, adding additives to impede browning, cure meats, slow down the growth of micro-organisms, and to add to flavour.

An **antioxidant** is a substance that can be added to food to increase its shelf life by delaying the onset of oxidative degradation. Naturally occurring antioxidants and their sources include: vitamin C in citrus fruits and most green vegetables, vitamin E in nuts, seeds, soya beans, whole grains, and some vegetable oils like canola oil, ß-carotene in vegetables such as carrots and broccoli as well as fruits such as tomatoes and peaches and selenium in fish, shellfish, meat, eggs and grains.

Synthetic antioxidants include BHA, BHT, PG, THBP and TBHQ. Almost all have phenolic type structures: they have a hydroxyl group attached to a benzene ring.

Natural antioxidants are perceived to be safer and known to reduce the risk of cancer and heart disease by reacting with free radicals. Vitamin C is vital for the production of hormones and collagen, whilst ß-carotene can act as a precursor for vitamin A. However, these are more expensive than synthetic antioxidants.

Many people think that synthetic antioxidants can have harmful side effects. Even though synthetic antioxidants are more effective than the natural ones they require strictly enforced codes for their safe use in foods, which may be difficult to police, especially in developing countries and many feel that their safety has yet to be satisfactorily proven.

Many substances traditionally used in different cultures as promoting good health are rich in natural antioxidants such as green tea, turmeric, oregano, blueberries, cranberries and dark chocolate with claims of lowering levels of LDL cholesterol, blood sugar levels and high blood pressure as well as preventing cancerous cell development.

There are three main types of antioxidants: (i) Antioxidants that reduce free radical formation or free radical quenchers which react with the free radicals present during the propagation step and produce less reactive free radicals; examples include HBA and BHT. (ii) Chelating agents that form stable complex ions with transition metals and hence reduce free radicals which may be formed by the reaction of transition metal ions with the hydroperoxides; Examples include plant extracts from rosemary, tea and mustard and salts of EDTA. (iii) Reducing agents (electron donors) can react with both oxygen in the food and with the hydroperoxides such as vitamin C and carotenoids.

A **dye**, a coloured compound, either synthetic or from a different natural source, is often added to enhance the appearance of processed products. A pigment is a colouring material naturally present in food. Colour is due to the fact that a dye or a pigment absorbs certain frequencies of visible light, whilst emitting others which are able to stimulate the retina in the eye.

Anthocyanins are the most commonly found pigments, responsible for red, pink, purple and blue colours found in fruits and vegetables and many flowers. They all have very similar 3-ring $C_6C_3C_6$ structures with conjugated double bonds, but vary in the number and position of the hydroxyl groups and alkoxy side chains. Anthocyanins are often found bonded to sugar side chains which also modify their precise colour, and are water soluble.

Carotenoids are widely found in all living things, especially in algae. A precursor for vitamin A, they are responsible for yellow, orange and red colours in bananas, tomatoes, carrots and saffron. The essential feature of carotenoid structure is the long hydrocarbon chain, which may also have methyl groups attached. In some cases there may be ring structures at the ends of the chain, in other cases not. Similarly some caretenoids have hydroxyl groups near the end of the chain or on the ring, whereas others, sometimes called carotenes have a hydrocarbon structure and are fat soluble.

Chlorophyll is the green coloured pigment responsible for catalysing the photosynthetic process in green plants and hence is widely found in green vegetables. Its structure contains magnesium at the centre of the ring which has extensive conjugation. There are actually two very closely related forms of chlorophyll, chlorophyll a and chlorophyll b, which differ only in whether a side chain is a methyl group (a) or an aldehyde group (b). Heme is the red pigment found in the red blood cells of higher animals. Its structure is similar to that of chlorophyll, but contains iron(II) rather than magnesium. The essential features of both chlorophyll and heme are the planar ring systems in which the metal ion is bonded to four nitrogen atoms, which act as ligands. This is referred to as a porphyrin ring.

These compounds absorb light in the visible region of the spectrum and hence appear coloured because they all have alternate single and double bonds ("conjugated" double bonds) with extensive systems of delocalised π-bonding. The greater the extent of delocalisation the closer together in energy the bonding and antibonding π-orbitals become and hence they region in which photons can excite an electron from one to the other shifts from the ultraviolet region (as in benzene) into the visible region.

Factors that affect the colour stability of pigments include the effects of oxidation, temperature, pH and the presence of metal ions. Anthocyanins are more stable and highly coloured at low temperature and pH. Carotenoids are subject to auto-oxidation due to the presence of many C=C double bonds. Chlorophyll reaction with heat is pH dependent being stable in basic solution of pH 9 and unstable in acid solution of pH 3. During heating, plant cells break down and release acids, decreasing the pH of the solution and hydrogen ions displace the magnesium ion from the ring into solution, resulting in a colour change to olive-brown. These changes also make the pigment less stable to light and photodegradation can occur. In muscles heme is found associated with myoglobin, a protein molecule, and this has a purplish-red colour. It binds easily to oxygen molecules and results in a colour change to bright red. A much slower reaction with oxygen, called auto-oxidation, results in the oxidation of the iron from iron(II) to iron(III), forming metmyoglobin and the colour changes to a brownish red colour.

Cooking foods often causes them to turn brown; there are two processes that lead to the colour change, the Maillard reactions and caramelization. In the Maillard condensation reactions the aldehyde group in reducing sugars (such as glucose and lactose) reacts with the free amino group of an amino acid, or amino groups on the side chains of peptides and proteins. The polymeric products are often brown and hence responsible for the colour change, whilst the lower molar mass products are responsible for many of the aromas of cooking and resulting changes in flavour. Caramelisation occurs when foods with a high carbohydrate concentration are heated. The rate of caramelisation varies with the sugar involved with fructose most easily caramelised. Extremes of pH, both high and low, also promote caramelisation. Because the Maillard reaction requires proteins or amino acids the browning of foods that do not contain these, such as making toffee from sugar, or the crisp sugar topping of *crème brulée*, results from caramelisation. In practice however the browning of food on cooking usually involves both processes.

GM foods

Modern biological techniques mean that it is possible to artificially modify the DNA sequence of micro-organisms, plants and animals. Using organisms modified in this way, it is possible to produce foods that are different from those that occur naturally. Foods produced from these organisms are collectively known as genetically modified (or GM) foods. There are a number of possible advantages to GM foods, which include: pest and disease resistance, improved quality and range and production of medicinal and other novel products. There are however concerns about the proliferation of genetically modified organisms and food produced from them. The main reasons for this concern are: Are GM foods safe for consumption? Will the production of GM foods damage natural ecosystems? Do we understand enough about genetic modification?

Dispersed systems

A dispersed system is a stabilised, macroscopically homogenous mixture of two immiscible phases.

A **suspension** or sol comprises solid particles suspended in a liquid; an example is blood in which the solid red and white cells remain suspended in the plasma. An emulsion is a stable blend of two immiscible liquids for example mayonnaise, which is a suspension of oil droplets in an aqueous system. Foams are comprised of gas bubbles trapped in a liquid medium for example whipped cream or egg whites. Emulsifiers are frequently used to promote mixing of the two phases, and stabilisers are often added to slow down their separation. Emulsifiers are molecules that can bond to both phases so they are found at the surface between the phases and hence are known as surfactants; this is very similar to the action of soap.

An **enantiomer** that rotates the plane of polarized light clockwise is dextrorotatory, labeled + or (d); an enantiomer that rotates the plane of polarized light anticlockwise is levorotatory, labeled – or (l). The D,L system is used for sugars and amino acids. In this the configuration of the molecule is related to that of glyceraldehydes and the configuration of other sugars about each chiral centre is then named by analogy, that is, if the molecule is viewed along the chain with the C=O pointed away, the D-isomer has the –OH group on the right. The system is also applied to amino-acids, where a useful rule of thumb is the "CORN" rule. The molecule is viewed with the C-H bond pointing away from the observer (fortunately the same as in the R,S system below). If the groups **CO**OH, **R**, **N**H$_2$ (where R- is the side chain) are arranged clockwise around the carbon atom then it is the D-form. If anticlockwise, it is the L-form. The R,S system is used for most other groups of compounds.

Different enantiomeric forms of molecules found in food often have different smells, tastes and toxicity.

(Shaded areas indicate AHL material)

Electrophilic addition to alkenes

Electrophile - a species that attacks a centre of negative charge, such as a π-bond, by acting as an electron pair acceptor?

Mechanism: Addition across the double bond takes place in two stages;

- Electrophilic attack on the double bond to form an intermediate cation (e.g. $CH_2Br–CH_2^+$)
- Reaction of this carbocation with an anion.

For example in the reaction between ethane and bromine:

$$CH_2 = CH_2 + \quad Br — Br \quad \rightarrow \quad CH_2Br–C^+H_2 + \quad :Br^- \quad \rightarrow \quad CH_2Br–CH_2Br$$
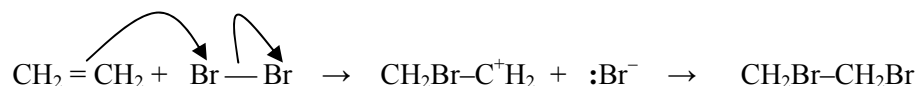
Unsymmetrical additions: When an unsymmetrical molecule (HX) adds to an unsymmetrical alkene ($^A{>}C{=}C{<}^B$) then two products are possible:

$$
\begin{array}{cc}
A \quad B & A \quad B \\
| \quad | & | \quad | \\
-C - C - & -C - C - \\
| \quad | & | \quad | \\
H \quad X & X \quad H
\end{array}
$$

A mixture of these is usually produced, but the one from the more stable intermediate carbocation will predominate.

Stability of carbocations: The stability increases when the charge is spread out, so the greater the number of alkyl groups attached to the carbon with the charge, the more stable the carbocation because alkyl groups have an electron releasing inductive effect ($CH_3 \rightarrow$). As a result the stability decreases in the order tertiary > secondary > primary.

Markovnikov's rule: When HX adds to an unsymmetrical alkene, as a result of carbocation stability, the hydrogen atom attaches to the carbon atom that already has the larger number of hydrogen atoms. For example:

$$(CH_3)_2C{=}CH_2 + H\text{-}Br \rightarrow (CH_3)_2CBr–CH_3$$

Nucleophilic Addition Reactions

Mechanism: The nucleophile (for example CN^-) attacks the carbon of the $C{=}O$ which carries a partial positive charge. The addition is completed by the anion formed gaining a hydrogen ion:

$$R_1R_2C^{\delta+}{=}O^{\delta-} + :CN^- \rightarrow R_1R_2C–O:^- \xrightarrow{H^+} R_1R_2C–OH$$
$$\qquad\qquad\qquad\qquad\qquad\quad | \qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\qquad\qquad CN \qquad\qquad\quad CN$$
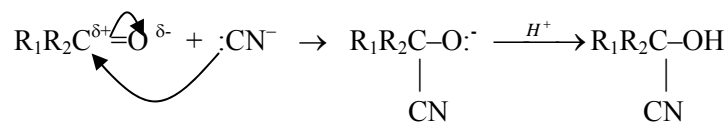
The product is an alcohol with a nitrile group sometimes called a cyanohydrin. The nitrile group can then be hydrolysed to –COOH to form a 2-hydroxycarboxylic acid which contains one more carbon in the chain than the original carbonyl compound:

$$R_1R_2C(OH)–C{\equiv}N + 2\,H_2O \rightarrow R_1R_2C(OH)–COOH + NH_3$$
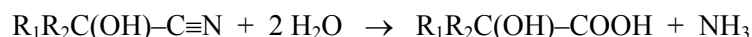
Addition-Elimination Reactions

Carbonyl compounds undergo addition reactions, similar to that above, with nucleophiles containing the -NH_2 group, but the initial product eliminates water to form a C=N double bond. Using the reaction of ethanal with 2,4-dinitrophenylhydrazine as an example:

$$CH_3CHO + H_2N\text{-}NHC_6H_3(NO_2)_2 \rightarrow CH_3CH(OH)\text{-}NH\text{-}NHC_6H_3(NO_2)_2 \rightarrow CH_3CH=N\text{-}NHC_6H_3(NO_2)_2 + H_2O$$

The products are bright yellow-orange coloured crystalline solids, so this test can be used to detect the presence of an aldehyde or ketone and their sharp melting points, were used to identify the specific compound.

Elimination reactions

Elimination is the removal of two atoms, or groups of atoms, from a molecule resulting in the formation of a multiple bond.
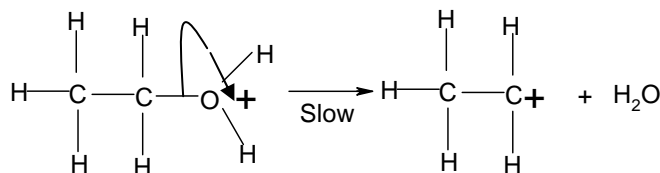
When heated with concentrated phosphoric acid (H_3PO_4) or sulfuric acid, alcohols dehydrate to form an alkene:
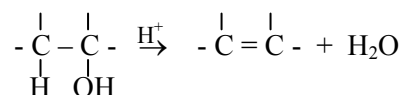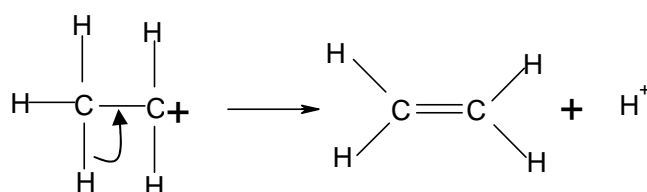

Mechanism: The acid catalyst, protonates the hydroxyl group of the alcohol:
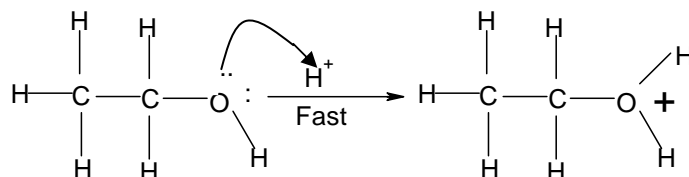
The protonated alcohol, dissociates into water and a carbocation:

A proton is eliminated from the carbon next to the one with the positive charge, reforming the catalyst:

Arenes

Benzene is a hydrocarbon with the formula C_6H_6. There are however many pieces of evidence that lead to the conclusion that 'cyclohexatriene' with alternate single and double bonds is not in fact the correct structure for benzene. Briefly these are:

- 'Cyclohexatriene' would not be symmetrical owing to the fact that double bonds are shorter than single bonds, but all the bonds in benzene are found to be an equal length.

- Benzene undergoes substitution rather than the addition reactions that characterise alkenes.

- Benzene is thermochemically more stable than 'cyclohexatriene' would be.

Aryl halides, with the halogen bonded to the ring, unlike halogenoalkanes, do not undergo nucleophilic substitution reactions for several reasons:

- The C–Cl bond is stronger owing to π-bonding with the benzene ring.

- Attack from the side opposite to the halogen is blocked by the benzene ring.

- The delocalisation reduces the $\delta+$ charge on the carbon atom attached to the halogen.
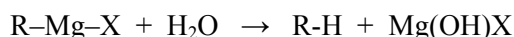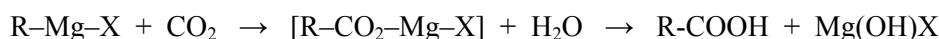
Grignard reagents

Formation: Grignard reagents can be prepared by the direct reaction of magnesium metal with halogenoalkanes in a solvent such as anhydrous (dry) ethoxyethane and are used in this solution:

$$R–X + Mg \rightarrow R–Mg–X \qquad (X = Cl, Br, I)$$

Reaction with water: Grignard reagents react readily with water to give an alkane:

$$R–Mg–X + H_2O \rightarrow R\text{-}H + Mg(OH)X$$

Reaction with water carbon dioxide: Grignard reagents react with carbon dioxide to give a product that is readily hydrolysed to a carboxylic acid. This is a way of lengthening a carbon chain:
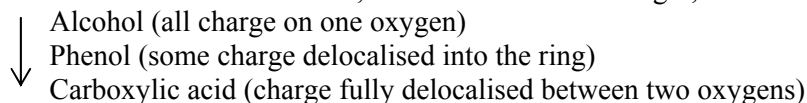
$$R–Mg–X + CO_2 \rightarrow [R–CO_2–Mg–X] + H_2O \rightarrow R\text{-COOH} + Mg(OH)X$$

Reaction with carbonyl compounds: Grignard reagents react with aldehydes and ketones to give a product that is readily hydrolysed to an alcohol. Again this is a way of lengthening a carbon chain:

$$R–Mg–X + C{=}O \rightarrow [R–C–O–Mg–X] + H_2O \rightarrow R\text{-}C\text{-}OH + Mg(OH)X$$
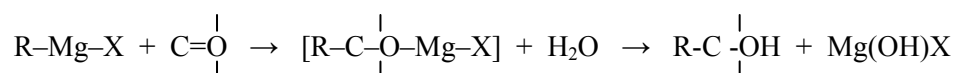
Acid-Base reactions

The more the charge on an ion can be spread out, by inductive effects or delocalisation, the more stable the ion is.

Acidity of hydroxyl groups: A hydroxyl group can dissociate and act as an acid (-OH $\rightarrow$ -O$^-$ + H$^+$) The extent to which this occurs, and hence the acid strength, increases in the order:

⬇ Alcohol (all charge on one oxygen)
Phenol (some charge delocalised into the ring)
Carboxylic acid (charge fully delocalised between two oxygens)

Acidity of substituted phenols: Electron donating groups, such as -CH$_3$, on the benzene ring increase the negative charge on the oxygen making the substituted phenol a weaker acid. Conversely electron withdrawing groups, such as –NO$_2$, decrease the electron density making it a stronger acid. Hence the acid strength, increases in the order:

$$CH_3\text{-}C_6H_4\text{-}OH \qquad\qquad C_6H_5\text{-}OH \qquad\qquad O_2N\text{-}C_6H_4\text{-}OH \longrightarrow$$
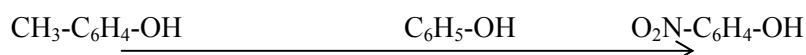
Acidity of substituted carboxylic acids: Electron donating groups, such as -CH$_3$, near to the –COOH group increase the negative charge on the oxygen making the carboxylic acid weaker. Conversely electron withdrawing groups, such as –Cl decrease the electron density making the acid stronger.

$$CH_3\text{-}COOH \qquad\qquad H\text{-}COOH \qquad\qquad Cl\text{-}CH_2\text{-}OH \longrightarrow$$
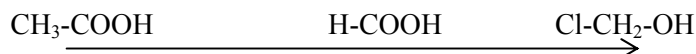
Base strength of compounds containing the –NH$_2$ group: The –NH$_2$ group, found in amines, like ammonia, can act as a base and form a cation –NH$_3^+$. Electron donating groups, such as -CH$_3$, near to the – NH$_2$ group decrease the positive charge on the nitrogen making the base stronger. Hence the base strength, increases in the order:

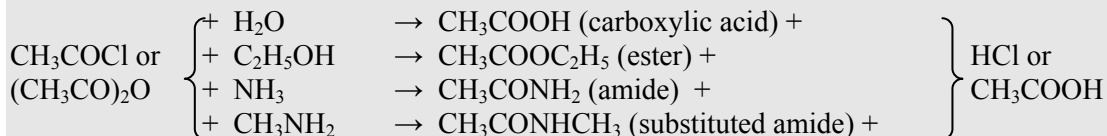$$NH_3 \qquad\qquad CH_3\text{-}NH_2 \qquad\qquad (CH_3)_2NH \qquad\qquad (CH_3)_3N \longrightarrow$$

Amides

The lone pair on the nitrogen of the amide group (-CO-NH$_2$) appears to be involved in a delocalised π-bond with the >C=O group, so that it is not available for donation. As a result amides do not act as bases.

## Addition-elimination reactions

The carbonyl groups in ethanoyl chloride, CH_3COCl, and ethanoic anhydride $(CH_3CO)_2O$ are both very polar and hence they are extremely susceptible to nucleophilic attack and addition-elimination reactions in which the –Cl and –O-CO-CH_3 groups are replaced by the nucleophile. Common examples are:

CH_3COCl or
$(CH_3CO)_2O$
$\begin{cases} + \text{ H}_2\text{O} & \rightarrow CH_3COOH \text{ (carboxylic acid) +} \\ + \text{ C}_2\text{H}_5\text{OH} & \rightarrow CH_3COOC_2H_5 \text{ (ester) +} \\ + \text{ NH}_3 & \rightarrow CH_3CONH_2 \text{ (amide) +} \\ + \text{ CH}_3\text{NH}_2 & \rightarrow CH_3CONHCH_3 \text{ (substituted amide) +} \end{cases}$
$\begin{cases} \text{HCl or} \\ CH_3COOH \end{cases}$

These reactions proceed by an addition-elimination mechanism, via an intermediate anion. The nucleophile initially attacks the very polar carbonyl group to give the anion. The leaving group is then lost allowing the >C=O bond to reform:
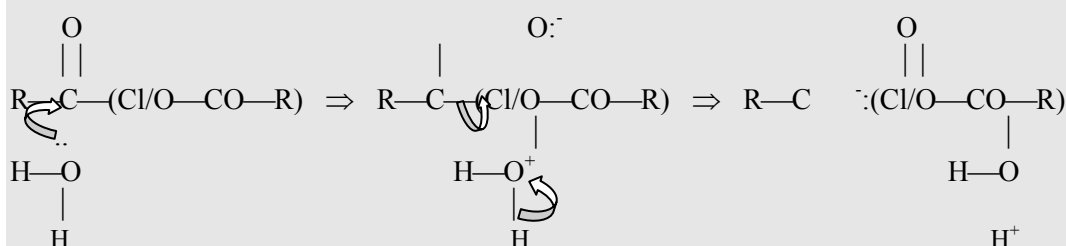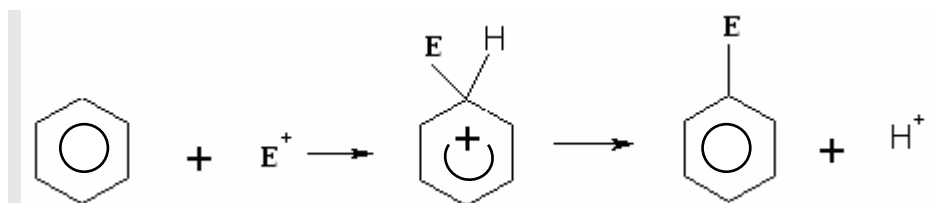

Electrophilic Substitution of the benzene ring

Because addition would lead to loss of delocalisation stabilisation, the carbocation formed by electrophilic attack on the benzene ring tends to lose a hydrogen ion, resulting in a substitution reaction.
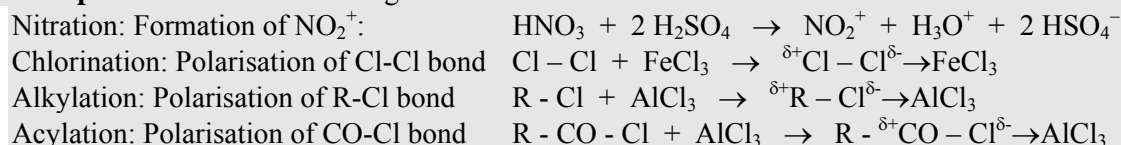
Typical electrophilic substitution reactions are:

- Nitration: $C_6H_6 + HNO_3 \xrightarrow{conc.\ H_2SO_4} C_6H_5NO_2 + H_2O$
- Chlorination: $C_6H_6 + Cl_2 \xrightarrow{Fe\ or\ FeCl_3} C_6H_5Cl + HCl$
- Alkylation: $C_6H_6 + CH_3Cl \xrightarrow{FeCl_3} C_6H_5CH_3 + HCl$
- Acylation: $C_6H_6 + CH_3COCl \xrightarrow{Fe\ or\ FeCl_3} C_6H_5COCH_3 + HCl$

Mechanism: The mechanism involves the attack of the electrophile (E^+) on the benzene ring to form the carbocation intermediate, followed by the loss of a hydrogen ion to form the final product:


**The electrophile** This varies according to the reaction:

Nitration: Formation of NO_2^+: $HNO_3 + 2\ H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2\ HSO_4^-$

Chlorination: Polarisation of Cl-Cl bond $Cl - Cl + FeCl_3 \rightarrow {}^{\delta+}Cl - Cl^{\delta-} \rightarrow FeCl_3$

Alkylation: Polarisation of R-Cl bond $R - Cl + AlCl_3 \rightarrow {}^{\delta+}R - Cl^{\delta-} \rightarrow AlCl_3$

Acylation: Polarisation of CO-Cl bond $R - CO - Cl + AlCl_3 \rightarrow R - {}^{\delta+}CO - Cl^{\delta-} \rightarrow AlCl_3$

Electrophilic substitution of methyl benzene: The methyl group is electron releasing (donating); it thus activates the benzene ring so it is more reactive than benzene. The electrophilic attack takes place at the 2- and 4-positions, so that nitration, chlorination, alkylation and acylation of methylbenzene produce a mixture of the corresponding 2- and 4-substituted products; for example:

$$CH_3C_6H_5 + 2\ HNO_3 \xrightarrow{H_2SO_4} \text{(2-nitro)} + \text{(4-nitro)} + 2\ H_2O$$
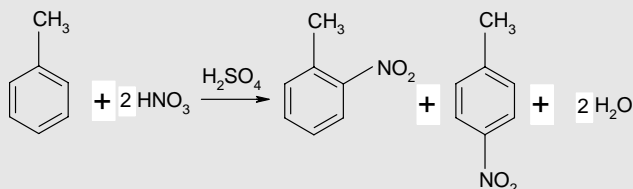
Chlorination of methylbenzene in the presence of $FeCl_3$ results in substitution on the ring (a mixture of 2- and 4-chloromethylbenzene), but in the presence of ultraviolet light it undergoes a side-chain substitution:

$$\text{Methyl benzene} + Cl_2 \xrightarrow{UV} \text{(chloromethyl) benzene} + HCl$$
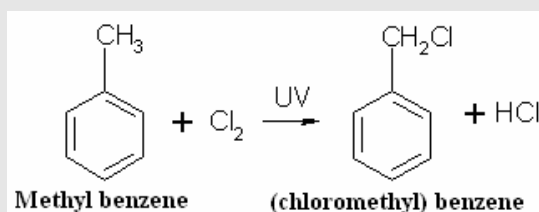
The effect of substituents on electrophilic substitution reactions of the benzene ring: A group on the benzene ring can change the reactivity of the aromatic ring (that the rate of substitution) and the position on the benzene ring at which the reaction occurs:

- Electron releasing groups such as the alkyl group, -R, and with electron pairs that can interact with the delocalised π-bond, such as –OH, increase the electron density and so activate the aromatic ring, especially at the 2- and 4- positions.
- Electron withdrawing groups, such as the nitro group, -NO$_2$, decrease the electron density and so deactivate the ring, especially at the 2- and 4- positions, so that 3-substitution occurs.
- The halogens are electron withdrawing and deactivate the ring, but the interaction of their electrons with the delocalised π-bond reduces this effect at the 2- and 4- positions, which are therefore the most reactive.

This is summarised in the table below:

2,4- directing groups			3- directing groups
Greatly activates the ring	Slightly activates the ring	Deactivates the ring	Deactivates the ring
Hydroxyl (–OH) Amino (-NH$_2$)	Alkyl (-R) -O-CH$_3$	Halogens (-Cl, -Br, -I)	Nitro (NO$_2$); Carbonyl (-CO-) -CN

(N.B. Shading indicates AHL material.)