

1 Atoms, Molecules and Stoichiometry

An **atom** is the smallest particle an element can be divided into without losing its identity.

Isotopes are atoms of the same element with the same number of protons in the nucleus but different number of neutrons.

A **molecule** is made up of a group of atoms held together by covalent bonds.

The **relative atomic mass** (A_r) of an element is the ratio of the average mass of one atom of that element to one-twelfth the mass of an atom of carbon-12.

The **relative isotopic mass** of an isotope of an element is the ratio of the mass of one atom of that isotope to one-twelfth the mass of an atom of carbon-12.

The **relative molecular mass** (M_r) of a molecule is the ratio of the average mass of one molecule to one-twelfth the mass of an atom of carbon-12.

The **relative formula mass** (M_r) of an ionic compound is the ratio of the average mass of one formula unit of that compound to one-twelfth the mass of an atom of carbon-12.

One **mole** is the amount of substance (n) that contains the same number of particles as there are atoms in exactly 12.0 g of pure carbon-12. The number of particles (N) in one mole of any substance is a constant known as **Avogadro's constant** (L), which is approximately equal to $6.02 \times 10^{23} \text{ mol}^{-1}$.

The **molar mass** (M) of a substance refers to the mass of one mole of that substance; it has units g mol^{-1} .

1.1 Stoichiometry Involving Gases

The **molar volume** of a gas is the volume occupied by one mole of a gas at a specified temperature and pressure. The molar volume at room temperature and pressure 298 K and 1 atm is 24.0 dm^3 , while the molar volume at standard temperature and pressure 273 K and 1 atm is 22.4 dm^3 .

1.2 Stoichiometric Calculations

Theoretical yield is the maximum amount of product that can be obtained from a given amount of reactants. Likewise, **actual yield** is the amount of product actually obtained from a reaction. **Percentage yield** is the ratio of actual yield to theoretical yield, expressed as a percentage.

In a reaction, the **limiting reagent** is the reactant that is completely used up at the end of the reaction. The amount of product formed is determined by the amount of the limiting reagent(s) at the start.

The **concentration** of a solution is the amount of solute, in grams or moles, per unit volume of solution. A **standard solution** is a solution with a known concentration.

Dilution is the process of adding more solvent to a known volume of solution to lower the concentration

of the solution, with the number of moles of solute remaining the same.

The **empirical formulae** of a compound is formula showing the simplest ratio of the number of atoms of each element in a compound.

The **molecular formula** is the exact formula showing the actual number of atoms of each element present in a compound.

A **part per million** (ppm) refers to a fraction out of a million. It is similar to a percentage.

1.3 Volumetric Analysis

Titration is a process involving the gradual addition of one solution to a fixed volume of another solution until stoichiometric amounts of the two solutions have reacted.

When direct titration is not possible, back titration is used. Titration is not possible when **(a)** one of the reactants is an insoluble solid; **(b)** there is no suitable indicator for the titration; or **(c)** the sample may contain impurities, which may interfere with direct titration.

Back titration involves a known excess of one reagent reacting with an unknown amount of another reagent, followed by a direct titration to find out the amount of excess reagent.

Table 1.1 details common indicators.

The **volume strength** of H_2O_2 is the volume of O_2 (at s.t.p.) that can be evolved by the decomposition of one volume of H_2O_2 . It is a ratio of volume of O_2 per volume of H_2O_2 .

2 Chemical Bonding

Chemical bonds are electrostatic forces of attraction that hold two or more atoms, ions, molecules, or any combinations of these together.

2.1 Ionic (electrovalent) bonding

Ionic bonds are strong electrostatic forces of attraction between oppositely charged ions in a giant ionic lattice structure. They are formed in ionic compounds when metal atoms lose electrons to form cations and non-metal atoms gain electrons to form anions, to achieve a stable noble gas configuration.

Generally, a large amount of energy is required to break ionic bonds. The strength of an ionic bond is directly proportional to the magnitude of the lattice energy of the bond, which is directly proportional to the product of the charges of the ions involved but inversely proportional to the distance between the two ions i.e. the sum of the ionic radii of the two ions. In other words,

$$\text{strength of ionic bond} \propto \left| \Delta H_{\text{latt}}^{\ominus} \right| \propto \frac{q_+ q_-}{r_+ + r_-}$$

The charge is generally the dominating factor that determines lattice energy and, by extension, strength.

Indicator	pH range	Acid	Endpoint	Alkali
Methyl orange	3–5	Red	Orange	Yellow
(screened)	3–5	Purple	Grey	Green
Phenolphthalein	8–10	Colourless	Pale pink	Red
Bromothymol blue	6–7.6	Yellow	Bluish-green	Blue

Table 1.1: Common indicators

When comparing bond strength, compare **(a)** ionic charges; and **(b)** radii.

2.2 Covalent bonding

Covalent bonds are strong electrostatic forces of attraction between the nuclei of the atoms and their shared pair of electrons in a simple or giant molecular structure. Covalent bonds are formed when non-metal atoms share valence electrons, forming molecules, to achieve a stable noble gas configuration.

A **dative bond** or coordinate bond is a covalent bond where the shared pair of electrons is provided by only one of the bonded atoms. The donor must have a lone pair of electrons and the acceptor must have vacant and energetically accessible orbitals to accept the lone pair of electrons.

Elements in period 3 and below may contain more than 8 electrons in their valence shell as they have vacant and energetically accessible *d* orbitals to expand the octet structure.

Aside from the above reason, some molecules cannot exist or are unstable due to steric repulsion, or overcrowding of the space around a central atom leading to repulsion between electron clouds of atoms.

2.2.1 Bond strength

Covalent bonding involves the effective overlap of valence orbitals of the two atoms involved. A bond involving the head-on overlap of *s* or *p* orbitals is a **σ bond**, while a bond involving the side-on or parallel overlap of *p* orbitals is a **π bond**. Generally, all single bonds are σ bonds, while double and triple bonds contain 1 σ bond and 1 or 2 π bonds respectively.

Covalent bonds generally require a large amount of energy to break. The strength of a covalent bond is directly proportional to the extent of overlap; thus σ bonds are generally stronger than π bonds.

The bond energy, bond length, and the radii of the atoms involved are indicators of bond strength. The greater the bond energy or the shorter the length or radii, the stronger the bond, and vice versa. **Bond energy** is the energy required to break 1 mole of a specific covalent bond in the gaseous state to form gaseous atoms under standard conditions. **Bond length** is the distance between the centres of two bonded atoms in a covalent bond. Generally, a triple bond is stronger than a double bond, which is stronger than a single bond.

Bond polarity is a measure of how equally electrons

are shared between 2 atoms in a chemical bond. It generally depends on the difference in electronegativity between the atoms. **Electronegativity**, or χ , is the tendency of an atom to attract electrons towards itself.

Atoms that have the same χ (usually, only identical atoms have the same χ) will form a covalent bond where the bonding electrons are equally shared, forming a **nonpolar covalent bond**. Otherwise, the bonding electrons are not equally shared, and a **polar covalent bond** is formed.

A polar covalent bond will create a **dipole moment**, which is a measure of the separation between the positive and negative charges in, and the extent of polarisation or distortion of a covalent bond. Dipole moments are vector quantities that point from the more electropositive atom to the more electronegative atom and have a magnitude that increases with the difference in χ between the atoms.

The **net dipole moment** is the sum of all the dipole moments in a molecule. If there is a net dipole moment i.e. the dipole moments do not cancel off, there will be permanent partial separation of charges; the more electronegative atom has a partial negative charge, and vice versa. The molecule is polar.

When deducing polarity, state **(a)** the shape of the molecule; **(b)** whether the dipole moments cancel off; **(c)** whether there is a net dipole moment; and **(d)** whether the molecule is polar.

2.2.2 Ionic bonds with partial covalent character

Some ionic bonds have a partial covalent character due to distortion or polarisation of the anion's electron cloud by the cation in an ionic compound. The extent of polarisation increases with the cation's charge density and the size and charge of the anion.

When comparing covalent character, **(a)** compare the ionic charge and radius and charge density of the cation; and **(b)** the ionic charge and size of the anion, where applicable.

Some metal and non-metals, like aluminium chloride, form a covalent bond instead of an ionic bond, due to the cation having a charge density high enough and the anion being large enough that the anion's electron cloud is polarised to such an extent that the bond becomes covalent.

2.2.3 Shapes of simple molecules

The **Valence Shell Electron Pair Repulsion (VSEPR)** model predicts the shapes of molecules. It is based on

the principles that **(a)** electron pairs around the central atom arrange themselves as far apart as possible to minimise inter-electron repulsion; and **(b)** the repulsion between lone pairs is greater than the repulsion between a lone pair and a bond pair, which is greater than the repulsion between bond pairs.

To explain the shape of a molecule,

- 1 state the number of bond pairs (b.p.) and lone pairs (l.p.) around the central atom.
- 2 state that to minimise repulsion and maximise stability, the electron pairs are directed to
 - 2 e.p.: opposite sides of each other
 - 3 e.p.: the corners of an equilateral triangle
 - 4 e.p.: the corners of a regular tetrahedron
 - 5 e.p.: the corners of a trigonal bipyramid
 - 6 e.p.: the corners of an octahedron
- 3 state, if there are any lone pairs,
 - 1 l.p.: l.p.–b.p. repulsion > b.p.–b.p. repulsion
 - 2 l.p.: l.p.–l.p. repulsion > l.p.–b.p. repulsion > b.p.–b.p. repulsion
- 4 state the bond angle and actual shape.

If the central atom is more electronegative than the surrounding atoms, bond pairs are drawn closer to the more electronegative central atom. The bond pairs will experience greater repulsion between one another and so the bond angle will be greater, and vice versa.

2.3 Intermolecular forces

Van der Waals' interactions are a class of intermolecular forces of attraction involving attraction between dipoles. There are three types of van der Waals' interactions, namely the **(a)** induced dipole-induced dipole attraction i.e. London dispersion force; **(b)** induced dipole-permanent dipole attraction i.e. Debye force; and **(c)** permanent dipole-permanent dipole attraction i.e. Keesom force.

London dispersion forces occur predominantly between nonpolar molecules. They form when electron clouds are temporarily distorted, forming dipoles that induce dipoles in neighbouring molecules, which attract.

Keesom forces occur only between polar molecules. They are simply the electrostatic forces of attraction between the permanent dipoles on polar molecules, and are relatively stronger than London forces.

The strength of van der Waals' forces depends on the size of the electron clouds of the molecules or atoms involved as well as the shape of the molecule. The greater the size of the electron cloud, the greater the extent of distortion of the electron cloud and so the greater the extent of van der Waals' forces of attraction. More energy is required to overcome more extensive van der Waals' interactions.

Straight chain isomers or longer molecules tend to have stronger van der Waals' interactions than branched chain molecules, as the surface area of contact is greater, leading to greater extent of distortion of the electron cloud, causing a greater extent of van der Waals' attraction.

Hydrogen bonds are bonds formed between a hydrogen atom bonded to N, O or F and an N, O or F atom with at least one lone pair. For molecules of similar size, hydrogen bonds are usually significantly stronger than van der Waals' interactions.

The average number of hydrogen bonds formed per molecule depends on the number of lone pairs available on the acceptor (the N, O or F with at least one lone pair), and the number of H atoms attached to N, O or F, whichever is lower.

Some molecules, like ammonia, alcohols, and carboxylic acids, dissolve in water by forming intermolecular hydrogen bonds with water molecules.

Some molecules have rather high melting and boiling points due to the presence of strong intermolecular hydrogen bonds, which require a greater amount of energy to overcome.

Some molecules, like ethanoic acid in an organic solvent (not water, as ethanoic acid will form hydrogen bonds with water), will dimerise due to intermolecular hydrogen bonds forming between pairs.

Some molecules have intramolecular hydrogen bonding, as the donor and acceptor groups are positioned in such a way (close to each other) that hydrogen bonds can be formed within a molecule.

Molecules with intramolecular hydrogen bonding will have lower melting and boiling points than isomers with intermolecular hydrogen bonding, as **(a)** the formation of intermolecular hydrogen bonds becomes less feasible; **(b)** so phase changes will involve overcoming only the less extensive intermolecular hydrogen bonds; and **(c)** this will require a lower amount of energy.

Molecules with intramolecular hydrogen bonding will also be less soluble in water than isomers with intermolecular hydrogen bonding, as **(a)** the formation of hydrogen bonds with water becomes less feasible; **(b)** so there is less extensive hydrogen bonding with water; and **(c)** this makes the molecule less soluble in water.

2.4 Metallic bonding

Metallic bonds are formed in metals, when metal atoms lose valence electrons to form cations, and the valence electrons become delocalised, free to move within the metallic lattice. The **metallic bond** is the strong electrostatic force of attraction between the cations and sea of delocalised electrons in a giant metallic structure.

Metallic bonds are generally strong; large amounts of energy are required to break them. The strength of a

metallic bond is directly proportional to the number of valence electrons contributed per atom, and the charge density of the metal cation.

When comparing metallic bond strength, compare **(a)** the number of valence electrons contributed per atom; and **(b)** the charge density of the metal cation.

2.5 Bonding and physical properties

2.5.1 Ionic compounds

The **giant ionic lattice structure** consists of oppositely charged ions held together by strong electrostatic forces of attraction (ionic bonds).

The coordination number of an ionic lattice is the number of nearest-neighbour ions to a central ion.

Ionic compounds **(a)** generally have high melting and boiling points, as a large amount of energy is required to overcome the strong electrostatic attraction between oppositely charged ions; **(b)** cannot conduct electricity in the solid state as ions can only vibrate about their fixed positions and there are no free mobile ions or electrons to conduct electricity; **(c)** can conduct electricity in the molten or aqueous state, as there are free mobile ions to do so; **(d)** are soluble in water as ion-dipole interactions form, which releases energy, causing the detachment of ions from the crystal lattice; **(e)** are insoluble in nonpolar solvents as no ion-dipole interactions can be formed to release energy to break down the crystal lattice; **(f)** are hard as oppositely charged ions are held together by strong electrostatic forces of attraction; and **(g)** are brittle as stress applied on an ionic lattice causes layers of ions to slide such that ions of similar charges come together; the resultant repulsion shatters the ionic lattice structure.

Ionic compounds can be used as refractories, which can withstand high temperatures due to their high melting points and relative inertness.

2.5.2 Giant molecules

Diamond is an example of a **giant molecule**, which has strong and extensive covalent bonding between carbon atoms, resulting in a giant three-dimensional tetrahedral molecular structure.

Diamond cannot conduct electricity, as there are no delocalised electrons or free mobile ions to do so. Diamond's strong and extensive covalent bonding between carbon atoms in a three-dimensional molecular structure causes it to **(a)** have a very high melting point, as a very large amount of energy is required to overcome the bonding; **(b)** be hard; and **(c)** be insoluble in both polar and nonpolar solvents as no solute-solvent forces are strong enough to break the bonding.

Diamond can be used as abrasives in cutting and boring rocks due to its high melting point and hardness.

Graphite is an example of a molecule with a **giant layered molecular structure**. In graphite, carbon atoms

are arranged in hexagonal flat parallel layers. Within layers, carbon atoms are covalently bonded to 3 other carbon atoms. Adjacent layers are held together by weak van der Waals' forces of attraction.

Graphite **(a)** has a high melting point, as a large amount of energy is required to overcome the strong and extensive covalent bonding between the atoms in the giant layered structure; **(b)** is a good conductor of electricity parallel to the layers as only three out of four valence electrons of carbon are used for bonding, and the fourth electron is delocalised over the whole layer and are free to move parallel layers to conduct electricity parallel to the layers; **(c)** is a non-conductor of electricity perpendicular to the layers, as electrons cannot flow between layers; **(d)** is soft and slippery as adjacent layers are held by weak van der Waals' forces, so layers can easily slide over each other when a force is applied; and **(e)** is insoluble in both polar and nonpolar solvents as no solute-solvent forces are sufficiently strong to overcome the strong and extensive covalent bonding between atoms in the giant layered structure.

Graphite can be used as lubricants in e.g. hot machines to reduce friction.

2.5.3 Simple molecules

Iodine is an example of a **simple molecule**. Atoms of iodine within molecules are bonded by strong covalent bonds, but separate molecules are held together only by weak van der Waals' forces of attraction. In the solid state, iodine molecules are arranged in a regular lattice structure.

Iodine **(a)** has low melting and boiling points, as a small amount of energy is required to overcome the weak intermolecular van der Waals' forces of attraction; **(b)** does not conduct electricity, as there are no free mobile ions or delocalised electrons to do so; **(c)** is insoluble in polar solvents as the strong intermolecular hydrogen bonds between water molecules are not compatible with the weak van der Waals' forces of attraction between iodine molecules; and **(d)** is soluble in nonpolar solvents like benzene as the weak van der Waals' forces between iodine molecules are compatible with the weak van der Waals' forces between benzene molecules.

Ice is another example of a simple molecule. Atoms of hydrogen and oxygen within molecules are bonded by strong covalent bonds, but separate molecules are held together by relatively strong hydrogen bonds.

The presence of two hydrogen atoms and two lone pairs in each water molecule creates a three dimensional tetrahedral structure, making ice not closely packed and forming an open-cage like structure.

Water **(a)** has a high boiling point, as a large amount of energy is required to overcome the strong hydrogen bonds between water molecules. This is important as otherwise, water would be a gas at r.t.p., and water

bodies would not exist, and there would be no rain; and **(b)** has a higher density than ice, as when ice melts the tetrahedral structure is partially broken down, causing water molecules to become closer and so there are more water molecules per unit volume, leading to a higher density, which is important as it allows marine life to survive during winter: ice only forms on the top of water bodies and the water below is insulated by the ice layer.

2.5.4 Metals

The **giant metallic lattice structure** consists of cations in a sea of delocalised electrons held together by strong electrostatic forces of attraction.

Metals **(a)** have high melting and boiling points, as a large amount of energy is required to overcome the strong electrostatic forces of attraction between the cations and the sea of delocalised electrons; **(b)** are good conductors of electricity as there are delocalised electrons present, which are free to move to conduct electricity; and **(c)** are malleable and ductile as when a force is applied, layers of ions can easily slide over each other without the metallic bond being broken; the metallic bond is easily reformed and the crystal lattice is restored.

Metals are usually alloyed to make them harder and less malleable, due to different sizes of cations inhibiting sliding. Examples of alloys include bronze, which is made from copper and zinc.

2.5.5 Finite resources

There is a limited amount of natural sources of raw materials like metals.

To overcome shortages of raw materials, humanity has come up with a few solutions. We can **(a)** find new sources of materials, through research and discovery; **(b)** develop new and more efficient methods of extracting and refining raw materials; and **(c)** recycling used products, by removing and reusing tin from scrap tin cans, copper from scrap electrical wires and pipes, steel from various materials and used cars, and aluminium from used aluminium cans, which is more economical as the extraction of aluminium from bauxite (aluminium ore) requires a lot of energy and is expensive, making recycling more worthwhile.

3 Atomic Structure

3.1 Structure and Particles

Atoms are made up of protons, electrons and neutrons. Protons and neutrons make up the nucleus while electrons orbit the nucleus.

Protons are subatomic particles with the symbol p^+ with a positive electric charge of $+1e$ and a mass of approximately 1.673×10^{-27} kg.

Neutrons are subatomic particles with the symbol n with no electric charge and a mass of approximately

1.675×10^{-27} kg.

Electrons are subatomic particles with the symbol e^- with an electric charge of $-1e$ and a mass of approximately 9.109×10^{-31} kg, or about $\frac{1}{1840}$ that of a proton.

An electric field shows the direction a positive particle would be deflected in if it were placed in the field; it goes from the positive terminal to the negative terminal. Protons in an electric field will be deflected towards the negative terminal, and electrons vice versa.

In an electric field, the force exerted on a particle is given by Coulomb's inverse square law. Simplifying things, the extent of deflection of a particle is directly proportional to its charge over mass (q/m) ratio.

The **mass number** of an element is the total number of protons and neutrons in an atom of the element.

The **atomic number** is the number of protons in an atom.

Nuclides are any species with a specified mass and atomic number. They can be represented as ${}_Z^AX$, where A represents the mass number, Z the atomic number, and X the element's symbol.

Isotopes are atoms of the same element containing the same number of protons but different number of neutrons.

3.2 Electronic Structure

Each electron in an atom occupies an orbital. An **orbital** can be defined as a region of space around the nucleus where there is a 90 % probability of locating an electron. The **electronic structure** of an atom is the arrangement of its electrons in their orbitals.

Electron orbitals are grouped into **subshells** l , which are then grouped into **principal quantum shells** n .

Electrons have a principal quantum number n , $n \in \mathbb{Z}^+$. Generally, the highest n found in a ground-state atom of an element is the period the element is in. The larger the n of an electron is, the further it is from the nucleus, the less strongly the electron is bound to the nucleus, and the higher the energy level of the electron.

Electrons also have an azimuthal quantum number l , $l \in \mathbb{Z}_0^+$. Electrons are grouped into subshells by their l , where 0 is the s subshell, 1 is p , 2 is d , 3 is f , 4 is g , and so on (except j). The highest l possible for any n is one less than the value of n . Thus the first shell ($n = 1$) only has a single $1s$ subshell, while the second has a $2s$ and $2p$ subshell, and so on.

Subshells are identified by their n and l , e.g. $l = 1$ in the $n = 2$ shell is referred to as the $2p$ subshell.

Electrons also have a magnetic quantum number m_l , $m_l \in \mathbb{Z}$. For a given l , $-l \leq m_l \leq l$.

Finally, electrons have a spin quantum number s , $s = \pm \frac{1}{2}$ (spin up or spin down).

These four quantum numbers n , l , m_l and s quantum mechanically fully describe an electron's quantum

state in an atom. By the **Pauli exclusion principle**, no two electrons in an atom can occupy the same quantum state, and so must have a unique combination of quantum numbers.

It follows from the above rules that the *s* subshell can have 2 electrons, the *p* subshell 6, the *d* subshell 10, and so on. It then follows that the first shell can contain 2 electrons, the 2nd 8, the 3rd 18, and so on.

In each quantum shell, there is one *s* orbital, which is spherical in shape, as well as three dumbbell-shaped *p* orbitals (p_x , p_y and p_z). The larger the *n*, the larger the orbital and the further the electrons in the orbital are from the nucleus. Orbitals in a given subshell are degenerate *IE* they are at the same energy level.

Orbitals with larger *n* are generally at a higher energy level than orbitals with a smaller *n*. Within a quantum shell, orbitals with larger *l* are at a higher energy level than orbitals with a smaller *l*. Orbitals with the same *n* and *l* in the same atom are at the same energy level.

This depends on each element, however. Elements up to calcium have 4*s* at a lower energy level than 3*d*, which is why 4*s* fills first for potassium and calcium.

In the 'A' level syllabus, the 4*s* subshell has a lower energy level than the 3*d* subshell when empty, but (magically somehow) jumps to a higher energy level when filled.

An orbital with two electrons (completely filled) is said to be paired; one with only one is unpaired.

The **Aufbau principle** states that electrons occupy the lowest energy orbital possible first before occupying higher energy orbitals. The **Hund principle** states that orbitals in a subshell are occupied singly with the same *s* before pairing occurs.

These rules together generally predict the ground state electronic configuration of an atom. When any electron is promoted to a higher energy level, the species is said to be excited.

Exceptions include chromium, which has a ground state electronic configuration of $[\text{Ar}]3d^5 4s^1$. Note the extra electron in 3*d* when compared to the configuration predicted by Aufbau. Another exception is copper, which has a ground state electronic configuration of $[\text{Ar}]3d^{10} 4s^1$. These exceptions occur because the elements are at a lower energy, or 'gain more stability' when they have such a configuration.

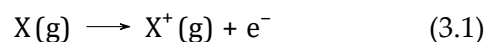
Atoms with similar electronic configurations or the same number of electrons are said to be **isoelectronic**.

For main group elements, the number of valence electrons is equal to the group number.

3.3 Ionisation Energies

The **first ionisation energy** (1st *IE*) is the energy required to remove one mole of electrons from one mole of gaseous atoms of an element to form 1 mole of singly

charged positive gaseous ions:



The *n*th *IE* is the energy required to remove one mole of electrons from one mole of (*n* – 1)ly positively charged gaseous ions to form one mole of *n*ly positively charged gaseous ions. The higher the ionisation energy of an element, the more difficult it is to remove an electron.

The **effective nuclear charge** (ENC) is the combined effect of the nucleus's charge and the screening effect, and is approximately equal to the nuclear charge minus the number of inner core electrons. The **nuclear charge** is simply the charge of the protons in the nucleus. The **screening effect** is the phenomenon where valence electrons seem 'shielded' from the electrostatic attraction from the positively charged nucleus by inner core electrons, *IE* electrons in inner quantum shells.

Generally, effective nuclear charge increases across the period.

3.3.1 Trends in Ionisation Energy

The *n*th *IE* is generally greater than the (*n* – 1)th *IE* as more energy is required to remove an electron from a more positive ion due to greater net electrostatic attraction between the nucleus and valence electrons.

Down a group, the *n*th *IE* generally decreases as (a) the atomic radius increases due to a greater number of quantum shells; (b) valence electrons are further away from the nucleus and experience greater shielding from the greater number of inner core electrons; (c) thus there is weaker electrostatic attraction between the nucleus and the valence electrons; and (d) so less energy is required to remove a valence electron.

Across a period, the *n*th *IE* generally increases as (a) the nuclear charge increases but the shielding effect remains relatively constant as the inner quantum shell of electrons remains the same; (b) effective nuclear charge increases; (c) there is stronger electrostatic attraction between the nucleus and valence electrons; and (d) so more energy is required to remove a valence electron.

An *IE* involving the removal of an ns^2 electron will be higher than one involving that of an np^1 electron as (a) the *np* electron is further away from the nucleus than the *ns* electron; (b) so there is weaker electrostatic attraction between the nucleus and the *np* electron; and (c) thus less energy is required to remove the *np* electron compared to the *ns* electron. E.g. 1st *IE* of B is less than 1st *IE* of Be.

An *IE* involving the removal of an np^3 electron will be higher than one involving that of an np^4 electron as (a) there is inter-electron repulsion between electrons in the doubly filled *np* orbital; and (b) so less energy is required to remove the *np* electron in the element with 4 electrons in the *np* subshell. E.g. 1st *IE* of O is less than 1st *IE* of N.

An *IE* involving the removal of an electron in the n th quantum shell will be higher than one involving that of an electron in the $(n + 1)$ th quantum shell, as **(a)** the valence $(n + 1)s$ electron is further away from the nucleus and more shielded compared to the $ns/p/d$ electron; **(b)** so there is weaker net electrostatic attraction between the nucleus and valence electron in the $(n + 1)$ th shell; and **(c)** thus less energy is required to remove the valence electron in the $(n + 1)$ th shell. E.g. 1st *IE* of Ne < 1st *IE* of Na.

When investigating successive *IEs* of an element, **(a)** a steady increase shows electrons in the same subshell; **(b)** a minor jump shows electrons in a subshell with lower l being removed; and **(c)** a sharp increase shows electrons in the next inner quantum shell being removed.

4 The Gaseous State

When dealing with gases, two sets of conditions are commonly used. **Standard temperature and pressure** (s.t.p.) refers to temperature and pressure of 273 K and 101 kPa respectively, while **room temperature and pressure** (r.t.p.) 298 K and 101 kPa respectively.

4.1 Gas Laws

Avogadro's law states that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of particles, i.e.

$$V \propto n \quad (4.1)$$

for constant T and p . It also means the volume ratio of reacting gases is equal to the mole ratio.

Boyle's law states that the volume of a fixed mass of gas is inversely proportional to its pressure at constant temperature, i.e.

$$p_1 V_1 = p_2 V_2 \quad (4.2)$$

for constant T and n .

Charles's law states that the volume of a fixed mass of gas is directly proportional to its thermodynamic absolute temperature at constant pressure, i.e.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (4.3)$$

for constant n and p .

The **combined gas law** is a combination of Boyle's law and Charles's law, which gives the relationship

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \quad (4.4)$$

The **ideal gas law** can be seen as a combination of the combined gas law and Avogadro's law, resulting in

$$pV = nRT \quad (4.5)$$

where R is the molar gas constant, approximately $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

From the ideal gas law, we have molar mass and density

$$M = \frac{mRT}{pV} \quad (4.6)$$

$$\rho = \frac{pM}{RT} \quad (4.7)$$

Dalton's law states that in a mixture of gases that do not react chemically, the total pressure of the mixture is equal to the sum of the partial pressures exerted by the constituent gases.

The **partial pressure** of a gas is the pressure that the gas would exert if it alone occupied the volume it currently occupies.

4.2 Ideal Gas Behaviour

An **ideal gas** is a gas that obeys the ideal gas law exactly. Ideal gases do not exist in reality.

A **real gas** is a gas that does not obey the ideal gas law. Under conditions of high temperature and low pressure, real gases approximate the behaviour of an ideal gas.

The ideal gas law describes gases that satisfy assumptions that **(a)** intermolecular forces of attraction between gas particles are negligible; **(b)** the total volume of gas particles is negligible compared to the volume of the container; **(c)** gas particles are in continuous random linear motion; and **(d)** all collisions between gas particles and between gas particles and the walls of their container are perfectly elastic, such that no kinetic energy is lost in a collision, so the total kinetic energy of gas particles at a constant temperature is constant.

At high temperatures, real gases tend toward ideal behaviour as **(a)** gas particles have high kinetic energy and do not attract each other as much during collisions; and **(b)** so the assumption that intermolecular forces of attraction between gas particles are negligible is valid.

At low temperatures, real gases deviate from ideal behaviour as **(a)** gas particles possess less kinetic energy so particles tend to attract each other more during collisions; **(b)** the intermolecular forces of attraction between gas particles become significant; **(c)** the impact of a given particle on the walls of the container during a collision is reduced; and **(d)** this causes p and thus pV to be smaller than if the gas was ideal.

At low pressures, real gases tend toward ideal behaviour as **(a)** gas particles are far apart and there are effectively no forces of attraction between gas particles; and **(b)** the assumption that the total volume of gas particles is negligible compared to the volume of the container is valid.

At high pressures, real gases deviate from ideal behaviour as **(a)** the volume of the container is decreased and gas particles come closer together; **(b)** the volume occupied by the gas particles becomes significant com-

pared to the container's volume; and (c) this causes V and thus pV to be larger than if the gas was ideal.

The extent of deviation of a gas from ideal behaviour depends on 3 factors. The lower the temperature or the higher the pressure, the greater the deviation, and the stronger the intermolecular forces of attraction between gas particles, the greater the deviation.

On a plot of pV/RT against p , the negative deviation is due to intermolecular forces between gas particles, while the positive deviation is due to the volume of the gas particles becoming significant.

5 Chemical Energetics

5.1 Enthalpy changes

The **enthalpy** of a substance (H) is a measure of the energy content of a substance.

The **enthalpy change** of a reaction (ΔH) is the amount of energy absorbed or released in a chemical reaction with respect to the number of moles of reactants or products specified.

$$\Delta H_{rxn} = \sum H_{pds} - \sum H_{rts} \quad (5.1)$$

An **endothermic reaction** is one in which $\Delta H > 0$. Energy is absorbed from the surroundings and so the temperature of the surroundings decreases. The products generally have a higher energy content than the reactants and so the products are said to be less stable than the reactants.

A very endothermic reaction is likely to proceed in the reverse direction (as the reverse reaction will be likewise very exothermic), so the products formed may be unstable and have a tendency to decompose or otherwise react to form the reactants of the forward reaction.

An **exothermic reaction** is one in which $\Delta H < 0$. Energy is released to the surroundings and so the temperature of the surroundings increases. The products generally have a lower energy content than the reactants and so are more stable than the reactants.

A very exothermic reaction may be explosive as a large amount of heat is evolved; reactions that have only solid or liquid reactants and gaseous products may also be so as there will be a great volume increase.

A reaction being exothermic indicates that the net energy absorbed in breaking bonds in the reactants is less than the net energy released in forming bonds in the products. Exothermic reactions are more thermodynamically feasible than endothermic reactions and so are more likely to occur spontaneously when initiated.

The enthalpy change of a reaction is affected by (a) the number of moles of reactants; (b) the states of reactants and products, due to latent heats of fusion and vaporisation; and (c) the temperature and pressure at which a reaction takes place.

5.1.1 Definitions

The **standard enthalpy change of reaction** ΔH^\ominus of a reaction is the amount of energy absorbed or released in the chemical reaction when molar quantities stated in the chemical equation react under standard conditions of 298 K and 1 atm.

Standard conditions, referred to by the plimsoll \ominus refers to a temperature of 298 K and pressure of 1 atm, with solutions at the concentration of 1 mol dm⁻³.

The **standard enthalpy change of combustion** ΔH_c^\ominus is the energy released when one mole of a substance is completely burnt in oxygen at 298 K and 1 atm.

The **standard enthalpy change of neutralisation** ΔH_n^\ominus is the energy released when an acid and a base react to form one mole of water at 298 K and 1 atm.

A neutralisation involving a strong acid and strong base will always have a ΔH_n^\ominus of $-57.3 \text{ kJ mol}^{-1}$. A neutralisation involving any weak acids or bases will have one that is less exothermic than that, as (a) weak acids or weak bases are only slightly dissociated in aqueous solution; (b) so some of the energy evolved from the neutralisation process is used to further dissociate the weak acid or weak base completely; and (c) this leads to a less exothermic standard enthalpy change of neutralisation.

The **standard enthalpy change of formation** ΔH_f^\ominus of a substance is the energy change when one mole of the substance is formed from its elements at 298 K and 1 atm. The ΔH_f^\ominus of elements is zero.

The **standard enthalpy change of atomisation** ΔH_{at}^\ominus of an element is the energy absorbed when one mole of gaseous atoms is formed from the element at 298 K and 1 atm.

The **standard enthalpy change of atomisation of a compound** is the energy absorbed when one mole of the gaseous compound is broken down into its constituent gaseous atoms at 298 K and 1 atm.

The **first ionisation energy** (1st IE) of an element is the energy absorbed when one mole of gaseous atoms loses one mole of electrons to form one mole of singly charged positive gaseous ions.

The **second ionisation energy** (2nd IE) of an element is the energy absorbed when one mole of singly charged positive gaseous ions loses one mole of electrons to form one mole of doubly charged positive gaseous ions.

The **first electron affinity** (1st EA) of an element is the energy released when one mole of gaseous atoms gains one mole of electrons to form one mole of singly charged negative gaseous ions. The 1st EA is always exothermic as the energy released when the nucleus attracts an electron is greater than the energy absorbed to overcome inter-electron repulsion.

The **second electron affinity** (2nd EA) of an element is the energy absorbed when one mole of singly charged negative gaseous ions gain one mole of electrons to form one mole of doubly charged negative gaseous ions. The 2nd EA is always endothermic as an electron is added to a negative ion; energy is needed to overcome the repulsion between the two negatively charged species.

The **lattice energy** $\Delta H_{\text{latt}}^{\ominus}$ of an ionic compound is the energy released when one mole of the ionic compound is formed from its constituent gaseous ions at 298 K and 1 atm.

The **bond energy** BE of an X–Y bond is the average energy absorbed when one mole of X–Y bonds in the gaseous state is broken in the gaseous state to form X and Y gaseous atoms at 298 K and 1 atm. The $\Delta H_{\text{at}}^{\ominus}$ of a non-metal element X is equal to half the bond energy of X–X.

The **standard enthalpy change of hydration** $\Delta H_{\text{hyd}}^{\ominus}$ of an ion is the energy released when one mole of the gaseous ion is hydrated at 298 K and 1 atm. $\Delta H_{\text{hyd}}^{\ominus}$ is generally directly proportional to the charge density q/r of the ion.

The **standard enthalpy change of solution** $\Delta H_{\text{sol}}^{\ominus}$ of a substance is the energy change when one mole of the substance is completely dissolved in a solvent to form an infinitely dilute solution at 298 K and 1 atm. The $\Delta H_{\text{sol}}^{\ominus}$ indicates the solubility of a substance, as it indicates the enthalpy change of the dissolution process. A more exothermic $\Delta H_{\text{sol}}^{\ominus}$ means the dissolution process of a substance is more exothermic, and thus that the substance is more soluble, and vice versa; a very positive $\Delta H_{\text{sol}}^{\ominus}$ means the substance is insoluble.

5.1.2 Calculations

Enthalpy changes can be calculated from experimental results using some equations.

The energy or heat Q absorbed or released by a substance to create a temperature change of ΔT is given by

$$Q = mc\Delta T \quad (5.2)$$

where m is the mass of the substance and c is the specific heat capacity of the substance.

When calculating enthalpy changes from experimental results, we assume that (a) there is negligible heat loss to the surroundings, as insulation is used, so any energy released or absorbed in the reactions is transformed into or from heat energy, changing the solution's temperature; (b) the density of the solution is 1.00 g cm^{-3} , which is approximately that of water; and (c) the specific heat capacity of the solution is $4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$, approximately that of water.

The enthalpy change of a reaction can be calculated from other enthalpy changes, where appropriate, using certain formulae.

If the $\Delta H_{\text{f}}^{\ominus}$ of all reactants and products are known,

$$\Delta H_{\text{rxn}}^{\ominus} = \sum \Delta H_{\text{f}}^{\ominus} \text{ p d t s} - \sum \Delta H_{\text{f}}^{\ominus} \text{ r x t s} \quad (5.3)$$

If the BE of all bonds broken and formed are known,

$$\Delta H_{\text{rxn}}^{\ominus} = \sum BE_{\text{rxts}} - \sum BE_{\text{p d t s}} \quad (5.4)$$

Calculating $\Delta H_{\text{rxn}}^{\ominus}$ using this method may produce a value that differs from the actual value as this method produces an approximation: bond energy values are only averages.

The algebraic method involves the manipulation of given equations to form equations that sum up to the equation of the desired reaction.

Hess' law involves using an alternative pathway of multiple reactions to form the same products.

5.2 Hess' Law and Born-Haber cycles

Hess' law states that the enthalpy change for a chemical reaction is the same regardless of the route by which the chemical change occurs, provided that the initial states of reactants and final states of the products are the same.

An energy level diagram is similar to an energy cycle, except that an energy level diagram shows the relative energies of reacting substances.

The **Born-Haber cycle** is a special energy cycle used to calculate lattice energies. It equates the overall enthalpy change of the atomisation of the elements in the ionic compound, the ionisation energy and electron affinity of the metal and non-metal respectively, and the lattice energy, to the enthalpy change of formation of the compound. In other words,

$$\Delta H_{\text{at}}^{\ominus} + IE + EA + \Delta H_{\text{latt}}^{\ominus} = \Delta H_{\text{f}}^{\ominus} \quad (5.5)$$

The lattice energies determined using the Born-Haber cycle are experimentally true i.e. they are accurate to reality. Lattice energies can also be theoretically determined based on the geometry of the crystal lattice, assuming a pure ionic compound is formed: ions are taken as point charges that exert electrostatic forces on their neighbours in the crystal lattice.

Lattice energies determined using theoretical models are usually in good agreement with experimental values for predominantly ionic compounds. However, for compounds with significant partial covalent character, theoretical values will tend to differ non-negligibly from the experimental values.

The standard enthalpy change of solution of an ionic compound can be determined using an energy cycle, equating the standard enthalpy change of solution to the standard enthalpy change of hydration of both ions in the substance minus the lattice energy of the ionic compound, i.e.

$$\Delta H_{\text{sol}}^{\ominus} = \Delta H_{\text{hyd}}^{\ominus} - \Delta H_{\text{latt}}^{\ominus} \quad (5.6)$$

5.2.1 Stability of compounds

A substance that has a lower enthalpy content than another substance i.e. a substance whose formation from the latter substance is exothermic is said to be energetically stable relative to the other substance.

A substance that is formed through a reaction with a high activation energy is said to be kinetically stable.

A substance can be energetically unstable but kinetically stable. This means that the substance, energetically speaking, should decompose, but the decomposition is so slow that it is negligible.

5.3 Thermodynamics

5.3.1 Entropy

Entropy is a measure of the disorder in a system.

An increase in temperature means that particles have a greater range of kinetic energies and speeds and move more randomly, so there is more disorder and more entropy.

An increase in the number of moles of liquid due to a solid melting, or an increase in that of gas due to a liquid boiling, means that there are more ways in which particles can arrange themselves i.e. particles are more randomly arranged, so there is more disorder, and thus more entropy.

When substances are mixed, there is always an increase in disorder and entropy, as there are more ways for particles to arrange themselves.

5.3.2 Gibbs free energy

A **spontaneous process** is one that can occur in a definite direction without being driven by some external force. Whether a reaction is spontaneous depends on the change in **Gibbs free energy** ΔG given by

$$\Delta G = \Delta H - T\Delta S \quad (5.7)$$

When $\Delta G < 0$, the reaction is spontaneous and feasible; when $\Delta G = 0$, the reaction is at equilibrium (and is feasible); and when $\Delta G > 0$, the reaction is not spontaneous and thus unfeasible.

Since ΔG depends on temperature, the spontaneity of a reaction also depends on temperature. When

- $\Delta H > 0$ and $\Delta S > 0$, $T\Delta S > \Delta H \Rightarrow \Delta G < 0$ at high $T \Rightarrow$ reaction is spontaneous and feasible at high T , v.v.
- $\Delta H < 0$ and $\Delta S < 0$, $T\Delta S > \Delta H \Rightarrow \Delta G < 0$ at low $T \Rightarrow$ reaction is spontaneous and feasible at low T , v.v.
- $\Delta H > 0$ and $\Delta S < 0$, $T\Delta S < \Delta H \Rightarrow \Delta G > 0 \forall T \Rightarrow$ reaction is not spontaneous nor feasible $\forall T$.
- $\Delta H < 0$ and $\Delta S > 0$, $T\Delta S > \Delta H \Rightarrow \Delta G < 0 \forall T \Rightarrow$ reaction is spontaneous and feasible $\forall T$.

Some reactions may not take place even if they are thermodynamically feasible i.e. $\Delta G < 0$ as their activation

energy may be too high for the reaction to occur at an appreciable rate.

6 Electrochemistry

6.1 Oxidation states

The **oxidation state** is an indicator of the degree of oxidation of an atom in a chemical compound. It is the hypothetical charge that an atom would have if all bonds to atoms of other elements were fully ionic. Oxidation states are integers, but some compounds may have elements with fractional average oxidation states e.g. iron(II,III) oxide (Fe_3O_4) where some iron atoms are in +2 state and others are in +3 state.

Oxidation states are assigned based on certain rules, such that **(a)** the oxidation state of a free element is zero; **(b)** for a monatomic ion, the oxidation state is equal to the net charge on the ion; **(c)** hydrogen has an oxidation state of 1 and oxygen has an oxidation state of -2 when they are present in most compound, except that hydrogen has an oxidation state of -1 in hydrides of active metals, e.g. LiH , and oxygen has an oxidation state of -1 in peroxides, e.g. H_2O_2 ; **(d)** the algebraic sum of oxidation states of all atoms in a neutral molecule must be zero, or in ions, equal to the charge on the ion; and **(e)** the less electronegative atom has the positive oxidation number.

6.2 Redox processes

Oxidation occurs when the oxidation number of an element increases. It occurs (generally) when an atom loses electrons or hydrogen, or gains oxygen. An **oxidising agent** is a substance that oxidises some other substance while itself being reduced; in redox reactions, it acts as an electron acceptor.

Conversely, **reduction** occurs when the oxidation number of an element decreases. It occurs (generally) when an atom gains electrons or hydrogen, or loses oxygen. A **reducing agent** is a substance that reduces some other substance while itself being oxidised; in redox reactions, it acts as an electron donor.

A **redox reaction** is one in which oxidation and reduction occurs at the same time. Electrons are always transferred from the reducing agent to the oxidising agent. **Disproportionation** is a redox reaction in which the same element in the same reactant is both oxidised and reduced simultaneously.

If substance A oxidises substance B, A is said to be a stronger oxidising agent than B. B is said to be a stronger reducing agent than A (as if A oxidises B, then B has reduced A).

6.2.1 Redox titrations

MnO_4^- in an acidic medium is generally the strongest oxidising agent in the syllabus. When performing MnO_4^- titrations, the acidic medium is generally provided by sulfuric acid; acids that are easily oxidisable (e.g. HCl)

cannot be used as the ion will be oxidised by manganate(VII), interfering with the titration. No indicator is used during the titration, and the colour change is colourless to pale pink. When titrating iron(II), the overall colour change is green to orange (pink + yellow); the end-point colour change is yellow (at the equivalence point) to orange, due to Fe^{3+} .

Acidified $\text{Cr}_2\text{O}_7^{2-}$ is a strong O.A., but weaker than acidified MnO_4^- . When performing $\text{Cr}_2\text{O}_7^{2-}$ titrations, the acidic medium is generally provided by sulfuric acid. An indicator, diphenylamine sulfonate is used; the end-point colour change is yellow to violet blue.

Iodometric titrations are used to determine the concentration of iodine, or substances that liberate iodine from potassium iodide. Sodium thiosulfate is usually used as the oxidising agent. The overall colour change is brown (from iodine) to colourless. The end-point colour change is yellow to colourless if no indicator is used. Starch is sometimes used as an indicator. When starch is added, the solution will turn blue-black as starch forms a complex with the iodine in the solution; when all the iodine has been reduced, the solution will sharply decolourise and turn colourless. Starch is only added near the end-point as if added too early, iodine will be strongly adsorbed onto starch, and the accuracy of the end-point will be reduced.

6.3 Electrode potentials

The **standard electrode potential** E^\ominus is the reduction potential set up when an electrode is in contact with a 1 mol dm^{-3} solution of ions at 1 atm and 298 K measured relative to a standard hydrogen electrode.

E^\ominus is a measure of how reducible a species is into another species; the more positive the value, the more reducible the species. Likewise, the more negative the value, the more oxidisable the species.

E^\ominus are taken with reference to the standard hydrogen electrode (S.H.E.). The S.H.E. consists of a platinised Pt electrode in a solution containing 1 mol dm^{-3} of H^+ (aq) and H_2 gas at 1 atm and 298 K bubbled through the solution.

To determine E^\ominus of some reduction reaction:

- 1 Use standard conditions of 1 atm and 298 K, with the concentrations of all solutions at 1 mol dm^{-3} .
- 2 The standard hydrogen electrode is used as the reference electrode and the two half-cells are connected by a salt bridge.
- 3 The potential difference set up when the half-cells are connected is measured by a voltmeter, which will show the E^\ominus of that reaction.

Electrode potentials depend on the position of the equilibrium. For a given reduction reaction, any change that shifts the equilibrium towards the right, favouring reduction, will increase E^\ominus , and vice versa.

6.4 Applications of electrode potentials

The E^\ominus of a reduction reaction is an indicator of the strength of the species in the equation as oxidising or reducing agents. The more positive the E^\ominus , the stronger the reactant species is as a reducing agent; the more negative the E^\ominus , the stronger the product species is as an oxidising agent.

The E^\ominus of a reaction involving metal ions (like the Fe^{3+} and Fe^{2+} pair) can predict the stability of the ions in different media. For the case of $\text{Fe}^{3+}/\text{Fe}^{2+}$, it can be seen that $E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$ is more positive while $E^\ominus(\text{Fe}(\text{OH})_3/\text{Fe}(\text{OH})_2) = -0.56 \text{ V}$ is more negative and so Fe^{2+} is less likely to be oxidised in acid and thus is more stable than Fe^{3+} in acid, while $\text{Fe}(\text{OH})_2$ is likely to be oxidised in alkali and so is less stable than $\text{Fe}(\text{OH})_3$ in a basic medium.

The **standard cell potential** E_{cell}^\ominus given by

$$E_{\text{cell}}^\ominus = E_{\text{red}}^\ominus - E_{\text{ox}}^\ominus \quad (6.1)$$

of a reaction or electrochemical cell can determine the thermodynamic feasibility of a reaction. If E_{cell}^\ominus is positive, the reaction is feasible; if it is zero, the reaction is at equilibrium; if it is negative, the reaction is not feasible. Typically, if E_{cell}^\ominus is positive but close to zero, the extent of the forward reaction is small.

To predict what happens when two species are mixed, we can pick out reduction equations involving the species. Any pair of equations where one species is reduced and the other is oxidised and $E_{\text{cell}}^\ominus \geq 0$ will occur.

However, E_{cell}^\ominus only deals with the feasibility of a reaction; it does not predict the rate of reaction. A reaction may not occur even if $E_{\text{cell}}^\ominus > 0$ as it may be kinetically too slow due to high activation energy. Also, E_{cell}^\ominus values are only valid for standard conditions.

6.5 Electrolytic cell

An **electrolytic cell** is one in which chemical reactions take place at electrodes as a result of a direct electrical current passing through the **electrolyte**, which is a molten compound or aqueous solution. The process of using an electric current to bring about chemical change is **electrolysis**.

In an electrolytic cell, the **anode** is the positive electrode connected to the positive terminal of the battery, and the **cathode** is the negative electrode connected to the negative terminal of the battery. Cations are attracted to the cathode where reduction occurs, and anions to the anode where oxidation occurs.

At the cathode, the cation that is most easily reduced i.e. most positive E^\ominus , as in section 6.3, and at the anode, the anion (or the anode) that is most easily oxidised i.e. most negative E^\ominus , is preferentially discharged, unless a species with an E^\ominus of similar but smaller magnitude is present in much larger concentration, in which case

that species is discharged instead – this usually occurs for anions only.

Faraday's 1st law states that the mass of a substance produced at an electrode during electrolysis is directly proportional to the quantity of electricity passed.

Faraday's 2nd law states that the number of Faraday required to discharge (i.e. reduce/oxidise) one mole of an ion equals the number of charges on the ion.

Calculations on the amount of substance discharged may not be accurate due to impurities in the electrolyte leading to some current not being used to discharge substances, or fluctuations in the current during electrolysis.

6.6 Applications of electrolysis

Aluminium can be **anodised** i.e. have its oxide layer thickened through electrolysis, in order to protect the metal from corrosion. An electrolyte of $\text{H}_2\text{SO}_4(\text{aq})$ is used, with a graphite cathode and the object as the anode. At the cathode, H^+ is discharged to H_2 while at the anode, H_2O is discharged to O_2 which reacts with Al to form the oxide layer.

Copper can be purified through electrolysis. An electrolyte of $\text{CuSO}_4(\text{aq})$ is used, with the impure copper as the anode and a thin sheet of pure copper as the cathode. At the anode, Cu is oxidised to Cu^{2+} and at the cathode, Cu^{2+} is reduced to Cu, with the net result being a transfer of Cu from the impure anode to the pure cathode. Metals with $E^\ominus < E^\ominus(\text{Cu}^{2+}/\text{Cu})$ are oxidised at the anode but do not get reduced; metals with $E^\ominus > E^\ominus(\text{Cu}^{2+}/\text{Cu})$ are not oxidised and fall to the bottom of the tank as anode sludge.

6.7 Galvanic cell

A **galvanic cell** is one that produces an electromotive force as a result of chemical reactions taking place at the electrodes, converting chemical energy to electrical energy. A reaction between two half-cells will occur according to predictions explained in section 6.4.

For a galvanic cell, the polarity of the anode is negative since electrons flow away from it, and the polarity of the cathode is positive, since electrons flow towards it.

6.8 Applications of galvanic cells

Galvanic cells tend to be used as batteries. **Primary cells** are electrochemical cells in which redox reactions are spontaneous but irreversible and so they cannot be recharged; **secondary cells** are cells in which the reactions are reversible and so can be recharged.

A fuel cell consists of a fuel like H_2 that is oxidised by an oxidant e.g. O_2 , with the energy produced converted to electrical energy. Reactants are continuously replaced as they are consumed and the products are continuously removed.

A common fuel cell is the $\text{H}_2\text{-O}_2$ fuel cell. Porous graphite electrodes are used in an electrolyte of HCl

or H_2SO_4 , or hot KOH or NaOH. At the anode, hydrogen is oxidised and at the cathode, oxygen is reduced, with the overall reaction being that of the formation of water.

Benefits of fuel cells include them being pollution free, having high power-to-mass ratios, and being highly efficient. However, they tend to be expensive due to the Ni and Pt used as catalysts (that are also easily poisoned due to impurities in the fuels), and the high temperatures required for the reaction to take place.

7 Equilibria

An **irreversible reaction** is a chemical reaction that proceeds to completion. A **reversible reaction** is a reaction in which the forward and backward reactions both occur.

Reversible reactions never reach equilibrium, but instead they reach dynamic equilibrium, which is when the rate of the forward reaction equals the rate of the backward reaction. At dynamic equilibrium, substances are still reacting together although the concentration of products and reactants remain constant.

7.1 Equilibrium constants

An **equilibrium constant** K_c is the value of the reaction quotient when the reaction has reached equilibrium. The **reaction quotient** is the product of the concentrations of the products raised to the power of their stoichiometric coefficients, over a similar product of the concentrations of the reactants.

When writing expressions for the equilibrium constant, solid substances, as well as any water acting as a solvent (i.e. there are substances in aqueous state), are omitted.

The equilibrium constant can also be written in terms of the partial pressures of reactants, in which case it is denoted K_p .

Equilibrium constants are affected by temperature. If the reaction is exothermic, then it varies inversely with temperature; if the reaction is endothermic, then it varies directly with temperature.

The **degree of dissociation** of a substance is the quotient of the number of moles of that substance that has dissociated over the initial number of moles of that substance.

7.2 Factors affecting chemical equilibria

Le Chatelier's principle states that when a system in equilibrium is subjected to a change or stress that disturbs the equilibrium, the system will react in a way so as to counteract the effect of the change or stress.

If the concentration of a product or reactant is changed, by Le Chatelier's principle, **(a)** the equilibrium position will shift left or right to increase or decrease the concentration of that substance; **(b)** the concentration of that substance increases or decreases towards the original

value until a new equilibrium is attained; and (c) the new equilibrium mixture will contain more products/reactants and less reactants/products.

If the pressure is changed, the system will try to change the pressure towards the original value. By Le Chatelier's principle, (a) the equilibrium position shifts left or right in the direction towards a *reduction or increase* in the total number of moles of gas; (b) *increasing or decreasing* pressure; and (c) the new equilibrium mixture will contain more products/reactants and less reactants/products. If there are the same total number of moles of gas for the reactants and products, then pressure will not affect the equilibrium composition or position.

If the temperature is changed, the system will try to remove or produce heat to shift temperature towards the original value. By Le Chatelier's principle, (a) the equilibrium position shifts left or right towards the exothermic or endothermic reaction to release or absorb heat; and (b) the new equilibrium mixture will contain more products/reactants and less reactants/products. The equilibrium constant varies with temperature.

Catalysts increase the rate of forward and backward reaction to the same extent so the position of the equilibrium remains unchanged, but as the rate of reaction increases, equilibrium is reached more quickly.

Le Chatelier's principle can be applied to the Haber process. The **Haber process** is a process for the manufacture of ammonia from nitrogen and hydrogen, which is an exothermic process.

Usually, the Haber process takes place under a high pressure of 250 atm and moderate temperature of 450 °C, in the presence of finely divided iron catalyst and with nitrogen and hydrogen in the ratio 1 : 3.

By Le Chatelier's principle, (a) an increase in pressure will cause the equilibrium position to shift right towards a reduction in the number of moles to decrease pressure, increasing yield of ammonia; and (b) an increase in temperature will cause the equilibrium position to shift right towards the exothermic reaction to release heat, increasing yield of ammonia.

However, too high a pressure would be too expensive to maintain, as thicker pipes need to be built to withstand higher pressure. Thus, a pressure of 250 atm is used. Too low a temperature would decrease the rate of reaction until it is too low, so a moderate temperature of 450 °C is used. There is a compromise between the conflicting demands of high yield and high rate of reaction.

The iron catalyst is used to increase the rate of reaction; it does not affect the yield of ammonia.

7.3 Brønsted-Lowry Theory of Acids and Bases

An **acid** is a substance that can donate a proton to another substance in solution. Conversely, a **base** is a sub-

stance that can accept a proton from another substance in solution. A **Brønsted-Lowry reaction** involves the transfer of a proton from the acid, which is a proton donor, to the base, which is a proton acceptor.

The **conjugate base** of a substance is the result of removing a proton from the substance; the **conjugate acid** of a substance is thus the result of adding a proton to the substance.

A **strong acid** or **base** is one that dissociates fully in solution to give protons or hydroxide ions respectively.

A **weak acid** or **base** is one that dissociates partially in solution to give protons or hydroxide ions respectively.

7.4 Acid and base equilibria

Pure water can **self-ionise**, where one water molecule donates a proton to another water molecule. There is thus a small degree of dissociation of pure water. This reaction is endothermic.

The ionic product of water at equilibrium is known as the water dissociation constant K_w . At 25 °C, $K_w = 10 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$; K_w increases with temperature.

The power of hydrogen pH of a solution is the negative base-10 logarithm of the concentration of hydrogen ions in solution in mol dm^{-3} . The pOH of a solution is similarly defined.

Due to the laws of logarithm, the following relationship arises:

$$\text{p}K_w = \text{pH} + \text{pOH} \quad (7.1)$$

A solution is said to be **neutral** when $[\text{H}^+] = [\text{OH}^-]$, **acidic** when $[\text{H}^+] > [\text{OH}^-]$, and **basic** when $[\text{H}^+] < [\text{OH}^-]$.

To calculate the pH of a strong acid, find the $[\text{H}^+]$ and from that the pH. When the concentration of protons from the acid is below $10 \times 10^{-5} \text{ mol dm}^{-3}$, the hydrogen ions ($10 \times 10^{-7} \text{ mol dm}^{-3}$) produced by water dissociation should be taken into account. This is done likewise for a base, and then calculating the pH from the pOH.

All acids have an acid dissociation constant K_a that measures its strength, given by

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (7.2)$$

For strong acids, the K_a is more than that of the hydrogen ion i.e. more than about 54.95. The larger the K_a , the stronger the acid.

Bases likewise have a base dissociation constant K_b , given by

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \quad (7.3)$$

The larger the K_b , the stronger the base.

The concentration of H^+ produced by a weak acid and

of OH^- by a weak base in solution are approximated by

$$[\text{H}^+] \approx \sqrt{[\text{HA}] \times K_a} \quad (7.4)$$

$$[\text{OH}^-] \approx \sqrt{[\text{B}] \times K_b} \quad (7.5)$$

Considering the expressions for K_w , K_a and K_b , the following relationship can be derived:

$$K_w = K_a K_b \quad (7.6)$$

where K_a is the dissociation constant of an acid and K_b is that of its conjugate base, or vice versa.

The conjugate base of a strong acid can be considered to be neutral, while that of a weak acid will be weakly basic as well. The same applies to bases.

7.5 Buffers

A **buffer solution** is one that is capable of maintaining a fairly constant pH when small amounts of acid or base are added to it.

An **acidic buffer** contains a weak acid and the salt of its conjugate base, while a **basic buffer** contains a weak base and the salt of its conjugate acid.

A buffer solution is most effective in resisting pH change when the concentration of the acid or base equals the concentration of its conjugate. This is known as **maximum buffer capacity**, which occurs when

$$\text{pH} = \text{p}K_a \vee \text{pOH} = \text{p}K_b$$

The pH of a buffer system can be calculated by

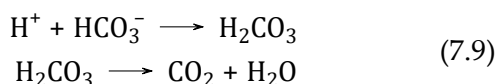
$$\text{pH} = \text{p}K_a + \lg \frac{[\text{A}^-]}{[\text{HA}]} \quad (7.7)$$

$$\text{pOH} = \text{p}K_b + \lg \frac{[\text{BH}^+]}{[\text{B}]} \quad (7.8)$$

A buffer works by removing any H^+ or OH^- added. When a small amount of acid, H^+ , is added, the added H^+ is removed as $[\text{H}^+]$ is only slightly changed and so pH remains fairly constant. When a small amount of base, OH^- , is added, the added OH^- is removed as $[\text{OH}^-]$ is only slightly changed and so pH remains fairly constant.

pH in blood is maintained by the $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ buffer pair.

When there is excess acid in the blood,



Excess acid in the blood reacts with the hydrogencarbonate ion to form carbonic acid, which then decomposes into water and carbon dioxide, which is exhaled.

When there is too little acid present,



By Le Chatelier's principle, the equilibrium position shifts right, causing an increase in $[\text{H}^+]$.

7.6 Acid-base titrations

An acid can be titrated against a base, or vice versa. The substance in the conical flask is titrated against the substance in the burette, or the substance in the burette is titrated into the substance in the flask.

The **equivalence point** of a titration is the theoretical point when stoichiometric amounts of the acid and base have reacted. There is usually a rapid pH change over this point.

The **endpoint** of a titration is the point where the indicator used changes colour. Any indicator selected should have a pH transition range that lies within the rapid change over the equivalence point.

A **titration curve** is simply a graph of pH against volume of titrant added.

Most titrations have only one equivalence point. However, titrations involving weak acids or bases that are polyprotic will have the same number of equivalence points as the number of protons that the acid or base can donate or accept.

For a titration with a weak acid or base, at the each equivalence point, the main species contributing to pH or pOH is the conjugate base or acid of the previous main species (or the weak acid or base itself).

For a titration of a weak diprotic acid with a strong base, at the first equivalence point,

$$\text{pH} \approx \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2}) \quad (7.11)$$

The endpoint of a weak base-strong acid or strong base-weak acid titration is acidic or basic respectively, due to salt hydrolysis causing $[\text{H}^+] > [\text{OH}^-]$ or $[\text{OH}^-] > [\text{H}^+]$ respectively.

7.7 Salt solubility

Soluble salts dissociate completely in solution into their constituent ions, but sparingly soluble salts dissociate only partially.

The **solubility product** is an equilibrium constant that is the product of the molar concentrations of the dissolved dissociated ions, each raised to their appropriate powers, in a saturated solution of the salt at a given temperature.

Solubility is a concentration term that refers to the maximum amount of solute that can be dissolved per dm^3 of solvent to make a saturated solution at a given temperature.

Common ion effect occurs when the solubility of a sparingly soluble salt is decreased in the presence of a common ion from an external source.

When a common ion is added, due to common ion effect, by Le Chatelier's principle, equilibrium position shifts left to decrease the concentration of the common ion. The solubility of the salt will be decreased.

The **ionic product** is a product of the molar concentrations of the dissolved dissociated ions, each raised to their appropriate powers, in the solution at a given temperature. Its value may vary with situation.

When the ionic product of a salt is less than the salt's solubility product, no precipitation occurs. When the ionic product equals the solubility product, the solution is saturated; no precipitation occurs yet. When the ionic product is greater than the solubility product, precipitation of the salt occurs until the ionic product equals the solubility product.

8 Reaction Kinetics

The **rate of reaction** is the change in the concentration of reactants or products per unit time. It is the magnitude of the gradient of a concentration-time graph, and has units of $\text{mol dm}^{-3} \text{ time}^{-1}$.

There are three general types of rate of reaction.

Instantaneous rate refers to the rate of change of concentration of a reactant or product at some t , and is represented by the gradient of the tangent to a concentration-time graph at the time t .

Initial rate is the instantaneous rate of reaction at $t = 0$.

Average rate refers to the change in concentration of a reactant or product over some time interval. It is represented by the gradient of the line connecting the two points on the concentration-time graph at the start and end of the time interval.

8.1 Rate equations and orders of reaction

The **rate equation** relates the rate of reaction to the concentration of reactants raised to some indices. It takes the form of $\text{rate} = k[A]^m[B]^n$, where k is a rate constant.

The **rate constant** k , a proportionality constant, is given by

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

where A is the Arrhenius constant, E_a is the activation energy of the reaction, R is the molar gas constant, and T is the temperature. For a reaction with overall order n , it has units of $\text{mol}^{1-n} \text{ dm}^{3n-3} \text{ s}^{-1}$.

A , the **Arrhenius constant**, is generally seen as the total number of collisions that occur (both effective and non-effective collisions) per unit time.

The **order of reaction** with respect to $[A]$ and $[B]$ are m and n respectively. It is the index to which the concentration of a reactant is raised in the rate equation, and must be experimentally determined.

The **overall order of reaction** is the sum of all the individual orders of reactions in the rate equation.

The **half-life** of a reaction ($t_{1/2}$) is the time taken for $[\text{reactant}]$ to decrease to half its original value.

A reaction that is zero-order with respect to a reactant will have its rate of reaction independent of the concen-

tration of that reactant. For such a reaction, **(a)** a rate-molarity graph will be a horizontal line at $\text{rate} = k$; and **(b)** a molarity-time graph will be a downward-sloping straight line with gradient $-k$.

A reaction that is first-order with respect to a reactant will have its rate of reaction directly proportional to the concentration of that reactant. For such a reaction, **(a)** a rate-molarity graph will be a straight line passing through the origin with positive gradient k ; and **(b)** a molarity-time graph will be a decreasing exponential graph that shows a constant half-life. The half-life of the reaction with respect to the reactant is given as

$$t_{1/2} = \frac{\ln 2}{k} \quad (8.1)$$

and the concentration of the reactant at any time t

$$[\text{reactant}] = \left(\frac{1}{2}\right)^{t/t_{1/2}} [\text{reactant}]_0 \quad (8.2)$$

A reaction that is second-order with respect to a reactant will have its rate of reaction directly proportional to the square of the concentration of that reactant. For such a reaction, **(a)** a rate-molarity graph will be a quadratic curve; and **(b)** a molarity-time graph will be a decreasing curve without a constant half-life.

A reaction with overall order of reaction greater than 1 can become a pseudo first-order reaction if all reactants except one that the reaction is first-order with respect to are present in large excess. This works as reactants that are present in large excess will exhibit negligible changes in concentration as the reaction progresses, so their concentrations remain effectively constant.

To find the order of reaction with respect to a reactant based on experimental concentration data, compare two experiments that differ only in the concentration of the reactant and possibly other reactants for which the order of reaction is known.

To find the order of reaction with respect to a reactant based on a molarity-time graph, **(a)** for the reactant on the y-axis, look at the half-life of the reaction; and **(b)** for any reactants for which multiple graphs are drawn for different concentrations, look at and compare the initial rate of reactions of two suitable graphs.

8.2 Activation energy and reaction mechanisms

Collision theory states that chemical reactions only occur if there are effective collisions, which occur when **(a)** reactant particles collide with energy greater than the activation energy E_a ; and **(b)** reactant particles collide with the correct orientation.

The rate of reaction is directly proportional to the frequency of effective collisions.

The **activation energy** (E_a) is the minimum amount of energy that molecular collisions must possess for a chemical reaction to occur. It is used mainly to break bonds in reacting particles, and overcome repulsive

forces present when reactant molecules are close to one another (steric repulsion).

A **Maxwell-Boltzmann distribution** curve shows the number of particles with a specific amount of energy at a given temperature. An activation energy is represented by a vertical line at $E = E_a$. The area under the graph to the right of the line gives the number of particles with energy greater than or equal to E_a .

For all chemical reactions, reactants form a transition state before forming products. Only reactant particles with at least the activation energy can attain the transition state before products are formed. The transition state is indicated on an energy profile diagram by the peak between the reactants and products.

An **elementary reaction** is a reaction with a single step. An energy profile diagram of such a reaction would show only one transition state. For elementary reactions, the orders of reaction correspond to the stoichiometric coefficients in the reaction equation. Since each step in a non-elementary reaction is an elementary reaction, this applies likewise.

A **non-elementary reaction** is a reaction with more than one step. An energy profile diagram of such a reaction would show a number of peaks corresponding to the number of steps. The slow step of the reaction would have the highest activation energy. For non-elementary reactions, the overall rate equation is the rate equation of the slow step, also known as the rate-determining step.

Reactions involving more than two molecules are usually not elementary reactions as it is very unlikely for three molecules to collide with the correct orientations with energy greater than the activation energy for the reaction to occur in a single step.

8.3 Factors affecting rate of reaction

The concentration of reactants affects the rate of reaction as **(a)** when concentration is increased, the number of reactant particles per unit volume increases; **(b)** frequency of effective collisions thus increases; and **(c)** since rate of reaction is proportional to the frequency of effective collisions, rate of reaction increases.

The pressure of gaseous reactants affects the rate of reaction as (similar to concentration) **(a)** when pressure is increased, gaseous reactant particles are brought closer together; **(b)** number of gaseous reactant particles per unit volume increases; and **(c)** frequency

The temperature of reactants affects the rate of reaction as **(a)** when temperature is increased, the Maxwell-Boltzmann curve is skewed to the right; **(b)** since the area under the curve is proportional to the number of reactant particles, the number of reactant particles with $E \geq E_a$ increases; and **(c)** frequency By increasing temperature, the rate constant k is increased.

The surface area of reactants affects the rate of reaction

as **(a)** when surface area is increased, there is a larger accessible area for collision since a larger total surface area is exposed; and **(b)** frequency Increasing the surface area increases A (the Arrhenius constant), in turn increasing k .

The level of light received by a photochemical reaction affects the rate of reaction as **(a)** when light intensity in a photochemical reaction is increased, amount of light energy absorbed by reactant particles increases;; **(b)** number of reactant particles with $E \geq E_a$ increases; and **(c)** frequency

8.4 Catalysts

A **catalyst** is a substance that increases the rate of reaction by providing an alternative reaction pathway with lower activation energy while remaining chemically unchanged at the end of the reaction. It increases the rate of reaction as **(a)** a catalyst provides an alternative reaction pathway with lower activation energy; **(b)** thus when a catalyst is used the number of reactant particles with $E \geq E_a$ increases; and **(c)** frequency By decreasing the E_a , the rate constant k of a reaction is increased. The energy profile diagram of a catalysed reaction has a lower peak than the same uncatalysed one.

8.4.1 Autocatalysis

An **autocatalyst** is a catalyst that is one of the products of the chemical reaction itself; it carries out its catalytic action as soon as it is formed in the reaction. E.g. $2 \text{MnO}_4^- + 5 \text{C}_2\text{O}_4^{2-}(\text{aq}) + 16 \text{H}^+(\text{aq}) \rightarrow 2 \text{Mn}^{2+}(\text{aq}) + 10 \text{CO}_2(\text{g}) + 8 \text{H}_2\text{O}(\text{l})$. The Mn^{2+} ion acts as the autocatalyst. At the beginning of the reaction, the rate of reaction is initially low as the autocatalyst Mn^{2+} has not been produced yet. As the reaction proceeds, the rate of reaction increases sharply as the autocatalyst Mn^{2+} has been produced; the rate of reaction will eventually peak out. Towards the end of the reaction, the rate of reaction decreases as the concentration of reactants begins to decrease to low levels; near the end, the rate is relatively constant as $[\text{Mn}^{2+}]$ is effectively constant and the concentration of reactants is very low.

8.4.2 Homogeneous catalysis

A **homogeneous catalyst** is a catalyst that is in the same physical state as the reactants. They provide an alternative reaction pathway by forming an intermediate that is then consumed to form the products, and are regenerated at the end of the reaction. E.g. $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2 \text{I}^-(\text{aq}) \rightarrow 2 \text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$ with catalyst $\text{Fe}^{3+}(\text{aq})$.

8.4.3 Heterogeneous catalysis

A **heterogeneous catalyst** is a catalyst that is not in the same physical state as the reactants. They provide an alternative reaction pathway by increasing the local concentration of the reactant particles on the catalyst surface as well as weakening the chemical bonds in

the reactants for reaction. E.g. Haber process; $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ with catalyst $\text{Fe}(\text{s})$.

8.4.4 Enzymatic catalysis

Enzymes are specialised globular proteins that increase the rate of biological reactions by providing an alternative reaction pathway of lower activation energy. Enzymes are highly specific i.e. they act only on certain substrates. They have enormous catalytic power but only at specific optimal pH and temperatures.

According to the **Michaelis-Menten theory**, enzymes catalyse reactions by combining with the reactants (substrates) to form enzyme-substrate complexes. The complexes then break down to form the free enzyme and the products.

Substrates must have the right shape to fit into the active sites of enzyme molecules to form the E-S complex; this is why they are highly specific. When all active sites are occupied by substrate molecules, the enzyme is said to be saturated.

For enzyme-catalysed reactions, the rate of reaction reaches a limit once reactant concentration reaches a certain level, as the enzyme becomes saturated. At low [substrate], the rate of reaction increases linearly with [substrate], and rate is proportional to [substrate] as active sites are not fully occupied; reaction is approximately 1st order w.r.t. [substrate]. As [substrate] increases, the rate of reaction increases to a lesser extent and rate is no longer proportional to [substrate] as more active sites begin to be occupied; reaction is mixed order w.r.t. [substrate]. At high [substrate], the rate of reaction is constant and independent of [substrate] as all active sites are occupied and the enzyme is saturated; reaction is zero-order w.r.t. [substrate].

9 Inorganic Chemistry

9.1 Chemical Periodicity

The **periodic table** is an arrangement of elements in order of increasing atomic number. Generally, the properties of elements are a periodic function of the atomic number.

A **group** refers to a vertical column in the table. The traditional group numbers (i.e. group I, II, etc.) show the number of valence electrons an atom of each element has. As a result, elements within the same group generally have similar chemical properties.

A **period** refers to a row in the table. The period number refers to the number of electron shells an atom of each element possesses.

9.1.1 Trends of period 3 elements

Atomic radius tends to decrease across periods, as (a) across a single period, electrons are added to the same valence shell; (b) the increase in nuclear charge

outweighs the negligible increase in shielding effect, so effective nuclear charge increases; and (c) thus there is stronger electrostatic attraction between the nucleus and valence electrons, so valence electrons are closer to the nucleus.

Atomic and ionic radius tends to increase down the group, as (a) down the group, there is an increasing number of quantum electron shells; (b) valence electrons are further away from the nucleus and experience more shielding by inner shells; and (c) thus there is weaker electrostatic attraction between the nucleus and valence electrons, so valence electrons are further from the nucleus.

For an element that forms a cation, its ionic radius is always smaller than its atomic radius, as (a) the cation has one less electron shell occupied than the neutral atom; (b) the nuclear charge of the nucleus stays the same, as the number of protons does not change; and (c) thus there is stronger electrostatic attraction between the nucleus and the cation's valence electrons, so the cation's valence electrons are closer to the nucleus.

For an element that forms an anion, its ionic radius is always larger than its atomic radius, as (a) the anion has more electrons in its valence shell than in the neutral atom, so the extent of repulsion between valence electrons is greater; (b) the nuclear charge of the anion stays the same, as the number of protons does not change; and (c) thus there is weaker electrostatic attraction between the nucleus and the anion's valence electrons, so the anion's valence electrons are further from the nucleus.

In an isoelectronic series of ions, the ionic radius decreases as the atomic number increases, as (a) the cations/anions are isoelectronic but; (b) the nuclear charge increases while screening effect is approximately constant as they have the same number of quantum electron shells; and (c) so the same number of electrons thus experiences stronger electrostatic attraction to the more positively charged nucleus, thus the valence electrons are closer to the nucleus. There is generally a sharp increase in ionic radius from group IV elements to group V elements as the anions have one more quantum electron shell occupied.

Electronegativity tends to increase across periods as (a) the increase in nuclear charge outweighs the negligible change in screening effect, so effective nuclear charge increases across the period; and (b) there is stronger electrostatic attraction between the nucleus and valence electrons, thus electron-attracting power of the atom increases.

Electronegativity tends to decrease down groups as (a) there is an increasing number of quantum electron shells, so the valence electrons are further away from the nucleus and better shielded by inner quantum electron shells; and (b) there is weaker electrostatic attraction

tion between the nucleus and valence electrons, so electron-attracting power of the atom decreases.

Melting point generally increases from group I to III, peaks at group IV, and then decreases, as **(a)** elements in group I to III have giant metallic structures; a large amount of energy is required to overcome the strong electrostatic attraction between the cations and the sea of delocalised electrons, leading to a high melting point; **(b)** the element in group IV has a giant molecular structure; a very large amount of energy is required to overcome the strong and extensive covalent bonding between atoms in a giant three-dimensional structure, leading to a very high melting point; and **(c)** elements in group V to 0 have simple molecular structures; a small amount of energy is required to overcome the weak van der Waals' attraction between molecules (or atoms, for group 0), leading to a low melting point.

Melting point generally increases from group I to III as **(a)** the number of valence electrons contributed per atom increases; **(b)** the ionic radius decreases while the ionic charge increases, so ionic charge density increases; and **(c)** so there is stronger electrostatic attraction between the metal cations and the sea of delocalised electrons requiring more energy to overcome, leading to a higher melting point.

Melting point generally decreases from group V to 0 in period 3 (P to Ar) as **(a)** the strength of van der Waals' attraction is proportional to the size of the electron cloud; **(b)** from P to Ar, the size of the element's electron cloud decreases (S_8 to P_4 to Cl_2 to Ar), so the extent of intermolecular van der Waals' attraction decreases; and **(c)** less energy is required to overcome the less extensive intermolecular van der Waals' attraction, so melting point decreases.

Electrical conductivity generally increases from group I to III and then decreases from group IV onwards as **(a)** from group I to III, the elements are metals, which are good conductors of electricity due to the sea of delocalised electrons present in their giant metallic lattice structure acting as charge carriers. Electrical conductivity increases as more valence electrons are contributed per atom from group I to III; **(b)** at group IV, the conductivity drops as metalloids are poor conductors of electricity; and **(c)** group V onward elements do not conduct electricity as there are no free mobile ions or delocalised electrons in their simple molecular structures to act as charge carriers.

Period 3 elements generally form oxides with oxidation states equal to their respective group numbers. However, P, S, and Cl can form oxides with oxidation number +3 (P_4O_6), +4 (SO_2), and +1 (Cl_2O) respectively.

Elements up to group V in period 3 generally form chlorides with oxidation states equal to their respective group numbers. However, P can form a chloride with oxidation state +3 (PCl_3), and S forms oxides with

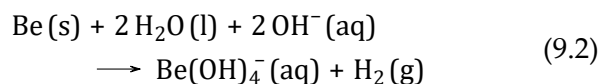
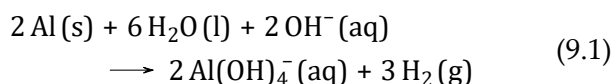
oxidation states +1 (S_2Cl_2) and +2 (SCl_2). Chlorine forms a rather obvious chloride.

Elements in period 3 form typical hydrides (for Na to Al) or hydrogen compounds (for the rest).

Generally, elements can attain up to oxidation states with the same numerical value as their group number.

Some elements have similar physical and chemical properties with those diagonally next to it. When this occurs, this is known as a **diagonal relationship**. Diagonal relationships occur due to similar charge densities.

Examples of diagonal relationships include **(a)** $LiNO_3$ decomposing in the same way as $Mg(NO_3)_2$; **(b)** Be and Al both dissolving in alkali; $BeCl_2$ and $AlCl_3$ both being covalent; **(c)** $Be(OH)_2$ and $Al(OH)_3$, and BeO and Al_2O_3 , all being amphoteric; and **(d)** Be and Al both reacting with alkalis, liberating hydrogen.



9.1.2 Trends of period 3 oxides

The melting point of period 3 oxides increases from Na_2O to MgO and decreases thereafter, as **(a)** Na_2O , MgO and Al_2O_3 have giant ionic lattice structures; a large amount of energy is required to overcome strong electrostatic forces of attraction between the oppositely charged ions, leading to a high melting point; **(b)** SiO_2 has a giant molecular structure; a large amount of energy is required to overcome the strong and extensive covalent bonding between atoms in a giant 3-dimensional molecular structure, leading to a high melting point; and **(c)** P_4O_{10} , SO_2 , SO_3 and Cl_2O_7 have simple molecular structures; a small amount of energy is required to overcome the weak van der Waals' attraction between simple molecules, leading to a low melting point.

The melting point of Na_2O is lower than that of MgO because the lattice energy of MgO is higher.

The melting point of MgO is higher than that of Al_2O_3 because Al^{3+} has a very high charge density, so it is able to polarise the anion O^{2-} 's electron cloud to a large extent, inducing partial covalent character, so Al_2O_3 has slightly weaker ionic bonds than MgO leading to MgO having a higher melting point.

9.1.3 Trends of period 3 chlorides

The melting point of period 3 chlorides decreases from $NaCl$ to $SiCl_4$, increases to PCl_5 , and decreases to S_2Cl_2 , as **(a)** $NaCl$ and $MgCl_2$ both have giant ionic lattice structures; they need a large amount of energy to overcome the strong electrostatic attraction between oppositely charged ions, thus a high melting point; and **(b)** Al_2Cl_6 , $SiCl_4$, PCl_5 , S_2Cl_2 , and Cl_2 all have simple molecular

structures; they require only a small amount of energy to overcome weak van der Waals' attraction and so have low melting points. (At r.t.p., PCl_5 exists as an ionic solid of $\text{PCl}_4^+\text{PCl}_6^-$, leading to its higher than expected melting point.)

MgCl_2 has a lower melting point than expected it because of covalent character due to Mg^{2+} 's high charge density.

9.2 Group II

Group II elements are the alkali earth metals. They are silvery-white, soft, and easily oxidised in air.

As with all other groups, down the group, their atomic and ionic radii increase, and their first ionisation energy, electronegativity and melting point decrease.

Group II metals are very good reducing agents, and their reducing power, and thus reactivity, increases down the group, as down the group, **(a)** the ionisation energy decreases thus valence electrons are more easily lost; and **(b)** they have a greater tendency to be oxidised, thus they are stronger reducing agents.

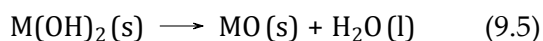
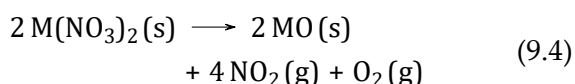
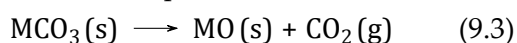
All group II metals burn with a bright flame to form basic oxides (except the amphoteric BeO). When burnt in oxygen, they produce flames of colours as in table B.7.

Group II metals generally react with water to produce hydroxides and H_2 gas, as in table B.7.

The hydroxides of Ca and Sr are sparingly soluble in water, while that of Ba is soluble in water. In general, the solubility of the hydroxides, and thus base strength, of group II metals increases down the group.

Group II oxides are basic except for BeO which is amphoteric. BeO behaves like Al_2O_3 when reacting with bases, and forms the $\text{Be}(\text{OH})_4^{2-}$ ion. The rest of the oxides are basic and react as per normal, as in table B.7.

Group II carbonates, nitrates, and hydroxides are thermally unstable and decompose on heat to form oxides.



The thermal stability of group II nitrates, carbonates and hydroxides increases down the group, as **(a)** down the group, ionic size of cation increases; **(b)** so charge density and polarising power of cation decreases; **(c)** the ability of the cation to distort the anion charge cloud and break the relevant bond decreases; and **(d)** thus thermal stability increases and decomposition temperature increases.

Group II metals have various uses.

- MgO is used as a refractory for furnace linings, and as an antacid.
- CaO , i.e. quicklime, is used as a drying agent and to reduce the acidity of soil.

- CaCO_3 , i.e. limestone, is used as building materials and in the manufacture of CaO .
- BaSO_4 is given to patients suffering from digestive disorders as it can be traced through the body by X-ray.

9.3 Group VII

Group VII elements are the halogens. All halogens exist as diatomic molecules X_2 , are nonpolar, and have simple molecular structures.

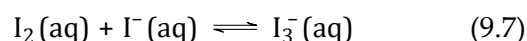
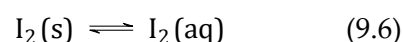
Volatility of the halogens decreases down the group, as down the group, **(a)** size of electron cloud increases; **(b)** there is a greater extent of distortion of the electron cloud; **(c)** more energy is required to overcome the more extensive intermolecular van der Waals' forces; **(d)** boiling and melting points increase; and **(e)** thus volatility decreases.

Intensity of the halogens' colour increases down the group.

Halogens are soluble in nonpolar solvents like CCl_4 as **(a)** both halogens and nonpolar solvents have simple molecular structures; and **(b)** the weak van der Waals' forces between halogen molecules are compatible with the weak van der Waals' forces between nonpolar solvent molecules.

Halogens are only slightly soluble in water as the weak van der Waals' forces between halogen molecules are not compatible with the stronger hydrogen bonds between water molecules.

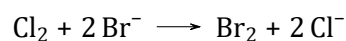
I_2 's solubility is increased in a solution of I^- in water as the brown I_3^- complex is formed:



Cl_2 , Br_2 and I_2 exhibit variable oxidation states as they all have empty and energetically accessible d orbitals enabling them to expand their octet configuration. F_2 does not as it has no energetically accessible and vacant d orbital to expand its octet configuration.

Oxidising power and reactivity of the halogens decreases down the group as down the group, **(a)** the E^\ominus values decrease; **(b)** there is a decrease in tendency to accept electrons and be reduced to X^- ; and **(c)** so oxidising power decreases.

It follows that halogens higher up in the group can displace the halide ions of halogens lower in the group out of their aqueous solutions e.g.



This can be used to detect the presence of Br^- and I^- ions in solution, by shaking an unknown with $\text{Cl}_2(\text{aq})$ then adding an organic solvent like CCl_4 . Chlorine will displace the halide forming its element, and the addition of the organic solvent will cause most of the displaced halogen to dissolve in it, with a bit left in the

water. Since water and organic solvents are immiscible, two layers of different colours will be formed, and the identity of the displaced halogen can be deduced.

The reactivity of halogens with hydrogen decreases down the group as down the group, **(a)** the total bond energy released in forming H–X decreases more significantly than the total bond energy absorbed in breaking X–X and H–H; and **(b)** thus ΔH_{rxn} becomes less exothermic and reactivity decreases.

All halogens oxidise $\text{S}_2\text{O}_3^{2-}$ but to varying degrees; Cl_2 and Br_2 oxidise it to SO_4^{2-} while I_2 only oxidises it to $\text{S}_4\text{O}_6^{2-}$. Cl_2 and Br_2 , being stronger oxidising agents, can oxidise $\text{S}_2\text{O}_3^{2-}$ all the way to SO_4^{2-} , increasing the oxidation state of S from +2 to +6 respectively. However, I_2 , being a weaker oxidising agent, can only oxidise $\text{S}_2\text{O}_3^{2-}$ to $\text{S}_4\text{O}_6^{2-}$, increasing the oxidation state of S from +2 to +2.5 only.

9.3.1 Trends of halides

HCl, HBr and HI are colourless gases with simple molecular structures.

The melting and boiling points of hydrogen halides increases down the group due to the increase in size of electron cloud

The thermal stability of hydrogen halides decreases down the group as down the group, **(a)** covalent bond length of H–X increases; **(b)** covalent bond strength decreases; and **(c)** bond dissociation energy decreases. The acid strength of hydrogen halides increases down the group as down the group, **(a)** covalent bond strength of H–X decreases; **(b)** bond dissociation energy decreases; **(c)** ease of breaking H–X increases; and **(d)** so H_3O^+ and X^- can be formed more easily.

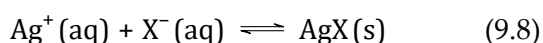
The reducing power of halides increases down the group as their E^\ominus decreases down the group.

Solubility of silver halides

An unknown halide ion can (other than being shaken with Cl_2) be identified by examining the solubility of the silver halide precipitate in dilute and concentrated NH_3 .

AgF is very soluble in pure water, while the other silver halides form precipitates.

AgCl is soluble in excess dilute ammonia, because



(a) its K_{sp} is relatively higher; **(b)** so when $\text{NH}_3(\text{aq})$ is added, it combines with $\text{Ag}^+(\text{aq})$ to form the colourless and soluble $[\text{Ag}(\text{NH}_3)_2]^+$ complex; **(c)** by Le Chatelier's principle, the position of equilibrium (9.8) shifts left; **(d)** ionic product of AgCl decreases to a value lower than its K_{sp} since the latter is relatively high; and **(e)** thus AgCl precipitate dissolves.

AgBr and AgI are insoluble in excess dilute ammonia as their K_{sp} are relatively low and their ionic products easily exceed their K_{sp} values.

When a stronger ligand like cyanide is added, AgBr will dissolve, as **(a)** CN^- is a stronger ligand than NH_3 and will form a more stable complex $[\text{Ag}(\text{CN})_2]^-$; **(b)** by Le Chatelier's principle, the equilibrium position (9.8) shifts right; **(c)** the ionic product of AgBr decreases below its K_{sp} ; and **(d)** thus AgBr dissolves.

AgCl and AgBr are soluble in excess concentrated ammonia while AgI is still insoluble.

9.4 Transition Elements

A **transition element** is a d-block element that forms at least one stable ion with partially filled *d* orbitals.

Based on the definition, Sc and Zn are not transition elements as the former forms only Sc^{3+} which has no *d* electron, while the latter forms only Zn^{2+} which has a completely filled *d* subshell.

9.4.1 Physical properties

Across the transition elements, atomic radius decreases slightly, as across the period, **(a)** nuclear charge increases but electrons are added to inner *3d* orbitals and thus provide more effective shielding of the *4s* electrons; **(b)** so the increase in nuclear charge is almost cancelled by the increase in shielding effect; **(c)** effective nuclear charge increases slightly; and **(d)** thus atomic and ionic radii decrease slightly.

This is contrasted to the period 2 and 3 elements, where across the period, **(a)** electrons are added to the same outermost quantum shell; **(b)** the increase in nuclear charge outweighs the negligible increase in shielding effect; **(c)** effective nuclear charge increases significantly; and **(d)** thus atomic and ionic radii decrease significantly

Transition metals are harder and denser than non-transition metals, as transition metals **(a)** have a relatively smaller atomic radius, and thus a more closely-packed structure; **(b)** they also have higher relative atomic mass; and **(c)** so atoms are attracted closer together, leading to higher mass per unit volume i.e. higher density.

Across the transition metals, 1st *IE* and 2nd *IE* increase slightly, as **(a)** 1st *IE* and 2nd *IE* involve the removal of *4s* electrons; **(b)** across the period, the added inner *3d* electrons provide effective shielding of outer *4s* electrons; **(c)** effective nuclear charge increases slightly; and **(d)** thus there are only small increases in 1st *IE* and 2nd *IE*.

Across the transition metals, 3rd *IE* and 4th *IE* increase rapidly, as **(a)** 3rd *IE* and 4th *IE* involve the removal of *3d* electrons; **(b)** the remaining *d* electrons provide a relatively poor shielding effect; **(c)** across the period, there is a significant increase in effective nuclear charge; and **(d)** thus there is an rapid increase in 3rd *IE* and 4th *IE*.

The 1st *IE*s of Cr and Cu are slightly lower than expected, as the removal of an outer electron results in

the attainment of a stable half-filled $3d^5$ or fully-filled $3d^{10}$ configuration, which is a favourable process, so less energy is required.

The 2nd IEs of Cr and Cu are slightly higher than expected, as the removal of an outer electron results in the disruption of the stable half-filled $3d^5$ or fully-filled $3d^{10}$ configuration, which is unfavourable, so more energy is required.

The 3rd IE of Fe is lower than expected, as inter-electron repulsion is predominant between paired d electrons in the doubly-filled d orbital, resulting in less energy needed to remove a valence electron from Fe^{2+} .

Transition metals have higher melting points and boiling points than s-block metals, as (a) they have giant metallic structures with stronger metallic bonds as both $3d$ and $4s$ electrons are involved in delocalisation; (b) melting and boiling involves overcoming the stronger electrostatic forces of attraction between the cations and the sea of delocalised electrons; (c) more energy is thus required; and (d) so they have higher melting and boiling points than typical metals.

For s-block metals, only s electrons contribute to delocalisation in metallic bonding, resulting in weaker metallic bonds.

Transition elements possess good mechanical qualities like high tensile strength, malleability and ductility, as the layers of closely-packed atoms easily slip over one another without disrupting the electrostatic attraction between cations and delocalised electrons.

Transition metals are better thermal and electrical conductors than main group metals, as both $3d$ and $4s$ electrons are available for delocalisation, so there are more of mobile electrons to act as charge carriers.

9.4.2 Chemical properties

Transition elements possess variable oxidation states as the $3d$ and $4s$ orbitals are close in energy, so a variable number of $3d$ and $4s$ electrons can be removed, forming ions of similar stability.

The highest oxidation state a transition metal can take is equal to the number of $4s$ electrons plus the number of unpaired $3d$ electrons.

Negative E^\ominus values for Ti, V and Cr indicate that reduction is less feasible, so $M^{3+}(aq)$ is more stable than $M^{2+}(aq)$. $M^{2+}(aq)$ would be easily oxidised, so M^{2+} is a good reducing agent.

Positive E^\ominus values for Mn to Cu indicate that reduction is more feasible, so $M^{2+}(aq)$ is more stable than $M^{3+}(aq)$. $M^{3+}(aq)$ would be easily reduced, so $M^{3+}(aq)$ is a good oxidising agent.

Mn^{2+} is more stable than Mn^{3+} as the removal of a third electron from Mn is more difficult due to disruption of the stable half-filled $3d^5$ configuration, so oxidation is less likely to occur and E^\ominus is more positive than expected.

Another anomaly is Fe^{3+} being more stable than Fe^{2+} , which occurs as the removal of third electron is easier due to inter-electron repulsion between d electrons in the doubly-filled d orbitals in Fe^{2+} , so oxidation is more likely to occur and E^\ominus is less positive than expected.

9.4.3 Complex formation

A **complex ion** is an ion containing a central metal atom or ion closely surrounded by ions or molecules, called ligands, bonded through dative bonds.

A **ligand** is a molecule or anion which contains at least one lone pair of electrons available for forming dative bonds with a central metal atom or ion.

The **coordination number** is the number of dative bonds that each central metal atom or ion can form with its ligands.

A monodentate ligand forms only one dative bond per ligand, a bidentate ligand forms two, a hexadentate ligand forms six, and so on.

Complexes with coordination number 2 are linear; those with 4 are tetrahedral or sometimes square planar, and those with 6 are octahedral.

9.4.4 Colour of complexes

Transition metal complexes are usually coloured.

Explanation

A transition metal complex has partially filled d orbitals. When ligands approach the central metal atom/ion for dative bonding, repulsion causes the d orbitals to be split into two groups; this effect is known as d orbital splitting.

A lower energy d electron can undergo $d-d$ transition and be promoted to an available higher energy d orbital. During the transition, the d electron absorbs a certain wavelength of light from the visible region of the electromagnetic spectrum. The remaining wavelengths not absorbed appears as the colour of the complex.

$3d^0$ and $3d^{10}$ complexes give colourless solutions or white solids as there is either no lower energy d electron to be promoted, or there is no available higher energy d orbital to accommodate d electron promotion.

Factors affecting colour

The colour of a complex or compound depends on the splitting energy ΔE , which in turn depends on several factors.

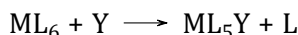
- As the oxidation state of the metal increases, the splitting energy also increases.
- The shape of the complex results in different groupings of orbitals, also affecting the splitting energy.
- Different ligands split the energy levels to different extents. Weak-field ligands result in small splitting energies while strong-field ligands result in large splitting energies.

Differences in colour between complexes can be explained by comparing their splitting energy, the wavelength absorbed, and the wavelengths that are not absorbed.

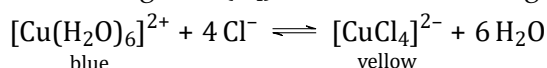
9.4.5 Ligand exchange and stability

A stronger ligand can replace a weaker ligand from a cation complex through **ligand exchange**.

For example, if ligand Y is a stronger ligand than L, then ML_5Y is more stable than ML_6 , and the following reaction occurs.

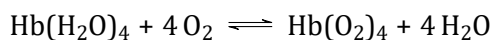


For example, when concentrated HCl is added to a solution containing Cu^{2+} (aq), the solution turns green.



The stronger Cl^- ligands replace H_2O ligands in blue $[Cu(H_2O)_6]^{2+}$ to form yellow $[CuCl_4]^{2-}$. The presence of both complexes result in a green colour.

Another example is haemoglobin.



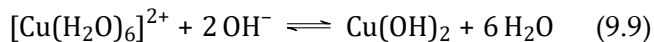
In a haemoglobin molecule, each of the four Fe^{2+} is octahedrally bonded to five N atoms and to an O atom from a water molecule. The H_2O ligand may be replaced by an O_2 ligand to form oxyhaemoglobin in a reversible reaction. O_2 is thus taken up by blood and distributed to cells.

CN^- and CO are toxic because the H_2O ligand may be replaced by stronger CN^- and CO ligands in an irreversible reaction, preventing the formation of oxyhaemoglobin, eventually depriving cells of O_2 .

9.4.6 Dissolution of precipitates by complexation

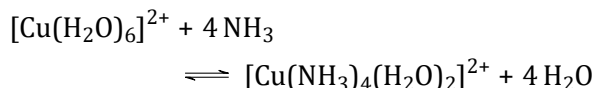
When dilute ammonia is gradually added to a solution containing Cu^{2+} (aq) ions, a pale blue precipitate is formed, which dissolves on adding more dilute ammonia.

When dilute ammonia is added gradually,



the ionic product of $Cu(OH)_2$ increases past its K_{sp} , so a pale blue precipitate of $Cu(OH)_2$ is formed.

In excess ammonia, both NH_3 and OH^- compete to combine with $[Cu(H_2O)_6]^{2+}$. NH_3 ligands replace H_2O ligands to form a deep blue complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$.



As concentration of $[Cu(H_2O)_6]^{2+}$ decreases, position of equilibrium (9.9) shifts left, and ionic product of $Cu(OH)_2$ decreases until it is less than its K_{sp} , and the pale-blue precipitate dissolves.

9.4.7 Catalysis

A **catalyst** is a substance that increases the rate of reaction without itself undergoing any permanent chemical

change, and provides an alternative pathway of lower activation energy for a reaction to occur.

Heterogeneous catalysis

A **heterogeneous catalyst** operates in a different physical state compared to the reactant. Transition metals and their compounds are good heterogeneous catalyst because of the availability of 3d and 4s electrons for temporary bond formation with reactants.

Heterogeneous catalysis function through adsorption, activation and desorption.

Adsorption occurs when temporary bonds are formed with reactant molecules when they adsorb on the catalyst surface (i.e. on the active sites).

Activation occurs when adsorption increases the surface concentration of reactants and weakens the covalent bonds within reactant molecules, lowering the activation energy. Reactant molecules are thus brought closer together and reaction can take place between the reactants molecules more easily.

Desorption occurs when resulting product molecules diffuse away from the catalyst's surface, leaving the active sites free for more reactant molecules to adsorb.

Homogeneous catalysis

Homogeneous catalysts operate in the same physical phase as the reactant. Transition metals and their compounds are good homogeneous catalysts because of their ability to exist in various oxidation states, facilitating the formation of reaction intermediates via alternative pathways of lower activation energy.

A substance acting as a homogeneous catalyst will react with one reactant to form an intermediate that then reacts with the other reactant. In most cases, the two separate reactions are more feasible than the two reactants reacting together.

An example is Fe^{3+} (aq) used to catalyse the reaction of $S_2O_8^{2-}$ (aq) and I^- (aq). The two reactants have the same charge, so they repel and the reaction is unfavourable. However, the reaction of both reactants with the catalyst is favourable as Fe^{3+} is oppositely charged, and they attract.

10 Organic Chemistry

10.1 Introductory topics

Organic chemistry is the study of compounds containing carbon, except its oxides and carbonates.

Carbon is a group IV element and can form up to four bonds. It usually does so in all compounds except when it is a cation (known as a carbocation).

10.1.1 Formulae of organic compounds

A **molecular formula** shows the actual number of each type of atom in a compound, but it does not show any form of structure or arrangement of atoms.

A **structural formula** shows the arrangement of atoms within the molecule; it shows the sequence in which atoms are bonded to each other.

A **displayed formula** or **full structural formula** shows all bonds in the molecule.

A **skeletal formula** is a simplified structural formula where all carbon atoms in alkyl chains and the hydrogens attached to them are removed, represented only by a carbon skeleton.

10.1.2 Basic nomenclature

Organic compounds can be classified into aliphatic, alicyclic and aromatic compounds. **Aliphatic compounds** are compounds without any aromatic ring like benzene; **alicyclic compounds** are simply cyclic aliphatic compounds like cyclopropane. Finally, **aromatic compounds** have an aromatic ring e.g. benzene.

Functional groups are specific groups of atoms that give a compound its characteristic chemical properties.

A **homologous series** is a series of compounds with the same functional group and general formula. Generally, each member has similar chemical properties and different physical properties, because they have the same functional group, but each successive compound differs by a methylene bridge ($-\text{CH}_2-$).

In IUPAC nomenclature, organic compound names are constructed using prefixes, suffixes and infixes. The primary functional group is used as the suffix; the number of carbon atoms in the longest chain containing the primary functional group is used as the stem, and any other secondary functional groups form the prefix. Prefixes are arranged in alphabetical order; the primary functional group is selected based on a priority.

All functional groups are numbered where needed if the name would otherwise be ambiguous. Each number is called a locant. Where there is a choice of locants, the selection is done based on the guidelines that (a) the suffix functional group should have the lowest locants, by the first point of difference rule; (b) any double or triple bonds should have the lowest locants, by the first point of difference rule; and (c) the prefix functional groups should have the lowest locants, by the first point of difference rule. E.g. 2,4,4-trimethylhexane, not 3,3,5-trimethylhexane.

The **first point of difference rule** is as follows. List the locants out in numerical order, and compare each term. At the first difference i.e. different locant, the locant set with the smaller locant is the correct one.

10.1.3 Isomerism

Isomers are compounds that have the same molecular formula but a different structural formula. There are two general types of isomerism: structural isomerism and stereoisomerism.

Structural isomerism is further divided into chain, positional and functional group isomerism. **Chain iso-**

merism is different arrangements of the carbon chain — straight or branched. **Positional isomerism** is having different positions of substituents or functional groups on a chain or ring e.g. 1-chloropropane and 2-chloropropane. **Functional group isomerism** is having different functional groups due to different arrangement of atoms e.g. ethanoic acid (CH_3COOH) and methyl methanoate (HCOOCH_3).

Stereoisomerism is further divided into geometric and optical isomerism.

Geometric isomerism occurs only when there is restricted rotation (e.g. due to a $\text{C}=\text{C}$ double bond) and there are two or more different substituents attached to the carbons of the double bond. This creates two geometric isomers with different physical properties but similar chemical properties.

Geometric isomers are named using *E/Z* or *cis-/trans-*nomenclature. If the substituents with higher CIP priority are on the same side, it is the *Z* or *cis* isomer, and if they are on different sides, then it is the *E* or *trans* isomer. E.g. (*E*)-but-2-ene and (*Z*)-but-2-ene.

The number of geometric isomers of a compound is 2^n , where n is the number of double bonds having geometric isomerism.

A carbon atom with 4 different substituents is a **chiral carbon**. If the compound it is in has no plane of symmetry, then the compound exhibits optical isomerism. An optical isomer is known as an **enantiomer**.

Optical isomers are named using *R/S* nomenclature. If the carbon atom is viewed with the lowest priority group pointing away, then the three remaining substituents appear to form a trigonal shape. If substituents go from highest priority to lowest priority in the clockwise direction, then it is the *R* isomer; otherwise, it is the *S* isomer.

Enantiomers are said to be optically active as they can rotate linearly polarised light. Enantiomers can also be named in the direction they rotate plane-polarised light; if it rotates clockwise, then it is the (+) enantiomer; otherwise it is the (-) enantiomer. (This is not related to the *R/S* system.) Enantiomers otherwise have identical chemical and physical properties.

The number of enantiomers of a compound is given by 2^m , where m is the number of chiral centres.

A **racemic mixture** is one with equal amounts of both (+) and (-) enantiomers. Such a mixture does not rotate plane-polarised light as there is exact cancellation of all possible rotation of plane polarised light.

CIP priority

In the CIP system, priority is assigned by comparing the atoms directly attached to the carbon atom. The group with the atom of highest atomic number has the highest priority, and so on.

If there is a tie, then atoms two bonds away from the carbon must be considered, by making a list of atoms, in descending atomic number order, connected to each atom one bond away from the carbon atom, and the group with the highest atomic number at the first point of difference wins.

This is repeated for more bonds away until the tie is broken. If groups differ only in *E/Z* or *R/S* isomerism, then the *R* and *Z* isomers are of higher priority. If a *R/S* descriptor is decided in such a manner, then the lowercase *r* and *s* are used instead. E.g. (1*R*,2*s*,3*S*)-1,2,3-trichlorocyclopentane.

10.1.4 Hybridisation

Hybridisation is the mixing of atomic orbitals to form hybrid orbitals suitable for the pairing of electrons to form chemical bonds in the valence bond theory.

In general, if a carbon is bonded to 2 atoms, it is *sp* hybridised; if it is bonded to 3, then it is *sp*² hybridised, and if it is bonded to 4, then it is *sp*³ hybridised.

sp hybrid orbitals are formed by one *s* and one *p* orbital to form 2 *sp* hybrid orbitals; 2 *p* orbitals remain unhybridised. The shape about the carbon is linear.

*sp*² hybrid orbitals are formed by one *s* and two *p* orbitals to form 3 *sp*² orbitals; 1 *p* orbital remains unhybridised. The shape about the carbon is trigonal planar.

*sp*³ hybrid orbitals are formed by one *s* and three *p* orbitals to form 4 *sp*³ orbitals. The shape about the carbon is tetrahedral.

Note that benzene is *sp*² hybridised; there is only 1 hydrogen bonded to each carbon, as each carbon-carbon bond is a 1.5-bond.

sp^{*x*} notation indicates the ratio of *s* to *p* character, which is 1 to *x*. Thus in *sp* orbitals, there is half *s* character and half *p* character; in *sp*² orbitals, there is one-third *s* character and two-thirds *p* character, and so on.

10.2 Physical properties

10.2.1 Polarity

The C–H bond is considered to be nonpolar as the electronegativities of carbon and hydrogen are extremely close. This means that all hydrocarbons regardless of shape are nonpolar.

Organic compounds with O like in –OH or =O groups, halogen substituents, or N like in –NH₂ can be polar.

10.2.2 Melting and boiling points

Hydrocarbons generally have low melting and boiling points, due to their simple molecular structure, where there are only weak intermolecular van der Waals' forces that require a small amount of energy to overcome.

Branched hydrocarbons generally have a lower boiling point than straight-chain isomers as branching gives molecules a more spherical shape, decreasing the surface area of contact, decreasing the extent of distortion of electron clouds, leading to less extensive van der Waals' forces that require less energy to overcome.

In general, *cis* isomers tend to have a higher boiling point than *trans* isomers as *cis* isomers are more likely to be polar. However, the reverse is true for melting point as *trans* isomers tend to pack better than *cis* isomers, so more energy is required to overcome the intermolecular forces in a crystal of a *trans* isomer.

Halogenoalkanes and carbonyl compounds, being polar, will generally have higher melting and boiling points than similar hydrocarbons, as the permanent dipole-permanent dipole forces between molecules of the former two are stronger and require more energy to overcome than the induced dipole-induced dipole forces between hydrocarbon molecules. A carbonyl compound will have a higher boiling point than a similar halogenoalkane.

Halogenoalkanes with larger halogens (in terms of electron cloud size) will have higher boiling points.

Alcohols and amines have higher boiling points than similar hydrocarbons, halogenoalkanes and carbonyl compounds as the hydrogen bonds between alcohol molecules are stronger and require more energy to overcome. Secondary or tertiary alcohols tend to have lower boiling points than primary alcohols as the –OH group experiences more steric hindrance in the former two, leading to weaker intermolecular hydrogen bonds. Amines have lower boiling points than similar alcohols as N–H is less polar than O–H.

Carboxylic acids have the highest boiling points if compared to other organic compounds with similar mass – except amino acids, as the electron-withdrawing carbonyl group results in an even more polar hydroxyl group, leading to stronger hydrogen bonding; more hydrogen bonds are also formed, so there is more extensive intermolecular hydrogen bonding that requires more energy to overcome.

Amino acids have the highest melting and boiling points compared to other organic compounds, as they exist as zwitterions. A high amount of energy is required to overcome the strong electrostatic attraction between zwitterions. Because of this, amino acids exist as solids at r.t.p. (their melting point is above 200 °C).

10.2.3 Solubility

Organic compounds that cannot form hydrogen bonds i.e. hydrocarbons and halogenoalkanes are insoluble in water as the hydrogen bonding between water molecules are incompatible with the weak van der Waals' attraction between these organic molecules. These compounds are soluble in organic solvents e.g.

CCl_4 as the weak van der Waals' attraction between these organic molecules is compatible with the weak van der Waals' attraction between organic solvent molecules.

Alcohols, carbonyl compounds, carboxylic acids, esters and amides of smaller molecular size are soluble in water and insoluble in organic solvents for the above reasons. However, as the alkyl group becomes bulkier, the solubility in water decreases as the bulkier alkyl group has a greater hydrophobic nature.

Amino acids are soluble in water as the ion-dipole interactions formed result in the release of energy that causes the detachment of zwitterions from the crystal lattice for solvation.

10.3 Acidity and basicity

A weak acid is a substance that dissociates partially in solution to give protons.

The strength of an acid depends on its tendency to dissociate, which depends on the stability of the conjugate base. If the negative charge on the anion is dispersed e.g. via intramolecular hydrogen bonding, lone pair delocalisation, or the presence of an electron-withdrawing group, the anion is stabilised, and vice versa.

Electron-withdrawing groups cause greater conjugate base stabilisation if there are more of them, they contain more electronegative atoms, or they are nearer to the acidic group.

Alcohols can behave as very weak acids — weaker than water. They are so weak because the electron-donating alkyl group intensifies the negative charge on the conjugate base (alkoxide), destabilising the conjugate base. Ethane-1,2-diol is more acidic than ethanol (and water) as intramolecular hydrogen bonds can be formed between the oxygen in the deprotonated alcohol group and the other alcohol group in the conjugate base. This only applies when the hydroxyl groups are on adjacent carbon atoms.

Phenol is more acidic than water as the phenoxide ion is stabilised by charge delocalisation where the lone pair of electrons on the oxygen atom of phenoxide is delocalised into the benzene ring, reducing the intensity of the negative charge on the oxygen atom of phenoxide, stabilising phenoxide, the conjugate base of phenol.

Carboxylic acids are more acidic than alcohols or phenols as the carboxylate anion is resonance stabilised by the delocalisation of the negative charge over the C atom and both O atoms. The carboxylate anion is thus more stable than the phenoxide or alkoxide anion, so carboxylic acids ionise more, thus being more acidic.

A base is a substance that can accept a proton. Amines are weak bases in water, as the lone pair on N can accept a proton.

The strength on a base depends on the availability of its lone pair, which depends on the electron density of the N atom's lone pair. Electron-donating groups will increase the availability of the lone pair on N, increasing basicity; electron-withdrawing groups (or a benzene ring, which allows the lone pair to be delocalised into the ring) will decrease the availability of the lone pair on N, decreasing basicity. As with acids, the number, distance and strength of substituents have similar effects.

10.4 Organic reactions

All organic compounds can undergo free radical substitution. Organic compounds with $\text{C}=\text{C}$ can undergo electrophilic addition; those with a benzene ring can undergo electrophilic substitution. Organic compounds with electron-withdrawing groups like $-\text{X}$ or $-\text{OH}$ can undergo nucleophilic substitution; organic compounds with $=\text{O}$ (ketones and aldehydes only!) can undergo nucleophilic addition.

10.4.1 Electrophilic addition

The rate of reaction of the electrophilic addition of X_2 and HX depends on the bond energies of $\text{H}-\text{X}$ and $\text{C}-\text{X}$.

Adding X_2 involves breaking $\text{X}-\text{X}$ and the pi bond of $\text{C}=\text{C}$, and the formation of $\text{C}-\text{X}$. Down the halogens, the decrease in energy released forming $\text{C}-\text{X}$ is more than the decrease in energy absorbed breaking $\text{X}-\text{X}$, so reactivity decreases down the group.

Adding HX involves breaking $\text{H}-\text{X}$ and the pi bond of $\text{C}=\text{C}$, and the formation of $\text{C}-\text{X}$ and $\text{C}-\text{H}$. Down the halogens, the decrease in energy absorbed breaking $\text{H}-\text{X}$ is more than the decrease in energy released forming $\text{C}-\text{X}$, so reactivity increases down the group.

In an addition where there are two possible products, the major product is the one where the nucleophile formed as an intermediate in the electrophilic addition attaches to the carbon that would form a more stable carbocation. In other words, (**Markovnikov's rule**) the electrophile attaches to the carbon with more H atoms.

10.4.2 Elimination

In general, if more than one alkene can be obtained as a result of elimination, the major product is the alkene which is more substituted i.e. the alkene with the greater number of R groups. This is **Saytzeff's rule**.

10.4.3 Electrophilic substitution

Since the reactivity of the benzene ring is due to the pi electron cloud, substituents affecting the pi electron density will also affect the reactivity of the ring. Groups with electronegative atoms that cannot delocalise their electrons into the ring are deactivating. They decrease the pi electron density of the ring, making it less reactive and decreasing the rate of reaction of electrophilic substitution. Common deactivating

groups include $-\text{NO}_2$, $-\text{CN}$, $-\text{COR}$, $-\text{COOR}$, $-\text{COOH}$, $-\text{CHO}$, and the halogens I, Br, Cl, and F. This is in ascending order of ring reactivity i.e. descending order of deactivating strength.

Electron-donating groups or groups that have lone pairs that can be delocalised are activating. They increase the pi electron density of the ring, making it more reactive and increasing the rate of reaction. Common activating groups include $-\text{NHCOR}$, $-\text{R}$, $-\text{OR}$, $-\text{OH}$, $-\text{NH}_2$, in similar order as above.

Substituents also have an effect on the position at which further substitutions take place. In general, saturated groups are 2-4- (ortho, para) directing, while unsaturated groups are 3- (meta) directing.

10.4.4 Nucleophilic substitution

There are two types of nucleophilic substitution — $\text{S}_{\text{N}}2$ i.e. bimolecular nucleophilic substitution, and $\text{S}_{\text{N}}1$ i.e. unimolecular nucleophilic substitution. The former is favoured when there is less steric hindrance around the electron-deficient C; the latter is favoured when the electron-deficient C forms a stable carbocation.

The $\text{S}_{\text{N}}2$ mechanism follows second order kinetics, and it is a one-step mechanism. Due to the nucleophile attacking from the backside of the electron-deficient C, products formed by this mechanism always have their optical configuration inverted compared to the original reactant. $\text{S}_{\text{N}}2$ is most favourable and has the highest rate for primary halogenoalkanes or alcohols, and becomes less favourable the more carbon neighbours the electron-deficient C has, due to steric hindrance.

The $\text{S}_{\text{N}}1$ mechanism follows first order kinetics, and it is a two-step mechanism. The rate equation involves only the compound being attacked. In the first step of the mechanism, a carbocation intermediate is formed, which is trigonal planar. In the second step, the nucleophile can attack from either the top or the bottom of the carbocation, and there is equal probability of either. Thus, a racemic mixture is formed when the attacked carbon is chiral. $\text{S}_{\text{N}}1$ is most favourable and has the highest rate for tertiary compounds, and becomes less favourable the less carbon neighbours the electron-deficient C has, as the carbocation intermediate formed is less stable.

The rate of reaction of nucleophilic substitution on halogenoalkanes depends on the ease of breaking the C–X bond. It follows that the rate of reaction for $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$.

A halogenoarene or phenol generally does not undergo nucleophilic substitution as one lone electron pair on the halogen or oxygen atom is delocalised into the benzene ring, strengthening the carbon-halogen bond due to partial double bond character, preventing nucleophilic substitution under normal conditions.

Similarly, a halogenoalkene (RCH=CXR') will not un-

dergo nucleophilic substitution under normal conditions as one lone electron pair of the halogen atom is delocalised with the adjacent $\text{C}=\text{C}$, strengthening the C–X bond due to partial double bond character, preventing nucleophilic substitution under normal conditions.

In an acyl chloride, the carbonyl C atom has 2 very electronegative atoms (O and Cl) bonded to it, so it has a large partial positive charge. It is thus highly electron deficient and will undergo nucleophilic substitution readily; this causes acyl chlorides to be extremely reactive.

10.4.5 Nucleophilic addition

In the nucleophilic addition of HCN to a carbonyl compound, HCN acts as an acid in the second step to donate a proton to form the final product. HCN also generates the CN^- nucleophile.

The slow first step involves the CN^- nucleophile, but HCN is a weak acid and so is a poor source of CN^- . Trace NaOH or NaCN is added to remedy this. NaOH will neutralise H^+ in the reaction mixture, decreasing $[\text{H}^+]$, and by Le Chatelier's principle, the equilibrium position in the dissociation of HCN shifts right to increase $[\text{H}^+]$, increasing $[\text{CN}^-]$ and the rate of reaction. NaCN will fully dissociate to produce the initial CN^- for the nucleophilic attack on the electron-deficient C atom, acting as a homogenous catalyst as CN^- is regenerated in the second step.

The temperature of the reaction is kept to 10°C to 20°C to prevent poisonous HCN gas from escaping to the environment. It is not brought lower than this to ensure a reasonable rate of reaction.

If the addition creates a chiral C, then a racemic mixture will be formed as there is equal probability of CN^- attacking the trigonal planar electron-deficient carbonyl C atom from either the top or bottom of the plane.

Ketones are usually less reactive than aldehydes as ketones have two alkyl groups attached to the carbonyl C while aldehydes only have one, resulting in steric hindrance; it is more difficult for the nucleophile to attack the electron-deficient carbonyl C atom in a ketone than in an aldehyde. The additional electron-donating R-group in ketones causes the partial positive charge on ketones' carbonyl C to be less than that on aldehydes, so ketones' carbonyl C is less susceptible to nucleophilic attack.

10.5 Uses and environmental concerns

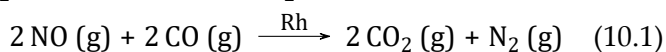
Alkanes are generally used as fuels: petrol is a mixture of C_5 to C_{10} alkanes. In car engines, petrol vapours are ignited in air causing an explosive reaction, driving the pistons of the engine.

When the combustion of fuel is not smooth, knocking occurs. Knocking reduces engine power, leads to wear and tear in the engine, and also wastes petrol. To reduce knocking, an antiknock agent, tetraethyllead(IV)

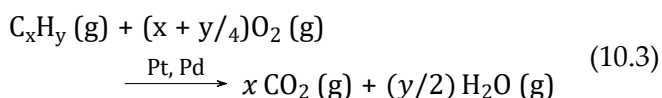
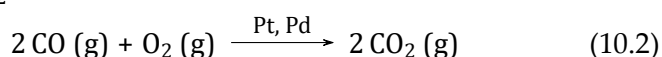
i.e. $\text{Pb}(\text{C}_2\text{H}_5)_4$ is added to petrol, which becomes leaded petrol. The weak $\text{Pb}-\text{C}$ bonds are easily broken, resulting in ethyl radicals that initiate smooth burning. However, this forms PbO which coats car cylinders. To prevent this, $\text{CH}_2\text{BrCH}_2\text{Br}$ is added to remove the lead content as volatile PbBr_2 which passes out as exhaust.

The use of petrol as fuels produces many pollutants. The incomplete combustion of fuel releases CO as well as unburnt hydrocarbons. CO causes carbon monoxide poisoning as it combines with haemoglobin in the blood, forming carboxyhaemoglobin, which prevents the transportation of O_2 to all parts of the body. Unburnt hydrocarbons become part of photochemical smog in strong sunlight, causing lung damage. The use of TEL releases PbBr_2 vapour, which can lead to lead poisoning, causing brain damage. Oxides of nitrogen are produced due to the reaction of N_2 with O_2 at high temperatures and pressures in the car engine. They form acid rain that corrodes buildings and destroys marine life, as well as causing respiratory problems in humans and interfering with nitrogen metabolism in plants. SO_2 produced due to trace sulfur compounds in fuels creates acidic gases that also form acid rain.

Catalytic converters, which are wire meshes coated with rhodium, platinum and palladium, reduce NO_x to N_2 and oxidise CO to CO_2 .

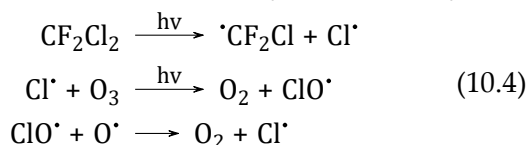


Unburnt hydrocarbons and CO are oxidised to CO_2 and H_2O .



Fluoroalkanes and fluorohalogenoalkanes are stable and unreactive due to the strong $\text{C}-\text{F}$ bond. They are good solvents with low boiling points and are non-flammable, non-toxic and odourless. Due to their lack of reactivity, they are useful as inert materials in fire extinguishers, refrigerants, and aerosol propellants. Their boiling points just below room temperature make them easy to liquefy by a slight increase in pressure, and conversely easy to vaporise by a slight decrease in pressure. This makes them useful as liquid refrigerants, and also aerosol propellants.

Chlorofluorocarbons, also known as CFCs, have been widely used as aerosols and refrigerants. However, due to their inertness, they tend to drift up into the stratosphere, where they undergo homolytic fission to form chlorine radicals that destroy the ozone layer.



Note that $\text{Cl}\cdot$ is regenerated. In general, only fluoroalka-

nes are safe for use as the $\text{C}-\text{F}$ bond will not break as easily as the other halogens'.

10.6 Amino acids and proteins

10.6.1 Amino acid properties

Amino acids exist as electrically neutral dipolar ions called zwitterions, formed when the carboxylic acid group donates its proton to the amino group.

The pH at which an amino acid exists as a zwitterion is known as its isoelectric point. Below this pH, amino acids exist as cations; above this pH, amino acids exist as anions.

Electrophoresis can be used to separate a mixture of amino acids by using an electric field. Depending on the pH of the medium, different amino acids will move towards the cathode or anode; the distance of movement depends on the q/m ratio.

Amino acids have different types depending on the number of C atoms between $-\text{NH}_2$ and $-\text{COOH}$. If there is only one C atom, it is an α -amino acid; if there are two, it is a β -amino acid; and so on.

α -amino acids have general formula $\text{RCH}(\text{NH}_2)\text{COOH}$.

The properties of amino acids, other than those caused by the α - NH_2 and α - COOH , depend on the R -groups of each amino acid. Amino acids can have R -groups that are one of nonpolar i.e. hydrophobic, uncharged and hydrophilic, negatively charged, or positively charged.

10.6.2 Proteins and basic properties

Proteins are polymers consisting of long peptide chains of amino acid residues. Peptide linkages are formed by the condensation of amino acids by removing a H_2O molecule between the $-\text{COOH}$ and $-\text{NH}_2$ groups of separate amino acid molecules.

Proteins have important functions in living systems. They act as **(a)** structural proteins, defining shapes and sizes of cells; **(b)** muscle fibres, providing mechanical force; **(c)** transport proteins, moving metabolites; **(d)** hormones, controlling cell activity; and **(e)** enzymes, catalysing metabolic processes.

Since peptide bonds are simply amide linkages, they can be hydrolysed similarly. They can also be broken in the presence of suitable enzymes.

10.6.3 Protein structures

Primary and secondary structure

The primary structure of proteins refers to the sequence of amino acids in polypeptide chains. By the nature of interactions between different amino acid residues, the primary structure determines the folding, shape, nature and function of the protein.

By convention, amino acid sequences are written with the N -terminus first (on the left).

The secondary structure of proteins refers to regular arrangements of the polypeptide chain stabilised by

hydrogen bonds between an O of an amide group and a H of another on the same chain.

The α -helix is a regular coiled configuration of the polypeptide chain, held in place by intra-chain hydrogen bonds. The O atom in the amide group of each amino acid is hydrogen-bonded to the H atom in the amide group of the fourth amino acid further down the chain, and there are 3.6 amino acids per helical turn. The R-groups on the α -carbon point outside of the helix and are perpendicular to the main axis of the helix. The formation of many hydrogen bonds within the helix gives a strong total binding effect, causing the helix to be flexible and elastic.

The β -pleated sheet consists of sections of polypeptide aligned side-by-side linked by intra-chain hydrogen bonding, with R-groups projected above or below the sheet. Hydrogen bonding between sections of the polypeptide results in a very stable structure. The β -pleated sheet is flexible but inelastic, and can either run parallel or antiparallel.

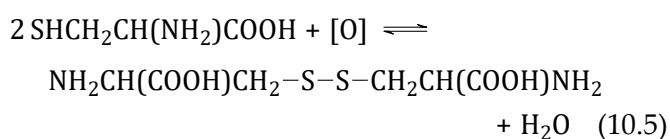
Tertiary structure

The tertiary structure of proteins is the overall three-dimensional shape of a protein that is formed when a polypeptide chain folds extensively to form a complex rigid three-dimensional structure. The tertiary structure is held together by R-group interactions, depending on the nature of the group.

Non-polar or hydrophobic groups interact via van der Waals' attraction with other non-polar groups only.

Polar or hydrophilic groups interact via permanent dipole-permanent dipole attraction with other polar groups, and hydrogen bonding with groups containing O-H, C=O or N-H.

Groups containing the thiol group (S-H can form disulfide bonds with other such groups i.e. cysteine residues), forming a cystine.



Ionic groups can form ionic bonds with oppositely charged groups, and hydrogen bonds with groups containing O-H, C=O or N-H.

Globular proteins have distinctive tertiary structures where almost all hydrophilic R-groups are on the outer surface, half or more of the hydrophobic R-groups are internally located, and the folding is compact with little or no room for water molecules in the interior. This allows them to be soluble in water.

Quaternary structure

The quaternary structure is the combination of two or more individually folded polypeptide chains interacting to form a complex structure. Individual polypeptide chains exist in their own tertiary structures and

are called subunits. Subunits in the quaternary structure are held together by van der Waals' interactions, ionic bonds and hydrogen bonds. Proteins where two or more subunits are identical polypeptide chains are said to be oligomeric.

Haemoglobin is a protein with a quaternary structure consisting of 4 subunits — 2 α -subunits and 2 β -subunits, each subunit being noncovalently linked to a haem group. Each haem group contains a Fe^{2+} ion that binds reversibly to O_2 . $\text{Hb} + 4 \text{O}_2 \rightleftharpoons \text{Hb}(\text{O}_2)_4$. Both the α - and β -subunits have 70% α -helical regions. There is little contact between two α -subunits and two β -subunits, but there is a lot of contact between α -subunits and their neighbouring β -subunits.

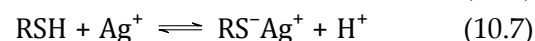
10.6.4 Denaturation

Denaturation refers to the breaking of weak bonds holding the secondary, tertiary and quaternary structures (but not the covalent bonds within the primary structures). The loss of shape of the protein causes the loss of protein function. Proteins can be denatured by heating, pH change, mechanical agitation, and addition of metal ions.

Heating and mechanical agitation disrupts the weaker bonds like van der Waals' forces that stabilise the tertiary and quaternary structures, and the hydrogen bonds that stabilise the secondary structure.

pH changes protonate or deprotonate acidic and basic R-groups. At low pH, excess H^+ protonates basic R-groups like -COO^- and -NH_2 , forming -COOH and -NH_3^+ respectively, disrupting ionic bonds and hydrogen bonds respectively. At high pH, excess OH^- deprotonates acidic R-groups like -COOH and -NH_3^+ , forming -COO^- and -NH_2 respectively, disrupting hydrogen bonds and ionic bonds respectively. Changes in pH thus disrupt the ionic bonds and hydrogen bonds between basic and acidic R-groups, which hold the secondary, tertiary and quaternary structure of proteins together, leading to changes in protein shape and loss of protein function.

Metal ions like Cu^{2+} , Ag^+ and Hg^+ disrupt the ionic interactions between charged ionic R-groups by forming ionic bonds with these groups. Metal ions can interact with anionic R-groups to form insoluble salts. They can also disrupt the formation of disulfide bonds as they have high affinity for sulfur in the thiol group, leading to the formation of precipitates.

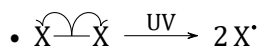


These effects disrupt the tertiary and quaternary structures of proteins.

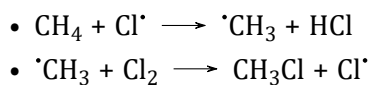
A Organic Mechanisms

A.1 Free Radical Substitution

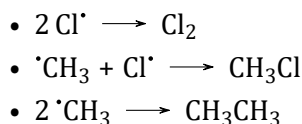
1 Initiation:



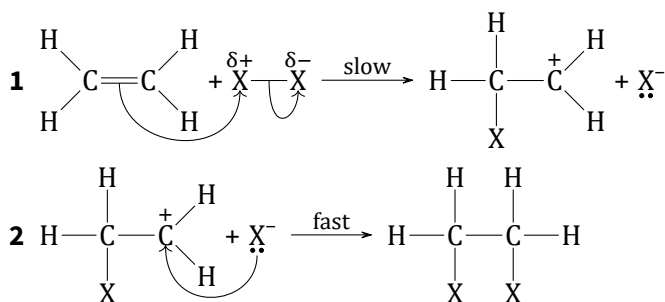
2 Propagation:



3 Termination

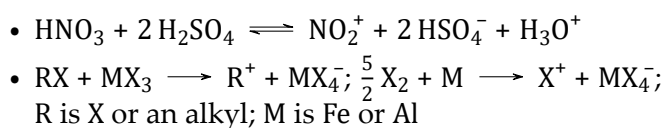


A.2 Electrophilic Addition

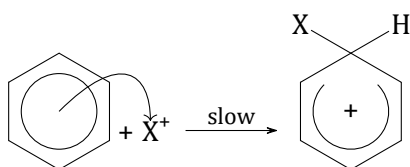


A.3 Electrophilic Substitution

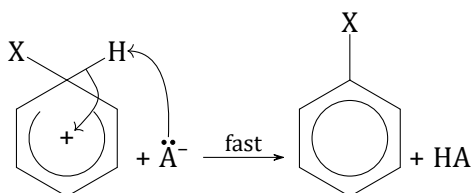
1 Formation of electrophile



2 Electrophilic attack

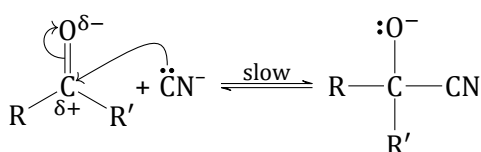


3 Neutralisation (deprotonation)

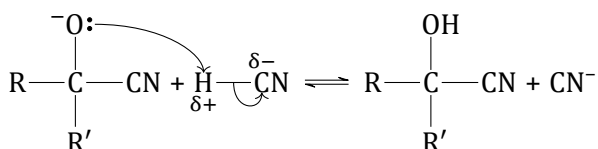


A.4 Nucleophilic Addition

1 Nucleophilic attack

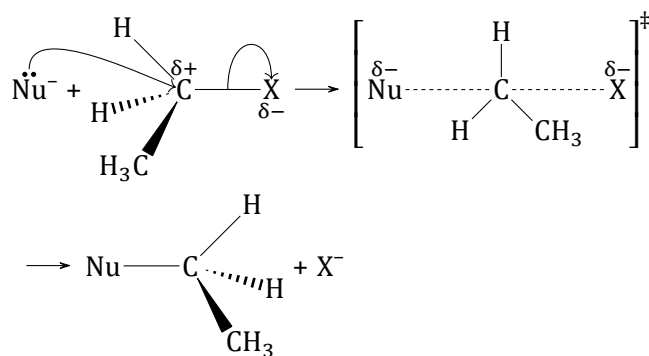


2 Neutralisation (protonation)

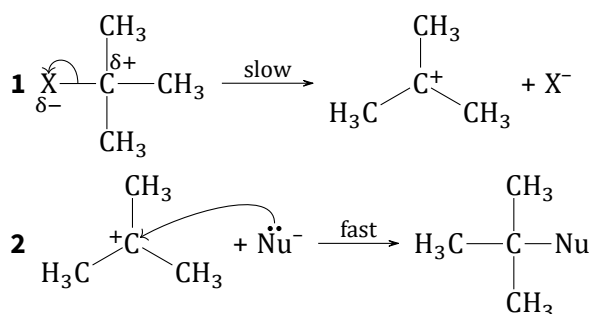


A.5 Nucleophilic Substitution

A.5.1 S_N2 (Bimolecular)



A.5.2 S_N1 (Unimolecular)



B Inorganic Chemistry Summary of Reactions

	Equation	Observations	Flame
Na	$2 \text{Na (s)} + \frac{1}{2} \text{O}_2 \text{(g)} \longrightarrow \text{Na}_2\text{O (s)}$	Burns very vigorously	Yellow
Mg	$\text{Mg (s)} + \frac{1}{2} \text{O}_2 \text{(g)} \longrightarrow \text{MgO (s)}$	Burns very vigorously	Bright white
Al	$4 \text{Al (s)} + 3 \text{O}_2 \text{(g)} \longrightarrow 2 \text{Al}_2\text{O}_3 \text{(s)}$	Must be heated to 800 °C due to the unreactive oxide layer	—
Si	$\text{Si (s)} + \text{O}_2 \text{(g)} \longrightarrow \text{SiO}_2 \text{(s)}$	Reacts slowly with strong heat	—
P	$\text{P}_4 \text{(s)} + 3 \text{O}_2 \text{(g)} \longrightarrow \text{P}_4\text{O}_6 \text{(s)}$ $\text{P}_4 \text{(s)} + 5 \text{O}_2 \text{(g)} \longrightarrow \text{P}_4\text{O}_{10} \text{(s)}$	Reacts vigorously, forming a dense white fume of P_4O_{10}	Brilliant yellow
S	$\text{S (s)} + \text{O}_2 \text{(g)} \longrightarrow \text{SO}_2 \text{(g)}$ $\text{SO}_2 \text{(g)} + \frac{1}{2} \text{O}_2 \text{(g)} \text{ (excess)} \longrightarrow \text{SO}_3 \text{(g)}$	Burns slowly	Blue

Table B.1: Reaction of period 3 elements with oxygen

	Chloride	Observations
Na	NaCl (s)	Reacts very vigorously
Mg	$\text{MgCl}_2 \text{(s)}$	Reacts vigorously
Al	$\text{AlCl}_3 \text{(s)}$	Reacts vigorously; dimerises to Al_2Cl_6
Si	$\text{SiCl}_4 \text{(l)}$	Reacts slowly
P ₄ (s)	$\text{PCl}_3 \text{(l)}$	In limited Cl_2 ; reacts slowly
P ₄ (s)	$\text{PCl}_5 \text{(s)}$	In excess Cl_2 ; reacts slowly
S	$\text{S}_2\text{Cl}_2 \text{(l)}$	Reacts slowly

Table B.2: Reaction of period 3 elements with chlorine

	Equation	Observations
Na	$2 \text{Na (s)} + 2 \text{H}_2\text{O (l)} \longrightarrow 2 \text{NaOH (aq)} + \text{H}_2 \text{(g)}$	Reacts very vigorously
Mg	$\text{Mg (s)} + \text{H}_2\text{O (g)} \longrightarrow \text{MgO (s)} + \text{H}_2 \text{(g)}$	Reacts with steam only
Al	$2 \text{Al (s)} + 3 \text{H}_2\text{O (g)} \longrightarrow \text{Al}_2\text{O}_3 \text{(s)} + 3 \text{H}_2 \text{(g)}$	Reacts with steam only
Cl ₂	$\text{Cl}_2 \text{(g)} + \text{H}_2\text{O (l)} \longrightarrow \text{HClO (aq)} + \text{HCl (g)}$	Hydrolyses to pH 2 solution
Rest	Does not react	

Table B.3: Reaction of period 3 elements with water

	Equation	Remarks	pH	UI
Na ₂ O	Na ₂ O (s) + H ₂ O (l) \longrightarrow 2 NaOH (aq)	Reacts vigorously	13	Violet
MgO	MgO (s) + H ₂ O (l) \rightleftharpoons Mg(OH) ₂ (aq)	Reacts less vigorously and dissolves sparingly as its lattice energy is high, leading to a high enthalpy of solution.	9	Blue
Al ₂ O ₃	Does not react; too much energy required to cause detachment of ions from the lattice structure			
SiO ₂	Does not react; too much energy required to break its very stable giant molecular structure			
P ₄ O ₆	P ₄ O ₆ (s) + 6 H ₂ O (l) \longrightarrow 4 H ₃ PO ₃ (aq)		2	Red
P ₄ O ₁₀	P ₄ O ₁₀ (s) + 6 H ₂ O (l) \longrightarrow 4 H ₃ PO ₄ (aq)			
SO ₂	SO ₂ (g) + H ₂ O (l) \longrightarrow H ₂ SO ₃ (aq)			
SO ₃	SO ₃ + H ₂ O (l) \longrightarrow H ₂ SO ₄ (aq)			
Cl ₂ O ₇	Cl ₂ O ₇ (aq) + H ₂ O (l) \longrightarrow 2 HClO ₄ (aq)			

Table B.4: Reaction of period 3 oxides with water

	Equation	Remarks
Na ₂ O	Na ₂ O (s) + 2 H ⁺ (aq) \longrightarrow 2 Na ⁺ (aq) + H ₂ O (l)	
MgO	MgO (s) + 2 H ⁺ (aq) \longrightarrow Mg ²⁺ (aq) + H ₂ O (l)	
Al ₂ O ₃	Al ₂ O ₃ (s) + 6 H ⁺ (aq) \longrightarrow 2 Al ³⁺ (aq) + 3 H ₂ O (l)	With acid
Al ₂ O ₃	Al ₂ O ₃ (s) + 2 OH ⁻ (aq) + 3 H ₂ O (l) \longrightarrow 2 Al(OH) ₄ ⁻ (aq)	With base
SiO ₂	SiO ₂ (s) + 2 OH ⁻ (aq) \longrightarrow SiO ₃ ²⁻ (aq) + H ₂ O (l)	
P ₄ O ₆	P ₄ O ₆ (s) + 8 OH ⁻ (aq) \longrightarrow 4 HPO ₃ ²⁻ (aq) + 2 H ₂ O (l)	
P ₄ O ₁₀	P ₄ O ₁₀ (s) + 12 OH ⁻ (aq) \longrightarrow 4 HPO ₄ ³⁻ (aq) + 6 H ₂ O (l)	
SO ₂	SO ₂ (g) + 2 OH ⁻ (aq) \longrightarrow SO ₃ ²⁻ (aq) + H ₂ O (l)	
SO ₃	SO ₃ (g) + 2 OH ⁻ (aq) \longrightarrow SO ₄ ²⁻ (aq) + H ₂ O (l)	
Cl ₂ O ₇	Cl ₂ O ₇ (aq) + 2 OH ⁻ (aq) \longrightarrow 2 ClO ₄ ⁻ (aq) + H ₂ O (l)	

Table B.5: Reaction of period 3 oxides with acid and base

	Equation	Remarks	pH	UI
NaCl	NaCl (s) \longrightarrow Na ⁺ (aq) + Cl ⁻ (aq)	Undergoes hydration	7	Green
MgCl ₂	MgCl ₂ (s) + 6 H ₂ O (l) \longrightarrow [Mg(H ₂ O) ₆] ²⁺ (aq) + 2 Cl ⁻ (aq) [Mg(H ₂ O) ₆] ²⁺ (aq) + H ₂ O (l) \rightleftharpoons [Mg(H ₂ O) ₅ (OH)] ⁺ (aq) + H ₃ O ⁺ (aq)		6.5	Orange
Undergoes hydration and then slight hydrolysis to form a slightly acidic solution, as the relatively high charge density of the hydrated Mg ²⁺ ion polarises the electron cloud of one of the surrounding water molecules, weakening and breaking the O–H bond, releasing a proton.				
Al ₂ Cl ₆	AlCl ₃ (s) + 6 H ₂ O (l) \longrightarrow [Al(H ₂ O) ₆] ³⁺ (aq) + 3 Cl ⁻ (aq) [Al(H ₂ O) ₆] ³⁺ (aq) + H ₂ O (l) \rightleftharpoons [Al(H ₂ O) ₅ (OH)] ²⁺ (aq) + H ₃ O ⁺ (aq)		3	Orange
Undergoes hydration and hydrolysis to form an acidic solution, for reasons similar to MgCl ₂ .				
SiCl ₄	SiCl ₄ (l) + 2 H ₂ O (l) \longrightarrow SiO ₂ (s) + 4 HCl (g)	Hydrolyses completely	2	Red
PCl ₃	PCl ₃ (l) + H ₂ O (l) \longrightarrow H ₃ PO ₃ (aq) + 3 HCl (g)			
PCl ₅	PCl ₅ (s) + 4 H ₂ O (l) (excess) \longrightarrow H ₃ PO ₄ (aq) + 5 HCl (g)	(hot)		
PCl ₅	PCl ₅ (s) + H ₂ O (l) \longrightarrow POCl ₃ (aq) + 2 HCl (aq)	(cold)		
POCl ₃	POCl ₃ (aq) + 3 H ₂ O (l) \longrightarrow H ₃ PO ₄ (aq) + 3 HCl (aq)			
S ₂ Cl ₂	2 S ₂ Cl ₂ (l) + 2 H ₂ O (l) \longrightarrow 3 S (s) + SO ₂ (g) + 4 HCl (g)			
Cl ₂	Cl ₂ (g) + H ₂ O (l) \longrightarrow HClO (aq) + HCl (g)			

Table B.6: Reaction of period 3 chlorides with water

Element		Reaction with water		Oxide		
	Flame	Cold	Steam	Solubility	pH	UI
Be	—	—	—	BeO	Insoluble	
Mg	brilliant white	—	Forms oxide	MgO	Slightly	9 Blue
Ca	red	Forms hydroxide		CaO	Yes	10–13 Violet
Sr	crimson	Forms hydroxide		SrO	Yes	10–13 Violet
Ba	green	Forms hydroxide		BaO	Yes	10–13 Violet

Table B.7: Reactions of group II elements and oxides

Colour in state					
	Gas	Liquid	Solid	Aqueous	Organic
Cl ₂	Greenish-yellow	—	—	Greenish-yellow	Yellow
Br ₂	Reddish-brown	—	—	Yellow	Orange
I ₂	Violet	—	Black	Brown	Violet

Table B.8: Colours of group VII elements

Equation		Observations
F ₂	H ₂ (g) + F ₂ (g) → 2 HF(g)	Explosive even in the dark
Cl ₂	H ₂ (g) + Cl ₂ (g) → 2 HCl(g)	Explosive in sunlight; does not react at r.t.p. or in the dark
Br ₂	H ₂ (g) + Br ₂ (g) → 2 HBr(g)	Heat and Pt catalyst
I ₂	H ₂ (g) + I ₂ (g) → 2 HI(g)	Reacts reversibly at 400 °C with Pt catalyst

Table B.9: Reactions of group VII elements with hydrogen

Equation		Remarks
X ₂	2 OH [−] (aq) + X ₂ (aq) → X [−] (aq) + XO [−] (aq) + H ₂ O(l)	R.t.p. dilute NaOH and Cl ₂ or 0 °C dilute NaOH and Br ₂
XO [−]	3 XO [−] (aq) → 2 X [−] (aq) + XO ₃ [−] (aq)	On warming
X ₂	6 OH [−] (aq) + 3 X ₂ (aq) → 5 X [−] (aq) + XO ₃ [−] (aq) + 3 H ₂ O(l)	Hot concentrated NaOH (70 °C) and Cl ₂ or Br ₂ or I ₂

Table B.10: Reactions of group VII elements with NaOH(aq)

Equation		Remarks
F ₂ , Cl ₂	NaX(s) + H ₂ SO ₄ (l) → HX(g) + NaHSO ₄ (s)	HX is not further oxidised by H ₂ SO ₄ as the latter is not powerful enough an oxidising agent
Br ₂	NaBr(s) + H ₂ SO ₄ (l) → HBr(g) + NaHSO ₄ (s) 2 HBr(g) + H ₂ SO ₄ (l) → Br ₂ (g) + SO ₂ (g) + 2 H ₂ O(l)	HBr forms white fumes; SO ₂ is pungent
I ₂	NaI(s) + H ₂ SO ₄ (l) → HI(g) + NaHSO ₄ (s) 8 HI(g) + H ₂ SO ₄ (l) → 4 I ₂ (g) + H ₂ S(g) + 4 H ₂ O(l)	HI forms white fumes; H ₂ S is pungent

Table B.11: Reactions of group VII elements with concentrated H₂SO₄

Ion	Species and colour		
V(II)	$[\text{V}(\text{H}_2\text{O})_6]^{2+}$: violet		
V(III)	$[\text{V}(\text{H}_2\text{O})_6]^{3+}$: green		
V(IV)	$[\text{VO}(\text{H}_2\text{O})_5]^{2+}$: blue		
V(V)	$[\text{VO}_2(\text{H}_2\text{O})_4]^+$: yellow		
Cr(II)	$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$: blue		
Cr(III)	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$: green	$[\text{Cr}(\text{OH})_6]^{3-}$: deep green	$[\text{Cr}(\text{NH}_3)_6]^{3+}$: purple
Cr(VI)	CrO_4^{2-} : yellow	$\text{Cr}_2\text{O}_7^{2-}$: orange	
Mn(II)	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$: pink/colourless		
Mn(III)	$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$: red		
Mn(IV)	MnO_2 : brown solid		
Mn(VI)	MnO_4^{2-} : green		
Mn(VII)	MnO_4^- : purple		
Fe(II)	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$: pale green	$[\text{Fe}(\text{CN})_6]^{4-}$: yellow	
Fe(III)	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$: yellow	$[\text{Fe}(\text{CN})_6]^{3-}$: orange-red	$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$: blood red
Co(II)	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$: pink	$[\text{Co}(\text{NH}_3)_6]^{2+}$: pale brown	$[\text{CoCl}_4]^{2-}$: blue
Co(III)	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$: dark brown		
Ni(II)	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$: green	$[\text{Ni}(\text{NH}_3)_6]^{2+}$: blue	$[\text{Ni}(\text{CN})_6]^{4-}$: yellow
Cu(I)	Cu_2O : reddish-brown solid		
Cu(II)	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$: blue	$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$: dark blue	$[\text{CuCl}_4]^{2-}$: yellow
Ag(I)	$[\text{Ag}(\text{H}_2\text{O})_2]^+$: colourless		
	$[\text{Ag}(\text{NH}_3)_2]^+$: colourless		

Table B.12: Colours of transition metal compounds and complexes

Precipitate	Colour	Soluble in excess of	Complex	Colour
$\text{Cr}(\text{OH})_3$	Green	$\text{NaOH}(\text{aq})$	$[\text{Cr}(\text{OH})_6]^{3-}$	Deep green
$\text{Zn}(\text{OH})_2$	White	$\text{NaOH}(\text{aq})$	$[\text{Zn}(\text{OH})_4]^{2-}$	Colourless
$\text{Zn}(\text{OH})_2$	White	$\text{NH}_3(\text{aq})$	$[\text{Zn}(\text{NH}_3)_4]^{2+}$	Colourless
$\text{Cu}(\text{OH})_2$	Blue	$\text{NH}_3(\text{aq})$	$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	Deep blue
$\text{Co}(\text{OH})_2$	Blue	$\text{NH}_3(\text{aq})$	$[\text{Co}(\text{NH}_3)_6]^{2+}$	Pale brown
$\text{Ni}(\text{OH})_2$	Green	$\text{NH}_3(\text{aq})$	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	Blue

Table B.13: Transition metal precipitates soluble when excess ligand added

C Organic Chemistry Summary of Reactions

C.1 Free Radical Substitution

1 $\text{R-CH}_3 + \text{X}_2 \longrightarrow \text{R-CH}_2\text{X} + \text{HX}$; reagents: X_2 (g); conditions: r.t.p., UV light

C.2 Electrophilic Addition

1 $\text{CH}_2=\text{CH}_2 + \text{X}_2 \longrightarrow \text{CH}_2\text{XCH}_2\text{X}$; reagents: X_2 (CCl_4); conditions: r.t.p., dark; observations: decolourisation of reddish-brown Br_2 or greenish-yellow Cl_2 solution

2 $\text{CH}_2=\text{CH}_2 + \text{HX} \longrightarrow \text{CH}_3\text{CH}_2\text{X}$; reagents: dry HX (g) or HX (CCl_4); conditions: r.t.p.

3 $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}_2\text{OH}$; reagents: H_2O (g) or H_2O (l); conditions: 300 °C, 65 atm, conc. H_3PO_4 cat. or cold conc. H_2SO_4 then hot water

C.3 Electrophilic Substitution

1 $\text{C}_6\text{H}_6 + \text{HNO}_3 \longrightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$; reagents: conc. HNO_3 , conc. H_2SO_4 cat.; conditions: 55 °C

2 $\text{C}_6\text{H}_6 + \text{X}_2 \longrightarrow \text{C}_6\text{H}_5\text{X} + \text{HX}$; reagents: X_2 ; conditions: r.t.p., dark, ahd. FeX_3 or AlX_3 or Fe cat.; observations: white fumes of HX

3 $\text{C}_6\text{H}_6 + \text{RX} \longrightarrow \text{C}_6\text{H}_5\text{R} + \text{HX}$; reagents: RX ; conditions: r.t.p., ahd. FeX_3 or AlX_3 cat.

4 $\text{C}_6\text{H}_5\text{OH} + \text{HNO}_3 \longrightarrow \text{o-/p-C}_6\text{H}_4(\text{OH})(\text{NO}_2) + \text{H}_2\text{O}$; reagents: dil. HNO_3 ; conditions: r.t.p. (heat for disub.)

5 $\text{C}_6\text{H}_5\text{OH} + 3 \text{HNO}_3 \longrightarrow \text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3 + 3 \text{H}_2\text{O}$; reagents: conc. HNO_3 ; conditions: r.t.p.

6 $\text{C}_6\text{H}_5\text{OH} + \text{X}_2 \longrightarrow \text{o-/p-C}_6\text{H}_4(\text{OH})(\text{X}) + \text{HX}$; reagents: X_2 (CCl_4); conditions: r.t.p.

7 $\text{C}_6\text{H}_5\text{OH} + 3 \text{X}_2 \longrightarrow \text{C}_6\text{H}_2(\text{OH})(\text{X})_3 + 3 \text{HX}$; reagents: X_2 (aq); conditions: r.t.p. Test for phenol with Br_2 ; observations: white ppt of 2,4,6-tribromophenol

8 $\text{C}_6\text{H}_5\text{NH}_2 + 3 \text{X}_2 \longrightarrow \text{C}_6\text{H}_2(\text{NH}_2)(\text{X})_3 + 3 \text{HX}$; reagents: X_2 (aq); conditions: r.t.p. Test for phenylamine with Br_2 ; observations: white ppt of 2,4,6-tribromophenylamine. Note: same observations as phenol!

C.4 Nucleophilic Substitution

1 $\text{RX} + \text{NaOH} \longrightarrow \text{ROH} + \text{NaX}$; reagents: NaOH (aq) or KOH (aq); conditions: heat. Test for RX ; observations: ppt (white: RCl ; cream: RBr ; yellow: RI) forms with AgNO_3 (aq)

2 $\text{RX} + \text{KCN} \longrightarrow \text{RCN} + \text{KX}$; reagents: KCN in ethanol; conditions: heat

3 $\text{RX} + 2 \text{NH}_3 \longrightarrow \text{RNH}_2 + \text{NH}_4\text{X}$; reagents: exc. conc. NH_3 in ethanol; conditions: heat in sealed tube

4 $\text{RCOOH} + \text{R'OH} \rightleftharpoons \text{RCOOR'} + \text{H}_2\text{O}$; reagents: RCOOH or R'OH (Nu: R'O^-); conditions: conc. H_2SO_4 cat., heat
Note: R' cannot be benzene in this case (phenol will not undergo N.S. with $-\text{COOH}$.)

5 $\text{RCOCl} + \text{R'OH} \longrightarrow \text{RCOOR'} + \text{HCl}$; reagents: RCOCl or R'OH (Nu: R'O^-); conditions: r.t.p.

6 $\text{RCOCl} + \text{NHR'R''} \longrightarrow \text{RCONR'R''} + \text{HCl}$; reagents: NHR'R'' ; conditions: r.t.p.

7 $3 \text{ROH} + \text{PX}_3 \longrightarrow 3 \text{RX} + \text{H}_3\text{PO}_3$; reagents: dry PX_3 or X_2 with red phosphorus; conditions: heat

8 $\text{ROH} + \text{HCl} \longrightarrow \text{RCl} + \text{H}_2\text{O}$; reagents: HCl (g) or conc. HCl , ahd. ZnCl_2 cat. (Lucas' reagent); conditions: heat

9 $\text{ROH} + \text{PCl}_5 \longrightarrow \text{RCl} + \text{POCl}_3 + \text{HCl}$; reagents: ahd. PCl_5 ; conditions: r.t.p. Test for alcohol; observations: white fumes of HCl

10 $\text{ROH} + \text{SOCl}_2 \longrightarrow \text{RCl} + \text{SO}_2 + \text{HCl}$; reagents: ahd. SOCl_2 ; conditions: r.t.p.

11 $\text{ROH} + \text{HBr} \longrightarrow \text{RBr} + \text{H}_2\text{O}$; reagents: NaBr , conc. H_2SO_4 cat. or HBr (g); conditions: heat

12 $\text{RCOOH} + \text{PCl}_5 \longrightarrow \text{RCOCl} + \text{HCl} + \text{POCl}_3$; reagents: ahd. PCl_5 ; conditions: r.t.p.

13 $3 \text{RCOOH} + \text{PCl}_3 \longrightarrow 3 \text{RCOCl} + \text{H}_3\text{PO}_3$; reagents: ahd. PCl_3 ; conditions: heat

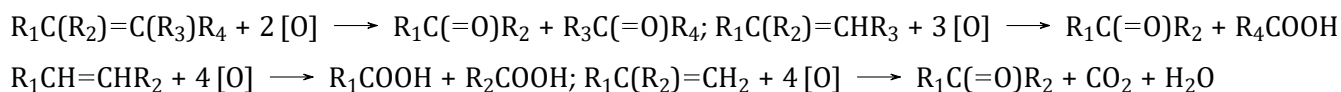
14 $\text{RCOOH} + \text{SOCl}_2 \longrightarrow \text{RCOCl} + \text{HCl} + \text{SO}_2$; reagents: ahd. SOCl_2 ; conditions: r.t.p.

C.5 Nucleophilic Addition

1 $\text{RC(=O)R'} + \text{HCN} \longrightarrow \text{RC(OH)(CN)R'}$; reagents: HCN , trace NaCN or NaOH cat.; conditions: 10 °C to 20 °C

C.6 Oxidation

- 1 $\text{CH}_2=\text{CH}_2 + [\text{O}] + \text{H}_2\text{O} \longrightarrow \text{CH}_2\text{OHCH}_2\text{OH}$; reagents, conditions: cold KMnO_4 in $\text{H}_2\text{SO}_4/\text{NaOH}$; observations: decolourisation of purple KMnO_4 , brown ppt of MnO_2
- 2 Strong oxidation of alkenes; reagents, conditions: hot KMnO_4 in $\text{H}_2\text{SO}_4/\text{NaOH}$; observations: decolourisation of purple KMnO_4 ; effervescence of CO_2 (if terminal alkene)



- 3 $\text{C}_6\text{H}_5\text{R} + 3 [\text{O}] \longrightarrow \text{C}_6\text{H}_5\text{COOH} + (\text{CO}_2)$; reagents: KMnO_4 in H_2SO_4 (aq); conditions: heat; observations: purple KMnO_4 is decolourised, white ppt of benzoic acid. Note: R is any alkyl group with at least one H attached to the C attached to the ring. CO_2 if R contains more than one C. Balance accordingly.
 - 4 $\text{RCH}_2\text{OH} + [\text{O}] \longrightarrow \text{RCHO} + \text{H}_2\text{O}$; reagents: $\text{K}_2\text{Cr}_2\text{O}_7$ (aq) in H_2SO_4 (aq); conditions: heat under distillation; observations: orange $\text{K}_2\text{Cr}_2\text{O}_7$ turns green.
 - 5 $\text{RCH}_2\text{OH} + 2 [\text{O}] \longrightarrow \text{RCOOH} + \text{H}_2\text{O}$; reagents: KMnO_4 (aq) or $\text{K}_2\text{Cr}_2\text{O}_7$ (aq) in H_2SO_4 (aq); conditions: heat; observations: purple KMnO_4 decolourises or orange $\text{K}_2\text{Cr}_2\text{O}_7$ turns green
 - 6 $\text{RCHOHR}' + [\text{O}] \longrightarrow \text{RC}(=\text{O})\text{R}' + \text{H}_2\text{O}$; reagents: KMnO_4 (aq) or $\text{K}_2\text{Cr}_2\text{O}_7$ (aq) in H_2SO_4 (aq); conditions: heat; observations: purple KMnO_4 decolourises or orange $\text{K}_2\text{Cr}_2\text{O}_7$ turns green. Test for 1° and 2° alcohol – 3° alcohol has no colour change.
 - 7 $\text{RCHO} + [\text{O}] \longrightarrow \text{RCOOH}$; reagents: KMnO_4 (aq) or $\text{K}_2\text{Cr}_2\text{O}_7$ (aq) in H_2SO_4 (aq); conditions: heat; observations: purple KMnO_4 decolourises or orange $\text{K}_2\text{Cr}_2\text{O}_7$ turns green
 - 8 $\text{RCHOHCH}_3 + 4 \text{I}_2 + 6 \text{NaOH} \longrightarrow \text{CHI}_3 + 5 \text{NaI} + \text{RCOO}^-\text{Na}^+ + 5 \text{H}_2\text{O}$; reagents: I_2 (aq) in NaOH ; conditions: heat; observations: pale yellow ppt
 - 9 $\text{RC}(=\text{O})\text{CH}_3 + 3 \text{I}_2 + 4 \text{NaOH} \longrightarrow \text{CHI}_3 + 3 \text{NaI} + \text{RCOO}^-\text{Na}^+ + 3 \text{H}_2\text{O}$; reagents: I_2 (aq) in NaOH ; conditions: heat; observations: pale yellow ppt
- Note: R must be an alkyl or aryl; the $(=\text{O})$ group cannot be part of a carboxylic acid, ester, or acyl chloride.
- 10 $\text{RCHO} + 2 [\text{Ag}(\text{NH}_3)_2]^+ + 3 \text{OH}^- \longrightarrow \text{RCOO}^- + 2 \text{Ag} + 4 \text{NH}_3 + 2 \text{H}_2\text{O}$; reagents: Tollens' reagent (NH_3 (aq) with AgNO_3); conditions: heat; observations: silver mirror or black ppt. Test for all aldehydes.
 - 11 $\text{RCHO} + 2 \text{Cu}^{2+} + 5 \text{OH}^- \longrightarrow \text{RCOO}^- + \text{Cu}_2\text{O} + 3 \text{H}_2\text{O}$; reagents: Fehling's reagent; conditions: heat; observations: reddish-brown ppt. Test for aliphatic (only) aldehydes.

C.7 Reduction

- 1 $\text{CH}_2=\text{CH}_2 + 2 [\text{H}] \longrightarrow \text{CH}_3\text{CH}_3$; reagents: H_2 (g); conditions: Ni cat., h.t.p. **or** Pd cat. or Pt cat, r.t.p.; observations: decrease in pressure
- 2 $\text{RCHO} + 2 [\text{H}] \longrightarrow \text{RCH}_2\text{OH}$; reagents, conditions: LiAlH_4 in dry ether or NaBH_4 in (m)ethanol or Na in ethanol or H_2 with Pd/Pt cat., r.t.p. **or** H_2 with Ni cat., heat
- 3 $\text{RC}(=\text{O})\text{R}' + 2 [\text{H}] \longrightarrow \text{RCHOHR}'$; reagents, conditions: LiAlH_4 in dry ether or NaBH_4 in (m)ethanol or Na in ethanol or H_2 with Pd/Pt cat., r.t.p. **or** H_2 with Ni cat., heat
- 4 $\text{RCOOH} + 4 [\text{H}] \longrightarrow \text{RCH}_2\text{OH} + \text{H}_2\text{O}$; reagents: LiAlH_4 in dry ether; conditions: r.t.p.
- 5 $\text{RCOOR}' + 4 [\text{H}] \longrightarrow \text{RCH}_2\text{OH} + \text{R}'\text{OH}$; reagents: LiAlH_4 in dry ether; conditions: r.t.p.
- 6 $\text{RCONR}'\text{R}'' + 4 [\text{H}] \longrightarrow \text{RCH}_2\text{NR}'\text{R}'' + \text{H}_2\text{O}$; reagents: LiAlH_4 in dry ether; conditions: r.t.p.
- 7 $\text{RCN} + 4 [\text{H}] \longrightarrow \text{RCH}_2\text{NH}_2$; reagents, conditions: LiAlH_4 in dry ether or H_2 , Pd/Pt cat., r.t.p. **or** H_2 , Ni cat., heat. Note: if using H_2 , then use H_2 in equation
- 8 $\text{C}_6\text{H}_5\text{NO}_2 + 6 [\text{H}] \longrightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2 \text{H}_2\text{O}$; reagents, conditions: Sn in exc. conc. HCl, heat then NaOH (aq), r.t.p.

C.8 Elimination

- 1 $\text{CH}_3\text{CH}_2\text{X} + \text{KOH} \longrightarrow \text{CH}_2=\text{CH}_2 + \text{KX} + \text{H}_2\text{O}$; reagents: ethanolic KOH; conditions: heat.
- 2 $\text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$; reagents, conditions: exc. conc. H_2SO_4 cat, 180°C or exc. conc. H_3PO_4 cat., 250°C or Al_2O_3 cat., 350°C


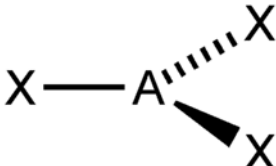
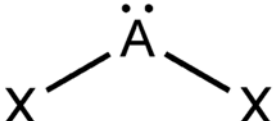
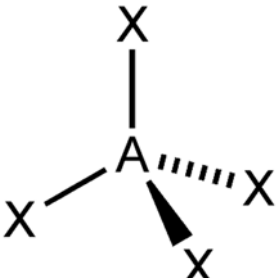

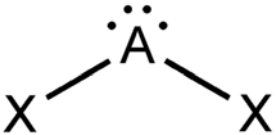
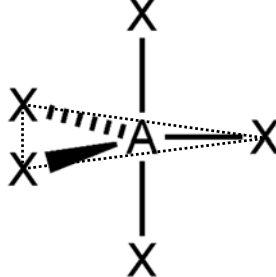
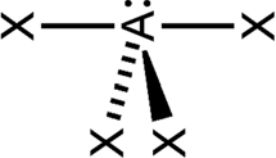
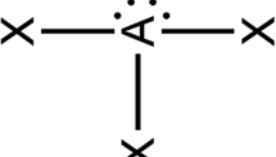
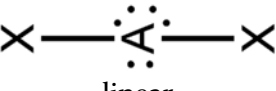
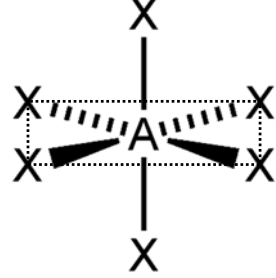
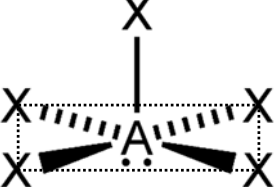

C.9 Hydrolysis

- 1 $\text{RCN} + 2 \text{H}_2\text{O} + \text{H}^+ \longrightarrow \text{RCOOH} + \text{NH}_4^+$; reagents: HCl (aq) or H_2SO_4 (aq); conditions: heat
- 2 $\text{RCN} + \text{H}_2\text{O} + \text{OH}^- \longrightarrow \text{RCOO}^- + \text{NH}_3$; reagents: NaOH (aq) or KOH (aq); conditions: heat
- 3 $\text{RCOOR}' + \text{H}_2\text{O} \rightleftharpoons \text{RCOOH} + \text{R}'\text{OH}$; reagents: HCl (aq) or H_2SO_4 (aq); conditions: heat
- 4 $\text{RCOOR}' + \text{NaOH} \rightleftharpoons \text{RCOO}^-\text{Na}^+ + \text{R}'\text{OH}$; reagents: NaOH (aq) or KOH (aq); conditions: heat
- 5 $\text{RCONR}'\text{R}'' + \text{H}_2\text{O} \rightleftharpoons \text{RCOOH} + \text{N}^+\text{H}_2\text{R}'\text{R}''$; reagents: HCl (aq) or H_2SO_4 (aq); conditions: heat
- 6 $\text{RCONR}'\text{R}'' + \text{NaOH} \longrightarrow \text{RCOO}^-\text{Na}^+ + \text{NHR}'\text{R}''$; reagents: NaOH (aq) or KOH (aq); conditions: heat

C.10 Miscellaneous

- 1 $\text{ROH} + \text{Na} \longrightarrow \text{RO}^-\text{Na}^+ + \frac{1}{2} \text{H}_2$; reagents: Na or K ; conditions: r.t.p.; observations: effervescence of H_2 ; ToR: acid-metal displacement
- 2 $\text{RCOOH} + \text{Na} \longrightarrow \text{RCOO}^-\text{Na}^+ + \frac{1}{2} \text{H}_2$; reagents: Na or K ; conditions: r.t.p.; observations: effervescence of H_2 ; ToR: acid-metal displacement
- 3 $\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \longrightarrow \text{C}_6\text{H}_5\text{O}^-\text{Na}^+ + \text{H}_2\text{O}$; reagents: NaOH ; conditions: r.t.p.; ToR: neutralisation
- 4 $\text{RCOOH} + \text{NaOH} \longrightarrow \text{RCOO}^-\text{Na}^+ + \text{H}_2\text{O}$; reagents: NaOH ; conditions: r.t.p.; ToR: neutralisation
- 5 $2 \text{RCOOH} + \text{Na}_2\text{CO}_3 \longrightarrow 2 \text{RCOO}^-\text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2$; reagents: Na_2CO_3 ; conditions: r.t.p.; ToR: neutralisation
- 6 $\text{RNH}_2 + \text{HCl} \longrightarrow \text{RNH}_3^+\text{Cl}^-$; reagents: mineral acid; conditions: r.t.p.; ToR: neutralisation
- 7 $\text{RC}(=\text{O})\text{R}' + \text{o,p-C}_6\text{H}_3(\text{NHNH}_2)(\text{NO}_2)_2 \longrightarrow \text{o,p-C}_6\text{H}_3(\text{NHN}=\text{C}(\text{R})\text{R}')(\text{NO}_2)_2 + \text{H}_2\text{O}$;
reagents: 2,4-dinitrophenylhydrazine (2,4-DNPH i.e. Brady's reagent); conditions: heat; observation: orange crystals of hydrazone; ToR: condensation. Test for all aldehydes and ketones.
- 8 $\text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{FeCl}_3} \text{violet complex}$; reagents: neutral FeCl_3 (aq); conditions: r.t.p.; observations: violet complex formed; ToR: complexation. Test for phenol.

Annex: Shapes of Molecules

e.p.	Basic shape	l.p.	Shape	\angle	P	E.g.
2	 linear	0	(same)	180°	N	CO ₂
3	 trigonal planar	0	(same)	120°	N	BF ₃
		1	 bent	119°	Y	SnCl ₂
4	 tetrahedral	0	(same)	109.5°	N	CH ₄
		1	 trigonal pyramidal	107°	Y	NH ₃
		2	 bent	104.5°	Y	H ₂ O
5	 trigonal bipyramidal	0	(same)	120° on plane; 90° on perpendicular axis	N	PCl ₅
		1	 distorted tetrahedral	119° on plane; $<90^\circ$ on perpendicular axis	Y	SF ₄
		2	 T-shaped	$<90^\circ$ on perpendicular axis	Y	ClF ₃
		3	 linear	180°	N	XeF ₂
6	 octahedral	0	(same)	90°	N	SF ₆
		1	 square pyramidal	$<90^\circ$	Y	IF ₅
		2	 square planar	90°	N	XeF ₄