

# Chem Notes

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This compilation of notes are made as a reference for the GCE "A"-level Chemistry Paper, focusing on brief explanations on theories as well as (ideally) exhaustive collections of writing for answering technique. These notes are meant for free, public use, but at the reader's own risk.  
Good luck with your exams.

# 1 Stoichiometry

## 1.1 Particles and Relative Mass

### Definition 1.1: Proton Number / Atomic Number

The Proton Number is the number of protons in an atom of that element. This determines the identity of the atom.

### Definition 1.2: Nucleon Number / Mass Number

The Nucleon Number is the total number of protons and neutrons in the nucleus of an atom.

### Definition 1.3: Nuclide

A Nuclide is a species of atom with a specific proton number and nucleon number, written  $\frac{\text{Nucleon Number}}{\text{Proton Number}}\text{X}$

### Definition 1.4: Isotope

Isotopes of an element are atoms with the same proton number but different nucleon numbers. Isotopes tend to have similar chemical properties but differing physical properties (melting point, boiling point etc).

### Definition 1.5: Relative Isotopic Mass

Relative Isotopic Mass is the mass of an atom of a specific isotope divided by  $\frac{1}{12}$  the mass of a carbon-12 atom, and is unitless

### Definition 1.6: Relative Atomic Mass

Relative Atomic Mass is the weighted average of the masses of naturally occurring species of a specific element, and is unitless. The value is calculated as

$$A_r = \frac{\sum \text{Nucleon number} \times \text{Fractional abundance}}{\frac{1}{12} \text{ the mass of a carbon-12 atom}}$$

### Definition 1.7: Relative Molecular / Formula Mass

Relative Molecular Mass is the relative mass of one covalent molecule of a certain substance, obtained as the sum of the  $A_r$ s of its constituent atoms. Relative Formula Mass is similar but used for ionic compounds and is calculated using the smallest collection of atoms from which a formula can be made (AKA a formula unit).

## 1.2 The Mole

### Definition 1.8: Mole

A mole of substance is the amount of a substance which contains as many elementary elements (molecules, ions, electrons, atoms, particles etc) as there are atoms in 12 grams of carbon-12. Alternatively, it is the amount of substance which contains  $6.0 \times 10^{23}$  elementary elements, also known as the Avogadro constant and written as  $L$ .

### Definition 1.9: Molar Mass

Molar mass is the mass of a mole of substance with units grams per mole.

## 1.3 Chemical Formulae

### Definition 1.10: Empirical Formula

The Empirical Formula of a compound is the simplest ratio of different element's atoms in one molecule.

### Definition 1.11: Molecular Formula

The Molecular Formula of a compound is the actual number of atoms of each element in one molecule of the compound.

A molecular formula of a substance is always a multiple of its empirical formula. Since ionic compounds do not exist in single molecules, they do not have a molecular formula.

## 1.4 Stoichiometry

### Definition 1.12: Stoichiometry

Stoichiometry is defined as the study of the proportions of which molecules react with each other.

### Definition 1.13: Stoichiometric Amounts

Stoichiometric Amounts of a substance are the amounts which undergo reaction.

From a balanced equation, one can obtain ratios of moles of reactants and products, masses of reactants and products and volumes of gases evolved.

### 1.4.1 Limiting Reagent

When reacting substances, reactants may exceed stoichiometric amounts and not be reacted.

### Definition 1.14: Limiting Reagent

The Limiting Reagent in a reaction is the reactant which is deficient and consumed completely in a reaction.

### 1.4.2 Yield

### Definition 1.15: Theoretical Yield

The Theoretical Yield of a reaction is the mass of product formed calculated using the chemical equation and the amount of limiting reagent used.

### Definition 1.16: Actual Yield

The Actual Yield of a reaction is the mass of product that is actually obtained after reaction.

### Definition 1.17: Percentage Yield

The Percentage Yield is the ratio of actual yield to theoretical yield presented in percent.

### 1.4.3 Volume of Gases

Avogadro's hypothesis states that at constant temperature and pressure, any volume of gas will have the same number of molecules.

#### Definition 1.18: Molar Volume

The Molar Volume  $V_m$  is the volume taken up by 1 mole of gas at a certain temperature and pressure. Common temperatures and pressures include:

Standard Temperature and Pressure (s.t.p.) at 273 K and 100 000 Pa or 1 bar gives  $V_m = 22.7 \text{ dm}^3 \text{ mol}^{-1}$ .

Room Temperature and Pressure (r.t.p.) at 293 K and 101 325 Pa or 1 atm gives  $V_m = 24 \text{ dm}^3 \text{ mol}^{-1}$ .

## 1.5 Concentration

#### Definition 1.19: Solution

A Solution is a homogeneous mixture of two or more substances, with the more abundant substance being the solvent and the less abundant substance the solute.

#### Definition 1.20: Concentration

The Concentration of a substance is the amount or mass of substance dissolved per unit of solvent or solution. The molar concentration is written by enclosing the name of substance in square brackets and has units  $\text{mol dm}^{-3}$ . The mass concentration has units  $\text{g dm}^{-3}$ .

#### Definition 1.21: Standard Solution

A Standard Solution is a solution of known constitution and concentration.

## 1.6 Acid-Base Titration

#### Definition 1.22: Volumetric Analysis

Volumetric Analysis, otherwise called Titrimetric Analysis, is a category of experiments which involve the precise measurement of volumes of solutions which react, typically involving the reaction of a standard solution (titrant) with a solution of unknown concentration (titre) to obtain the concentration of the unknown solution by adding one solution to another solution until stoichiometric amounts of reactants have reacted.

### 1.6.1 Acids and Bases

#### Definition 1.23: Arrhenius Acids and Bases

Arrhenius Acids are substances which increase the concentration of  $\text{H}^+$  in a solution while an Arrhenius Base increases the concentration of  $\text{OH}^-$  in a solution. Both react to form  $\text{H}_2\text{O}$ .

#### Definition 1.24: Brønsted Acids and Bases

Brønsted-Lowry Acids are substances which donate protons while Brønsted-Lowry Bases receive protons.

#### Definition 1.25: Lewis Acids and Bases

Lewis Acids are substances which receive electron pairs while Lewis Bases are substances which donate electron pairs.

#### Definition 1.26: Strength of Acid / Base

The Strength of an Acid or a Base is the extent of which it dissociates in an aqueous solution. Strong acids and bases exist as completely disassociated solutions while weak acids and bases are observed to exist in their complete molecules. The acidity constant,  $K_a$  or  $\text{p}K_a$  of an acid HA is defined by  $\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$  when the dissociation is in equilibrium.

#### Definition 1.27: Basicity

The Basicity of an acid is how many  $\text{H}^+$  ions it ionizes per molecule.

### 1.6.2 Titration Curves and Indicators

#### Definition 1.28: Equivalence Point

The Equivalence Point is said to be reached when an acid-base mixture has undergone complete neutralization and is signified by a region of rapid pH change in the pH-Volume curve.

The equivalence point of an acid-base titration depends on whether its acid and base used is strong or weak. Strong acid - weak base reactions have rapid pH change from 3.5 to 6.5 and call for indicators like methyl orange (red-orange-yellow) and screened methyl orange (violet-grey-green) while weak acid - strong base reactions call for thymol blue (yellow-green-blue), phenolphthalein (colorless-pink) and thymolphthalein (colorless-blue). For phenolphthalein and thymolphthalein, the endpoint colors depend on the titrant. Strong-acid strong-base reactions can use all of the above indicators while weak-acid weak-base reactions have no suitable indicator.

### 1.6.3 Back Titration

Back titrations are used when the qualities of a substance need to be assessed when they cannot be easily dissolved into a solution, such as solid carbonates. Samples are reacted fully with a standard solution and the standard solution is then titrated against to investigate the change in its concentration to determine the properties of the sample.

### 1.6.4 Double Indicator Method

The double indicator method is used when assessing titrations which have more than one region of rapid pH change. Multiple equivalence points suggest that there are multiple stages to a reaction and hence the amount of titrant used to reach a certain stage can be examined at multiple points and used to infer more data.

For a titration of a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ , phenolphthalein can be added as an indicator to find the

first equivalence point. After reaching that point, methyl orange is then added to find the second equivalence point.

## 1.7 Redox

### Definition 1.29: Oxidation

Oxidation occurs when a species of atom loses electrons.

### Definition 1.30: Reduction

Reduction occurs when a species of atom gains electrons.

### Definition 1.31: Redox

Redox reactions occur when reduction and oxidation occurs simultaneously.

### Definition 1.32: Disproportionation

Disproportionation reactions occur when the same element is simultaneously oxidized and reduced. The opposite reaction is called comproportionation.

	Oxidation	Reduction
O <sub>2</sub>	+	-
H	-	+
e <sup>-</sup>	-	+
Oxidation Number	+	-

### 1.7.1 Oxidation Number

1. Elements have 0 oxidation state. Elements bonded to the same element as itself only have 0 oxidation state.
2. All F in compounds have -1.
3. All H in compounds have +1, except for -1 in metal hydrides.
4. All O in compounds have -2, except for -1 in peroxides, -0.5 in superoxides and +2 in OF<sub>2</sub>.
5. All ions and compounds have net oxidation state equal to their charge.
6. More electronegative atoms have lower oxidation numbers than less electronegative atoms.

Fractional oxidation states exist.

### 1.7.2 Balancing Redox Equations

Note that given a reduction and oxidation process, the net amount of e<sup>-</sup> does not change. Use this to determine the ratio of other reactants and the amount of e<sup>-</sup> consumed or produced in an unknown reduction or oxidation reaction.

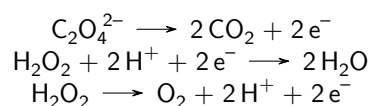
1. Write and balance half equations of products and reactants.
2. Balance O with H<sub>2</sub>O and H with H<sup>+</sup> or OH<sup>-</sup> depending on which is present.

3. Balance charges with e<sup>-</sup>.

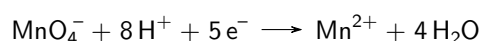
4. Combine both reactions to balance e<sup>-</sup> and remove common reactants and products.

### 1.7.3 Redox Titration

Common half-equations include:



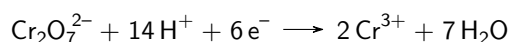
Manganate(VII) titrations involve the half-reaction



in acidic medium and  $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$  in basic medium. Due to the purple color of  $\text{MnO}_4^-$ , the reaction is self-indicating and the end point is reached whenever there is an appearance or disappearance of purple tint in the solution.

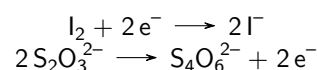
Fe<sup>3+</sup> solutions in  $\text{MnO}_4^-$  titrations are yellow before titration, while H<sub>2</sub>O<sub>2</sub> solutions are colorless.

Dichromate(VI) titrations involve the half-reaction



in acidic medium. Though orange  $\text{Cr}_2\text{O}_7^{2-}$  ions turn into green  $\text{Cr}^{3+}$  ions, green appears significantly before an endpoint is reached and hence requires indicators like barium / sodium diphenylamine p-sulphonate or diphenylamine (green to blue-violet) or N-phenylanthranilic acid (green to red-violet).

Iodine and thiosulphate react with each other with the half-equations:



And a titration of thiosulphate ions into a solution containing I<sub>2</sub> can be used to assess the amount of I<sub>2</sub> in said solution. Otherwise called Iodometric titrations, they usually involve the creation of I<sub>2</sub> by adding some substance to KI and then titrating with standard S<sub>2</sub>O<sub>3</sub><sup>2-</sup> solution until the solution turns near colorless, at which starch solution is added to create starch-iodine complexes which are blue-black and can easily identify an endpoint, with the color change of dark blue to colorless. Solutions left exposed to air will eventually turn blue again due to atmospheric oxidation of I<sup>-</sup>.

## 1.8 Miscellaneous

### Definition 1.33: Precipitation Reaction

Precipitation reactions involve the reaction of two solutions to form solid products.

## 2 Atomic Structure

### 2.1 Structure of the Atom

Atoms are made of the nucleus (diameter  $10 \times 10^{-14}$  m) which contains its protons and neutrons and the electron cloud (diameter  $10 \times 10^{-10}$  m) surrounding the nucleus.

#### 2.1.1 Deflection in an Electric Field

When a beam of particles are passed between two charged electric plates, charged particles experience an electric force which deflects them from the original direction of motion. Negatively charged particles are attracted to positive plates and positively charged particles are attracted to negatively charged plates. The magnitude of deflection or angle of deflection is observed to be proportional to the  $\frac{\text{charge}}{\text{mass}}$  ratio. The larger the charge on a particle the larger the electric force experienced, and the larger the mass the lesser the amount of deviation which results from the same amount of force.

#### 2.1.2 Orbitals

Electrons do not occupy fixed positions around a nucleus but rather are constantly present in regions of space around the nucleus known as atomic orbitals and have differing levels of energy.

##### Definition 2.1: Shell

A electronic shell is a collection of electrons which share a similar energy level.

##### Definition 2.2: Principal Quantum Number

The Principal Quantum Number (written as **n**) is a description of which shell an electron is in. Large values of **n** imply that the electron tends to move far away from the nucleus as well as having a larger sized orbital (AKA more diffuse), has a high amount of energy and has weaker electrostatic attraction between nucleus and electron.

##### Definition 2.3: Atomic Orbital

An Atomic Orbital is a certain space around a nucleus where electrons tend to move inside, and where there is a high probability of observing an electron inside. Each atomic orbital has a certain geometry and a certain amount of energy which is described by its principal quantum number. Each orbital can contain a maximum of two electrons.

##### Definition 2.4: Subshell

Shells are categorized into Subshells which then comprise of electrons with similar geometries. Subshells include the s, p, d and f shells.

s orbitals have a spherical shape. s subshells have 1 orbital and contain 2 electrons.

p orbitals have a dumbbell shape which are oriented along perpendicular axis, and are labeled as the  $p_x$ ,  $p_y$  and  $p_z$

orbitals. p subshells have 3 orbitals and contain 6 electrons.

d orbitals generally have a 4-lobed shape with three orbitals ( $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ ) pointing between axis, one orbital  $d_{x^2-y^2}$  and one orbital along the z axis as well as a torus along the x-y plane  $d_{z^2}$ . d subshells have 5 orbitals and contain 10 electrons.

The  $n^{\text{th}}$  shell will hence have **n** subshells and contain  $n^2$  orbitals and  $2n^2$  electrons.

#### 2.1.3 Electronic Configuration

##### Definition 2.5: Electronic Configuration

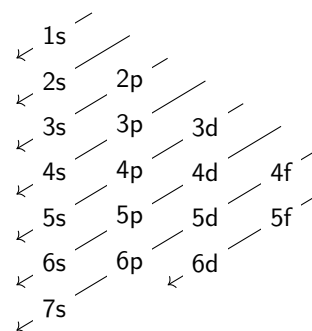
The Electronic Configuration of an atom or ion is a description of how its electrons are distributed among its shells, subshells and orbitals.

##### Definition 2.6: Isoelectronic Species

Isoelectronic Species are atoms or ions which have the same number of electrons, regardless of electronic configuration.

##### Definition 2.7: Aufbau Principle

The Aufbau Principle states that electrons fill the orbitals with the lowest energy level first. The energy level of an orbital is determined by experimentation and has been estimated by equations such as the Schrödinger equation.



Note that the 4s orbital fills before the 3d orbital.

##### Definition 2.8: Pauli Exclusion Principle

The Pauli Exclusion Principle states that one orbital can contain a maximum of two electrons and that they must be of opposite spins in order to reduce intra-electronic repulsion through magnetic attraction as a result of their opposite spin.

##### Definition 2.9: Hund's Rule

Hund's Rule states that orbitals in a subshell must all have at least one electron before any orbital can have two in order to minimise intra-electronic repulsion.

Exceptions governing electronic configuration:

**Group 6** elements have electronic configuration of  $d^5 s^1$  rather than  $d^4 s^2$  since inter-electronic repulsion is minimized.  $d^4$  shells are generally not observed. One example of such an element is Cr with configuration  $[\text{Ar}] 3d^5 4s^1$

**Group 11** elements have electronic configuration of  $d^{10} s^1$  rather than  $d^9 s^2$  since a fully filled d subshell is more stable than the 4s subshell due to geometric symmetry.  $d^9$  shells are generally not observed. One example of such an element is Cu with configuration  $[\text{Ar}] 3d^{10} 4s^1$

### 2.1.4 Written Electronic Configuration

Electronic configuration is written as a series of subshells and the amount of electrons present in the orbital.

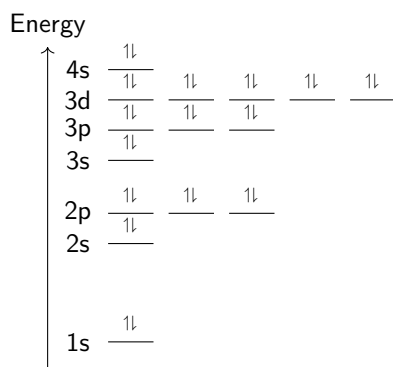
Electronic Configuration for Xenon:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 4d^{10} 5s^2 5d^{10}$

In long answer questions, when explaining electronic configuration, shorthand can be used.

Electronic Configuration for Cesium:  $[\text{Xe}] 6s^1$

### 2.1.5 Energy Level Diagrams

Energy level diagrams are used to represent the energy levels of differing orbitals. The y axis is labeled as energy while to the right each subshell's orbitals are represented as a dash, with electrons in an orbital represented as arrows.



### 2.1.6 Electronic Configuration of Ions

Anions have electrons added to the next energetically accessible orbital. Electronic configuration is calculated as usual.

Cations have their electrons removed from the orbital of highest energy. Electrons occupy the orbital of lowest energy level first (4s before 3d), but once inner orbitals are filled these inner orbitals will repel outermost orbitals and promote them to a higher energy level (hence 4s is removed before 3d when being ionized).

Keep in mind that electronically accessible  $\neq$  highest/lowest energy.

### 2.1.7 Excited Particles

#### Definition 2.10: Ground State

An atom or ion is in its ground state when all electrons are in orbitals of the lowest available energy level / at its most stable.

#### Definition 2.11: Excited State

An atom or ion in an excited state has absorbed energy and has electrons which are promoted to higher energy levels, which can then emit energy to return to ground state. Excited particles are denoted with an asterisk to the right ( $C^*$ ).

## 2.2 Periodic Table Trends

### 2.2.1 Common Properties

There are three main factors which affect properties of atoms:

#### Number of Electronic Shells :

The higher the principal quantum number of an atom, the larger the distance between the nucleus and its valence electrons and hence the weaker the electrostatic attraction between the nucleus and the valence electrons.

#### Size of Nuclear Charge :

The larger the number of protons in an atom, the stronger the electrostatic attraction between the nucleus and the valence electrons.

#### Shielding Effect by Inner Electrons :

The larger the number of inner shell electrons, the larger the shielding effect experienced by the valence electrons and hence the weaker the electrostatic attraction between the nucleus and the valence electrons.

All electrons repel each other due to their negative charge, hence electrons in inner shells repel electrons in outer shells and prevent outer electrons from experiencing the full nuclear charge.

#### Definition 2.12: Effective Nuclear Charge

The Effective Nuclear Charge is the combination of the effects of size of nuclear charge with shielding effect by inner electrons on the strength of electrostatic attraction between nucleus and valence electrons of a particle, typically used when comparing elements down a period.

Explanations tend to follow a pattern of [Down a group / Across a period]  $\rightarrow$  [# of shells + Nuclear Charge + Shielding]  $\rightarrow$  [Electrostatic Attraction increases/decreases]  $\rightarrow$  [Property].

Across a period:

**Number of Electronic Shells** remains constant.

**Effective Nuclear Charge** increases as number of protons increases to increase the nuclear charge and though the number of electrons increase, they are added to the same quantum shell which means shielding effect remains approximately constant.

**Electrostatic Attraction** between nucleus and valence electrons hence increases across a period.

Down a group:

**Number of Electronic Shells** increases, increasing the distance between valence electrons and the nucleus.

**Nuclear Charge** may increase, but is not as significant.

**Electrostatic Attraction** between nucleus and valence electrons hence decreases down a group.

### 2.2.2 Electronegativity

#### Definition 2.13: Electronegativity

Electronegativity is the tendency of an atom to attract bonding electrons.

Electronegativity increases as electrostatic attraction increases.

### 2.2.3 Atomic Radius

#### Definition 2.14: Atomic Radius

Atomic Radius is the shortest inter-nuclear distance found in the structure of an element. Metallic elements calculate radius from half the distance between to neighboring atoms in a metal. Covalent elements calculate radius from half the distance between two bonded atoms. Monatomic elements calculate radius from half the distance between two atoms which are not bonded.

Atomic radius increases as electrostatic attraction decreases.

### 2.2.4 Ionic Radius

#### Definition 2.15: Ionic Radius

Ionic Radius is the radius of the spherical ion in an ionic compound.

Ionic Radius of isoelectronic species increase as electrostatic attraction decreases.

### 2.2.5 First Ionization Energy

#### Definition 2.16: First Ionization Energy

The First Ionization Energy of a atom is the amount of energy required to be supplied to remove one mole of  $e^-$  from one mole of gaseous atoms.

First Ionization Energy increases as electrostatic attraction increases.

Two exceptions occur to this trend:

**Group 2 and 13** notices that group 13 elements have a lower first IE than group 2 elements, since the p electron in group 13 is at a higher energy level than that of the s electron in a group 2, hence less energy is needed to remove electrons from the group 13 element.

**Group 15 and 16** notices that group 16 elements have a lower first IE than group 15 elements since the paired p orbital in group 16 elements exhibits inter-electronic repulsion that is not present in the group 15 element with unpaired p orbitals, hence less energy is required to remove electrons from the group 16 element.

### 2.2.6 nth Ionization Energy

Successive IEs of an element increase since each successive electron being removed is being extracted from an ion of increasing positive charge which attracts its electrons more strongly.

There is a large increase of IE when electrons are removed from a different quantum shell and a smaller increase of IE when electrons are removed from a different subshell. Use these observations to infer the group of an element when given its successive IEs.

## 3 Chemical Bonding I

### 3.1 Chemical Bonding

#### Definition 3.1: Chemical Bonds

Chemical Bonds are binding forces of attraction between atoms, ions or molecules which result in a lower energy arrangement, involving the rearrangement of outer electrons of particles.

The "Octet rule" states that atoms tend to rearrange electrons until they have 8 electrons in a valence shell, but this "rule" has many exceptions. Usually it is only applied to noble gases other than helium and particles in the first and second periods of the periodic table.

Molecules with less than 8 electrons in their valence shell are described as electron deficient and are able to accept electrons to achieve an octet structure. Molecules with an odd number of electrons are described as radicals and readily form bonds with other radicals or other particles.

### 3.2 Covalent Bonds

#### Definition 3.2: Covalent Bonds

Covalent Bonds are the electrostatic forces of attraction between two positively charged nuclei and the shared pair of electrons.

Note that the definition states "positively charged nuclei" rather than "atom", the atom itself is not necessarily

charged.

Covalent bonds are generally formed by two atoms sharing electrons among each other, in order for an atom to gain electrons in its orbit to achieve the energetically stable octet / noble gas configuration.

Dative covalent bonds occur when a shared pair of electrons in a covalent bond are provided by only one of the bonding atoms, drawn in structural formula as a arrow pointing from the donor to the recipient atom rather than a solid line. Dative covalent bonds are received by atoms when they have vacant, low-lying orbitals to accept electrons.

### 3.2.1 Sigma and Pi Bonds

Sigma  $\sigma$  bonds involve the overlap of two electron orbitals head-on. Pi  $\pi$  bonds involve the overlap of two electron orbitals side-to-side. Single covalent bonds have one  $\sigma$  bond, while double or triple bonds have one  $\sigma$  and one or two  $\pi$  bonds.  $\sigma$  bonds are stronger than  $\pi$  bonds since head-on electron orbital overlap is stronger than side-to-side overlap. This is used to explain the fact that the strength of a double bond is less than twice that of a single bond (mathematically speaking,  $\sigma + \pi < 2\sigma$ ).

### 3.2.2 Factors Affecting Strength of Covalent Bonds

#### Definition 3.3: Strength of a Covalent Bond

The Strength of a Covalent Bond is measured by its Bond Energy / Bond Enthalpy, which is the average energy absorbed when one mole of a bond is broken in a gaseous state.

A larger number of bonds between atoms result in stronger covalent bonds. More electrons are shared between atoms, creating a higher density of electrons in the inter-nuclear region, hence there is increased electrostatic attraction between bond pairs and nuclei, hence increasing bond strength. This is used when comparing bonds of different

A larger atomic radius results in weaker covalent bonds. A larger electron cloud size among bonded atoms means that bonded electrons are more diffuse and spread out, hence there is a decrease in the "effectiveness of overlap" of larger atoms as compared to smaller atoms, hence there is a decrease in electrostatic attraction between bond pairs and nuclei and a reduction in bond strength. This is typically used to compare between bonds involving atoms with significantly different atomic radius and atoms of the same group.

A larger difference in electronegativity results in stronger covalent bonds. Differences in electronegativity in bonded atoms result in the formation of partial charges among the bonded atoms, where the more electronegative atom attracts bonded electrons strongly, hence there is stronger electrostatic attraction due to the presence of opposite partial charges, hence increasing bond strength. This is typically used to compare between bonds involving atoms

with significantly different electronegativities and in cases where bonds involve Fluorine.

### 3.2.3 Implications of Stronger Covalent Bonds

Stronger covalent bonds reduce the distance between two nuclei, reducing the bond length.

Strongly covalently bonded atoms are less likely to react.

## 3.3 Intermediate Bond Types

### 3.3.1 Covalent Bonds with Ionic Character

Some covalent bonds involve atoms with different degrees of electronegativity. With this difference in electronegativity, electrons are more strongly attracted to one nucleus than the other, making the electron pair(s) in a covalent bond unequally shared, giving rise to a polar covalent bond.

#### Definition 3.4: Dipole Moment

Dipole moment is the quantification of the degree of polarity of a bond, calculated as a product of the charge and distance between charges. The greater the dipole moment, the more polar the bond.

Dipole moment is drawn as an arrow with a perpendicular line at its other end, pointing towards the more electronegative atom. Dipole moment of a molecule is the vector sum of all dipole moments in its bonds, and a molecule with a non-zero dipole moment is considered a polar molecule.

### 3.3.2 Ionic Bonds with Covalent Character

Cations attract the electron cloud of the anion and distorts the electron cloud towards the cation, causing covalent character in an ionic bond. The degree of covalent character in an ionic bond is dependent on the ability of the cation to polarize the anion by having a dense positive charge (high charge and small radius) and the ability of the the anion to be polarized by having a large electron cloud.

Typically ionic compounds which have a large degree of covalency result in covalent bonds being formed. This gives rise tho the case where  $\text{AlF}_3$  is ionic but  $\text{AlCl}_3$  since Al has a high charge density and Cl has a larger electron cloud size than F. Therefore,  $\text{AlF}_3$  and  $\text{Al}_2\text{O}_3$  are ionic but  $\text{AlCl}_3$  is covalent.

## 3.4 Intermolecular Forces of Attraction

Simple Covalent substances exist as simple, small molecules. Physical state changes (melting, boiling) involve the manipulation of Intermolecular Forces of Attraction (IMF) rather than breaking or forming covalent bonds.



### 3.4.1 Instantaneous Dipole-Induced Dipole

Instantaneous dipole-induced dipole (id-id) interactions occur in all simple covalent molecules since all molecules have an electron cloud. At a point in time the random motion of electron orbitals may cause asymmetrical distribution of electrons to create an instantaneous dipole, which then induces a dipole in a neighboring particle, creating synchronized motion between two particles and hence a attraction between them. id-id interactions are short lived because instantaneous dipoles do not last as long. The strength of id-id interactions is hence considered weak.

The larger the number of electrons in a molecule and the larger the surface area of a molecule (straight chain hydrocarbons vs branched hydrocarbons), the stronger the id-id interaction.

### 3.4.2 Permanent Dipole-Permanent Dipole

Permanent dipole-permanent dipole (pd-pd) interactions occur in polar covalent molecules. Polar molecules align themselves such that their positive dipole is in line with the negative dipole of other molecules and vice versa, where the electrostatic attraction between dipoles gives rise to pd-pd interactions.

The larger the dipole moment of an electron, the stronger its pd-pd interactions.

In most cases where the number of electrons between molecules is similar, the molecule with a dipole has a higher melting or boiling point because it has pd-pd ON TOP OF the id-id which nonpolar molecules have. However, id-id interactions have a higher upper bound of strength and if the electron cloud size is large enough, id-id interactions can be stronger than pd-pd interactions of a smaller molecule.

### 3.4.3 Ion-Dipole Interactions

Ion-dipole interactions arise when ions are exposed to polar molecules, at which a favorable orientations between ionic charges and dipole moments allow for a reduction in energy level. This is the primary interaction involved when dissolving ionic solids in water and other polar solvents.

When drawing ion-dipole interactions, be sure to indicate regions of electron density  $\delta^-$  and electron deficiency  $\delta^+$  on the dipole as well as a dotted line between the ion and dipole, showing at least one interaction per possible pair of ion and dipole.

### 3.4.4 Hydrogen Bond

Hydrogen bonds are a special category of pd-pd interaction which is exceptionally strong due to the small but highly electronegative hydrogen atom. F, O or N bonded to H is highly polar and causes electron density to be highly withdrawn from the H atom, making the H atom

have a very high positive dipole, which then readily attracts a lone pair from another F, O or N from an adjacent molecule. F, O or N are required due to their high electronegativity which is able to induce a positive dipole on H and their small size which can then bring a lone pair close to the H atom for hydrogen bonds to form.

Hydrogen bonds are the strongest IMF. When comparing strength of H-bonding between different molecules which are capable of forming H-bonds, highlight the number of hydrogen bonds it can form on average per molecule, which is limited by the number of H bonded to F, O and N or the number of lone pairs in F, O and N, whichever is lower, and identify which molecule has more extensive H-bonding. Strength of a H-bond also depends on the dipole moment of a bond between H and some atom hence HF has higher melting/boiling points than  $\text{NH}_3$ .

$\text{H}_2\text{O}$ , when frozen, creates a highly-ordered tetrahedral lattice among molecules due to hydrogen bonding, where each oxygen atom is bonded to 4 hydrogen atoms, causing water to expand when frozen.

H-bonding in organic molecules with the carboxylic acid group  $\text{COOH}$  form dimers in gaseous state due to the presence of  $\text{O-H}$  bonds.

Intramolecular H-bonding can occur in molecules where its H and F/O/N molecules which could be used for hydrogen bonding instead bond within a molecule instead of between molecules, reducing sites available for H-bonding and reducing the overall IMF.

### 3.4.5 Solubility

For a solute to dissolve in a solvent, the intermolecular forces in the solute and solvent should be similar. This is because the energy released in the formation of IMF between solvent and solute needs to be large enough to overcome IMF between solvent and IMF between solute, and is hence ensured by having similar types of IMF.

Simple molecules with the same type of intermolecular bonds mix well. If the solute-solute interaction and the solvent-solvent interaction is the same as the solvent-solute interaction, dissolution will be favorable because there is sufficient energy released in the formation of IMF to break preexisting IMF. If not, dissolution will be unfavorable because one of the interactions are weaker than the other and energy released in formation of IMF is not sufficient to overcome preexisting IMF.

As an exception to this rule, ionic solids (pd-pd) also tend to dissolve in water (H-bonds) because of the strong ion-dipole interactions with polar molecules and compensate for overcoming strong ionic bonds in the solid and H-bonds among water molecules.

Another addition to this rule would be the case where a solute reacts with solvent to create products which are able to form favorable interactions with the solvent (to follow

the first or second rule).

### 3.5 Ionic Bonds

#### Definition 3.5: Ionic Bonds

Ionic Bonds are the electrostatic forces of attraction between two oppositely charged ions.

Ions are usually formed through the transfer of electrons from one (usually metallic) atom to another (usually non-metallic) atom. Ions in a solid are held in fixed and orderly arrangements.

#### Definition 3.6: Coordination Number

The Coordination number is the number of nearest neighbors to an atom

Ionic solids generally have high melting and boiling points above 500 °C and are all solids at room temperature. Ionic solids are generally soluble in polar solvents, conduct electricity in molten or aqueous states and are hard and brittle.

#### 3.5.1 Factors Affecting Strength of Ionic Bond

#### Definition 3.7: Lattice Energy

Lattice Energy is the energy released when one mole of ionic crystalline solid is formed from its constituent gaseous ions.

Ionic bonds are generally strong. The strength of an ionic bond, or its lattice energy is related to the charges on an ionic compound's constituent ions and their radii:

#### Equation 3.1: Lattice Energy

The Lattice Energy LE of an ionic compound is dependent on its cationic charge  $q_+$ , anionic charge  $q_-$  and interionic distance  $r_+ + r_-$ :

$$|LE| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$$

### 3.6 Giant Covalent Molecules

A giant covalent molecule is made of atoms held together in an extensive network by covalent bonds, such as graphite and quartz.

#### 3.6.1 Diamond

Diamond contains molecules of carbon which are covalently bonded to 4 other carbon atoms in a tetrahedral arrangement. Strong covalent bonds between carbon atoms mean that the molecule has a high melting and boiling point and is very strong. Diamond also has no unbonded electrons and hence is an insulator.

#### 3.6.2 Graphite

Graphite is carbon in a layered structure, made of planes of bonded hexagonal rings of carbon atoms. Each carbon atom is singly bonded with other carbon atoms at a 120

°angle, leaving one electron in a p orbital not involved in bonding, hence forming an extended  $\pi$  electron cloud above and below a layer of carbon atoms. This electron cloud contains delocalised electrons which conduct electricity.

Strong covalent bonds between carbon atoms mean that the boiling point of graphite is very high. However, layers of graphite are held together by weak IMF which then allow graphite to be malleable and soft as they can glide over each other.

#### 3.6.3 Quartz

Quartz  $\text{SiO}_2$  contains silicon atoms covalently bonded to 4 oxygen atoms in a tetrahedral shape while oxygen atoms are bonded to 2 silicon atoms. Due to strong covalent bonds and its rigid 3-dimensional structure, quartz is hard and insoluble as well as having a high melting and boiling point.

### 3.7 Metallic Bonds

Metals are composed of a rigid lattice of positive ions surrounded by a "sea of electrons".

Metals have high electrical conductivity in solid and liquid states due to the availability of free electrons as mobile charge carriers. Metals are also good conductors of heat as mobile electrons are fast-moving and mobile. Metals are also malleable and ductile as non-directional metallic bonds allow layers of metals to glide over each other without breaking metallic bonds. Metals are closely packed and have high densities. Metals generally have high melting and boiling points.

#### 3.7.1 Factors Affecting Strength of Metallic Bond

Metallic bonds are strong and non-directional, with each nucleus attracting electrons in its surroundings.

A higher number of valence electrons in a atom result in stronger metallic bonds.

A smaller cationic size of a metal atom results in stronger metallic bonds. A metallic cation of smaller radius will have a higher charge density and hence have a stronger attraction to delocalised electrons.

### 3.8 Geometry of Molecules

#### 3.8.1 Dot and Cross

Dot and cross representations aim to show the distribution of electrons in a particle, especially highlighting which electrons originate from which atom.

Ionic Dot and Cross diagrams are drawn using one formula unit of the ionic compound. Ions are drawn enclosed within square brackets with their charge written in superscript to the right. Multiple atoms in a ionic compound

are represented with a coefficient to the left of the dot and cross diagram. Typically, the metallic ion has no more electrons in its valence shell hence when required to draw valence electrons only the metallic atom typically has no electrons surrounding it. Be sure to show that the non-metallic atom has received electrons from an external source by drawing a suitable number of electrons with a different sign surrounding the nonmetal atom.

Covalent Dot and Cross diagrams are drawn such that the most number of atoms have a octet configuration, other than the H atom which only has two electrons. Make the most electronegative atoms the central atoms, give each other atom a single covalent bond between central atom and then provide electrons to the external nuclei to allow them to achieve octet structure. Afterwards, calculate the total number of electrons involved in bonding and insert the remaining electrons into the central atom. Rearrange the bonds to ensure octet structure throughout, making some bonds dative, double, triple as suitable.

For Dot and Cross diagrams of charged molecules, electrons are gained by the most electronegative atom and electrons are lost by the least electronegative atom, and overall charge must also be displayed as a square bracket with superscript.

**NOT TAUGHT: Formal Charge** is a calculated quantity of how stable a covalently bonded atom is in its current state of bonding, calculated as the number of valence electrons an atom has minus the number of lone electrons and minus the number of bonds pairs. Minimizing this number when drawing a covalently bonded molecule will ensure that it is a energetically feasible configuration.

### 3.8.2 VESPR

Covalent bonds are directional and hence have predictable shapes. Valence Shell Electron Pair Repulsion (VESPR) Theory is used to predict the shape of covalently bonded molecules, stating that electron pairs repel each other and are arranged such that repulsion is minimized. Lone pair-lone pair repulsion is stronger than lone pair-bond pair, which is stronger than bond pair-bond pair. Single, unpaired electrons have a weaker repulsion than all of these. Lone pairs exert larger repulsion than bond pairs because they are only attracted by one nucleus.

Shapes of covalently bonded molecules are derived by counting the number of areas of electron density (a lone electron/double bond/triple bond counts as one region) to derive electron-pair geometry. The number of lone electron pairs and bond electron pairs are then used to infer the molecular geometry of a molecule.

Specific bond angles to remember would be that tetrahedral molecules with 4 bond pairs or 4 lone pairs at  $109.5^\circ$ , 3 bond pairs at about  $107^\circ$  and 2 bond pairs at about  $105^\circ$  (Water at  $104.5^\circ$ ). An decreasing electronegativity of the central atom also results in an increased deviation of bond angle since the bond pairs are further from the

central nucleus and exert less repulsion.

Molecules with 5 regions of electron density have lone pairs first occupy orbitals in the trigonal planar region.

Three dimensional bonds are drawn with triangles instead of lines. One vertex resides at the central atom while two reside at the external atom. Shaded triangles mean that a bond extends out of the paper, while a triangle of vertical lines mean that a bond extends into the paper.

Please refer to page 10 of the lecture notes for the full VESPR table.

## 3.9 Interpretation of Physical Properties

High melting and boiling points are an indicator of strong interactions between particles: IMF in simple covalent molecules, covalent bonds in giant covalent molecules, ionic bonds in ionic substances and metallic bonds in metals.

Conduction of electricity indicates the presence of mobile charge carriers like electrons or ions in a substance.

### 3.10 Exam Technique

#### Definition 3.8: Bulk Property

A Bulk Property is a physical property which is constant no matter the size or amount of substance in a system.

#### 3.10.1 In Terms of Structure and Bonding

When prompted with "in terms of structure and bonding", be sure to identify the type of molecule (simple covalent, giant covalent, ionic, metallic) and its type of bond (covalent + IMF, covalent, ionic, metallic).

For questions regarding simple covalent molecules, identify the molecular shape and whether the molecule is polar using VESPR and other concepts.

#### 3.10.2 Melting / Boiling Points

[Insert property here], hence the [high/low] electrostatic forces of attraction of [type of bond or whatever] mean that a [large/small] amount of energy is required to overcome these electrostatic forces of attraction, hence there is a [high/low] melting and boiling point.

#### 3.10.3 Drawing Giant Covalent Structures

Draw at least 5 "ring units" of a giant covalent structure.

## 4 Gases

### 4.1 Gases

Gases are made of particles which are separated by large distances due to weak IMF. The particles in a gas are

constantly moving, resulting in collisions with the surface of its container and giving rise to pressure. The average speed of gas particles is dependent on its total internal kinetic energy, AKA its temperature.

## 4.2 Ideal Gas Law

The chemical analysis of gases involve the quantities of

- Pressure  $p$  measured in Pa or  $\text{N m}^{-2}$  or  $\text{kg m}^{-1} \text{s}^{-2}$
- Volume  $V$  measured in  $\text{m}^3$
- Temperature  $T$  measured in K
- Amount of gas  $n$  measured in mol

### Definition 4.1: Boyle's Law

Boyle's Law states that for a fixed  $n$  and  $T$ ,  $V \propto p^{-1}$

### Definition 4.2: Charles' Law

Charles' Law states that for a fixed  $n$  and  $p$ ,  $V \propto K$

### Definition 4.3: Gay-Lussac's Law

Gay-Lussac's Law states that for a fixed  $n$  and  $V$ ,  $p \propto K$

### Definition 4.4: Avogadro's Law

Avogadro's Law states that for a fixed  $T$  and  $p$ , for any gas,  $n \propto V$

A combination of all these laws as well as experimental calculation of their proportionality constants gives us the ideal gas equation:

### Equation 4.1: Ideal Gas Equation

Where  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

$$pV = nRT$$

To sketch graphs related to the ideal gas equation, rearrange the terms algebraically to find the form of the graph.

## 4.3 Kinetic Theory of Gases

The Kinetic Theory of gases is a mathematical model to examine the behavior of gases. In order for the equation  $pV = nRT$  to be valid, certain assumptions need to be made:

**Volume of Particles** is assumed to be zero. Particles in an ideal gas are assumed to be point masses which have no volume. In reality, at high concentrations of gas the volume of gas particles is significant as compared to its container, hence using the volume of the container is no longer a suitable estimate of volume.

**Attraction of Particles** is assumed to be negligible. Particles exert IMF on each other which when strong enough result in dampening of collision between gas particles and the walls of a container as IMF attracts particles away from the walls of a container.

**Constant Random Motion** assumes that pressure is constant.

**Elasticity of Collision** assumes that kinetic energy is constant and that no energy is lost to other forms of energy like sound.

### Energy is Proportional to Temperature

The main concerns of ideal gas are the first two assumptions, as they cause significant deviation from ideality in most real gases whose values have been experimentally obtained. The last three are precedents for the other gas laws to be valid.

## 4.4 Deviation from the Ideal Gas Law

For a gas to approach ideality, there needs to be

**Low Pressure** to ensure that particles are far apart and have negligible volume compared to its container and have negligible IMF due to the large distance,

**High Temperature** to ensure that particles have high enough kinetic energy to overcome IMF and hence making IMF negligible.

For a gas to deviate from ideality, there can be

**High Pressure** where gas particles are closer together and occupy a significant volume as compared to the volume of the container, on top of having significant IMF.

**Low Temperature** where particles have less kinetic energy which is less able to overcome IMF, making the effect of IMF significant.

### 4.4.1 Graphs of Deviation from ideality

Graphs of  $pV/RT$  against  $p$  curves typically originate at the value of 1.0, decrease at moderately high pressures of around 150 atm and then rises above 1.0 at higher pressures.

At moderately high pressures, the spaces between particles of real gas are close enough for IMF to become significant, making a particle approaching a wall be attracted by molecules near to it and lessening the impact of the particle on the wall, resulting in a decreased gas pressure. The stronger the IMF of the gas molecules and the lower the temperature, the greater this effect, and the larger the value of  $p$  which the  $pV/RT$  against  $p$  graph cuts the line  $pV/RT = 1$  and the lesser the minimum of the curve.

At high pressures, gas particles are close together and space between them is significantly reduced, the space taken up by gas particles cause free volume to be significantly less than the volume of the container, resulting in an overstated volume. The larger the size of the gas particle, the stronger the effect, and the higher the gradient of the  $pV/RT$  graph as  $p$  increases beyond a high value.

Gas particles with the same type of IMF and same size electron clouds generally have similar  $pV/RT$  against  $p$  graphs.

Note that graphs which show gases decreasing without a minimum usually have the rightmost bound of the  $x$  axis at a moderately high  $p$ , where the minimum has not yet been drawn.

When comparing graphs at different temperature, lower temperatures will have a earlier and deeper minimum, cross the ideal gas value at a later  $x$  coordinate and have a larger final gradient. Substances at temperatures more than 1000 K typically do not have a significant minimum. When comparing graphs of different substance, substances with stronger IMF will have a earlier and deeper minimum.  $H_2$  and He gas typically do not have a significant minimum.

## 4.5 Partial Pressure

### Definition 4.5: Dalton's Law of Partial Pressures

Dalton's Law of Partial Pressures states that the total pressure of a mixture of non-reacting gases is equal to the sum of the pressure of the individual gases as if each gas alone occupies the container.

### Equation 4.2: Dalton's Law of Partial Pressures

For pressure  $p$ , of gases A B and C, the total pressure is given by the equation

$$p_{\text{total}} = p_A + p_B + p_C$$

Because of Avogadro's law, the total pressure of a mixture of gases can be calculated by using the sum of the amount of gas particles to obtain  $p_{\text{total}}$ . The partial pressures of a gas like  $p_A$  can be calculated by  $p_{\text{total}} \times \frac{n_A}{n_{\text{total}}}$ .

Questions using this concept are usually basic stoichiometry questions, just with the added dimension of using volumes of gas and pressure of gas to obtain amount of gas.

## 4.6 Vapor Pressure

### Definition 4.6: Volatility

The Volatility of a liquid is its tendency to evaporate.

### Definition 4.7: Vapor Pressure

Vapor Pressure is the pressure that particles of an evaporated liquid exerts.

### Definition 4.8: Saturated Vapor Pressure

Saturated Vapor Pressure the pressure of vapor particles when the rate of evaporation is the same as the rate of condensation.

"Boiling" occurs when temperature is sufficient for liquid particles to evaporate and establish a saturated vapor

pressure equal to that of its surroundings. Substances with strong IMF are less volatile and have lesser saturated vapor pressures, meaning more energy is required to overcome IMF for boiling to occur and hence increasing its boiling point.

# 5 Energetics

## 5.1 Chemical Reactions and Energy

### Definition 5.1: Chemical Energetics

Chemical Energetics is the study of energy changes that occurs during reactions and phase changes.

### Definition 5.2: State Function

A State Function is a function whose values only depend on the state of a system, rather than the pathway used to reach a state.

### Equation 5.1: State Function Change

The change in a state function  $\Delta f$  is obtained using its beginning  $f_{\text{initial}}$  and final  $f_{\text{final}}$  values by the equation:

$$\Delta f = f_{\text{final}} - f_{\text{initial}}$$

### 5.1.1 Enthalpy

#### Definition 5.3: Enthalpy

The Enthalpy  $H$  of a substance is a quantification of its energy content. Substances with lower  $H$  or lower enthalpy have less energy and are more stable. Enthalpy is a state function. Measured in J

Absolute enthalpy cannot be obtained, but rather the change in enthalpy  $\Delta H$  has a real value and is calculated like a state function.

#### Definition 5.4: Endothermic

An Endothermic reaction is one where energy is released to the surroundings, i.e.  $\Delta H > 0$

#### Definition 5.5: Exothermic

An Exothermic reaction is one where energy is released to the surroundings, i.e.  $\Delta H < 0$

#### Definition 5.6: Activation Energy

Activation Energy  $E_A$  is the amount of energy required for reactant particles to possess before they can collide successfully to form products.

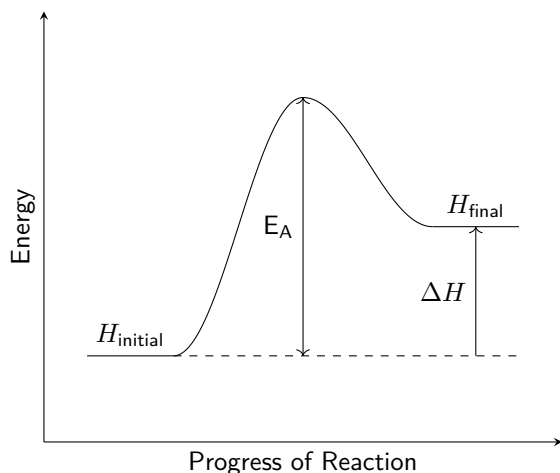
As particles form bonds, they become more stable and release energy, whereas when breaking bonds particles are excited and absorb energy. Hence, bond formation is typically exothermic and bond breaking is endothermic.

Exothermic reactions are energetically feasible and are more likely to occur. However, energetic stability is insufficient to assess the speed of which reactions will happen, which can be very slow (like  $C_{\text{Diamond}} \rightarrow C_{\text{Graphite}}$ )

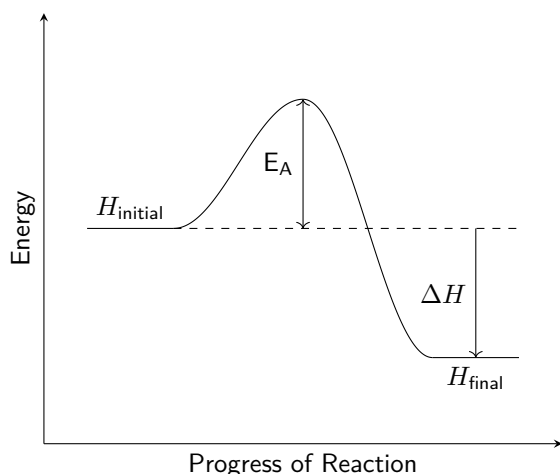
## 5.2 Energy Profile Diagram

Energy profile diagrams describe the potential energy stored in a substance as a reaction progresses, showing the relative energy levels of its reactants, products and the activation energy required.

Endothermic Reaction



Exothermic Reaction



Note that the arrows for  $E_A$  have two arrowheads while  $\Delta H$  only has one. The number of peaks in energy of a molecule indicate an intermediate step in the mechanism.

## 5.3 Standard Enthalpy Definitions

### Definition 5.7: Standard Conditions

Standard Conditions (subscript  $\ominus$ , pronounced naught and symbol is called a plimsoll) refer to situations where temperature is 298 K, pressure is 1 bar and solutions have concentration  $1 \text{ mol dm}^{-3}$ . Standard conditions  $\neq$  s.t.p or r.t.p.

### Definition 5.8: Standard States

Standard States are the physical and chemical states at which a substance is most stable at standard conditions. Standard states of substances with the same chemical formula follow their most stable sample ( $C_{\text{graphite}}$  rather than  $C_{\text{diamond}}$ ,  $\text{H}_2\text{O}$  at liquid rather than gas).

Note for each reaction that  $\Delta H$  is defined for 1 mol of the reaction rather than of a product or reactant if not

stated, as well as the physical states of all substances.

Definitions of standard enthalpies follow the general form of:

The standard enthalpy change of [process] is the energy (changed/released/absorbed) when [amount to be observed] of [specific substance with physical state] is [description of process] under conditions of [temperature, pressure, concentration and other conditions].

### 5.3.1 List of Standard Enthalpies

**Standard enthalpy change of reaction**  $\Delta H_r^\ominus$  is the energy change in a reaction when one mole of reaction occurs with stated quantities of a reaction under standard conditions.

**Standard enthalpy change of formation**  $\Delta H_f^\ominus$  is the energy released when one mole of substance is formed from its elements under standard conditions.

**Standard enthalpy change of combustion**  $\Delta H_c^\ominus$  is the energy released when one mole of substance is completely burnt under standard conditions.

**Standard enthalpy change of neutralization**  $\Delta H_{\text{neut}}^\ominus$  is the energy change when one mole of  $\text{H}_2\text{O}$  is formed through reacting an acid and a base under standard conditions.

Neutralization between strong acid and strong base typically has enthalpy change of  $-57.3 \text{ kJ mol}^{-1}$ . Neutralization can be endothermic in the case of a weak acid or base, as the endothermic disassociation of  $\text{H}^+$  and  $\text{OH}^-$  combined with the exothermic hydration of ions may result in a net endothermic effect which is larger than the energy released due to formation of  $\text{H}_2\text{O}$ , hence it may be endothermic.

**Standard enthalpy change of atomization**  $\Delta H_{\text{atom}}^\ominus$  is the energy required for when gaseous element molecules are atomized into one mole of gaseous atoms or one mole of gaseous compound is atomized into constituent gaseous atoms.

**Bond Dissociation Energy** BDE is the energy required to break one mole of a particular bond in a compound when the compound is in gaseous state.

**Bond Energy** BE is the average energy required to break one mole of a type of bond between two atoms. BE is obtained when BDE is averaged out.

**Ionization Energy** IE is the energy required to form one mole of gaseous electrons and one mole of charged gaseous atoms from one mole of gaseous atoms.

**Electron Affinity** EA is the energy change when one mole of gaseous atoms acquire one mole of gaseous electrons.

Note that the first EA can be exothermic or endothermic, but the second EA is endothermic because electrons are being introduced to a negatively charged species and will experience repulsion.

**Lattice Energy** LE is the amount of energy released when gaseous cation and anion react to form one mole of solid ionic compound under standard conditions.

**Standard enthalpy change of hydration**  $\Delta H_{\text{hyd}}^{\ominus}$  is the energy released when one mole of gaseous ion is hydrated under standard conditions.

$\Delta H_{\text{hyd}}^{\ominus}$  is proportional to the charge density of an ion, i.e.  $\Delta H_{\text{hyd}}^{\ominus} \propto \left| \frac{q}{r} \right|$

**Standard enthalpy change of solution**  $\Delta H_{\text{soln}}^{\ominus}$  is the energy change when one mole of substance is completely dissolved in solvent to form an infinitely dilute solution under standard conditions.

When asked to define standard enthalpies in a question, ensure that responses are defined with respect to reactants specified in the question rather than just a generic definition. Answer with context.

## 5.4 Energy Cycles

### Definition 5.9: Hess' Law

Hess' Law states that the enthalpy change of a reaction is determined by its initial and final states of the system and independent of the pathways taken. i.e. Enthalpy is a state function.

Given a list of  $\Delta H$  and the data from the information booklet,  $\Delta H$  of other reactions can be found by exploiting this rule. No matter how many steps of a reaction is taken, so long as the reactants and products are the same, the total  $\Delta H$  will be the same.

When drawing cycles:

- Always show state symbols of substances
- Label reactions/arrows with the correct  $\Delta H_{\text{subscript}}$ , value of enthalpy change and introduced or removed elements (and their state) if there are any
- Only use  $\ominus$  when data given is applicable to standard conditions
- Ensure that all introduced elements are also removed at some point in a cycle
- Write "By Hess' Law," before calculations of enthalpy change.
- As a worst case scenario, ensure that cycles are complete in order to salvage marks.
- Be especially careful with BE values; For  $\frac{3}{2} \text{Cl}_2 \rightarrow 3 \text{Cl}$ ,  $\Delta H$  is  $\frac{3}{2} \text{BE}(\text{Cl}-\text{Cl})$  rather than  $3 \text{BE}(\text{Cl}-\text{Cl})$

### 5.4.1 Energy Cycle Shortcuts

Given the  $\Delta H_{\text{f}}$  or  $\Delta H_{\text{c}}$  of both products and reactants,  $\Delta H_{\text{r}}$  of a reaction can be calculated with:

Equation 5.2:  $\Delta H_{\text{r}}$  given  $\Delta H_{\text{f}}$  of products and reactants

$$\Delta H_{\text{r}} = -\Delta H_{\text{f}}(\text{reactants}) + \Delta H_{\text{f}}(\text{products})$$

Equation 5.3:  $\Delta H_{\text{r}}$  given  $\Delta H_{\text{c}}$  of products and reactants

$$\Delta H_{\text{r}} = +\Delta H_{\text{f}}(\text{reactants}) - \Delta H_{\text{f}}(\text{products})$$

### 5.4.2 Energy Level Diagrams

Energy level diagrams are a special type of energy cycle which are drawn with energy as a vertical axis where each state of a set of substances occupy a vertical position. In addition to the above, when drawing energy level diagrams:

- Label the vertical axis and the " $\text{kJ mol}^{-1}$ " unit.
- Attempt to maintain proportion between changes in enthalpy: larger  $\Delta H$  should have a larger vertical gap than smaller  $\Delta H$
- One arrow corresponds to one kind of reaction with one  $\Delta H$  value, do not have multiple reactions occurring at once.
- Up arrows show endothermic reactions, down arrows exothermic
- Label a zero at the energy level where all reactants are at its standard state.

For drawing energy level diagrams to obtain LE of a substance, follow the steps:

- Draw standard state of metal and nonmetal, label as zero energy.
- Draw state of ionic solid and arrow from standard state to ionic solid for formation of ionic solid.
- Draw state of gaseous atoms of metal and nonmetal from standard state.
- Draw state of cations and anions from gaseous atoms. Note that cations need to be formed first. Gaseous  $\text{e}^-$  also needs to be included.
- Join cations and anions to ionic solid with arrow labeled as LE.

Note that the first  $E_{\text{A}}$  may be negative for the nonmetal and its corresponding vertical position with respect to the other states needs to be calculated and shown properly. If it dips below a previous state it should be shown properly.

## 5.5 Lattice Energy

Theoretical calculations for lattice energy can be obtained through using the previously shown formula of  $|\text{LE}| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$ . This obtains values similar to experimentally obtained results for compounds which are mostly ionic. However, partial covalent character in some ionic compounds

(usually involving transition metals) causes measured LE to have a discrepancy with the theoretical equation, where partial covalent character strengthens the bond between anions and cations, causing an increase in LE.

## 5.6 Solubility

The process of dissolving an ionic solid involves two steps: the endothermic disassociation of ionic bonds between the solid followed by the exothermic hydration of the ions due to the formation of ion-dipole interactions. Applying Hess' Law:

### Equation 5.4: Standard Enthalpy of Solution

For a ionic solid MX:

$$\Delta H_{\text{soln}}^{\ominus}(\text{MX}) = \Delta H_{\text{hyd}}^{\ominus}(\text{M}^+) + \Delta H_{\text{hyd}}^{\ominus}(\text{X}^-) - LE(\text{MX})$$

Ionic solids are more likely to be soluble if  $\Delta H_{\text{soln}}^{\ominus}$  is negative, where the energy released by hydration is sufficient to compensate for the lattice dissociation energy required to break down the ionic solid.

## 5.7 Entropy

### Definition 5.10: Entropy

Entropy is the measure of disorder of a system. A system with higher entropy has more ways to organize itself.

Zero entropy is defined as the entropy of any substance at absolute zero. For the purposes of chemical energetics, entropy is treated as a state function where change in entropy is derived from comparing its initial and final states. Negative entropy change indicates that the final state is more ordered, while a positive entropy change indicates that the final state is more disordered.

### 5.7.1 Entropy Changes

An **increase in the number of gas particles in a system** increases the entropy of a system as an increase in gas particles creates an increase in particles in random motion, hence reactions which have a net increase of gas particles have a positive entropy change.

**Mixing of particles** increases entropy as there are more ways to organize particles. Mixing gas particles causes these particles to occupy a larger container, allowing them more ways to be arranged in the larger volume. Mixing soluble liquid particles cause these liquid particles to have greater disorder than their unmixed state.

**Dissolution of ionic solids in water** can cause both increases and decreases in entropy. Disruption of the ordered ionic lattice structure which causes ionic solids to lose their orderly form increases entropy significantly as they are free to move about the solvent, however there is also a decrease in entropy due to the process of hydration as ion-dipole interactions between water and ions puts these particles into an orderly arrangement. For NaCl, the

dissolution process results in a net increase in randomness as breaking of ionic structure is more predominant than the process of hydration. For  $\text{CaSO}_4$ , the dissolution process decreases entropy as the process of hydration is more predominant than breaking of ionic structure.

### Definition 5.11: Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann Distribution graph is a plot of number of molecules with a given energy level against kinetic energy. Though the temperature of a substance is constant, its individual particles still have differing energy levels. Increasing the temperature of a substance will broaden the Maxwell-Boltzmann Distribution and also shift the peak lower and to the right.

An **increase in temperature** results in an increase in entropy. As temperature increases, there is a broadening of the Maxwell-Boltzmann distribution of the particles, providing more energy states which any individual particle can hold at one point in time and hence causing an increase in entropy.

State changes from solid to liquid to gas cause an increase in entropy, since the structural order in a solid is destroyed by melting into a liquid and since changes to the gaseous state are accompanied with a large increase in volume. The entropy in a similar amount of gas is significantly higher than that of a liquid, which is higher than that of a solid.

## 5.8 Gibbs Free Energy

### Definition 5.12: Standard Gibbs Free Energy Change

The Standard Gibbs Free Energy Change  $\Delta G^{\ominus}$  of a reaction is the overall change in the total energy content of a reaction, once accounted for both changes in enthalpy and changes in entropy.

### Equation 5.5: Standard Gibbs Free Energy Change

For the enthalpy change  $\Delta H^{\ominus}$ , entropy change  $\Delta S^{\ominus}$  and current temperature  $T$  of a reaction, the Standard Gibbs Free Energy Change  $\Delta G^{\ominus}$  of a reaction is given as:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

Note that in most calculations  $\Delta H$  is in kJ while  $\Delta S$  is in J, do remember to convert units.

Note that in most cases where reactions take place in standard conditions, all  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  values should be followed by a superscript  $\ominus$  to indicate standard conditions or the use of values obtained at standard conditions, despite temperature being different.  $\Delta H^{\ominus}$  and  $\Delta S^{\ominus}$  are assumed to not vary with different temperature. When in doubt, follow the notation of the question.

### 5.8.1 Thermodynamic Feasibility

Studying thermodynamic feasibility allows us to predict if reactions will occur.



**Definition 5.13: Thermodynamic Spontaneity**

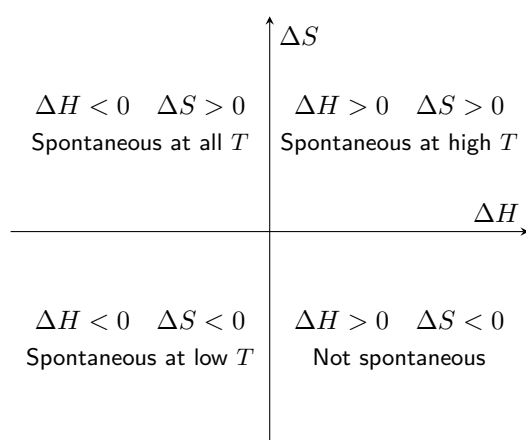
A Thermodynamically Spontaneous reaction is a irreversible reaction that can occur without any external assistance in terms of energy input, involving a system which moves from a unstable to a stable state.

**Definition 5.14: Endergonic**

An Endergonic reaction has a positive  $\Delta G$  value and is not thermodynamically spontaneous.

**Definition 5.15: Exergonic**

An Exergonic reaction has a negative  $\Delta G$  value and is thermodynamically spontaneous.

**Types of Thermodynamic Feasibility**

To explain the thermodynamic feasibility of a reaction:

1. State and explain sign of  $\Delta H$
2. State and explain sign of  $\Delta S$
3. Comment on sign on  $\Delta G$ :

**(Not) Spontaneous at all T** is because  $\Delta H$  and  $T\Delta S$  both have the same sign, hence  $\Delta G$  will be (positive/negative) regardless of T

**T dependent** is because at low T  $\Delta G$  is (positive/negative) since  $\Delta H$  outweighs  $T\Delta S$ , but at high T  $\Delta G$  is (negative/positive) since  $T\Delta S$  outweighs  $\Delta H$ .

**5.9 Experimental Energetics**

Experimental methods to find  $\Delta H$  of reactions are in syllabus.

**5.9.1 Highest Reading Method**

This method involves the derivation of enthalpy change by direct reading of temperature change. A reaction is conducted in an insulated environment with known volumes and amount of reactants. The maximum/minimum temperature reading of the system is then read and used to calculate  $\Delta H$  through calculating the heat capacity of the system, using temperature change to find the total amount of heat change and finally calculating heat change

per unit of reaction.

**Equation 5.6: Highest Reading Method**

For a resultant volume of system  $V$ , density of water  $\rho_{H_2O}$ , specific heat capacity of water  $c_{water}$ , measured temperature change  $\Delta T$  which then gives the amount of heat transfer  $q$ , and finally amount of reaction  $n$ , the enthalpy of a reaction  $\Delta H$  is given by the equations:

$$q = mc\Delta T$$

$$\Delta H = -\frac{q}{n}$$

This experiment assumes that:

- There is negligible heat loss to surroundings
- The resultant solution is infinitely dilute: its density and its heat capacity is equal to that of water

**5.9.2 Graph Method**

This method involves the derivation of enthalpy change by estimating temperature change and compensating for heat loss through using a graphical method. A reaction is conducted in an insulated environment with known volumes and amount of reactants, and the temperature of the system is taken at regular intervals before and after reaction takes place. A graph of temperature against time is plotted, and the temperature change reading is obtained through intersecting two lines: one line of  $x =$  time of start of reaction and one best fit line of the temperature readings after reaction takes place and temperature change due to reaction is complete. This experiment, after graphing, uses similar equations to the Highest Reading method to obtain  $\Delta H$ .

This experiment assumes that:

- Heat loss to surroundings is at a constant rate and is accounted for via extrapolation
- Reaction is instantaneous
- The resultant solution is infinitely dilute: its density and its heat capacity is equal to that of water

**5.10 Exam Technique**

When a question specifies "with the use of an energy cycle" or "with the use of an energy level diagram", diagrams must be drawn.

**6 Kinetics****6.1 Reaction Kinetics****Definition 6.1: Reaction Kinetics**

Reaction Kinetics is the study of rate of chemical reactions, investigating the factors which affect rate of reaction and the mechanisms of reaction.

### Definition 6.2: Rate of Reaction

Rate of Reaction is the rate of which a reaction takes place with respect to time, measured through the change in concentration of reactants or products over time, with units  $\text{mol s}^{-1}$ .

Average rate of reaction is the rate of reaction over a large time, calculated by finding the gradient of the line drawn between two points on the concentration-time graph. Instantaneous rate of reaction is rate of reaction over an infinitesimally small amount of time, obtained by reading the gradient of a tangent to the curve at a point in time.

## 6.2 Order of Reaction

It can be experimentally observed that the speed of a reaction is dependent on the concentrations of individual reactants.

### Equation 6.1: Rate Equation

For a proportionality constant  $k$ , concentration of reactants  $[A]$  and  $[B]$  and order of reaction w.r.t A and B  $m$  and  $n$ , the rate of reaction can be obtained with the equation:

$$\text{rate} = k[A]^m[B]^n$$

### Definition 6.3: Rate Equation

The Rate Equation of a reaction is the mathematical expression which shows the dependence of rate of reaction on concentrations and the powers which concentrations are raised to. Rate equations can only be obtained through experiment, cannot be deduced theoretically or from stoichiometric equation and may not even involve all reactants in a chemical equation.

### Definition 6.4: Rate Constant

The Rate Constant of a reaction is the constant of proportionality in the rate equation of the reaction, with sufficient units such that the total RHS ends with units  $\text{mol s}^{-1}$ , defined for a specific temperature and presence of a certain catalyst.

### Definition 6.5: Order of Reaction

The Order of Reaction of a reactant is the power which it is raised to in the rate equation. The order of reaction of a reactant must be found experimentally and must be a rational number. Order of reaction is used to infer reaction mechanism.

### Definition 6.6: Overall Order of Reaction

The Overall Order of Reaction is the sum of powers in the rate equation. Overall order of reaction can be used to assess the shape of concentration-time graphs as well as the units of the rate constant.

### 6.2.1 First order Reactions

First order reactions are reactions whose rate is directly proportional to the concentration of a single reactant.

First order reactions hold the special property that the half life of its reactants is constant.

### Definition 6.7: Half-life

The Half-life  $t_{1/2}$  of a system is the time taken for a property to decrease by half.

To prove that a reaction is first order from its concentration against time graphs, find different durations at which concentration decreases by half. If these times are the same,  $t_{1/2}$  can be said to be constant and the reaction is said to be first order w.r.t. reactant. Additionally, given the rate constant of a reaction, the half life can also be mathematically calculated.

### Equation 6.2: Half-Life of First Order Reaction

For the rate constant of a first-order reaction  $k$ , its half life  $t_{1/2}$  is given by the equation:

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

## 6.3 Pseudo-order Reactions

When experimentally studying rates of reaction, the rate of a chemical reaction may appear to be dependent on less concentrations than theoretically examined / reactions appear to be zero order when they are in fact non-zero order:

**Reactant is in excess** causes the rate of a reaction to seemingly be independent of the concentration of the reactant in excess. Usually this occurs when a reactant is present in 1 order of magnitude larger than the limiting reactant.

**Solvent is reactant** is a special case of having a reactant in excess. Reactions in aqueous solution where  $\text{H}_2\text{O}$  is involved have  $\text{H}_2\text{O}$  present in a concentration of about  $65 \text{ mol dm}^{-3}$ .

**Presence of catalyst** causes the rate of reaction to seemingly be independent of the concentration of a catalyst. The concentration-time graph of a catalyst seems to be a straight line and hence zero order, but since catalysts remain constant in concentration throughout a reaction as they are consumed and re-generated it is in fact non-zero order.

Pseudo-order reactions can have their rate equations simplified. For a reaction pseudo- $m^{\text{th}}$ -order to A but in fact is  $(m+n)^{\text{th}}$ -order, its rate equation would be  $\text{rate} = k'[A]^m$  where  $k' = k[B]^n$ .

## 6.4 Deriving Order of Reaction

In order to identify the order of a reaction with respect to its reactants, data is obtained to describe the variances of the rate of reaction in scenarios with initial different concentration of reactants, which is then used to find order of reaction.

When comparing two sets of data with one variable changed and the ratio between their (initial) rate of reaction, state that as [reactant] changed by [factor], (initial) rate of reaction changed by [factor], hence the order of reaction with respect to the reactant is [order].

When comparing two sets of data with more than one variable change (of which all but one has known order) and the ratio between their (initial) rate of reaction, answer in a similar format to:

**Equation 6.3: Deriving Order from Experiments with Multiple Variables**

For a reaction of rate equation  $\text{rate} = k[A]^m[B]^n$  where  $m$  is known but  $n$  is unknown and given two sets of data with  $[A]$ ,  $[B]$  and rate, they are related by the equation

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]_1^m[B]_1^n}{k[A]_2^m[B]_2^n}$$

$$\left(\frac{[B]_1}{[B]_2}\right)^n = \frac{\text{rate}_1}{\text{rate}_2} \div \left(\frac{[A]_1}{[A]_2}\right)^m$$

## 6.5 Reaction Mechanism

**Definition 6.8: Reaction Mechanism**

The Reaction Mechanism is the collection of elementary steps in sequence showing how reactants are converted into products.

**Definition 6.9: Elementary Step**

An Elementary Step is a distinct step in a reaction mechanism which describes a single molecular event that involves breaking and/or making bonds, and cannot be broken down into simpler steps.

**Definition 6.10: Molecularity of a Elementary Step**

The Molecularity of a Elementary Step is a description of the number of reactant molecules that are involved in an elementary step.

**Definition 6.11: Intermediate**

An Intermediate species is a molecule which is formed in one step and consumed in another, and cannot be observed outside of a reaction.

The rate equation of a reaction is governed by its reaction mechanism. For a given reaction mechanism, its “rate determining step” or “slow” step is the step which is the limiting factor to the speed of reaction and has the largest activation energy. The rate equation is then deduced from the molecules involved in the rate determining step as well as the prior fast steps which produce intermediate species consumed in the rate determining step.

For a elementary reaction of  $x\text{A} + y\text{B} \longrightarrow \text{C}$ , its rate equation is  $\text{rate} = k[\text{A}]^x[\text{B}]^y$ .

## 6.6 Theories of Rate of Reaction

### 6.6.1 Collisions and Reactions

Collision Theory states that reactions occur when reactant particles collide in an effective manner where they are in a favorable orientation with correct collision geometry to form new bonds and where particles have a sufficient amount of energy to allow for re-organization of bonds in colliding particles.

### 6.6.2 Transition State Theory

Transition State Theory states that upon successful/effective collision, reactant species form an unstable transition state with a large amount of potential energy which then form the more stable products. This gives rise to the rise observed in energy profile diagrams, where the highest point in a reaction on the potential energy axis is the point at which the transition state exists.

### 6.6.3 Maxwell-Boltzmann Distribution Curves

The kinetic energy of particles in a gas always changes due to the large number of collisions which change their speeds, but the overall distribution of molecular speeds / kinetic energy of a system follows the Maxwell-Boltzmann distribution. As temperature increases, the maximum of the curve is displaced to the right and takes a lower value and there is a greater spread of kinetic energies as the curve broadens. As such, there is a larger amount of molecules above a set amount of energy and hence more particles which are able to collide with sufficient energy to form a effective collision.

## 6.7 Factors Affecting Rate of Reaction

### 6.7.1 Physical State of Reactants

In order for a reaction to occur, particles need to mix, collide and react, hence frequency of successful collisions depends on the physical states of reactants.

Reactants in a fluid state or a finely divided solid state have a larger available surface area per unit volume, allowing for a larger frequency of collision and hence a larger probability of effective collision, hence increasing the rate of reaction.

Reactions involving ions are faster than reactions involving molecules as reactions involving molecules require covalent bonds to be broken, rather than in reactions involving ions which usually already have mobile ions.

### 6.7.2 Concentration of Reactants

As concentration of a reactant increases, the reactant particles become closer together and the frequency of collisions increase, leading to the increase of probability of effective collisions with the correct geometry and sufficient energy, hence increasing the rate of reaction.

For gases, indicate that the increase of partial pressure of a gas is equivalent to an increase in concentration of a gas on top of the above explanation. Note that this does not apply to zero order reactions.

### 6.7.3 Temperature

As temperature increases, the average kinetic energy of the reactant increases, leading to a broadening of the Maxwell-Boltzmann distribution where more particles have energy greater than or equal to the activation energy of the reaction, leading to an increase in effective collision frequency and hence increasing the rate of reaction.

The Arrhenius Equation, the general formula for the rate constant  $k$  relating it to temperature and activation energy also shows that an increase in temperature or a decrease in activation energy increases the rate constant.

#### Equation 6.4: Arrhenius Equation

For Arrhenius constant  $A$ , activation energy  $E_a$ , molar gas constant  $R$  and temperature  $T$ , the rate constant  $k$  is given by the equation:

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

### 6.7.4 Presence of Catalyst

#### Definition 6.12: Catalyst

A Catalyst is a substance which increases rate of reaction but does not undergo permanent chemical change.

The presence of a catalyst provides an alternative reaction pathway with lower activation energy than an uncatalysed reaction, hence more reactants have sufficient energy to have effective collisions as seen by observing a Maxwell-Boltzmann distribution, resulting in increased effective collision frequency and hence an increase in rate of reaction.

## 6.8 Catalysts

#### Definition 6.13: Inhibitor

An Inhibitor is a substance which decreases the rate of a chemical reaction.

#### Definition 6.14: Promoter

A Promoter is a substance which increases the efficiency of a catalyst.

#### Definition 6.15: Catalyst Poison

A Catalyst Poison is a substance which inhibits the efficiency of a catalyst.

#### Definition 6.16: Homogeneous Catalysts

Homogeneous Catalysts are catalysts in the same physical state as the reactants.

Homogeneous catalysts typically act by reacting with some reactants to form an intermediate, which is then reacted to form product while the catalyst is regenerated. The reaction mechanism involving a catalyst would have lesser activation energy due to the presence of the intermediate step, hence proceeding much faster than the uncatalyzed reaction.

#### Definition 6.17: Heterogeneous Catalysts

Heterogeneous Catalysts are catalysts in different physical states as the reactants.

Heterogeneous catalysts involve the reactants adsorbing onto the catalyst surface to form weak bonds between the surface and the reactant, which then weakens the covalent bonds in the adsorbed molecule as well as increasing the concentration of reactant on the surface of the catalyst, hence reducing the activation energy of reaction. Reaction occurs on the surface of the catalyst, after which the reactants desorb from the surface of the catalyst.

Catalyst Poisoning can occur when chemicals uninvolved in the desired reaction are more readily adsorbed onto the catalyst surface than desired reactants, hence reducing the amount of active sites which would otherwise speed up the reaction.

#### Definition 6.18: Autocatalysis

Autocatalysis occurs when a reaction's products catalyzes the reaction itself.

For an autocatalytic reaction, its initial rate is slow since it is not catalyzed, but then as product is formed the rate of reaction increases as the product catalyses the reaction. When approaching the end of the reaction, the rate of reaction decreases due to the low concentration of reactants despite the adequate supply of catalyst. To test for autocatalysis, artificially adding product at the start of the reaction would result in a sharp increase of rate of reaction.

### 6.8.1 Enzymes

#### Definition 6.19: Enzymes

Enzymes are proteins which catalyze chemical reactions in biological systems.

Enzymes are globular proteins with active sites in their three dimensional structure. Enzymes are efficient in small amounts as they are regenerated at the end of a reaction. Enzymes are specific to a reaction due to the specialization of its active site. Enzymes require body temperature and a narrow pH range to operate at maximum efficiency, where sub-optimal conditions hinder the activity of an enzyme and too high a temperature will denature enzymes.

Enzymes catalyze reactions by providing an alternative reaction pathway with a lower activation energy by forming an enzyme-substrate complex.

## 6.9 Experimental Technique

### 6.9.1 Method of Initial Rates

The Method of Initial Rates involves the repetition of experiments with varying concentrations of reactant to obtain the initial rates of each iteration and hence assess the order of reactants. Initial rate of reaction can be obtained by varying methods:

**Volumetric Analysis** involves sampling, quenching and titrating a system to obtain the concentration of reactant at different time intervals, after which a graph is plotted and its initial rate is obtained.

**Clock Reaction** involves the recording of amount of time for a reaction to produce a certain amount of product, at which a physical or chemical cue indicates when a clock has been reached. As the amount of product required to trigger clock stays constant, the initial rate of reaction can be said to be inversely proportional to the amount of time taken for a clock to be reached.

### 6.9.2 Method of Isolation

The Method of Isolation involves the continuous assessment of data to monitor the change of concentration of a specific reactant over time and hence assess the order of a single reactant. The reaction in question is made pseudo-order with respect to the specified reactant by adding other reactants in excess, and the progress of reaction is then assessed by varying methods:

**Volumetric Analysis** involves sampling, quenching and titrating a system to obtain the concentration of reactant at different time intervals.

**Volume/Pressure** of a system can be read and then translated into rate of change in volume / partial pressure which then is used to obtain the concentration of reactant or product over time.

**Conductivity** of a system can be observed to identify change in concentration of charge-carrying particles in a solution over time which is then used to obtain the concentration of reactant or product over time.

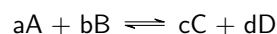
**Colorimetry** involves the continuous recording of color intensity of a solution due to the presence of a colored reactant or product, after which comparison of concentration readings against a calibration curve allows data to be translated into the concentration of the colored substance over time.

### 6.10 Exam Technique

When reading instantaneous rate off a concentration-time graph, use a stapler or similar reflective object to simulate the graph before  $t = 0$ , and use a set square to find the normal to the position of the reflective surface to obtain a tangent at  $t = 0$ .

## 7 Equilibrium I

### 7.1 Dynamic Equilibrium



#### Definition 7.1: Reversible Reaction

A Reversible Reaction is a reaction which does not proceed to completion and can proceed both in forward and reverse, where eventually a mixture of reactants and products are acquired.

#### Definition 7.2: Dynamic Equilibrium

A Dynamic Equilibrium is the state in a reversible reaction when the macroscopic properties (concentration, pressure) appear to remain constant, implying that the rate of forward reaction is equal to the rate of reverse reaction which leads to zero net change.

### 7.2 Equilibrium Properties

Consider a reaction as above. From Kinetics, we understand the rate of reactions of the forward reaction has a rate equation of rate  $= k_{\text{fwd}}[A]^a[B]^b$  while the reverse reaction has a rate equation of rate  $= k_{\text{rev}}[C]^c[D]^d$ .

In a dynamic equilibrium, the rate of the forward and reverse reactions are equal. Through manipulating the above equations, we obtain a special quantity  $K_C$ , known as the equilibrium constant, for values of concentrations once equilibrium has been reached.

$$k_{\text{fwd}}[A]^a[B]^b = k_{\text{rev}}[C]^c[D]^d$$
$$K_C = \frac{k_{\text{fwd}}}{k_{\text{rev}}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Calculating the value of  $K_C$  when using values of concentrations not at equilibrium will instead obtain the value of  $Q_C$ , the reaction quotient. Reaction will hence continue so that  $Q_C \rightarrow K_C$  and finally  $Q_C = K_C$ .

#### Definition 7.3: Position of Equilibrium

The Position of Equilibrium is a description of the relative composition of products and reactants in a reaction mixture.

In a gaseous reaction environment, the concentration of gaseous reactants will be proportional to the partial pressures of the reactants, hence an alternative equilibrium constant  $K_P$  can be used, where

$$K_P = \frac{p_A^a p_B^b}{p_C^c p_D^d}$$

From the above derivation, the equilibrium constant could be expressed as the ratio between two rate constants. From the Arrhenius equation,  $K_C$  can be inferred to be dependent on temperature.  $K_C$  is not affected by catalysts, changes in total pressure or concentrations.

A large/small value of  $K_C$  suggests the position of equilibrium of a reaction lies to the right/left, implying there is complete/no reaction.

### 7.2.1 Manipulating Equilibrium Constants

The equilibrium constant of a forward reaction is the reciprocal of the equilibrium constant of the reverse reaction.

$$K_{\text{forward}} = K_{\text{reverse}}^{-1}$$

For a multi-step reaction, the overall equilibrium constant is the product of all the reactions.

$$K_{\text{total}} = K_1 \times K_2 \times K_3 \dots$$

When the stoichiometric coefficient of a reaction is multiplied by a product  $n$ , the equilibrium constant is raised to the same power  $n$ .

$$K_{\text{new}} = K_{\text{old}}^n$$

## 7.3 Gibbs Free Energy and Equilibria

The  $\Delta G^\ominus$  of a reaction determines if a reaction is spontaneous. The  $\Delta G$  value, defined as the instantaneous change in  $\Delta G^\ominus$  for a certain composition of a reaction mixture, can be seen to be a description of the instantaneous change in  $\Delta G^\ominus$ . Combine this with the knowledge that energetic systems tend towards the lowest energy level and we conclude that equilibrium is reached when  $\Delta G = 0$ .

The graph of the  $\Delta G^\ominus$  of a system against progress of reaction is a U-shaped curve, because  $\Delta S$  increases as product and reactant is mixed and hence leading to a U-shaped dip due to the  $-T\Delta S$  term is superimposed on the straight line of the  $\Delta H$  term.

From the graphs, we observe that the position of equilibrium is solely dependent on  $\Delta G^\ominus$ , leading to the equation:

$$\Delta G^\ominus = RT \ln(K_C)$$

## 7.4 Homogeneous and Heterogeneous Equilibria

Equilibrium systems can be classified according to what physical state its reactants are in.

### Definition 7.4: Homogeneous Equilibrium

A Homogeneous Equilibrium is one whose reactants and products are all in the same physical state.

### Definition 7.5: Heterogeneous Equilibrium

A Heterogeneous Equilibrium is one whose reactants and products are in different states.

Pure reactants and products which are liquid (not aqueous) and solid form have a fixed concentration at a fixed

temperature, and hence can be ignored when calculating  $K_C$ . Water, since it is present in large quantities in an aqueous system, can also be ignored in calculation of  $K_C$  should the reaction involve water since its concentration is approximately constant.

## 7.5 ICE Tables

When given information about the reactants and products in an equilibrium system, the quantities of each substance can be calculated through the use of an Initial-Change-Equilibrium table. The header of each column corresponds to a balanced reversible reaction (with state symbols for safety) and each row is labeled as "Initial Concentration/Pressure/Amount" with the corresponding units.

Quantities such as the concentration, amount or partial pressures of reactants can be used to fill in the ICE table because all of these quantities are stoichiometrically related. However, when calculating or using  $K_C$  or  $K_P$  the volumes of the system need to be accounted for in the case where the two sides of a reaction have different amounts of products.

The total pressure may also be a useful quantity when constructing ICE tables.

### Definition 7.6: Degree of Dissociation

The Degree of Dissociation  $\alpha$  is the fraction of a reactant that is dissociated at a particular temperature, where

$$\alpha = \frac{\text{Amount of reactant dissociated}}{\text{Initial amount of reactant}}$$

## 7.6 Le Chateliers' Principle

### Definition 7.7: Le Chateliers' Principle

Le Chateliers' Principle (informally abbreviated LCP) states that when a system in equilibrium is disturbed, it will attempt to counteract the change by favoring the reaction which reverses the disturbance.

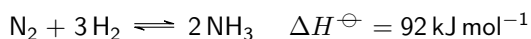
LCP is a convenient explanation which amalgamates the observed reactions to disturbances in equilibrium systems. Disturbances in the form of adding or subtracting reactants, increasing or decreasing pressure or volume all change  $Q_C$  that happen to follow this rule. Disturbances in the form of temperature changes affect  $K_C$  also happen to follow this rule since  $K_C$  is effectively a ratio between rate constants and rate constants are dependent on temperature.

In exams, just write the following standard answer:

[Change in System], equilibrium system counteracts by favoring [forward/reverse] reaction which [exo/endergonic, more/less gaseous particles, more reactant/product etc], [product/reactant increases/decreases].

## 7.7 Industrial Processes

Industrial processes involving obtaining products from an equilibrium reaction are tasked with obtaining a product cost-effectively, therefore maximizing yield, maximizing speed of reaction and minimizing cost (in equipment needed to maintain the equilibrium environment). One such process would be the Haber Process to obtain Ammonia.



The Haber Process is conducted at 450 °C as a compromise to increase the speed of reaction by supplying a large amount of heat and also to use a moderate temperature so as to have a higher yield of  $\text{NH}_3$  at equilibrium.

The Haber Process is conducted at 200 atm to shift the equilibrium to the right by favoring the reaction which decreases gaseous molecules but also to moderate the cost of maintaining a industrial setup at high pressures.

The Haber Process also involves the addition of iron catalyst and aluminum oxide promoter to speed up reaction, a continuous removal of ammonia gas to shift equilibrium to the right and increase yield and finally also introduces reactants in stoichiometric quantities to minimize excess.



Another industrial process is the Contact Process used to form Sulfur Trioxide, where the reaction takes place at 450 °C, 1 atm and with the presence of Vanadium Oxide  $\text{V}_2\text{O}_5(\text{s})$  catalyst to obtain 99% yield.

## 8 Chemical Bonding II

### 8.1 Hybridization

Electronic Orbital theory states that electrons fill orbitals of the lowest energy first, arising to a situation of electronic configuration  $1s^2 2s^2 2p^2$  with two lone electrons. However atoms with this configuration readily form 4 bonds, implying the presence of 4 lone electrons. Additionally, all of these bonds are of same length and require the same amount of energy to break, implying that these are of the same energy level.

#### Definition 8.1: Hybridization

Hybridization occurs when multiple orbitals combine to form hybrid orbitals with intermediate properties of the orbitals.



Atoms with hybrid orbitals increase the number of lone pairs they have in order to form more bonds, creating a

net lower energy state. The hybridization state of an atom is determined by the number of regions of electron density it has.

$sp^3$  hybridized orbitals are formed by the mixing of 1 s and 3 p orbitals, forming 4  $sp^3$  hybrid orbitals and hence 4 regions of electron density arranged in a tetrahedral orientation.

$sp^2$  hybridized orbitals are formed by the mixing of 1 s and 2 p orbitals, forming 3  $sp^2$  hybrid orbitals and hence 3 regions of electron density arranged in a trigonal planar orientation.

$sp$  hybridized orbitals are formed by the mixing of 1 s and 1 p orbitals, forming 2  $sp$  hybrid orbitals and hence 2 regions of electron density arranged in a linear orientation.

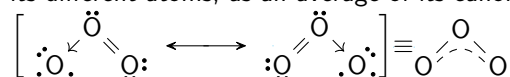
As the s-character of a hybrid orbital increases, the size of the orbital decreases and electrons are more tightly held together, therefore increasing the effectiveness of overlap when this orbital is covalently bonded and therefore increasing bond strength and decreasing bond length.

### 8.2 Resonance

#### Definition 8.2: Resonance

Resonance is the continuous overlapping of p-orbitals.

In some molecules,  $\pi$  bonds are delocalised over more than two nuclei because multiple p-orbitals are overlapping and are able to share the electrons. The Resonance Hybrid of a molecule describes how electrons are delocalised across its different atoms, as an average of its canonical forms.



Resonant structures are more stable because electrons are able to delocalize onto the overlapping  $\pi$  orbitals.

### 8.3 Graphite

With understanding of hybridization and resonance, graphite's high melting point as compared to diamond can be explained. Graphite covalent bonds are stronger due to the orbitals being  $sp^2$  hybridized as compared to  $sp^3$  in diamond, and resonance in graphite allows delocalised electrons to form a cloud whose additional electron density holds nuclei closer together.

## 9 Intro to Organic

#### Definition 9.1: Organic Chemistry

Organic Chemistry is the study of chemistry with respect to molecules involving Carbon and Hydrogen.

## 9.1 Carbon in Organic Chemistry

Carbon  ${}^6\text{C}$  is able to form many compounds because of its properties when having 4 electrons in its valence shell.

- 4 covalent bonds can be formed
- All the electrons in a fully bonded Carbon are bond pairs
- Single, double and triple bonds can be formed

Organic compounds are stable and unreactive because:

- $\text{C-H}$  and  $\text{C-C} / \text{C=C} / \text{C}\equiv\text{C}$  are strong
- Carbon has no low-lying vacant orbitals / cannot expand octet and hence cannot form extra bonds
- Skeletal carbon have no lone pairs for reaction

Carbon causes varied geometries in organic molecules:

- $\text{sp}^3$  hybridized carbon occurs with 4 single bonds with a tetrahedral structure and a  $109.5^\circ$  angle.
- $\text{sp}^2$  hybridized carbon occurs with 3 bonds (2 single and 1 double) or in benzene rings (delocalised  $\pi$  e<sup>-</sup> cloud) with a trigonal planar structure and a  $120^\circ$  angle
- $\text{sp}$  hybridized carbon occurs with 2 bonds (two double / 1 single and 1 triple) with a linear structure and a  $180^\circ$  angle

## 9.2 Functional Groups

### Definition 9.2: Functional Group

A Functional Group comprises an atom or a group of atoms to be bonded to the organic compound which determines its chemical properties.

### Definition 9.3: Homologous Series

A Homologous series is a family of compounds with the same functional group.

Homologous series usually share chemical and physical properties, and therefore can be prepared by similar processes. Homologous series may differ with a member through the addition of a  $\text{CH}_2$  group and its chemical formula follows a general pattern.

## 9.3 Structural Chemical Formula

In addition to empirical and molecular formula as discussed in Stoichiometry, organic chemistry now requires the understanding of structural formula due to the large size and convoluted bonding of organic molecules.

### Definition 9.4: Condensed Structural

Condensed Structural formula describes each C in the skeletal chain and what groups are bonded to it. For example,  $\text{CH}_2\text{CH}_1\text{CH}_3$  for but-1-ene.

### Definition 9.5: Displayed / Full Structural

Full Structural formula describes each atom using labels, what bonds form between which atoms and also the arrangement of groups around carbon (4 groups drawn in orthogonal directions, 3 groups in trigonal).

### Definition 9.6: Stereochemical

Stereochemical formula describes each atom using labels and the 3-dimensional distribution of bonded molecules. Solid lines are parallel to the plane of the paper, wedged bonds move out of the paper while hashed bonds move into the paper.

### Definition 9.7: Skeletal

Skeletal formula describes primarily all atoms which are not carbon or hydrogen in a compound. Lines representing bonds are drawn in a imaginary hexagonal grid with each unlabeled vertice representing a carbon, functional groups are drawn and finally all vacant lone electrons are implicitly filled with hydrogen. Multiple bonds are drawn as multiple parallel lines.

Cyclic carbon are drawn by their skeletal formula with a line from the cycle to whatever other miscellaneous groups it is bonded to, and all C or H are implicit.

## 9.4 Functional Groups and Nomenclature

To name an organic compound:

1. Identify the functional group
2. Identify the longest C chain which includes the functional group.
3. Number Cs from one end to other
4. Identify side-chains, add di/tri prefixes
5. Order prefixes alphabetically, ignoring di/tri prefixes
6. Combine prefix, root, multiple bond infixes and suffix.

A chain must either not include cyclic C or must all be cyclic. Number of C determines the root. If the root is a cycle, cyclo- is added to the front. Root names are: meth, eth, prop, but, pent, hex, hept, oct, non, dec and so on.

### 9.4.1 Functional Groups

Functional groups are selected (in increasing priority):

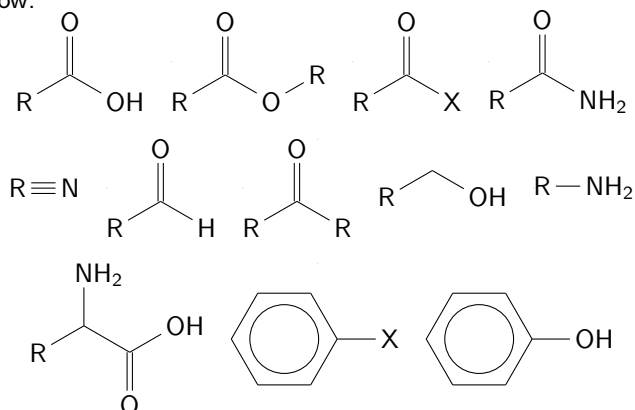
- Carboxylic Acids (-oic acid)  $\text{COOH}$
- Carboxylic Acid Derivatives: Esters ([Name of R]-yl [Root]-ate) COR, Acyl Halides (-oyl [halide]-ide) COX, Amide (-amine)  $\text{CONH}_2$
- Nitrile (-nitrile)  $\text{C}\equiv\text{N}$
- "Oxygen groups": Aldehyde (-al) OH Ketone (-one) O, Alcohol (-ol)  $-\text{O}-\text{H}$
- Amine (-amine)  $\text{NH}_2$



Other functional groups not in this list include:

- Amino Acids
- Halogenarenes
- Phenols

All these functional groups have been drawn in order below.



#### 9.4.2 Tiebreakers

Candidate carbon chains and C numbers are allocated by (in increasing priority):

- Minimizing the number of the functional group
- Minimizing the sum of the prefixes
- Minimizing the number of the alphabetically first prefix

Prefix names of functional groups are:

- Bromo-/Chloro-/Iodo- for halide groups
- Oxo- for aldehyde and ketone groups
- Alkoxy- for esters, Hydroxy- for alcohol groups
- Cyano- for nitrile groups
- Amino- for amine groups, Nitro- for  $\text{NO}_2$
- Phenyl- for benzene ring
- Methyl-/Ethyl-/Propyl- for alkane groups

## 9.5 Organic Reactions

### 9.5.1 Organic Species

#### Definition 9.8: Lewis Acids and Bases

Lewis Acids are particles which readily accept  $e^-$  pairs. Lewis Bases are particles which readily donate  $e^-$  pairs.

#### Definition 9.9: Electrophile

An Electrophile is a species of particle which is electron-deficient or readily accepts electrons. This arises when the particle has vacant orbitals or has electrons strongly pulled from it such as a protonic H.

#### Definition 9.10: Nucleophile

A Nucleophile is a species of particle which has a lone pair of electrons, is electron-rich or readily donates electrons. This arises when the particle has one or more lone pairs of electrons.

#### Definition 9.11: Free Radical

A Free Radical is an electrically neutral species with an unpaired electron.

Electrophiles are attracted to electron rich sites of molecules while Nucleophiles are attracted to electron deficient sites.

#### Definition 9.12: Degree of Substitution

The Degree of Substitution of a atom in an organic molecule is determined by how many carbon it is bonded to. The degree of substitution of a hydrogen atom is the degree of the atom which it is bonded to.

### 9.5.2 Reaction Mechanisms

#### Definition 9.13: Reaction Mechanism

A Reaction Mechanism describes the movement of electrons and atoms throughout the process of an organic reaction, hence determining the energetics and kinetics of a reaction.

#### Definition 9.14: Homolytic Fission

Homolytic Fission involves a covalent bond breaking and donating one electron to both previously bonded atoms, creating free radicals. Homolytic Fission is indicated by drawing 'Fish-hook' arrows from the bond to the atoms.

#### Definition 9.15: Heterolytic Fission

Heterolytic Fission involves a covalent bond breaking and donating both electrons to one specific atom, charging both atoms. Heterolytic Fission is indicated by drawing a double-headed arrow from the bond to one atom. The recipient of the electron pair is the more electronegative atom, forming a carbocation or a carboanion.

#### Definition 9.16: Carbocation

A Carbocation  $\text{C}^+$  is a positively charged species of carbon, usually present in intermediate species of reactions involving heterolytic fission.

A mechanism of a reaction is classified as one of Free Radical, Nucleophilic or Electrophilic depending on what species other than the organic molecule is reacted with in the slow step of a mechanism.

### 9.5.3 Types of Reactions

#### Definition 9.17: Addition

Addition Reactions involve the combination of multiple reactants to form one product, typically involving the breakage of the  $\pi$  bond in a double bond.

#### Definition 9.18: Substitution

Substitution Reactions involve the combination of multiple reactions to form multiple products.

#### Definition 9.19: Elimination

Elimination Reactions involve the removal of molecules from one reactant to form  $\pi$  bonds.

#### Definition 9.20: Condensation

Condensation involves the combination of two large molecules together and the removal of a small molecule ( $H_2O$  or  $HCl$ ).

#### Definition 9.21: Hydrolysis

Hydrolysis involves the breaking of a bond using water.

#### Definition 9.22: Oxidation

Oxidation involves the removal of O, addition of H, loss of  $e^-$  or increase in oxidation number.

#### Definition 9.23: Reduction

Reduction involves the addition of O, removal of H, gain of  $e^-$  or decrease in oxidation number.

#### Definition 9.24: Rearrangement

Rearrangement involves the migration of functional groups within a chain of carbon atoms.

#### Definition 9.25: Step Up/Step Down

Step Up and Step Down reactions involve the formation of and removal of C—C bonds respectively.

### 9.5.4 Miscellaneous Terminology

#### Definition 9.26: Electronic Effect

Compounds are electron-withdrawing or electron-donating if they decrease or increase the electron density in a compound respectively.

Electronic effect arises due to a difference in electronegativity in atoms which may affect delocalize electrons or a contribution to the electrons or the orbitals constituting a  $\pi$  electron cloud.

#### Definition 9.27: Steric Effect

Steric Effect, or Steric Hindrance, is the phenomena where the reactivity of a atom is reduced because it is bonded to groups which are large enough to prevent a reaction.

## 9.6 Isomerism

### 9.6.1 Cis-trans Isomerism

#### Definition 9.28: Cis-trans Isomers

Cis-trans Isomers contain the same bonding structure but differ in the arrangement of groups due to a restriction in rotation.

Cis-trans isomers occur when there are:

- Restricted rotation due to the presence of a C=C double bond or a ring structure
- For alkenes, different functional groups attached to each carbon.
- For ring, different functional groups attached to different carbon.

By right cis-trans notation should only be used in cases where there are the same two types of groups on each carbon in an alkene, after which cis-trans is used to describe how the parent carbon chain passes through the double bond and finally cis-trans is deprecated for the IUPAC E-Z notation which is out of syllabus.

Cis-trans isomers have similar but not identical chemical properties and have differing physical properties, due to the polarization of cis isomers and the better packing ability of trans isomers.

### 9.6.2 Enantiomerism

#### Definition 9.29: Enantiomers

Enantiomers (ee-nan-shi-oh-merh-s) exists where the mirror image of an atom's structure is non-superimposable with its original structure.

Enantiomers have similar physical properties except for a noticeable difference in its optical activity, where different enantiomers rotate polarized light an angle specific to a pair of enantiomers.

When drawing enantiomers, draw two structures separated by a plane of symmetry, using wedges and hashes to indicate bonds out of and into the plane of the paper respectively. Orbitals must be in a tetrahedral shape.

#### Definition 9.30: Chiral Carbon

Chiral Carbons have 4 different groups bonded to it, and tend to indicate the presence of an enantiomer.

When identifying chiral carbons, eliminate all carbons without 4 bonds (connected to double or triple bond, two bonds in a skeletal formula etc) to speed up process.

#### Definition 9.31: Meso Compounds

Meso Compounds contain chiral centers but also have planes of symmetry and are hence able to produce superimposable mirror images.

## 10 Alkanes

### 10.1 Structure of Alkanes

Alkanes are chains of singly-bonded carbon which are saturated with hydrogen, following the general molecular formula  $C_nH_{2n+2}$ . Cycloalkanes are rings of singly-bonded carbon which are saturated with hydrogen, following the general molecular formula  $C_nH_{2n}$ .

### 10.2 Physical Properties of Alkanes

The boiling points of alkanes increase as the number of carbon increase due to the increase in electron cloud size and later decrease with greater extents of branching due to the decrease in electron cloud surface area.

Even-numbered carbon alkanes are able to pack more closely together than odd-numbered carbon alkanes, hence even-numbered carbon alkanes have generally higher boiling points than odd-numbered carbon alkanes, up until hexane and heptane from which there is a smooth upward trend no matter even or odd number.

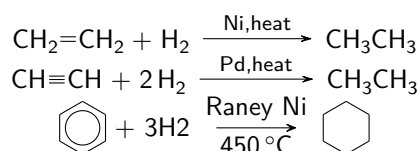
Alkanes are often nonpolar and are generally insoluble in polar solvents.

The density of alkanes increase as the number of carbon increase, but tend toward  $0.8 \text{ g cm}^{-3}$  and hence are always less dense than water.

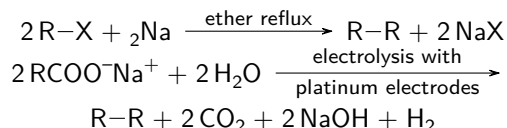
### 10.3 Reactions with Alkanes

#### 10.3.1 Formation of Alkanes

Unsaturated hydrocarbon chains can be hydrogenated in the presence of different catalysts to form alkanes.



Alkanes can also be recovered from monohalogenalkanes and carboxylates using the Wurtz and Kolbe's reactions respectively.



#### 10.3.2 Reaction of Alkanes

Alkanes do not react with hydroxide, acid, oxidizing or reducing agents. However, they do burn in the presence of oxygen and alkanes decolorize bromine when exposed to sunlight.

Alkanes are generally unreactive because they are nonpolar with no centers of electric charge, are saturated with hydrogen and hence have little irregular regions of electron

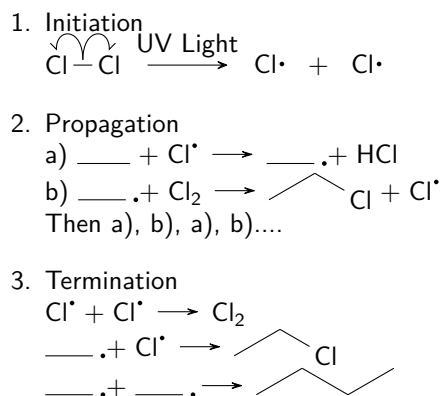
density (no rich or deficient sites) and also because the C-H and C-C bonds are strong.

Alkanes can be burnt in air to form carbon dioxide or water. In the event of incomplete combustion due to a limited amount of oxygen, incomplete combustion may occur to produce carbon for a sooty flame and carbon monoxide.

#### 10.3.3 Free Radical Substitution

Reagents:  $X_2$  ( $X \in \text{Cl, Br, I}$ )

Conditions: (Flash of) UV light



If monohalogenated alkenes are desired, introduce  $X_2$  in limiting amounts.

### 10.4 Alkanes and the Environment

Burning fuel produces multiple pollutants:

- Carbon Dioxide which has contributed towards global warming due to its property as a greenhouse gas.
- Carbon Monoxide, formed by incomplete combustion, is poisonous to humans by deactivating hemoglobin.
- Excess hydrocarbons can lead to formation of photochemical smog which causes respiratory ailments for both humans and plants.
- Nitrogen Oxides, formed at high temperatures when nitrogen is used in place of oxygen, can contribute towards acid rain.
- Sulfur Oxides, formed due to trace amounts of sulfur being present in crude oil, can contribute towards acid rain.
- Lead Compounds, formed when lead is added to engines to prevent knocking, are harmful to humans due to lead poisoning.

Catalytic converters in internal combustion engines help to reduce the production of carbon monoxide, uncombusted hydrocarbons and nitrogen oxides by reacting them to form  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$ .

### 10.4.1 Sustainable Resources

Crude oil is a natural source of hydrocarbons but does not regenerate quickly, and can hence be said to be a finite resource. Alternative sources need to be discovered and exploited to keep up with modern day energy demands.

Recycling, where waste materials are made reusable again, reduces the need for new raw materials and also reduces cost of resource extraction by supplying an alternative, consumes waste in the process and is a net benefit to the environment.

## 11 Alkenes

### 11.1 Structure of Alkenes

Alkenes are organic molecules which contain C=C double bonds.

#### 11.1.1 Cis-trans Isomerism

Alkenes commonly display cis-trans isomerism as its C=C double bonds provide the restricted rotation about a bond.

Cis-trans isomers of the same alkene have varying physical properties. Trans isomers tend to have higher melting points as they generally tessellate better than cis isomers in the solid state. Cis isomers on the other hand have higher boiling points because their structure forms a dipole moment which leads to more energy being required for the state change from liquid to gas.

### 11.2 Formation of Alkenes

Alkenes are generally formed through condensation of halogenoalkanes or alcohols.

#### 11.2.1 Elimination

Elimination reactions may produce more than one product, but typically the major product is the more stable alkene, which has more alkyl substituents attached to the double bonded carbons.

#### Halogenoalkanes to Alkenes

Refer to 'Elimination' in Halogenoalkanes.

#### Alcohols to Alkenes

Refer to 'Elimination' in Hydroxy Compounds.

### 11.3 Reaction of Alkenes

Alkenes are typically more reactive than their alkane counterparts due to the high electron density of the C=C bond which tends to polarize surrounding molecules and attract electrophiles. Alkenes will typically undergo electrophilic addition reactions which break the double bond to form single bonds.

### 11.3.1 Reduction

Unsaturated alkenes can undergo reduction reactions which replace the C=C  $\pi$  bond with H to form a saturated hydrocarbon.

Reagents:  $H_2$

Conditions: Ni + 150 °C OR Pd + Heat OR Pt

### 11.3.2 Electrophilic Addition

Alkene species typically undergo Electrophilic Addition reactions which remove the C=C  $\pi$  bond in order to form two new bonds with various side molecules and usually react readily and quickly due to the exothermic processes. These reactions typically involve the formation of an electrophilic species, the slow addition of the electrophilic species and finally the addition of a nucleophilic species.

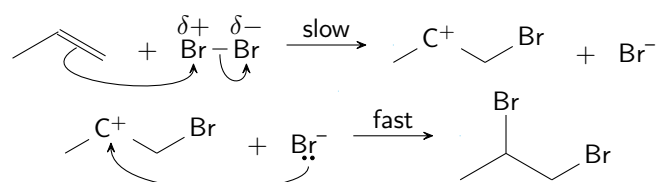
Carbocations that are bonded to more C atoms are more stable as they can tap on the electrons of other carbon. As such, electrophilic addition reactions which involve the formation of a carbocation will form more molecules with more substituted carbocations, leading to the formation of a major product. Note that minor products may still form.

Reactions involving formation of  $C^+$  involve states where  $C^+$  is  $sp^2$  hybridized. As such, any further reactions have an equal probability of nucleophilic attack from both upper and lower planes as compared to the plane of bonds to  $C^+$ . A resultant racemic mixture of enantiomers will result if the  $C^+$  is eventually chiral.

#### Addition of Halogen Gas

Reagents:  $X_2$  ( $X \in Cl, Br, I$ )

Conditions: In inert solvent ( $CCl_4$ ), dark, room temperature



#### Addition of Hydrogenhalide

Reagents: HX ( $X \in Cl, Br, I$ )

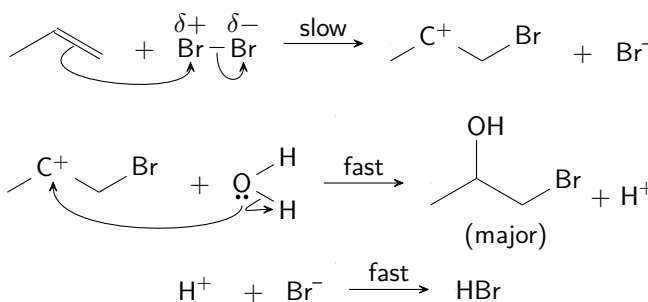
Conditions: Room temperature, dark, anhydrous

H acts as the electrophile.

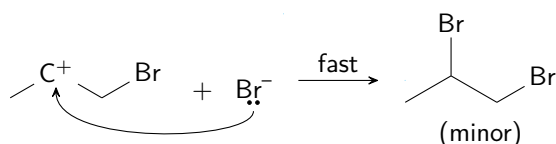
#### Addition of Halohydrin

Reagents:  $X_2$  ( $X \in Cl, Br, I$ )

Conditions: Aqueous, room temperature



OR



### Formation of Alcohol

Reagents:  $\text{H}_2\text{O}$

Conditions: Cold concentrated  $\text{H}_2\text{SO}_4$  then warm  $\text{H}_2\text{O}$

Conditions (Industrial):  $\text{H}_3\text{PO}_4(\text{l})$  in celite,  $300^\circ\text{C}$

### 11.3.3 Oxidation

#### Mild Oxidation / Formation of Diol

Reagents:  $\text{KMnO}_4$

Conditions:  $\text{NaOH}$  cold

#### Strong Oxidation

Reagents:  $\text{KMnO}_4$

Conditions:  $\text{H}_2\text{SO}_4$ , warm or heat under reflux

Reactant alkene first undergoes mild oxidation and is saturated with  $-\text{OH}$  groups, afterward the heat supplied allows for the cleavage of a  $\sigma$  bond between two C with OH groups attached to each of them due to the electron-withdrawing effect of an  $-\text{OH}$  group.

Terminal / primary C are reacted into  $\text{CO}_2 + \text{H}_2\text{O}$ , secondary C are converted into terminal  $\text{COOH}$  groups and tertiary C are converted into ketone groups.

$\text{HOOC}-\text{COOH}$  or Ethanedioic acid as well as  $\text{CHOOH}$  or Methanoic acid will be oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in acidic  $\text{KMnO}_4$ . Methanoic acid is also oxidized by acidic  $\text{K}_2\text{Cr}_2\text{O}_7$ .

#### Strong Oxidation in Alkaline Medium

Reagents:  $\text{KMnO}_4$

Conditions:  $\text{NaOH}$ , warm

$\text{CO}_3^{2-}$  is obtained instead of  $\text{CO}_2$  and  $\text{COO}^-$  is obtained instead of  $\text{COOH}$ . Addition of acidic solution will revert the products to  $\text{CO}_2$  and  $\text{COOH}$ .

## 12 Arenes

### 12.1 Structure of Benzene

A Benzene ring is a cyclic chain of 6 carbon atoms which are all  $\text{sp}^2$  hybridized. Each carbon atom has one remaining electron in an unhybridized p orbital, which eventually pool together to form a  $\pi$   $\text{e}^-$  cloud. This resonance structure ensures that the benzene ring is especially stable, providing its aromatic properties.

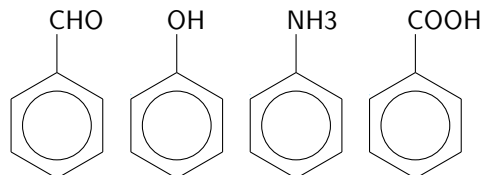
Benzene rings have been found to have this special property as all C-C bonds have been found to have the same bond length and also because the enthalpy of three  $\text{C}=\text{C}$  double bonds result in a energy change significantly larger than that of a Benzene ring. As such, reactions involving benzene tend to maintain its resonance/aromatic structure and rarely convert Benzene into Cyclohexene.

### 12.2 Physical Properties of Benzene

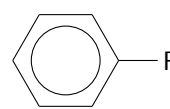
Benzene is a colorless liquid at room temperature and pressure. It freezes at  $5.5^\circ\text{C}$  and melts at  $80^\circ\text{C}$ . Benzene is insoluble in water and less dense than water.

### 12.3 Aromatic Nomenclature

Most benzene derivatives involve their functional group's prefix being added to 'benzene'. Four unique names need to be memorized: benzaldehyde, phenol, phenylamine and benzoic acid.

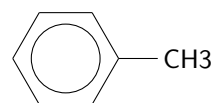


A benzene ring that does not contain the functional group is a 'phenyl' (abbreviated Ph) group.

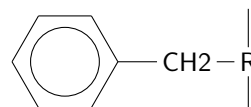


### 12.4 Methylbenzene

Methylbenzene is the simplest alkylbenzene, characterized by a methyl group attached to a benzene ring. Due to the presence of these two groups, methylbenzene is able to undergo both reactions involving the benzene ring as well as an alkyl chain.



A  $\text{C}_6\text{H}_5\text{CH}_2$  group is a 'benzyl' group.



## 12.5 Reaction of Arenes

Arenes are typically reactive due to the presence of its electron-dense  $\pi$   $e^-$  cloud. However, benzene rings tend to preserve their aromaticity even after reactions due to its unique stability. Arenes will typically undergo electrophilic substitution reactions.

Side chains of benzene rings are typically more reactive than their counterparts without benzene rings as the  $\pi$   $e^-$  cloud of the benzene ring can disassociate across C atoms in the side chain, making them more reactive. Otherwise, side chains can undergo any reactions as if they lacked its benzene ring substituent.

### 12.5.1 Reduction

Reagents:  $H_2$

Conditions: Raney Ni, High T, High P

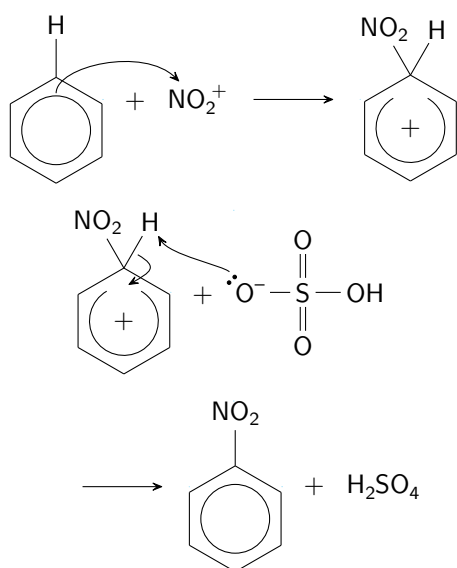
### 12.5.2 Electrophilic Substitution

#### Nitration

Reagents: Concentrated  $HNO_3$

Conditions: Concentrated  $H_2SO_4$ , 55 °C in benzene, 30 °C in methylbenzene

Generation of Electrophile:  $HNO_3 + 2 H_2SO_4 \rightleftharpoons NO_2^+ + 2 HSO_4^- + H_3O^+$



#### Halogenation

Reagents:  $X_2$  ( $X \in Cl, Br, I$ )

Conditions: Anhydrous,  $AlX_3$  OR  $FeX_3$  or Fe

Generation of Electrophile:  $Cl-Cl + AlCl_3 \rightarrow Cl^+ + AlCl_4^-$

#### Friedel-Craft Alkylation

Reagents:  $R-Cl$

Conditions:  $AlCl_3$

Generation of Electrophile:  $R-Cl + AlCl_3 \rightarrow R^+ + AlCl_4^-$

#### Friedel-Craft Acylation

Reagents:  $R-COCl$

Conditions:  $AlCl_3$

Generation of Electrophile:  $R-COCl + AlCl_3 \rightarrow RCO^+ + AlCl_4^-$

### 12.5.3 Oxidation

Though the benzene ring itself is unreactive, any alkyl chains bonded to a benzene ring can undergo oxidation, replacing the alkyl group with a  $COOH$  group. However, the reaction requires that the benzylic carbon has at least 1 H or 1 O atom bonded to it, otherwise a case such as a tert-butyl benzene will not be oxidised due to steric effect of  $CH_3$  groups attached to the benzylic C.

Reagents:  $KMnO_4$

Conditions: Warm

## 12.6 Activating and Deactivating Groups

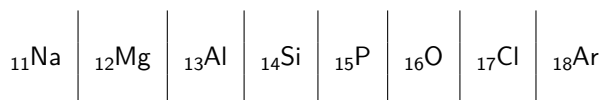
Functional groups bonded to a benzene ring will distort the electron cloud of the benzene ring through two mechanisms. Groups bonded to benzene rings can donate or withdraw electrons by 'Resonance Effect' which arises when there is lone pairs (increasing reactivity) or  $\pi$  bonds (decreasing reactivity) at functional groups adjacent to the benzene. Groups can also affect reactivity through 'Inductive Effect' which arises due to electronegativity of attached groups and may supply or withdraw  $e^-$  to the aromatic  $\pi$   $e^-$  cloud.

The functional groups presently on a benzene ring can determine the locations of where further electrophilic substitution reactions attach their functional groups onto. 'Meta'-directing groups prefer addition to the third carbon in the benzene ring whereas 'Ortho/Para'-directing groups prefer addition to the second or fourth carbon in the benzene ring.

When there is more than one group on a benzene ring, follow the locations as determined by the strongest activating group on the benzene.

## 13 Periodicity I

### 13.1 Period 3



Period 3 comprises the elements of Na to Ar.

### 13.2 Atomic and Physical Properties

Please refer to Atomic Structure.

## 13.3 Period 3 and Oxygen

### 13.3.1 Oxides

Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>6</sub> P <sub>4</sub> O <sub>10</sub>	SO <sub>2</sub> SO <sub>3</sub>	<u>Cl<sub>2</sub>O</u> <u>Cl<sub>2</sub>O<sub>7</sub></u>
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*Note: Properties of underlined compounds are not in the A level syllabus.*

Oxides of Na, Mg and Al are ionic compounds, Si is macro-molecular and P, S and Cl are simple covalent molecules. All are solid at room temperature save for SO<sub>3</sub> which is an orange liquid.

### 13.3.2 Period 3 and Oxygen

Na and Mg react vigorously and burns with a orange and white flame respectively to form their oxides.

Al initially reacts vigorously but slows down due to the formation of an impervious layer of Al<sub>2</sub>O<sub>3</sub>.

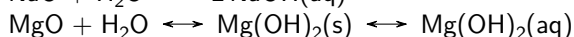
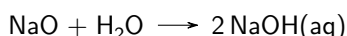
Si reacts slowly with oxygen to form SiO<sub>2</sub>.

P reacts vigorously and burns with a yellow flame to form its oxide.

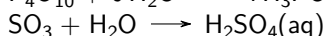
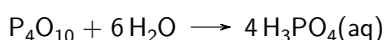
S reacts slowly and burns with a blue flame to form its oxide.

### 13.3.3 Oxides and Water

Most oxides except for Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> which have very strong lattice energies and covalent bonds are able to dissolve in water. MgO is sparingly soluble.



Oxides of Na and Mg are basic as they readily accept H<sup>+</sup> in water and hence release OH<sup>-</sup> in aqueous solution. MgO is significantly less basic because it does not dissolve well.

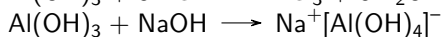
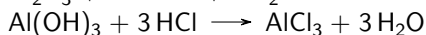
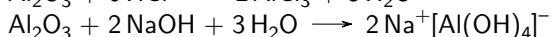
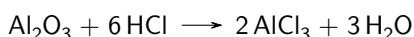


Oxides of P and S are highly acidic because their bonding with many O render them electron deficient and prone to nucleophilic attack by OH<sup>-</sup>, causing the release of H<sup>+</sup> into aqueous solution.

### 13.3.4 Acid-Base Properties

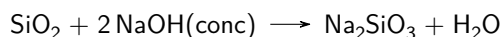
Across Period 3, oxides of elements progress from basic to amphoteric to acidic.

Na<sub>2</sub>O and MgO act as bases whereas P<sub>4</sub>O<sub>10</sub> and SO<sub>3</sub> act as acids.



Oxides and hydroxides of Al are amphoteric and react with

both acids and bases.



SiO<sub>2</sub> is classified as an acidic oxide because of its ability to react with concentrated bases.

## 13.4 Period 3 and Chlorine

### 13.4.1 Chlorides

NaCl	MgCl <sub>2</sub>	AlCl <sub>3</sub>	SiCl <sub>4</sub>	PCl <sub>5</sub> <u>PCl<sub>3</sub></u>	<u>S<sub>2</sub>Cl<sub>2</sub></u>
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*Note: Properties of underlined compounds are not in the A level syllabus.*

Chlorides of Period 3 elements demonstrate the property of maximum oxidation state, where the theoretical limit on the number of covalent bonds an atom can form is equal to the number of valence electrons in its unbonded atom because electrons can be promoted to low-lying 3d orbitals and form as many bonds as it can supply electrons.

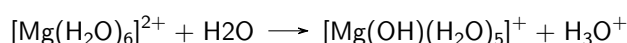
Chlorides of Na and Mg are ionic compounds while the rest are simple covalent molecules. NaCl and MgCl are solids at room temperature, AlCl<sub>3</sub> is solid but can sublime and dimerize into Al<sub>2</sub>Cl<sub>6</sub> at higher temperatures, SiCl<sub>4</sub> is liquid and PCl<sub>5</sub> is gaseous.

### 13.4.2 Period 3 and Chlorine

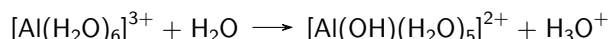
Na, Mg, Al and P react vigorously and burns with an orange, white, white and yellow flame respectively to form their chlorides.

### 13.4.3 Chlorides and Water

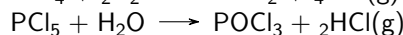
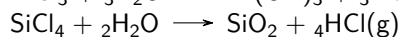
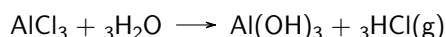
NaCl is a strong electrolyte and disassociates readily in water to form a neutral solution.



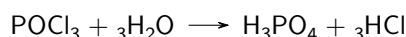
MgCl<sub>2</sub> disassociates readily in water and exhibits slight hydrolysis.



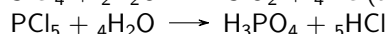
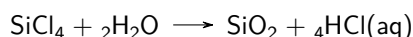
AlCl<sub>3</sub> disassociates readily in water and exhibits moderate hydrolysis.



In conditions with limited amount of water, AlCl<sub>3</sub>, SiCl<sub>4</sub> and PCl<sub>5</sub> or when cold water is added to PCl<sub>5</sub>, fumes of HCl are released.



In excess water, POCl<sub>3</sub> can complete its reaction.



In excess water,  $\text{SiCl}_4$  and  $\text{PCl}_5$  react to form acidic solutions.

### 13.5 Period 3 and Water

Na reacts vigorously with water to form NaOH.

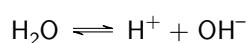
Mg reacts vigorously with steam to form MgO and reacts slowly with water to form  $\text{Mg}(\text{OH})_2$ .

Al reacts vigorously with steam to form  $\text{Al}_2\text{O}_3$  but slows down due to its impervious oxide layer.

$\text{Cl}_2$  reacts with water to form HCl solution.

## 14 Ionic Equilibria

### 14.1 Ionic Product of Water



#### Definition 14.1: Ionic Product of Water $K_w$

The product of concentrations of  $\text{H}^+$  and  $\text{OH}^-$  are always  $K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  at 298 K.

As a result of this property of the equilibrium between disassociating  $\text{H}_2\text{O}$ , the concentration of one ion can be calculated once the concentration of the other is known.

### 14.2 pH and pOH

#### Equation 14.1: p Function

For some quantity  $X$ :

$$pX = \log_{10} X$$

#### Definition 14.2: pH

pH is a measure of the concentration of  $\text{H}^+$  in a solution, calculated as:

$$pH = \log_{10} [\text{H}^+]$$

#### Definition 14.3: pOH

pOH is a measure of the concentration of  $\text{OH}^-$  in a solution, calculated as:

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

Note that at 298 K,  $pH + pOH = pK_w = 14$ .

### 14.3 Acid and Base Models

Ionic Equilibria typically use the Brønsted Acid and Base model, which involves the transfer of  $\text{H}^+$ .

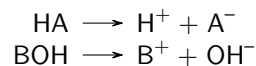
#### Definition 14.4: Brønsted Acids and Bases

Brønsted-Lowry Acids are substances which donate protons while Brønsted-Lowry Bases receive protons.

#### Definition 14.5: Conjugate Acids and Bases

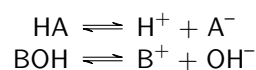
A Conjugate Acid or Base is the chemical substance obtained after a base receives  $\text{H}^+$  or an acid donates  $\text{H}^+$  respectively.

### 14.4 Strength of Acids and Bases



#### Definition 14.6: Strong Acids and Bases

Strong Acids and Bases are substances which fully disassociate into  $\text{H}^+$  and  $\text{OH}^-$  in aqueous solution.

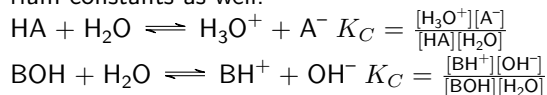


#### Definition 14.7: Weak Acids and Bases

Weak Acids and Bases are substances which only partially disassociate into  $\text{H}^+$  and  $\text{OH}^-$  in aqueous solution.

### 14.5 Weak Acids and Bases

Weak acids and bases disassociate according to an incomplete reaction and exist in equilibrium, hence acid and base disassociation reactions can be quantified through equilibrium constants as well.



Notice that the non-simplified reactions of weak acid and weak base disassociation are pseudo-order with respect to  $\text{H}_2\text{O}$  because  $\text{H}_2\text{O}$  is present in large excess. As such, a simplified equilibrium constant for weak acid and weak base disassociation can be used instead.

#### Equation 14.2: Weak Acid Equilibrium Constant

For a weak acid which dissociates to equilibrium concentrations  $[\text{H}^+]$ ,  $[\text{A}^-]$  and  $[\text{HA}]$ , its equilibrium constant  $K_A$  is given by the equation

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

#### Equation 14.3: Weak Base Equilibrium Constant

For a weak base which dissociates to equilibrium concentrations  $[\text{B}^+]$ ,  $[\text{OH}^-]$  and  $[\text{BOH}]$ , its equilibrium constant  $K_B$  is given by the equation

$$K_B = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}$$

As with other equilibrium constants, the values of  $K_A$  and  $K_B$  are constant at any given temperature and do not vary with concentration.



**Definition 14.8: Disassociation Constant**

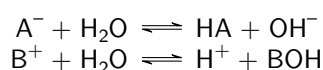
The disassociation constant  $\alpha$  of a weak acid or base is the proportion of disassociated acid or base to original concentration of acid or base.

**Equation 14.4: Disassociation Constant**

$$\alpha = \frac{[A^-]_{\text{equilibrium}}}{[HA]_{\text{initial}}}$$

**14.6 Salt Hydrolysis****Definition 14.9: Salt Hydrolysis**

The disassociation of acids and bases will form  $H^+$  or  $OH^-$  as well as a conjugate base  $A^-$  or acid  $B^+$ . If a solution contains these conjugate bases or acids, their reverse reaction of Salt Hydrolysis can occur.



As such, a 'fully reacted' weak acid or base solution still contains conjugate base or acids which will alter their pH.

Also notice that the product of the equilibrium constants of the initial disassociation reaction and the salt hydrolysis equation will be equal to that of  $K_w$ .

**Equation 14.5: Relationship of  $K_A$  and  $K_B$** 

$$K_A \times K_B = K_w$$

**14.7 Buffer Solutions****Definition 14.10: Buffer Solution**

A Buffer Solution is a solution which can resist change in its pH. Usually it contains a weak acid and its conjugate base in comparable proportions or a weak base and its conjugate acid in comparable proportions.

**Equation 14.6: Henderson Hasselbach Equation**

$$\begin{aligned} pH &= pK_A + \lg \frac{[A^-]}{[HA]} \\ pOH &= pK_B + \lg \frac{[B^+]}{[BOH]} \end{aligned}$$

**Definition 14.11: Effective Buffer Region**

The effective buffer region is the region of pH where a buffer solution is able to resist changes in pH, typically present within  $pK_A \pm 1$  or  $pK_B \pm 1$

**Definition 14.12: Maximum Buffer Capacity**

A Buffer solution is at maximum buffer capacity if it can resist the addition of acid and the addition of base equally well.

At maximum buffer capacity, the concentration of acid or base is equal to the concentration of conjugate salt. At this point in time, the lg term is numerically equal to zero, hence  $pH = pK_A$  or  $pK_B$ . As a result of this property, the point of maximum buffer capacity in a titration occurs at half of the volume of the equivalence point, where  $pH = pK_A$ .

**14.8 Acid-Base Titration Curves**

For a titration of weak acid against strong base:

**Equation 14.7: Initial pH**

Assuming  $[HA]_{\text{initial}} \approx [HA]_{\text{equilibrium}}$

$$pH = -\lg \sqrt{K_A [HA]}$$

**Equation 14.8: pH in Buffer Region**

When  $|\lg \frac{[A^-]}{[HA]}| < 1$

$$pH = pK_A + \lg \frac{[A^-]}{[HA]}$$

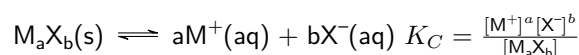
**Equation 14.9: Equivalence Point pH**

Assuming  $[HA]_{\text{initial}} \approx [A^-]_{\text{endpoint}}$

$$pH = 14 - pOH = 14 + \lg \sqrt{\frac{K_w}{K_A} [HA]}$$

**14.9 Solubility Product****Definition 14.13: Solubility**

The solubility of a salt is how much salt can be dissolved per unit volume of water.



Since  $[M_aX_b]$  is approximately constant, the equilibrium constant of dissociation of a sparingly soluble salt can be presented as pseudo-order with respect to its solid salt.

**Equation 14.10: Solubility Product  $K_{sp}$** 

The Solubility Product  $K_{sp}$  of a sparingly soluble salt which disassociates to equilibrium concentrations  $[M^+]$  and  $[X^-]$  is given by the equation

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

As with other equilibrium constants, the value of  $K_{sp}$  is constant at any given temperature and do not vary with concentration.

### 14.9.1 Ionic Product

#### Equation 14.11: Ionic Product $IP$

The Ionic Product  $IP$  of a sparingly soluble salt which disassociates to instantaneous concentrations  $[M^+]$  and  $[A^-]$  is given by the equation

$$IP = [M^+]^a [X^-]^b$$

Ionic Product is analogous to  $Q_C$  as  $K_{sp}$  is to  $K_C$ .

In any system containing ions of a sparingly soluble salt, the  $IP$  is always less than or equal to  $K_{sp}$ , or else precipitation will occur to remove sufficient aqueous ions to bring  $IP$  lower.

For a solution already containing some of one ion of a sparingly soluble salt, the overall solubility of a salt will drop drastically due to the inflated ionic product. Explain with Le Chatelier's Principle.

### 14.9.2 $K_{sp}$ of Metal Hydroxides

Metal hydroxides in the syllabus typically fall into three main categories.

Hydroxides of Cr, Al and Fe have a low  $K_{sp}$  ranging from  $1 \times 10^{-23}$  to  $1 \times 10^{-29}$  and precipitate with even  $NH_3(aq)$  with  $NH_4Cl$  present.

Hydroxides of Zn, Mg, Mn, Ni and Co have moderate  $K_{sp}$  ranging from  $1 \times 10^{-11}$  to  $1 \times 10^{-20}$  and will form ppt in NaOH solution and  $NH_3(aq)$ , but tend to dissolve when  $NH_4Cl$  is added in the latter case.

Hydroxides of Ba and Ca have very high  $K_{sp}$  values of approximately  $1 \times 10^{-6}$  and will only form ppt when concentrate NaOH is added.

### 14.10 Complex Ions

$[Al(OH)_4]^-$	$[Zn(OH)_4]^{2-}$	$[Cr(OH)_6]^{3-}$
$[Cu(NH_3)_4]^{2+}$	$[Zn(NH_3)_4]^{2+}$	$[Ag(NH_3)_2]^+$

#### Definition 14.14: Complex Ions

A Complex Ion is a ion consisting of a central ion with one or more surrounding ions or molecules (called ligands) bonded to the central ion through dative covalent bonds.

Complex ions are typically more soluble in water due to their ability to form ion-dipole interactions with water.

Reactions which form complex ions typically have very high  $K_{sp}$ . As such, when the necessary reactants are introduced into a system which contains insoluble salts, the formation of complex ions will readily react away whatever ions are left in the solution, increasing the solubility of the insoluble salt.

## 15 Halogenoalkanes

### 15.1 Structure of Halogenoalkanes

Halogenoalkanes are derivatives of alkanes compounds with F, Cl, Br, I groups. Halogenoarenes are derivatives of arenes with benzylic H replaced by a F, Cl, Br, I group.

Halogenoalkanes can be classified according to the degree of substitution of C that the halogen is bonded to.

### 15.2 Physical Properties of Halogenoalkanes

Halogenoalkanes contain polar R-X bonds which increase their melting and boiling point. For compounds with the same R group, the molecule with a larger X electron cloud has stronger id-id interactions and hence a larger melting and boiling point.

Though they are polar, halogenoalkanes are still poorly soluble in water. Fluoroalkanes and monochloroalkanes are less dense than water while other R-X compounds are denser than water.

### 15.3 Formation of Halogenoalkanes

#### Alkanes to Halogenoalkanes

Mono and polyhalogenated products can be formed from alkanes. Refer to 'Free Radical Substitution' in Alkanes.

#### Alkenes to Halogenoalkanes

Mono and dihalogenated products can be formed from alkenes. Refer to 'Electrophilic Substitution' in Alkenes.

#### Alcohols to Halogenoalkanes

Monohalogenated products can be formed from alcohols. Refer to 'Nucleophilic Substitution' in Hydroxy Compounds.

### 15.4 Reaction of Halogenoalkanes

Halogenoalkanes typically undergo nucleophilic substitution reactions.

The rate of reaction primarily depends on the nature of the R-X bond, with weaker bonds reacting faster despite the change in electronegativity, hence rate of reaction increases in the order C-Cl, C-Br and C-I.

#### 15.4.1 Nucleophilic Substitution

##### Definition 15.1: Nucleophile

A Nucleophile Nu is a particle which has at least one pair of free electrons and can act as an electron donor. Nucleophiles are attracted to electron-poor sites.

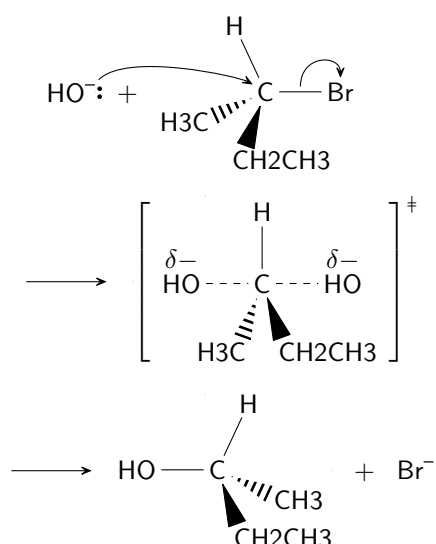
Note that nucleophiles are not necessarily charged.

Nucleophilic substitution can occur through two mechanisms, characterized by the study of these mechanism's kinetic properties.

#### Definition 15.2: S<sub>N</sub>2

The S<sub>N</sub>2 mechanism of nucleophilic substitution involves two molecules in its slow (and only) step.

S<sub>N</sub>2 reactions involve the backside attack of a nucleophile to the halogenoalkane at the opposite side of the C–X bond, forming an intermediate molecule both bonded to the nucleophile and X, after which X is ejected. This reaction preserves the enantiomeric quality of a molecule if the original alkane displays enantiomerism about the C with X due to the spatial requirements of a backside attack.

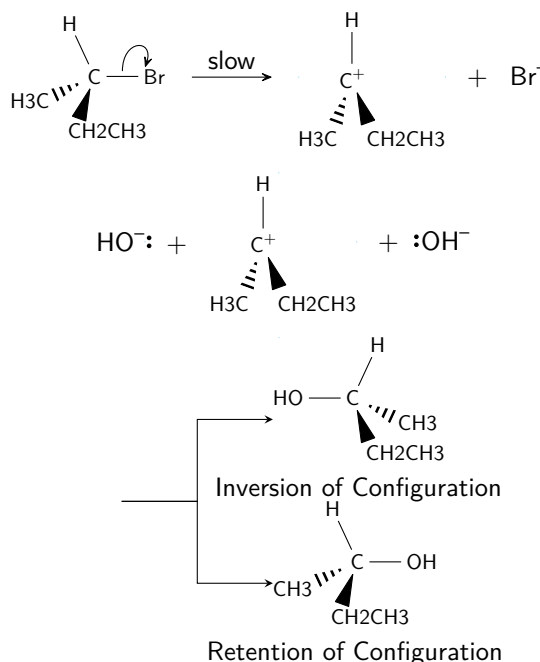


Label partial charges on atoms as they 'develop' charges throughout the reaction. A negatively charged nucleophile will progress to a neutral charge whereas a neutrally charged nucleophile will develop a positive charge.

#### Definition 15.3: S<sub>N</sub>1

The S<sub>N</sub>1 mechanism of nucleophilic substitution involves 1 molecule in its slow step.

S<sub>N</sub>1 reactions involve the spontaneous ejection of the X group in its slow step to form a carbocation which will then react with a nucleophile. The later addition of the nucleophile will happen at equal probabilities at either side of the planar C<sup>+</sup>, hence any enantiomeric products about C will be racemic.



Draw stereochemistry of a reaction if the original molecule displays enantiomerism about the C bonded to X. Also indicate by annotating 'Retention of Configuration' and 'Inversion of Configuration' below the resultant molecules.

The mechanism at which a S<sub>N</sub> reaction occurs depends primarily on the bonding of the C bonded to X. C with more alkyl groups bonded to it will generally follow the S<sub>N</sub>1 mechanism because it will form a more stable C<sup>+</sup> whereas C with less alkyl groups bonded to it will follow the S<sub>N</sub>2 mechanism due to the free space around C leaving it susceptible to backside attack. When explaining why a reaction follows one mechanism, explain why one is favored and why the other is less likely.

#### Formation of Alcohol

Reagents: NaOH

Conditions: Aqueous, heat

A polyhalogenoalkane may react to form multiple alcohol groups on the same carbon (also known as gem-diols), which may then decompose into ketone and carboxylic acid groups.

#### Formation of Amines

Reagents: Excess concentrated NH<sub>3</sub>

Conditions: Alcoholic, heat, sealed tube

If NH<sub>3</sub> is not in excess, a primary amine can act as a nucleophile in later reactions and form a chain reaction to eventually form secondary and tertiary amines and finally a quaternary ammonium salt because more-substituted amine compounds are stronger nucleophiles than their primary counterparts.

Indicate all reactions (including proton transfer) when describing the mechanism.

#### Formation of Nitriles

Reagents: KCN

Conditions: Alcoholic, heat

In practice, a mixture of alcohol and water is used so that all reactants can be dissolved. Nitriles can be further reduced to form primary amines ( $\text{H}_2$ , Ni and Heat OR  $\text{LiAlH}_4^-$ , dry ether and heat) or undergo hydrolysis to form carboxylic acids ( $\text{H}_2\text{SO}_4(\text{aq})$ , heat) and carboxylate ions ( $\text{NaOH}(\text{aq})$ , heat).

### Williamson Ether Synthesis

Reagents: Alcohol, Na OR  $\text{R}-\text{O}^-\text{Na}^+$

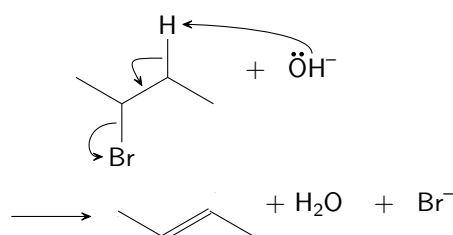
Conditions: Heat

### 15.4.2 Elimination

#### Dehydrohalogenation

Reagents: NaOH

Conditions: Alcoholic, heat



Dehydrohalogenation can only occur if there is a H in some C adjacent to the C-X group.

## 15.5 Halogenoarenes

Halogenoarenes are compounds with X bonded to benzene rings.

Halogenoarenes burn with a sooty flame and are insoluble in and denser than water.

Refer to 'Electrophilic Substitution' in Arenes for methods of preparation.

Halogenoarenes generally do not undergo nucleophilic substitution reactions. Extension of the  $\pi$   $e^-$  cloud over C-X causes the formation of a partial double bond character, the benzene ring physically blocks approaching nucleophiles, the  $e^-$  density of the benzene ring repels approaching nucleophiles and the presence of the  $e^-$  cloud prevents the formation of  $\text{C}^+$ . However, reactions may occur under extreme conditions (150 atm, 350 °C).

Halogenoarenes can also undergo electrophilic substitution, much like other arenes. However, X are electron-withdrawing and electronegative, hence they are deactivating groups and the reactivity of the arene decreases as more X groups are added. X is a 2,4-directing group.

## 15.6 Distinguishing Tests

### 15.6.1 '4-step Test'

1. Heat with  $\text{NaOH}(\text{aq})$  (liberate  $-\text{X}$  group)
2. Cool (prevent decomposition of  $\text{AgNO}_3$ )

3. Acidify with  $\text{HNO}_3$  (remove OH)

4. Add  $\text{AgNO}_3$  (form ppt)

Positive tests will form a  $\text{AgX}$  precipitate. The identity of X can be determined according to the color of the precipitate.

### 15.6.2 Ethanolic $\text{AgNO}_3$

1. Heat with ethanolic  $\text{AgNO}_3$

Ethanol acts as a nucleophile which will displace the halide group, which then causes the precipitation of  $\text{AgX}$ .

## 15.7 Applications of Halogenoalkanes

Strong C-F and C-Cl bonds mean that organic molecules saturated with F and Cl are highly unreactive. As a result, Chlorofluorocarbon (CFC) / 'Freon' compounds are also usually non-toxic, non-flammable (or even flame retardant), odorless, volatile and easily liquifiable. However, their high stability and low density mean that these compounds can rise to high altitudes before decomposition, after which  $\text{Cl}^\bullet$  radicals can easily form to deplete  $\text{O}_3$  in a chain reaction.

As a replacement, the use of HCFC compounds and HFC compounds are proposed as the presence of C-H bonds allow them to be destroyed at lower altitudes before being able to extensively damage the  $\text{O}_3$  layer.

## 16 Hydroxy Compounds

### 16.1 Structure of Hydroxy Compounds

Hydroxy compounds, also known as alcohols, are organic molecules with a  $-\text{OH}$  group.

### 16.2 Physical Properties of Hydroxy Compounds

Due to the presence of  $-\text{OH}$  groups and the preceding hydrocarbon chain, Hydroxy Compounds are able to form strong Hydrogen bonds with polar solvents like water as well as within other Hydroxy molecules. As a result, Hydroxy Compounds are soluble in both organic and polar solvents and can be used as an emulsifier and also have relatively high melting and boiling points, which also increases as the number of Hydroxy groups increases.

### 16.3 Formation of Hydroxy Compounds

#### Alkenes to Alcohols

Refer to 'Electrophilic Addition' in Alkenes.

#### Halogenoalkanes to Alcohols

Refer to 'Nucleophilic Substitution' in Halogenoalkanes.

#### Reduction of Carboxylic Acid / Aldehyde / Ketone to Alcohols

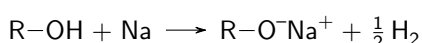
Refer to 'Reduction' in Carbonyl Compounds and Carboxylic Acids.

## 16.4 Reaction of Hydroxy Compounds

### 16.4.1 Reduction

Alcohols are able to donate  $H^+$  in organic solutions and can hence act as weak acids, therefore reducing metals like Na. However, in aqueous solution  $H_2O$  acts as a stronger acid and hence alcohols do not act as an acid. Across different alkyl chains, the more substituted chain is the weaker acid because the electron-donating C will destabilize  $O^-$ .

Reagents: Na



### 16.4.2 Elimination

#### Dehydrohalogenation

Reagents: Concentrated  $H_2SO_4$

Conditions: Heat at  $170^\circ C$

As with other reactions involving elimination of  $H_2O$ , the presence of a  $\beta$ -H is required for successful elimination.

### 16.4.3 Nucleophilic Substitution

In the presence of other nucleophiles, an  $R-OH$  is a suitable leaving group and can make way for nucleophiles such as X.

After being treated with Na in anhydrous conditions, an alkoxide  $R-O^-$  is obtained which can then act as a nucleophile, allowing it to take place in reactions such as ether synthesis and acylation.

#### Halogenation

Reagents:  $HCl(aq)$  OR  $Br_2$ ,  $H_2SO_4$  OR  $I_2$ ,  $H_3PO_4$

Conditions: Heat

Reagents:  $PCl_3$  OR  $PBr_3$  OR red P,  $I_2$  (1:3 Ratio)

Conditions: Anhydrous, room temperature

Reagents:  $PCl_5$  (1:1 Ratio)

Conditions: Room temperature

Observation: White fumes formed (HCl)

Reagents:  $SOCl_2$  (1:1 Ratio)

Conditions: Room temperature

Observation: White fumes formed (HCl)

#### Ether Synthesis

Reagents:  $R-Cl$

Conditions: Heat

#### Ester Synthesis

Reagents:  $RCOOH$

Conditions: Concentrated  $H_2SO_4$ ,  $60^\circ C$

Reagents:  $RCOCl$

Conditions: Room temperature

Observation: White fumes formed (HCl)

### 16.4.4 Oxidation

#### Oxidation of Primary Alcohol to Aldehyde

Reagents:  $K_2Cr_2O_7$

Conditions: With dilute  $H_2SO_4$ , heat, immediate distillation

#### Oxidation of Primary Alcohol to Carboxylic Acid and Secondary Alcohol to Ketone

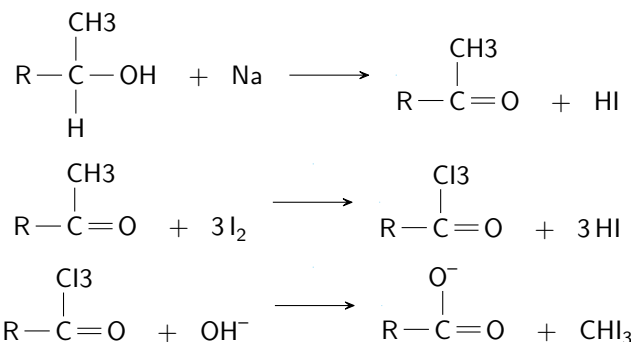
Reagents:  $K_2Cr_2O_7$  OR  $KMnO_4$

Conditions: Dilute  $H_2SO_4$ , heat

### 16.4.5 Iodoform Formation

Reagents: Na,  $I_2$

Observation: Yellow ppt ( $CHI_3$ )



The Iodoform reaction requires the presence of a  $CH_3$  and H group next to COH in the alcohol reactant.

The Iodoform reaction results in the formation of a  $COO^-$  compound and also the precipitation of  $CHI_3$ .

## 16.5 Structure of Phenols

A Phenol group is a benzene ring with an OH group bonded to a carbon in the ring.

The  $Ph-OH$  group is electron donating and hence an activating group, making them very reactive. Phenols are 2,4-directing.

Due to the presence of the  $\pi e^-$  cloud in the benzene ring,  $Ph-OH$  can deprotonate to  $Ph-O^-$  and the negative charge on  $O^-$  can be dispersed across the ring, hence phenols can act as acids. The acidity of a phenol is strengthened by attaching electron-withdrawing groups on the benzene ring (such as  $NO_2$ ) or can be weakened by attaching electron-donating groups on the benzene ring (such as  $CH_3$ ).

## 16.6 Physical Properties of Phenols

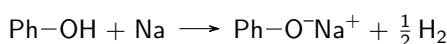
Pure phenols are colorless crystalline solids at room temperature. Phenols melts at 42 °C and boil at 217 °C due to their ability to form hydrogen bonds between molecules. However, the extent of these hydrogen bonds can be diminished if the species of phenol is able to exhibit intramolecular H bonds which then reduces the strength of intermolecular bonds.

Phenol compounds are sparsely soluble in water due to the presence of a hydrophobic benzene ring, but are soluble in NaOH solution.

## 16.7 Reactions of Phenols

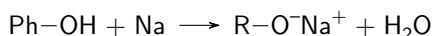
### 16.7.1 Reduction

Reagents: Na



### 16.7.2 Acid-base

Reagents: NaOH



### 16.7.3 Electrophilic Substitution

Due to the presence of the electron-donating OH group, the electron density in a phenol ring is increased, leaving it more reactive to electrophilic substitution reactions. Compared to reactions of arenes, reactions of phenols typically do not require heating or the presence of a catalyst.

#### Halogenation

Reagents:  $\text{X}_2$  ( $\text{X} \in \text{Cl}, \text{Br}$ )

Conditions: Aqueous, room temperature

Halogenation of phenols in a aqueous substrate forms a polysubstituted product. A tribromophenol is an insoluble white precipitate.

Reagents:  $\text{X}_2$  ( $\text{X} \in \text{Cl}, \text{Br}$ )

Conditions:  $\text{CCl}_4$ , room temperature

Halogenation of phenols in a aqueous substrate forms a monosubstituted product.

#### Nitration

Reagents: Concentrated  $\text{HNO}_3$

Conditions: Room temperature

Nitration of phenols in a concentrated solution forms a polysubstituted product.

Reagents: Dilute  $\text{HNO}_3$

Conditions: Room temperature

Nitration of phenols in a dilute solution forms a monosubstituted product.

### 16.7.4 Acylation

Reagents:  $\text{R-OCl}$

Conditions: Na, room temperature

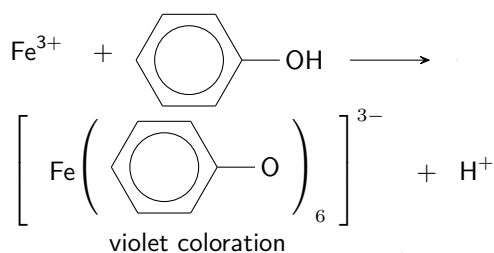
Observation: White fumes formed ( $\text{HCl}$ )

Na is added to form a carboxylate salt which can then readily react with acyl halides to form an ester.  $\text{Ph-OH}$  is not a strong enough nucleophile to undergo esterification with carboxylic acids.

### 16.7.5 Complexation

Reagents: Neutral  $\text{FeCl}_3$

Observation: Violet coloration



Phenols form complexes with  $\text{Fe}_3^+$  and obtain a violet color. Phenols with different groups attached to them may have varying colors.

## 17 Carbonyl Compounds

### 17.1 Structure of Carbonyl Compounds

Carbonyl compounds are organic molecules with a  $\text{C=O}$  group.

Aldehydes are compounds with a  $\text{R-CO-H}$  (more commonly written  $\text{R-CHO}$ ) structure while ketones are compounds with a  $\text{R-CO-R}$  structure.

### 17.2 Physical Properties of Carbonyl Compounds

Aldehydes and ketones have higher boiling points than similar alkene chains, but have lower boiling points than similar alcohols, typically due to the presence of the  $\text{C=O}$  bond with its permanent dipole but the lack of corresponding H bonding between carbonyl molecules.

Lone pairs of  $e^-$  on O allow carbonyl compounds to form H bonds with water, giving them good solubility in water so long as the carbon chain is small in number (less than 5C). Carbonyls such as propanone (common name 'acetone') are used as industrial solvents.

### 17.3 Formation of Carbonyl Compounds

#### Oxidation of Alcohols to Aldehydes and Ketones

Refer to 'Oxidation' in Hydroxy Compounds.

## 17.4 Reaction of Carbonyl Compounds

### 17.4.1 Reduction

Aldehydes and ketones can be reduced to primary alcohols and secondary alcohols respectively.

Reagents:  $\text{H}_2$ , Ni

Conditions: Heat

Reagents:  $\text{LiAlH}_4$  in dry ether or  $\text{NaBH}_4$  in methanol

Conditions: Room temperature

$\text{NaBH}_4$  is a source of  $\text{H}^-$  and reduces aldehydes and ketones.

Use  $\text{LiAlH}_4$  when avoiding reduction of alkene groups and  $\text{NaBH}_4$  when specifically reducing carbonyl compounds.

### 17.4.2 Oxidation

Aldehydes can be completely oxidized to carboxylic acids.

Reagents: Acidic  $\text{KMnO}_4$  or Acidic  $\text{K}_2\text{Cr}_2\text{O}_7$

Conditions: Heat

### 17.4.3 Nucleophilic Addition

Carbonyl compounds contain a  $\text{C}=\text{O}$  structure. Due to the electronegativity of O as compared to C, C holds a partial positive charge which is then able to attract electron-rich nucleophiles. Compounds are added across the unsaturated  $\text{C}=\text{O}$  bond, hence leaving carbonyl compounds susceptible to Nucleophilic Addition.

Carbonyl compounds with alkyl groups or aromatic groups bonded to the  $\text{C}=\text{O}$  structure decrease susceptibility to nucleophilic addition due to electronic effect reducing the intensity of the partial positive charge in the former and due to resonance effect in the latter.

#### Addition of Nitriles / Formation of Cyanohydrins

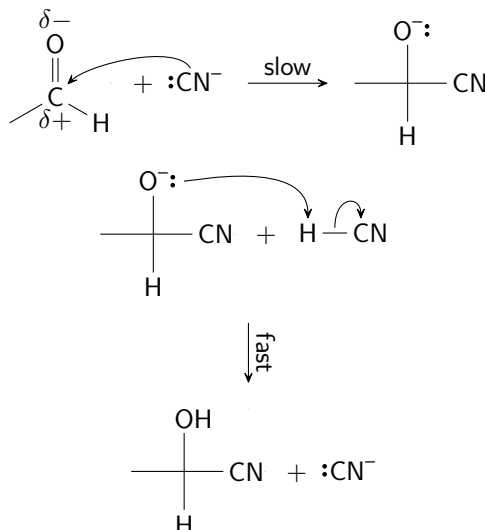
Reagents:  $\text{HCN}$ , trace  $\text{KCN}$  OR  $\text{HCN}$ , trace  $\text{KOH}$  OR  $\text{KCN}$ ,  $\text{H}_2\text{SO}_4$

Conditions: **Room temperature**

Nucleophilic addition of  $\text{C}\equiv\text{N}$  is an endothermic process. Heating the reaction will in fact slow the rate of reaction.

Generation of Electrophile:  $\text{KCN} \rightleftharpoons \text{K}^+ + \text{CN}^-$ , OR

Generation of Electrophile:  $\text{HCN} + \text{KOH} \rightleftharpoons \text{H}_2\text{O} + \text{K}^+ + \text{CN}^-$



Study of this reaction's kinetics determines that the rate of reaction is determined by the concentration of carbonyl and  $\text{CN}^-$ . As a result, for higher rates of reaction there needs to be trace amounts of  $\text{KCN}$  or  $\text{KOH}$  to catalyze reactions.

Note that in the case of ( $\text{KCN}$ ,  $\text{H}_2\text{SO}_4$ ) the reaction consumes  $\text{H}_2\text{SO}_4$  rather than using it as a catalyst.  $\text{H}_2\text{SO}_4$  needs to be added in comparable amounts rather than in trace amounts.

Nucleophilic addition of  $\text{CN}$  produces a structure known as a cyanohydrin, a  $\text{CN}^-$  adjacent to  $\text{C-OH}$ . Cyanohydrins, similar to nitrile compounds in halogenoalkanes, can be further hydrolyzed in acidic or basic conditions and can also be reduced to form primary amines. Carboxylic acid, carboxylate and primary amines adjacent to a  $\text{C-OH}$  suggest that the product may have been obtained through a cyanohydrin.

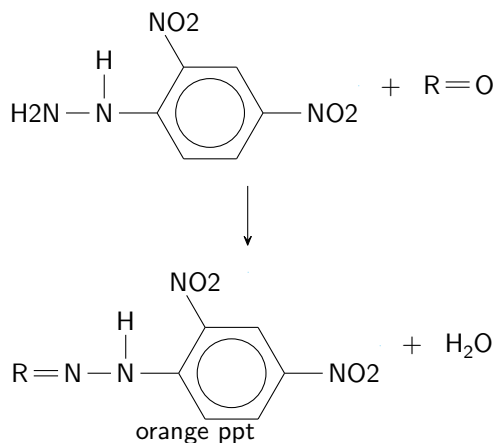
Carbonyl compounds are typically  $\text{sp}^2$  hybridized with respect to C in  $\text{C}=\text{O}$ . The trigonal planar geometry of  $\text{C}=\text{O}$  containing molecules mean that nucleophiles have equal chance of attacking from either plane, eventually forming a racemic mixture which is optically inactive.

### 17.4.4 Characteristic Reactions

Carbonyl compounds can be better differentiated through the use of several chemical tests, typically involving either condensation or oxidation reactions.

#### Condensation and 2,4-DNPH

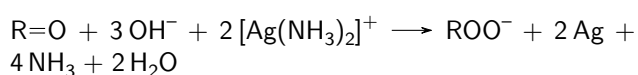
Aldehydes and Ketones both react with 2,4-dinitro phenyl hydrazine (2,4-DNPH) to form 2,4-dinitro phenyl hydrazones which are orange precipitates.



2,4-DNPH does not react with carboxylic acids as the interference of the C—OH renders lone pairs on C=O unable to undergo condensation.

### Oxidation using Tollen's Reagent

Aldehydes are oxidized by Tollen's reagent to form a silver mirror.



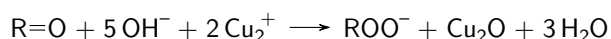
Reagents: Tollens' Reagent  $[\text{Ag}(\text{NH}_3)_2]^+$ , NaOH

Conditions: Heat

Observation: Silver mirror formed

### Oxidation using Fehling's Solution

Aliphatic aldehydes are oxidized by Fehling's solution to form a red-brown ppt of  $\text{Cu}_2\text{O}$ .



Reagents: Fehling's solution  $\text{Cu}_2^+(\text{aq})$ , NaOH

Conditions: Heat

Observation: Reddish-brown ppt formed

### 2,4-DNPH / Tollens / Fehlings

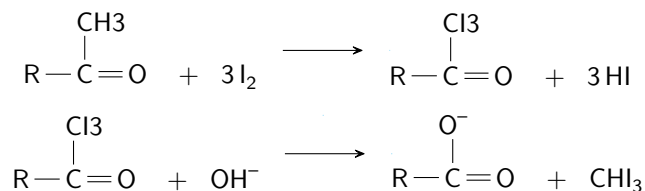
Using these three tests sequentially allows for identification of carbonyl compounds and further differentiation between ketones, aldehydes and aromatic aldehydes.

#### 17.4.5 Iodoform Formation

Carbonyl compounds with a  $\text{R}-\text{CO}-\text{CH}_3$  structure form yellow ppt of  $\text{CHI}_3$  when heated with  $\text{I}_2$  and NaOH. As a result, 2-carbonyls and ethanaldehyde can be identified through this test.

Reagents: Na,  $\text{I}_2$

Observation: Yellow ppt ( $\text{CHI}_3$ )



## 17.5 Aromatic Carbonyls

Carbonyl groups on a benzene ring are deactivating due to the presence of the electron deficient  $\text{C}=\text{O}$  structure, in addition to the fact that these compounds are typically strengthened due to resonance structures.

## 18 Carboxylic Acids

### 18.1 Structure of Carboxylic Acids

Carboxylic Acids (combination between carbonyl and hydroxyl groups) are organic molecules with the  $\text{COOH}$  group.

### 18.2 Physical Properties of Carboxylic Acids

Carboxylic acids have higher boiling points than similar alkanes as they are able to form intermolecular hydrogen bonds. Carboxylic acids also have higher boiling points than similar alcohols as the O—H bond is more polar due to the presence of electron withdrawing  $\text{C}=\text{O}$ .

Due to the presence of intermolecular hydrogen bonds, carboxylic acids tend to dimerize when in a gaseous state.

Carboxylic acids with four or less carbon atoms are soluble in water due to the formation of hydrogen bonds with  $\text{COOH}$  as well as the formation of ion-dipole interactions with  $\text{COO}^-$ . Longer chains have hydrophobic carbon chains which reduce their solubility.

### 18.3 Formation of Hydroxy Compounds

#### Alcohols / Aldehydes to Carboxylic Acids

Refer to 'Oxidation' in Alcohols and Carbonyls.

#### Nitriles to Carboxylic Acids

Refer to 'Nucleophilic Substitution' in Halogenoalkanes and 'Nucleophilic Addition' in Carbonyl Compounds.

#### Alkenes to Carboxylic Acids

Refer to 'Oxidation' in Alkenes.

#### Phenyls to Carboxylic Acids

Refer to 'Oxidation' in Arenes.



## 18.4 Reaction of Carboxylic Acids

### 18.4.1 Acid-Base Reactions

Carboxylic Acids are the most acidic organic functional group in the syllabus. The C–OH group contributes acidic character where its H can be easily lost, which is then intensified by the C=O group due to it withdrawing  $e^-$  from C. Additionally, the conjugate base of a carboxylic acid, also known as the carboxylate group  $COO^-$  is highly stable due to it having two equivalent resonance structures.

As a result, carboxylic acids are able to react with not only Na(s) and NaOH, but can also react with carbonates to produce salt and  $CO_2(g)$ , and hence are more acidic than C–OH and Ph–OH.

### 18.4.2 Reduction

Carboxylic Acids are able to be reduced back to primary alcohols.

Reagents:  $H_2$ , Ni

Conditions: Heat

Reagents:  $LiAlH_4$  in dry ether

Conditions: Room temperature

### 18.4.3 Acyl Chloride Formation

Carboxylic Acids can be reacted to form another acidic species known as the Acyl Chloride  $COCl$ . Acyl Chlorides are more reactive than carboxylic acids and are hence more often used for ester formation and amide formation.

Reagents:  $PCl_3$  (1:3 Ratio)

Conditions: Room temperature

Reagents:  $PCl_5$  (1:1 Ratio)

Conditions: Room temperature

Observation: White fumes formed (HCl)

Reagents:  $SOCl_2$  (1:1 Ratio)

Conditions: Room temperature

Observation: White fumes formed (HCl)

### 18.4.4 Condensation

In the presence of other nucleophiles, an R–OH is a suitable leaving group and can make way for nucleophiles such as X.

After being treated with Na in anhydrous conditions, an alkoxide  $R-O^-$  is obtained which can then act as a nucleophile, allowing it to take place in reactions such as ether synthesis and acylation.

Reagents: ROH, NO Phenol

Conditions: Concentrated  $H_2SO_4$ ,  $60^\circ C$

Reagents: Acyl Chloride and ROH

Conditions: Room temperature

Observation: White fumes formed (HCl)

## 18.5 Acyl Chlorides and Esters

Acyl chlorides are organic compounds with a  $R-COCl$  structure. Esters are compounds which have  $ROO-R'$  structures.

Carboxylic acid derivatives such as these typically have lower boiling points than the original carboxylic acids due to their inability to form H bonds with other molecules.

Esters are generally insoluble in polar solvents due to long hydrophobic chains while acyl chlorides are soluble in polar solvents as it readily hydrolyzes to its carboxylic acid form. Both compounds are readily soluble in organic compounds.

## 18.6 Reactions of Acyl Chlorides

### Hydrolysis

Reactants:  $H_2O$

Observation: White fumes formed (HCl)

On solution with water, acyl chlorides will readily react with  $H_2O$  to produce  $ROOH$  and white fumes of HCl. The end solution is usually very acidic due to the presence of a large amount of dissolved HCl.

### Condensation

The presence of the C=O structure in acyl chlorides renders the C positive and hence nucleophiles tend to be attracted towards it to undergo condensation reactions.

Reactive acyl chlorides can form  $RC-R'$  bonds very rapidly due to the  $COCl$  group. Acyl chlorides react with alcohols, phenols (but preferably the more nucleophilic phenoxide), primary and secondary amides to form esters.

Reactants: ROH OR  $Ph-O^-$  OR  $NH_3$  OR  $RNH_2$  OR  $RR'NH_2$

Conditions: Room temperature

This reaction proceeds much more rapidly as compared to ester formation with  $RCOOH$  due to the higher reactivity of  $RCOCl$ . Phenolic esters can only be formed through the use of acyl chlorides.

## 18.7 Reactions of Esters

### Hydrolysis

Reactants: HCl OR NaOH

Conditions: Heat under reflux

Ester bonds can be broken in acidic and basic medium, forming carboxylic acids and alcohols in their respective protonated or deprotonated states. Note that when breaking ester bonds between a carboxylic acid and phenol, additional reactant may be required to re-protonate

the phenoxide after reaction.

## 19 Organic Nitrogen Compounds

### 19.1 Structure of Organic Nitrogen Compounds

Organic Nitrogen Compounds are organic molecules with N atoms present.

Amides are molecules with N bonded to an aliphatic group, whereas Amines are molecules with a C=O group adjacent to N, and are classified as so due to their differing properties.

### 19.2 Physical Properties of Organic Nitrogen Compounds

Ammonia, Methylamine and Ethylamine are gases at room temperature, while other aliphatic amines with up to 4 C as well as Phenylamine are liquid at room temperature.

Amines typically have higher boiling points than other similar alkanes due to their ability to form H bonds, but still have lower boiling points than alcohols as the N—H...N bond is weaker than the O—H...O bond. Boiling points of amines decrease from primary to tertiary species due to their decreasing ability to form H bonds and their decreasing dipole moment.

Amines are generally soluble in water as they can form H bonds with water molecules. Amines with short carbon chains are also volatile, where warming of solutions containing ammonia or short-chain amides will give a pungent odor.

On the other hand, amides are able to form N—H...O bonds between molecules, hence most primary amides other than methanamide are crystalline solids. Primary and secondary amines have high melting and boiling points whereas tertiary amides have much lower boiling and melting points. Amides regardless of order are able to dissolve in water given short hydrophobic carbon chains.

### 19.3 Formation of Organic Nitrogen Compounds

#### Halogenoalkanes to Amines

Refer to 'Nucleophilic Substitution' in Halogenoalkanes.

#### Nitriles to Amines

Refer to 'Nitriles' in Halogenoalkanes and in Carbonyl Compounds.

#### Amides to Amine

Reagents:  $\text{LiAlH}_4$  in dry ether

Conditions: Room temperature

C=O groups are reduced to  $-\text{CH}_2^-$ .

#### Nitrobenzene to Phenylamine

Reagents:  $\text{Sn}$  with concentrated HCl, then aqueous NaOH

Conditions: First step reflux, second step room temperature

Nitrobenzene can be reduced and then neutralized to form phenylamine.

#### Amides to Amine

Refer to 'Hydrolysis' in Organic Nitrogen Compounds.

### 19.4 Reaction of Organic Nitrogen Compounds

Amines typically undergo reactions as either bases or nucleophiles.

#### 19.4.1 Acid-Base Reactions

Amines can react with acids to form amine salts which are non-volatile and hence odorless. Amines can be then regenerated through reacting the salt with base such as NaOH.

Various amines have differing degrees of basicity, depending on the nature of its side chains, degree of substitution and their physical state.

Basic strength increases from phenylamine to ammonia to amide. Phenylamine is the least basic species as the lone pair of  $e^-$  in N is partially disassociated to the  $e^-$  cloud of benzene. Amides are more basic because it has electron donating  $e^-$  groups which can stabilize its conjugate acid.

Amides are completely neutral because the lone pair of N is disassociated across the C=O double bond, leaving the  $e^-$  pair unavailable to act as a Lewis base.

Basic strength increases from primary to tertiary amides in gaseous state as the number of  $e^-$  donating alkyl groups increases. However, in an aqueous state the presence of large methyl groups in tertiary amines cause it to be less basic than primary and secondary amines.

#### 19.4.2 Nucleophilic Substitution

Refer to 'Nucleophilic Substitution' in Halogenoalkanes.

### 19.5 Condensation Reactions

Most amines undergo condensation reactions with acid halides to form amides. Tertiary amines do not react as they lack the H molecule to be condensed.

Reagents: ROCl

Conditions: Anhydrous, room temperature

Observations: White fumes of HCl

To form amines, a reaction with acyl halides must occur instead of with carboxylic acids as in the latter case an acid-base reaction will occur instead.

## 19.6 Reaction of Phenylamine

Phenylamine is a strongly activating group to benzene, more so than hydroxy groups.

### Halogenation

Reagents:  $X_2$  ( $X \in \text{Cl, Br}$ )

Conditions: Aqueous, room temperature

Halogenation of phenylamine in an aqueous substrate forms a polysubstituted product. A tribromophenol is an insoluble white precipitate.

To obtain a monosubstituted product, phenylamine needs to be deactivated before reaction.

Reagents:  $\text{CH}_3\text{COCl}$ , then  $X_2$  ( $X \in \text{Cl, Br}$ ), then NaOH

Conditions: Room temperature, then aqueous and room temperature, then aqueous and heat

### Nitration

Phenylamine will not undergo nitration. Under acidic conditions, phenylamine is protonated into deactivating phenylammonium which will not react.

## 19.7 Hydrolysis

Amide bonds between  $\text{R}-\text{C}=\text{O}$  and  $\text{N}-\text{H}_2$  are susceptible to breakdown when heated in acidic or alkaline mediums. Acidic hydrolysis produces carboxylic acids and ammonium whereas basic hydrolysis produces carboxyl ions and amines.

Conditions: Acidic or Alkaline, Heat

To differentiate between amines and amides, gentle heating to liberate  $\text{NH}_3$  or other amides can be used as a differentiating test.

## 19.8 Amino Acids

Amino acids are organic molecules with at least one carboxylic acid group and one amine group. They are classified according to the location of the amine relative to the  $\text{COOH}$  group, with  $n$ -amino acid referring to the amine on carbon  $n$  from  $\text{COOH}$ .

The most important amino acids are the 20  $\alpha$ -amino acids which make up biological proteins. These amino acids generally display optical activity with the exception of amino-ethanoic acid.

### 19.8.1 Zwitterions

Due to amino acids having weak acid and weak base groups, amino acids change in makeup depending on the pH of its environment. Zwitterions are the form of amino acids which consist of one  $\text{RNH}_3^+$  and one  $\text{COO}^-$  group. This dipolar form is its most stable state at its pH, as compared to if the functional groups were in their neutral state. The pH at which the most number of zwitterions are present is also known as its isoelectric point, written  $pI$ .

By being able to form zwitterions, amino acids generally form crystalline solids with high melting points, are very soluble and have a moderate acidity and basicity as compared to their pure carboxylic acid and pure amine counterparts.

### 19.8.2 Amino Acid Separation

Through taking advantage of different amino acid's mass and their differing charges at various pH, amino acids can be separated through paper or gel Electrophoresis. A mixture of amino acids with preferably different  $pI$  are placed in the center of a medium with a known pH, after which a voltage is applied on either side of the paper and the different amino acids will migrate according to:

- Their net charge determines which end of the paper it migrates to
- Their varying masses vary the speed which the molecules move

## 19.9 Peptides and Proteins

A peptide bond is a specific name for an amide bond between two amino acids formed via condensation reaction. Dipeptides, tripeptides and so on describe molecules with the according number of amino acid components. Molecules of this form with molar mass smaller than  $5000 \text{ g mol}^{-1}$  are called polypeptides, whereas molecules with molar mass larger than this are considered to be proteins.

Polypeptides and proteins can be broken down via hydrolysis.

### 19.9.1 Industrial Hydrolysis

#### Complete Hydrolysis

Conditions:  $6\text{M HCl(aq)}$  OR  $\text{NaOH(aq)}$  at  $100^\circ\text{C}$  for 20 h in an evacuated tube

#### Partial Hydrolysis

Conditions:  $\text{H}_2\text{SO}_4(\text{aq})$  OR  $\text{HCl(aq)}$  OR  $\text{NaOH(aq)}$ , heat for few hours

Acid or base catalyzed hydrolysis of proteins breaks down all amide bonds regardless of their adjacent components, creating a mixture of amino acids in their relative concentrations. If the reaction is conducted in less extreme

conditions and given less time to react, a collection of partially hydrolyzed peptides can be obtained, from which the structure of the entire protein may be derived from.

### 19.9.2 Enzymatic Hydrolysis

Various biological enzymes can selectively hydrolyze amide bonds at specific ends of specific amino acids. Common enzymes used include trypsin, chymotrypsin and pepsin. By using two or more enzymes, analysis of the remaining polypeptides can be used to determine the sequence of amino acids in the protein.

## 20 Electrochemistry

### 20.1 Redox

Refer to 'Redox' in Stoichiometry.

### 20.2 Electrolytes

#### Definition 20.1: Electrolyte

An Electrolyte is a compound which can conduct electricity in the molten or aqueous state, primarily through the flow of charged ions.

#### Definition 20.2: Strong / Weak Electrolyte

Strong or Weak electrolytes are compounds which fully or partially ionize in molten or aqueous medium respectively.

#### Definition 20.3: Non-electrolyte

A Non-electrolyte is a compound which does not ionize and does not conduct electricity in molten or aqueous state.

### 20.3 Electrode Potentials

#### 20.3.1 Half-cell Potential

When metals are submerged in aqueous solution, an equilibrium between its solid and aqueous ion species is established. Positive ions are dissolved into solution while electrons are left on the surface of the metal, forming a difference in charge and therefore a potential difference.

This formation of an electric potential difference can then be extended to many other redox half-reactions (e.g. a potential difference between an inert electrode and solution is also established in a solution containing  $\text{Fe}_2^+$  and  $\text{Fe}_3^+$ ).

As probing the potential of a half-cell will inevitably interfere with the reaction system (e.g. submerging a voltmeter into the solution may redistribute positive ions in solution), electrode potentials of half-cells are measured relative to each other, with the global standard of 'zero potential'

being that of the 'Standard Hydrogen Electrode'.

#### 20.3.2 Standard Electrode Potential

To ensure consistent measurements of electrode potentials, the values are measured under specific conditions and concentrations of reactive species:

- All temperatures are at 25 °C aka 298 K
- All aqueous species are at 1 mol dm<sup>-3</sup>
- All gaseous species are at 1 bar
- Electrodes with no solid metal species use inert Pt or graphite electrodes

#### Definition 20.4: Standard Electrode Potential $E^\ominus$

The Standard Electrode Potential  $E^\ominus$  of a half cell is the electromotive force between a half cell and the Standard Hydrogen Electrode, at temperature 25 °C and where all reacting species are 1 mol dm<sup>-3</sup> and all gases are at 1 bar.

Standard electrode potentials are denoted with a  $\ominus$  to indicate standard conditions, written as a superscript.

Note: Though water is a reacting species, it is present in liquid and not aqueous form, and thus does not need to be present in 1 mol dm<sup>-3</sup>.

#### Standard Hydrogen Electrode

The Standard Hydrogen Electrode (S.H.E.) is a platinum electrode covered in platinum black (to increase surface area), immersed in a solution of 1 mol dm<sup>-3</sup>  $\text{H}^+$  and surrounded by 1 bar of  $\text{H}_2$  gas at 25 °C.

#### 20.3.3 Measuring Electrode Potentials

A half cell to be measured and a S.H.E. are setup adjacent to each other and a salt bridge is used to connect both pools of solution, which provides ions to readily migrate and maintain charge neutrality in each cell. A high-resistance voltmeter is then connected between the two electrodes and the potential difference  $E^\ominus$  is read from the voltmeter.

Electrode potentials are assigned to their respective reduction half equations as 'redox potentials' or 'reduction potentials', where electrons are present on the left side of the equation. A more positive electrode potential indicates that equilibrium in this half cell lies far to the right and is hence more likely to be reduced.

Reversing redox half equations will also reverse their awarded redox potential, but multiplying a half-reaction with coefficients will not affect redox potentials.

### 20.4 Redox Series

Once data has been collected across multiple half-cells, what reaction occurs between a system of two connected

half-cells can be predicted. The half cell with a more positive reduction potential will be more likely to undergo reduction while the half cell with a more negative reduction potential will be more likely to undergo oxidation.

## 20.5 Standard Cell Potentials

### Definition 20.5: Standard Cell Potential $E_{\text{cell}}^{\ominus}$

The Standard Cell Potential  $E_{\text{cell}}^{\ominus}$  of two half cells is the potential difference between the two standard half cells and is equal to the difference between the standard redox potentials of the two cells.

### Definition 20.6: Anode

The Anode of a electrochemical setup is the electrode at which a oxidation reaction occurs.

### Definition 20.7: Cathode

The Cathode of a electrochemical setup is the electrode at which a reduction reaction occurs.

Once current is allowed to flow between the two electrodes in an electrochemical cell, the redox reaction is allowed to occur, with electron flow from the cathode to the anode.

### Equation 20.1: Standard Cell Potential

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

### 20.5.1 Non-standard Cell Potentials

If the half-cells are not under standard conditions, the potential difference between the two electrodes may change. By considering  $E^{\ominus}$  as a representation of equilibrium constant, changes to individual half-cells can be analyzed using half-reactions of the cell, therefore predicting the effect on its equilibrium constant and finally predicting the change of  $E^{\ominus}$  and  $E_{\text{cell}}^{\ominus}$ .

## 20.6 Cell Potentials and Energetics

### Equation 20.2: Gibbs Free Energy of Redox Reaction

Where  $n$  is the number of electrons transferred in one mole of reaction and  $F$  is Faraday's constant of  $96\,500\text{ C mol}^{-1}$

$$\Delta G^{\ominus} = -nFE^{\ominus}$$

If two species of compounds which can undergo redox reaction are mixed, the spontaneity of the redox reaction can be predicted by comparing their redox potentials as if they were in half-cell setups, where from there the change of Gibbs Free Energy of the system can be calculated.

## 20.6.1 Fuel Cells

### Definition 20.8: Fuel Cells

Fuel Cells are voltaic cells where controlled reaction of redox processes are used to convert chemical energy into electrical energy from a continuous supply of reactants.

A commonly studied fuel cell is the hydrogen fuel cell, where  $\text{H}_2$  and  $\text{O}_2$  gas are introduced into the cell and reacted to form water. The location of where water is produced depends on whether the electrolyte is basic or acidic.

Fuel cells are advantageous in that they are space saving, light, reusable, highly efficient as compared to fossil fuels and in the case of the  $\text{H}_2$  fuel cell, non polluting. Disadvantages include the fact that  $\text{H}_2$  fuel is gaseous at room temperature and explosive and thus difficult and dangerous to store.

### 20.6.2 Practical Power Sources

Increasing research is needed to develop smaller, lighter, higher voltage and higher capacity batteries due to increasing demands for portable power and environmental sustainability.

## 20.7 Electrolytic Cells

By supplying external electromotive force to a system, redox reactions which are otherwise not spontaneous at specific conditions can be forced to occur. Reactions are often accompanied with observations of effervescence, color changes and deposition or solution of metal electrodes.

## 20.8 Selective Discharge

When power is supplied to a electrolytic cell, the reaction which requires the least amount of power to drive occurs, resulting in only some species of molecules undergoing reaction. Identifying which species is discharged involves examining:

- The physical state of the electrolyte, where an aqueous electrolyte may allow for the redox of  $\text{H}_2\text{O}$  rather than a ionic species.
- The reactivity of the electrode, where a reactive electrode is a possible candidate to be reduced
- The concentrations of present species, where non-standard concentrations of reactants may affect the reduction potential of half-reactions and thus change which species is selectively discharged
- The actual electrode potentials of the present species

Electrodes connected to the negative terminal of a power source are supplied with electrons and cause the reaction with the most positive reduction potential to occur. Electrodes connected to the positive terminal of a power source

receive electrons and cause the reaction with the most negative reduction potential to occur.

## 20.9 Faraday's Laws of Electrolysis

### Definition 20.9: Faraday's Constant

The Faraday's Constant  $F$  is the amount of charge carried per mole of electrons.

### Equation 20.3: Faraday's Constant

$$F = Le$$

### Definition 20.10: Faraday's First Law of Electrolysis

Faraday's First Law of Electrolysis states that the mass of substance produced or volume of gas liberated is proportional to the amount of charged passed through the cell.

### Definition 20.11: Faraday's Second Law of Electrolysis

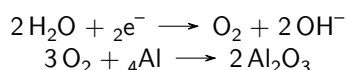
Faraday's Second Law of Electrolysis states that the amount of charge required to discharge 1 mol of an element depends on the charge of its ion.

Using Faraday's Laws of Electrolysis and knowledge of the exact chemical reaction that takes place in a electrolytic cell, the amount of charge passed through and the amount of reaction that has taken place can now be calculated.

## 20.10 Uses of Electrolysis

### 20.10.1 Anodized Aluminum

When current is passed through aluminum electrodes in dilute  $\text{H}_2\text{SO}_4$  electrolyte,  $\text{O}_2$  is produced at the cathode, which then can react with Al to form corrosion-resistant, electrically insulating and colorable  $\text{Al}_2\text{O}_3$ .



### 20.10.2 Copper Purification

In order to purify crude copper which may have Zn and Ag impurities, an impure copper electrode is used as an anode while a pure copper electrode is used as a cathode in a  $\text{CuSO}_4$  electrolyte.

Impurities with a larger  $E^\ominus$  than Cu cannot be dissolved, leaving Ag sludge which settles to the bottom of the electrolytic cell. Impurities with a smaller  $E^\ominus$  than Cu cannot be reformed at the cathode, leaving  $\text{Zn}_2^+$  ions suspended in the electrolyte.

## 21 Periodicity II

### 21.1 Group 2

Group 2 comprises the alkali earth metals, specifically Be, Mg, Ca, Sr and Ba.

#### 21.1.1 Reactivities

The reactivity of group 2 elements increase down the group.

As the number of electronic shells increases, the radius of valence  $ns^2$  electrons increases and thus the attractive strength decreases. Ionization energy thus decreases down the group, reducing the first two ionization energies and thus making lower elements more easily lose their valence electrons.

#### 21.1.2 Stability of Carbonates

The thermal stability of group 2 carbonates decreases down the group.

Down the group, the ionic radius of elements increases, decreasing the charge density of element's +2 charge. There is hence a decreasing extent of distortion of the electron cloud of  $\text{CO}_3^{2-}$  and a decreasing extent of weakening of covalent bonds in  $\text{CO}_3^{2-}$ . As a result, more heat energy is required to break the covalent bonds in  $\text{CO}_3^{2-}$ , increasing the thermal stability down the group.

## 21.2 Group 17

Group 17 comprises the halogen gases, specifically F, Cl, Br, I and At.

### 21.2.1 Bond Dissociation Energy

The BDE of diatomic group 17 elements decreases down the group, with the exception of F which has a lower BDE than Cl.

Down the group, the number of electron shells increases, increasing the size of the valence orbitals. As the orbitals become more diffuse, there is a decreased effectiveness of overlap between orbitals, hence reducing the bond strength.

The F–F bond is weaker than the Cl–Cl bond as the small size of F causes inter-orbital repulsion of lone pairs and bonded pairs.

### 21.2.2 Oxidizing Power

The oxidizing strength of group 17 elements decreases down the group.

As the number of electronic shells increases, the radius of valence orbitals increases, therefore decreasing the attraction experienced by valence electrons. Atoms are hence less able to attract electrons to form anions, decreasing their ability to be reduced and hence decreasing their oxidizing strength.

F and Cl have positive  $E^\ominus$ , indicating that they are able to oxidize water in aqueous solution to form HF and HCl. Br and I on the other hand have negative  $E^\ominus$  and thus

will not oxidize water in standard conditions.

A more oxidizing halogen can displace a less oxidizing halogen from a compound. A halogen further up in the group is able to oxidize a halogen lower in the group.

### Reactions with Thiosulfate

$\text{Cl}_2$  and  $\text{Br}_2$  is able to oxidize  $\text{S}_2\text{O}_3^{2-}$  to  $\text{SO}_4$ , but  $\text{I}_2$  can only oxidize  $\text{S}_2\text{O}_3^{2-}$  to  $\text{S}_4\text{O}_6^{2-}$ .

### 21.2.3 Hydrogen Halides

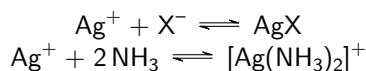
The thermal stability of hydrogen halides decreases down the group.

Down the group, the larger number of electron shells increases the radius of valence electrons, therefore resulting in less effective overlap of covalent bonds. Additionally, there is a decrease in electronegativity difference down the group, reducing bond polarity and hence bond strength. As a result the H–X bond strength decreases down the group, decreasing the amount of thermal energy needed to break covalent bonds and thus the thermal stability decreases down the group.

### 21.2.4 Silver Halides and $\text{NH}_3$

Halides form precipitates when added to solutions containing  $\text{Ag}^+$ .

In order to differentiate between different silver halides, the concentration of  $\text{OH}^-$  is altered in order to bring the ionic product of the various silver halides below their  $K_{\text{sp}}$ .



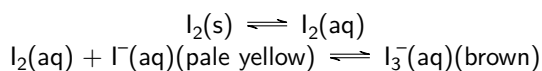
After a silver halide precipitate is formed,  $\text{NH}_3(\text{aq})$  is added to solution which will form  $[\text{Ag}(\text{NH}_3)_2]^+$  complex. As the formation of  $[\text{Ag}(\text{NH}_3)_2]^+$  has a very large equilibrium constant, the concentration of  $\text{Ag}^+$  will drop sharply, which then shifts the first equilibrium far to the left and possibly dissolving more  $\text{AgX}$ .

As  $K_{\text{sp}}$  of silver halides decreases from Cl to I,  $\text{AgCl}$  will be soluble when  $\text{NH}_3(\text{aq})$  is added while  $\text{AgBr}$  will be soluble once  $\text{NH}_3(\text{conc})$  is added.

Exposing silver halides to sunlight also turns white  $\text{AgCl}$  gray and turns cream  $\text{AgBr}$  yellow.

### 21.2.5 Solubility of $\text{I}_2$

$\text{I}_2$  is sparingly soluble in water, but very soluble once a slight amount of KI is present.



Once a small amount of KI is added, the second equilibrium is established which lies far to the right, allowing for the formation of the triiodide  $\text{I}_3^-$  complex. This decreases

the concentration of  $\text{I}_2(\text{aq})$ , where then the first equilibrium now lies far to the right as well, allowing for more solution of solid  $\text{I}_2$ .

## 22 Transition Metals

### 22.1 Period 3 and the 3d Orbital

The 3d block contains 10 elements ranging from Sc to Zn, characterized by their trend to add electrons to a inner d-shell orbitals rather than to an outermost electron shell orbital.

#### 22.1.1 d Orbital Shapes

Refer to 'Orbitals' in Atomic Structure.

#### 22.1.2 Electronic Configuration of d-block elements

Refer to 'Electronic Configuration' in Atomic Structure.

Key points to note are that Cr and Cu have a  $4s^1$  configuration.

#### 22.1.3 The Transition Elements

##### Definition 22.1: Transition Element

A Transition Element is a d-block element which can form one or more stable ions with a partially filled d orbital.

Zn is not a transition element as  $\text{Zn}_2^+$  has a fully filled 3d orbital. Cu may seem as if it is not a transition element as it readily forms  $\text{Cu}^+$  with a fully filled 3d orbital, but in fact it forms a stable  $\text{Cu}_2^+$  with a  $[\text{Ar}] 3d^9$  configuration and is hence a transition element.

### 22.2 Physical Properties of Transition Metals

Varying physical properties across the 3d block can be derived from numerous changing characteristics:

#### Number of electronically accessible electrons :

Due to the similar energy levels of the 3d and 4s electrons, both sets of electrons are available for donation and disassociation. Across the block, there is an increase in number of 3d electrons.

#### Number of Protons :

Number of protons increases across the block, increasing nuclear charge but also increasing the mass per atom of metal.

#### Effective Nuclear Charge :

Electrons are added to the penultimate electron shell which DOES impact the amount of shielding experienced by the 4s orbital.

Across the block, as nuclear charge increases and

shielding effect increases, there is an overall small increase in effective nuclear charge but it is effectively constant past Group 5 elements.

### 22.2.1 Melting and Boiling Points

Across the block, as the number of electronically accessible electrons increases, strength of metallic bonding increases, therefore requiring more thermal energy to overcome these metallic bonds and increasing both melting and boiling points across the period.

### 22.2.2 Electrical Conductivity

Across the block, as the number of electronically accessible electrons increases, the number of mobile charge carriers also increases, therefore reducing the resistance of a metal.

### 22.2.3 Atomic Radius

Atomic Radius decreases across the period as effective nuclear charge increases, but is approximately constant past Group 5.

### 22.2.4 Ionic Radius

Ionic Radius of the  $2+$  ions decreases across the 3d block. As now all 4s orbitals are vacant, ionic radius is provided by the 3d orbitals. Shielding effect only slightly increases due to 3d orbitals shielding each other but nuclear charge still increases, hence effective nuclear charge increases consistently and attraction of valence electrons increases.

### 22.2.5 Density

Density is determined by the atomic radius of metal atoms and their relative masses. As the atomic radius of 3d block elements is constant but their mass numbers still increase across the block, density increases across the block.

### 22.2.6 Ionization Energy

As effective nuclear charge slightly increases across the block, first ionization energy also gradually increases.

Subsequent ionization energies of 3d block elements will be abnormally low compared to their left neighbors if they:

- Involve the ionization of a  $3d^6$  to  $3d^5$  configuration; OR
- Involve the ionization of a  $4s^1$  electron while neighbors are already removing electrons from the 3d shell (Mn and Zn 1<sup>st</sup> I.E.s).

## 22.3 Variable Oxidation States

Due to the similarity of energy levels of electrons in the 3d and 4s subshells, electrons in both sets of orbitals are available for bond formation and electron donation, allowing them to display multiple oxidation states.

The maximum oxidation state of the transition metals is equal to the number of unpaired d-electrons plus the two 4s electrons. Mn is able to form the highest maximum oxidation state of +7.

Compounds with TM elements in low oxidation states are typically basic (e.g. MnO) while compounds with TM elements in high oxidation states are acidic (e.g.  $Mn_2O_6$ ).

### 22.3.1 Redox Potentials of TM Cations

Many of the TM elements exist in common oxidation states of +2 or +3. The relative stabilities of their +2 and +3 oxidation states can be quantified by examining their reduction potentials, where the more positive the reduction potential from +3 to +2 the more stable their +2 oxidation state.

Across the d-block, the reduction potential from +3 to +2 cations becomes more positive over the group, except for Fe which has an abnormally low reduction potential due to the transition from a  $3d^5$  to  $3d^6$  configuration being less stable due to electron repulsion within an orbital.

## 22.4 Transition Metal Catalysis

Transition metals are able to act as catalysts to speed up many reactions.

Due to the presence of partially-filled 3d subshells, transition metals are able to exchange electrons with other molecules to form weak bonds, whether through donating 3d electrons or by accepting electrons into low-lying orbitals. These weak bonds facilitate adsorption of molecules to the surface of metals and allow for heterogeneous catalysis to occur.

Common use-cases of heterogeneous catalysis include the use of powdered Ni during reduction of alkenes and Fe/ $Fe_2O_3$  in the Haber Process.

Transition metals' ability to form compounds with variable oxidation states, and the ease of reacting between these compounds mean they easily facilitate the formation and removal of intermediate compounds within a reaction as homogeneous catalysts, most commonly in reaction schemes involving redox steps.

Common use-cases of homogeneous catalysis include the use of  $Fe_3^+$  when encouraging the reaction of  $S_2O_8^{2-} + I^- \rightarrow 2SO_4^{2-} + I_2$ .  $Fe_3^+$  is an effective catalyst in this scenario as the uncatalyzed reaction has a high activation energy from the collision between two negatively charged species, while the catalyzed reaction involves two steps between anions and  $Fe_2^+/Fe_3^+$  cations and is hence of a much lower activation energy.



## 22.5 Transition Metal Complexes

### Definition 22.2: Complex

A Complex is a chemical species which comprises of a central metal atom or ion, bonded to one or more surrounding atoms or molecules with dative covalent bonds.

### Definition 22.3: Complex Ion

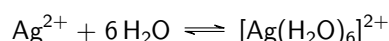
A Complex Ion is a Complex with a non-zero charge.

### Definition 22.4: Ligand

A Ligand is a species of molecule or ion which has at least one lone pair of electrons which can be donated into a low-lying vacant orbital of a central metal atom or ion to form a dative covalent bond, thus forming a complex.

The number of bonds in a complex ion typically exceeds the current oxidation state of the actual metal atom.

### 22.5.1 Complex Formation



Transition Metals and their cations commonly form complexes due to the presence of low-lying vacant orbitals which can accept donated electrons from ligands, as well as their generally large charge-to-mass ratio which can then more strongly attract electron pairs from free ligands.

S-block metals typically do not form complexes as they lack the electronically accessible low-lying vacant orbitals to accept bonds from ligands, and also generally have a smaller charge-to-mass ratio which is unable to hold ligands in place.

### 22.5.2 Ligands and Complex Geometry

Ligands are often classified according to how many dative bonds they can form with metal atoms. Most ligands are monodentate ( $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{NH}_3$ ,  $\text{CN}^-$ ), some are bidentate ( $\text{C}_2\text{O}_4^{2-}$ ), some tetradentate (haem) and some hexadentate ( $\text{edta}^{4-}$ ).

### Definition 22.5: Coordination Number

The Coordination Number of a complex is the number of dative bonds formed between the central metal atom or ion and its ligands.

Dative bonds of complexes (not necessarily the ligands themselves) arrange themselves around central metal ions similar to how electrons rearrange themselves into specific geometries as suggested by VESPR. Complexes with two dative bonds may have a linear geometry, four bonds may have tetrahedral or square planar geometry and six bonds may have an octahedral geometry.

## 22.5.3 Complex Salts

### Definition 22.6: Complex Salts

Complex Salts are salts with one or more constituent complex ions.

Written formulas of complex salts may be ambiguous in describing how many species are ligands and how many others are anions, such as  $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$  which is a neutral complex while  $\text{Cr}(\text{NH}_3)_5\text{Cl}_3$  which is a complex salt made of  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$  and  $2 \text{Cl}^-$ .

The species which is a ligand can be differentiated by species which is an ion as the ion is completely disassociated in water and can react elsewhere while the ligand is typically unreactive - in the latter case 1 mol of salt will form 2 mol of  $\text{AgCl}$  ppt, with the last  $\text{Cl}^-$  being kept in the complex ion.

### 22.5.4 Common Complex Ions

**Bolded** ions are in the QA syllabus.

Complex	Color	Properties
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	Light Blue	Aqua complex
<b><math>[\text{Cu}(\text{NH}_3)_4]^{2+}</math></b>	Deep Blue	Soluble in $\text{NH}_3$
$[\text{Cu}(\text{Cl})_4]^{2-}$	Yellow	May appear green due to mixing with aqua complex
$[\text{Cu}(\text{Cl})_2]^-$	-	Complex of Copper (I)
$[\text{Ag}(\text{H}_2\text{O})_6]^+$	Colorless	Aqua complex
<b><math>[\text{Ag}(\text{NH}_3)]^{4+}</math></b>	Colorless	Complex in $\text{NH}_3$ , used when testing halides
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	Green	Acidic from 3+ cation
<b><math>[\text{Cr}(\text{OH})_6]^{3-}</math></b>	Green	Soluble in $\text{NaOH}$
<b><math>[\text{Cr}(\text{NH}_3)_6]^{3+}</math></b>	Green	Soluble in $\text{NH}_3$
<b><math>[\text{Al}(\text{OH})_4]^-</math></b>	Colorless	Not a TM, but complex
<b><math>[\text{Zn}(\text{OH})_4]^{2-}</math></b>	Colorless	Soluble in $\text{NaOH}$
<b><math>[\text{Zn}(\text{NH}_3)_4]^{2+}</math></b>	Colorless	Soluble in $\text{NH}_3$

## 22.6 Complex Chemistry

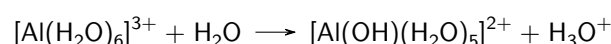
### 22.6.1 Aqua Complexes

### Definition 22.7: Aqua Complex

An Aqua Complex is a complex species with only  $\text{H}_2\text{O}$  as a ligand.

Most complexes with water have a coordination number of 6, except for  $\text{Pt}_2^+$  and  $\text{Pd}_2^+$ .

Transition metals form aqua complexes in water, as compared to s-block metals which form hydration spheres from ion-dipole interactions.

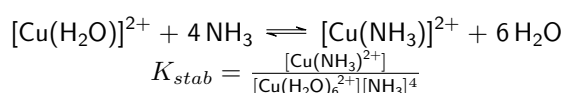


Aqua complexes of 3+ metal cations have sufficiently large charge-to-mass ratios which give them very high polarizing

power. This polarization leads to distortion of the electron clouds of H<sub>2</sub>O ligands, weakening the O–H bond and allowing other free H<sub>2</sub>O molecules to take in protons from the ligands, forming H<sub>3</sub>O<sup>+</sup>. Solutions of  $\frac{1}{3}$  ions are hence slightly acidic.

## 22.6.2 Ligand Exchange

Ligand exchange reactions occur when one complex is formed from another, involving the removal of one species of ligand and the addition of the other. When a solution containing one complex has another ligand added to solution, further equilibria are established involving ligand exchange.



### Definition 22.8: Stability Constant $K_{stab}$

The Stability Constant  $K_{stab}$  of the formation of a complex salt is the equilibrium constant for the formation of a new complex from an aqua complex. The greater its value, the more stable a complex is with respect to its aqua complex of the same metal ion.

### Equation 22.1: Stability Constant $K_{stab}$

The Stability Constant  $K_{stab}$  of the formation of a complex salt with chemical formula  $[\text{M}(\text{ligand})_n]^{x+}$ , in a solution at equilibrium with concentrations  $[\text{M}(\text{ligand})_n^{x+}]$ ,  $[\text{M}(\text{H}_2\text{O})_6^{x+}]$  and  $[\text{ligand}]$  is given by the equation

$$K_{stab} = \frac{[\text{M}(\text{ligand})^{x+}]}{[\text{M}(\text{H}_2\text{O})_6^{x+}][\text{ligand}]^n}$$

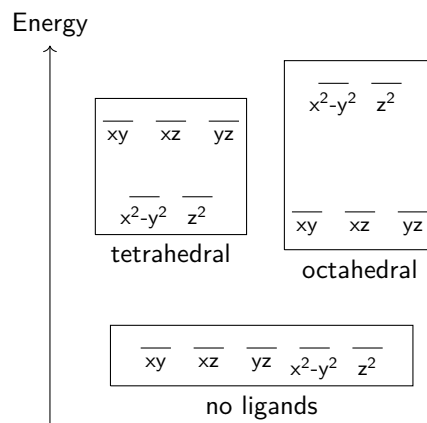
As with other equilibrium constants, the value of  $K_{stab}$  is constant at any given temperature and do not vary with concentration.

If a solution contains ligands to form multiple possible complexes, the various  $K_{stab}$  values can be used to identify which species, generally the complex with the highest  $K_{stab}$ , will be the main complex present.

## 22.6.3 Color of Transition Metals

As ligands approach the central metal ion, the dative bonds formed become regions of higher electron density which then repel inner electron orbitals of the metal ion. Due to the geometry of the various 3d orbitals, electron orbitals are repelled to different extents and now have an energy gap between partially filled orbitals. Small energy gaps such as these correspond to the energies of visible light particles, allowing these central ions to now absorb energy corresponding to specific wavelengths to promote electrons from a filled to empty but higher-energy orbital, leading to the occurrence of color.

Complexes with octahedral geometry have its ligands approach along the x, y and z axes, thus repelling orbitals which are along the axis more, leading to the higher energy levels of the  $x^2-y^2$  and  $z^2$  orbitals. Complexes with tetrahedral geometry have its ligands approach between the x, y and z axes and thus leading to higher energy levels of the xy, xz and yz orbitals.



When complexes absorb color of one specific wavelength, the color that is observed later on is the complement of said absorbed color. Complementary color pairs include red-green, orange-blue and yellow-purple.

Various complexes of the same central metal ion but different ligands may exhibit different colors. This is because various ligands are able to split the d orbitals to different extents. In terms of increasing splitting effect (and hence decreasing wavelength of absorbed light), the spectrochemical series orders the species of:

Halide Anions (Starting with I), OH<sup>−</sup>, Ethanedioate, H<sub>2</sub>O, edta, NH<sub>3</sub>, NO<sub>2</sub><sup>−</sup>, CN<sup>−</sup>, CO

## 22.6.4 Haemoglobin

Haemoglobin is a molecule in blood which is used in the transport of O<sub>2</sub> around the body. Haemoglobin is a complex, with a central Fe<sup>2+</sup> ion, one tetradentate haem ligand which surrounds the xy plane, one monodentate globin protein and finally one extra empty site for O<sub>2</sub> ligands to bind to. The binding of O<sub>2</sub> to haemoglobin allows for efficient transport of O<sub>2</sub> throughout the human body via its circulatory system.

Species such as CN<sup>−</sup> and CO are much stronger ligands than O<sub>2</sub>, and will bind to haemoglobin molecules much more strongly than O<sub>2</sub>. This renders the haemoglobin molecule unable to bind to and transport O<sub>2</sub> throughout the body, leading to what we know as carbon monoxide poisoning and an additional side effect of cyanide poisoning.

Other animals such as horseshoe crabs have blue-colored blood. This is due to the presence of haemocyanin, a haemoglobin-like molecule but with Cu<sup>2+</sup> instead of Fe<sup>2+</sup> as its central metal ion.