

Chem Notes

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(ver 0.1.0)

This compilation of notes are meant to be used 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 $\overset{\text{Atomic Number}}{\text{Nucleon Number}}\text{X}$

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 6.0×10^{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 number of atoms of different elements 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 bar 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 mol dm^{-3} . The mass concentration has units 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 H^+ in a solution while an Arrhenius Base increases the concentration of OH^- in a solution. Both react to form H_2O .

Definition 1.24: Brønsted Acids and Bases

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

Definition 1.25: 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 1.26: Basicity

The Basicity of an acid is how many H^+ ions it ionizes per molecule.

1.6.2 Titration Curves and Indicators

Definition 1.27: 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 a 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 Na_2CO_3 and 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 1.28: Redox

Redox reactions occur when reduction and oxidation occurs simultaneously.

Definition 1.29: Disproportionation

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

	Oxidation	Reduction
O ₂	+	-
H	-	+
e ⁻	-	+
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 OF₂.
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.

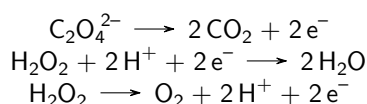
1.7.2 Balancing Redox Equations

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

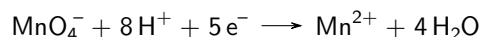
1. Write and balance half equations of products and reactants.
2. Balance O with H₂O and H with H⁺ or OH⁻ depending on which is present.
3. Balance charges with e⁻.
4. Combine both reactions to balance e⁻ and remove common reactants and products.

1.7.3 Redox Titration

Common half-equations include:



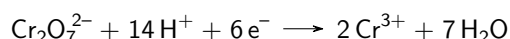
Manganate(VII) titrations involve the half-reaction



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 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.

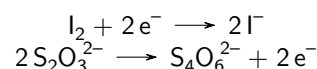
Fe³⁺ solutions in MnO_4^- titrations are yellow before titration, while H₂O₂ solutions are colorless.

Dichromate(VI) titrations involve the half-reaction



in acidic medium. Though orange $\text{Cr}_2\text{O}_7^{2-}$ ions turn into green Cr^{3+} ions, green appears significantly before an end-point 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 I₂ can be used to assess the amount of I₂ in said solution. Otherwise called Iodometric titrations, they usually involve the creation of I₂ by adding some substance to KI and then titrating with standard S₂O₃²⁻ 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⁻.

1.8 Miscellaneous

Definition 1.30: 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 10×10^{-14} m) which contains its protons and neutrons and the electron cloud (diameter 10×10^{-10} m) surrounding the nucleus.

2.1.1 Deflection in an Electric Field

When a beam of particles is 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^{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 a 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.

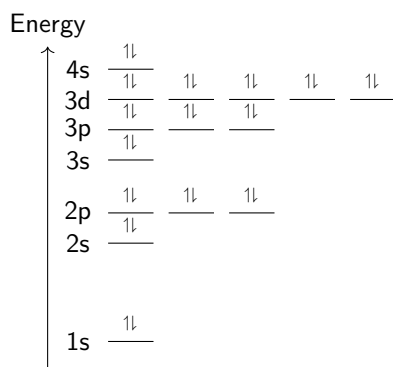
Electronic Configuration for Xenon: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 4d^{10} 5s^2 5d^{10}$

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 σ bonds involve the overlap of two electron orbitals head-on. Pi π bonds involve the overlap of two electron orbitals side-to-side. Single covalent bonds have one σ bond, while double or triple bonds have one σ and one or two π bonds. σ bonds are stronger than π 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 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 AlF_3 is ionic but AlCl_3 since Al has a high charge density and Cl has a larger electron cloud size than F. Therefore, AlF_3 and Al_2O_3 are ionic but 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 all 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 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 F, O and N with lone pairs, 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 NH₃.

H₂O, 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 COOH form dimers in gaseous state due to the presence of 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.

3.4.4 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 π 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 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.

3.8 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 an 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.

3.9 Geometry of Molecules

3.9.1 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 an 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 an 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 an energetically feasible configuration.

3.9.2 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° , 3 bond pairs at about 107° and 2 bond pairs at about 105° (Water at 104.5°). 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.

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.

3.10 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.

3.11 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.

3.11.1 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.

3.11.2 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.

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 N m^{-2} or $\text{kg m}^{-1} \text{s}^{-2}$
- Volume V measured in 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.

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_{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 Δf is obtained using its beginning f_{initial} and final f_{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 ΔH 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. $\Delta > 0$

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

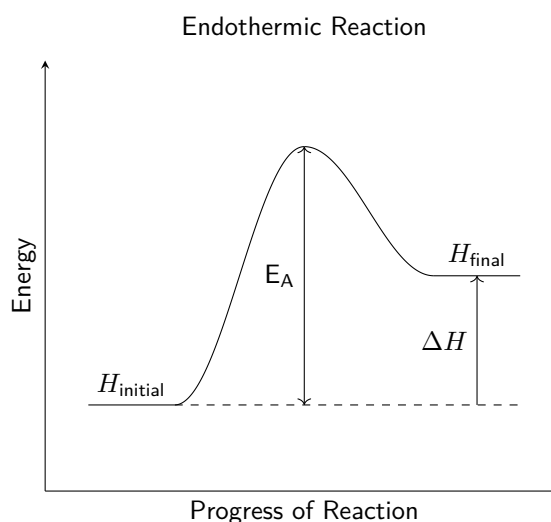
Activation Energy E_A is the amount of energy required for reactant particles to possess before they can collide successfully to form products.

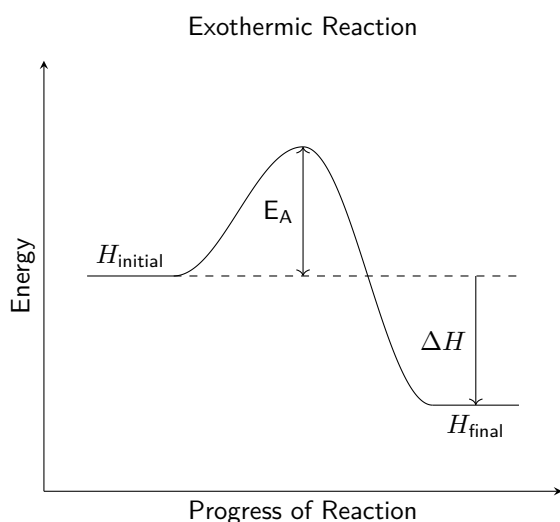
As particles form bonds, they become more stable and release energy, whereas when breaking bonds particles are excited and absorb energy. Hence, bond formation is typically exothermic and bond breaking is endothermic.

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.





Note that the arrows for E_A have two arrowheads while ΔH only has one.

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 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_{graphite} rather than C_{diamond} , H_2O at liquid rather than gas).

Note for each reaction that ΔH 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 ΔH_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 ΔH_f^\ominus is the energy released when one mole of substance is formed from its elements under standard conditions.

Standard enthalpy change of combustion ΔH_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 H_2O 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 H^+ and 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 H_2O , 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.

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 ΔH and the data from the information booklet, ΔH 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 ΔH 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 $\frac{3}{2} \text{Cl}_2 \rightarrow 3 \text{Cl}$, ΔH 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 ΔH_f or ΔH_c of both products and reactants, ΔH_r of a reaction can be calculated with:

Equation 5.2: ΔH_r given ΔH_f of products and reactants

$$\Delta H_r = -\Delta H_f(\text{reactants}) + \Delta H_f(\text{products})$$

Equation 5.3: ΔH_r given ΔH_c of products and reactants

$$\Delta H_r = +\Delta H_f(\text{reactants}) - \Delta H_f(\text{products})$$

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 " kJ mol^{-1} " unit.
- Attempt to maintain proportion between changes in enthalpy: larger ΔH should have a larger vertical gap than smaller ΔH

- One arrow corresponds to one kind of reaction with one ΔH 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:

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

Note that the first E_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:

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

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 CaSO₄, 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 ΔG^\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 ΔH^\ominus , entropy change ΔS^\ominus and current temperature T of a reaction, the Standard Gibbs Free Energy Change ΔG^\ominus of a reaction is given as:

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

Note that in most calculations ΔH is in kJ while ΔS is in J, do remember to convert units.

Note that in most cases where reactions take place in standard conditions, all ΔG , ΔH and ΔS 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. ΔH^\ominus and ΔS^\ominus are assumed to not vary with different temperature. When in doubt, follow the notation of the question.

5.8.1 Thermodynamic Feasibility

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.

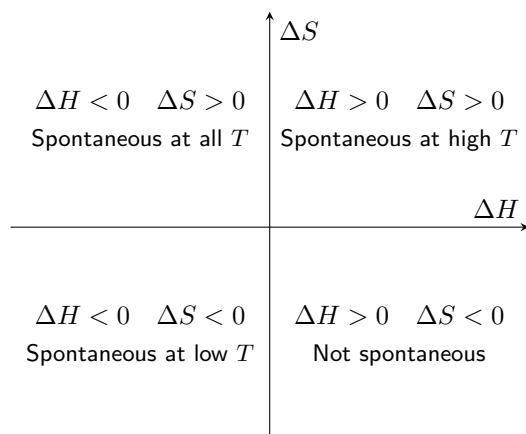
Definition 5.14: Endergonic

An Endergonic reaction has a positive ΔG value and is not thermodynamically spontaneous.

Definition 5.15: Exergonic

An Exergonic reaction has a negative ΔG value and is thermodynamically spontaneous.

Types of Thermodynamic Feasibility



To explain the thermodynamic feasibility of a reaction:

1. State and explain sign of ΔH
2. State and explain sign of ΔS
3. Comment on sign on ΔG :

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

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

5.9 Experimental Energetics

Experimental methods to find ΔH 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 ΔH 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 ρ_{H_2O} , specific heat capacity of water c_{water} , measured temperature change ΔT which then gives the amount of heat transfer q , and finally amount of reaction n , the enthalpy of a reaction ΔH 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 ΔH .

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 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 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 H_2O is involved have H_2O present in a concentration of about 65 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 regenerated it is in fact non-zero order.

Pseudo-order reactions can have their rate equations simplified. For a reaction pseudo- m^{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 $x\text{A} + y\text{B} \rightarrow \text{C}$, its rate equation is $\text{rate} = k[A]^x[B]^y$.

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 where the catalyst is regenerated. The reaction mechanism involving a catalyst would have lesser activation energy due to the presence of the intermediate step.

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 $t = 0$.