Chem Notes

Chang Si Yuan

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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 $^{\text{Atomic Number}}_{\text{Nucleon Number}}\text{X}$

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

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

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_rs 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 $V_m = 22.7\,dm^3\,mol^{-1}$.
Room Temperature and Pressure (r.t.p.) at 293 K and 101 325 Pa or 1 bar gives $V_m = 24\,dm^3\,mol^{-1}$.

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 pK_a of an acid HA is defined by $\frac{[H^+][A^-]}{[HA]}$ 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 Doule 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 $NaHCO_3$, phenophthalein 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 OF_2.
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 H_2O 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:

$$C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^-$$
$$H_2O_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$$
$$H_2O_2 \longrightarrow O_2 + 2\,H^+ + 2\,e^-$$

Manganate(VII) titrations involve the half-reaction

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$$

in acidic medium and $MnO_4^- + 4\,H^+ + 3\,e^- \longrightarrow MnO_2 + 2\,H_2O$ 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.

Fe^{3+} solutions in MnO_4^- titrations are yellow before titration, while H_2O_2 solutions are colorless.

Dichromate(VI) titrations involve the half-reaction

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

in acidic medium. Though orange $Cr_2O_7^{2-}$ ions turn into green Cr^{3+} ions, green appears significantly before an endpoint is reached and hence requires indicators like barium / sodium dipheylamine 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:

$$I_2 + 2\,e^- \longrightarrow 2\,I^-$$
$$2\,S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2\,e^-$$

And a titration of thiosulphate ions into a solution containing I_2 can be used to assess the amount of I_2 in said solution. Otherwise called Iodometric titrations, they usually involve the creation of I_2 by adding some substance to KI and then titrating with standard $S_2O_3^{2-}$ 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^-.f

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} msurrounding 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 $d_{x^2\text{-}y^2}$ 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

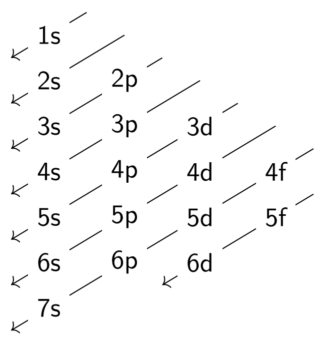
The Electronic Configuration of a atom or ion is a description of how its electrons are distributed among its shells, subshells and orbitals.

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 [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 [Ar] $3d^{10}$ $4s^1$

2.1.4 Written Electronic Configuration

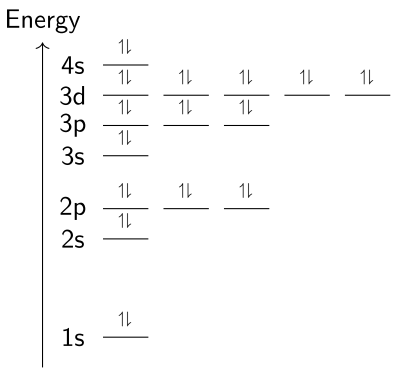
Electronic configuration is written as a series of subshells and the amount of electrons present in the orbital.

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: [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 NH_3.

H_2O, 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 $r_+ + r_-$:

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

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 rigit 3-dimensional structure, quartz is hard and insoluble as well has 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 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.

3.9 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 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.

3.9.2 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 vertice 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 $\mathrm{N\,m^{-2}}$ or $\mathrm{kg\,m^{-1}\,s^{-2}}$
- Volume V measured in $\mathrm{m^3}$
- 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 $R = 8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$

$$pV = NRT$$

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 $p_{\text{total}} \times \frac{n_A}{n_total}$.

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 Standard Enthalpy Definitions

5.2 Energy Cycles

5.3 Energy Level Diagrams

5.4 Energetic Feasibility

5.5 Solubility

5.6 Entropy

5.6.1 Entropy Changes

5.7 Gibbs Free Energy

5.7.1 Thermodynamic Feasibility

6 Kinetics

6.1 Order of Reaction

6.2 Pseudo-Order Reactions

6.3 Kinetic Feasibility