Chem Notes

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

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_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 273K and 100000Pa or 1bar gives $V_m = 22.7$ dm^3 mol^{-1}.
Room Temperature and Pressure (r.t.p.) at 293K and 101325Pa or 1bar 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:

$$C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^-$$
$$H_2O_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$$
$$H_2O_2 \longrightarrow O_2 + 2\,H^+ + 2\,e^-$$
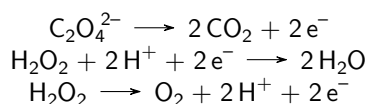
Manganate(VII) titrations involve the half-reaction

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$$
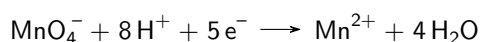
in acidic medium and $MnO_4^- + 4\,H^+ + 3\,e^- \longrightarrow MnO_2 + 2\,H_2O$ in basic medium. Due to the purple color of MnO_4^-, the reaction is self-indicating and the end point is reached whenever there is an appearance or disappearance of purple tint in the solution.

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

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$
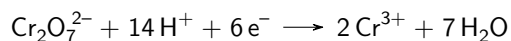
in acidic medium. Though orange $Cr_2O_7^{2-}$ ions turn into green Cr^{3+} ions, green appears significantly before an endpoint is reached and hence requires indicators like barium / sodium dipheylamine p-sulphonate or diphenylamine (green to blue-violet) or N-phenylanthranilic acid (green to red-violet).

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

$$I_2 + 2\,e^- \longrightarrow 2\,I^-$$
$$2\,S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2\,e^-$$
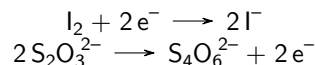
And a titration of thiosulphate ions into a solution containing I_2 can be used to assess the amount of I_2 in said solution. Otherwise called Iodometric titrations, they usually involve the creation of I_2 by adding some substance to KI and then titrating with standard $S_2O_3^{2-}$ solution until the solution turns near colorless, at which starch solution is added to create starch-iodine complexes which are blueblack 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^{-14}m) which contains its protons and neutrons and the electron cloud (diameter 10^{-10}m) surrounding the nucleus.

2.1.1 Deflection in an Electric Field

When a beam of particles are passed between two charged electric plates, charged particles experience an electric force which deflects them from the original direction of motion. Negatively charged particles are attracted to positive plates and positively charged particles are attracted to negatively charged plates. The magnitude of deflection or angle of deflection is observed to be proportional to the $\frac{charge}{mass}$ 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 nth shell will hence have n subshells and contain n^2 orbitals and $2n^2$ electrons.

2.1.3 Electronic Configuration
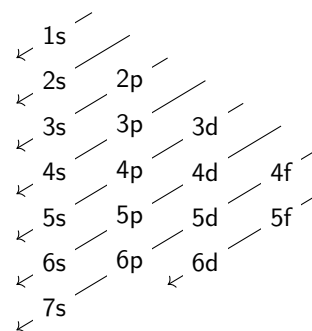
Definition 2.5: Electronic Configuration

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.

$$
\begin{array}{llll}
1s & & & \\
2s & 2p & & \\
3s & 3p & 3d & \\
4s & 4p & 4d & 4f \\
5s & 5p & 5d & 5f \\
6s & 6p & 6d & \\
7s & & &
\end{array}
$$

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.
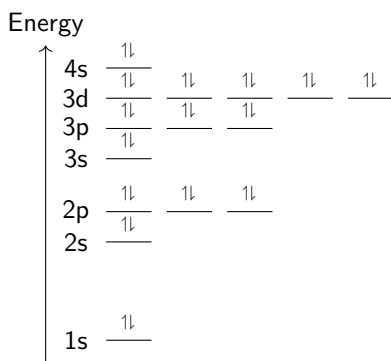
2.1.6 Electronic Configuration of Ions

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 Geometry of Molecules

3.1.1 Dot and Cross

3.1.2 VESPR

3.2 Covalent Bonds

3.2.1 Factors Affecting Strength of Covalent Bonds

3.3 Ionic Bonds

3.3.1 Factors Affecting Strength of Covalent Bond

3.4 Solubility

4 Gases

4.1 Ideal Gas Law

4.2 Deviation from the Ideal Gas Law

4.3 Partial Pressure

4.4 Graphing

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