

9647 H2 Chemistry

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What you will find here is definitions and short answers that will be tested. That means you should find them familiar, especially those who are studying in the same junior college with me. I have done something similar for physics.

You do need to memorise the definitions all around. They are points that you are expected to secure.

However, you do need to understand the concepts to apply them. Do note that you have used the essential key words and phrases in your answer.

You also need to know how to apply the skills that you have learnt. It is common to find equations to balance in chemistry, including redox ones. Calculations can sometimes be tedious, but they are the easier points to score. Structural elucidation can be a challenge. There is also a planning question. I will need to leave the reinforcement of these skills in the practices that you should have been doing. You are expected to finish up the entire TYS.

You will also need to fulfil the basic requirement of the question: answer the question. Describing a chemical reaction will need naming of the reactant, type of reaction and the product. Change will require description of what is before and after.

You need to be precise in the terms that you use. Enthalpy, entropy, cell potentials need to be signed, and to describe a difference, use: "more/less positive/negative". Also, do note that modifiers ("MORE electronegative") are important at times. These are just some of them.

You might see that there is a lack of diagrams. I might add them some time later, but since there is a plenty of space now, you can use this opportunity to scribble on the margins.

You can use this as a framework to create your own notes. The process of making this has allowed me to expose my learning gaps and bridge them accordingly.

If you happen to use this as your revision, do keep in mind that I am also a student. There can also be mistakes.

There is no better way to appreciate my work other than pointing out these problems. It will be a feedback for me, and also allow me to correct it for users like you. If you found this from owlcove, the comments section is just below.

I am just doing what I hope others could have done, and this is what I came up with. If you do feel the same, you can also make the learning process easier for us and the future cohorts.

Enjoy!

Atomic Structure

Isotopes are atoms of an element that have the **same number of protons** but **different number of neutrons**.

They have the same chemical properties but similar physical properties.

(Same number of) Isotopic (proton) Isotonic (nucleon) Isoelectronic (electrons)

Nuclide refers to any species with a specified number of protons and neutrons.

Atomic / Proton number is the number of protons in the nucleus of an atom.

Mass / Nucleon number is the total number of protons and neutrons in the nucleus of an atom.

Angle of deflection $\theta \propto \frac{a}{m}$

The greater the **charge** of the particle, the more the **attractive force** exerted on it, the **greater the deviation** from original direction of motion.

The greater the **mass** of the particle, the larger the **kinetic energy** of the particle, the **larger the force** must be exerted for it to deflect, the **lesser the deviation**.

Electrically neutral particles, like the neutron, are undeflected.

Electronic configuration refers to the distribution of electrons amount the various orbitals in the atom or ion.

Electrons are not fixed in place; they are spread out in the nucleus in electron clouds, forming orbitals.

s-orbital: spherically symmetrical about the nucleus

p-orbital: dumbbell shaped, mutually at **right angles** with each other

Energy level (state) of an orbital is the energy of the electron(s) occupying the orbital.

Ground state refers to **lowest possible energy level** available to the atoms or ions, where orbitals of lowest energy level are **filled with electrons first**.

The orbitals of the same type in the same shell are degenerate, i.e., they have the same energy level.

Quantum numbers of an electron in an atom

Principal quantum number	(n)	principal quantum shell
Orbital quantum number	(l)	type of subshell
Magnetic Quantum number	(m _l)	orbital of the subshell
Spin quantum number	(m _s)	up-spin / down-spin

Commented [HK1]: Use group 3 elements as case study

Commented [HK2]: Tbc

Meanwhile what can occupy this space?

The Aufbau Principle

Electrons are added to orbitals in **order of increasing orbital energy**.

As the nuclear charge increases due to the increase in the number of protons, the energies of all orbitals decrease.

However, because of their **proximity** to the nucleus, the energies of **s** orbitals **decrease more rapidly than other types** of orbitals.

The **energy** of the 4s orbital becomes **lower** than that of the 3d orbitals, thus the **4s orbital is filled before the 3d orbital**.

(However electronic configuration is **written** numerical order, despite that energy in 4s orbital is lower than 3d orbital, it is written as $1s^2 2s^2 2p^6 3s^2 3p^1 4s^2$)

Electrons are **removed** in the **reverse order** that they are filled.

However, despite that the **4s** orbital are **filled first** before the **3d** orbitals, the **3d** orbitals are **removed after** the **4s** orbital.

This is because once occupied by electrons, the inner 3d subshell **screens** the 4s electrons from the nuclear charge and causes the latter to be at a **higher energy level**.

Anomalous electronic configuration for chromium and copper

Chromium : $[Ar] 3d^5 4s^1$ Copper : $[Ar] 3d^{10} 4s^1$

Electronic configuration with **half-filled** or **fully filled 3d subshells** is **unusually stable** due to the **symmetrical distribution of charge** around the nucleus.

The even spread of charges results in **similar amount of electrostatic repulsion** at **each point in space**.

Such a state has **lower energy**, thus **more stable** as compared to a state of asymmetrical distribution.

Pauli Exclusion Principle

No two electrons in any atoms may have the same set of quantum numbers.

This implies that **only two electrons** can **occupy the same orbital** but **with opposite spins**.

Hund's Rule

When filling **degenerate orbitals**, electrons **occupy the orbitals singly** with **parallel spins** before any pairing occurs, due to inter electronic repulsion.

Factors affecting ionisation energy

Nuclear charge – due to the number of **protons** in the nucleus – increased electrostatic attraction between the valence electrons and protons

Screening effect – due to the **inner quantum shells** of **electrons shielding** (partially cancelling attraction) the valence electrons from attraction by the nucleus

Commented [HK3]: Also seen in transition elements

Commented [THK4]: Need housekeeping "atomic radius"
"orbitals get more diffused"
"type of orbitals"
"effective nuclear charge"
"subshell anomalies"

Trend of first ionisation energy

(The amount of energy absorbed to remove one mole of electrons from one mole of the gaseous atoms to form one mole of singly charged gaseous cations)

Down the group, first ionisation energy **decreases**.

The **number of electron shells increases** down the group.

Valence electrons are further away from the nucleus and **experience less electrostatic attraction by the nucleus**. (Screening effect)

Hence, less energy is required to overcome the electrostatic forces in the atom and remove the electrons

Across the period, first ionisation energy generally **increases**.

Nuclear charge increases across the period. However, **screening effect is relatively unchanged**. **Effective nuclear charge increases**.

Hence, more energy is required to overcome the electrostatic forces in the atom and remove the electrons.

However, first ionisation energy **decreases** between **Group II and III**.

Beryllium : $1s^2 2s^2$ Magnesium : $1s^2 2s^2 2p^6 3s^2$

Boron : $1s^2 2s^2 2p^1$ Aluminium : $1s^2 2s^2 2p^6 3s^2 3p^1$

The electron from the **2p** (3p) orbital in Boron (Aluminium) is **further to the nucleus** than the electron from the **2s** (3s) orbital in Beryllium (Magnesium).

Hence less energy is required to remove the electron less strongly attracted to the nucleus.

Also, first ionisation energy also **decreases** between **Group V and VI**.

Nitrogen : $1s^2 2s^2 2p^3$ Phosphorous : $1s^2 2s^2 2p^6 3s^2 3p^3$

Oxygen : $1s^2 2s^2 2p^4$ Sulfur : $1s^2 2s^2 2p^6 3s^2 3p^4$

The **paired electron** in the **2p** (3p) orbital in Oxygen (Phosphorous) experience **more inter-electronic repulsion** in the **p⁴** configuration compared to the **unpaired electron** in the **2p** (3p) orbital in Nitrogen (Sulfur).

Hence less energy is required to remove the **paired p** electrons, resulting in lower first ionisation energy for Oxygen (Phosphorous).

Deductions of electronic configuration of elements

Successive I.E. generally increase because when electrons are successively removed from the atom, the remaining electrons experience **less inter-electronic repulsion**, resulting in **stronger attractive forces for the remaining electrons**.

A large increase in I.E suggests the next electron is removed from the inner quantum shell.

(A sharp increase in ionisation energy occurs when the nth electron is removed. The nth electron comes from an inner quantum shell.

Hence there are (n – 1) electrons in the outer shell)

Commented [THK5]:

Hindsight – group 3 elements – case study?

IR/AR/IE

- Primary
No. of quantum shells

- Secondary
Effective nuclear charge

Nuclear charge
Inter-electronic repulsion

Commented [HK6]: ...because?

Chemical Bonding

Structure	Giant ionic lattice	Giant metallic lattice	Giant molecular	
			Rigid	Layered
Examples	Sodium chloride, Magnesium oxide	Sodium, Aluminium, Iron	Diamond, Silicon dioxide	Graphite, Boron nitride
Type of bonding	Ionic bonding	Metallic bonding	Covalent bonding	Covalent bonding Weak van der Waals
	Strong electrostatic attraction between the positively charged ions and the negatively charged ions.	Strong electrostatic attraction between metal cations and the sea of delocalised electrons.	Strong covalent bonds between atoms.	Strong covalent bonds between atoms within layers. Weak van der Waals' in between atoms of different layers.*
Constituents	Metal cations Sea of delocalised electrons	Cations Anions	Atoms	Atoms
Melting and boiling points	Large amount of heat is required to overcome the strong electrostatic attraction between the oppositely charged ions that hold the giant ionic lattice.	Large amount of heat is required to overcome the strong electrostatic attraction between the metal ions and the surrounding sea of delocalised electrons in the giant metallic lattice.	A very large amount of energy is required to overcome the <u>extensive</u> and strong covalent bonds that hold the atoms in the giant molecular structure.	
Factors affecting strength	The smaller the ionic radius , the smaller the inter-ionic distance , the stronger the electrostatic attraction.	The smaller the ionic radius , the stronger the electrostatic attraction.	The larger the atomic size , the larger and diffused the valence orbitals, the less strong the strong electrostatic attraction between the bonding pair of electrons and the two bonding nuclei .	
	The larger the charge size , the stronger the electrostatic attraction.	The larger the charge size , the higher the density of delocalised electrons , the stronger the electrostatic attraction	For multiple bonds, there are more bonding electrons within the inter-nuclei region for multiple bonds, hence stronger attractive forces.	
Malleability and ductility	When a stress is applied, the lattice of alternating positive and negative ions held by strong electrostatic attraction may be displaced, leading to contact between like charges , causing them to repel from one another and the crystal disintegrate.	The layers of metal atoms in an orderly arrangement can slide past one another when a force is applied, without disrupting the metallic bonding.	The giant molecular structure is held by strong covalent bonds between the atoms in an extensive network, holding them tightly in fixed positions even when a force is applied.	The carbon atoms of graphite are held by strong covalent bonds within extensive layers in the giant molecular structure. Each C is sp^2 hybridised. 3 out of the 4 valence electrons are used for σ bonds. The layers are free to slide past one another, therefore the graphite is soft.

Commented [HK7]: Needs review (i.e. read more answer key)

Commented [THK8]: FYI

Much of them are not specifically stated in the syllabus, however, the lattice structures are.

describe, in simple terms, the lattice structure of a crystalline solid which is:

- (i) ionic, as in sodium chloride, MgO
- (ii) simple molecular, as in iodine
- (iii) giant molecular, as in graphite; diamond
- (iv) hydrogen-bonded, as in ice
- (v) metallic, as in copper

Commented [HK9]: FYI Giant Covalent Structure of diamond and graphite

The carbon atoms of the diamond are held by strong covalent bonds in a tetrahedral arrangement in the giant molecular structure.

A large amount of heat is required to overcome such bonds.

Each C is sp^3 hybridised. All the four valence electrons are used for σ bonds. There are no mobile electrons to conduct electricity.

The carbon atoms of the graphite are held by strong covalent bonds in a hexagonal arrangement on extensive layers in the giant molecular structure.

Each C is sp^2 hybridised. 3 out of the 4 valence electrons are used for σ bonds.

The unhybridised 2p orbitals of the C atom overlap continuously to form delocalized π electron clouds.

These π electrons can act as mobile charge carriers to conduct electricity along the plane.

Commented [THK10]: Arrangement – hexagonal- how to put it in?

Electrical conductivity	In solid state, cation and anions are held tightly in fixed positions by strong electrostatic attraction in the giant ionic lattice and are not mobile to conduct electricity. At aqueous or molten state, ions are mobile to conduct electricity.	Metal is made up of metal cations which are surrounded by the sea of delocalised electrons which are mobile to conduct electricity.	Exist as electrically neutral atoms held by strong covalent bonds in giant molecular structure. Hence there is an absence of mobile charged particles to conduct electricity.	The unhybridised 2p orbitals of the carbon atom overlap continuously to form delocalized π electron clouds which can act as mobile charge carriers to conduct electricity along the plane .
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Most ionic salts are soluble because the energy released from the formation of strong ion-dipole interactions between the ions and the polar solvent molecules is sufficient to separate the oppositely charged ions in the ionic solids.

Lattice is a three dimensional structure consisting of a **regular arrangement** of point in space, occupied by atom, ions or molecules.

Co-ordination number refers to the number of ions that surround another ion of opposite charge in the crystal lattice.

When there is large difference in the ratio of the ionic radius, it is unstable to have many larger ions surrounding a smaller ion due to strong repulsive forces.

Covalent bond is formed by **overlapping** of two valance atomic orbitals, constituting of **strong electrostatic attraction** between the **pair of electrons** and the **two bonding nuclei** to hold the two atoms together in a molecule.

Sigma (σ) bonds – formed when atomic orbitals overlap **collinearly (head-on)**

Pi (π) bonds – formed when atomic orbitals overlap **collaterally (side-on)**

Double bond – consists of a σ bond and a π bond

Triple bond – consists of a σ bond and two π bond

Dative bond – a covalent bond which is formed when the shared pair of electrons is provided only by one of the bonding atoms.

The donor atom need to have a lone pair of electrons, and are unlikely to be very electronegative.

The recipient atoms need to be **electron deficient**, to receive the donated electrons. Dative bond has the same strength as a covalent bond.

Dimerization is a reaction where two electron deficient molecules react to form a single molecule to achieve an octet of valence electrons for the central atom.

Expansion of octet

Cl atom has **low-lying, vacant 3d orbitals** to expand its octet of electrons to form double bonds with O atoms.

Non-existence of F_2O

F_2O does not exist as F atom **does not have vacant low-lying/** energetically favourable orbitals to **expand its octet**.

The other alternative would be for the F atom to provide two electrons for **dative** bonds to O atoms. However, the F atom is **too electronegative** for dative bonding.

Commented [THK11]: FYI: Electrical conductivity of graphite and h-BN TBA

Commented [THK12]: Graphite is still a poor conductor – perhaps it is not made up of uniform continuous layers, it is not an excellent conductor of electricity?

Commented [HK13]: Draw bonding of Cl_2O , ClO_2 , NO_2 , and N_2O , CO

Bottomline: Not period 3 and above, cannot expand octet configuration

Commented [THK14]: Do they always need an empty orbital?

Commented [HK15]: CCl_4 does not react (or hydrolyse) in water due to the absence of empty low-lying 3d orbitals to accommodate the lone pair of electrons from water molecules.

Intermolecular forces of attraction

Ion-dipole interaction is the force between a full charge of an ion and a partial charge of a polar molecule.

Type	Instantaneous dipole induced dipole	Permanent dipole – permanent dipole	Hydrogen bonding
Nature of bonding	<p>Momentary fluctuation of the electron density of all electrons in a molecule can cause a temporary polarisation or distortion of the electron cloud in the molecule forming an instantaneous dipole.</p> <p>The partial negative end δ^- of the temporary dipole in one molecule repels the electron cloud and induces an δ^+ end and an δ^- end on another nearby molecule.</p>	<p>Due to the difference in electronegativity, the bonding electrons will be drawn towards the more electronegative atom, creating a dipole moment. As the moments do not cancel out one another, the net dipole moment causes the polarity of the molecule.</p> <p>The permanent separation of charges results in a partial positive and negative charges that attract the nearby polar molecules.</p>	<p>The bonding electrons between hydrogen and any of F/O/N atoms are pulled closer towards the highly electronegative F/O/N atom, causing the hydrogen atom in the molecule to become an almost a bare proton.</p> <p>The strong partial charge on the hydrogen atom is strongly attracted to the negative charge of the lone pair of the F/O/N atom of a nearby molecule.</p>
Factors affecting strength of bond	<p><u>Size of electron cloud</u> From BF_3 to BI_3, the electron cloud size increases. The electron cloud is more easily polarised. This result in stronger instantaneous dipole-induced dipole attraction between molecules.</p> <p><u>Shape of molecule</u> Pentanol is an elongated molecule which provides a greater surface area for i.d.-i.d. attractions between molecules to operate as compared to the more compact and spherical 2-methylbutanol. Hence, boiling point of pentanol is higher.</p>	<p><u>Difference in electronegativities</u> Molecules that higher polarities (due to stronger net dipole moment) have stronger permanent dipole – permanent dipole forces of attraction which results in a higher boiling point.</p> <p>However, for molecules with considerable difference in M_r, i.d.-i.d. is more significant.</p>	<p><u>Extent of hydrogen bonding</u> The hydrogen bonding between H_2O molecules (2 bonds per molecule) is more extensive than between HF molecules or between NH_3 molecules (1 bond per molecule).</p> <p><u>Electronegativity of atom $\text{F} > \text{O} > \text{N}$ bonded to H</u> F atoms have a higher electronegativity than O and N, there is stronger attraction between the lone pair on the F atom, which the hydrogen is strongly attached to.</p>

Commented [HK16]: FYI organic chem
Liquid CO_2 is the suitable solvent for organic compounds, because CO_2 can be easily removed by evaporation and can be recycled for repeated use.
Polar ends of CO_2 can solvate the polar caffeine molecule, resulting in caffeine being soluble in CO_2 . In addition, CO_2 is not toxic.

Implications of hydrogen bonding

Ice has higher density than water – because of the empty space between **tetrahedrally** arranged water molecules that are held by hydrogen bonds.

Abnormally high melting and boiling points – HF, H_2O and NH_3 have higher melting and boiling points than expected in their corresponding groups.

Anomalous relative molecular mass M_r – ethanoic acid CH_3COOH has an apparent M_r of 120 instead of the expected 60.

Some substances are miscible in water – by forming hydrogen bonds with water molecules.

VSEPR (Valence Shell Electron Pair Repulsion) theory

Electron pairs (bond pairs and lone pairs) around the central atom of a molecule are **arranged as far apart as possible** to minimise their mutual repulsion.

Lone pairs of electrons are **closer to the central atoms** than bonding pairs of electrons; hence lone pair exerts a **greater repulsion** against the other electron pairs.

Therefore, **lone pair – lone pair > lone pair – bond pair > bond pair – bond pair**

“Carbon is in _____ (linear – bent – trigonal planar – tetrahedral – T-shape – trigonal/square bipyramidal – octahedral) shape with respect to atoms bonded to it.”

Commented [THK17]: Draw shapes (TBA long later)

Bond angle of atoms that has four electron pairs but different number of lone pairs: **CH₄-109.5°** **NH₃-107°** **H₂O-105°**

The extra lone pair in the molecule **compresses** the two bond pairs to a greater extent.

For simple compounds with a **lone pair**:

Modification 1 – **Electronegativity** of the terminal atom (example: 93° NF₃ and 107° NH₃)

Fluorine is more electronegative than hydrogen, drawing bonding electrons in N – F bond towards F.

Less inter-electronic repulsion between the electron pairs around the F atom, repulsion from the lone pair is comparatively more significant. Bond angle is smaller.

Modification 2 – **Electronegativity** of the central atom (example: 105° in H₂O and 92° in H₂S)

Oxygen is more electronegative than sulfur, drawing bonding electrons in O – H bond towards O.

More inter-electronic repulsion between the electron pairs around O atom, repulsion from the lone pair is comparatively less significant. Bond angle is larger.

Modification 3 – **Size** of the central atom

The size of the electron cloud increases for larger atoms, the distance between the electron pairs is now larger.

There is less difference in magnitude of repulsion for the different combinations of electron pairs, bond angle is smaller.

Commented [THK18]: Is electronegativity (as above) dependent on size – so is this double counting?

Gaseous State

Ideal gas is a **hypothetical gas** whose pressure, volume and temperature are **completely described** by the ideal gas equation:

$$pV = nRT$$

Basic Assumptions of the Kinetic Theory

Volume of gas molecules is **negligible** compared to the **volume it occupies**.

Intermolecular forces of attraction between gas molecules are **negligible**.

All molecular collisions are perfectly **elastic**. There is **no loss of kinetic energy** during collisions.

Conditions for ideality in real gases

At **low pressure**, the gas molecules are **far apart**.

The **volume of the gas molecules** therefore becomes **insignificant** compared to the **volume occupied by the gas**.

At **high temperatures**, the gas molecules have higher kinetic energy and **move faster**.

The **intermolecular forces of attraction** become **negligible**.

Gases that have **weak intermolecular forces of attraction** have greater ideality.

Such gases are **non-polar** (without the relatively stronger **p.d.-p.d.**), **monoatomic** and have **small atomic size** (hence **smaller electron cloud** for weaker **i.d.-i.d.**)

Deviations from Ideality

At **high pressure**, gas molecules are packed closer together as the volume of the container is reduced.

The volume of gas molecules is no longer negligible compared to the volume of the container.

$$V_{\text{real}} = V_{\text{ideal}} + V_{\text{molecules}} \quad pV_{\text{real}}/RT > pV_{\text{ideal}}/RT = n \text{ (positive deviation)}$$

At **low temperature**, the **average kinetic energy** of gas molecules decreases, molecules move more slowly, attractive forces between molecules is now more significant.

For large molecules (significant **i.d.-i.d.**) or polar molecules (**p.d.**), the **intermolecular forces of attraction** are more significant.

The **force** of the molecules **striking** on the **surfaces** of the container is **weaker**; hence pressure of the gas is **lower** than ideal.

$$p_{\text{real}}V/RT < p_{\text{ideal}}V/RT = n \text{ (negative deviation)}$$

The gas is **not ideal** due to the **significant p.d.-p.d. attraction** between the polar molecules.

Hence for the **same partial pressure**, there are **more moles of** (non-ideal gas) **present than calculated**.

Commented [THK19]: The point where two curves offset each other and achieve ideality? (Is this how R is derived?)

Chemical Energetics

ΔH_f^\ominus	+/-	absorbed or evolved	when molar quantities of reactants	as shown in the chemical equation			react together				
ΔH_f^\ominus	+/-			absorbed	a substance	in its standard state		is formed from its constituent elements			
ΔH_{at}^\ominus (element)	+					free gaseous atoms		is formed from its element			
ΔH_{at}^\ominus (compound)	+					a compound		in the standard state		is broken into atoms of its constituent elements in the gaseous state	
Bond Energy	+					a particular X-Y bond		in a particular compound in the gaseous state		is broken	
The amount of heat			when one mole of	electrons	is removed	from one mole of	to form one mole of	singly	charged gaseous cations.		
1 st Ionisation Energy	+	absorbed						gaseous atoms		doubly	
2 nd Ionisation Energy	+				singly charged gaseous ions						
1 st Electron Affinity	+/-	absorbed or evolved			is added			gaseous atoms		singly	charged gaseous anions.
2 nd Electron Affinity	+			singly charged gaseous ions		doubly					
ΔH_c^\ominus	-	evolved		a substance		in its standard state		is completely burned in excess oxygen.			
ΔH_{latt}^\ominus	-			the solid ionic compound				is formed from its constituent free gaseous ions.			
ΔH_{neut}^\ominus	-			water		is formed from neutralisation		between an acid and a base.			
ΔH_{hyd}^\ominus	-			free gaseous ions		is dissolved in an infinite volume of water		forming a solution at infinite dilution.			
ΔH_{sol}^\ominus	+/-	absorbed or evolved		a solute							

under the standard conditions of 298K and 1atm.

Commented [HK20]: If bond energy calculated (using data booklet) differs from actual answer, you can state 'values in data booklet are average bond energy values./ or if applicable, the compound is not in the gaseous state.

Equations

$$\Delta H_f^\ominus(\text{element in standard state}) = 0$$

$$\begin{aligned}\Delta H_r^\ominus &= \Sigma \Delta H_f^\ominus(\text{products}) - \Sigma \Delta H_f^\ominus(\text{reactants}) \\ &= \Sigma \Delta H_c^\ominus(\text{reactants}) - \Sigma \Delta H_c^\ominus(\text{products}) \\ &= \Sigma \text{B. E.}(\text{reactants}) - \Sigma \text{B. E.}(\text{products})\end{aligned}$$

$$\Delta H_c^\ominus(\text{H}_2) = \Delta H_f^\ominus(\text{H}_2\text{O}), \text{ and likewise for other elements}$$

$$\Delta H_{\text{sol}}^\ominus = -\Delta H_{\text{latt}}^\ominus + \Delta H_{\text{hyd}}^\ominus(\text{cations}) + \Delta H_{\text{hyd}}^\ominus(\text{anions})$$

$$\Delta H_{\text{latt}}^\ominus(\text{or L. E.}) \propto \left| \frac{q^+ q^-}{r^+ + r^-} \right|$$

$$Q = mc\Delta T \text{ (Mass of the solution only)}$$

Hess' Law (of Constant Heat Summation) states that ΔH of any chemical reaction is dependent only on the **initial state of the reactant** and the **final state of the product**, and is **independent of the reaction pathway** taken.

Entropy S is the measure of disorder in a system. Disorder applies to the **arrangement and energy of the particles**.

Factors affecting entropy

Temperature – **kinetic energy distributed** over a wider range – more ways to distribute the energy.

State of substance – $S^\ominus(\text{s}) < S^\ominus(\text{l}) \ll S^\ominus(\text{g})$ – more ways to rearrange particles and energy

No. moles of gas – more gas molecules moving randomly – more ways to distribute particles and energy

Mixing particles – more ways to rearrange the particles

Dissolving solids – ions breaking away from the solid lattice results in greater entropy, however gathering of water molecules orderly around ions results in lower entropy.

The net change in entropy is usually positive.

The standard Gibbs free energy change of a reaction ΔG^\ominus is the free energy for a reaction when it occurs under standard conditions.

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

(assuming ΔH and ΔS do not change with temperature, although in reality, there is a slight change)

Spontaneous reaction occurs in a **definite direction** without external interference, and **irreversible** (cannot be brought back to its original state).

Commented [HK21]: Energy diagram should help.

Commented [HK22]: Explain why magnesium carbonate decomposes at a temperature lower than that of calculated.

Increase in entropy of gaseous CO_2 is greater than that of solid MgO and MgCO_3 thus, the ΔS is greater than ΔS_{cal} used in $e(i)$.

The Periodic Table

Element	Sodium	Magnesium	Aluminium	Silicon	Phosphorous	Sulfur	Chlorine
Melting point	High They have giant metallic structures with strong electrostatic forces of attraction between the metal cations and the ‘ sea of delocalised electrons ’. Increase from Na to Al because more delocalised electrons are available for metallic bonding which results in stronger electrostatic forces of attraction.			Extremely high It has a giant molecular structure with strong, extensive covalent bonds between the Si atoms .	Low They have simple molecular structures with only weak van der Waals’ forces of attraction holding the discrete molecules together. Increases with along with the number of electrons per molecule, as the greater polarisability results in stronger van der Waals forces of attraction.		
Electrical Conductivity	Good conductor Their metallic lattices contain delocalised electrons. Electrical conductivity increases from Na to Al as the number of delocalised electrons increases.			Poor (Semiconductor) Electrons in the covalent bonds are held tightly and are not easily delocalised.	Non-conductor There are no delocalised electrons in their simple molecular structures.		
Atomic radius	Across the period, there is an increase in the nuclear charge while the screening effect remains relatively constant . The stronger attraction pulls electrons more closely to the nucleus.						
First ionisation energy	The stronger attraction also results in the increasing first ionisation energy.						
		Exception – see Chemical bonding			Exception – see Chemical bonding		
Ionic radius	Across each isoelectronic series, there is an increasing attraction between the increasing number of protons and the same number of electrons. Thus, the ionic radius in both isoelectronic cations and anions decreases. From Si ⁴⁺ to P ³⁻ , there is an additional third quantum shell which is screened. Thus ionic radius increases from Si ⁴⁺ to P ³⁻ .						

Commented [HK23]: Pretty much repeated stuff from chemical bonding.

Oxides	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₆ / P ₄ O ₁₀	SO ₂ / SO ₃
Melting point	High – they have giant ionic lattice with strong electrostatic forces of attraction between the ions			similar to element		
formation	Very rigorous, yellow flame $4\text{Na} + \text{O}_2 \rightarrow 2\text{Na}_2\text{O}$	Very rigorous, bright white flame $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$	Rigorous, white flame $4\text{Al} + 3\text{O}_2 \rightarrow \text{Al}_2\text{O}_3$	Heat required $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$	Rigorous reaction $\text{P}_4 + 3\text{O}_2 \rightarrow \text{P}_4\text{O}_6$ In excess oxygen: $\text{P}_4 + 5\text{O}_2 \rightarrow \text{P}_4\text{O}_{10}$	Heat required $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$ In excess oxygen: $2\text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3$
Oxides of elements change generally from being ionic and basic to being amphoteric and finally to being covalent and acidic, due to the decreasing difference in electronegativity between the element and oxygen.						
The large electronegative difference with oxygen causes the metal atom to lose valence electrons to oxygen atom to form metal ions and basic oxide ions O ²⁻			*covalent behaviour	The small electronegativity difference with oxygen causes it to share electrons with oxygen atom to form the covalent bond.		
Acid/base	basic		amphoteric	acidic		
pH in water	13	9	7 (insoluble)		2	1
Reaction with acid/water	$\text{Na}_2\text{O} + 2\text{H}^+ \rightarrow 2\text{Na}^+ + \text{H}_2\text{O}$	$\text{MgO} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 3\text{H}_2\text{O}$	Dissolves readily in water to give strongly acidic solutions		
	$\text{NaOH} + \text{H}^+ \rightarrow 2\text{Na}^+ + \text{H}_2\text{O}$	$\text{Mg}(\text{OH})_2 + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2\text{O}$	$\text{Al}(\text{OH})_3 + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}$	$\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_3$	$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$	
Reaction with water/alkali				$\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4$	$\text{SO}_3 + 2\text{OH}^- \rightarrow \text{H}_2\text{SO}_4$	
	Dissolves readily to give NaOH, which dissociates completely. $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$	Dissolves sparingly to give a white suspension of Mg(OH) ₂ which dissociate partially to give a weakly alkaline solution. $\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$	$\text{Al}_2\text{O}_3 + 2\text{OH}^- + 3\text{H}_2\text{O} \rightarrow 2[\text{Al}(\text{OH})_4]^-$ $\text{Al}(\text{OH})_3 + \text{OH}^- \rightarrow [\text{Al}(\text{OH})_4]^-$	$\text{SiO}_2 + 2\text{OH}^- \rightarrow \text{SiO}_3^{2-} + \text{H}_2\text{O}$	$\text{P}_4\text{O}_6 + 12\text{OH}^- \rightarrow 4\text{PO}_3^{3-} + 6\text{H}_2\text{O}$ $\text{P}_4\text{O}_{10} + 12\text{OH}^- \rightarrow 4\text{PO}_4^{3-} + 6\text{H}_2\text{O}$	$\text{SO}_2 + 2\text{OH}^- \rightarrow \text{SO}_3^{2-} + \text{H}_2\text{O}$ $\text{SO}_3 + 2\text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O}$
Oxidation number	+1	+2	+3	+4	+3/+5	+4/+6
	Always positive because oxygen and chlorine are more electronegative				Several O.N. as have energetically available 3d subshells for the expansion of the octet to accommodate more than 8 electrons.	

Commented [HK24]: Metal ions (not the pure metal) that have **high charge density** (small and highly charged) undergo hydrolysis to give an acidic solution.
The high polarising power of metal ions polarises the O – H bond in the co-ordinated H₂O molecules giving the H⁺ atoms a highly positive charge, which may be **extracted** by free water molecules, forming H₃O⁺ ions, giving an acidic solution.

Commented [HK25]: Of what?

Chlorides	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃ / PCl ₅
Melting point	High – they have giant ionic lattice with strong electrostatic forces of attraction between the ions			similar to simple molecules	
formation	Very rigorous $2\text{Na} + \text{Cl}_2 \rightarrow \text{NaCl}$	Rigorous $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$	Rigorous $2\text{Al} + 3\text{Cl}_2 \rightarrow \text{AlCl}_3$	Heat required $\text{Si} + 2\text{Cl}_2 \rightarrow \text{SiCl}_4$	Rigorous reaction $\text{P}_4 + 6\text{Cl}_2 \rightarrow 4\text{PCl}_3$ In excess chlorine $\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$
Reaction with water	Dissolves to form a neutral solution $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$	Mg ²⁺ ions are hydrated to $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$	Al ³⁺ ion are hydrated to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	Reactions are very rigorous with fumes of HCl gas produced which results in strongly acidic solutions.	
		The high charge density and polarises and weaken the O – H bond in water molecules which encourages deprotonation to produce H ⁺ to form a slightly acidic solution		$\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$	$\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
		$[\text{Mg}(\text{H}_2\text{O})_6]^{2+} \rightleftharpoons [\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]^+ + \text{H}^+$	$[\text{Al}(\text{H}_2\text{O})_6]^{3+} \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+} + \text{H}^+$ $\rightleftharpoons [\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^+ + \text{H}^+$		Limited amount of water: $\text{PCl}_5 + \text{H}_2\text{O} \rightarrow \text{POCl}_3 + 2\text{HCl}$ Large amount of water: $\text{PCl}_5 + 4\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 5\text{HCl}$
pH	7	6	2	1	1

The large electronegativity difference of Al and oxygen makes AlCl₃ an ionic compound.

Al³⁺ has a **small ionic radius** and is **highly charged**, giving rise to a **high charge density** and hence **high polarising power** to **distort** the electron cloud of the anion.

Cl[–] has a **large ionic radius** which has valence electrons that are **less tightly bound** to the nucleus,

resulting in a **greater ease of distortion of the electron cloud (polarisability)**, leading to sharing of electrons.

Hence AlCl₃ is ionic with partial covalent character and amphoteric.

Group II

	Magnesium	Calcium	Strontium	Barium
Reaction with oxygen	The metals burn vigorously in oxygen to form a white solid.			
	$M + \frac{1}{2}O_2 \rightarrow MO$			
	White flame	Brick-red flame	Brick-red flame	Apple-green flame
Reaction with water	The metals react with water to form the hydroxide and hydrogen gas.			
	$M + 2H_2O \rightarrow M(OH)_2 + H_2$			
	Reacts slowly in cold water, but reacts quickly in steam.	React readily with cold water in increasing vigour.		
	The oxides are ionic and basic in nature. The increasingly soluble oxide dissolves in water to form alkaline solution of increasing strength.			
Thermal stability of nitrates	Down Group II, the thermal stabilities increase/ ease of thermal decomposition decreases.			
	$M(NO_3)_2 \rightarrow MO + NO_2 + \frac{1}{2}O_2$ $MO_2 \rightarrow MO + \frac{1}{2}O_2$ $M(OH)_2 \rightarrow MO + H_2O$ $MCO_3 \rightarrow MO + CO_2$ $MSO_3 \rightarrow MO + SO_2$			
	Down the group, the ionic radius of M^{2+} increases.			
	As a result, the charge density of M^{2+} decreases, the M^{2+} ions become less polarising .			
	The electron cloud of $NO_3^- / CO_3^{2-} / OH^-$ anion is less distorted .			
	The N – O / C – O / O – H covalent bond within the $NO_3^- / CO_3^{2-} / OH^-$ anion is weakened to a smaller extent down the group.			
	Hence the thermal stabilities increase/ ease of thermal decomposition decreases down the group.			

Group VII

	fluorine	chlorine	bromine	iodine
Colour in CCl ₄	very pale yellow	very pale green	reddish brown	violet
Colour in H ₂ O		yellow-green	yellowish brown	reddish brown
Volatility	Halogens are volatile due to the weak van der Waals forces of interactions between the simple molecules. Down the group, the boiling and melting points of halogens increases, volatility decreases. As a result of decreasing volatility down the group, the physical state of the halogens changes from gas (F ₂ and Cl ₂) to liquid (Br ₂) to solid (I ₂). Halogens exist as simple molecules of X ₂ . As the molecular size of X ₂ increases, the number of electrons increases, leading to a greater ease of distortion of the larger electron cloud in the molecule. This leads to stronger instantaneous dipole-induced dipole attraction between the X ₂ molecules, requiring more energy to overcome these intermolecular forces.			
Relative reactivity of the elements as oxidising agents	E [⊖] _{F₂/F⁻ = +2.87}	E [⊖] _{Cl₂/Cl⁻ = +1.36}	E [⊖] _{Br₂/Br⁻ = +1.07}	E [⊖] _{I₂/I⁻ = +0.54}
	F ₂ has the most positive electrode potential, it has the greatest tendency to accept electrons, it undergoes reduction most readily.	Down the group, E [⊖] _{X₂/X⁻ becomes less positive. The ease of reduction decreases. There is a lower tendency for X₂ to be reduced into X⁻. The oxidising power of halogens decreases from F₂ to I₂. Each halide ion can be oxidised by the halogen above it.}		
		S ₂ O ₃ ²⁻ + 4X ₂ + 5H ₂ O → 2SO ₄ ²⁻ + 10H ⁺ + 8X ⁻ The oxidation number of sulfur increases from +2 to +6.		S ₂ O ₃ ²⁻ + I ₂ → S ₄ O ₆ ²⁻ + 2I ⁻ O.N. increases from +2 to +2.5.
reactions of halide ions with:	When solid halides are heated with concentrated H ₂ SO ₄ , HX is produced. NaX + H ₂ SO ₄ → HX + NaHSO ₄			
	Concentrated H ₂ SO ₄ is not able to oxidise the HF/HCl formed.		Concentrated H ₂ SO ₄ oxidises the HX formed.	
concentrated sulfuric acid			2HBr + H ₂ SO ₄ → Br ₂ + SO ₂ + 2H ₂ O	8HI + H ₂ SO ₄ → 4I ₂ + H ₂ S + 4H ₂ O
	Steamy fumes of HF/HCl observed.		Brown fumes of Br ₂ observed. Purple fumes of I ₂ observed.	
aqueous silver ions followed by aqueous ammonia	Silver halide is precipitated when halide ions react with aqueous silver nitrate. Ag ⁺ + X ⁻ ⇌ AgX			
	No ppt	White ppt	Cream ppt	Yellow ppt
	Ag ⁺ + 2NH ₃ ⇌ [Ag(NH ₃) ₂] ⁺ Adding of NH ₃ removes free Ag ⁺ , [Ag ⁺] decreases, position of equilibrium shifts to the left.			

Commented [HK26]: Halogens are p-block elements with an outermost electronic configuration of $ns^2 np^5$. The most common and stable oxidation state for halogen is -1 . All halogens, except fluorine, exhibit variable oxidation states.

Commented [HK27]: Explain why this occurs?

Commented [HK28]: Why is it soluble? (or is it)

Reactions of the elements with hydrogen	B. E. (F – F) = 158	B. E. (Cl – Cl) = 244	B. E. (Br – Br) = 193	B. E. (I – I) = 151
	B. E. (H – F) = 562	B. E. (H – Cl) = 431	B. E. (H – Br) = 366	B. E. (H – I) = 299
	Very rapid reaction, explodes with H ₂ under all conditions	Rapid reaction, explodes with H ₂ in the presence of light	Slow reaction, heat at 200°C in the presence of catalyst	No reaction, unless strongly heated. Reaction is incomplete.
	The reactivity with hydrogen decreases down the group as the strength of the H – X bond formed decreases. Less energy is evolved when HX is formed.			
Relative thermal stabilities of the hydrides	Do not decompose under heat.		Decomposes slightly under heat Brown fumes of Br ₂ observed.	Easily decomposed under heat. Gives out dense purple fumes of I ₂ on gentle heating.
	Down the group, the atomic radius of X increases, the bonding pair of electrons is further away from the nuclei of H and X. Bonding electrons are less strongly attracted to the nucleus. H – X bond becomes weaker. H – X bond energy increases.			
	HX is extremely soluble in water. In aqueous solution, the H – X bond is broken and the hydroxonium ions H ₃ O ⁺ are formed. HF is a very weak acid, not only because of the high bond energy of HF, but also because HF forms hydrogen bonds with water and other HF molecules.			

Commented [HK29]: “H – I bond is weaker than H – Cl bond. Reaction of I₂ with H₂ is less vigorous/favourable and the HI formed is easily decomposed, hence the reaction is reversible.”

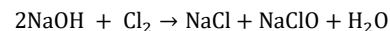
Commented [HK30]: Side note (which is not quite relevant to the cases)
The increasing atomic radius down the group usually imply longer and hence weaker covalent bonds. One exception in this trend is fluorine, which has a weak F-F bond. This could be due to the lone pairs of electrons on the fluorine atoms being close together that they strongly repel each other, hence weakening the bond.

Commented [HK31]: The notes specified that the acidity decreases down the period. It is really the case? i.e. HCl already completely dissociates in water, given the same no. of moles, there should not be a stronger monoprotic acid.

When Cl₂ reacts with NaOH, it undergoes disproportionation.

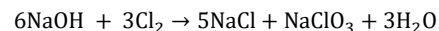
Cold (15°C) aqueous NaOH

The oxidation state of Cl₂ increases from 0 in Cl₂ to +1 in chlorate(I), and decreases from 0 in Cl₂ to –1 in chloride.

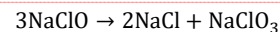


Hot (70°C) aqueous NaOH

The oxidation state of Cl₂ increases from 0 in Cl₂ to +5 in chlorate(V), and decreases from 0 in Cl₂ to –1 in chloride.



The chlorate that was first produced undergoes further disproportionation to form chloride and chlorate (V)



Commented [HK32]: Clarify reaction pathway.

Chemical Equilibrium

Reversible reactions are reactions that proceed in both forward and backward directions.

Dynamic Equilibrium is a state in a reversible reaction in which the **rate** of the **forward** reaction **equals** to the rate of the **backward** reaction which has no change in the concentrations of the reactants and the products.

Le Chatelier's Principle states that if a change occurs in one of the conditions (concentration, temperature, or pressure) under which a reversible reaction is in dynamic equilibrium, the position of equilibrium shifts so as to **minimise that change** and to re-establish equilibrium.

The system **cannot completely cancel** the change in the external factor but it shifts its equilibrium position in the direction that will minimise the change.

At any given temperature, the equilibrium constant K_p/K_c is equal to the product of the concentrations/partial pressure of the **products**, each raised to the power equal to its **stoichiometric coefficient** in the balanced reaction, **divided** by the product of the concentrations/partial pressure of the **reactants**, each raised to the power equal to its stoichiometric coefficient in the balanced **reaction**.

Only temperature affects the value of the equilibrium constant K_p/K_c .

When **extra reactant is added** to an equilibrium mixture, the **[reactant]** increases, by Le Chatelier's principle, the **position of equilibrium** will **shift** to the **right** to **remove some of the excess reactant**, **[reactant] decreases**, **[product] increases**. K_c is unchanged. (Subsequently for reactant/product added/removed)

When the **volume** container decreases at constant temperature, the **partial pressure** of reactants and products increases, by Le Chatelier's principle, the **position of equilibrium** will **shift** to the **[side with fewer no. of moles of gas]** to decrease pressure **by producing fewer gas molecules**, p_{reactant} increases/decreases, p_{product} increases/decreases, total pressure of the gas mixture decreases. K_p is **unchanged**. (Subsequently for volume increase)

Catalyst increases the rate of both forward and backward reactions to the same extent. Position of equilibrium and equilibrium constant K_p/K_c remains unchanged. However, **catalyst increases the rate** (decreases the time taken) for the **re-establishment** of the equilibrium.

When the **temperature increases**, the **forward/backward endothermic reaction** is favoured (because rate increases more quickly than the other) the **equilibrium position shifts to the right/left** to **absorb the extra heat**. The **concentration of products** increases/decreases. Thus K_c increases/decreases. (Subsequently for temperature decrease)

Commented [HK33]: This is asked for

Commented [HK34]: The rate equation is not necessary the stoichiometric ratio
- however this problem has yet to be encountered.

Commented [HK35]: FYI
$$K_c = \frac{[\text{product}]^m}{[\text{reactant}]^n}$$

If $K_c > 1$, the position of equilibrium lies on the right as there is a higher proportion of products

Commented [HK36]: When the concentration of one reactant decrease, can the concentration of the other reactant increase?

Commented [HK37]: Also really for increase in temperature/concentrate/pressure?

Factors of consideration in **applications** in industrial processes

Time efficiency – percentage yield, rate in reaching equilibrium

Resource efficiency – cost of equipment

The Haber process

Since the forward reaction is exothermic, applying Le Chatelier's principle, the **production** of NH_3 is **favoured** by low temperature.

However, if the temperature is too low, the **rate of reaction** will be too slow, making the process uneconomical.

Hence a moderate temperature of 450°C is used to obtain an optimum yield of NH_3 at a reasonable rate.

Since there is a lesser no. of moles of gaseous products than reactants, applying Le Chatelier's principle, the **production** of NH_3 is **favoured** by a very high pressure.

However a very high pressure demands higher **costs** of plant construction and maintenance for more expensive thicker vessels.

Hence a moderately high pressure of 250atm is used.

To increase the rate of the establishment of equilibrium, iron is used the catalyst for the reaction.

Iron is finely divided to increase the total surface area of the catalyst so that the rate of the forward reaction can be **further** increased.

Expression for K_p/K_c does not include solids (because it has a constant density, therefore it has no effect on pressure/concentration)

In a homogeneous equilibrium (esterification/hydrolysis), K_c include the concentration of water.

In a heterogeneous equilibrium (acid-base), K_c does not include the concentration of water (because change in concentration of water is negligible.)

Ionic Equilibrium

In the Brønsted-Lowry Theory,

an **acid** is a proton (H^+) donor

a **base** is a proton (H^+) acceptor

an acid-base reaction is proton transfer from an acid to a base, forming conjugate base and conjugate acid respectively.

A **strong** acid/base undergoes **complete dissociation** in water. $[\text{H}^+] = [\text{HX}]_{\text{initial}}$

A **weak** acid/base undergoes **partial dissociation** in water. $[\text{H}^+] < [\text{HX}]_{\text{initial}}$

The degree of dissociation α refers to the fraction of molecules which is ionised in water. $\alpha = \text{dissociated}/\text{initial} = \sqrt{K_a/[\text{HA}]_{\text{initial}}}$

$$\text{pH} = -\lg[\text{H}^+]$$

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

$$\text{pH} + \text{pOH} = \text{p}K_w = -\lg([\text{H}^+][\text{OH}^-]) = 14.0 \text{ at } 298\text{K}$$

pH, pOH and degree of dissociation α are **not good indicators** of the strength of an acid (base) as they are dependent on the **concentration** of the acid (base) used.
The relative strength of acids of bases should be determined by K_a or K_b , which are only affected by temperature.

The strength of weak acids (bases) is a **measure of how good a proton donor (acceptor)** it is. Stronger acid (base) has larger K_a (K_b).

For weak acids, $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \approx \frac{[\text{H}^+]^2}{[\text{HA}]_{\text{initial}}}$$

For weak bases, $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{BH}^+$

$$K_b = \frac{[\text{OH}^-][\text{BH}^+]}{[\text{B}]} \approx \frac{[\text{OH}^-]^2}{[\text{B}]_{\text{initial}}}$$

Commented [HK38]: Need to see what is really relevant

Commented [HK39]: H^+ does not exist on its own, as it is very small with high charge density. It exists as hydronium ions H_3O^+

Commented [HK40]: pH is a measure of total concentration of H^+ ions in the aqueous system.

You need to calculate pOH then pH in alkaline conditions.

Commented [HK41]: K_w is the ionic product of water. K_w (and $\text{p}K_w$) are constant at constant temperature.

Commented [HK42]: FYI

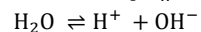
(I don't know how come K_c is involved)

Determining of which of the conjugate acid/base pair is stronger
 $\text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{BH}^+$
 K_c is large (small). Position of equilibrium lies more to the right (left).
 HA and B (A^- and BH^+) are stronger acid and base respectively, as
 HA and B (A^- and BH^+) as a better proton donor and acceptor respectively.

Commented [HK43]:

$$\text{pH} = \text{p}K_a - \lg \frac{[\text{acid}]}{[\text{salt}]}$$

Decrease of pK_w over an **increase** in **temperature**



When **temperature increases**, the **forward endothermic reaction** is favoured, the **equilibrium position shifts to the right** to **absorb the extra heat**.

$[H^+][OH^-]$ increases. As $pH = -\log_{10}[H_3O^+]$ and $pOH = -\log_{10}[OH^-]$, pH and pOH decreases.

Since $pK_w = pH + pOH$, pK_w decreases.

Total **yield** of hydrogen gas of **weak vs. strong acid**

HX is a strong acid that undergoes complete dissociation to give n moles of H^+ ions to form m volume of H_2 .

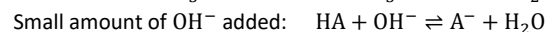
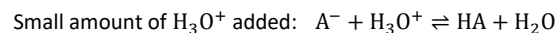
HA is a weak acid that undergoes partial dissociation. However H^+ is removed by reacting with (metal).

As $[H^+]$ decreases, dissociation of HA is shifted completely to the right.

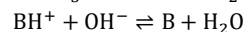
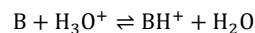
Eventually all HA will dissociate, producing the same amount of H^+ as HX, forming the same amount of H_2 .

A buffer solution is one whose **pH remains almost constant** when small amounts of acid or alkali are added.

Acidic buffer



Alkaline buffer



At the **maximum buffer capacity**, $[A^-] = [HA]$

$$pH = pK_a$$

$[B] = [BH^+]$

$$pOH = pK_b$$

An indicator is a weak acid; the acid HIn is a different colour from its conjugate base In^- .

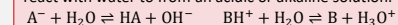
To distinguish the colour change, one conjugate has to be 10 times of the concentration of the **other**.

The indicator is suitable if the pH transition range of the indicator lies within the rapid pH change over the equivalence point.

The pK_a of the indicator matches the rapid pH change of the titration curve at the equivalence point.

Commented [HK44]: Salt hydrolysis?

Salt hydrolysis is a reaction in which ions (from a weak acid or base) react with water to form an acidic or alkaline solution.



"At equivalence point, only the hydrolysis of the salt is considered."

Don't how this sentence came about either

Commented [THK45]: Capacity of a buffer is the quantity of H^+ or OH^- it can remove before its pH changes. (really don't change?)

Effective buffer range is the pH range covered which the buffer is effective in maintaining the pH.

In this effective buffer range, both weak acid HA (weak base B) and the conjugate base A^- (conjugate acid BH^+) are present (in relatively significant amounts.)

$$pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$$

Commented [HK46]: Draw a pH titration graph

Solubility

Soluble salts dissociate completely to give separate hydrated ions in the solution.

	NO_3^-	NO_2^-	Cl^-	Br^-	I^-	CrO_4^{2-}	SO_4^{2-}	SO_3^{2-}	CO_3^{2-}	OH^-	
$\text{Na}^+/\text{K}^+/\text{NH}_4^+$											$\text{Na}^+/\text{K}^+/\text{NH}_4^+$
Ca^{2+}											Ca^{2+}
Ba^{2+}											Ba^{2+}
Pb^{2+}			soluble in hot water								Pb^{2+}
Ag^+											Ag^+

K_{sp} is known as solubility product, and is dependent on the ionic formula of the salt. It is constant at constant temperature.

$$K_{sp} = [\text{M}^{y+}]^x [\text{A}^{x-}]^y = x^x y^y s^{m+n}$$

It is valid for sparingly soluble salts only.

When ionic product $< K_{sp}$,

the solution has not reach saturation. More solute can dissolve in the solution.

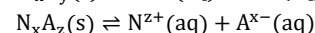
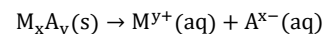
When ionic product $= K_{sp}$,

the solution is exactly at saturation point, addition of more solute will remain undissolved.

When ionic product $> K_{sp}$,

not all the solid has dissolved in water. Equilibrium is established between the undissolved salt and the dissolved ions.

The common ion effect is the phenomenon of reduced solubility with the addition of common ions to a sparingly soluble salt.



With the increase in concentration of common ion $[\text{A}^{x-}]$ due to the added M_xA_y , the **position of the equilibrium will shift** to the left to remove the extra ions.

This will result in precipitation of the salt N_xA_z .

Commented [HK47]: Table – show Ksp values

Commented [HK48]: FYI

Saturated solution is one that contains the maximum amount of solute in a given amount of solvent such that the ions are in equilibrium with the solid.

The solubility s of a substance is the quantity that dissolves in 1 dm³ of water to form a saturated solution at a stated temperature.

Commented [HK49]: Complex ion is a central metal cation that is surrounded by anions or molecules called ligands.

The ligands have at least a lone pair of electrons that can form a dative bond with the central ion. Example of such ligands includes halides, ammonia and hydroxide.

Formation of such complex ions from the metal cations reduces the concentration of the metal cations.

The equilibrium shifts left and hence increases the solubility of the salts.

(Covered in transition metals)

Acid-base reaction may take place changing the concentration of ions, and hence solubility of the solid

CrO_4^{2-} ion undergoes acid-base reaction in the presence of H^+ to form $\text{Cr}_2\text{O}_7^{2-}$ ion.

$[\text{CrO}_4^{2-}]$ decreases and equilibrium shifts to the right and more BaCrO_4 dissolves.

Selective precipitation is the separation of ions based on the difference in solubilities of the salts under different conditions.

A common reagent is added to an aqueous solution containing mixtures of ions.

The salt that requires a lower minimum concentration of ion will precipitate first.

Reaction Kinetics

The rate of reaction is how the concentration of a product P increases (OR how the concentration of reactant R decreases) with time.

$$\text{rate} = \frac{d[P]}{dt} = -\frac{d[R]}{dt}$$

Rate of reaction at a point in time can be deduced from the gradient of concentration-time graph.

The rate equation states the relationship between the rate of reaction and the concentrations of each reactant.

Rate = $k[A]^m[B]^n$ (Units of rate = $\text{mol dm}^{-3} \text{s}^{-1}$)

k is the rate constant (and its unit is such that the equation is homogenous)

The reaction is in m^{th} **order** with respect to A. ($m + n$) is the overall order of reaction.

For a reaction mechanism to be **consistent** with a rate equation,

the sum of individual steps in the mechanism must **give the overall balanced chemical equation**, and

the **orders** of reaction in the rate equation are the **coefficients** of the reactant species in the **slow step (rate determining step)**.

The **rate determining step** (slow step) is the step in the reaction mechanism that has the **highest activation energy**.

It is usually the first step of the reaction mechanism;

otherwise, the rate determining step will require intermediates, and the rate equation will then include all reactants in the previous steps.

Energy profile diagram – intermediates (minima) and transition state (maxima)

Commented [HK50]: FYI

Instantaneous Rate of a chemical reaction is defined as the rate of change of reactant or product concentration at any specific time. Initial rate is defined as the rate which the reactant used up (or the product being formed) at the beginning of the reaction.

Commented [HK51]: $k = Ae^{-E_a/RT}$

Commented [HK52]: FYI

The order of a reaction with respect to a reactant is the power to which the concentration of that reactant is raised in the experimentally determined rate equation.

Commented [HK53]: draw

The initial concentration of the other reactants are much higher so that its relative change in concentration is relatively small, and not affect the rate of reaction, if it does.

Commented [HK54]: AIC MYCT 2014

Derivation of **Rate Equation** from experimental data

Inspection method using **rates**

"Comparing expt 1&3, when $[H_2O_2]$ increases to 2 \times , initial rate increases to 2 \times . Hence, reaction is 1st order w.r.t. $[H_2O_2]$ "

"Without a change in $[H^+]$, the rate of reaction should decrease to $\frac{1}{2} \times$, as reaction 1st order w.r.t. $[H_2O_2]$. Hence reaction is zero order w.r.t. $[H^+]$ "

$$\frac{r_1}{r_2} = \frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]^a[B]^b[C_1]^n}{k[A]^a[B]^b[C_2]^n} = \left(\frac{[C_1]}{[C_2]}\right)^n$$

The **rate-concentration**ⁿ graph

Straight line through origin implies rate is nth order w.r.t. concentrationⁿ (rate = $k[A]^n$)

Half-life of the reaction is the time taken for the concentration of a reactant to be **reduced to half its original concentration**.

Constant half-life implies rate = $k[A]$

[R]-time graph can be deduced from [P]-time graph, however the final [P] needs to be known.

Commented [HK55]: Possible to use half-life to calculate initial rate? (or do we even need to do so?)

If rate-concentration graph is downward sloping curve with a constant gradient, it implies that the reaction is 0th order w.r.t. the reactant.

Experimental determinations for the of Rate of Reaction

Commented [HK56]: Discontinuous and continuous types

Physical

Volume of gas (liberation of hydrogen from acid-metal reaction, collected in syringe, volume measured and recorded at regular intervals)

Decrease in mass (liberation of carbon dioxide from carbonates, mass recorded at regular time intervals)

Change in colour intensity (formation of brown nitrogen dioxide from nitrogen monoxide and ozone) using colorimeter

Change in conductivity (formation of ionic products from non-ionic reactants)

Change in pressure using a manometer

Chemical

Sampling (quenching with dilution/cooling/removal of catalyst/reactant, then titrimetric analysis)

Clock method (oxidation of aqueous iodide I^- by peroxodisulphate $S_2O_8^{2-}$) (**time** taken for prominent visual change = **1/ initial rate**)

Collision Theory

For a reaction to take place, an effective collision must occur.

An effective collision must be **correctly oriented** and must occur with a minimum amount of energy called **activation energy**.

Activation energy is the **minimum amount of energy required** for an effective collision to occur.

Energy profile diagram

Minima correspond to the energy level of the intermediate.

Maxima correspond to the energy level of the transition state.

No. of steps in a mechanism corresponds to the number of maxima in the energy profile diagram. Slowest step have the highest activation energy E_a .

The activation energy of a step in the reaction mechanism is measured from the previous minima to the next maxima.

Increase in surface area (of solid reactants/catalysts) increases the rate of reaction.

The smaller the size of the solid, the higher the total surface area exposed for reaction to occur increases.

Frequency of effective collisions increases. The rate of reaction increases.

Increase in concentration / pressure (for gas) increases the rate of reactions.

The increase in concentration / pressure implies more number of particles per unit volume.

The frequency of effective collision increases. The rate of reaction increases.

The **Boltzmann distribution curve** shows the distribution of collision energies with respect to collision frequency, where very few molecules have very low or very high energies, and most of the molecules have the moderate amount of energy.

Increase in temperature increases the rate of reaction.

The average kinetic energy of the molecules increases (as shown by the maxima of the curve shifting to the right)

The number of reactant molecules with energy greater than or equal to the activation energy E_a will increase (energies are more spread out)

This results in an increase in the frequency of effective collisions. The rate of reaction increases.

Presence of catalyst increases the rate of reaction.

By providing an alternative pathway for the reaction, the activation energy of the catalysed reaction is lower. ($E_a' < E_a$)

More molecules have energies greater than or equal to the lowered activation energy E_a' (area under curve above E_a' increases)

This results in an increase in the frequency of effective collisions. The rate of reaction increases (higher k value).

Commented [HK57]: Draw the Boltzmann distribution curves

Commented [HK58]: (f) explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction

(g) show understanding, including reference to the Boltzmann distribution, of what is meant by the term activation energy

(h) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and hence, on the rate) of a reaction

(i) (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy, giving a larger rate constant

(ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution

Commented [HK59]: Show on distribution curve

A **catalyst** increases the rate of reaction by providing another reaction pathway which has lower activation energy.

Heterogeneous catalysts exist in a different phase from the reactants, often metals or metal oxides interacting with gaseous or liquid reactants.

Iron acts as a heterogeneous catalyst in the Haber process. Nitrogen and hydrogen **migrate** to the catalyst surface.

Adsorption now occurs. New bonds are formed between the reactants and the catalyst.

Bonds within each reactant molecule are **weakened**. New bonds between the reactant molecules form.

Desorption takes place when all bond formation is completed. The product molecules migrate away from the catalyst surface.

Homogenous catalysts exist in the same phase as the reactants (for example: NO_2 in the oxidation of SO_2 into SO_3 that forms acid rain)

The reactant and the catalyst combine to form a **reactive intermediate**. $\text{NO}_2 + \text{SO}_2 \rightarrow \text{SO}_3 + \text{NO}$

The product is formed with the **regeneration** of the catalyst. $\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2$

The activation energies are much lower than the uncatalysed reactions.

Another example of homogenous catalyst is Fe^{2+} in the formation of I^- by peroxodisulphate $\text{S}_2\text{O}_8^{2-}$.

Autocatalyst is a product of the chemical reaction that can catalyse the reaction as well.

Mn^{2+} in the redox reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$

Enzymes are naturally occurring biologically active **catalysts**.

As enzymes are **large** protein molecules bound with hydrogen bonds, they operate best at a certain **optimum** temperature and pH range.

Due to the **specific configuration** in the **active site** enzyme allows only substrates that have a **complementary structure** to bind there.

Hence enzymes are very **specific** in the type of reaction they catalyse.

Enzymes + substrate \rightarrow Enzyme substrate complex

Enzyme-substrate complex \rightarrow Enzyme-products complex (slow)

Enzyme-products complex \rightarrow Enzyme + products

At the end, the products are released and the active site is free to allow action on other substrate molecules.

When the concentration of substrate is high, the active sites on all enzymes are **occupied**, and the order of reaction becomes zero with respect to substrate concentration.

Hence rate of reaction no longer increase with substrate concentration.

Commented [HK60]: (j) outline the different modes of action of homogeneous and heterogeneous catalysis, including: (i) the Haber process

(ii) the catalytic removal of oxides of nitrogen in the exhaust gases from car engines (see also Section 10.2)

(iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide

(iv) catalytic role of Fe^{2+} in the $\text{I}^-/\text{S}_2\text{O}_8^{2-}$ reaction

(k) describe enzymes as biological catalysts which may have specific activity

(l) explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems

Electrochemistry

The standard **electrode** potential E^\ominus of an element is defined as the potential difference between a standard hydrogen electrode and a half cell of the element in a solution of its ions at 1 mol dm^{-3} under the standard conditions of 298K and 1atm.

The standard hydrogen electrode (SHE) consists of an inert platinum electrode (coated with finely divided platinum) dipping into an aqueous solution of H^+ ions at 1 mol dm^{-3} , with hydrogen gas bubbling in at a pressure of 1 atm and 298K. The standard electrode potential of SHE $E_{\text{H}^+/\text{H}_2}^\ominus$ is defined to be zero.

The standard cell potential E_{cell}^\ominus is the **maximum** potential difference between two half-cells which are operated under standard conditions.

$$E_{\text{cell}}^\ominus = E_{\text{reduction}}^\ominus - E_{\text{oxidation}}^\ominus$$

Cell diagram ("left" and "right" refer to the species of the reduction reaction in the data booklet)

anode | (if it is not the anode) right, left | (electrolyte if shared) | left, right (if it is not the cathode) | **cathode**

The electrons will flow

from the more negative (less positive) electrode (**anode**, where **oxidation** occurs)

to the less negative (more positive) electrode (**cathode**, where **reduction** occurs).

Under standard conditions, the reaction is usually feasible if $E_{\text{cell}}^\ominus > 0$. (The reaction is not feasible if $E_{\text{cell}}^\ominus < 0$) To calculate E_{cell}^\ominus :



$$E_{\text{cell}}^\ominus = +0.80\text{V} - (+0.77\text{V}) = +0.03\text{V} > 0\text{V} \quad \text{Reaction is feasible.}$$



However, under non-standard conditions, the use of standard cell potentials may not predict the feasibility of a reaction.

At high [reactant] / [product], the **position of equilibrium** shift to the right / left and the E is more / less positive than E^\ominus .

Hence (the species) is **preferentially discharged** and (product) is evolved/formed at the cathode/anode.

Even under standard conditions, the reaction may be very slow because of high activation energy that is not overcome. $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$

One Faraday $F = Le = 96500\text{C}$ is the charge on one mole of electrons.

Commented [HK61]: Balancing of ionic half-equation to be moved here.

Commented [HK62]: It is to increase total surface area of electrodes to allow reactions at electrode to occur more rapidly.

The membrane is porous to allow selective ions to pass through to maintain electrical neutrality.

Commented [HK63]: show w.r.t. E^\ominus values and data booklet half reaction.

Commented [HK64]: As a result, the tendency of Ag^+ (aq.) to be reduced will decrease

Commented [HK65]: In electrolysis of sodium halide, a higher concentration of halide ion will lower its reduction potential and in most cases, make it more likely to be oxidized, unless its fluorine.

The H_2/O_2 fuel cell

Electrolyte: hot conc. KOH (aq.)

Electrodes: Carbon with a sprinkling of platinum

At the anode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$

At the cathode: $2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$

Anodising of aluminium (for corrosion resistance and decoration)

At the cathode (steel): $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

At the anode (aluminium object): $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

Oxygen released at the anode oxidises the aluminium, artificially thickening the surface oxide Al_2O_3 layer to about 20 micrometres.

Purification of copper

Electrolyte: CuSO_4 (aq.)

The cell potential is adjusted such that Cu dissolves.

At the anode (impure copper): $\text{Cu} \rightarrow 2\text{e}^- + \text{Cu}^{2+}$

Impurities with E^\ominus values which are less positive than $E^\ominus_{\text{Cu}^{2+}/\text{Cu}}$ dissolve, while impurities with E^\ominus values which are more positive than $E^\ominus_{\text{Cu}^{2+}/\text{Cu}}$ remain undissolved

At the cathode (purified copper): $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

Electrolysis of brine

Electrolyte: Purified brine (concentrated NaCl)

At the anode (titanium): $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ (electrode preferred due to the corrosive nature of Cl_2)

At the cathode (steel): $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$

The porous asbestos diaphragm prevents the mixing of NaOH (formed at the cathode) and Cl_2 (formed at the anode), which disproportionate Cl_2 to Cl^- and ClO^- .

It also serves to prevent highly reactive H_2 (formed at the cathode) and Cl_2 formed at the anode from coming into contact as they can be sold as useful chemical separately.

Purification of brine is necessary to remove Ca^{2+} and Mg^{2+} which would precipitate insoluble hydroxides and block the pores of the diaphragm.

Relationship between electrochemistry and thermodynamics:

$$\Delta G = -nFE^\ominus_{\text{cell}} = \Delta H^\ominus - T\Delta S^\ominus$$

A positive E^\ominus_{cell} indicates a spontaneous reaction and the reaction is likely to be exothermic.

Commented [HK66]: Picture

Commented [HK67]: "state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and improved batteries (as in electric vehicles) in terms of **smaller size**, **lower mass** and **higher voltage**"

Advantages of the fuel cell

High energy/mass ratio – can be used in space shuttles

High efficiency – current is directly produced from the reaction of hydrogen and oxygen

No pollution / greenhouse effect – chemical product is water

Transition Elements

A transition element is a d block element that can form at least one stable ion with a partially filled d subshell.

Element	$_{21}\text{Sc}$	$_{22}\text{Ti}$	$_{23}\text{V}$	$_{24}\text{Cr}$	$_{25}\text{Mn}$	$_{26}\text{Fe}$	$_{27}\text{Co}$	$_{28}\text{Ni}$	$_{29}\text{Cu}$	$_{30}\text{Zn}$
Electronic configuration	$[\text{Ar}]3d^14s^2$	$[\text{Ar}]3d^24s^2$	$[\text{Ar}]3d^34s^2$	$[\text{Ar}]3d^54s^1$	$[\text{Ar}]3d^54s^2$	$[\text{Ar}]3d^64s^2$	$[\text{Ar}]3d^74s^2$	$[\text{Ar}]3d^84s^2$	$[\text{Ar}]3d^{10}4s^1$	$[\text{Ar}]3d^{10}4s^2$

$[\text{Ar}] = 1s^22s^22p^63s^23p^6$

In a transition metal atom, the **increase in the nuclear charge** with an addition of a proton is **shielded** by the **increase in electrons** in the **inner 3d** subshell. Effective nuclear charge remains relatively constant.

First ionisation energies (which involves removal of the **4s** electron), **atomic and ionic radii**, and of the transition elements are **relatively invariant**.

As the **shielding effect** provided by **d** electrons is **poor**, the s electrons experience a greater **effective** nuclear charge. Therefore the d-block elements have a **smaller atomic/ionic radius** than the s-block elements.

With the increasing relative atomic mass (and also smaller atomic size for s-block), there is a **gradual increase in density** in the s-block to d-block.

In transition metals, the close similarity in energy of the 4s and 3d electrons allows **more electrons** to be **available** for **delocalisation**.

In addition the metal ions has **higher charge density**, resulting in **stronger metallic bonding** makes d-block elements to have a **higher melting point**, **less malleable**, and be better **electrical conductors** than the s-block elements, which only has 4s electrons that can be delocalised to act as mobile charge carriers. (Mn have a low melting point among transition metals because **electrons in the half-filled 3d subshell are stable** and thus not readily available for metallic bonding.)

The **s-block** elements are **limited** to **oxidation states** of +1 (for Group I) or +2 (for Group II), Once the outer s electrons are removed, the further removal of inner shell p electrons would require too much energy.

The **transition elements** have **variable oxidation states** because 4s and 3d electrons are similar in energy.

Once the 4s electrons are removed, **some or all the 3d** electrons may also be removed or shared without requiring much more energy.

The **maximum** oxidation state **corresponds** to the sum of the **number of 4s and unpaired 3d electrons**.

Commented [HK68]: 3 reactions
acid-base
ligand exchange
redox involving E

Commented [HK69]: Some colours
Cr³⁺ is a green solution; Cr(OH)₃ is a grey-green ppt. CrO₄²⁻ is a yellow solution. MnO₄²⁻ is a green solution. MnO₂ is a brown solid. MnO₄²⁻ is a purple solution.

Commented [HK70]: Configuration of Cu⁺, Cu²⁺

Commented [HK71]: View from another perspective

Commented [HK72]: "Melting point for transition elements depends on the number of unpaired 3d electrons that can be delocalised for metallic bonding."

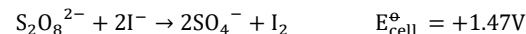
Commented [HK73]: However, some of the most malleable metals is a transition metal, e.g. gold

Commented [HK74]: "The elements exhibit higher oxidation states when they form covalently bonded oxo-anions or compounds with oxygen. They exhibit lower oxidation states when they exist as cations."

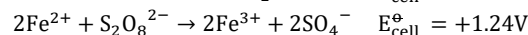
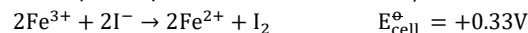
Commented [HK75]: Due to inter-electronic repulsion, converting d₆ to d₅ involved less energy.
 $\text{Co}^{3+} \rightarrow \text{Co}^4 + e^-$

Commented [HK76]: Consider Copper

Transition elements are able to exist in **variable oxidation states**. Inter-conversion of oxidation states enable transition elements and their compounds to form **intermediate** compounds and then revert to original state at the end of the catalysed reaction.



The reaction is **thermodynamically feasible** ($E_{\text{cell}}^\ominus > 0$) but **kinetically slow (high activation energy)** due to **electrostatic repulsion** between **two negatively charged ions**. $\text{Fe}^{2+}/\text{Fe}^{3+}$ acts as a catalyst by providing an alternative reaction pathway **via the intermediate** $\text{Fe}^{3+}/\text{Fe}^{2+}$:



Since in both steps it involves collision between **two oppositely charged ions**, the **activation energy is much lower** than that of the uncatalysed reaction.

Transition elements and their compounds can be used as **heterogeneous catalysts** because they have **empty or partially-filled d orbitals** which can be used to form **temporary bonds** with reactant molecules which **weaken** the existing bonds in these molecules, **lowering the activation energy**. The rate of reaction increases also because of the **higher reactant concentrations** as the molecules are brought closer in the active sites.

Reaction	$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$	$\text{RCH}=\text{CH}_2 + \text{H}_2 \rightleftharpoons \text{RCH}_2\text{CH}_3$	$2\text{SO}_2 + \text{O}_2 \rightleftharpoons \text{SO}_3$
Catalyst	$\text{Fe}/\text{Fe}_2\text{O}_3$	Ni	V_2O_5

Transition metal ions form **complexes** by allowing dative bonds to be made by **ligands** because the metal ions are small and highly charged resulting it to have a **high charge density** and have **vacant 3d orbitals of low energy level** that can accommodate electrons donated by the ligands.

Ligands are neutral molecules or anion which possess **at least one lone pair of electrons** which can be used to form **dative bond** to the central metal ion or atom.

Stronger ligands such as NH_3 have **more available lone pair** than ligands such as H_2O , as **effective nuclear charge** on N is less than on O atom, forming **stronger dative bonds** with the metal ion.

However, complexes of **polydentate** ligands tend to be more stable than complexes of monodentate ligands because

they form **multiple dative bonds** which are more difficult to break, and the formation of the **chelate** complex is accompanied by an **increase in entropy**.

For example, competition between ligands takes place in the **haemoglobin**.

When there is a high $[\text{O}_2]$ (in the lungs), oxygen molecules displace the water ligands in forming a dative bond with iron (II) ion.

Oxyhaemoglobin is transported to the tissues, where there is a low $[\text{O}_2]$, O_2 is displaced and released to the cells.

Stronger ligands such as CO molecules **interact irreversibly** with Fe atom in the haem group. Compared to the $\text{Fe} - \text{O}_2$ dative bond, the $\text{Fe} - \text{CO}$ **dative bond** is stronger which **better stabilises** the iron (II) centre and **cannot** be broken easily. Hence CO poisons the haemoglobin and disables bonding with O_2 .

Commented [HK77]: Also in reaction kinetics

Commented [HK78]: Really?
For example, Cu^{2+} , it can only accommodate 2 electrons

Commented [HK79]: Terms
ligands – only after they form dative bonds?
“stronger” “weaker” “more stable/stabilising”
Who forms the dative bond? The l.p. or the molecule or the atom

Commented [HK80]: How to draw a ligand

Depending on the **ionic radius/charge density/polarising power** of the metal ion, the aqua complexes (metal ion with H_2O ligands) undergo hydrolysis (due to weakening of $\text{O} - \text{H}$ covalent bond), forming an acidic solution.

When $\text{NH}_3(\text{aq.})$ is added, NH_3 deprotonates free H_2O molecules into OH^- ions. Cu^{2+} ions is **precipitated** as **pale blue** $\text{Cu}(\text{OH})_2$.
 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 2\text{OH}^- \rightleftharpoons \text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4 + 6\text{H}_2\text{O}$

Upon adding excess $\text{NH}_3(\text{aq.})$, NH_3 molecules **displace** H_2O molecules by making a **stronger dative bond** with copper (II) ion, forming $[\text{Cu}(\text{NH}_3)_6]^{2+}$
 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 4\text{H}_2\text{O}$

This result in $[[\text{Cu}(\text{H}_2\text{O})_6]^{2+}]$ to decrease, by Le Chatelier's principle, the position of equilibrium shifts to the left to increase $[[\text{Cu}(\text{H}_2\text{O})_6]^{2+}]$.
Hence the pale blue precipitate dissolves forming a **deep blue solution**.

Under **ligand field influence**, the 3d orbitals of V^{3+} is split into **two** levels.

The energy gap ΔE between the non-degenerate orbitals is **small** and corresponds to that in the **visible light spectrum**.

Energy is **absorbed** from the visible region when an electron is **promoted** from a lower energy d-orbital to a vacant higher energy level d-orbital in a **d-d transition**.

The **colour** of the complex ion observed is the **complement** of the colours that are absorbed.

Ca^{2+} and Sc^{3+} are **colourless** because the energy required for electronic transition from 3p to 4s is **large** and falls **outside** the energies of the **visible light spectrum**.

Ti^{4+} , Cu^+ and Zn^{2+} are colourless because they have a **fully filled 3d subshell** which do not allow for a **d-d transition** of an 3d electron.

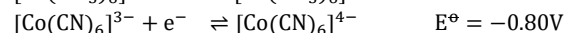
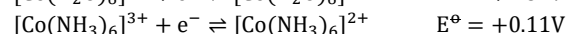
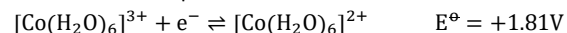
Spectrochemical series: $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} \approx \text{H}_2\text{O} < \text{CH}_3\text{CN} < \text{NH}_3 < \text{C}_2\text{H}_4(\text{NH}_2)_2 < \text{NO}_2^- < \text{CN}^- \approx \text{CO}$

NH_3 has **greater ligand field strength** as compared to H_2O .

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ absorbs light in the orange region of the spectrum and so it appears **turquoise**.

$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ absorbs light in the yellow region (which is of smaller wavelength due to larger ΔE) of the spectrum and so it appears **deep blue**.

Formation of complexes can affect the relative stabilities of oxidation states in transition metals.



$\text{Co}(\text{III})$ is less readily reduced to $\text{Co}(\text{II})$ when it is bonded to NH_3 ligands.

As the lone pair of electrons on the NH_3 ligand is more available than the H_2O , the **cobalt metal centre** of $[\text{Co}(\text{NH}_3)_6]^{3+}$ is **more electron rich** than $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, making the former less likely to accept an electron.

$[\text{Co}(\text{CN})_6]^{3-}$ is also **negatively charged** so it is less likely to accept an electron to undergo reduction.

Commented [HK81]: Insoluble because it is a neutral complex
 $\text{Cr}^{3+} \rightarrow \text{Cr}(\text{OH})_3 \rightarrow [\text{Cr}(\text{OH})_6]^{3-}$
The neutral complex is amphoteric

Commented [HK82]: For d-d transition to occur there must be at least one d electron and an empty d orbital in the higher energy level).

Commented [HK83]: Not possible for an electron to move from a lower level d-orbital to a higher level d orbital in the higher energy level.

Commented [HK84]: Ligands arranged on the left end of this spectrochemical series are **generally** regarded as weaker ligands and cannot cause forcible pairing of electrons within 3d level and thus form outer orbital octahedral complexes.
On the other hand ligands lying at the right end are stronger ligands and form inner orbital octahedral complexes after forcible pairing of electrons within 3d level.

Ligands with greater ligand field strength are more stabilising?

Organic Chemistry

Isomerism is the property of two or more compounds (called isomers) having the same molecular formula but different arrangement of atoms.

	Type of isomers	Physical properties	Chemical properties
Structural isomers are compounds with the same molecular formula but different arrangement of atoms.	Functional group isomers contain different functional groups. They have different chemical properties.	Different	Different
	Chain isomers have the same functional groups but with different carbon backbones.	Slightly different (straight/branched chain)	Slightly different (different type of products)
	Positional isomers have the same carbon backbones but differ in the position of the functional groups.	Similar	Slightly different (different type of products)
Stereoisomers contain the same atoms bonded to one another, and the bonding and functional groups are identical, however they differ only in the way the atoms are arranged in 3-dimensional space.	Cis-trans isomers (geometrical isomers) have the same molecular and structural formula but different spatial arrangement due to the restriction of rotation about a multiple bond or about a ring. (cis - same side, trans - opposite side)	Cis-trans isomers may have different melting and boiling points if they have different polarities.	Almost identical
	Optical isomers (enantiomers) are molecules that have the same molecular and structural formula but different spatial arrangement of atoms. They contain a chiral carbon and they exist as non-superimposable mirror image of each other.	Identical except the direction they rotate in plane polarised light	Identical except in their interactions with another chiral molecule (different biological properties)

Commented [HK85]: Cyclohexene occurs only in the cis form. The introduction of a trans double bond in the 6 membered ring causes greater strain than the bond of the ring can accommodate.

Optical isomers (enantiomers) contain a **chiral centre** (a single atom with **four different groups attached** to it in tetrahedral directions / absence of a plane of symmetry)

Optical activity is the ability to rotate the plane of a plane-polarised light.

They have identical physical properties except in the direction they rotate in plane polarised light.

Solutions containing one enantiomer (or an excess over the other) are optically active as they rotate plane polarised light.

However a **racemic** mixture which contains equal amount amounts of each enantiomer is optically inactive.

Commented [THK86]: Can I have nitrogen to be the chiral centre?

They have identical chemical properties except in their interactions with another chiral molecule, and exhibit different biological properties.

Enzymes have specific configuration in the active site enzyme allows only substrates that have a complimentary structure to bind there, so they are very specific and can only work on one of the enantiomer and has no effect on the other. Hence enantiomers have different biological properties.

The (+) isomer of **thalidomide** is a very successful, non-toxic **sedative** that can be used for the treatment of **morning sickness**.

The other (–) enantiomer, however, can damage the foetus and result in **badly deformed babies**.

Commented [THK87]: Meso compounds

Comparing the acidity of ethanol, phenol and carboxylic acid

Ethanol is a **weaker** acid than water. The alkyl group is **electron donating**. This **further intensifies** the negative charge on the oxygen atom of the anion, thus **destabilising** the ethoxide ion. The dissociation to alkoxide ion and H^+ is not favoured.

Phenol is a **stronger** acid than water. The lone pair of electrons in oxygen in the phenoxide anion is **delocalised** into the **π -electron cloud** of the benzene ring, thus **dispersing** the **negative charge**, **stabilising** the phenoxide ion by **resonance**. The dissociation into the phenoxide ion and H^+ is **favoured**.

Carboxylic acid is a stronger acid than phenol. The p orbital of the C atom overlaps sideways with the p-orbitals of the 2 neighbouring O atoms, dispersing the negative charge of the carboxylate ion, **stabilising** of the carboxylate ion. The dissociation into the carboxylate ion and H^+ is favoured. As the charge dispersal between 2 O atoms in $-COO^-$ is more effective than between the O and C atoms in the benzene ring, $-COOH$ is **more acidic** than phenol.

The alkyl group (halide/carboxylic acid) is electron donating (withdrawing). This intensifies (further disperses) the negative charge on the carboxylate/phenoxide/ethoxide ion and destabilising it. The dissociation of the molecule to give the conjugate base and H^+ ions becomes less favourable. Hence the acid becomes weaker (stronger).

For benzoic acid, the p-orbital on the C-atom overlaps with the orbitals of the 2 neighbouring O as well as the π orbitals of the benzene ring. Hence the negative charge of the benzoate ion can be dispersed into the ring as well into the carbonyl group, resulting in the most stable conjugate base.

The **second** pK_a value is higher because it is energetically unfavourable to remove a positively charged H^+ from a negatively charged ion.

Comparing the basicity of ammonia, phenylamine and alkylamine

Amines (including ammonia) are basic because the lone pair of electrons on the N atom can form a dative bond with a proton to form an acid.

Alkyl group is **electron donating** and increases the **electron density** around the N atom in alkylamine.

This increases the **availability** of the lone pair on the N atom to accept a proton.

This results in a stronger base than ammonia.

The lone pair of electrons on the N atom in phenylamine is **delocalised into the π electron cloud** of the benzene ring.

This **decreases the availability** of the lone pair of electrons on the N atom to accept a proton.

This results in a weaker base than ammonia.

The electronegative Cl is an electron withdrawing group.

This causes a **greater extent of delocalisation** of the lone pair of electron on the N atom into the **π electron cloud** of the benzene ring.

The lone pair is now **even less available** to accept a proton, making chloroaniline a weaker base than phenylamine.

Commented [HK88]: The lone pair in phenol is not easily available because it is delocalised into the pi electron cloud.

Commented [HK89]: According to the K_a values, H_2CO_3 is a stronger acid than phenol. Hence H_2CO_3 will react with the phenoxide ion to form phenol.

Commented [HK90]: "The first deprotonation of oxalic acid forms a mono-anion which is stabilised by intramolecular hydrogen bonding, hence the dissociation lies much on the right and pK_1 is lower than that of formic acid."
"The presence of the electron withdrawing $-COOH$ group disperses the negative charge on the mono-anion."

Commented [HK91]: FYI
Some mono-anions formed are stabilised by intramolecular hydrogen bonding with the unionised $-COOH$ group, which has to be overcome during the dissociation of the second $-COOH$ group, resulting in an even higher second pK_a value.

In some compounds, intramolecular hydrogen bonding may be able to stabilize the conjugate base, making it more basic.

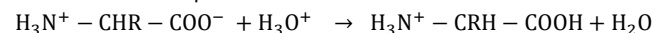
Commented [HK92]: Trimethylamine (tertiary amine) has 3 bulky alkyl substituents, which (sterically) hinder the formation of dative bond between the lone pair of electrons on the N atom and the proton / hinder approach of the proton. Hence, trimethylamine is less basic than methylamine (primary amine).

Amino acids and proteins

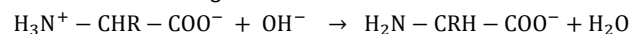
The proton of the --COOH group is donated to the --NH_2 group of the same molecule to give a zwitterion.

Amino acid zwitterions are amphoteric since they contain an **acidic functional group** NH_3^+ and a basic functional group --COO^- .

Zwitterions act as a base by accepting a proton from the acid to form a positive ion



Zwitterions act as an acid by donating a proton from the base to form a negative ion



The isoelectronic point pI is the pH at which an amino acid carries no net charge.

The **primary structure** refers to the sequence of amino acids held by **peptide** bonds in a polypeptide chain.

The **secondary structure** refers to the regular arrangement of the polypeptide chain in α -helices and β -pleated sheet, stabilised by hydrogen bonding between $\text{C} = \text{O}$ and $\text{N} - \text{H}$ groups of peptide bonds.

α -helix is a **regular coiled spiral polypeptide** chain held in place by intramolecular hydrogen bonds

between the $\text{C} = \text{O}$ group of the peptide bond and the $\text{N} - \text{H}$ group of the 4th peptide bond further down the protein chain.

As all the intramolecular hydrogen bonds are linear, this result in **maximum stability** as the total binding effect is strong.

All side chains point towards the outside of the helix and are perpendicular to the main axis of the helix.

The α -helix is **flexible and elastic**. When pulled, the α -helix elongates and the hydrogen bonds weaken.

When released, the hydrogen bonds reform and the α -helix returns to its original state.

β -pleated sheet consists of polypeptide chain arranged in a parallel fashion, running in the parallel or anti-parallel directions to each other, with hydrogen bonds formed between the chains.

They are **flexible but inelastic** as the chains of the amino acids are already extended.

Tertiary structure of a protein describes how the entire protein chain coils and folds into an overall three dimensional shape. It is held by:

van der Waals's forces between non-polar alkyl groups,

electrostatic forces of attraction between charged alkyl groups,

hydrogen bonding between polar R groups with N-H , O-H and C=O bonds

disulphide bonds between two cysteine $-\text{CH}_2\text{SH} + \text{HSCH}_2 - + [\text{O}] \rightarrow -\text{CH}_2\text{S} - \text{SCH}_2 - + \text{H}_2\text{O}$

Commented [HK93]: Note that in the zwitterion of lysine, the ammonium group is in the unconventional position (at the side group)

Commented [HK94]: Picture
Summarise

Commented [HK95]: Picture
Summarise

Quaternary structure of a protein describes how two or more polypeptide chains with tertiary structures come together to give large aggregate structures.

A haemoglobin molecule is a tetramer made up of four globular protein polypeptide chains / subunits, of which two are α -subunits (each with 144 amino acid residues) and two are β -subunits (each with 146 amino acid residues)

Denaturation of proteins involves the disruption of the **secondary, tertiary and quaternary** structures as these are held together by weak intermolecular interactions, resulting in the loss of protein function and changes in physical properties of the protein.

Solubility is drastically **reduced** as the protein chain **unfolds** and **exposes the hydrophobic R groups** to the aqueous surroundings.

Most enzymes **lose all catalytic activity** since a precise tertiary structure is required for the substrate to fit.

Heat overcomes the interactions that hold the secondary (hydrogen bonds), tertiary and quaternary structures (R group interactions).

Changing pH causes the acidic or alkali groups to protonate or deprotonate, breaking the electrostatic forces of attraction between charged R groups.

Heavy metal ions break the electrostatic forces of attraction between the charged R groups and **prevents the formation** of disulphide bonds by reacting with $-SH$ groups.

Commented [HK96]: Does it affect the bonds that are already formed?

Enzymes (amylase), which are protein, catalyse chemical reaction (hydrolysis of starch into maltose) in our bodies.

Protein (haemoglobin) is used to transport materials (oxygen) within our bodies.

Protein hormones (insulin) act as chemical messengers within and between cells for cell growth and co-ordination, in this case to control blood sugar level.

Miscellaneous

Carbon monoxide CO is formed from the incomplete combustion of fuel in car engine.

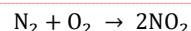
CO is very toxic to mammals as it **forms a stable compound with haemoglobin**, rendering it ineffective in transporting oxygen around the body.

Commented [HK97]: Refer to ligand – transition elements

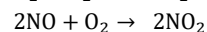
Unburnt hydrocarbons are carcinogenic and contribute to photochemical smog, which can cause respiratory problems.

At high temperatures (1000°C) inside the **engines**,

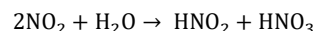
nitrogen and oxygen react to form nitrogen monoxide.



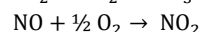
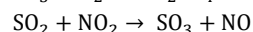
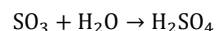
NO gas is readily oxidised into oxygen to form NO_2 gas.



NO_2 is a pungent acidic gas which contributes to acid rain.



Moreover, NO_2 **exacerbates** acid rain formation from sulfur dioxide by catalysing its oxidation to sulfur trioxide, and regenerating at the end of the mechanism.

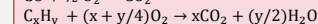
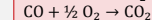
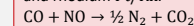


Commented [HK98]: FYI

(also covered in reaction kinetics)

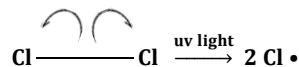
Catalytic converters speed up the conversion of pollutant gases to harmless gases by redox reactions.

They employ metals such as platinum Pt, or a mixture of platinum and rhodium Pt/Rh.



Free radical substitution

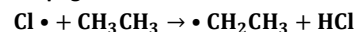
Initiation



under ultraviolet light or heat, the homolytic fission of Cl — Cl bond takes place and chlorine free radicals Cl • are formed.

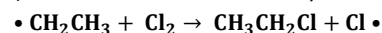
(H • is unlikely to be formed because it is highly unstable and therefore energetically unfavourable to be generated)

Propagation



The highly reactive chlorine free radical, on colliding with alkanes such as methane, **abstracts a hydrogen atom** to produce HCl and a dimethyl radical • CH₂CH₃.

(Iodoalkanes cannot be made by free radical substitution as the first propagation step is endothermic)



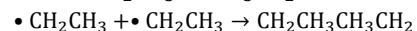
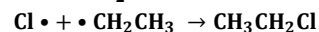
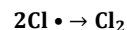
The dimethyl radical reacts further with another chlorine molecule. The product monochloromethane is produced and a chlorine free radical is **regenerated**.

Only a flash of ultraviolet light is required as the regenerated of chlorine free radical can react in the first propagation step leading to a **chain reaction**.

Commented [THK99]: Effect on product composition with prolonged radiation?
What is the rate equation and rate of reaction for this mechanism.

Termination

When any two free radical collides, the unpaired electrons pair up to form a stable product, **terminating the chain reaction**.



Terminations are highly exothermic as they involve bond forming only.

At any one time there is a **very low concentration** of free radicals, the **likelihood** of two radicals colliding is **small**.

As a free radical is highly reactive and can react with almost any molecule in the reaction mixture,

the chloroethane formed can undergo further substitution via the same mechanism to yield multi substituted halogenoalkanes in the propagation step.

Excess alkane or limited chlorine can be used to maximise the probability of chlorine radical colliding with the pentane molecule

and reduces the probability of the chlorine radical colliding with the monochloropentane formed that leads to a multi-substituted product.

Chlorine atoms abstract each primary and secondary hydrogen atoms with equal probability, however

due to the **inductive effect** of the alkyl groups, CH₃ — ĊH — CH₃ radical is more stable than CH₃ — CH₂ — ĊH₂ radicals,

secondary hydrogen atoms is more likely to be abstracted, resulting in a higher rate of formation of secondary radicals, and thus a deviation from the ratio.

Electrophilic addition

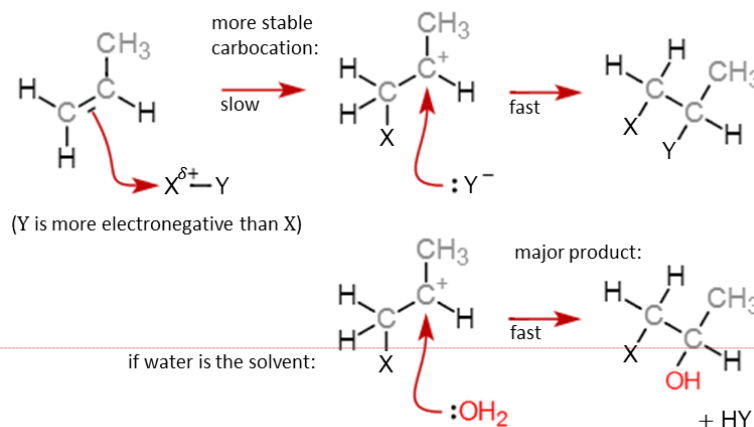
Markovnikov's rule:

the more stable carbocation has a **more substituted carbon** atom, because electron releasing alkyl group eases the positive charge on the carbocation.

For the addition of X_2 (aq.) to alkene:

the much higher concentration of water, a nucleophile,

results in the major product which also contains the hydroxyl group



Commented [HK100]: Also, in an organic compound contains a C atom with two -OH bonds attached to it, it is unstable, so it automatically becomes C=O instead.

Elimination of water

Saytzeff's rule:

the major product has a more substituted carbon (because it is more stable)

Nucleophilic substitution

S_N1

Applies to a **more substituted carbon**

because a more stable carbocation is formed in the first step.

Product is **racemic** (equal quantities of both enantiomers)

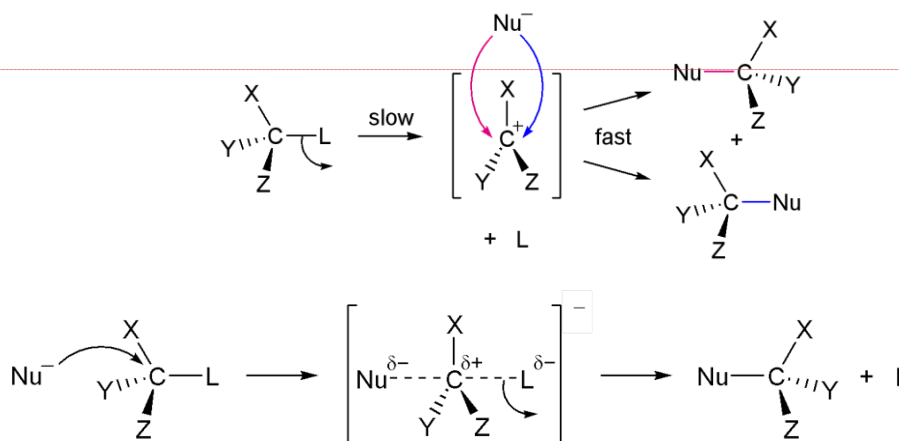
S_N2 :

Applies to a **less substituted carbon**

because there is less steric hindrance to the nucleophile

The mechanism has only one step.

If the carbon is chiral, the product's configuration is inverted



Commented [HK101]: In a halogenoalkene, in a C-X bond, if the same C is involved in a C=C bond, then the electrons from the X atom is delocalised into the pi C=C bond, strengthening the C-X bond, so making it unreactive. Pie orbital overlap.

The **carbon** of the acyl group is highly electron deficient because it is bonded to two highly electronegative atoms, oxygen and chlorine. This makes the carbon very susceptible to attack by nucleophiles, even a weak nucleophile like H_2O can hydrolyse it.

The more alkyl groups attached to the C atom bearing the X atom, the more crowded at the electrophilic C centre, the more difficult for the nucleophile to approach it. As alkyl groups are electron donating, the stability of carbocation increases with increasing alkyl substitution.

Determining the identity of halides

Aryl halides undergo hydrolysis, releasing the X^- ion. The X^- ion released forms a precipitate with Ag^+ from AgNO_3 .

Bond **strength** decreases from $\text{C} - \text{Cl}$ (340kJmol^{-1}) to $\text{C} - \text{Br}$ (280kJmol^{-1}) to $\text{C} - \text{I}$ (240kJmol^{-1}).

The ease at which these bonds break increases in this order, and also for the **rate** of reaction

$\text{C} - \text{F}$ (485kJmol^{-1}) bond is very strong and is difficult to break, hence no nucleophilic substitution occurs.

In $\text{C}_6\text{H}_5\text{Cl}$, the p-orbital on the Cl atom overlaps with the π -electron cloud of the benzene ring.

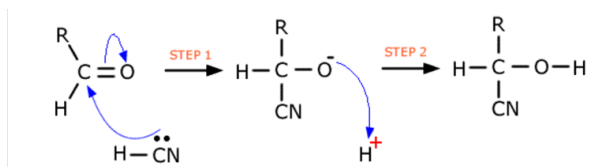
The lone pair of electrons on the Cl atom can delocalise into the ring, creating some **double bond character**. Hence, no substitution occurs and no ppt is formed.

The aryl carbon concerned bonded to chlorine does not undergo nucleophilic substitution.

The p-orbital on Cl overlaps with the π electron cloud of the aromatic ring.

The $\text{C} - \text{Cl}$ bond, having partial double bond character, is stronger and thus not easily **cleaved**.

Nucleophilic addition



The product is called a cyanohydrin.

Product is **optically inactive** because it is a racemic mixture as the nucleophile may attack the carbonyl carbon from either side with equal probability.

Commented [HK102]: The carbon atom in the acyl chloride is highly electron deficient as it is bonded to two highly electron withdrawing atoms, chlorine and oxygen. A weak nucleophile like H_2O and less harsh conditions allow for hydrolysis.

The carbon atom in the halogenoalkane is electron deficient because of the electron withdrawing effect of the halide atom. A strong nucleophile like OH^- and moderately harsh conditions like heating under reflux can result in hydrolysis

Commented [HK103]: Include electronegativity antithesis

The greater the difference in polarity of the C-X bond, the more susceptible the C atoms is to the attack by nucleophiles. However the two factors are in opposition. Bond strength is a more significant factor.

Commented [HK104]: From the notes and N1999:

Heat RX in a test tube with aqueous NaOH

Acidify resultant mixture with dilute HNO_3 to remove excess NaOH

Add aqueous AgNO_3

Why there is a matter with speed?

(rate of breaking bond only matter in hydrolysis, not formation of ppt I thought?)

Commented [HK105]: Halogenoalkane from alcohols - precursor to produce HX

$\text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow \text{HBr} + \text{NaHSO}_4$

Concentrated H_2SO_4 cannot be used to prepare HI because H_2SO_4 oxidises HI into I_2 .

Phosphoric acid and iodine is used instead to produce HI.

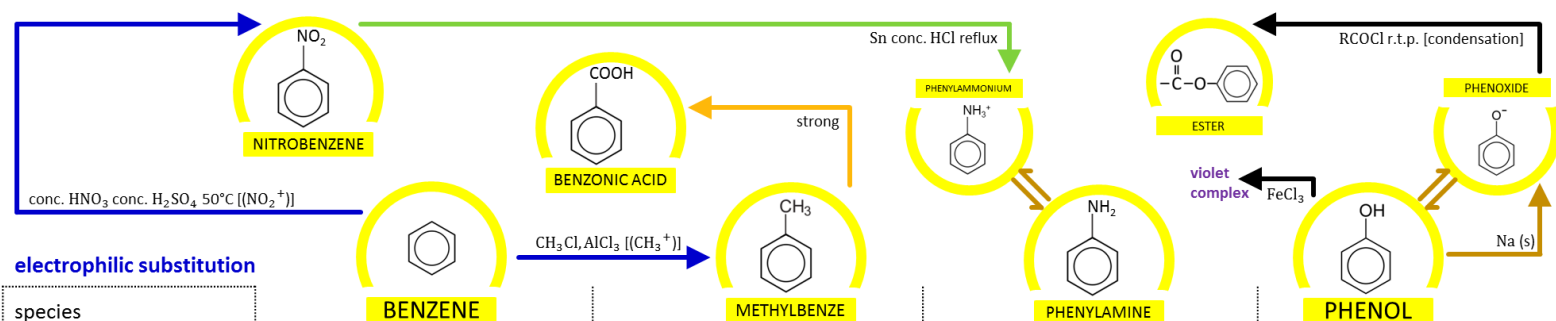
$3\text{ROH} + \text{PX}_3 \rightarrow 3\text{RX} + \text{H}_3\text{PO}_3$

$\text{ROH} + \text{PX}_5 \rightarrow \text{RX} + \text{POX}_3 + \text{HX}$

$\text{ROH} + \text{SOCl}_2 \rightarrow \text{RCl} + \text{SO}_2 + \text{HCl}$

Commented [HK106]: Step 1 is fast

H^+ is from H-CN

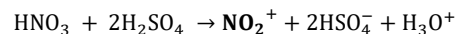


electrophilic substitution

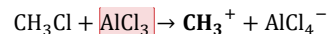
species		BENZENE		METHYLBENZE		PHENYLAMINE		PHENOL	
reactivity		—		weakly activating		strongly activating			
orientation		2,4,6 —directing							
—NO ₂	mono	conc. HNO ₃	50°C	conc. HNO ₃	30°C	dil. HNO ₃			
	tri	conc. H ₂ SO ₄ (to generate NO ₂ ⁺)	100°C	conc. H ₂ SO ₄ (to generate NO ₂ ⁺)	(warmer)	conc. HNO ₃			
—X	mono	X ₂ (l) FeX ₃ /AlX ₃ /Fe(s) (to generate X ⁺)				X ₂ in CCl ₄			
	tri	(at a higher temperature)				X ₂ (aq.)			

Electrophilic substitution

The electrophile E⁺ is first generated from the reactant and the Lewis catalyst.



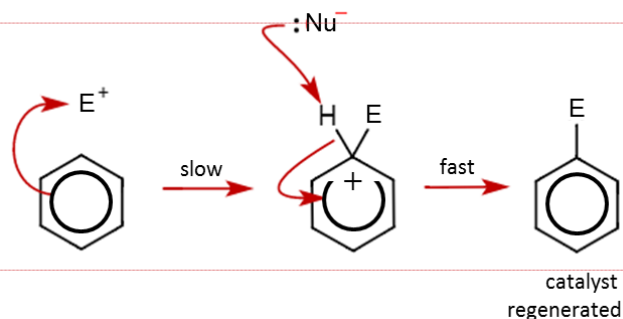
if generating the reactant in-situ: $2\text{Fe} + 3\text{X}_2 \rightarrow 2\text{FeX}_3$



The Lewis catalyst is regenerated at the end of the substitution.

In phenol/phenylamine, the **delocalisation** of the **lone pair of electrons** on O/N atom into the **π electron cloud** of the benzene ring makes it electron rich.

This makes phenol **more susceptible** to attack by electrophiles and hence it is not required to generate a strong electrophile (by AlCl₃) for this electrophilic substitution.



Commented [HK107]: Update booster pack. Then update this section

Commented [HK108]: It acts as a Lewis Acid catalyst because it only has 6 electrons around it and is electron –deficient; it can accept 2 more electrons from lone pair of Cl- to achieve an octet configuration.

Commented [HK109]: "If the first carbon, is a tertiary carbon (attached to 4 c atoms) then complete side chain oxidation does not occur."

