9647 H2 Chemistry

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!

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# 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

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.

**-orbital**: **spherically symmetrical** about the nucleus  
**-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 principal quantum shell Orbital quantum number type of subshell  
Magnetic Quantum number orbital of the subshell  
Spin quantum number up-spin / down-spin

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 orbitals **decrease more rapidly than other types** of orbitals.   
The **energy** of the orbital becomes **lower** than that of the orbitals, thus the  **orbital is filled before the orbital**.  
(However electronic configuration is **written** numerical order, despite that energy in orbital is lower than orbital, it is written as)

**Electrons** are **removed** in the **reverse order** that they are filled.However, despite that the orbital are **filled first** before the orbitals, the orbitals are **removed after** the 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 : Copper :   
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 valance 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

**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 : Magnesium :    
Boron : Aluminium : The electron from the () orbital in Boron (Aluminium) is **further to the nucleus** than the electron from the () orbital in Beryllium (Magnesium).  
Hence less energy is required remove the electron less strongly attracted to the nucleus.

Also, first ionisation energy also **decreases** between **Group V and VI**.  
Nitrogen : Phosphorous :   
Oxygen : Sulfur :   
The **paired electron** in the () orbital in Oxygen (Phosphorous) experience **more inter-electronic repulsion** in the configuration compared to   
the **unpaired electron** in the () orbital in Nitrogen (Sulfur).  
Hence less energy is required to remove the **paired** 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 electron is removed. The electron comes from an inner quantum shell.  
Hence there are () electrons in the outer shell)

# 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 extensive 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 larger the **charge size**, the stronger the electrostatic attraction. | The smaller the **ionic radius**, the stronger the electrostatic attraction.  The larger the **charge size**, the higher the density of **delocalised electrons**, the stronger the electrostatic attraction | The larger the **atomic** **size**, the larger and diffused the valance orbitals, the less strong the **strong electrostatic attraction** between the **bonding pair of electrons** and the **two bonding nuclei.**  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 is 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. |
| 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 orbitals of the carbon atom overlap continuously to form delocalized electron clouds which can act as mobile charge carriers to conduct electricity along the plane. |

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

Double bond – consists of a bond and a bond  
Triple bond – consists of a bond and two bond

Dative bond – a covalent bond which is formed when the shared pair of electrons is provided only be 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  
 atom has **low-lying**, **vacant 3d orbitals** to expand its octet of electrons to form double bonds with atoms.

Non-existence of   
 does not exist as atom **does not have vacant low-lying**/ energetically favourable orbitals to expand its octet.  
The other alternative would be for the atom to provide two electrons for **dative** bonds to atoms. However, the atom is **too electronegative** for dative bonding.

**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 | **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**.  The partial negative end of the temporary dipole in one molecule repels the electron cloud and induces an end and an end on another nearby molecule. | 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.  The **permanent separation of charges** results in a **partial positive and negative** charges that attract the nearby polar molecules. | 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**.  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. |
| Factors affecting strength of bond | Size of electron cloud From BF3 to BI3, the **electron cloud size increases**. The **electron cloud** is **more easily polarised**. This result in **stronger instantaneous dipole-induced dipole attraction** between molecules.  Shape of molecule  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. | Difference in electronegativities  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. | Extent of hydrogen bonding The hydrogen bonding between molecules (2 bonds per molecule) is more **extensive** than between molecules or between molecules (1 bond per molecule).  Electronegativity of atom bonded to  atoms have a higher electronegativity than and, there is stronger attraction between the lone pair on the atom, which the hydrogen is strongly attached to. |
| However, for molecules with considerable **difference in**, i.d.-i.d. is more significant. | |

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 –, and have higher melting and boiling points than expected in their corresponding groups.  
Anomalous relative molecular mass – ethanoic acid has an apparent of 120 instead of the expected 60.  
Some substances are miscible in water – by forming hydrogen bonds with water molecules.

**VSEPR (Valance 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.”

Bond angle of atoms that has four electron pairs but different number of lone pairs: **-109.5o -107o -105o** 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: 93o and 107o)   
Fluorine is more electronegative than hydrogen, drawing bonding electrons in bond towards.  
Less inter-electronic repulsion between the electron pairs around the atom, repulsion from the lone pair is comparatively more significant. Bond angle is smaller.

Modification 2 – **Electronegativity** of the central atom (example: 105o in and 92o in)   
Oxygen is more electronegative than sulfur, drawing bonding electrons in bond towards.  
More inter-electronic repulsion between the electron pairs around 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.

# Gaseous State

Ideal gas is a **hypothetical gas** whose pressure, volume and temperature are **completely described** by the ideal gas equation:  
Basic Assumptions of the Kinetic Theory  
**Volume of gas molecules** is **negligible** compared to the **volume it occupies**.  
**Intermolecular forcers 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.

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.

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**.

# Chemical Energetics

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | The amount of heat | absorbed or evolved | when molar quantities of reactants | | | | as shown in the chemical equation | | react together | | | under the standard conditions of 298K and 1atm. |
|  |  | when one mole of | a substance | | | in its standard state | | is formed from its constituent elements | | |
| (element) |  | absorbed | free gaseous atoms | | | | | is formed from its element | | |
| (compound) |  | a compound | | | | in the standard state | is broken into atoms of its  constituent elements in the gaseous state | | |
| Bond Energy |  | absorbed | a particular X-Y bond | | | | in a particular compound  in the gaseous state | is broken | | |
| 1st Ionisation Energy |  | absorbed | electrons | is removed | from one mole of | | gaseous atoms | to form one mole of | singly | charged gaseous cations. |
| 2nd Ionisation Energy |  | singly charged gaseous ions | doubly |
| 1st Electron Affinity |  | absorbed or evolved | is added | gaseous atoms | singly | charged gaseous anions. |
| 2nd Electron Affinity |  | absorbed | singly charged gaseous ions | doubly |
|  |  | evolved | a substance | | | | in its standard state | is completely burned in excess oxygen. | | |
|  |  | the solid ionic compound | | | | | is formed from its  constituent free gaseous ions. | | |
|  |  | water | | | is formed from neutralisation | | between an acid and a base. | | |
|  |  | free gaseous ions | | | is dissolved in an  infinite volume of water | | forming a solution at infinite dilution. | | |
|  |  | absorbed or evolved | a solute | | |

Equations

, and likewise for other elements

(Mass of the solution only)

**Hess’ Law** (of Constant Heat Summation) states that 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 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 – – 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 is the free energy for a reaction when it occurs under standard conditions.

(assuming and 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).

# 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’**. | | | **Extremely high**  It has a **giant molecular structure** with **strong, extensive covalent bonds** between the **atoms**. | **Low**  They have **simple molecular structures** with only  **weak van der Waals’ forces of attraction** holding the **discrete molecules** together. | | |
| Increase from Na to Al because more delocalised electrons are available for metallic bonding which results is stronger electrostatic forces of attraction. | | | 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. | | | **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. | | |
| Electrical conductivity increases from Na to Al as the number of delocalised electrons increases. | | |
| 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 to, there is an additional **third quantum shell** which is screened. Thus ionic radius increases from to. | | | | | | |

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Oxides |  |  | |  | |  | |  | |  |
| 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 | Very rigorous, bright white flame | | Rigorous,  white flame | | Heat required | | Rigorous reaction  In excess oxygen: | | Heat required  In excess oxygen: |
|  | 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 valance electrons to oxygen atom to form metal ions and basic oxide ions | | | \*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 |  |  | |  | |  | | Dissolves readily in water  to give strongly acidic solutions | | |
|  | |  |
| Reaction with water/alkali | Dissolves readily to give, which dissociates completely. | Dissolves sparingly to give a white suspension of which dissociate partially to give a weakly alkaline solution. | |  | |  | |  | |  |
| Oxidation number |  |  | |  | |  | |  | |  |
| Always positive because oxygen and chlorine are more electronegative | | | | | | | Several O.N. as have energetically available **subshells** for the **expansion** of the octet to accommodate more than 8 electrons. | | |
| Chlorides |  | |  | |  | |  | |  | |
| Melting point | **High –** they have **giant ionic lattice** with **strong electrostatic forces of attraction** between the **ions** | | | | similar to simple molecules | | | | | |
| formation | Very rigorous | | Rigorous | | Rigorous | | Heat required | | Rigorous reaction  In excess chlorine | |
| Reaction with water | Dissolves to form a neutral solution | | ions are hydrated to | | ion are hydrated to | | Reactions are very rigorous with fumes of gas produced which results in strongly acidic solutions. | | | |
|  | | Limited amount of water:  Large amount of water: | |
| The high charge density and polarises and weaken the bond in water molecules which encourages deprotonation to produce to form a slightly acidic solution | | | |
|  | |  | |
| pH | 7 | | 6 | | 2 | | 1 | | 1 | |

The large electronegativity difference of and oxygen makes an ionic compound.  
 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.  
 has a **large ionic radius** which has valance 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 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. | | | |
| 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. | | | |
| 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.  Down the group, the **ionic radius** of increases.  As a result, the **charge density** of decreases, the ions become **less polarising**. The electron cloud of // anion is **less distorted**.  The / / covalent bond within the // 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 | very pale yellow | very pale green | reddish brown | violet |
| Colour in |  | 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 ( and) to liquid () to solid ().  Halogens exist as simple molecules of.  As the molecular size of 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 themolecules, requiring more energy to overcome these intermolecular forces. | | | |
| **Relative reactivity** of the elements as oxidising agents |  |  |  |  |
| has the most positive electrode potential, it has the greatest tendency to accept electrons, it undergoes reduction most readily. | Down the group, becomes less positive. The ease of reduction decreases. There is a lower tendency for to be reduced into. The oxidising power of halogens decreases from to.  Each halide ion can be oxidised by the halogen above it. | | |
|  | The oxidation number of sulfur increases from +2 to +6. | | O.N. increases from +2 to +2.5. |
| reactions of halide ions with:  concentrated sulfuric acid | When solid halides are heated with concentrated, is produced. | | | |
| Concentrated is not able to oxidise the formed. | | Concentrated oxidises the formed. | |
|  |  |
| Steamy fumes of observed. | | Brown fumes of observed. | Purple fumes of observed. |
| aqueous silver ions followed by aqueous ammonia | Silver halide is precipitated when halide ions react with aqueous sliver nitrate. | | | |
| No ppt | White ppt | Cream ppt | Yellow ppt |
|  | | |
| Adding of removes free, decreases, position of equilibrium shifts to the left. | | |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Reactions** of the elements **with hydrogen** |  |  |  |  |
|  |  |  |  |
| Very rapid reaction, explodes with  under all conditions | Rapid reaction, explodes with  in the presence of light | Slow reaction, heat at 200oC  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 bond formed decreases.  Less energy is evolved when is formed. | | | |
| **Relative thermal stabilities of the hydrides** | Do not decompose under heat. | | Decomposes slightly under heat  Brown fumes of observed. | Easily decomposed under heat. Gives out dense purple fumes of on gentle heating. |
| Down the group, the atomic radius of increases, the bonding pair of electrons is further away from the nuclei of and. Bonding electrons are less strongly attracted to the nucleus. bond becomes weaker. bond energy increases. | | | |
| is extremely soluble in water.  In aqueous solution, the bond is broken and the hydroxonium ions are formed.  is a very weak acid, not only because of the high bond energy of, but also because forms hydrogen bonds with water and other HF molecules. | | | |

When reacts with, it undergoes disproportionation.

Cold (15oC) aqueous  
The oxidation state of increases from in to in chlorate(I), and decreases from in to in chloride.

Hot (70oC) aqueous  
The oxidation state of increases from in to in chlorate(V), and decreases from in to in chloride.  
The chlorate that was first produced undergoes further disproportionation to form chloride and chlorate (V)

# 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/ 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/.

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. Kc 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**,  
 increases/decreases, increases/decreases, total pressure of the gas mixture decreases. 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 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 increases/decreases. (Subsequently for temperature decrease)

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 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 450oC is used to obtain an optimum yield of 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 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 / does not include solids (because it has a constant density, therefore it has no effect on pressure/concentration)  
In a homogeneous equilibrium (esterification/hydrolysis), include the concentration of water.  
In a heterogeneous equilibrium (acid-base), 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 () donor  
a **base** is a proton () 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. A **weak** acid/base undergoes **partial dissociation** in water.

The degree of dissociation refers to the fraction of molecules which is ionised in water.

, and degree of dissociation 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 or, 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 ().

For weak acids,

For weak bases,

Decrease of 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**.   
increases. As and, and decreases.   
Since, decreases.

Total **yield** of hydrogen gas of **weak vs. strong** acid  
 is a strong acid that undergoes complete dissociation to give moles of ions to form volume of .  
 is a weak acid that undergoes partial dissociation. However is removed by reacting with (metal).  
**As decreases, dissociation of is shifted completely to the right.**  
Eventually all will dissociate, producing the same amount of as, forming the same amount of .

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

Acidic buffer Alkaline buffer  
Small amount of added:   
Small amount of added:

At the maximum buffer capacity,

An indicator is a weak acid; the acid is a different colour from its conjugate base.  
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 change over the equivalence point.  
The of the indicator matches the rapid pH change of the titration curve at the equivalence point.

# Solubility

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

|  |  |  |  |  |  |  |  |  |  |  |  |
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| // |  |  |  |  |  |  |  |  |  |  | // |
|  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  | soluble in hot water | | |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |

is known as solubility product, and is dependent on the ionic formula of the salt. It is constant at constant temperature.  
   
It is valid for sparingly soluble salts only.

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

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

When,   
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 due to the added, the **position of the equilibrium will shift** to the left to remove the extra ions.   
This will result in precipitation of the salt .

# Reaction Kinetics

**The rate of reaction** is how the concentration of a product increases (OR how the concentration of reactant decreases) with time.   
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.  
()   
 is the rate constant (and its unit is such that the equation is homogenous)   
The reaction is in order with respect to. 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)

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.

Derivation of **Rate Equation** from experimental data

Inspection method using **rates**  
“Comparing expt 1&3, when increases to, initial rate increases to. Hence, reaction is 1st order w.r.t.”  
“Without a change in, the rate of reaction should decrease to, as reaction 1st order w.r.t. . Hence reaction is zero order w.r.t.”

The **rate-concentration**n graph  
**Straight line** through origin implies rate is order w.r.t. concentrationn

**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   
-time graph can be deduced from -time graph, however the final needs to be known.

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

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 by peroxodisulphate) (**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.  
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** in 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 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. (’ < )  
More molecules have energies greater than or equal to the lowered activation energy (area under curve above increases)   
This results in an increase in the frequency of effective collisions. The rate of reaction increases (higher value).

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: in the oxidation of into that forms acid rain)  
The reactant and the catalyst combine to form a **reactive intermediate**.   
The product is formed with the **regeneration** of the catalyst.   
The activation energies are much lower than the uncatalysed reactions.  
Another example of homogenous catalyst is in the formation of by peroxodisulphate.

**Autocatalyst** is a product of the chemical reaction that can catalyse the reaction as well.  
 in the redox reaction between and

**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 **complimentary structure** to bind there.   
Hence enzymes are very **specific** in the type of reaction they catalyse.  
Enzymes + substrate Enzyme substrate complex  
Enzyme-substrate complex Enzyme-products complex (slow)   
Enzyme-products complex 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.

# Electrochemistry

The standard electrode potential 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 dm3 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 dm3, with hydrogen gas bubbling in at a pressure of 1 atm and 298K. The standard electrode potential of SHE is defined to be zero.

The standard cell potential is the **maximum** potential difference between two half-cells which are operated under standard conditions.

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. (The reaction is not feasible if) To calculate:

Reaction is feasible.   
 is reduced to, is oxidised into :

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 is more / less positive than.  
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.

One Faraday is the charge on one mole of electrons.

The fuel cell  
Electrolyte: hot conc. (aq.)   
Electrodes: Carbon with a sprinkling of platinum  
At the anode:   
At the cathode :

Anodising of aluminium (for corrosion resistance and decoration)  
At the cathode (steel):   
At the anode (aluminium object):   
Oxygen released at the anode oxidises the aluminium, artificially thickening the surface oxide layer to about 20 micrometres.

Purification of copper  
Electrolyte: (aq.)   
The cell potential is adjusted such that dissolves.  
At the anode (impure copper):   
Impurities with values which are less positive than dissolves, while impurities with values which are more positive than remain undissolved  
At the cathode (purified copper):

Electrolysis of brine  
Electrolyte: Purified brine (concentrated)   
At the anode (titanium): (electrode preferred due to the corrosive nature of)  
At the cathode (steel):

The porous asbestos diaphragm prevents the mixing of (formed at the cathode) and (formed at the anode), which disproportionate to and.  
It also serves to prevent highly reactive (formed at the cathode) and formed at the anode from coming into contact as they can be sold as useful chemical separately.  
Purification of brine is necessary to remove and which would precipitate insoluble hydroxides and block the pores of the diaphragm.

Relationship between electrochemistry and thermodynamics:   
A positive indicates a spontaneous reaction and the reaction is likely to be exothermic.

# 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 |  |  |  |  |  |  |  |  |  |  |
| Electronic configuration |  |  |  |  |  |  |  |  |  |  |

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 and 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.  
(have a low melting point among transition metals because **electrons in the half-filled subshell are stable** and thus not readily available for metallic bonding.)

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

The **transition elements** have **variable oxidation states** because and electrons are similar in energy.  
Once the 4s electrons are removed, some or all the electrons may also be removed or shared without requiring much more energy.   
The **maximum** oxidation state corresponds to the sum of the **number of and unpaired electrons**.

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 sate at the end of the catalysed reaction.   
The reaction is **thermodynamically feasible** () but **kinetically slow** (**high activation energy**) due to **electrostatic repulsion** between **two negatively charged ions**.  
 acts as a catalyst by providing an alternative reaction pathway **via the intermediate**:   
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 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 |  |  |  |
| Catalyst |  |  |  |

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 orbitals of low energy level** that can accommodate electrons donated by the ligands.  
**Ligands** are neutral molecules or anion which process **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 have **more available lone pair** than ligands such as, as **effective nuclear charge** on is less than on 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 (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, is displaced and released to the cells.

Stronger ligands such asmolecules **interact irreversibly** with atom in the haem group. Compared to the dative bond, the**dative bond** is stronger which **better** **stabilises** the iron (II) centre and **cannot** be broken easily. Hence poisons the haemoglobin and disables bonding with.

Depending on the **ionic radius/charge density/polarising power** of the metal ion, the aqua complexes (metal ion with ligands)   
undergo hydrolysis (due to weakening of covalent bond), forming an acidic solution.

When(aq.) is added, deprotonates free molecules into ions. ions is **precipitated** as **pale blue** .

Upon adding excess (aq.), molecules **displace** molecules by making a **stronger dative bond** with copper (II) ion, forming

This result in to decrease, by le Chatelier’s principle, the position of equilibrium shifts to the left to increase.   
Hence the pale blue precipitate dissolves forming **a deep blue solution**.

Under **ligand field influence**, the orbitals of is split into **two** levels.  
The energy gap 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-orbital to a vacant higher energy level-orbital in a- transition.  
The **colour** of the complex ion observed is the **complement** of the colours that are absorbed.

and are **colourless** because the energy required for electronic transition from to is **large** and falls **outside** the energies of the **visible light spectrum**.   
, and are colourless because they have a **fully filled subshell** which do not allow for a - transition of an electron.

Spectrochemical series:   
 has greater **ligand field strength** as compared to.  
 absorbs light in the orange region of the spectrum and so it appears **turquoise**.   
 absorbs light in the yellow region (which is of smaller wavelength due to larger) of the spectrum and so it appears **deep blue**.

Formation of complexes can affect the relative stabilities of oxidation states in transition metals.  
 is less readily reduced to when it is bonded to ligands.   
As the lone pair of electrons on the ligand is more available than the, the **cobalt metal centre** of is **more electron rich** than,   
making the former less likely to accept an electron.  
 is also **negatively charged** so it is less likely to accept an electron to undergo reduction.

# 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) |

**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.

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**.

**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 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**-electron cloud** of the benzene ring, thus **dispersing** the **negative charge**, **stabilising** the phenoxide ion by **resonance**. The dissociation into the phenoxide ion and is **favoured**.

**Carboxylic acid** is a stronger acid than phenol. The orbital of the atom overlaps sideways with the-orbitals of the 2 neighbouring atoms,   
dispersing the negative charge of the carboxylate ion, **stabilising** of the carboxylate ion. The dissociation into the carboxylate ion and is favoured.  
As the charge dispersal between 2 atoms in is more effective than between the and atoms in the benzene ring, 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 ions becomes less favourable. Hence the acid becomes weaker (stronger).

For benzoic acid, the-orbital on the-atom overlaps with the orbitals of the 2 neighbouring as well as the 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 value is higher because it is energetically unfavourable to remove a positively charged 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 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 atom in alkylamine.  
This increases the **availability** of the lone pair on the atom to accept a proton.  
This results in a stronger base than ammonia.

The lone pair of electrons on the atom in phenylamine is **delocalised into the electron cloud** of the benzene ring.  
This **decreases the** **availability** of the lone pair of electrons on the atom to accept a proton.  
This results in a weaker base than ammonia.

The electronegative is an electron withdrawing group.  
This causes a **greater** **extent of delocalisation** of the lone pair of electron on the atom into the  **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.

**Amino acids and proteins**

The proton of the group is donated to the group of the same molecule to give a zwitterion.   
Amino acid zwitterions are amphoteric since they contain an acidic functional group and a basic functional group.  
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 is the 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 and groups of peptide bonds.

α-helix is a **regular coiled spiral polypeptide** chain held in place by intramolecular hydrogen bonds   
between the group of the peptide bond and the 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

**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 tetrameter 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 breaks the electrostatic forces of attraction between the charged R groups and prevents the formation of disulphide bonds by reacting with –SH groups.

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 is formed from the incomplete combustion of fuel in car engine.  
 is very toxic to mammals as it **forms a stable compound with haemoglobin**, rendering it ineffective in transporting oxygen around the body.

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

At high temperatures (1000oC) inside the engines,  
nitrogen and oxygen react to form nitrogen monoxide.   
 gas is readily oxidised into oxygen to form gas.

is a pungent acidic gas which contributes to acid rain.

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

# Free radical substitution

**Initiation**   
under ultraviolet light or heat, the homolytic fission of bond takes place and chlorine free radicals are formed.  
( is unlikely to be formed because it is highly unstable and therefore energetically unfavourable to be generated)

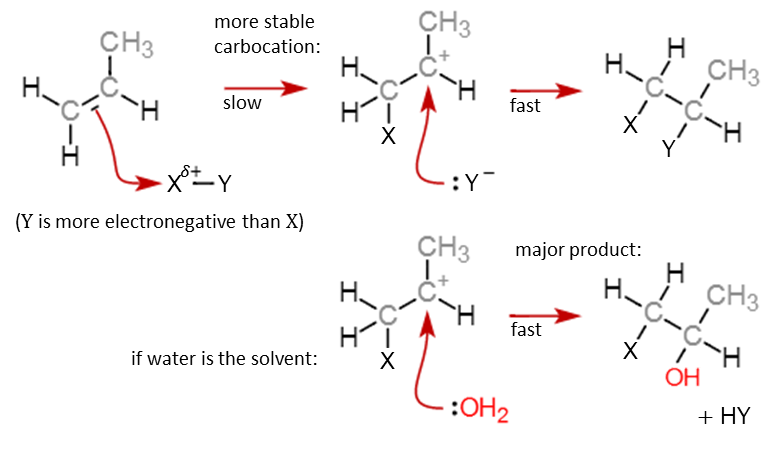
**Propagation**  
The highly reactive chlorine free radical, on colliding with alkanes such as methane, **abstracts a hydrogen atom** to produce and a dimethyl radical.  
(Iodoalkanes cannot be made by free radical substitution as the first propagation step is endothermic)  
The dimethyl radical reacts 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**.

**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, radical is more stable than 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 (aq.) to alkene:   
the much higher concentration of water, a nucleophile,   
results in the major product which also contains the hydroxyl group

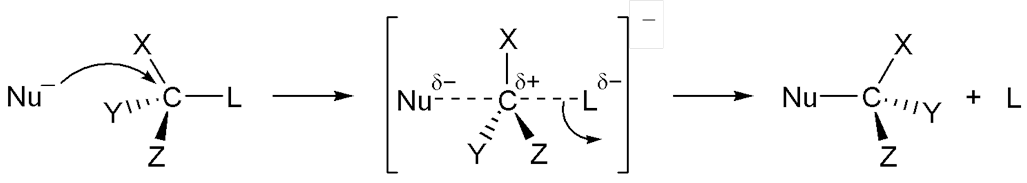
**Elimination of water**

Saytzeff’s rule:   
the major product has a more substituted carbon (because it is more stable)

# http://upload.wikimedia.org/wikipedia/commons/b/bb/SN1_reaction_mechanism.pngNucleophilic substitution

SN1  
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)

SN2:   
Applies to a **less substituted carbon**   
because there is less stearic hindrance to the nucleophile

The mechanism has only one step.

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

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 can hydrolyse it.

The more alkyl groups attached to the atom bearing the atom, the more crowded at the electrophilic 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.

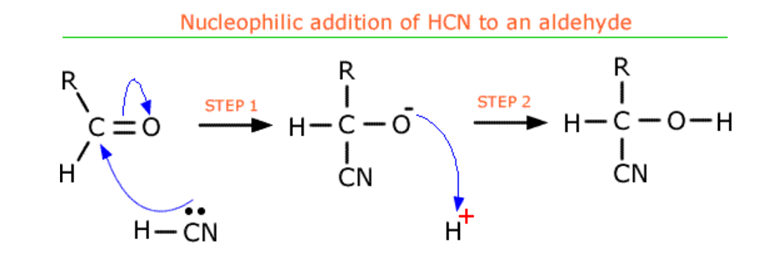
**Determining the identity of halides**

Aryl halides undergo hydrolysis, releasing the ion. The ion released forms a precipitate with from.  
Bond strength decreases from (340kJmol-1) to (280kJmol-1) to (240kJmol-1).   
The ease at which these bonds break increases in this order, and also for the rate of reaction

(485kJmol-1) bond is very strong and is difficult to break, hence no nucleophilic substitution occurs.  
In, the-orbital on the atom overlaps with the-electron cloud of the benzene ring.  
The lone pair of electrons on the 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-orbital on overlaps with the electron could of the aromatic ring.   
The bond, having partial double bond character, is stronger and thus not easily cleaved.

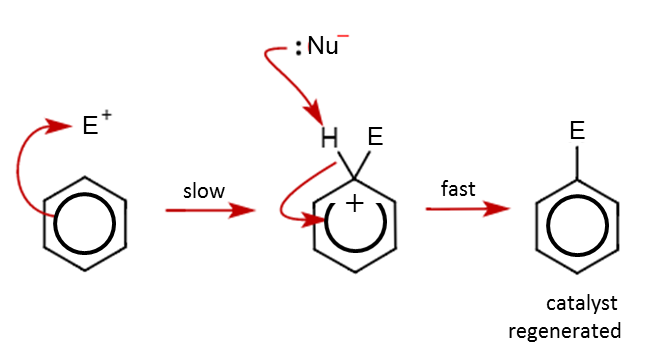
# Nucleophilic addition

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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.

# Flowchart for aromatic reactions

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# Electrophilic substitution

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

if generating the reactant in-situ:

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

In phenol/phenylamine, the **delocalisation** of the **lone pair of electrons** on / 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) for this electrophilic substitution.

# Flowchart for aliphatic reactions