

First Edition



# AS Level Chemistry

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# Physical Chemistry

## Atomic Structure

### Structure of an Atom

- An atom is the smallest particle of an element that can exist independently
- an atom consists of a nucleus with protons and neutrons, electrons orbit around the nucleus
- protons are positively charged, neutrons have no charge, electrons are negatively charged
- the nucleus has an overall positive charge
- an atom has an overall neutral charge

### Subatomic particles

- The protons, neutrons, and electrons in an atom are subatomic particles
- their masses and charges are measured in relation to each other
- Such as Relative Atomic Mass and Relative Atomic Charge

Subatomic Particle	Relative Atomic Charge	Relative Atomic Mass
Proton	+1	1
Neutron	0	1
Electron	-1	1/1836

### Atomic Number and Mass Number

- *Atomic Number/Proton Number* is the number of protons in the nucleus of an atom
- The atomic number is equal to the number of electrons in a neutral atom
- The *Mass Number/Nucleon Number* is the total number of protons and neutrons in an atom
- The number of neutrons can be calculated by *Mass Number - Atomic Number*

### Atomic Radius

- The atomic radius of an element is half the distance between the two nuclei of covalently bonded atoms of the same type
- The atomic radius generally decreases across a period and increases down a group
- The atomic radius decreases across the period because with higher proton number there is higher nuclear charge and more electrons are added in the same quantum shell with approximately constant shielding, resulting in greater attraction between nucleus and electrons, pulling them closer.
- Down the group, the quantum shells increase and there is increased shielding, resulting in greater atomic radius.

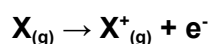
### Ionic Radius

- Size of cation is always smaller than that of its parent atom
- Size of anion is always greater than that of its parent atom
- Size of cation is always lesser than the size of anion provided they are in the same period.

### Ionisation Energy

- Ionisation energy is the amount of energy required to remove one mole of electrons from one mole of gaseous atoms of an element to form one mole of gaseous ions
- Ionisation energy is measured under standard conditions of temperature and pressure
- The unit of I.E is Kilo joule per mole ( $\text{KJmol}^{-1}$ )
- Ionisation energy is always endothermic as we are breaking the electrostatic force between proton and electron
- The first ionisation energy is the amount of energy required to remove one mole of electrons from one mole of isolated gaseous atoms to form one mole of  $1+$  ions

The first I.E of an element X can be represented by the equation:



- Second I.E is always larger than the first I.E as upon removing electrons radius will become smaller, and there will be less repulsion, and greater nuclear force of attraction thus we need more I.E for the removal of second electron

### Factors affecting Ionisation Energy

- The ionisation energy increases across a period and decreases down the group
- The I.E depends on factors of atomic radius, nuclear charge, shielding effect, and spin-pair repulsion

**Atomic Radius:** As the electrons get further from the nucleus, they experience lesser attraction from the nucleus and are easier to remove

**Nuclear Charge:** As the nuclear charge increases, the electrons experience greater force of attraction and are more difficult to remove

**Shielding Effect:** Electrons repel each other so the inner quantum shell electrons pushes the outer quantum shells away from the nucleus, reducing the nuclear attraction and making the electrons easier to remove

**Spin pair repulsion:** it occurs when two electrons are paired in the same orbital, they repel each other making one electron easier to remove

- Across a period, the nuclear charge increases, which results in stronger attraction between the nucleus and electrons, pulling the electrons closer and decreasing the atomic radius, the shielding effect remains constant as the electron shell is the same. This requires more energy to remove an electron, increasing the I.E
- Down the group, the atomic radius and shielding effect increases, which decreases the I.E

### Ionisation Energy trends (Exceptions)

- An increase in subshell will decrease the I.E as outer subshell electrons are further away from the nucleus such as between Beryllium and Boron
- Another example would be Magnesium and Aluminium
- There is a decrease in I.E when a second electron enters the px subshell as it experiences spin-spin repulsion make it easier to remove an electron such between Nitrogen and Oxygen
- Another example would be Phosphorus and Sulfur
- There is a large decrease in ionisation energy between the last element in a period and the first element of the next to the change in quantum shell

### Successive Ionisation Energies of an Element

- The successive ionisation energies of an element increases
- it is harder to remove an electron from an ion as compared to its neutral atom
- this is due to the decreased shielding effect and increased nuclear attraction
- A change in quantum shell causes a large increase in successive ionisation energy
- The large jump can be used to deduce the group number of an element
- For example, a large increase between the third and fourth I.E indicates that the element belongs to group 3

### Isotopes

- Isotopes are atoms of the same element that contain the same number of protons but different number of neutrons
- An Isotope is represented by the name of the element followed by dash and mass number
- For example Carbon-12
- Isotopes have similar chemical properties but different physical properties
- Due to the same number of electrons, isotopes react in the same manner
- Due to the different number of neutrons, isotopes have differences in mass and density

### Electron Shells

- Electronic configuration is the arrangement of electrons in an atom
- Electrons are arranged around the nucleus in principal energy levels or principal quantum shells
- The energy level or quantum shell is represented by the Principal Quantum Number (n)
- A higher principal quantum number means the shell is further from the nucleus
- Each quantum shell can hold a fixed number of electrons

### Subshells

- The principal quantum shells are split into subshells
- Subshells are represented by s, p and d
- The energy of the subshells increases in the order  $s < p < d$
- s subshell contains 2 electrons
- p subshell contains 6 electrons
- d subshell contains 10 electrons

### Orbitals

- Subshells contain one or more atomic orbitals
- Orbitals exist at specific energy levels and electrons can only be found at these specific levels
- Each orbital can have a maximum of 2 electrons
- Hence, s subshell has 1 orbital, p subshell has 3, and d subshell has 5
- Each orbital has a specific shape
- the three orbitals of p subshell are  $p_x$ ,  $p_y$  and  $p_z$

n	Electrons ( $2n^2$ )	Subshells
1	2	$1s^2$
2	8	$2s^2, 2p^6$
3	18	$3s^2, 3p^6, 3d^{10}$
4	32	$4s^2, 4p^6, 4d^{10}, 4f^{14}$

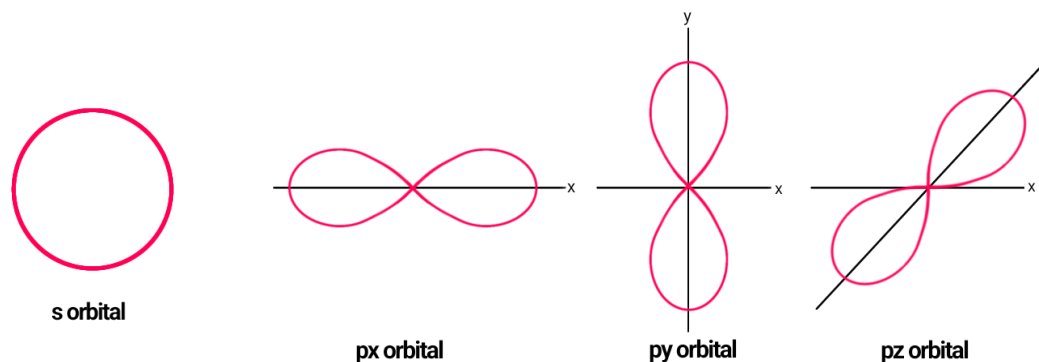
### Ground State

- The Ground state is the most stable electronic configuration of an atom which has the lowest amount of energy
- The subshells with lower energy levels are filled first
- The pattern is disrupted at quantum shells  $n=3$  and above
- 4s has a lower energy level than 3d and hence is filled first
- Orbitals in the same subshell have the same energy and are known as degenerate
- $p_x$ ,  $p_y$  and  $p_z$  all have the same energy levels



## S & p orbitals

- s orbitals are spherical in shape
- the s orbitals are bigger at a higher principal quantum number
- p orbitals are dumbbell shaped
- every p subshell has 3 orbitals except for when  $n=1$
- the p orbitals become larger and longer with increasing quantum number



## Electronic Configuration

- subshells are filled in increasing order of energy levels
- electrons are spinning charges rotating clockwise or anticlockwise about their own axis
- electrons with similar spin repel each other, causing spin-pair repulsion
- electrons occupy different orbitals in the same subshell first to avoid spin-pair repulsion
- they are paired when there are no more empty orbitals
- the paired electrons spin in opposite directions to minimise repulsion
- if there are three electrons in the p subshell, all three orbitals will have one electron each
- a fourth electron in the p subshell will pair in px subshell

## Periodic Table Blocks

- Group 1 and 2 elements are known as s block elements
- s block elements have their electrons in an s subshell
- Group 13 to 18 elements are p block elements
- their valence electrons are located in the p subshell
- Transition block elements are d block elements
- Their valence electrons are in the d subshell

## Exceptions

- Copper has configuration  $3d^5, 4s^1$  instead of  $3d^4, 4s^2$
- Chromium has configuration  $3d^5, 4s^1$  instead of  $3d^4, 4s^2$
- This is because the configuration is more stable when the d subshell is half full or full as compared to having one lesser, so one electron moves from 4s subshell to 3d subshell

# Moles & Stoichiometry

## Relative Mass

- *Relative Atomic Mass* is the average mass of all the isotopes of an element relative to 1/12th of the mass of Carbon-12
- *Relative Molecular Mass* is the average mass of a molecule of an element or compound relative to 1/12th of the mass of Carbon-12
- *Relative Formula Mass* is the average mass of a formula unit of an ionic compound relative to 1/12th of the mass of Carbon-12
- *Relative Isotopic Mass* is the mass of an isotope of an element relative to 1/12th of the mass of Carbon-12

## Mole and Avogadro Constant

- One mole of any substance contains  $6.02 \times 10^{23}$  atoms
- This number is known as Avogadro's constant
- One mole of a substance has mass equal to its Relative Atomic or Molecular Mass
- One mole of a gas at room temperature and pressure occupies  $24 \text{ dm}^3$  volume

## Formulae

- Moles =  $\text{Mass} / A_r$  or  $M_r$
- Moles =  $\text{Volume} \times \text{Concentration} / 1000$
- Moles =  $\text{Volume of gas at r.t.p} / 24$
- Percentage Yield =  $\text{actual mass} / \text{predicted mass} \times 100$

## Empirical and Molecular Formula

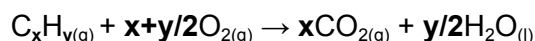
- Empirical formula is the simplest whole number ratio of atoms in a molecule
- Molecular formula is the actual number of atoms of all the elements present in a molecule

## Steps to Calculate Empirical Formula

- Divide the mass of the elements present by the atomic mass to get the moles
- Divide all the values calculated by the smallest value calculated to get ratio
- The ratio corresponds to the number of atoms of each element in the Empirical Formula

## Combustion

- Combustion is the burning of a substance in air ( $\text{O}_2$ )
- General equation for combustion of gaseous Hydrocarbons:





# Chemical Bonding

## Electronegativity

- Electronegativity is the ability of an atom to attract or gain electrons
- Fluorine is the most electronegative atom
- Hydrogen is the least electronegative non-metal

## Electronegativity Factors & Trends

- Electronegativity increases left to right across a period
- Electronegativity decreases down the group
- Increased nuclear charge results in increased electronegativity
- Increased atomic radius results in decreased electronegativity
- Increased shielding through increased quantum shells or subshell will decrease electronegativity
- Metals are less electronegative than nonmetals

## Electronegativity and Bonding

- A large difference in electronegativities between bonded atoms means the bond is ionic
- Small or no difference means the bond is covalent

## Bond Energy

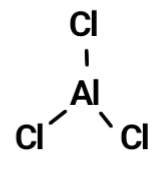
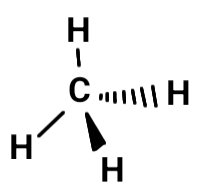
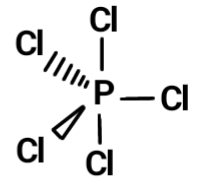
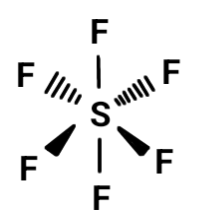
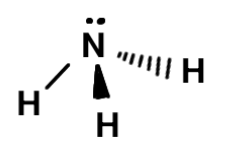
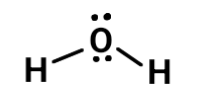
- It is the energy required to break one mole of a covalent bonds in gaseous state
- Bond Energy has units  $\text{KJmol}^{-1}$
- Bond Energy is always endothermic
- The higher the bond energy, the stronger the covalent bond

## Bond Length

- It is the distance between the nuclei of two covalently bonded atoms
- The greater the nuclear attraction, the lesser the bond length
- The lower the bond length, the stronger the covalent bond
- Hence, the lower the bond length, the higher the Bond Energy

## Shapes of covalent molecules

- The shapes of covalent molecules are predicted by the Valence Shell Electron Pair Repulsion Theory (VSEPR)
- Electrons are negatively charged and repel each other when close
- The repulsion in bonding pair of electrons a molecule causes it to adopt a shape to minimise the repulsion
- Lone pairs repel each other more than bond pairs
- Lone pair-lone pair > lone pair-bond pair > bond pair-bond pair repulsion

Bond Pairs	Lone Pairs	Shape Name	Bond Angles	Example
2	0	Linear	180	$\text{O}=\text{C}=\text{O}$
3	0	Triangular Planar	120	
4	0	Tetrahedral	109.5	
5	0	Triangular Bipyramidal	90 & 120	
6	0	Octahedral	90	
3	1	Triangular Pyramidal	107	
2	2	Bent non-linear	104.5	

### Hydrogen Bonding

- Hydrogen Bonding is the strongest form of intermolecular bonding
- It is a type of a permanent dipole-permanent dipole bonding
- It is present in molecules where Hydrogen is covalently bonded to small, highly electronegative atoms; F, O, N only
- Due to the electronegativity difference, the bond becomes highly polarised
- The H becomes so partial positive charged that it can bond with the lone pair of an O or N atom of another molecule
- Hydrogen bonding causes high melting and boiling points, such as in water
- It causes high surface tension in water

### Polarity

- Bond Polarity is the charge separation in a covalent molecule to a difference in electronegativities between bonded atoms
- when two covalently bonded atoms have the same electronegativity, the bond is nonpolar
- The lesser electronegativity atom gains a partial positive charge ( $\delta^+$ )
- The higher electronegativity atom gains a partial negative charge ( $\delta^-$ )
- The greater the difference in electronegativity, the more polar the bond becomes

### Dipole

- The dipole moment is a measure of how polar a bond is
- It is represented by an arrow pointing towards the partial negative end of dipole

### Polarity in Molecules

- The polarity of a molecule is determined by the polarity of each bond and the arrangement of bonds
- Equal and opposite dipoles cancel each other out
- Symmetrical molecules like linear, planar or tetrahedral are non-polar as dipoles are equal and opposite
- Molecules having lone pairs are polar because they distort symmetry

### Van der Waals forces

- Intermolecular forces between covalent molecules are known as Van der Waals forces
- There are two types of Van der Waals forces:
  1. temporary/induced dipole - induced dipole forces
  2. Permanent dipole - permanent dipole forces

### **Instantaneous dipole - Induced dipole forces**

- present in non-polar covalent molecules
  - when two nonpolar molecules come close together, electrons of the molecules repel each other
  - The repulsion causes electrons to be unevenly distributed, inducing a dipole
  - the partial positive end of a molecule attracts the partial negative end of another
  - this attraction is induced dipole - induced dipole force
- induced dipole - induced dipole forces increase with increasing electrons and greater surface area of molecules to allow more points of contact

### **Permanent dipole - permanent dipole forces**

- polar molecules have permanent dipoles
  - the molecules always have partial positive and partial negative ends
  - the forces between two polar molecules are permanent dipole-permanent dipole forces
  - the partial positive end of one molecule attracts the partial negative end of another
- Permanent dipole-permanent dipole forces are stronger than induced dipole-induced dipole forces in molecules having same number of electrons
- Hence, polar molecules have higher melting and boiling points

### **Coordinate/Dative bonding**

- A dative bond is formed when one atom provides both electrons for a covalent bond
- The sharing is not mutual
- It is represented by an arrow pointing away from the lone pair of electrons that form the bond
- $\text{Al}_2\text{Cl}_6$  is a dimer formed by dative bonding, a chlorine atom of one  $\text{AlCl}_3$  gives two electrons to the Aluminium atom of another

### **Incomplete and Expanded Octet**

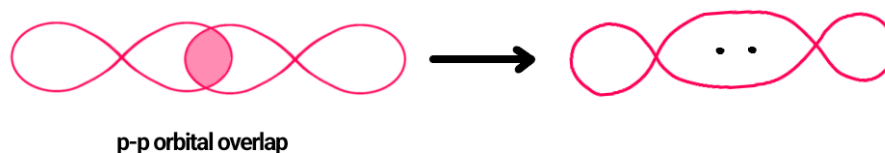
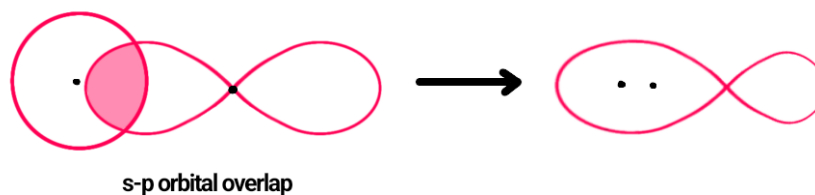
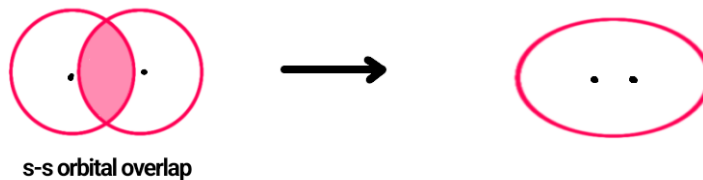
- Some species can have more or less than eight electrons in their outer shell
- $\text{GaCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{BeCl}_2$ ,  $\text{BF}_3$ ,  $\text{BCl}_3$  are examples of molecules having incomplete octet
- $\text{PCl}_5$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{SF}_6$ ,  $\text{SeF}_6$  are examples of expanded octet

### **Sigma and Pi bonding**

- It is the overlapping of two half filled atomic orbitals
- The greater the atomic orbital overlap, the stronger the bond

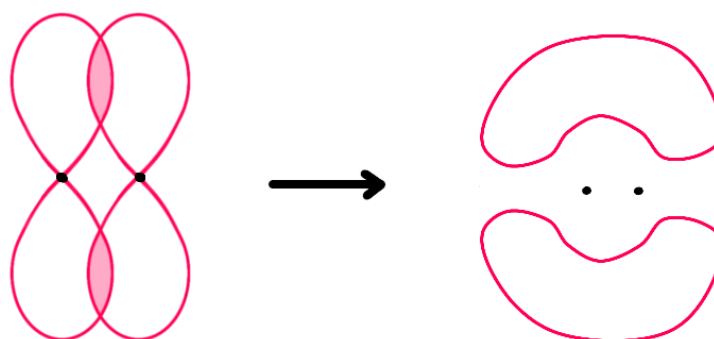
### Sigma bonds

- They are formed by the end to end overlapping of atomic orbitals
- Both s and p orbitals overlap this way
- the pair of electrons is found between the two nuclei
- the force between the electrons and nuclei bonds the atoms together
- All single covalent bonds are sigma bonds



### Pi bonds

- are formed from the sideways overlap of adjacent p orbitals
- double covalent bonds contain 1 sigma and 1 pi bond
- Triple covalent bonds contain 1 sigma and 2 pi bonds



# States of Matter

## Kinetic Theory of Gases

- No intermolecular forces are present between gas molecules
- The actual volume of gas molecules is negligible compared to the volume occupied
- All collisions between gas molecules are elastic, no energy is lost
- The kinetic energy of gas molecules is directly proportional to temperature

## Ideal Gases & Real Gases

- Gases that follow the kinetic theory are known as ideal gases, however, gases, in reality, do not follow this theory exactly even though they come close, they are known as real gases
- Under conditions of low temperature and high pressure, real gases deviate from ideal behaviour
- Under conditions of high temperature and low pressure, real gases show ideal behaviour
- Non-polar and small size gases behave more ideally; e.g He, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>
- Polar with Hydrogen Bonding and large molecule gases deviate from ideal behaviour; NH<sub>3</sub>

## Ideal Gas Equation

$$pV = nRT$$

p = pressure (Pa)

V = volume (m<sup>3</sup>)

n = number of moles of gas (mol)

R = gas constant (8.31 JK<sup>-1</sup>mol<sup>-1</sup>)

T = temperature (Kelvin)

It's necessary to convert to the correct units

## Lattice Structures

- most ionic, covalent and metallic structures are lattice structures
- The ions, atoms or molecules are arranged in a regular and repeating arrangement

## Giant Ionic Lattices

- An ionic bond is formed by the transfer of electrons from a metal to a non metal atom
- The ions have an electrostatic force of attraction between them
- Ionic compounds are arranged in giant ionic lattices
- The positive and negative ions are arranged in an alternating order
- For example, NaCl and MgO
- They are strong but brittle
- They have high melting and boiling points due to strong electrostatic forces
- Soluble in water as they can form ion-dipole bonds
- Only conduct electricity in molten or aqueous states as ions can move around

### Covalent Lattices

- Covalent bonds are formed by the sharing of electrons between nonmetals
- Covalent compounds can have simple molecular or giant molecular lattices
- Iodine and Ice have simple molecular lattices
- Sand, Graphite and Diamond have giant molecular lattices
  
- Simple covalent structures have low melting and boiling points
- Mostly insoluble in water unless they are polar or can form Hydrogen bonds
- Do not conduct electricity in solid or liquid state
  
- Giant covalent compounds have high melting and boiling points
- Can be hard or soft depending on structure
- Mostly insoluble in water
- Mostly do not conduct electricity unless free electrons available

### Metallic Lattices

- Metals form giant metallic lattices where metal ions are surrounded by a sea of delocalised electrons
- are often packed in hexagonal layers or cubic arrangement
- Metallic compounds are malleable
- The metal layers can slide
- Metallic compounds are strong and hard due to strong forces between ions and electrons
- Metals have high melting and boiling points
- Pure metals are insoluble in water
- Can conduct electricity in solid or liquid states due to delocalised electrons

	M.P/ B.P	Conductivity	Solubility	Hardness	Forces	Examples
<b>Giant Ionic</b>	high	Molten or aqueous	soluble	Hard, brittle	Electrostatic attraction	NaCl
<b>Giant Metallic</b>	high	Solid or liquid	insoluble	Hard, malleable	Attraction between Electrons and Ions	Copper
<b>Simple Covalent</b>	low	No	Insoluble unless polar	Soft	Weak intermolecular	Cl <sub>2</sub>
<b>Giant Covalent</b>	V.high	No except graphite	insoluble	Very hard except graphite	Strong covalent bonds	SiO <sub>2</sub>

# Chemical Energetics

## Enthalpy Changes

- Total chemical energy inside a substance is called enthalpy
- the change in chemical energy during a chemical reaction is the enthalpy change
- Enthalpy change is represented by  $\Delta H$
- An enthalpy change can be positive or negative
- The activation energy is the minimum amount of energy needed for a reaction to take place
- The activation energy is represented by  $E_a$

## Exothermic Reactions

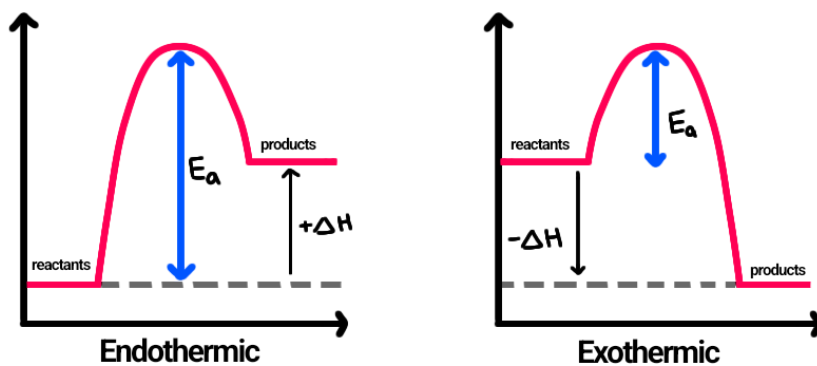
- A reaction is exothermic when the products have lesser energy than the reactants
- Heat energy is given off to the surroundings
- The enthalpy decreases so  $\Delta H$  is negative
- They have a lower  $E_a$  than endothermic reactions
- Bond making is exothermic
- If more energy is released when new bonds are formed than energy is required to break bonds, the reaction is exothermic

## Endothermic Reactions

- A reaction is endothermic when the products have greater energy than the reactants
- Heat energy is absorbed from the surroundings
- The enthalpy increases so  $\Delta H$  is positive
- Have a higher  $E_a$  than exothermic reactions
- Bond breaking is endothermic
- If more energy is required to break bonds than energy is released when new bonds are formed, the reaction is endothermic

## Energy Level Diagrams

- It is a graph of the energies of reactants and products against time





### Enthalpy Changes at Standard Conditions

- Enthalpy changes are measured at standard conditions for fair comparison between reactions
- Pressure 101kPa
- Temperature of 298 K (25 degrees)
- Aqueous solutions should be at concentration of 1.0mol dm<sup>-3</sup>
- Enthalpy change under standard conditions is represented by  $\Delta H^\circ$

### Enthalpy Change of Formation ( $\Delta H^\circ_f$ )

The enthalpy change when one mole of a compound is formed from its constituent elements under standard conditions.

### Enthalpy Change of Combustion ( $\Delta H^\circ_c$ )

The enthalpy released when one mole of a substance is burnt in air completely under standard conditions

### Enthalpy Change of Neutralisation ( $\Delta H^\circ_{neut}$ )

The enthalpy released when one mole of water is formed by the reaction between an acid and an alkali under standard conditions

### Bond Energy

- Exact bond energy is the amount of energy required to break one mole of a specific covalent bond
- Average bond energy is the average of bond energies in different environments
- Average bond energy is calculated through enthalpy changes
- Average bond energy = total bond energy/number of bonds

### Calculating Enthalpy Change with Bond Energies

$\Delta H = \text{Total bond energy of reactants} - \text{total bond energy of products}$

### Measuring Enthalpy Change

$$Q = mc\Delta T$$

Q = energy transferred (J)

m = mass (g)

c = specific heat capacity (Jg<sup>-1</sup>K<sup>-1</sup>)

$\Delta T$  = change in temperature

### Hess's Law

- The law states that the total enthalpy change in a reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same
- whatever route the reaction takes, the enthalpy change will be the same
- this is used to calculate enthalpy changes that can't be measured
- it can be calculated through the enthalpy change of formation, combustion

### Calculating $\Delta H$ from standard enthalpy change of formation

$\Delta H = \text{total standard enthalpy change of formation of products} - \text{total enthalpy change of formation of reactants}$

#### Steps

1. Write down balanced equation
2. Write down all the elements that the compounds involved in the reaction form from
3. Draw arrows correctly from elements to compounds
4. Apply Hess Law, energy change of direct route should equal indirect route, subtract the enthalpy going the opposite direction of an arrow and add when going in the same direction

### Calculating $\Delta H$ from standard enthalpy change of combustion

$\Delta H = \text{total standard enthalpy change of combustion of reactants} - \text{total standard enthalpy change of combustion of products}$

#### Steps

1. Write down balanced equation
2. Write down all the products of combustion of reactants and products
3. Draw arrows correctly from reactants and products to combustion compounds
4. Apply Hess Law, energy change of direct route should equal indirect route, subtract the enthalpy going the opposite direction of an arrow and add when going in the same direction

### Calculating standard enthalpy change of formation from standard enthalpy change of combustion

$\Delta H_f = \text{total standard enthalpy change of combustion of reactants} - \text{total standard enthalpy change of combustion of products}$

#### Steps

1. Write down balanced equation
2. Write down all the products of combustion of reactants and products
3. Draw arrows correctly from reactants and products to combustion compounds
4. Apply Hess Law, energy change of direct route should equal indirect route, subtract the enthalpy going the opposite direction of an arrow and add when going in the same direction

# Electrochemistry

## **Oxidation Numbers**

- oxidation number is a number that tells the electrons in an atom or ion
- a loss of electrons is represented by a positive oxidation number
- a gain of electrons is represented by a negative oxidation number
- The total oxidation state of a neutral compound is zero
- The total change in oxidation state in a reaction is equal

## **Redox**

- Reduction is the gain of electrons or loss of oxidation state
- Oxidation is the loss of electrons or gain of oxidation state
- Reactions in which reduction and oxidation take place are known as redox
- A substance that oxidises another substance and reduces itself is known as an oxidising agent
- A reducing agent is a substance that reduces another substances and oxidises itself
- A redox reaction must have both a reducing and oxidising agent

## **Disproportionation reaction**

- A reaction in which one substance is both oxidised and reduced

# Equilibria

## Reversible Reactions

- In a reversible reaction the products can react to form the reactants back
- the reaction can proceed in both the forward and backward directions
- Reversible reactions are represented by a double arrow  $\rightleftharpoons$

## Dynamic Equilibrium

- When the rate of the forward reaction is equal to the rate of the backward direction in a closed system

## Le Chatelier's principle

When any dynamic equilibrium is disturbed, it will shift the equilibrium in the forward or backward direction to undo the disturbance and restore the equilibrium.

**1. Temperature:** Increasing temperature shifts the equilibrium towards the endothermic reaction, decreasing shifts towards exothermic

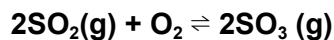
**2. Pressure:** Increasing pressure shifts equilibrium towards lesser number of moles of gas

**3. Concentration:** Increasing concentration of reactants or decreasing concentration of products will shift equilibrium towards forward reaction. Decreasing concentration of reactants or increasing concentration of products shifts equilibrium towards backward reaction.

## Equilibrium Constant - Concentrations

- The equilibrium constant  $K_c$  is the ratio of concentrations of products in a reaction to the concentrations of the reactants
- Square brackets [ ] represent concentration
- $K_c = \frac{[\text{products}]}{[\text{reactants}]}$
- The concentrations of different products and reactants are multiplied with each other, the moles of each substance are taken as a power in the calculation
- The unit of  $K_c$  is deduced from its calculation
- Only a change in temperature affects the value of  $K_c$

### **K<sub>c</sub> calculation example**



$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^3 [\text{O}_2]}$$

### **Mole fraction**

it is the number of moles of one gas divided by the total number of moles of gas at equilibrium

### **Partial Pressure**

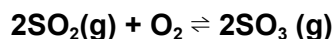
It is the pressure exerted by one gas in a mixture of gases

Sum of partial pressures = total pressure

Partial pressure = mole fraction x total pressure

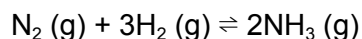
### **Equilibrium Constant - Partial Pressures**

- The equilibrium constant  $K_p$  is the ratio of the partial pressures of the products to the partial pressure of the reactants
- $K_p = \text{partial pressure of products} / \text{partial pressure of reactants}$
- Only a change in temperature affects the value of  $K_p$



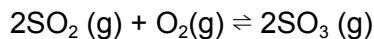
$$K_c = \frac{p(\text{SO}_3)^2}{p(\text{SO}_2)^3 p(\text{O}_2)}$$

### **Conditions used in Haber's process**



- The Haber's process is carried out under the conditions of 450 - 500 degrees temperature, 200 - 250 atm, and Fe or Fe<sub>2</sub>O<sub>3</sub> as catalyst
- Although temperature increases the rate of reaction, it shifts equilibrium backward since the backward reaction is endothermic which decreases the yield of ammonia. Therefore, a compromising temperature of 450-500 degrees is used.
- Increasing pressure increases both the rate of reaction but also shifts equilibrium forward and increases yield. Thus, pressure is kept at 200-250 atm, however, maintaining higher pressures is expensive.

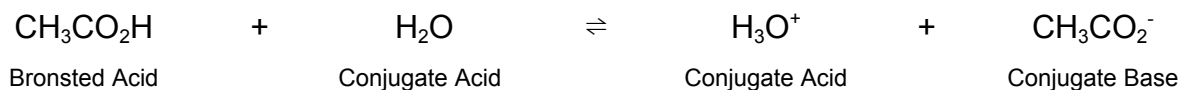
### Conditions used in the Contact Process



- Increasing pressure shifts equilibrium forward
- However the reaction is carried out at 1 atm
- This is because the  $K_p$  is already high, higher pressures are expensive and unnecessary
- Although temperature increases the rate of reaction, it shifts equilibrium backward since the backward reaction is endothermic which decreases the yield of ammonia. Therefore, a compromising temperature of 450 degrees is used.

### Lowry-Bronsted acid-base theory

- According to this theory, acids are proton donors ( $\text{H}^+$  ions) and bases are protons accepters
- A lowry-bronsted acid is a substance that gives away  $\text{H}^+$  ions
- A Lowry-Bronsted base is a substance that accepts  $\text{H}^+$  ions



### pH Scale

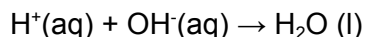
- it is a scale that shows how acidic or alkaline a substance is
- Acids have pH below 7
- Alkalis have pH above 7
- pH 7 is neutral, water has pH 7
- the lower the pH, the more acidic a substance is
- the higher the pH, the more alkaline a substance is
- the most accurate way to measure pH is with a pH metre
- it can also be measured using a universal indicator which changes colour according to the pH of the solution; acids are red/orange, neutral solutions are green, bases are blue/purple

### Strong & Weak Acids

- Strong acids fully dissociate  $\text{H}^+$  ion in water
- The greater the concentration of the  $\text{H}^+$  ions, the more acidic the substance
- Weaker acids only partially dissociate  $\text{H}^+$  ions
- Stronger acids conduct electricity better due to the concentration of  $\text{H}^+$  ions
- Stronger acids are more reactive

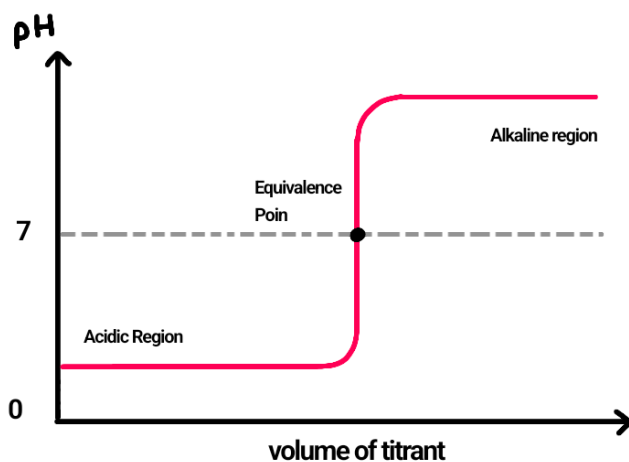
### Neutralisation Reaction

- A reaction between an acid and an alkali to produce a salt and water
- The ionic equation of any neutralisation reaction is the same



### pH Titration Curve

- Titration is a technique used to carry out neutralisation reactions
- It involves adding a titrant from a burette to a solution in a conical flask with an indicator
- The titrant is added till the end point, which is when solution changes colour
- Neutralisation takes place at the end point
- It is also known as the equivalence point



- The curve is drawn with the volume of titrant in  $\text{cm}^3$  at the x axis and pH on y axis
- It starts from the pH of the solution in the conical flask and goes to the pH of the titrant
- At the equivalence point, the line is vertical
- The shape of the curve changes according the pH of the solution and titrant

# **Reaction Kinetics**

## **Rate of Reaction**

- The rate of reaction is the speed at which a reaction takes place
- rate of reaction = change in reactants or products (mol dm<sup>-3</sup>)/time

## **Collision Theory**

- For a reaction to take place, the particles need to collide with each other in correct orientation and with enough energy
- The minimum energy required for successful collisions is known as the activation energy
- When particles don't have enough energy or correct orientation, the collision is ineffective and the particles bounce off each other

## **Factors of Rate of Reaction**

- The collision frequency is the number of collisions per unit time
- When collision frequency increases, more particles have energy above  $E_a$
- Thus, increasing the collision frequency, increases the rate of reaction

## **Catalyst**

- a substance that speeds up the rate of reaction without taking part in the reaction
- it increases the rate by lowering the energy of activation

## **Concentration**

- The greater the concentration of a fluid, the more the particles in a given volume
- This increases the chances of collisions and hence the collision frequency
- Increased collision frequency thus means increased rate of reaction
- Reducing concentration reduces collision frequency and rate of reaction
- The rate of reaction keeps changing through a reaction because the concentration of reactants and products keeps changing as more products are formed

## **Pressure**

- Increasing the pressure pushes particles closer and there are more particles in a volume
- Thus the collision frequency increases and the rate of reaction

## **Temperature**

- Increasing the temperature gives the particles more kinetic energy
- The particles then move faster, increasing the collision frequency and rate of reaction

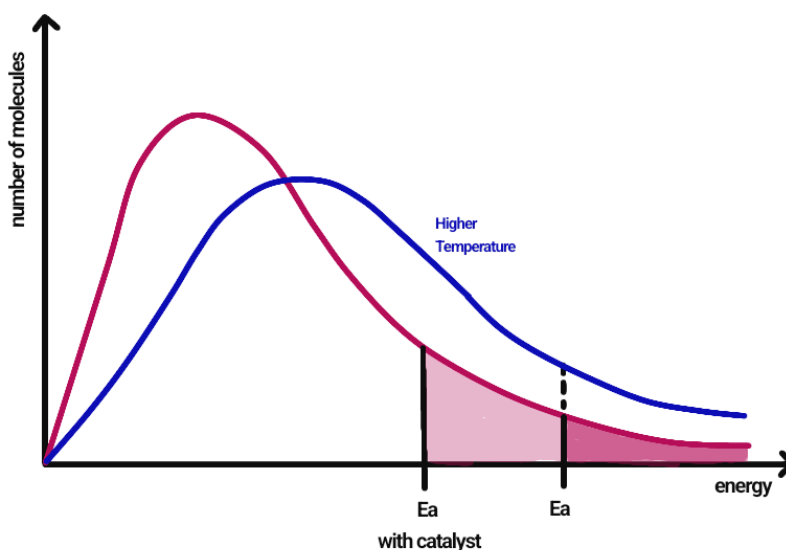


### Boltzmann Distribution Curve

- It is a graph of the distribution of energies in particles at a given temperature
- A few particles have very low and high energy, most particles will be in between
- This shows only a small amount of particles will have enough energy for successful collisions and to chemically react

### Changes in Temperature

- When the temperature is increased, particles gain more energy
- The collision frequency is increased and the rate of reaction increases
- On the Boltzmann distribution curve, this flattens the curve more and shifts the peak towards higher energy
- The area under the curve remains same as it represents the total number of particles



### Catalysts

- Since catalysts lower the activation energy, the point marked  $E_a$  on the curve shifts to the left
- Hence, more particles have a higher energy than the  $E_a$  which increases the rate of reaction

### Homogeneous and Heterogeneous Catalysts

- Homogeneous catalysts are catalysts that are in the same state as the reactants
- Heterogeneous catalysts are in a different state than the reactants

# Inorganic Chemistry

## Period 3

### Elements of 3rd Period Properties

#### 1, Atomic Radius

- The atomic radius decreases across the period
- Since the nuclear charge and number of electrons increase, there is greater attraction which results in smaller atomic radius
- The smaller the atomic radius, the more the number of valence electrons, the stronger the metallic bonding

#### 2. Ionic Radius

- Ionic radius is the distance between the nucleus and the outermost electron of an ion
- For isoelectronic species, ionic radius decreases when nuclear charge increases

#### 3. Melting Point & Boiling Point

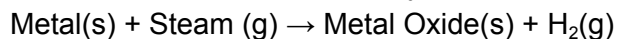
- The M.P/B.P increases left to right in the period, reaching a maximum at silicon then sharply decreasing to reach a minimum at Argon
- Na, Mg, and Al are metallic elements that form giant ionic lattices
- The metallic bonding strength increases from Na to Al due to valence electrons
- Si has a giant covalent structure with a network of strong covalent bonds so it has the highest melting point
- S<sub>8</sub> molecules have stronger Vander Waals force hence have higher melting point than P<sub>4</sub>
- P, S, Cl, and Ar are non-metals with simple molecules and have low melting points due to weak temporary dipole-dipole attraction

#### 4. Electrical Conductivity

- metals are good conductors of electricity due to free valence electrons
- electrical conductivity of metals depends on the number of valence electrons
- the electrical conductivity increases from Na to Al
- From Si onwards, the elements are nonmetals and are non-conductors

## Reactions of Period 3 elements

### 1. With water or steam



- Na reacts with cold water vigorously to form NaOH and H<sub>2</sub> and Na dissolves quickly
- Mg reacts with cold water extremely slowly, solution formed is weak alkaline
- Mg reacts with steam vigorously to make MgO and H<sub>2</sub>, white solid left behind
- Cl will undergo disproportionation reaction to give acidic solution

### 2. With Oxygen

	Equation	Conditions	Rate	Flame	Product
Na	$4\text{Na(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{Na}_2\text{O(s)}$	heat	vigorous	Bright yellow	White solid
Mg	$2\text{Mg(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{MgO(s)}$	heat	vigorous	Bright white	White solid
Al	$4\text{Al(s)} + 3\text{O}_2(\text{g}) \rightarrow 2\text{Al}_2\text{O}_3(\text{s)}$	Powdered	fast	Bright white	White solid
Si	$\text{Si(s)} + \text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{s)}$	Powdered & heat	slow	Bright white	White solid
P	$4\text{P(s)} + 5\text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s)}$	heat	vigorous	Yellow/White	White clouds
S	$\text{S(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$	Powdered & heat	gentle	Blue	Toxic fumes

### 3. With Chlorine

	Equation	Conditions	Rate
Na	$2\text{Na(s)} + \text{Cl}_2(\text{g}) \rightarrow 2\text{NaCl(s)}$	heat	vigorous
Mg	$\text{Mg(s)} + \text{Cl}_2(\text{g}) \rightarrow 2\text{MgCl(s)}$	heat	vigorous
Al	$2\text{Al(s)} + 3\text{Cl}_2(\text{g}) \rightarrow \text{Al}_2\text{Cl}_6(\text{s)}$	heat	vigorous
Si	$\text{Si(s)} + 2\text{Cl}_2(\text{g}) \rightarrow \text{SiCl}_4(\text{l})$	heat	slow
P	$2\text{P(s)} + 5\text{Cl}_2(\text{g}) \rightarrow 2\text{PCl}_5(\text{l})$	heat Excess chlorine	slow

### Acid Base Nature of Period 3 Oxides

Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>10</sub>	SO <sub>2</sub> / SO <sub>3</sub>
Basic	Basic	Amphoteric	Acidic	Acidic	Acidid

### Reactions of Period 3 Oxides

#### 1. With Water

	Equation	pH
Na <sub>2</sub> O	$\text{Na}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH}(\text{aq})$	12-14 (strong alkaline)
MgO	$\text{MgO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Mg}(\text{OH})_2(\text{aq})$	8-10 (weak alkaline)
P <sub>4</sub> O <sub>10</sub>	$\text{P}_4\text{O}_{10}(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{H}_3\text{PO}_4(\text{aq})$	3-4 (weak acid)
SO <sub>2</sub>	$\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_3(\text{aq})$	1-2 (strong acid)
SO <sub>3</sub>	$\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$	1-2 (strong acid)

*Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> do not react with water since they are insoluble*

#### 2. With Acids/Bases

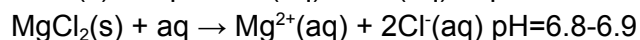
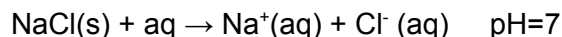
	Equation
Na <sub>2</sub> O	$\text{Na}_2\text{O}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
MgO	$\text{MgO}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
Al <sub>2</sub> O <sub>3</sub>	$\text{Al}_2\text{O}_3(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 2\text{AlCl}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
	$\text{Al}_2\text{O}_3(\text{s}) + 2\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaAl}(\text{OH})_4(\text{aq})$
SiO <sub>2</sub>	$\text{SiO}_2(\text{s}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SiO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
P <sub>4</sub> O <sub>10</sub>	$\text{P}_4\text{O}_{10}(\text{s}) + 12\text{NaOH}(\text{aq}) \rightarrow 4\text{Na}_3\text{PO}_4(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$
SO <sub>2</sub>	$\text{SO}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
SO <sub>3</sub>	$\text{SO}_3(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$

### Amphoteric Nature of $\text{Al}_2\text{O}_3$

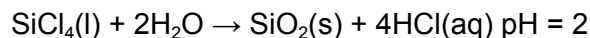
- $\text{Al}_2\text{O}_3$  acts as a base in the presence of an acid
- $\text{Al}_2\text{O}_3 + 6\text{HCl (aq)} \rightarrow 2\text{AlCl}_3(\text{aq}) + 3\text{H}_2\text{O (l)}$
- $\text{Al}_2\text{O}_3$  acts as an acid to react with  $\text{NaOH}$  and produces an aluminate salt
- $\text{Al}_2\text{O}_3 (\text{s}) + 3\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O} \rightarrow 2\text{NaAl}(\text{OH})_4 (\text{aq})$

### Reactions of Chlorides with Water

- $\text{NaCl}$  and  $\text{MgCl}_2$  simply dissolve in water and form their respective aqueous ions
- No reaction takes place
- This is because as polar water molecule is attracted to ions dissolving the chlorides and breaking down the giant ionic structures, the metals and chloride ions become hydrated ions



- The reaction of  $\text{SiCl}_4$  with water is known as hydrolysis of  $\text{SiCl}_4$
- white ppt, steamy white fumes are produced



- $\text{PCl}_5$  also undergoes hydrolysis



### Reaction of $\text{AlCl}_3$ with water



- $\text{Al}^{3+}$  ion has high charge and small ionic radius
- Hence it has high polarising power.
- Polarising power is the tendency of a cation to distort electrons (electron cloud) of anion.
- Or to attract lone pair of electrons of water
- Distortion results in forming some covalent character in that compound.
- When water is added to  $\text{AlCl}_3$  the  $\text{Al}^{3+}$  ions become hydrated
- The bonded water molecule loses an  $\text{H}^+$  ion
- The  $\text{H}^+$  ion and  $\text{Cl}^-$  ions reacted together to form white fumes of  $\text{HCl}$



## Group 2 Elements

- Group 2 elements are called alkaline earth metals
- Beryllium is the least reactive while Barium is the most reactive
- Beryllium exhibits a non-metallic character; high charge density and high polarising power
- Down the group rate of reaction increases and reaction becomes more exothermic
- Down the group the density of group 2 metal increases

### Reactions of Group 2 Elements

#### 1. With water

- All group 2 metals react with water to form respective hydroxide and H<sub>2</sub> gas
- Except for Beryllium it has no reaction with water
- The reactivity increases down the group
- The reaction becomes more vigorous down the group

#### 2. With oxygen

- Group 2 metals react with oxygen gas when heated over bunsen flame, forming respective oxides

Group 2 Metal	Flame Colour
Mg	white
Ca	Brick red
Sr	red
Ba	Apple green

#### 3. With dilute acid HCl

- Group 2 metals undergo displacement/redox reactions with dilute acid
- Beryllium reacts rapidly and the rest reacts vigorously
- Metal + dil HCl → Respective Chloride Salt + H<sub>2</sub>

#### 4. With dilute acid H<sub>2</sub>SO<sub>4</sub>

- Group 2 metals undergo displacement/redox reactions with dilute acid
- Metal + dil H<sub>2</sub>SO<sub>4</sub> → Respective Chloride Salt + H<sub>2</sub>
- SrSO<sub>4</sub> and BaSO<sub>4</sub> are insoluble salts formed
- Down the group, reaction slows down due to the formation of insoluble sulfate layer on the metal surface

## Reactions of Group 2 oxides

### 1. With water

- All group 2 oxides are basic oxides
- Except for BeO which is amphoteric
- They react with water to form respective hydroxides
- The solubilities of oxides and hydroxides increase down the group
- The solution produced becomes more alkaline down the group

### 2. With dilute HCl

- All group 2 oxides react with dilute acid to form salt and water through neutralisation
- $\text{MetalOxide} + 2\text{HCl} \rightarrow \text{MetalCl}_2 + \text{H}_2\text{O}$

### Reactions of Group 2 Carbonates with HCl



### Thermal Decomposition

- Thermal decomposition is breakdown of a compound into 2 or more different substances using heat
- The temperature at which thermal decomposition of G2 elements take place increases down the group

### Thermal Decomposition of Group 2 Carbonates

- All group 2 carbonates decompose upon heating
- They form respective oxide and  $\text{CO}_2$
- Thermal stabilities of group 2 carbonates increases, higher temperature is required to decompose carbonates down the group
- $\text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2$

### Thermal Decomposition of Group 2 Nitrates

- All group 2 nitrates decompose upon heating, forming respective oxide,  $\text{NO}_2$  and  $\text{O}_2$
- $\text{NO}_2$  gas has brown colour
- White solid remains and brown gas is released during reaction
- $2\text{M}(\text{NO}_3)_2 \rightarrow 2\text{MO} + 4\text{NO}_2 + \text{O}_2$

### Trend in solubilities of group 2 hydroxides and sulfates

- The solubility of group 2 hydroxides increases down the group
- The solubility of group 2 sulfates decreases down the group

## Group 17 Halogens

All group 17 elements are diatomic covalent molecules

F<sub>2</sub> (g) : Pale Yellow gas

Cl<sub>2</sub>(g) : Yellow-green gas

Br<sub>2</sub>(l) : Orange-Brown liquid

I<sub>2</sub> (s) : Shiny blue-black crystals

At (s): Black solid

### **Trend in the Melting Point, Boiling Point and Volatility**

- The melting and boiling points increase down the group
- The volatility decreases down the group
- Moving down, the number of electrons increase, strength of induced dipole-induced dipole attraction increases, hence the M.P and B.P increase and volatility decreases

Note: Solid iodine sublimes upon heating to give violet/purple vapours

### **Trend in reactivity**

- The relative reactivities of halogens depends on the electronegativity and relative oxidising ability of halogens.
- All halogens are oxidising agents
- The relative oxidising ability decreases down the group, hence the relative reactivity decreases down the group

### **Halide ions as reducing agents**

- The halide ions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) are reducing agents
- they reduce other species and are oxidised to form respective halogen
- The relative reducing ability of halide ions increases down the group
- Going down the group. Halide ions become larger, outermost electrons gets further away from nucleus making it less tight to lose electron and thus reducing agent increases

### **Reaction with H<sub>2</sub> gas**

- F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub> all react with H<sub>2</sub> to form respective halogen halides
- Cl<sub>2</sub>(g) + H<sub>2</sub> (g) → 2HCl(g)
- The reactivity decreases down the group
- All halogen halides are colourless gases at r.t.p and when added to water form strong acids



### Trend in thermal stabilities of Hydrogen Halides

- The thermal stabilities of hydrogen halides decreases down the group
- This is because the Bond Energy decreases as H-X bond length increases
- Fluorine atoms have smaller bond enthalpy than Chlorine and Bromine because the atomic size of F is smaller than that of Cl and Br, making it easier for F atoms to break bonds and escape the molecule.
- When a hot metal wire or hot glass rod is taken into a glass jar containing HI gas, HI decomposes into H<sub>2</sub> and I<sub>2</sub> vapours since it is the least thermally stable
- The same hot metal wire or glass will not decompose HBr and HCl

### Displacement reactions of halogens

- The more reactive halogen can displace less reactive halogen from its halide salt solution
- $\text{Cl}_2(\text{aq}) + 2\text{KI}(\text{aq}) \rightarrow 2\text{KCl}(\text{aq}) + \text{I}_2(\text{aq})$
- Cl<sub>2</sub> has oxidised I<sup>-</sup> ions to I<sub>2</sub>; I<sup>-</sup> ions have reduced Cl<sub>2</sub> to Cl<sup>-</sup> ions

### Reactions of halide ions with AgNO<sub>3</sub> (aq) followed by NH<sub>3</sub> (aq)

- When acidified AgNO<sub>3</sub> is added to an aqueous solution of Cl<sup>-</sup> ions, a white precipitate of AgCl forms
- When an excess of dilute aqueous NH<sub>3</sub> is added, the white ppt dissolves completely.
- $\text{NaCl}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow 2\text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$
- When acidified AgNO<sub>3</sub> is added to aqueous bromide, a pale cream precipitate forms
- The precipitate is partially soluble in dilute aqueous NH<sub>3</sub> and is fully soluble in concentrated aqueous NH<sub>3</sub>
- $\text{MgBr}_2(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow 2\text{AgBr}(\text{s}) + \text{Mg}(\text{NO}_3)_2(\text{aq})$
- When acidified AgNO<sub>3</sub> is added to Iodide ions, a yellow precipitate is formed
- The precipitate is insoluble in dilute and concentrated NH<sub>3</sub>(aq)
- $\text{KI}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgI}(\text{s}) + \text{KNO}_3(\text{aq})$

### Reaction of Halide ions with Concentrated H<sub>2</sub>SO<sub>4</sub>

- Metal halides do not react with Dilute acids
- Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> will react with concentrated H<sub>2</sub>SO<sub>4</sub> and will produce one or more toxic gases

Reaction	Observations
$\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$	White fumes of HCl
$\text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HBr}$	-
$2\text{HBr} + \text{H}_2\text{SO}_4 \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$	Red-brown fumes of Br <sub>2</sub>
$\text{NaI} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HI}$	-
$2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$	Purple vapours of I <sub>2</sub>
$6\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 3\text{I}_2 + \text{S} + 4\text{H}_2\text{O}$	Yellow solid (S) formed
$8\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$	Smell of rotten egg of H <sub>2</sub> S

### Uses of Halogens

Fluorine: used to make insulating handles for pans

Chlorine: used for water purification and as bleaches agents

Bromine: used as Flame retardants and fire extinguishers

Iodine: used as antiseptic and disinfectant agents

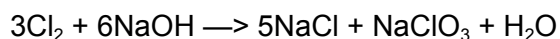
### Disproportionation reaction

- It is a reaction in which the same species are both oxidised and reduced

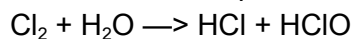
Chlorine in cold alkali



Chlorine in hot alkali



Chlorine in water purification



- Chlorine can be used to clean water and make it drinkable
  - Chloric acid (HClO) sterilised water by killing bacteria
  - Chloric acid can further dissociate in water to form ClO<sup>-</sup>
- $$\text{HClO} \rightarrow \text{H}^+ + \text{ClO}^-$$
- ClO<sup>-</sup> also acts as a sterilising agent cleaning the water

# Nitrogen and Sulfur

## Reactivity of Nitrogen

- Nitrogen is a diatomic molecule
- Nitrogen gas is unreactive because of its triple covalent bond and lack of polarity
- It has a very high bond energy required to overcome the triple bond
- Nitrogen is non-polar which also makes it unreactive
- Nitrogen gas only reacts in very high temperatures such as during lightning

## Ammonia

- Ammonia is an alkaline gas
- It turns damp red litmus paper blue
- It has a pungent smell

## Preparation of Ammonia

- It is produced at a large scale in industries using the Haber process
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- It can be prepared in a laboratory by heating an ammonium salt with a base
- This is known as displacement of  $\text{NH}_3$  from ammonium salt
- $\text{NH}_4\text{Cl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{NH}_3$

## Basicity of Ammonia

- Ammonia is a base because of the lone pair of electrons of Nitrogen
- It acts as a proton acceptor
- $\text{NH}_3$  reacts with acids to form respective ammonium salts

## Structure and formation of Ammonium Ion

- the  $\text{NH}_4^+$  ion is formed when  $\text{NH}_3$  accepts a proton ( $\text{H}^+$ ) from an acid
- A dative bond is formed between  $\text{NH}_3$  and  $\text{H}^+$
- $\text{NH}_3$  has a pyramidal shape
- $\text{NH}_4^+$  ion has tetrahedral shape

## Oxides of Nitrogen

- Nitrogen reacts with oxygen in air under extreme conditions of lightning to form nitrogen oxides
- Nitrogen can also form oxides in the high temperature and pressure of car engine
- The oxides are atmospheric pollutants as they mix with rain to form acid rain
- Catalytic converter are used in car exhausts to convert harmful gases into harmless gases
- The nitrogen oxides are reduced to nitrogen gas with a hot catalyst like platinum
- $2\text{CO}(\text{g}) + 2\text{NO}(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{N}_2(\text{g})$
- NO forms acid rain and respiratory problems

### **Nitrogen Dioxide as a Catalyst**

- NO<sub>2</sub> oxidises SO<sub>2</sub> gas to SO<sub>3</sub> and is reduced to NO
- NO is readily oxidised in the air to form NO<sub>2</sub>
- SO<sub>2</sub>(g) + NO<sub>2</sub>(g) → SO<sub>3</sub>(g) + NO (g)
- SO<sub>3</sub> reacts with water to form sulfuric acid
- This way NO<sub>2</sub> also acts as a catalyst to form acid rain

### **Oxides of Sulphur Dioxide**

- SO<sub>2</sub> is produced through volcanic eruption or through flue gases in industries like brick kilns
- It can be found in extraction of metal ores and combustion in car engines
- SO<sub>2</sub> inhibits growth of bacteria and yeasts etc
- SO<sub>2</sub> can be used as food preservatives or to bleach the wood pulp for paper production
- This acidic oxide works as a reducing agent as well
- SO<sub>2</sub> can be reduced in air by process of flue gases desulfurization

### **Harmful effects of Acid Rain**

- Acid rain causes respiratory problems such as asthma, and skin irritation
- It corrodes marble and limestone buildings
- It increases the acidity of soil, and affects root growth
- It destroys aquatic life

### **Treatment of soil**

- Acid rain increases the acidity of soil which is harmful for the plant growth
- Acidic soil can be neutralised by adding CaO, Ca(OH)<sub>2</sub> and CaCO<sub>3</sub>
- Excess of CaCO<sub>3</sub> has no effect but adding others will make the soil basic
- Ca(OH)<sub>2</sub> should not be mixed with fertiliser, as upon reaction NH<sub>3</sub> gas will produce, which will decrease the nitrogen content in soil
- Alkaline soil can be neutralised by adding (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

### **Eutrophication**

- The rapid biological growth of algae on the surface of water due to presence of nitrates and phosphates
- It is caused by industrial wastes and detergents rich in nitrate and phosphate are drained into water sources
- It causes dysentery
- Developing foetus fails to separate oxygenated blood from deoxygenated blood, and as a result child will be born with blue skin
- Growth of algae blocks the sunlight to and it kills the plants underneath
- Bacterial cells decompose the remaining O<sub>2</sub> from the soil which destroys marine life
- Farmers can reduce watercourse nitrates with timely, cost-effective fertilisation.

# Organic Chemistry

## Homologous Series

- Organic chemistry is the chemistry of carbon compounds
- except  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^{1-}$ , CO and  $\text{CO}_2$
- Hydrocarbons are compounds containing Carbon and Hydrogen only
- Members of a homologous series have same general formula
- Successive members of a homologous series differ by a  $\text{CH}_2$
- Members of a homologous have similar chemical properties
- They have similar chemical reactions and prepared the same way

### Functional Group

- A functional group is a specific atom or group of atoms that confers certain physical and chemical properties onto a molecule
- Functional groups are used to classify organic compounds
- Organic compounds with the same functional group are known as homologous series

Series	General Formula	Functional Group
Alkene	$\text{C}_n\text{H}_{2n}$	$\text{C}=\text{C}$
Halogenoalkanes	$\text{C}_n\text{H}_{2n+1}\text{X}$	R-X
Alcohol	$\text{C}_n\text{H}_{2n+1}\text{OH}$	R-OH
Aldehydes	$\text{C}_n\text{H}_{2n+1}\text{CHO}$	R-CHO
Ketones	$\text{C}_n\text{H}_{2n+1}\text{COC}_n\text{H}_{2n+1}$	R-CO-R
Carboxylic Acids	$\text{C}_n\text{H}_{2n+1}\text{COOH}$	R-COOH
Esters	$\text{C}_n\text{H}_{2n+1}\text{COOC}_n\text{H}_{2n+1}$	R-COOC-R
Amines	$\text{C}_n\text{H}_{2n+1}\text{NH}_2$	R-NH <sub>3</sub>
Nitriles	$\text{C}_n\text{H}_{2n+1}\text{CN}$	R-C $\equiv$ N

## Formulae

- **Molecular Formula** represents the actual number of atoms of all the elements in a molecule
- **Displayed Formula** represents the arrangement of atoms by showing all the covalent bonds in a molecule
- **Structural Formula** shows how the atoms are bonded to each carbon atom in a molecule
- **Empirical Formula** shows the simplest whole number ratio of atoms in a molecule
- **Skeletal Formula** gives the simplest representation of an organic molecule without showing Carbon and Hydrogen atoms of the hydrocarbon chain

## Aliphatic Hydrocarbons

These are open chain hydrocarbons such as alkanes and alkenes

## Naming organic compounds

- The prefix of an organic compound's name is determined by the number of carbon atoms in the longest chain

Name Prefix	Number of Carbon Atoms
Meth-	1
Eth-	2
Prop-	3
But-	4
Pent-	5
Hex-	6
Hept-	7
Oct-	8
Non-	9
Dec-	10

- Branched chains and functional groups are indicated by the number of the carbon atom they are attached to, counting from the end that gives the smallest number
- The branched side chain is known as an alkyl group and is added to start of the name
- In structural formulas, the branched side chains are indicated by brackets
- Multiple alkyl groups are represented by 'di-', 'tri-' or 'tetra'
- Numbers and words are separated by a hyphen

### IUPAC Rules (Nomenclature)

- Select the longest continuous carbon chain, also known as parent chain
- Double bond always forms part of the longest chain
- Give numbers to carbon atoms of longest chain, start numbering from that end where:
  - The branches are at lowest position
  - Functional group has lowest position
  - Greater number of branches present
- If more than 1 functional group is present, only one group is treated as principal group based on dominance  
(*Most dominant to Least Dominant*)
- Carboxylic acid, Ester, Aldehyde
- Nitrile
- Ketone
- Alcohol
- Amine
- Nitro
- Halogens
- Alkyl
- Write name of branches in alphabetical order along their position
- Similar groups are represented by commas between their numerical positions

## Organic Chemistry Terminology

### Saturated Hydrocarbons

Hydrocarbons which contain only single bonds, they have maximum hydrogen atoms

### Unsaturated Hydrocarbons

Hydrocarbons which contain carbon-carbon double or triple bonds

### Homolytic Fission

The breaking of a covalent bond such that each atom takes an electron from the broken bond to form two radicals

### Heterolytic Fission

The breaking of a covalent bond such that the higher electronegativity atom takes both electrons to form a negative ion and leaving behind a positive ion

### Radical Chain Reactions

- A free radical is a species with one or more unpaired electrons
- A free radical reaction involves free radicals and has three steps
- Initiation: A covalent bond is broken by energy from UV light to form free radicals
- Propagation: free radicals attack molecules to form more free radicals
- Termination: two free radicals react to form a product molecule

### Nucleophiles

- Species which is attracted towards partial positive charged carbon of polar covalent bond
- Species that can donate a lone pair of electrons
- Attracted towards positively charged species
- can be negatively charged or may contain lone pair of electrons
- Examples,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{Cn}^-$ ,  $\text{OH}^-$ ,  $\text{NH}_3$

### **Electrophiles**

- Species which is attracted towards carbon-carbon double bond of alkenes
- They can accept a pair of electrons
- They are attracted to negatively charged species
- Positively charged specie
- Examples,  $H^+$ ,  $Br^+$ ,  $Cl^+$ ,  $C^+$

## **Types of Reactions**

### **Addition Reactions**

- Two or more molecules combine to form a single product with no other products

### **Substitution Reactions**

- An atom or group of atoms replaces another atom or group of atoms

### **Elimination Reactions**

- A small molecule such as  $H_2O$  is removed from an organic molecule

### **Hydrolysis**

- Reaction in which a compound is broken down by water

### **Condensation**

- Two molecules combine together, eliminating small molecule such as  $H_2O$

### **Oxidation**

- Gain of oxygen or loss of hydrogen

### **Reduction**

- Gain of hydrogen or loss of oxygen

## **Reaction Mechanisms**

### **Curly Arrows**

Curly arrows represent the movement of electron pairs, pointing towards the species that accepts the lone pair from the bond or lone pair

### **Free Radical Substitution**

- A reaction in which halogen atoms substitute for hydrogen atoms in alkanes

### **Electrophilic Addition**

- A reaction where an electron-rich region of an organic molecule is attacked by an electrophile followed by addition of a small molecule to give one product only

### **Nucleophilic Substitution**

- A nucleophile displaces a halogen atom

### **Nucleophilic Addition**

- A reaction in which a nucleophile attacks a partial positive charge of an organic molecule followed by the addition of a small molecule to give one product only



## Shapes of Organic Molecules

### Straight Chain

- Compounds where carbon atoms are connected in one continuous chain

### Branched

- Branched molecules have side groups attached to the main chain

### Cyclic

- Compounds where carbon atoms are connected in a ring shape

## Hybridisation

### Sp<sup>3</sup> hybridisation

- Carbon atoms that form four sigma bonds are said to be sp<sup>3</sup> hybridised
- The four pairs of electrons repel each other
- Due to the repulsion, the bonds are as far from each other as possible
- The molecule forms a tetrahedral shape with bond angles of 109.5

### Sp<sup>2</sup> hybridisation

- Carbon atoms that form three sigma bonds are said to be sp<sup>2</sup> hybridised
- Each carbon atom will have a p orbital with one spare electron
- A pi bond is formed when two p orbitals overlap with each other
- The three bonds repel to form a trigonal planar shape with 120 bond angle

### Sp hybridisation

- Carbon atoms that form only one sigma bond are said to be sp hybridised
- They have two p orbitals with one spare electron each
- Four p orbitals can overlap to form two pi bonds
- The molecule has a linear arrangement with 180 bond angle

# Isomerism

## Structural Isomerism

- Structural isomers are compounds that have the same molecular formula but different structural formula
- There are three types of structural isomerism
  1. Chain isomerism
  2. Positional isomerism
  3. Functional group isomerism

### Chain Isomerism

- Chain isomers have the same molecular formula but their longest carbon chain is different due to branching

### Positional Isomerism

- Positional isomerism is caused by the functional group being on different carbon atoms
- For example pentanol and 2-pentanol

### Functional Group Isomerism

- Functional group isomers are compounds having same molecular formula but different functional groups
- For example ethanoic acid and methyl methanoate both share the same molecular formula  $C_2H_4O_2$

## Stereoisomerism

- Stereoisomers are compounds that have the same molecular formula and same structural formula but the atoms are differently arranged in space

### Geometrical (cis-trans) Isomerism

- Occurs in unsaturated compounds only
- Atoms or group of atoms bonded to carbon atoms across C=C double bond must differ
- Cis isomers have functional groups on the same side of the double bond
- Trans isomers have functional groups on opposite sides of the double bond
- This causes the isomers to have different physical and chemical properties
- Melting point of cis isomer is higher than melting point of trans
- Cis-trans isomerism occurs naturally in 1:1 ratio

## Optical Isomerism

- Arise when a carbon is bonded to four different atoms or groups of atoms
- These compounds are asymmetric
- Such a carbon is known as a chiral carbon
- Optical isomers are also called enantiomers
- Enantiomers are mirror images of each other that cannot be superimposed
- An equimolar solution of (+) and (-) enantiomers is called racemate. It is optically inactive

## Alkanes

- Alkanes are the simplest hydrocarbons with no functional group
- Alkanes have general formula  $C_nH_{2n+2}$

Alkane	Number of Carbons	Formula
Methane	1	CH <sub>4</sub>
Ethane	2	C <sub>2</sub> H <sub>6</sub>
Propane	3	C <sub>3</sub> H <sub>8</sub>
Butane	4	C <sub>4</sub> H <sub>10</sub>
Pentane	5	C <sub>5</sub> H <sub>12</sub>

## Production of Alkanes

- Alkanes can be produced by the Hydrogenation of Alkenes and Cracking

### Cracking

- Long chain alkanes are broken down into smaller chain alkanes and alkenes
- The long chain hydrocarbons are not very useful
- Short chain hydrocarbons have more demand and can be used as a fuel
- The large hydrocarbons are heated in a steel chamber with Al<sub>2</sub>O<sub>3</sub> catalyst
- Cracking is done in the absence of air and oxygen

### **Combustion**

- Combustion is a chemical process in which a substance reacts rapidly with oxygen and gives off heat
- Combustion is always exothermic
- Takes place in the presence of oxygen
- Can be incomplete or complete combustion
- Problems caused by incomplete combustion
  - Release of CO which causes blood poisoning
  - Wastage of fuel
  - Less energy produced

### **Free radical substitution reaction**

- Alkanes undergo free radical substitution reactions with halogens
- A halogen free radical replaces a hydrogen of alkane
- Ultraviolet light is required for the reaction to occur
- It occurs in the three steps of initiation, propagation and termination
- In initiation, a halogen's bond breaks in UV light to form two free radicals
- It is a homolytic fission reaction
- In propagation, the radicals react with reactant molecules to create more free radicals
- It is a chain reaction, C-H bond breaks heterolytically to form alkyl free radical
- In termination, two free radicals combine to form single unreactive molecule

### **Unreactivity**

- A lot of energy is required to break strong C-C and C-H bonds
- Alkanes are nonpolar because of nearly same electronegativities
- They can't react with polar reagents like electrophiles and nucleophiles
- Alkanes only dissolve in non-polar solvents

## Alkenes

- Alkenes are unsaturated hydrocarbons
- They have a carbon-carbon double bond
- The smaller alkenes are all gases at rtp and can be collected over water
- Double bond of alkene cannot be reduced with  $\text{LiAlH}_4$  and  $\text{NaBH}_4$
- Aqueous bromine decolourises in alkenes in unsaturation test

### Preparation of Alkenes

- Alkenes are prepared industrially by cracking
- Alkenes can be prepared in the lab by the dehydration of alcohol or dehalogenation

### Dehydration of Alcohols

Reagent: concentrated  $\text{H}_2\text{SO}_4$  +heat OR  $\text{Al}_2\text{O}_3$  +heat or pumice or pieces of porous pot

- H and OH are eliminated from adjacent carbon atoms to produce  $\text{H}_2\text{O}$
- A carbon-carbon double bond is formed between the adjacent carbons

**Alcohol  $\longrightarrow$  Alkene +  $\text{H}_2\text{O}$**

### Dehalogenation/Elimination

Reagent: Ethanolic KOH or Ethanolic NaOH with heat

- Alkenes can also be produced by removing H and a halogen atom from halogenoalkanes
- A carbon-carbon double bond is formed between the adjacent carbon atoms

**Halogenoalkane + NaOH (eth)  $\longrightarrow$  Alkene +  $\text{H}_2\text{O}$  + NaX**

- X may be any halogen atom

### Inductive Effect

- Carbocations are positively charged carbon atoms with only three bonds
- There are three types of carbocations: primary, secondary and tertiary
- Alkyl groups attached to carbocations are known as 'electron donating groups'
- Alkyl groups push electrons away from themselves to positively charged carbon atom
- This is represented by an arrowhead
- The carbocation becomes less positively charged
- The charge spreads out in the carbocation, making it more stable
- More alkyl groups makes the carbocation more stable
- Hence, tertiary carbocations are most energetically stable due to the positive inductive effect of alkyl group
- Carbocations are electrophiles due to the positive charge on carbon atoms

### Markovnikov's Rule

- Electrophiles react with the double bond of alkenes in addition reactions
- The electrophile will add to the carbon to give the most stable carbocation
- The nucleophile will be bonded to the carbon with the most alkyl groups
- Markovnikov's rule states that in an addition reaction of hydrogen halide with an alkene, the halogen atom bonds with the carbon atom which has the most number of hydrogen atoms

## Reactions of Alkenes

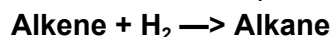
### Electrophilic Addition

- The carbon-carbon double bond is an electron concentrated region
- Electrophiles attack the carbon-carbon double bond
- The electrophile accepts a pair of electrons from the double bond
- In the mechanisms of electrophilic addition, there are two steps
- First step is slow. It is the addition of electrophile (positive specie) and formation of carbocation
- Second step is fast and nucleophile is attached with carbocation

### Hydrogenation

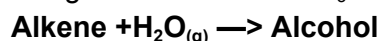
Reagent: Pt at rtp or Ni and heat at 140 degrees

- Although molecule  $H_2$  has no polarity, it is still able to behave as an electrophile
- Because when  $H_2$  molecule approaches the double bond, a dipole is induced due to repulsion between two bond pair of electrons ( $C=C$ ,  $H-H$ )



### Steam/Hydration

Reagent: concentrated  $H_3PO_4$  at 300 degrees and pressure of 600 atm



### Hydrogen Halide

Reagent: room temperature

- If there is symmetrical alkene then there will be only one product
- If there is asymmetrical alkene then there will be two products; minor halogeno alkane and major halogeno alkane
- The hydrogen acts as an electrophile and accepts a pair of electrons from the double bond
- When asymmetric molecule adds to an asymmetric alkene, the major product is the one where the halide is bonded to the most substituted carbon according to Markovnikov's rule
- Yield of minor product is always low due to fewer electron donating alkyl chains in carbocation which has the lower positive inductive effect and higher charge density



## Halogen

Reagent: Br<sub>2</sub> or Cl<sub>2</sub>

- This is the unsaturation test which decolourise bromine water
- Br<sub>2</sub> (aq) is an orange/yellow solution called bromine water
- The unknown compound is shaken with bromine water and the solution will decolourise

Alkene + Br<sub>2</sub> → HalogenoAlkane

## Combustion of Alkenes

- Alkenes are burnt on a large scale as fuel
- In excess oxygen, all the carbon and hydrogen will be oxidised to CO<sub>2</sub> and H<sub>2</sub>O
- In limited supply of oxygen, the carbon produces carbon monoxide

## Oxidation

- Alkenes can be oxidised with acidified KMnO<sub>4</sub>
- K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> can never react with alkenes
- In cold dilute KMnO<sub>4</sub>, a diol is formed, turning the purple solution colourless

**Alkene + H<sub>2</sub>O + [O] → Alcohol**

- In hot concentrated KMnO<sub>4</sub>, the double bond is completely broken to form aldehydes, ketones or carboxylic acids depending on the atoms bonded to the carbon atoms
- The reaction of alkene with hot KMnO<sub>4</sub> can be used to determine the position of double bond in larger alkene
- If carbon atom is bonded to two hydrogen atoms, oxidation to carbon dioxide
- If carbon atom is bonded to one hydrogen atom and one alkyl group, oxidation to aldehyde and carboxylic acid
- If carbon atom is bonded to two alkyl groups, oxidation to ketone
- Water is formed in each of the reactions

## Halogenoalkanes

- Halogenoalkanes are derivatives of alkanes
- The General formula  $C_nH_{2n+1}$  is only applicable if there is only one halogen atom

### Properties

- Halogenoalkanes have high melting and boiling point temperature as compared to hydrocarbon of comparable  $M_r$
- This is due to high bond polarity Carbon Halogen bond
- Chloroalkanes are less dense than water so they float over the surface of water
- Bromo and Iodo alkanes are denser than water
- Halogenoalkanes form immiscible liquid
- Halogenoalkanes experience permanent dipole permanent dipole interactions
- But they are not strong enough to form hydrogen bonds with water, hence slightly soluble in water
- Their solubilities further decrease by increasing the hydrophobic carbon unit
- Non polar substance that do not combine with water molecules are known as hydrophobic unit

### Preparation

- They can be produced by free radical substitution of alkanes, electrophilic addition of alkenes and substitution of alcohols

### Classification of Halogenoalkanes

- Halogenoalkanes can be classified into primary, secondary or tertiary
- Primary halogenoalkanes have one alkyl group directly bonded to carbon atom
- Secondary halogenoalkanes have two alkyl groups directly bonded to carbon atom
- Tertiary halogenoalkanes have three alkyl groups directly bonded to carbon atom

### Nucleophilic substitution reactions of halogenoalkanes

- Halogenoalkanes are much more reactive than alkanes due to electronegative halogens
- The halogen-carbon bond is polar
- In nucleophilic substitution reactions, nucleophiles are attracted towards partial positive charge of carbon atoms
- The nucleophile replaces a partial negative charged atom



### Reaction with NaOH or KOH

Reagent:  $\text{NaOH}_{(\text{aq})}$  or  $\text{KOH}_{(\text{aq})}$  + Heat under reflux

- This reaction is also known as formation of alcohol or hydrolysis
- Heat under reflux means that it will condense vertically
- Halogenoalkanes react with aqueous alkali to form alcohols
- The  $\text{OH}^-$  ion replaces the halogen
- The  $\text{OH}^-$  ion acts as a nucleophile by donating pair of electrons to carbon bonded to halogen



### Reaction with KCN

Reagent: Ethanolic KCN + heat under reflux

- The  $\text{CN}^-$  ion acts as a nucleophile
- Nitriles are formed when ethanolic KCN is heated under reflux with halogenoalkane
- This reaction adds an extra carbon atom to the carbon chain



### Reaction with $\text{NH}_3$

Reagent: concentrated ammonia dissolved in ethanol

- The  $\text{NH}_3$  molecule acts a nucleophile in this reaction
- Ethanolic excess  $\text{NH}_3$  is heated under pressure in closed vessel with halogenoalkane
- Primary amine is formed
- Since  $\text{NH}_3$  is in excess, the primary amine can undergo another reaction to form secondary amine



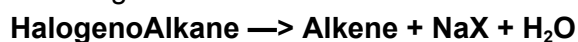
### Reaction with aqueous AgCl

- Halogenoalkanes can be broken down to form alcohols by hydrolysis
- The water molecules in aqueous AgCl act as nucleophiles
- The halogen is replaced by  $-\text{OH}$  to form alcohol
- Similar to reaction with aqueous alkali but slower
- Different halogenoalkanes have different rates of hydrolysis

### Elimination reactions of halogenoalkanes

Reagent:  $\text{KOH}(\text{eth})$  or  $\text{NaOH}(\text{eth})$  + Heat under reflux

- Organic molecules lose a small molecule in elimination reactions
- In halogenoalkanes, the small molecule is a hydrogen halide
- The C-X bond break heterolytically when heated with ethanolic NaOH
- A halogen ion is formed and alkene is left behind



- If the adjacent carbon atom of C-X bond does not contain any hydrogen atom then elimination reaction will not proceed
- Tertiary halogenoalkane will have no reaction

## Sn1 and Sn2 reaction mechanisms

- Nucleophilic substitution reactions occur in two ways depending on the structure of halogenoalkane
- SN2 refers to bimolecular nucleophilic substitution
- SN1 refers to unimolecular nucleophilic substitution

### Sn2

- Primary halogenoalkanes undergo Sn2 mechanism reactions
- Primary halogenoalkanes have one alkyl group bonded to the carbon with halogen
- The rate of Sn2 reactions is determined by the concentration of both halogenoalkane and the nucleophile
- It is a one step reaction
- Nucleophile donates a pair of electrons to partial positive carbon atom to form new bond
- C-X bond breaks with heterolytic fission at the same time
- OH<sup>-</sup> will attack the nucleophile from the opposite side of leaving nucleophile
- The halogen leaves as a negative ion

### Sn1

- Tertiary halogenoalkanes undergo Sn1 mechanism reactions
  - Tertiary halogenoalkanes have three alkyl groups with the C-X carbon atom
  - The rate of reaction depends on the concentration of only the halogenoalkane
  - It is a two step reaction
  - C-X bond breaks heterolytically in slow rate determining step to form halogen ion
  - A tertiary carbocation is formed which reacts with nucleophile in the second step
- 
- Sn2 reactions do not form carbocations because primary carbocations are not stable
  - Secondary halogenoalkanes undergo a mixture of Sn1 and Sn2 reactions depending on structure
  - If solvent is non polar then SN2 mechanism is favourable as formation of carbocation is difficult
  - If solvent is polar then SN1 mechanism is favourable as formation of carbocation is easier

### Reactivity of Halogenoalkanes

- Halogens undergo substitution reactions at different rates
- The relative reactivities of halogenoalkanes increases down the group
- This is because the C-X bond energy decreases down the group
- The C-X bond is broken during substitution reactions
- Since it's easier to break the C-X bond down the group, the relative reactivity increases

### Uses of HalogenoAlkanes

- Chloroalkanes are used as insecticides and pesticides as their bond strength is strong the expiry date will increase
- Bromoalkanes are used in fire extinguishers
- CFCs are inert so they cause global warming as they are greenhouse gas
- When CFC enters stratosphere they react with ozone layer and depletes it
- C-Cl bond breaks in presence of UV light, whereas C-F, C-C and C-H bonds are strong enough and cannot be broken by UV light
- Ozone depletion potential is directly proportional to the number of Cl atoms in CFCs

# Hydroxy Compounds

## Production of Alcohols

- Alcohols contain at least one hydroxy -OH group
- Alcohols can be prepared by
  - Electrophilic addition of Alkenes (Steam/Hydration)
  - Oxidation of Alkenes (cold dilute  $\text{KMnO}_4$ )
  - Nucleophilic substitution of Halogenoalkanes ( $\text{NaOH}_{(\text{aq})}$ )
  - Reduction of Aldehydes and Ketones
  - Reduction of Carboxylic Acids
  - Hydrolysis of Esters

## Properties

- Alcohol has more melting and boiling point than halogenoalkanes as it has hydrogen bonding
- Lower Alcohols are highly water soluble due to formation of hydrogen bonds between water and alcohol molecules
- Solubility decreases with increase in molecular mass due to increase in hydrophobic unit
- Alcohols are relatively weaker acid than water
- Alcohols cannot liberate  $\text{CO}_2$  from carbonates and bicarbonates

## Reactions of Alcohols

### Combustion of alcohols

- Alcohols react with oxygen in air when ignited to produce carbon dioxide and water by complete combustion
- Lower alcohols do not produce any pollutants such as CO or unburnt hydrocarbons

### Reaction with Na

- Na is the only metal that reacts with alcohols
- This is the redox reaction



### Nucleophilic Substitution of Alcohols

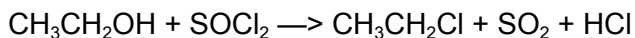
- The -OH group of alcohols can be replaced by halogens to produce halogenoalkanes
- Substitution to halogenoalkanes, e.g. by reaction with HX or KBr with  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ ; or with  $\text{PCl}_3$  and heat; or with  $\text{PCl}_5$ ; or with  $\text{SOCl}_2$

### Conversion of Alcohol in Chloroalkanes:

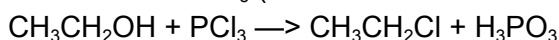
Reaction with  $\text{PCl}_5$  (rtp)



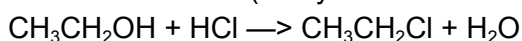
Reaction with  $\text{SOCl}_2$



Reaction with  $\text{PCl}_3$  (heat under reflux and then distilled)



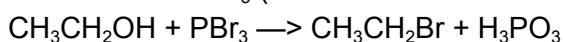
Reaction with  $\text{HCl}$  ( anhydrous  $\text{Zn}$  + heat)



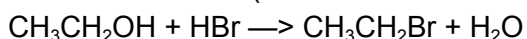
- This reaction is also known as Lucas Test and is used for the identification of primary, secondary and tertiary alcohols

### Conversion of Alcohol in Bromoalkanes:

Reaction with  $\text{PBr}_3$  (heat under reflux and then distilled)

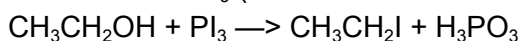


Reaction with  $\text{HBr}$  (heat under reflux and then distilled)



### Conversion of Alcohol in Iodoalkanes:

Reaction with  $\text{PI}_3$  (heat under reflux and then distilled)



### Oxidation of Alcohols

- Primary alcohols can be oxidised to aldehydes which can be further oxidised to carboxylic acids

- Secondary alcohols can be oxidised to form ketones

- Tertiary alcohols can not be oxidised

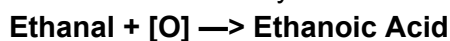
- Alcohols can be oxidised by acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  or acidified  $\text{KMnO}_4$

- Oxidation of primary alcohol (acidified  $\text{KMnO}_4$  + heat under reflux)

- Formation of Aldehyde

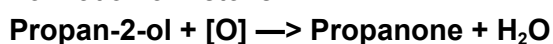


- Formation of Carboxylic acid



- Oxidation of secondary alcohol (acidified  $\text{KMnO}_4$  + heat under reflux)

- Formation of Ketone



### Dehydration of Alcohols

Reagent: concentrated  $\text{H}_2\text{SO}_4$  + heat or  $\text{Al}_2\text{O}_3$  powder or  $\text{H}_3\text{PO}_4$  or  $\text{P}_4\text{O}_{10}$

- When alcohol vapour is passed over hot catalyst  $\text{Al}_2\text{O}_3$  powder, it undergoes dehydration
- A water molecule is eliminated from the alcohol to produce alkene
- If the adjacent carbon atom of C-X bond does not contain any hydrogen atom then reaction will not proceed

**Alcohol  $\rightarrow$  Alkene +  $\text{H}_2\text{O}$**

### Uses of Alcohol

- Alcohol is used as an antiseptic and in medicines ( spirit-100% pure alcohol)
- Alcohol are used for drinking purposes (ethanol only)

# Carbonyl Compounds

## Production of Aldehydes and Ketones

- Aldehydes and ketones are carbonyl compounds containing C=O functional group
- They can be prepared by the oxidation of alcohols
- Acidified  $K_2Cr_2O_7$  and acidified  $KMnO_4$  can be used as the oxidising agents

### Aldehydes synthesis

- Primary alcohols are oxidised to form aldehydes
- The warm primary alcohol is slowly added to oxidising agent
- The aldehyde has to be separated as soon as it forms so that it does not oxidise further
- Aldehyde can be distilled off due to lower boiling point than alcohol
- It is collected as a liquid by condensing

### Ketones synthesis

- Secondary alcohols are oxidised to form ketones
- Ketones can not be oxidised further so they don't have to be distilled immediately

### Physical Properties

- Boiling and melting point is lower than alcohol but greater than hydrocarbons
- Aldehydes and ketones with water will make hydrogen bond
- Carbonyl compounds are simple covalent molecules with permanent dipole permanent dipole force of attraction between them

## Reactions of Aldehydes and Ketones

### Reduction of Aldehydes and Ketones

- Aldehydes can be reduced to primary alcohols
- Ketones can be reduced to secondary alcohols
- They can be reduced by agents such as  $NaBH_4$  in methanol and  $LiAlH_4$  in dry ether

### Nucleophilic Addition with HCN

- Aldehydes and ketones react with HCN in nucleophilic addition reaction
- $CN^-$  ion acts as a nucleophile
- It is added across the C=O bond
- The nucleophile is attracted to the partial positive charge of carbon atom
- It is a two step process
- An intermediate is formed in the first step when nucleophile attacks carbon atom
- The negatively charged oxygen atom reacts with  $H^+$  from HCN or  $H_2O$  to form hydroxynitrile

- KCN is used as catalyst with heat in slightly alkaline conditions
- Hydroxynitriles are produced

**Alkanal + HCN → Cyanohydrin**

Alkanone + HCN → Cyanohydrin

**2,4-DNPH Carbonyl Test**

- Carbonyls can be tested with 2,4-dinitrophenylhydrazine (2,4-DNPH)
- Aldehydes undergo a condensation reaction
- 2,4-DNPH forms a deep orange precipitate in presence of aldehydes and ketones
- The precipitate can be purified and the melting point can be checked to see if it's an aldehyde or ketone

**Fehling's Solution**

- It is an alkaline solution containing  $\text{Cu}^{2+}$  ions
- It acts as an oxidising agent
- When it is warmed with aldehyde, the aldehyde is oxidised to carboxylic acid
- The  $\text{Cu}^{2+}$  ions are reduced to  $\text{Cu}^+$  ions
- The colour of the solution changes from clear blue to opaque red
- Ketones do not give a positive test because they can not be oxidised

**Tollen's Agent**

- It is an alkaline solution of silver nitrate in excess ammonia
- When warmed at 80 degrees with aldehyde, the aldehyde is oxidised to carboxylic acid
- The  $\text{Ag}^+$  ions are reduced to Ag atoms
- The Ag atoms form a silver mirror in the test tube
- Ketones do not give a positive test because they can not be oxidised

**Iodoform Reaction**

- Tri-iodomethane or iodoform test gives yellow precipitate - In primary alcohol, it gives positive test with ethanol only
- In secondary alcohols, it gives positive test with those in which OH is bonded to 2<sup>nd</sup> carbon only
- In aldehydes, it gives positive test with ethanal only
- In ketones, it gives positive test with methyl ketones in which C=O is bonded to 2<sup>nd</sup> carbon only
- Methyl ketones are compounds containing  $\text{CH}_3\text{CO}$ - group
- The reagent is heated with alkaline solution of iodine
- It undergoes halogenation, replacing all three hydrogens of methyl group with iodine
- The compound is hydrolysed immediately by alkaline solution to form a sodium salt and yellow precipitate of  $\text{CHI}_3$



# Carboxylic Acids

## Production of Carboxylic Acids

- Carboxylic acids can be produced by the oxidation of primary alcohols or aldehydes
- Heating ester with dilute acid or alkali makes it undergo hydrolysis to produce its constituent carboxylic acid and alcohol

## Hydrolysis of Nitriles

- The hydrolysis of nitriles can be used to produce carboxylic acids
- With dilute acids, carboxylic acids can be produced along with ammonium salt through heat under reflux



- With dilute alkali, sodium carboxylate salt is produced, which can be used to produce carboxylic acid by acidification through heat under reflux
- The -CN group is converted to -COOH



## Reactions of Carboxylic Acids

Reaction	Products
Redox with reactive metals	Salt + Hydrogen gas
Neutralisation with alkalis	Salt + Water
Acid-base with carbonates	Salt + Water + Carbon dioxide gas
Esterification with alcohols - $\text{H}_2\text{SO}_4$ catalyst	Ester + Water
Reduction by $\text{LiAlH}_4$	Primary Alcohol + Water

## Properties

- Melting and boiling point are higher than those of alcohols of comparable Mr due to extensive hydrogen bond
- Carboxylic acids exist as a dimer

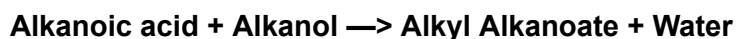
## Esters

- Esters have functional group -COOR
  - They have a sweet and fruity smell
  - It is used as solvent for adhesives
  - Due to its sweet odour it is used in cosmetics and perfumes
- The first part of the ester's name represents the alcohol while the second part comes from the carboxylic acid

### **Esterification**

- Esters are prepared from carboxylic acids and alcohols by condensation reaction with concentrated  $\text{H}_2\text{SO}_4$  as catalyst

Conditions: Heat under reflux

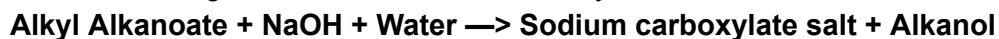


### **Hydrolysis of Esters**

- Heating ester with dilute acid or alkali makes it undergo hydrolysis to produce its constituent carboxylic acid and alcohol
- With dilute acid, the reaction is reversible



- With dilute alkali, the reaction is not reversible as it forms sodium carboxylate salt which needs to undergo acidification to form carboxylic acid



- Both of the reactions take place through heat under reflux

# Nitrogen Compounds

## Primary Amines

- Amines are compounds with  $\text{-NH}_2$  functional group
- Can be produced by nucleophilic substitution reaction of halogenoalkanes when heated with ethanolic ammonia under pressure
- The lone pair of electrons on nitrogen of  $\text{NH}_3$  acts as nucleophile
- The nucleophile is attracted towards partial positive charged carbon atom of C-X bond
- The C-X bond is broken, replacing the halogen with an amine

## Nitriles

- Nitriles are compounds with  $\text{-CN}$  functional group
- Can be produced by nucleophilic substitution reaction of halogenoalkanes
- Ethanolic KCN is heated under reflux with halogenoalkane
- The  $\text{CN}^-$  ion acts as a nucleophile
- Nucleophile attacks partial positive charged carbon of C-X
- The halogen is replaced by  $\text{-CN}$

## Hydroxynitriles

- Hydroxynitriles are compounds with both  $\text{-OH}$  and  $\text{-CN}$  groups
- They can be prepared by nucleophilic addition of aldehydes and ketones
- HCN is added to carbonyl compounds
- The reaction is a two step process
- In step 1, a negatively charged intermediate is formed when the  $\text{CN}^-$  ion attacks carbonyl carbon
- In step 2, the negative charged oxygen of intermediate reacts quickly with aqueous  $\text{H}^+$  ions from water or HCN to form 2-hydroxynitrile

# Polymerisation

Alkane  $C_nH_{2n+2}$

CycloAlkane  $C_nH_{2n}$

Alkene  $C_nH_{2n}$

CycloAlkene  $C_nH_{2n-2}$

## Monomer

- Small molecules that react together to make long chain molecules

## Polymer

- A long chain molecule made up of many repeating units derived from the monomers

## Polymerisation

- The process in which many small molecules chemically combine each other to form long chain molecules

## Addition Polymerisation

- A polymer is a long-chain molecule made up of many repeating units
- Additional polymerisation is an addition reaction of alkenes
- Many monomers combine to form one polymer
- The monomers should have at least one carbon-carbon double bond
- The pi bond in each C-C bond breaks to link monomers with new single bonds
- The addition reaction gives only one product

## Characteristics of addition polymerisation

- No mass loss during polymerisation hence empirical formula of monomer and polymer remains the same
- Pi bond will break and sigma will form
- The monomers are unsaturated and the polymers are usually saturated
- Additional polymers are generally synthetic and are plastics and they are non-biodegradable

## Disposal of Polymers

- Polymers are unreactive and don't chemically react
- They are non-biodegradable so they fill-up landfill site
- They cause pollution of the environment
- Polymers releases harmful greenhouse gases by combustion

# Analytical Techniques

## IR Spectroscopy

- Infrared spectroscopy is used to identify compounds by changes in vibrations of atoms
- Resonance frequency is the frequency at which molecules vibrate significantly more
- Each vibration absorbs a specific amount of infrared radiation
- It is measured in wavenumbers ( $\text{cm}^{-1}$ )
- Specific Absorptions have characteristics of width and intensity
- Unknown compounds can be identified by comparing to known IR spectrums

Bond	Functional Groups	IR absorption range/ $\text{cm}^{-1}$	Appearance of Peak
C-O	alcohols, esters	1040-1300	strong
C-C	aromatic compounds, alkenes	1500-1680	weak
C=O	amides, ketones, aldehydes, esters	1640-1690 1670-1740 1710-1750	strong
$\text{C}\equiv\text{N}$	nitriles	2200-2250	weak
C-H	alkanes, alkenes	2850-2950 3000-3100	strong weak
N-H	amines, amides	3300-3500	weak
O-H	carboxylic acids, alcohols	2500-3000 3200-3600	strong

## Mass Spectroscopy

- It is a technique used to identify unknown compounds
- molecules are bombarded with high energy electrons
- The molecules can lose electrons to form charged molecular ions
- Molecular ions can make further fragments such as ions, molecules and radicals
- Mass spectrometer only detects the positive ions
- Fragments are accelerated by electric fields
- They are deflected onto detector according to their mass/charge ratio
- Each fragment produces a corresponding m/e peak
- the most abundant ion's peak is known as the base peak

## Calculating Relative Atomic Mass

- Mass spectroscopy can be used to calculate the relative atomic mass
- The abundance of each isotope of an atom can be determined from the mass spectrum
- The heights of the peaks show the abundance of each isotope present

$$A_r = \frac{\text{sum of mass } \times \text{percentage abundance for each isotope}}{100}$$

## Deducing Molecular Formula

- The peak with the highest m/e value is the M+ ion peak
- [M+1] is a smaller peak due to the natural abundance of carbon-13 isotope
- The height of the [M+1] peak depends on the number of carbon atoms
- The greater the number of carbon atoms, the greater the height of the [M+1] peak
- The m/e value of a peak can be compared to known m/e values to identify fragments

## Calculating number of carbon atoms from [M+1] Peak

- [M+1] peaks are due to presence of carbon-13 isotopes which are 1.1% of all carbon atoms

$$\text{Number of carbon atoms (n)} = \frac{100 \times \text{abundance of [M+1]}}{1.1 \times \text{abundance of M+ ion}}$$

## Using [M+2] peaks to detect Chlorine and Bromine atoms

- Chlorine and bromine atoms cause [M+2] and [M+4] peaks

### Chlorine:

- Chlorine has two isotopes  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$
- The  $^{35}\text{Cl}$  isotope produces the M+ peak while the  $^{37}\text{Cl}$  isotope produces [M+2] peak
- The ratio of abundance of the isotopes and the height of the peaks is 3:1
- Peaks are caused by the different possible combinations of isotopes
- The number of peaks of a compound will be the number of possible combinations with the number of atoms
- A compound with two atoms of chlorine will produce three peaks in the ratio 9:6:1
- $^{35}\text{Cl} + ^{35}\text{Cl}$  – M+ peak
- $^{35}\text{Cl} + ^{37}\text{Cl}$  – [M+2] peak
- $^{37}\text{Cl} + ^{37}\text{Cl}$  – [M+4] peak

### Bromine:

- Bromine also has two isotopes  $^{79}\text{Br}$  and  $^{81}\text{Br}$
- The  $^{79}\text{Br}$  isotope gives rise to the M+ peak while the  $^{81}\text{Br}$  isotope gives rise to the [M+2] peak
- The ratio of abundance and ratio of heights is 1:1
- A compound with two atoms of bromine will produce three peaks in the ratio 1:2:1
- $^{79}\text{Br} + ^{79}\text{Br}$  – M+ peak
- $^{79}\text{Br} + ^{81}\text{Br}$  – [M+2] peak
- $^{81}\text{Br} + ^{81}\text{Br}$  – [M+4] peak

### **A Note from Mojza**

These notes for Chemistry (9701) have been prepared by Team Mojza, covering the content for GCE A Levels 2022-24 syllabus. The content of these notes has been prepared with great care. We apologise for any issues overlooked: factual, grammatical or otherwise. We hope that you benefit from these and find them useful towards achieving your goals for your Cambridge examinations.

If you find any issues within these notes or have any feedback, please contact us at [support@mojza.org](mailto:support@mojza.org).

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