



CHEMISTRY

A-LEVEL

VW SCHOOLS

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ORGANIC CHEMISTRY 2

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ENERGETICS



Chapter

Topic

P-CHEM-1
MEASURING ENTHALPY CHANGES



Practical

Practical Number

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ATOMIC STRUCTURE



WHAT IS THE STRUCTURE OF AN ATOM?

- Nucleus: made of protons and neutrons
- Electrons surround nucleus in shells

PROPERTIES OF PROTONS, NEUTRONS, AND ELECTRONS

Mass

- Proton mass relatively same mass as neutron
- Electron mass is 1/1836th the mass of a proton

Charge

- Protons have a positive charge
- Electrons have a negative charge
- Neutron has no charge

Atomic Number

- Number of protons

Isotopes

- Atoms of the same element with the same number of protons but a different number of neutrons
- Isotopes of the same element react in the same way as they have the same number of electrons
- Eg: **heavy water**. D₂O instead of H₂O (D-Deuterium instead of Hydrogen)

Ions

- **Cations**: positive ions, more protons than electrons
- **Anions**: Negative ions, more electrons than protons

HOW TO WRITE FORMULAE

- Overall charge is zero and ionic charges must balance
- Sum of positive charges is the same as the sum of the negative charges

STRONG NUCLEAR FORCE

- Protons and neutrons are called nucleons
- Held together by strong nuclear force which is stronger than electrostatic forces of attraction that hold protons and electrons together in the nucleus
- Strong nuclear force acts in small distances

MASS DEFECT

- To find the total mass, we cannot combine the masses of protons, neutrons, and electrons
- As there is a concept called **the mass defect**
- This is due to the strong nuclear force holding and protons and neutrons together in the nucleus reducing the total mass

So..how is relative mass calculated?

- **Relative Atomic/Molecular Mass**: average mass of an atom of an element/molecule relative to 1/12th of the mass of an atom of carbon-12
- **Relative Isotopic Mass**: Average mass of an isotope relative to 1/12th of the mass of an atom of carbon-12

So..how is relative mass determined?

- 1) Sample placed in **mass spectrometer** (instrument used to measure relative mass)
- 2) Sample is vaporised and then ionised to form positive ions
- 3) Ions are accelerated--> heavier ions move more slowly and more difficult to deflect than lighter ions--> ions of each isotope are separated
- 4) Ions detected on a mass spectrum as a mass to charge ratio (m/z). Each ion reaching detector contributes to the signal--> greater the abundance the larger the signal

m/z = relative mass of ion/relative charge on ion

Binary Compounds, Polyatomic Ions

- **Binary Compound** has 2 elements only
- Eg; sodium and oxygen form sodium oxide
- **Polyatomic Ions**: ions that contain atoms of more than one element



MORE ON PAGE 7

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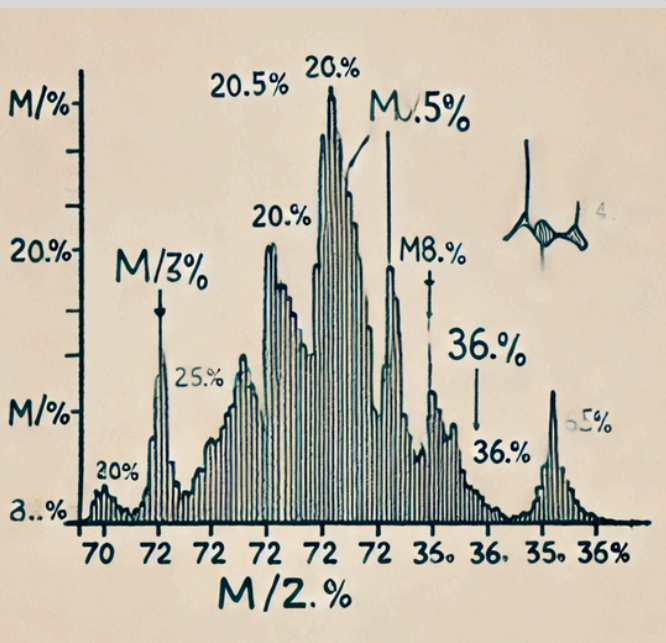
ATOMIC STRUCTURE



ATOMIC HISTORY

- **Boyle:** said there are substances that cannot be made simpler- elements
- **Dalton:** elements made of invisible atoms, all atoms of a particular element had the same mass, atoms of different elements had different masses, atoms cannot be broken down
- **Becquerel:** discovered radioactivity, showed particles were inside the atom
- **JJ Thompson:** discovered the electron (first subatomic particle to be discovered)--> plum pudding model (electrons were in circular arrays within atom, like plums in a pudding of positive charge)
- **Rutherford:** most of the mass, all of the positive charge was restricted to central area of nucleus--> gold foil experiment
- **Bohr:** atom consists of a tiny positive nucleus orbited by electrons which are in shells
- **Schrodinger:** electrons behaved like waves--> constructed mathematic equation--> quantum mechanics
- **Chadwick:** discovered the neutron
- **Lewis:** noble gases were inert (non-reactive) as they had full shells, ions were formed by atoms losing or gaining electrons, atoms can bond by sharing electrons to form full outer shells

INTERPRETING MASS SPECTRA



TOF MASS SPECTROMETRY

What is it?

- Way of separating a sample into its constituent ions
- Based on the mass to charge ratio (m/z)

What happens in it?

- **Vacuum:** whole apparatus under vacuum to prevent ions produced from colliding with air
- **Ionisation:** 2 types--> **electrospray:** sample dissolved in volatile solvent and forced through a fine hollow needle that is connected to positive terminal of a high voltage supply, produced positively charged small droplets that have gained a proton from the solvent, solvent evaporates and droplets get smaller and smaller until they contain only a single positively charged ion.
Electron impact: sample is vapourised and high energy electrons are fired at it from an electron gun which fires high energy electrons (hot wire filament with a current running through it)- $X(g) + e^- \rightarrow X^+ + 2e^-$
- **Acceleration:** positive ions are attracted towards a negatively charged plate, accelerate towards it, lighter ions and more highly charged ions achieve a higher speed
- **Ion drift:** ions pass through a hole in the negatively charged plate, forms a beam, travels along a tube, called the flight tube, to a detector
- **Detection:** Ions pass through a hole in the negatively charged plate, forming a beam and travel along a flight tube to the detector
- **Detection:** When ions with the same charge arrive at detector, lighter ones are first as they have higher velocities, flight times recorded. Positive ions pick up an electron from the detector, which enables a current flow
- **Data analysis:** signal from the detector is passed to a computer--> generates mass spectrum

High resolution vs low resolution

- High res: machine determines relative atomic masses to five decimal places
 - Low res: two decimal places
- **On y axis:** relative abundance as a percentage
 - **On x axis:** m/z ratio or mass number

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ATOMIC STRUCTURE



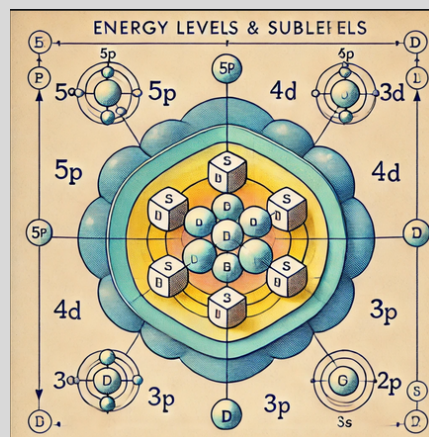
ELECTRON ARRANGEMENTS

Energy levels

- Shells that electrons are in are the main energy levels (labelled 1, 2, 3)
- Each main energy level can hold a maximum number of electrons given by the formula $2n^2$ (n is the number of the main energy level)
- Each main energy level is divided into sub-energy levels which have slightly different energies
- Main energy level 1 only has the s sub level

NUMBER OF ELECTRONS IN DIFFERENT LEVELS AND SUB-LEVELS

ELECTRON ENERGIES



Main Energy Level	1	2	3	4
Sub-level(s)	s	s, p	s, p, d	s, p, d, f
No. of orbitals in each sub-level	1 (2 electrons)	s: 1 (2 e ⁻), p: 3 (6 e ⁻)	s: 1 (2 e ⁻), p: 3 (6 e ⁻), d: 5 (10 e ⁻)	s: 1 (2 e ⁻), p: 3 (6 e ⁻), d: 5 (10 e ⁻), f: 7 (14 e ⁻)
Total number of electrons in main energy level	2	8	18	32

SPIN

Property of electrons

- Electrons in the same orbital must have opposite spins
- Electrons are usually represented by arrows pointing up or down to show the different directions of spin

IONISATION ENERGY (IE)

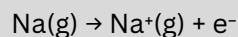
- Energy required to remove one mole of electrons from a mole of atoms in the gaseous state, measured in kJ per mole
- First IE: needs least energy to remove as it is the furthest away from the positive nucleus--> least electrostatic forces of attraction

RULES OF ELECTRON ALLOCATION TO ORBITALS

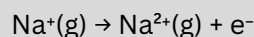
- 1) Atomic orbitals of lower energy are filled first
- 2) Atomic orbitals of the same energy fill singly before pairing starts--> because electrons repel each other
- 3) No atomic orbital can hold more than 2 electrons

IE's OF SODIUM

1st Ionisation Energy (IE):



For the 2nd Ionisation Energy of sodium:



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ATOMIC STRUCTURE



TRENDS IN 1st IONISATION ENERGY

Across a period

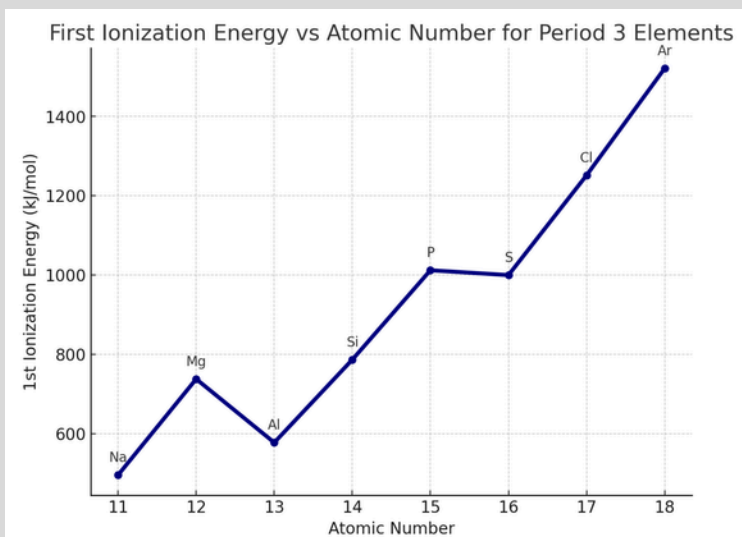
- Generally ionisation energies increase across a period
- As nuclear charge increases (number of protons)
- And atomic radius decreases (atoms get smaller)
- So outer electron is closer to the positively charged nucleus--> harder to remove the electron
- BUT there is a drop in IE (see diagram below) between phosphorous (1s², 2s², 2p⁶, 3s², 3p³) and sulfur (1s², 2s², 2p⁶, 3s², 3p⁴) as in phosphorous each of the three 3p orbital contains 1 electron, but in sulfur, one of the 3p orbitals must contain 2 electrons--> so repulsion between these makes it easier to remove that electron--> lowering IE
- ALSO there is a drop between Mg (1s², 2s², 2p⁶, 3s²) and Al. (1s², 2s², 2p⁶, 3s², 3p¹). Outer electron of Al is in a 3p orbital compared to 3s orbital in Mg (3p energy > 3s energy) so easier to remove/less energy needed

Down a group

- IE decreases
- Because atomic radius increases--> outer electron further away from positive nucleus so easier to remove
- Nuclear charge increases but this is offset by shielding effect (inner electrons reduce the positive electrostatic attraction 'felt' by the outer electrons)

ALL THE POLYATOMIC IONS YOU NEED TO KNOW

Ion Name	Formula	Charge
Ammonium	NH ₄ ⁺	+1
Hydroxide	OH ⁻	-1
Nitrate	NO ₃ ⁻	-1
Nitrite	NO ₂ ⁻	-1
Sulfate	SO ₄ ²⁻	-2
Sulfite	SO ₃ ²⁻	-2
Hydrogensulfate	HSO ₄ ⁻	-1
Carbonate	CO ₃ ²⁻	-2
Hydrogencarbonate	HCO ₃ ⁻	-1
Phosphate	PO ₄ ³⁻	-3
Hydrogenphosphate	HPO ₄ ²⁻	-2
Dihydrogenphosphate	H ₂ PO ₄ ⁻	-1
Chromate	CrO ₄ ²⁻	-2
Dichromate	Cr ₂ O ₇ ²⁻	-2
Permanganate	MnO ₄ ⁻	-1
Cyanide	CN ⁻	-1
Thiosulfate	S ₂ O ₃ ²⁻	-2
Peroxide	O ₂ ²⁻	-2
Acetate (Ethanoate)	CH ₃ COO ⁻	-1
Oxalate	C ₂ O ₄ ²⁻	-2



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AMOUNT OF SUBSTANCE



RELATIVE ATOMIC MASS

Relative Atomic Mass (A_r):

- The actual mass of atoms is too small to measure directly, so relative atomic masses are used.
- Historically, hydrogen was assigned a relative atomic mass of 1. Oxygen, for example, has a relative atomic mass of 16.
- Today, carbon-12 is the standard reference. One twelfth of the mass of a carbon-12 atom is exactly 1. The relative atomic mass (A_r) is the weighted average mass of an atom relative to carbon-12.

Relative Molecular Mass (M_r):

- The relative molecular mass (M_r) is the mass of a molecule compared to one twelfth of the mass of carbon-12.
- To calculate the relative molecular mass, add up the relative atomic masses (A_r) of all atoms in the molecule.

Relative Formula Mass (M_r):

- For ionic compounds, use the term "relative formula mass" (M_r) as they don't exist as molecules. This is calculated similarly to relative molecular mass.

Avogadro Constant and the Mole:

- Atoms are too small to weigh individually, so chemists use the Avogadro constant (6.022×10^{23}) to count atoms.
- The Avogadro constant is the number of particles (atoms, molecules) in 1 mole of a substance.
- The mass in grams of one mole of an element equals its relative atomic mass (A_r).
- For molecules, the mass in grams of one mole equals the relative molecular mass (M_r).

Number of Moles (n):

- To calculate the number of moles in a given mass:
 - $n = \text{mass (g)} / \text{mass of 1 mole (M)}$
 - For elements, use the relative atomic mass (A_r); for molecules or compounds, use the relative molecular/formula mass (M_r).

THE MOLE

Solutions and Concentration:

- A solution consists of a solute dissolved in a solvent.
- Concentration indicates how much solute is present in a given volume of solution and is measured in mol dm^{-3} .
 - 1 mol dm^{-3} means 1 mole of solute is dissolved in 1 cubic decimeter of solution.
 - 2 mol dm^{-3} means 2 moles of solute are dissolved per cubic decimeter, and so on.

Calculating Moles in a Solution:

- To find the number of moles (n) in a solution with a known concentration (c in mol dm^{-3}) and volume (V in cm^3), use the formula:
- $n = (c \times V) / 1000$

This formula helps you determine the number of moles in any given volume of a solution.

THE IDEAL GAS EQUATION

Gas Laws:

1. **Boyle's Law:** At constant temperature, the product of pressure and volume is constant.
 - $P \times V = \text{constant}$
2. **Charles' Law:** At constant pressure, volume is proportional to temperature.
 - $V/T = \text{constant}$
3. **Gay-Lussac's Law:** At constant volume, pressure is proportional to temperature.
 - $P/T = \text{constant}$

Combined Gas Law:

- Combining the above laws gives:
 - $(P \times V) / T = \text{constant}$ (for a fixed mass of gas)

Ideal Gas Equation:

- The ideal gas law connects pressure (P), volume (V), number of moles (n), and temperature (T) through the gas constant ($R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$):
 - $PV = nRT$
 - This equation can be rearranged to solve for:
 - Volume (V): $V = (nRT) / P$
 - Pressure (P): $P = (nRT) / V$
 - Number of moles (n): $n = (PV) / (RT)$

Notes on Units:

- P (pressure) in Pa
- V (volume) in m^3
- T (temperature) in K
- R (gas constant) = $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

Applications:

- At room temperature and pressure, the volume of one mole of any gas is approximately 24 dm^3 .
- The ideal gas equation can be used to find the number of moles (n) and calculate the relative molecular mass of gases by determining the mass of one mole.

01-CHEM-2

AMOUNT OF SUBSTANCE



EMPIRICAL FORMULAE AND MOLECULAR FORMULAE

Empirical Formula:

- The empirical formula represents the simplest whole-number ratio of atoms of each element in a compound.
 - Example: Carbon dioxide (CO_2) has an empirical formula showing a 1:2 ratio of carbon to oxygen atoms.

Steps to Find an Empirical Formula:

- Find the masses of each element present (via experiment).
- Calculate the moles of each element:
 - Number of moles = mass of element / molar mass of element
- Convert moles to a whole-number ratio by dividing each value by the smallest number of moles.

Simplifying Ratios:

- If the ratio isn't a whole number, divide each number by the smallest value to simplify.

Molecular Formula:

- The molecular formula shows the actual number of atoms of each element in a molecule.
 - Example: Ethene (C_2H_4) has a molecular formula, but its empirical formula is CH_2 .

Finding Molecular Formula:

- Divide the relative molecular mass by the relative mass of the empirical formula.
- Multiply the empirical formula by the result to get the molecular formula.
 - Example: Ethene's relative molecular mass is 28, and the empirical formula mass is 14. Since $28 \div 14 = 2$, the molecular formula is $(\text{CH}_2)_2$ or C_2H_4 .

CHEMICAL EQUATIONS: WRITING AND BALANCING

Equations in Chemical Reactions:

- Chemical equations represent the changes in a reaction, showing reactants on the left and products on the right.
- Word equations only show the names of reactants and products, e.g., hydrogen + oxygen $\rightarrow$ water.
- In reactions, atoms combine in simple whole-number ratios, known as the stoichiometry of the reaction.

Balanced Symbol Equations:

- Balanced symbol equations use chemical formulae, ensuring the same number of atoms for each element on both sides.
- These equations show how many moles of substances react and what products are formed.
- State symbols indicate the physical state: (s) solid, (l) liquid, (g) gas, (aq) aqueous.

Steps to Write a Balanced Equation:

- Write the word equation.
 - Example: aluminium + oxygen $\rightarrow$ aluminium oxide
- Write the correct formulae for each substance.
 - $\text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$
- Balance the equation by adjusting coefficients to equalize the number of atoms of each element.
 - Adjust aluminium: $2\text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$.
 - Adjust oxygen: $2\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$.
 - Final balanced equation: $4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$.
- Add state symbols.

Ionic Equations:

- In some reactions, ions that don't participate are called spectator ions.
- For example, in the reaction between hydrochloric acid (HCl) and sodium hydroxide (NaOH), the simplified ionic equation is:
 - $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$.
 - Sodium (Na^+) and chloride (Cl^-) are spectator ions.

Tips for Balancing Equations:

- Use the correct formulae for each substance.
- You can only adjust the coefficients in front of formulae to balance.
- The total charge in ionic equations must be balanced on both sides.

Working Out Amounts:

- A balanced symbol equation helps in calculating how much product is produced by comparing moles.
- Example: For $4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$:
 - 4 moles of Al react with 3 moles of O_2 to produce 2 moles of Al_2O_3 .
 - You can calculate the mass of reactants and products using their molar masses.

01-CHEM-2

AMOUNT OF SUBSTANCE



TITRATION CALCULATIONS

Titrations determine the concentration of a solution by reacting it with a solution of known concentration, using a suitable indicator.

Steps in a Titration:

1. Fill the burette with the solution of known concentration (acid).
2. Measure a specific volume of the solution to be tested (alkali) using a calibrated pipette and pipette filler.
3. Add the alkali to a conical flask, along with a few drops of an appropriate indicator.
4. Titrate by slowly adding the acid from the burette until the indicator shows a color change, indicating neutralization.
5. Repeat the titration, adding the acid dropwise near the endpoint, until you obtain consistent volume readings for the acid used.

Key Terms:

- Burette: For delivering the titrant (acid).
- Pipette: For measuring precise volumes of alkali.
- Conical Flask: Where the reaction occurs.
- Indicator: Shows the end point of the reaction.
- End Point: When the indicator changes color, signifying neutralization.

ATOM ECONOMY

Atom Economy: Atom economy measures the efficiency of a chemical reaction in terms of the proportion of reactants that form the desired product. It is calculated using the formula:

Atom Economy (%) = (Mass of desired product / Total mass of reactants) × 100

Example 1: Sodium Chlorate Production For the reaction: $2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{NaOCl}$

Given:

- Total mass of reactants = 151.0 g
- Mass of desired product (sodium chlorate) = 74.5 g

Atom Economy (%) = $(74.5 / 151.0) \times 100 = 49.3\%$

Example 2: Ethene Production For the reaction: $\text{C}_2\text{H}_4 + \text{Br}_2 \rightarrow \text{CHBr}_2\text{CHBr}_2$

Given:

- Total mass of reactants = 188.0 g
- Mass of desired product (1,2-dibromoethane) = 188.0 g

Atom Economy (%) = $(188.0 / (28.0 + 160.0)) \times 100 = 100\%$

Percentage Yield: Percentage yield indicates the practical efficiency of a reaction, considering the actual amount of product obtained compared to the theoretical maximum.

Percentage Yield (%) = (Actual yield / Theoretical yield) × 100

Example Calculation: For the reaction: $\text{Pb}(\text{NO}_3)_2 + 2\text{KI} \rightarrow \text{PbI}_2 + 2\text{KNO}_3$

Given Data:

- Theoretical yield of lead iodide = 4.61 g
- Actual yield obtained = 4.00 g

Percentage Yield (%) = $(4.00 / 4.61) \times 100 = 86.8\%$

Calculating Atom Economy of a Reaction:

1. Find the theoretical maximum number of moles or grams of the product.
2. Use the formula for atom economy to determine how efficiently the reactants are converted into the desired product.

Example: For the reaction of calcium carbonate: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$

Given:

- Theoretical maximum number of moles of CaO from 3.32 g of CaCO_3

Calculate Atom Economy: $\text{Atom Economy} = \frac{\text{Mass of CaO}}{\text{Total mass of CaCO}_3} \times 100$

Reversible Reactions: In reversible reactions, achieving 100% yield is challenging due to equilibrium. For example, the Haber process for ammonia synthesis cannot achieve 100% yield, but optimising conditions can improve yield.

01-CHEM-3

BONDING



WHY DOES CHEMICAL BONDING HAPPEN?

Chemical bonds form to achieve a more stable electron arrangement, similar to the full outer electron shells of noble gases. Atoms bond by either sharing or transferring electrons to reach this stable configuration. There are three main types of chemical bonds: ionic, covalent, and metallic.

IONIC BONDING

Definition: Ionic bonding occurs between metals and non-metals, involving the transfer of electrons from metal atoms to non-metal atoms. This process results in the formation of positively and negatively charged ions that are held together by electrostatic forces.

Process:

- **Metal Atoms:** Metals have one, two, or three electrons in their outer shell. They lose these electrons to achieve a noble gas configuration.
- **Non-Metal Atoms:** Non-metals have space in their outer shell to gain electrons, achieving a full outer shell and a noble gas configuration.

Example: Sodium Chloride

- Sodium (Na): Has 11 electrons with the configuration $1s^2 2s^2 2p^6 3s^1$. Sodium loses its single 3s electron to become Na^+ .
- Chlorine (Cl): Has 17 electrons with the configuration $1s^2 2s^2 2p^6 3s^2 3p^5$. Chlorine gains an electron to become Cl^- .

The ionic bond forms as the Na^+ and Cl^- ions are attracted to each other, creating a stable ionic lattice (Figure 4).

Ionic Bonding in Magnesium Oxide

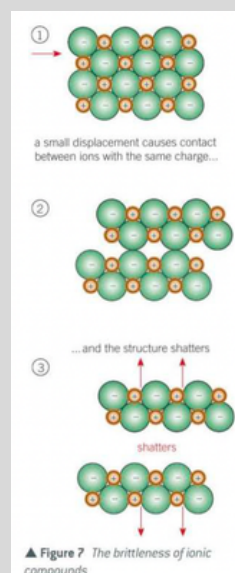
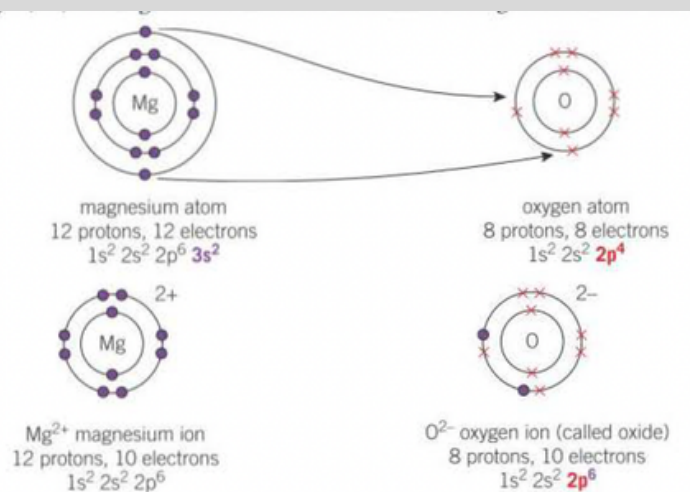
Process:

- Magnesium (Mg): Has 12 electrons with the configuration $1s^2 2s^2 2p^6 3s^2$. Magnesium loses two 3s electrons to become Mg^{2+} .
- Oxygen (O): Has 8 electrons with the configuration $1s^2 2s^2 2p^4$. Oxygen gains two electrons to become O^{2-} .

The ionic bond forms between Mg^{2+} and O^{2-} , resulting in the formation of magnesium oxide (MgO) (Figure 5).

Properties of Ionic Compounds

- **State at Room Temperature:** Ionic compounds are typically solid due to their high melting points, which are a result of the strong ionic bonds forming a lattice structure.
- **Conductivity:** They conduct electricity when molten or dissolved in water because the ions are free to move. However, they do not conduct electricity when solid because the ions are fixed in place within the lattice.
- **Brittleness:** Ionic compounds are brittle and can shatter easily. A sharp blow can shift the ions within the lattice, causing like-charged ions to come into contact and repel each other, leading to the material breaking apart.



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BONDING



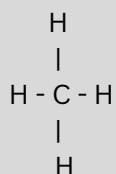
IONIC BONDING

Formation of Covalent Bonds:

- Covalent Bonds: Formed when non-metal atoms share pairs of electrons to achieve a stable electron arrangement similar to that of noble gases.
- Molecules: A molecule is a small group of atoms covalently bonded together. For example, chlorine gas (Cl_2) is made of Cl_2 molecules where two chlorine atoms share one pair of electrons, resulting in a stable noble gas configuration.

Representation:

- Single Covalent Bond: Represented by a single line (e.g., $\text{Cl}-\text{Cl}$) indicating one shared pair of electrons.
- Example: Methane (CH_4): Carbon (C) shares its four outer electrons with four hydrogen (H) atoms, each contributing one electron. The resulting molecule is CH_4 , with a structure:



Holding Atoms Together:

- Electrostatic Attraction: Atoms are held together by the electrostatic forces between the positively charged nuclei and the shared pair of electrons.

Double Covalent Bonds:

- Double Bonds: Involves sharing two pairs of electrons between atoms. For example, in an oxygen molecule (O_2), each oxygen atom shares two pairs of electrons:
- $\text{O}=\text{O}$

Properties of Covalent Compounds:

- State and Melting Points: Covalent compounds can be gases, liquids, or solids with low melting temperatures due to weak intermolecular forces compared to the strong covalent bonds within the molecules.
- Electrical Conductivity: These substances are poor conductors of electricity as the molecules are neutral and lack free charged particles. Solutions of covalent compounds in water do not conduct electricity if they remain as molecules.

CO-ORDINATE BONDING

Concept of Co-ordinate Bonding:

- Single Covalent Bond: Typically involves a pair of electrons shared between two atoms, with each atom contributing one electron.
- Co-ordinate Bond: Occurs when one atom provides both electrons in the bond, while the other atom accepts them. This type of bond is also known as dative covalent bonding.

Characteristics:

- Electron-Deficient Atom: The atom accepting the electron pair is electron-deficient and lacks a filled outer electron shell.
- Lone Pair: The donating atom provides a lone pair of electrons that is not involved in other bonding.

Example: Ammonium Ion (NH_4^+)

- Ammonia (NH_3): Contains a lone pair of electrons on the nitrogen atom.
- Formation of Ammonium Ion:
 - In the ammonium ion (NH_4^+), the nitrogen atom donates its lone pair of electrons to an H^+ ion (a proton with no electrons), forming a co-ordinate bond.
 - The nitrogen atom is now fully bonded, and the H^+ ion achieves a stable electron configuration.

Representation:

- Coordinate Bond Symbol: Represented by an arrow ($\rightarrow$) pointing from the atom donating the lone pair to the atom accepting it.
 - Example: $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$



CO-ORDINATE BONDING CONTNUED

Properties:

- Strength and Length: Co-ordinate bonds have the same strength and length as ordinary covalent bonds between the same pair of atoms.
- Symmetry: In a molecule like the ammonium ion, all bonds are of equal strength and length, resulting in a symmetrical structure.

Visual Representation:

- Ammonium Ion Diagram:
- mathematica
- Copy code
- H|H-N-H|H
 - The lone pair from nitrogen is donated to form the bond with H⁺.

CO-ORDINATE BONDING CONTNUED

Properties:

- Strength and Length: Co-ordinate bonds have the same strength and length as ordinary covalent bonds between the same pair of atoms.
- Symmetry: In a molecule like the ammonium ion, all bonds are of equal strength and length, resulting in a symmetrical structure.

Visual Representation:

- Ammonium Ion Diagram:
- mathematica
- Copy code
- H|H-N-H|H
 - The lone pair from nitrogen is donated to form the bond with H⁺.

CO-ORDINATE BONDING CONTNUED

Concept of Metallic Bonding:

- Electron Delocalization: In metals, outer electrons become delocalized and are not associated with any specific atom. This creates a "sea" of delocalized electrons surrounding a lattice of positive metal ions.
- Metallic Lattice: Metals consist of a lattice of positive ions embedded in a sea of delocalized electrons.

Properties of Metallic Bonding:

- Electrostatic Attraction: Positive metal ions are attracted to the delocalized electrons, which balances the repulsion between the positively charged ions.
- Giant Structure: The metallic bonding extends throughout the metal, forming a giant structure.

Properties of Metals:

1. Good Conductors:

- Electricity: Delocalized electrons can move freely through the metal, allowing it to conduct electricity effectively. An electron from the negative terminal of a power source enters one end of the metal, while another exits the positive terminal, enabling the flow of electric current.
- Heat: High thermal conductivity is due to the movement of delocalized electrons and the transfer of kinetic energy through vibrating metal ions.

2. Strength of Metals:

- Charge of Ions: Metals with ions of higher charge have more delocalized electrons and stronger electrostatic attractions, increasing strength.
- Size of Ions: Smaller metal ions have stronger bonds because their electrons are closer to the nucleus.

3. Malleability and Ductility:

- Malleable: Metals can be hammered or rolled into different shapes without breaking. The malleability arises because, upon distortion, metal ions remain in a similar environment.
- Ductile: Metals can be drawn into thin wires due to the ability of metal ions to slide past one another while maintaining their bond with delocalized electrons.

4. High Melting and Boiling Points:

- Giant Structures: Metals generally have high melting and boiling points because of the strong attractions between metal ions and the delocalized electron sea, which require substantial energy to overcome.

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BONDING



ELECTRONEGATIVITY

Electronegativity:

- Definition: Electronegativity is the ability of an atom in a covalent bond to attract the shared electron density toward itself.
- Electron Density: In chemistry, the term electron density is used to describe how the negative charge from electrons is distributed around atoms in a molecule.
- Pauling Scale: A numerical scale that measures electronegativity, ranging from 0 to 4, where higher values indicate stronger attraction for electrons. Fluorine, with an electronegativity of 4.0, is the most electronegative element.

Factors Affecting Electronegativity:

1. Nuclear Charge: A higher nuclear charge (more protons) increases electronegativity.
2. Atomic Radius: Smaller atoms have higher electronegativity because the nucleus is closer to the outer electrons.
3. Shielding Effect: Electrons in inner shells shield the outer electrons from the full nuclear charge. Less shielding increases electronegativity.

Trends in Electronegativity:

- Across a Period: Electronegativity increases as you move across a period in the Periodic Table. This is due to increasing nuclear charge and decreasing atomic size, with constant shielding.
- Down a Group: Electronegativity decreases as you move down a group because atoms get larger, and there is more shielding by inner electrons.

Most Electronegative Elements:

- The most electronegative elements are found in the top right corner of the Periodic Table (excluding noble gases). These elements include fluorine, oxygen, nitrogen, and chlorine.

ELECTRONEGATIVITY

• Non-polar Covalent Bonds:

- When two atoms in a covalent bond are the same (e.g., in a fluorine molecule, F_2), the electrons are shared equally because both atoms have the same electronegativity.
- This creates a non-polar bond where the electron cloud is uniformly spread between the atoms.

• Polar Covalent Bonds:

- In covalent bonds between atoms with different electronegativities, the electrons are not shared equally. The more electronegative atom pulls the electron density closer, causing a distortion in the electron cloud.
- Example: In hydrogen fluoride (HF), fluorine has an electronegativity of 4.0 and hydrogen has 2.1. The electrons in the bond are pulled toward fluorine, making fluorine partially negative (δ^-) and hydrogen partially positive (δ^+).
- Such bonds are polar covalent bonds.

Ionic Character in Polar Covalent Bonds:

- The greater the difference in electronegativity between two atoms, the more polar the bond becomes.
- In extreme cases, a polar covalent bond can exhibit ionic character, where the electron distribution begins to resemble that of an ionic bond with distinct charges.

Partial Charges in Polar Bonds:

- The partial charges (δ^+ and δ^-) show the relative distribution of electron density in a polar bond.
- H-F Example: The fluorine end (F) of the H-F molecule becomes δ^- (negative), while the hydrogen end (H) becomes δ^+ (positive).

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BONDING



THREE TYPES OF INTERMOLECULAR FORCES

There are three types of intermolecular forces that vary in strength and arise from different molecular interactions:

1. van der Waals Forces (weakest)
2. Dipole-Dipole Forces
3. Hydrogen Bonding (strongest)

DIPOLE-DIPOLE FORCES

Dipole Moments:

- Molecules with polar bonds can have a dipole moment, which is the net effect of the polarities of individual bonds.
- Molecular Shape: The shape of the molecule influences whether these dipoles cancel each other out or reinforce each other.
 - Examples:
 - Carbon Dioxide (CO_2): A linear molecule where dipoles cancel out, resulting in no net dipole moment.
 - Tetrachloromethane (CCl_4): A tetrahedral molecule where dipoles cancel, leading to no dipole moment.
 - Dichloromethane (CH_2Cl_2): A tetrahedral molecule where the dipoles do not cancel, so it has a dipole moment.

How Dipole-Dipole Forces Work:

- Molecules with permanent dipoles (e.g., hydrogen chloride, HCl) attract one another because the negative end of one dipole is attracted to the positive end of another.

VAN DER WAALS FORCES

How Hydrogen Bonding Works:

- Hydrogen bonding is a strong intermolecular force that involves hydrogen atoms "sandwiched" between two highly electronegative atoms (such as oxygen, nitrogen, or fluorine).
- Conditions for Hydrogen Bonding:
 - a. A hydrogen atom bonded to a very electronegative atom (O, N, or F).
 - b. A lone pair of electrons on the electronegative atom.
- Example: In water (H_2O), oxygen is much more electronegative than hydrogen, making the molecule polar. The small, positively charged hydrogen atoms are attracted to the lone pairs on nearby oxygen atoms in other water molecules, creating hydrogen bonds.

Hydrogen Bonding Examples:

- Water (H_2O): Hydrogen bonding between water molecules contributes to water's high boiling point and unique properties, such as the structure of ice.
- Ammonia (NH_3): Forms hydrogen bonds with water through nitrogen-hydrogen interactions.

Boiling Points and Hydrogen Bonding:

- The boiling points of water (H_2O), hydrogen fluoride (HF), and ammonia (NH_3) are higher than expected compared to other hydrides in their respective groups due to hydrogen bonding. These stronger intermolecular forces make the molecules more difficult to separate, raising their boiling points.

VAN DER WAALS FORCES

- Also known as: Instantaneous dipole-induced dipole forces.
- How they arise: Even in neutral atoms, electron clouds fluctuate momentarily, creating temporary dipoles. These dipoles can induce dipoles in neighboring atoms or molecules, resulting in weak electrostatic attractions.
- Key Points:
 - They exist between all atoms and molecules.
 - They are additive to other intermolecular forces.
 - Strength depends on electron number: Larger atoms or molecules with more electrons exhibit stronger van der Waals forces.
- Impact on boiling points:
 - Noble gases: Boiling points increase with increasing atomic number because of stronger van der Waals forces.
 - Hydrocarbons: As chain length increases, van der Waals forces increase, raising boiling points.

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BONDING

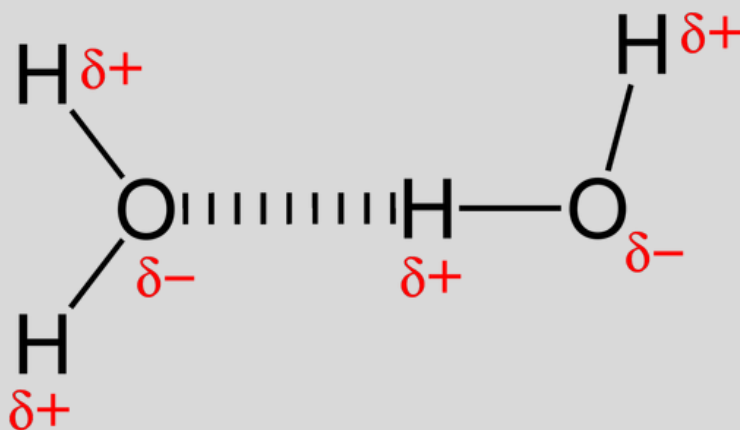
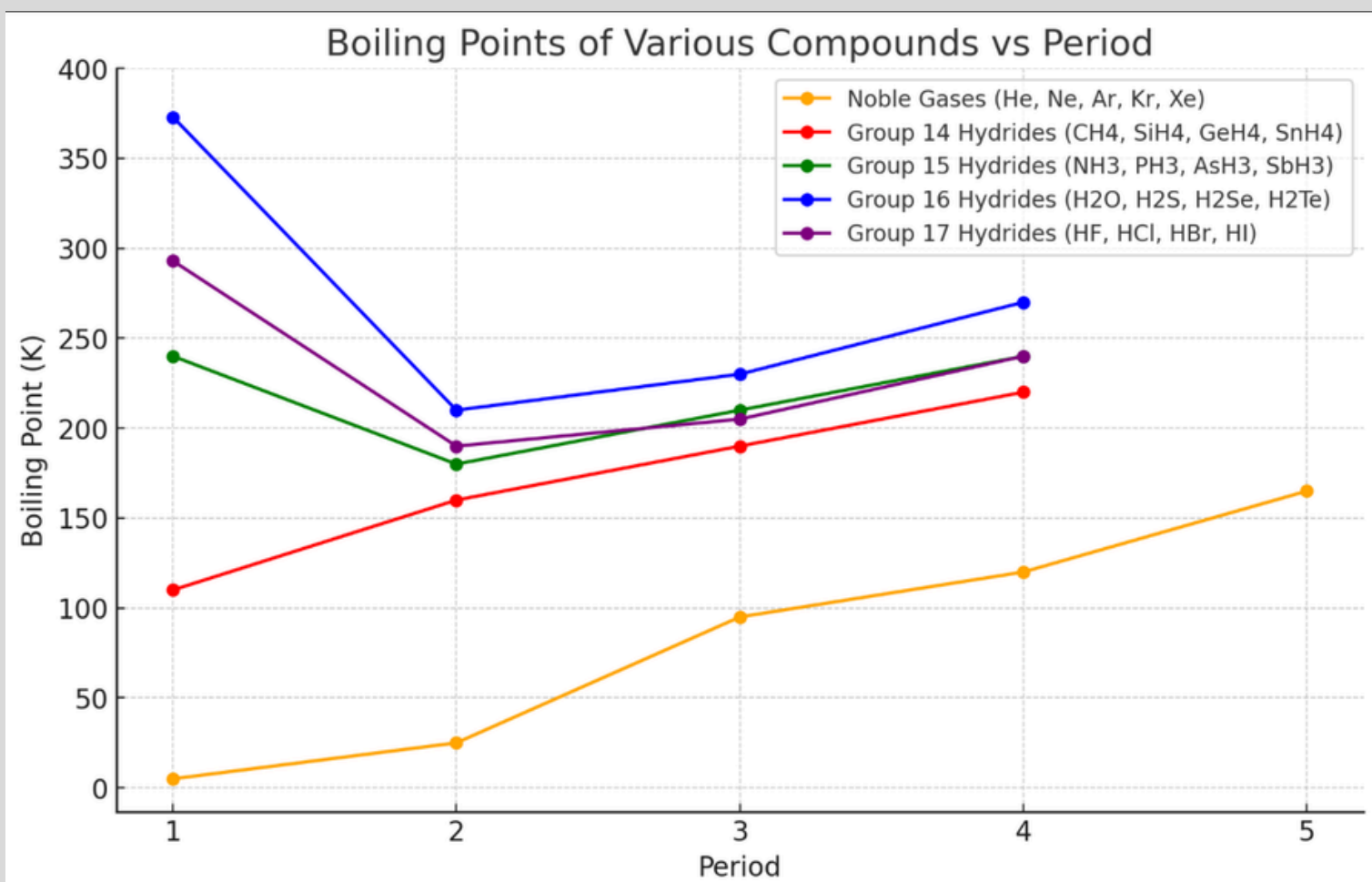


HYDROGEN BONDING- IN REAL LIFE

Importance of Hydrogen Bonding:

- Although hydrogen bonds are only about 10% the strength of covalent bonds, they are crucial in determining the properties of substances.
 - Example: The hydrogen bonds in water give it a unique density structure, allowing ice to be less dense than liquid water, causing ice to float. This property of ice has ecological importance as it insulates water bodies, enabling aquatic life to survive in cold climates.

DIAGRAMMATIC REPRESENTATION OF EACH TYPE OF FORCE



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BONDING



SHAPES OF MOLECULES AND IONS

Electron Pair Repulsion Theory:

Electron pair repulsion theory is based on the idea that pairs of electrons (whether in bonds or as lone pairs) repel each other. This repulsion influences the shape of molecules because the electron pairs will arrange themselves as far apart as possible to minimize repulsion.

Key Principles:

1. Electron pairs around an atom will repel each other.
2. Shapes of molecules are determined by the number of electron pairs around the central atom.
3. Electron pairs can be either shared (bonding pairs) or unshared (lone pairs).
4. Lone pairs repel more strongly than bonding pairs, affecting bond angles.

Molecular Shapes and Bond Angles:

Two Pairs of Electrons:

- Shape: Linear
- Bond Angle: 180°
- Example: Beryllium chloride (BeCl_2)
 - In BeCl_2 , the two bonding pairs of electrons are arranged as far apart as possible, resulting in a linear shape.

Three Pairs of Electrons:

- Shape: Trigonal Planar
- Bond Angle: 120°
- Example: Boron trifluoride (BF_3)
 - The three bonding pairs in BF_3 are arranged in a flat, triangular shape with bond angles of 120° .

Four Pairs of Electrons:

- Shape: Tetrahedral
- Bond Angle: 109.5°
- Example: Methane (CH_4), ammonium ion (NH_4^+)
 - The four bonding pairs form a tetrahedral shape, maximizing their separation.

Five Pairs of Electrons:

- Shape: Trigonal Bipyramidal
- Bond Angles: 90° and 120°
- Example: Phosphorus pentachloride (PCl_5)
 - The five pairs form a shape with three pairs arranged in a trigonal plane and two pairs above and below.

Six Pairs of Electrons:

- Shape: Octahedral
- Bond Angle: 90°
- Example: Sulfur hexafluoride (SF_6)
 - The six bonding pairs arrange themselves in an octahedral shape.

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BONDING



SHAPES OF MOLECULES AND IONS IN THE PRESENCE OF LONE PAIRS

Lone Pairs and Molecular Shape:

Lone pairs of electrons affect the shape of a molecule by repelling bonding pairs more strongly, which can reduce bond angles.

Ammonia (NH₃):

- Shape: Trigonal Pyramidal
- Bond Angle: 107°
- Electron Pair Geometry: Tetrahedral
 - Ammonia has four electron pairs around nitrogen (three bonding, one lone pair). The lone pair pushes the bonding pairs closer together, reducing the bond angle from 109.5° to 107°.

Water (H₂O):

- Shape: V-shaped (bent)
- Bond Angle: 104.5°
- Electron Pair Geometry: Tetrahedral
 - Water has four electron pairs around oxygen (two bonding, two lone pairs). The lone pairs repel the bonding pairs, reducing the bond angle to 104.5°.

Chlorine Tetrafluoride Ion (ClF₄⁻):

- Shape: Square Planar
- Bond Angle: 90° (approx.)
 - ClF₄⁻ has six electron pairs around chlorine (four bonding, two lone pairs). The lone pairs are positioned above and below the square plane formed by the bonding pairs, giving it a square planar shape.

Summary of Electron Pair Repulsion:

- Bonding pair - Bonding pair: Least repulsion
- Lone pair - Bonding pair: More repulsion
- Lone pair - Lone pair: Most repulsion

The increasing repulsion between electron pairs follows this order, influencing the final geometry of the molecule.

THREE STATES OF MATTER

State	Arrangement of Particles	Spacing	Movement	Properties
Solid	Regular	Close	Vibrating about a point	Definite shape, incompressible, expands on heating
Liquid	Random	Close	Rapid 'jostling'	Takes shape of the container, incompressible, evaporates
Gas	Random	Far apart	Rapid	Fills the container, easily compressible, exerts pressure

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BONDING



ENERGY CHANGES ON HEATING

- Heating a solid: Increases vibration, expanding the solid.
- Melting (fusion): Requires energy to weaken intermolecular forces, no temperature change during the process.
- Heating a liquid: Particles gain kinetic energy and move faster, slightly increasing in distance.
- Boiling (vaporization): Energy supplied to break intermolecular forces completely, turning liquid into gas.
- Heating a gas: Particles gain kinetic energy, moving much farther apart and expanding significantly.

CRYSTALS AND BONDING TYPE

Crystals are solid substances where particles are arranged in a regular structure. The type of bonding affects the properties of the crystals.

1. Ionic Crystals:

- Bonding: Strong electrostatic attractions between oppositely charged ions.
- Example: Sodium chloride (NaCl).
- Properties: High melting point due to strong attractions, does not conduct electricity when solid, but conducts when molten or dissolved.

2. Metallic Crystals:

- Bonding: Positive metal ions in a sea of delocalized electrons.
- Example: Metals like copper.
- Properties: High melting point due to strong metallic bonds, conducts electricity both in solid and molten states.

3. Molecular Crystals:

- Bonding: Molecules held by weak intermolecular forces (van der Waals, dipole-dipole, hydrogen bonds).
- Example: Iodine (I₂).
- Properties: Soft, low melting temperature, does not conduct electricity.

4. Macromolecular Crystals:

- Bonding: Covalent bonds extending throughout the structure.
- Examples: Diamond, graphite.
- Properties: High melting point due to strong covalent bonds, diamond is hard and non-conductive, graphite conducts electricity along planes of carbon atoms due to delocalized electrons.

SUMMARY OF PROPERTIES BASED ON BONDING TYPE

Bonding Type	Melting/Boiling Point	Electrical Conductivity	Example
Ionic	High	Conducts when molten/dissolved	NaCl
Metallic	High	Conducts in solid and liquid states	Copper
Covalent (Simple Molecular)	Low	Does not conduct (except for some cases like graphite)	I ₂
Covalent (Macromolecular)	High	Does not conduct (except graphite and graphene)	Diamond, graphite

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ENERGETICS



ENDOTHERMIC AND EXOTHERMIC REACTIONS

Thermochemistry is the study of heat changes during chemical reactions. Chemical bonds are broken and formed during reactions, leading to energy changes.

- Breaking bonds requires energy input.
- Forming bonds releases energy.
- The overall energy change determines whether the reaction is exothermic or endothermic.

Exothermic Reactions:

- Heat is released to the surroundings.
- Example: Neutralisation of an acid with an alkali.

Endothermic Reactions:

- Heat is absorbed from the surroundings.
- Example: The thermal decomposition of calcium carbonate:
- $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

Reversible Reactions:

- Endothermic in one direction is exothermic in the reverse.
- Example: Dehydrating copper sulfate:
- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightarrow \text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{g})$ (Endothermic)
- Adding water reverses the process and releases heat (Exothermic).

Quantities:

The energy change depends on the amount of reactants, typically measured in kJ mol^{-1} . For instance:

- Combustion of methane:
- $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
- Energy released: -890 kJ mol^{-1}

Examples of Useful Enthalpy Changes:

- Combustion of carbon:
- $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- Energy released: $-393.5 \text{ kJ mol}^{-1}$
- Endothermic cold packs (used in sports injuries) involve ammonium nitrate:
- $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4\text{NO}_3(\text{aq})$
- Energy absorbed: $+26 \text{ kJ mol}^{-1}$

ENTHALPY CHANGES

The enthalpy change (ΔH) is the heat change during a reaction at constant pressure. It is measured under standard conditions:

- **Pressure:** 100 kPa
- **Temperature:** 298 K (25°C)

The standard enthalpy change is denoted as ΔH° , which is pronounced as delta H standard.

Exothermic and Endothermic Reactions:

- Exothermic reactions release heat; the products have less energy than the reactants, so ΔH is negative.
- Endothermic reactions absorb heat; the products have more energy than the reactants, so ΔH is positive.

Pressure and State:

- Pressure affects reactions involving gases. Higher pressure requires more energy to push away the atmosphere, so less heat is released.
- Physical states (solid, liquid, gas) impact ΔH , as changes in state (e.g., liquid to gas) involve heat. Always include state symbols in equations.

Example of hydrogen combustion:

1. Formation of liquid water:
2. $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ $\Delta H = -285.8 \text{ kJ mol}^{-1}$
3. Formation of steam:
4. $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$ $\Delta H = -241.8 \text{ kJ mol}^{-1}$

The difference between ΔH values is due to the heat required to convert water into steam.

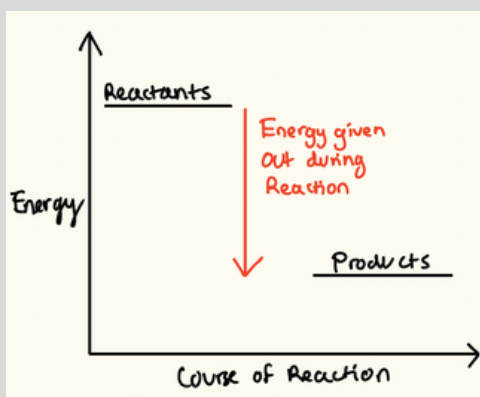
ENTHALPY DIAGRAMS

Enthalpy level diagrams (or energy level diagrams) visually represent enthalpy changes. They compare the enthalpy of reactants and products:

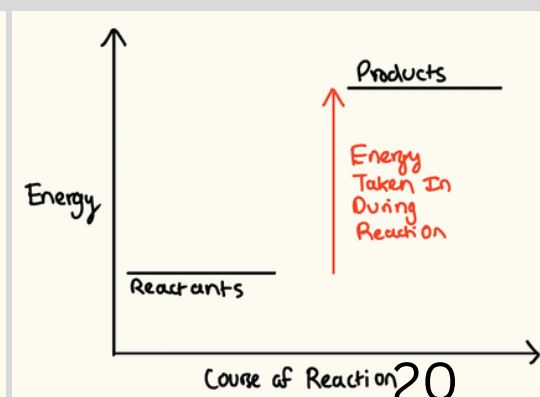
- **Exothermic:** Products have lower enthalpy than reactants.
- **Endothermic:** Products have higher enthalpy than reactants.

These diagrams plot enthalpy on the vertical axis and the progress of the reaction on the horizontal axis.

Exothermic



Endothermic



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MEASURING ENTHALPY CHANGES



HOW TO MEASURE ENTHALPY CHANGES

Standard Enthalpies

Common enthalpy changes:

- Enthalpy of formation ($\Delta_f H^\circ$): The enthalpy change when one mole of a substance is formed from its elements under standard conditions (298 K, 100 kPa).
- Enthalpy of combustion ($\Delta_c H^\circ$): The enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions.

Heat and Temperature

- Temperature relates to the average kinetic energy of particles and is independent of the number of particles.
- Heat is the total energy of all particles and depends on the quantity of the substance. Heat flows from high to low temperature.

Measuring Enthalpy Changes

To measure enthalpy change ($q = mc\Delta T$), you need:

1. Mass of the substance
2. Temperature change (ΔT)
3. Specific heat capacity (c), e.g., water = $4.18 \text{ J g}^{-1} \text{ K}^{-1}$.

Calorimetry

A calorimeter measures heat from a reaction. For example, when burning a fuel, a simple calorimeter can compare $\Delta_c H$ values. To improve accuracy, a flame calorimeter has features to minimize heat loss:

- Copper spiral chimney
- Enclosed flame
- Burns fuel in pure oxygen.

Reactions in Solution

For reactions in solution, heat is measured within the solution using polystyrene beakers to reduce heat loss. The specific heat capacity of solutions is usually assumed to be the same as water ($4.18 \text{ J g}^{-1} \text{ K}^{-1}$).

Neutralization Reactions

Neutralization reactions are exothermic. For example, the neutralization of HCl by NaOH: $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$

Displacement Reactions

More reactive metals displace less reactive ones, often releasing heat (exothermic). For example: $\text{Zn(s)} + \text{CuSO}_4\text{(aq)} \rightarrow \text{ZnSO}_4\text{(aq)} + \text{Cu(s)}$

Allowing for Heat Loss

Even with insulated polystyrene cups, some heat is lost. A cooling curve can be used to estimate the correct temperature change.

Example Calculation:

For the reaction between HCl and NaOH:

- Temperature rise (ΔT): 6.9°C
- Heat energy (q):
- $q = m \times c \times \Delta T = 100 \text{ g} \times 4.2 \text{ J g}^{-1} \text{ K}^{-1} \times 6.9 \text{ K} = 2898 \text{ J}$
- Moles of acid and alkali: 0.05 mol
- Enthalpy change (ΔH):
- $\Delta H = 2898 \text{ J} \div 0.05 \text{ mol} = -58 \text{ kJ mol}^{-1}$

The negative sign indicates an exothermic reaction.



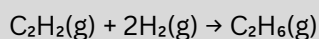
HESS'S LAW

Hess's Law states that the enthalpy change for a chemical reaction is the same, no matter which route is taken from reactants to products. This is a consequence of the law of conservation of energy, which states that energy cannot be created or destroyed. Therefore, as long as the starting and finishing points of a reaction are the same, the total energy change must also be the same, regardless of the path taken.

Using Hess's Law

Let's look at an example where ethyne (C_2H_2) is converted to ethane (C_2H_6) by two different routes. How can we find the enthalpy of reaction?

Route 1: The reaction happens directly, where ethyne reacts with two moles of hydrogen to produce ethane.



Enthalpy change: ΔH_1

Route 2: The reaction takes place in two stages.

- Stage 1: Ethyne (C_2H_2) reacts with one mole of hydrogen to give ethene (C_2H_4).
- $\text{C}_2\text{H}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g})$
- Enthalpy change: $\Delta H_2 = -176 \text{ kJ mol}^{-1}$
- Stage 2: Ethene (C_2H_4) then reacts with another mole of hydrogen to give ethane (C_2H_6).
- $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
- Enthalpy change: $\Delta H_3 = -137 \text{ kJ mol}^{-1}$

Applying Hess's Law

According to Hess's Law, the total enthalpy change for the reaction should be the same for both routes. Therefore:

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

$$\Delta H_1 = -176 + (-137) = -313 \text{ kJ mol}^{-1}$$

So, regardless of whether the reaction takes place directly (Route 1) or through the intermediate ethene (Route 2), the total enthalpy change remains the same: -313 kJ mol^{-1} .

HESS'S LAW AND ENTHALPY CALCULATIONS

Hess's Law states that the total enthalpy change for a chemical reaction is independent of the route taken, provided the starting and finishing points are the same.

This reflects the law of conservation of energy, which asserts that energy cannot be created or destroyed.

Example: Conversion of Ethyne to Ethane

Ethyne (C_2H_2) can be converted to ethane (C_2H_6) by two different routes:

1. Direct Reaction: C_2H_2 reacts with 2 moles of hydrogen (H_2) to form C_2H_6 .
2. Two-Step Reaction: a. C_2H_2 reacts with 1 mole of H_2 to form ethene (C_2H_4), $\Delta H_1 = -176 \text{ kJ mol}^{-1}$. b. C_2H_4 reacts with 1 mole of H_2 to form C_2H_6 , $\Delta H_2 = -137 \text{ kJ mol}^{-1}$.

According to Hess's Law, the total enthalpy change is the same for both routes.

Using Enthalpy Changes of Formation

The enthalpy change of formation ($\Delta_f H$) is the enthalpy change when one mole of a compound is formed from its elements under standard conditions. The reverse of a formation reaction has the negative enthalpy value.

To find the enthalpy change for converting ethyne to ethane:

- Step 1: Break ethyne into its elements (carbon and hydrogen). This is the reverse of its formation: $\Delta H_1 = +228 \text{ kJ mol}^{-1}$.
- Step 2: Form ethane from carbon and hydrogen: $\Delta H_2 = -85 \text{ kJ mol}^{-1}$.

Using Hess's Law:

$$\Delta H = \Delta H_1 + \Delta H_2 = -228 + (-85) = -313 \text{ kJ mol}^{-1}$$

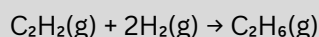


ENTHALPY OF COMBUSTION CALCULATIONS

Thermochemical Cycles Using Enthalpy Changes of Combustion

Example: Reaction Between Ethyne (C_2H_2) and Hydrogen (H_2) to Form Ethane (C_2H_6)

We will now use enthalpy changes of combustion to find the enthalpy change for this reaction:



In this case, we consider the combustion products (CO_2 and H_2O). The enthalpy changes of combustion for ethyne, hydrogen, and ethane are measurable because all three substances burn readily. The thermochemical cycle involves these reactions:

Thermochemical Cycle:

- Ethyne, hydrogen, and ethane all combust to form carbon dioxide and water.

Enthalpy changes of combustion:

- $\Delta H_c(\text{C}_2\text{H}_2) = -1301 \text{ kJ mol}^{-1}$
- $\Delta H_c(\text{H}_2) = -285.8 \text{ kJ mol}^{-1}$ (per mole of H_2)
- $\Delta H_c(\text{C}_2\text{H}_6) = -1560 \text{ kJ mol}^{-1}$

Using Hess's Law: To find ΔH_1 (the enthalpy change for the reaction), follow the cycle:

- $\Delta H_1 = (-1301) + 2(-285.8) - (-1560)$
- $\Delta H_1 = -313 \text{ kJ mol}^{-1}$

Finding Enthalpy of Formation (ΔH_f) Using Combustion Data

Enthalpy changes of formation are often hard to measure directly. For instance, forming ethanol from carbon, hydrogen, and oxygen is not a direct process. However, all elements involved burn in oxygen, allowing us to use their enthalpy changes of combustion.

For example:

- $\text{C}_2\text{H}_5\text{OH}$ formation from elements
- $2\text{C}(\text{s}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$
- does not occur directly, but their combustion values can be used.

Combustion Data:

- $\Delta H_c(\text{C}(\text{s}, \text{graphite})) = -393.5 \text{ kJ mol}^{-1}$
- $\Delta H_c(\text{H}_2(\text{g})) = -285.8 \text{ kJ mol}^{-1}$
- $\Delta H_c(\text{C}_2\text{H}_5\text{OH}(\text{l})) = -1367.3 \text{ kJ mol}^{-1}$

Using Hess's Law: To find ΔH_f for $\text{C}_2\text{H}_5\text{OH}$, reverse the combustion cycle:

- $\Delta H_f(\text{C}_2\text{H}_5\text{OH}) = 2(-393.5) + 3(-285.8) - (-1367.3)$
- $\Delta H_f = -277.1 \text{ kJ mol}^{-1}$

Note: Oxygen does not affect the enthalpy change because the same number of moles of O_2 appear on both sides.



BOND ENTHALPIES AND CALCULATIONS INVOLVING MEAN BOND ENTHALPIES

Breaking a covalent bond requires energy, making it an endothermic process. The energy required to break a bond is known as the bond dissociation enthalpy. The same amount of energy is released when a bond is formed, which is an exothermic process.

Key Definitions:

- Bond dissociation enthalpy: Energy needed to break a covalent bond with all species in the gaseous state.
- Mean bond enthalpy: The average bond energy for a bond in different molecules.

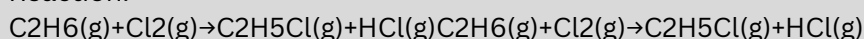
Example:

- The dissociation enthalpy of $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$ is $+436 \text{ kJ mol}^{-1}$.
- For $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})$, the bond energy for C-H is calculated as:
 - $\Delta H = +1664 \text{ kJ mol}^{-1}$ for breaking all C-H bonds, so the mean C-H bond energy = $1664 \div 4 = +416 \text{ kJ mol}^{-1}$.

Calculating Enthalpy Changes Using Mean Bond Enthalpies

You can use mean bond enthalpies to estimate the enthalpy change of a reaction. For example:

Reaction:



Steps:

1. Draw the displayed formula and show all bonds.
2. (Ethane and chlorine react to form chloroethane and hydrogen chloride.)
3. Break the bonds in the reactants:
 - $6 \times \text{C-H} = 6 \times 413 = 2478 \text{ kJ mol}^{-1}$
 - $1 \times \text{C-C} = 347 \text{ kJ mol}^{-1}$
 - $1 \times \text{Cl-Cl} = 243 \text{ kJ mol}^{-1}$
 - Total energy to break bonds = 3068 kJ mol^{-1}
4. Form bonds in the products:
 - $5 \times \text{C-H} = 5 \times 413 = 2065 \text{ kJ mol}^{-1}$
 - $1 \times \text{C-C} = 347 \text{ kJ mol}^{-1}$
 - $1 \times \text{C-Cl} = 346 \text{ kJ mol}^{-1}$
 - $1 \times \text{Cl-H} = 432 \text{ kJ mol}^{-1}$
 - Total energy released = 3190 kJ mol^{-1}
5. Calculate the difference:
 - Energy released - Energy required = $3190 - 3068 = +122 \text{ kJ mol}^{-1}$
 - Since more energy is released than absorbed, the reaction is exothermic with $\Delta H = -122 \text{ kJ mol}^{-1}$.

Shortcut Method

In reactions where only certain bonds are made or broken, you can simplify the process:

For the same reaction:

- Bonds broken:
 - $1 \times \text{C-H} = 413 \text{ kJ mol}^{-1}$
 - $1 \times \text{Cl-Cl} = 243 \text{ kJ mol}^{-1}$
 - Total = 656 kJ mol^{-1}
- Bonds formed:
 - $1 \times \text{C-Cl} = 346 \text{ kJ mol}^{-1}$
 - $1 \times \text{Cl-H} = 432 \text{ kJ mol}^{-1}$
 - Total = 778 kJ mol^{-1}
- Energy difference:
 - $778 - 656 = +122 \text{ kJ mol}^{-1}$
 - The reaction is exothermic with $\Delta H = -122 \text{ kJ mol}^{-1}$.

This approach simplifies complex bond enthalpy calculations, providing a quick estimate of the enthalpy change.

01-CHEM-5

KINETICS



COLLISION THEORY AND ACTIVATION ENERGIES

For a reaction to occur between two particles, they must collide with:

1. **Sufficient energy to break bonds.**
2. **The correct orientation so that the reacting parts of the molecules interact.**

Not every collision results in a reaction. Many collisions fail because:

- The particles don't have enough energy.
- The particles collide in the wrong orientation.

Factors Affecting Reaction Rates

Several factors can increase the rate of a chemical reaction:

1. Increasing Temperature:

- As temperature rises, particle speed increases. Faster-moving particles have more energy and collide more frequently, raising the chances of a successful reaction.

2. Increasing Concentration (in solutions):

- Higher concentration means more particles per unit volume, leading to more collisions and a faster reaction. However, as the reaction progresses, reactant concentration drops, slowing the reaction rate.

3. Increasing Pressure (in gases):

- Higher pressure compresses gas molecules into a smaller volume, increasing the frequency of collisions and accelerating the reaction.

4. Increasing Surface Area (in solids):

- Breaking a solid into smaller pieces increases its surface area. More surface area means more particles are available to react, resulting in a faster reaction.

5. Using a Catalyst:

- Catalysts speed up reactions by lowering the activation energy needed for the reaction to proceed, without being consumed in the reaction.

Activation Energy

The activation energy (E_a) is the minimum amount of energy required for a reaction to occur. Only a small fraction of collisions have enough energy to surpass this threshold and result in a reaction.

Reaction Profiles and Activation Energy:

• Exothermic Reactions:

- In exothermic reactions, the products have less energy than the reactants, meaning energy is released.
- Reactions with high activation energy occur slowly because few collisions have enough energy to overcome the activation barrier.
- Reactions with low activation energy occur quickly because more collisions have sufficient energy.

• Endothermic Reactions:

- In endothermic reactions, the products have more energy than the reactants, meaning energy is absorbed.
- These reactions require significant energy input to overcome the activation barrier.

Transition State

At the highest point on the enthalpy diagram, the reacting species form a transition state or activated complex, where:

- Some bonds are in the process of being broken.
- New bonds are being formed.
- This state is highly unstable, like a ball balanced at the top of a hill.

The activation energy is measured from the energy level of the reactants to the top of this curve, where the transition state exists.

01-CHEM-5

KINETICS



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KINETICS



MAXWELL-BOLTZMANN DISTRIBUTIONS

The Maxwell-Boltzmann distribution describes the spread of kinetic energies among particles in a gas or solution:

- No particles have zero energy.
- Most particles have intermediate energies, clustered around the peak of the curve.
- A few particles have very high energies (represented on the right-hand side of the curve), with no upper limit.

Key Points of the Distribution:

- The average energy of particles is not the same as the most probable energy. The most probable energy is the energy corresponding to the peak of the curve.
- The distribution curve is asymmetrical, with a longer tail on the right side, representing the particles with very high energies.

Activation Energy (E_a)

For a chemical reaction to occur, particles must collide with enough energy to start breaking bonds. This minimum amount of energy required is called the activation energy (E_a).

On a Maxwell-Boltzmann distribution graph:

- If you mark E_a on the x-axis, the area under the curve to the right of this line represents the number of particles that have enough energy to react.
- Only particles with energy equal to or greater than E_a can successfully participate in the reaction.

This concept explains why not all reactions, even exothermic ones, happen spontaneously at room temperature. Many particles do not have enough energy to overcome the activation barrier.

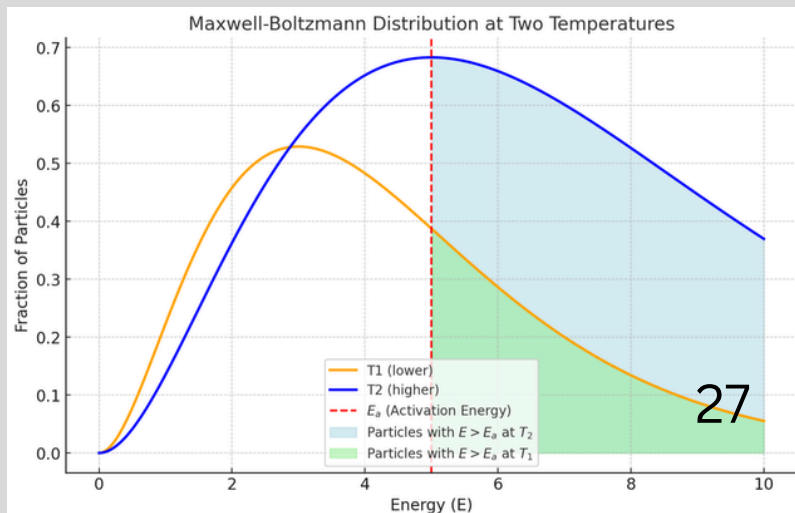
Why Activation Energy is Crucial:

- Fuels are stable at room temperature because the particles do not have enough energy to react spontaneously. However, a small spark can provide the necessary activation energy to start a combustion reaction.
 - For example, in a petrol station, the energy from a spark can initiate combustion, as the heat from the initial reaction provides the E_a for subsequent reactions.
- Friction can provide activation energy, like striking a match, where the heat generated by friction ignites the chemicals in the match head.
- Even a tiny electrical spark, such as from a light switch, can provide enough energy to trigger a gas explosion if there's a gas leak.

In conclusion, the Maxwell-Boltzmann distribution helps explain why certain reactions require specific conditions, such as heat or a spark, to overcome the activation energy barrier and begin.

EXPLAINING THE EFFECTS OF TEMPERATURE ON RATE

- **Maxwell-Boltzmann Distribution:** Shows the distribution of energies among particles in a gas.
- **Higher Temperatures:**
 - Peak of the curve shifts right and lowers.
 - More particles have energy greater than the activation energy (E_a), increasing the rate of reaction.
 - The total number of particles remains constant (area under curve stays the same).
- **Reaction Rate:** Increases with temperature due to a higher number of particles with energy exceeding E_a .
- **Effective Collisions:** Increase significantly with temperature, contributing more to the rate increase than the overall number of collisions.



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KINETICS



CATALYSTS

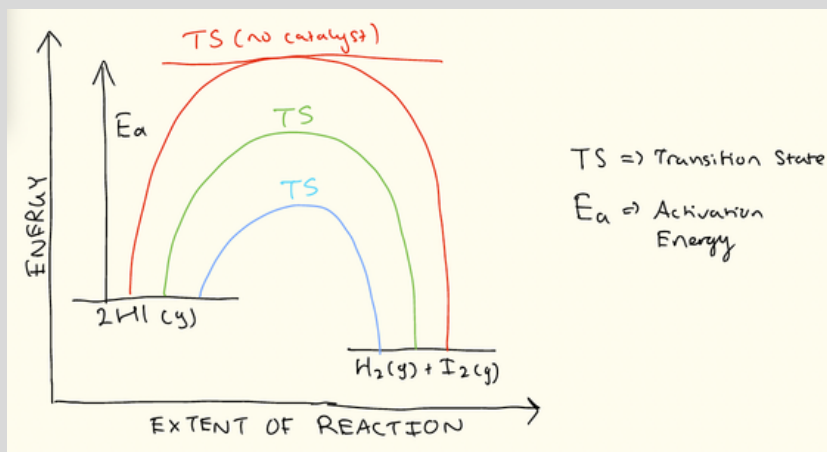
How Catalysts Work

Catalysts: Provide an alternative reaction pathway with a lower activation energy (E_a), increasing the rate of reaction without being consumed. Catalysts do not affect the enthalpy change or the position of equilibrium.

- **Activation Energy Example:**

- Without catalyst: 183 kJ mol^{-1}
- With gold catalyst: 105 kJ mol^{-1}
- With platinum catalyst: 58 kJ mol^{-1}

- **Maxwell-Boltzmann Distribution:** Catalysts increase the number of particles with energy greater than E_a , leading to more effective collisions.



CATALYSTS IN THE INDUSTRIAL SETTING

Reaction	Catalyst	Use
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$	Iron	Haber process (fertiliser production)
$4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$	Platinum & Rhodium	Ostwald process (nitric acid for fertilisers)
$\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3$	Nickel	Hydrogenation (hardening fats for margarine)
Cracking hydrocarbons	Zeolites (Aluminium oxide & silica)	Petrol production
Catalytic converters	Platinum & Rhodium	Reducing exhaust pollutants
Hydration of ethene to ethanol	Phosphoric acid (H_3PO_4)	Ethanol production (fuel additive & solvent)
Esterification ($\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CO}_2\text{CH}_3 + \text{H}_2\text{O}$)	Acid catalysts	Solvent production

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KINETICS



CATALYTIC CONVERTERS AND EFFECTS OF CHEMICALS ON THE ENVIRONMENT

Catalytic Converters

- Catalyst: Platinum and Rhodium.
- Function: Converts harmful gases (CO, NO_x, hydrocarbons) to less harmful products (N₂, CO₂, H₂O) through:
 - a. Adsorption: Gases bind to the catalyst surface, react.
 - b. Desorption: Products leave, freeing up space for more reactants.

Environmental Impact: CFCs and Ozone

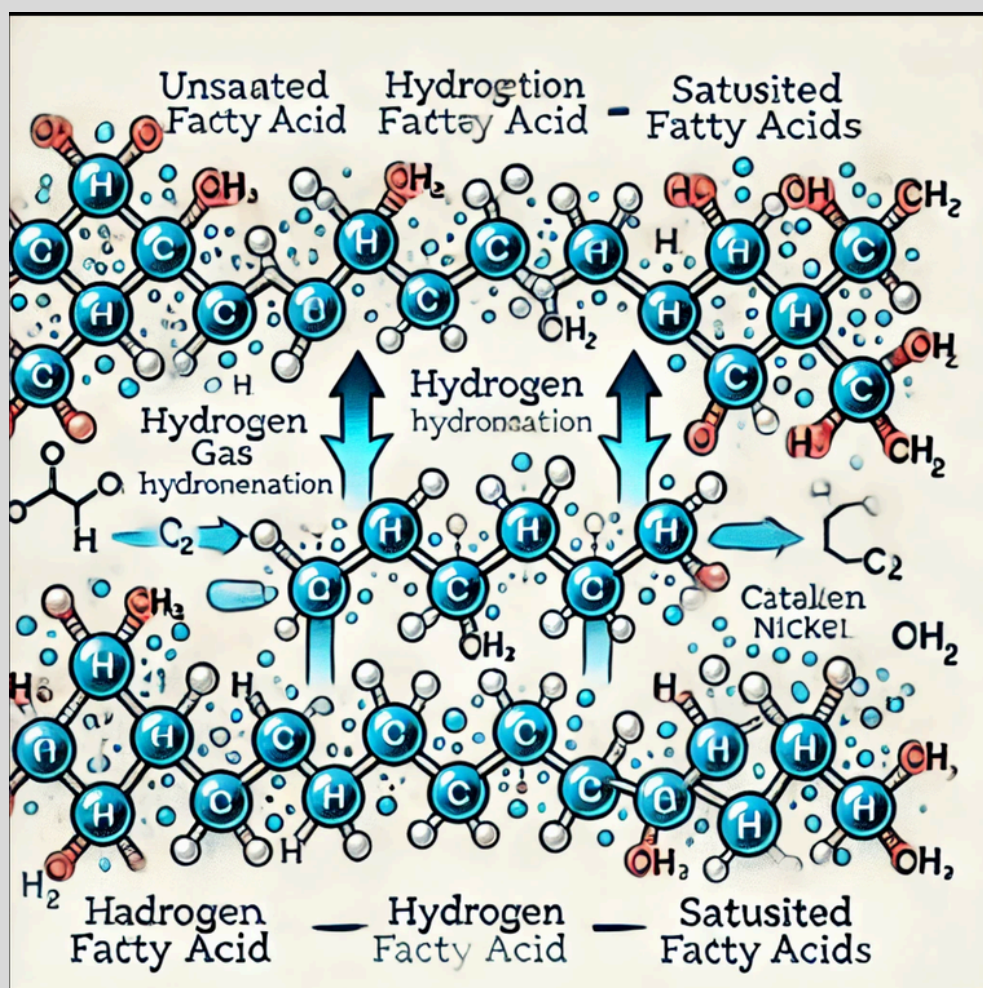
- Chlorofluorocarbons (CFCs): Previously used as solvents and propellants, CFCs break down ozone (O₃) in the atmosphere through catalytic reactions involving chlorine atoms.
- Montreal Protocol: Agreement to phase out CFCs, replaced by HCFCs and HFCs to reduce ozone depletion

ZEOLITE CATALYSTS AND HARDENING FATS

Zeolites: Minerals with an open pore structure that trap ions or molecules, altering their reactivity. Over 150 synthetic zeolites exist, with 48 naturally occurring. Zeolites are widely used in the petrochemical industry as catalysts.

Hydrogenation of Unsaturated Fats

In the production of margarine, hydrogen is added to unsaturated fats using a nickel catalyst, which is later filtered off. This process hardens the fat, allowing manufacturers to control its spreadability.



NO NEED TO
MEMORISE THIS!!!!

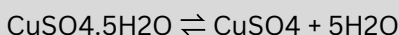
01-CHEM-6

EQUILLIBRIA



WHAT IS EQUILLIBRIA

- **Reversible reactions:** Reactions that can proceed in both forward and backward directions, e.g., hydration and dehydration of copper sulfate.



- **Dynamic equilibrium:** Reached in a closed system when the rates of the forward and reverse reactions are equal, and macroscopic properties (e.g., concentration, color) remain constant.

Key Features of Equilibrium:

1. Can only occur in a closed system.
2. Can be approached from either direction.
3. Is dynamic, with forward and reverse reactions continuing at the same rate.
4. Results in constant macroscopic properties.

Chemical Equilibrium:

- Starting with only reactants (A + B), the forward reaction is fast.
- As products (C + D) form, the reverse reaction speeds up.
- Equilibrium is reached when the rates of the forward and reverse reactions become equal.
- Equilibrium position can vary depending on conditions like temperature and pressure, but remains constant under fixed conditions.

EFFECTS OF CHANGING CONDITIONS ON EQUILLIBRIUM POSITION

The Equilibrium Mixture and Changing Conditions (AQA Key Points)

Position of Equilibrium

- Changing conditions like temperature, concentration, or pressure can shift the position of equilibrium.
 - Equilibrium shifts right (forward) if the proportion of products increases.
 - Equilibrium shifts left (backward) if the proportion of reactants increases.

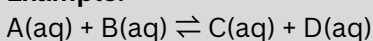
Le Chatelier's Principle

- Le Chatelier's Principle: If a system at equilibrium is disturbed, the equilibrium shifts to oppose the disturbance.

Changing Concentrations

- Increasing the concentration of a reactant causes the equilibrium to shift right, producing more products.
- Removing a product causes the equilibrium to shift right as well.

Example:



- Adding more A causes equilibrium to shift right, producing more C and D.

Changing Pressure

- Pressure changes affect reactions involving gases.
- If the number of gas molecules on each side is different:
 - Increasing pressure shifts equilibrium to the side with fewer molecules.
 - Decreasing pressure shifts equilibrium to the side with more molecules.

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EQUILLIBRIA



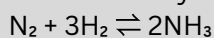
USE OF EQUILLIBRIA IN THE INDUSTRY

Ammonia in Industry

Ammonia is a crucial industrial chemical, with over 140 million tonnes produced annually. Approximately 80% is used in fertilisers like ammonium nitrate, ammonium sulfate, and urea. The rest is used in synthetic fibres (e.g., nylon), explosives, dyes, and plastics (e.g., polyurethane).

Making Ammonia

Ammonia is synthesised from nitrogen and hydrogen through a reversible reaction:



$$\Delta H = -92 \text{ kJ mol}^{-1}$$

The Haber Process

The Haber Process produces ammonia under the following conditions:

- **Pressure:** ~20,000 kPa (200 atm)
- **Temperature:** ~670 K
- **Catalyst:** Iron (increases reaction rate without altering equilibrium position)

In this process, only about 15% of nitrogen and hydrogen is converted to ammonia. The unreacted gases are recycled.

Key Points:

- Compromise conditions are used to balance yield and rate. Higher pressure favours ammonia production, while a lower temperature increases yield but slows the reaction.
- The ammonia is cooled to liquid form and removed.

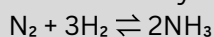
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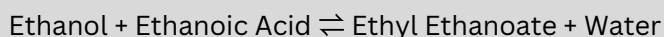
EQUILLIBRIA



THE EQUILLIBRIUM CONSTANT K_c

The Equilibrium Constant (K_c)

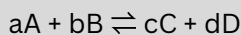
In reversible reactions, equilibrium is reached when the rates of the forward and reverse reactions are equal. For the reaction between ethanol and ethanoic acid to form ethyl ethanoate and water, the equilibrium can be expressed as:



When equilibrium is established, the concentrations of all substances remain constant. To analyze the equilibrium mixture, you can use a titration method to find the concentration of one of the reactants, such as ethanoic acid. With this information, you can calculate the concentrations of the other components.

The Equilibrium Constant (K_c)

For a general reversible reaction:



The equilibrium constant, K_c , is defined as:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Here:

- $[C]$ is the concentration of product C at equilibrium.
- $[D]$ is the concentration of product D at equilibrium.
- $[A]$ is the concentration of reactant A at equilibrium.
- $[B]$ is the concentration of reactant B at equilibrium.
- a, b, c, and d are the coefficients from the balanced equation.

Example:

For the reaction: $2A + B \rightleftharpoons 2C$

The equilibrium constant expression is: $K_c = \frac{[C]^2}{[A]^2 [B]}$

Units of K_c depend on the reaction. They are calculated by canceling out the units of each term in the expression. For example, if the concentrations are in mol/dm^3 , then:

$$K_c = \frac{(\text{mol/dm}^3)}{(\text{mol/dm}^3)^2} = \text{mol}^{-1}\text{dm}^3$$

Determining K_c

To find K_c :

1. Measure the equilibrium concentrations of all reactants and products.
2. Substitute these values into the K_c expression.
3. Calculate K_c using the appropriate units.

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EQUILLIBRIA



EXAMPLE K_c CALCULATIONS

Example 1: Ethanol and Ethanoic Acid Reaction

Reaction: Ethanol + Ethanoic Acid $\rightleftharpoons$ Ethyl Ethanoate + Water

Equilibrium Constant Expression: $K_c = \frac{[\text{Ethyl Ethanoate}] [\text{Water}]}{[\text{Ethanol}] [\text{Ethanoic Acid}]}$

Given:

- $K_c = 4.0$
- Initial moles: 1 mol each of ethanol and ethanoic acid

	Ethanol	Ethanoic Acid	Ethyl Ethanoate	Water
Start	1 mol	1 mol	0 mol	0 mol
Change	-x mol	-x mol	+x mol	+x mol
Equilibrium	(1 - x) mol	(1 - x) mol	x mol	x mol

Equilibrium Concentrations:

Assuming volume of the system is $V \text{ dm}^3$:

- $[\text{Ethanol}] = (1 - x) / V \text{ mol/dm}^3$
- $[\text{Ethanoic Acid}] = (1 - x) / V \text{ mol/dm}^3$
- $[\text{Ethyl Ethanoate}] = x / V \text{ mol/dm}^3$
- $[\text{Water}] = x / V \text{ mol/dm}^3$

Substitute into the equilibrium expression: $4.0 = \frac{(x / V) * (x / V)}{[(1 - x) / V] * [(1 - x) / V]}$ $4.0 = \frac{x^2}{(1 - x)^2}$

Solving: $x^2 = 4.0 * (1 - x)^2$ Taking the square root: $x = 3 / 4 = 0.75 \text{ mol}$

Equilibrium Composition:

- Ethanol = 0.25 mol
- Ethanoic Acid = 0.25 mol
- Ethyl Ethanoate = 0.75 mol
- Water = 0.75 mol

Example 2: Hydrogen Cyanide and Propanone Reaction

Reaction: $\text{CH}_3\text{COCH}_3 + \text{HCN} \rightleftharpoons \text{CH}_3\text{C}(\text{CN})(\text{OH})\text{CH}_3$

Equilibrium Constant Expression: $K_c = \frac{[\text{CH}_3\text{C}(\text{CN})(\text{OH})\text{CH}_3]}{[\text{CH}_3\text{COCH}_3] [\text{HCN}]}$

Given:

- $K_c = 30.0$
- Initial moles of propanone = 4.00 mol
- Volume = 2.00 dm^3
- Desired moles of product = 1.00 mol

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EQUILLIBRIA



EXAMPLE K_c CALCULATIONS CONTINUED

Example 2: Hydrogen Cyanide and Propanone Reaction (CONTINUED)

	Propanone	HCN	Product
Start	4.00 mol	x mol	0 mol
Change	-1.00 mol	-x mol	+1.00 mol
Equilibrium	3.00 mol	(x - 1.00) mol	1.00 mol

Equilibrium Concentrations:

- [Propanone] = 3.00 / 2.00 mol/dm³
- [HCN] = (x - 1.00) / 2.00 mol/dm³
- [Product] = 1.00 / 2.00 mol/dm³

Substitute into the equilibrium expression: $30.0 = \frac{1.00}{2.00} / \left[\frac{3.00}{2.00} * \frac{(x - 1.00)}{2.00} \right]$ $30.0 = \frac{1.00}{(3.00 * (x - 1.00))}$

Solving: $30.0 = 1.00 / (3.00 * (x - 1.00))$ $90.0 = 1.00 / (x - 1.00)$ $x - 1.00 = 1.00 / 90.0$ $x = 1.02$ mol

Required Moles of HCN:

- You need 1.02 mol of hydrogen cyanide to produce 1.00 mol of product in a 2.00 dm³ solution.

SUMMARY OF THE EFFECTS OF CHANGING CONDITIONS ON EQUILLIBRIA

Aspect	Summary
Effect of Temperature on K _c	Changing temperature affects K _c : - Exothermic reaction: Increasing temperature decreases K _c (equilibrium shifts left). - Endothermic reaction: Increasing temperature increases K _c (equilibrium shifts right).
Effect of Concentration on Equilibrium	Changing concentration affects equilibrium position: - Adding more reactant (e.g., ethanol) shifts equilibrium to the right (more product formed). - Adding more product shifts equilibrium to the left (more reactant formed).
Equilibrium Constant (K _c)	Describes equilibrium mixture composition: - K _c >> 1: Products predominate (equilibrium shifts right). - K _c << 1: Reactants predominate (equilibrium shifts left). - K _c ≈ 1: Significant amounts of both reactants and products.
Effect of Catalysts	Catalysts do not affect K _c . They speed up the attainment of equilibrium by lowering activation energy.
Gaseous Equilibria	Gaseous reactions obey equilibrium law using partial pressures instead of concentrations.

01-CHEM-7

REDOX



REDOX REACTIONS

Definition:

- Redox Reaction: A chemical reaction involving the transfer of electrons between species. It combines reduction and oxidation processes.

Concept	Description	Equation Example
Oxidation	Loss of electrons. The species undergoing oxidation increases its oxidation state.	$\text{Cu(s)} + \text{O}_2\text{(g)} \rightarrow \text{CuO(s)}$
Reduction	Gain of electrons. The species undergoing reduction decreases its oxidation state.	$\text{CuO(s)} + \text{H}_2\text{(g)} \rightarrow \text{Cu(s)} + \text{H}_2\text{O(l)}$
Oxidising Agent	Substance that accepts electrons and is reduced.	Oxygen (O_2) in the reaction $\text{Cu(s)} + \text{O}_2\text{(g)} \rightarrow \text{CuO(s)}$
Reducing Agent	Substance that donates electrons and is oxidised.	Hydrogen (H_2) in the reaction $\text{CuO(s)} + \text{H}_2\text{(g)} \rightarrow \text{Cu(s)} + \text{H}_2\text{O(l)}$
Electron Transfer	Movement of electrons between species in a redox reaction.	$\text{Cl}_2\text{(g)} + \text{H}_2\text{(g)} \rightarrow 2\text{HCl(g)}$

Half Equations:

- Oxidation Half Equation: Shows the loss of electrons.
 - Example: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
- Reduction Half Equation: Shows the gain of electrons.
 - Example: $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$

Key Points:

- Oxidation is losing electrons and Reduction is gaining electrons.
- Redox reactions involve the transfer of electrons, and these are also known as electron transfer reactions.
- Oxidising agents and reducing agents facilitate these electron transfers.

01-CHEM-7

REDOX



REDOX REACTIONS

Definitions:

- Oxidation: Loss of electrons.
- Reduction: Gain of electrons.
- Redox Reaction: Involves both oxidation and reduction (electron transfer).
- Oxidising Agent: Gains electrons (is reduced).
- Reducing Agent: Loses electrons (is oxidised).

Half Equations:

- Show electron transfer.
- Example 1 (Copper and Oxygen):
- Oxidation:
- $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
- Reduction:
- $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$
- Full Redox Reaction:
- $2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO}$

Spectator Ions:

- Do not participate in the redox reaction (e.g., O^{2-} in copper-magnesium reaction).

Worked Example:

Magnesium and Chlorine:

- Oxidation: $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$
- Reduction: $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$
- Overall Ionic Equation:
- $\text{Mg} + \text{Cl}_2 \rightarrow \text{Mg}^{2+} + 2\text{Cl}^-$

REDOX REACTIONS

Oxidation State:

- A number assigned to an element in a compound to indicate the loss or gain of electrons.
- Oxidation: Loss of electrons, resulting in a positive oxidation state.
- Reduction: Gain of electrons, resulting in a negative oxidation state.

Key Points:

- Uncombined Elements: Oxidation state = 0 (e.g., O_2 , H_2 , Na).
- Ionic Compounds: Oxidation state reflects the charge (e.g., $\text{Mg}^{2+} = +2$).
- Molecules: Oxidation state indicates electron distribution; more electronegative elements have negative states.

Rules for Finding Oxidation States:

1. Uncombined Elements: Always 0.
2. Common Elements:
 - Group 1: Always +1 (e.g., NaCl).
 - Group 2: Always +2 (e.g., CaCl_2).
 - Hydrogen: +1 (except in metal hydrides like NaH , where it's -1).
 - Oxygen: -2 (except in peroxides like H_2O_2 , where it's -1).
 - Fluorine: Always -1 (e.g., NaF).
 - Chlorine: -1 (except with F or O, where it can be positive).
3. Neutral Compounds: Sum of oxidation states = 0.
4. Complex Ions: Sum of oxidation states = charge on the ion (e.g., $\text{NH}_4^+ = +1$).
5. Most Electronegative Element: Always has a negative oxidation state.

Term	Definition	Example
Oxidation	Loss of electrons	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
Reduction	Gain of electrons	$\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$
Oxidising Agent	Gains electrons (is reduced)	O_2 in $\text{Cu} + \text{O}_2 \rightarrow \text{CuO}$
Reducing Agent	Loses electrons (is oxidised)	Mg in $\text{Mg} + \text{Cl}_2 \rightarrow \text{Mg}^{2+} + 2\text{Cl}^-$
Half Equation	Shows loss or gain of electrons	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
Spectator Ions	Ions that do not change in the reaction	O^{2-} in $\text{CuO} + \text{Mg} \rightarrow \text{MgO} + \text{Cu}$

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REDOX



WORKING OUT OXIDATION STATES

To determine oxidation states in compounds:

1. Identify Known Oxidation States: Use rules (e.g., O = -2, H = +1).
2. Deducing Unknown States: The sum of oxidation states in a neutral compound is zero, and for ions, it equals the ion's charge.

Compound	Oxidation States Explanation
PCl_5	Cl = -1 $\rightarrow$ P must be +5 (to balance sum to 0).
NH_3	H = +1 $\rightarrow$ N must be -3 (to balance sum to 0).
HNO_3	O = -2 (total -6), H = +1 $\rightarrow$ N must be +5.
H_2S	H = +1 $\rightarrow$ S must be -2 (to balance sum to 0).
SO_4^{2-}	O = -2 (total -8) $\rightarrow$ S must be +6 (sum = ion charge).
CuO	O = -2 $\rightarrow$ Cu must be +2 (to balance sum to 0).
Cu_2O	O = -2 $\rightarrow$ Cu must be +1 (to balance sum to 0).

Roman Numerals for Oxidation States:

- CuO = Copper(II) oxide (Cu = +2).
- Cu_2O = Copper(I) oxide (Cu = +1).

This approach ensures you correctly assign oxidation states using AQA mark scheme terms.

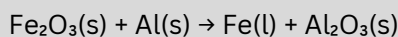
USING OXIDATION STATES IN REDOX EQUATIONS

You can determine which element has been oxidised or reduced in a redox reaction by looking at electron transfer or oxidation states:

- Oxidation is the loss of electrons (OIL), increasing oxidation state.
- Reduction is the gain of electrons (RIG), decreasing oxidation state.

Example 1: Thermite Reaction

Unbalanced:



1. Assign oxidation states:

- Fe in Fe_2O_3 : +3
- Al: 0
- Fe: 0
- Al in Al_2O_3 : +3

2. Only Fe and Al change oxidation states:

- $\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$ (Reduction)
- $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$ (Oxidation)

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REDOX

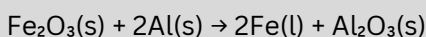


USING OXIDATION STATES IN REDOX EQUATIONS (CONTINUED)

Balance electrons:

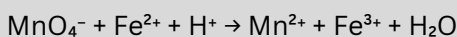
1. Each Fe atom gains 3 electrons, and each Al atom loses 3 electrons. There are 2 Fe atoms, so 2 Al atoms are needed.

Balanced equation:



Example 2: Aqueous Redox Reaction

Unbalanced:



1. Assign oxidation states:

- o Mn in MnO_4^- : +7
- o Fe^{2+} : +2
- o Mn^{2+} : +2
- o Fe^{3+} : +3

2. Identify redox changes:

- o Mn is reduced: $\text{Mn}^{7+} \rightarrow \text{Mn}^{2+}$ (gains 5 electrons)
- o Fe is oxidised: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ (loses 1 electron)

3. Balance electron transfer:

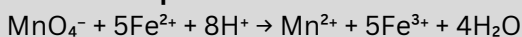
- o Multiply Fe^{2+} equation by 5 for electron balance: $5\text{Fe}^{2+} \rightarrow 5\text{Fe}^{3+} + 5\text{e}^-$

4. Add these to the equation: $\text{MnO}_4^- + 5\text{Fe}^{2+} + \text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + \text{H}_2\text{O}$

5. Balance remaining atoms:

- o Add $4\text{H}_2\text{O}$ on the right and 8H^+ on the left to balance oxygen and hydrogen.

Balanced equation:





THE PERIODIC TABLE AND ITS STRUCTURE

Metals and Non-metals:

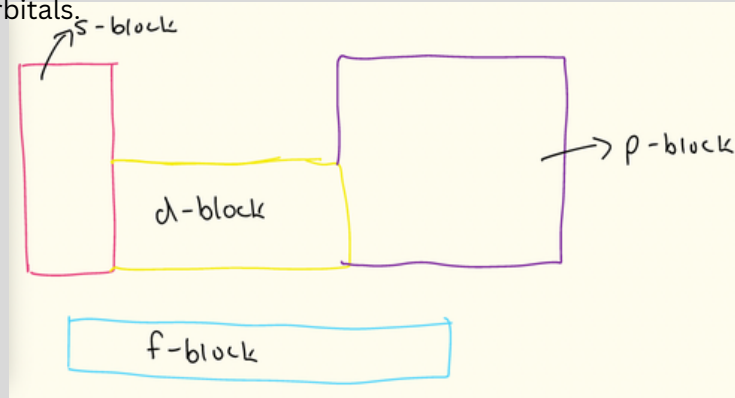
- The red staircase line divides metals (left) from non-metals (right).
- Metalloids (e.g., silicon) touch this line and have both metallic and non-metallic properties.

Blocks of the Periodic Table:

- s-block: Elements where the highest energy electrons are in s-orbitals (e.g., sodium, Na).
- p-block: Elements with the highest energy electrons in p-orbitals (e.g., carbon, C).
- d-block: Elements with the highest energy electrons in d-orbitals (e.g., iron, Fe).
- Note: Not all d-block elements are transition metals. Scandium (Sc) and zinc (Zn) are not considered transition metals because they don't form compounds with partially filled d-orbitals.

Origin of s, p, d, f Terms:

- These letters represent spectral lines:
 - s: Sharp
 - p: Principal
 - d: Diffuse
 - f: Fine



GROUPS AND PERIODS IN THE PERIODIC TABLE

Group Structure:

- A group is a vertical column in the Periodic Table.
- Elements in the same group have similar properties and the same number of electrons in their outer main level.
- Traditionally numbered I-VII in Roman numerals, plus zero for noble gases.
- Now commonly numbered as 1-7 and 0 (or 1-8) or 1-18 (including transition metals).

Reactivity Trends:

- s-block metals become more reactive as you go down a group.
- Non-metals become more reactive as you go up a group.
- Transition elements are generally unreactive metals, where most useful metals are found.

Lanthanides and Actinides:

- Lanthanides: Metals that mostly form +3 ions, with similar reactivity.
- Actinides: Radioactive metals, with thorium and uranium naturally occurring in significant amounts.

Periods:

- Periods are horizontal rows numbered from Period 1 (hydrogen and helium) onwards.
- Each period shows trends in physical properties and chemical behavior.

Placement of Hydrogen and Helium:

- Helium: Placed above noble gases (Group 0) but not a p-block element (its electron configuration is $1s^2$).
- Hydrogen: Often placed in Group 1 (forms +1 ions like alkali metals), but sometimes placed on its own or with halogens (due to forming H^- ions and covalent bonds).

TRENDS IN PROPERTIES OF ELEMENTS OF PERIOD 3

Explanation of Periodicity:

- Periodicity is explained by the electron arrangements of the elements.
- Groups 1, 2, and 3 elements (sodium, magnesium, and aluminium) are metals with giant structures that lose their outer electrons to form ionic compounds.
- Group 4 element silicon has four outer electrons forming four covalent bonds, and shows semi-metallic properties.
- Groups 5, 6, and 7 elements (phosphorus, sulfur, and chlorine) are non-metals. They either accept electrons to form ionic compounds or share electrons to form covalent compounds.
- Group 0 element argon is a noble gas, with a full outer shell and is unreactive.

Trends in Melting and Boiling Points:

- Giant structures (left side of Period 3) tend to have high melting and boiling points.
- Molecular or atomic structures (right side of Period 3) tend to have low melting and boiling points.

Metals (Na, Mg, Al):

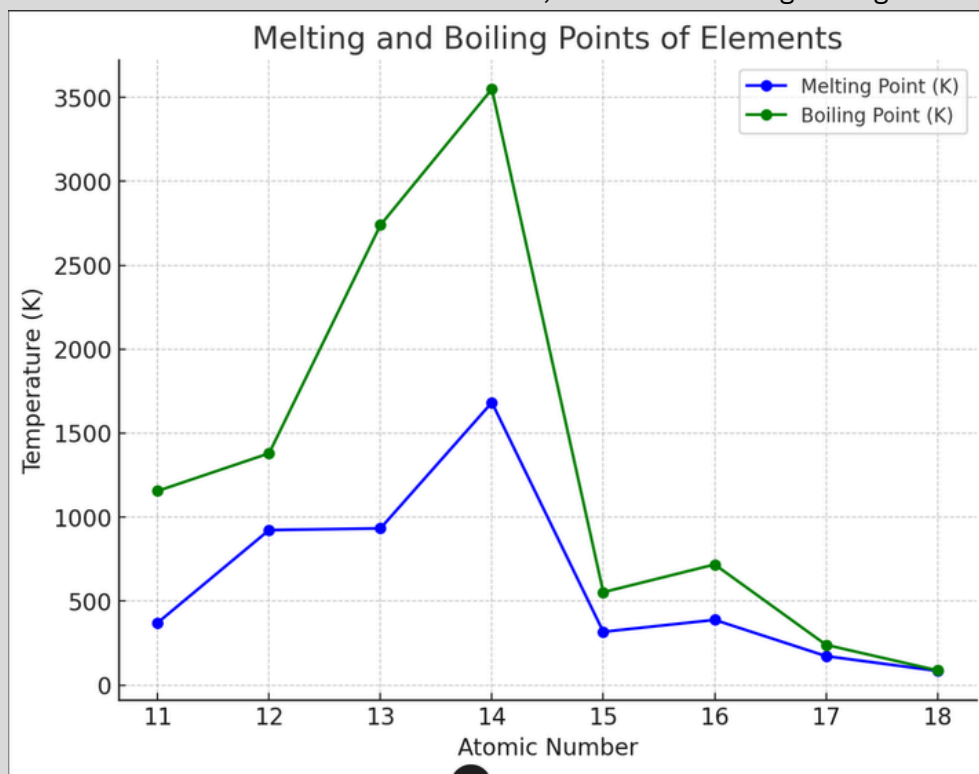
- The melting points and boiling points of metals increase from sodium (Na) to aluminium (Al) due to stronger metallic bonding.
- As you go across the period from left to right, the charge on the ion increases, and more delocalized electrons strengthen the metallic lattice.

Non-metals (P, S, Cl):

- Non-metals with molecular structures have melting points dependent on the strength of van der Waals forces.
- Melting points are ordered by molecular size: $S_8 > P_4 > Cl_2$.
- Silicon (Si), with its giant covalent structure, has a much higher melting point compared to other non-metals.

Boiling Points:

- Boiling points follow a similar pattern to melting points:
 - Metals increase across the period.
 - Non-metals follow the order $S_8 > P_4 > Cl_2$, with silicon having the highest due to its giant covalent structure.





TRENDS IN ATOMIC RADII ACROSS PERIOD 3

Concept:

- The atomic radius refers to the size of an atom, measured as half the distance between the centers of two identical atoms bonded together.
- The radius can differ depending on the type of bond the atom forms (e.g., covalent, ionic, metallic, van der Waals).
- Covalent radius is commonly used to measure atomic size.

Trends in Atomic Radii:

1. Across a Period:

- Atomic radius decreases as you move from left to right across a period.
- This is because, while electrons are added to the same energy level, the number of protons in the nucleus increases. This higher positive charge attracts electrons more strongly, pulling them closer to the nucleus.
- No additional electron shells are added to provide more shielding, so the effective nuclear charge increases, reducing atomic size.

2. Down a Group:

- Atomic radius increases as you move down a group.
- This is due to the addition of extra electron shells (energy levels), which outweighs the increase in nuclear charge. The outer electrons are farther from the nucleus, and there is increased electron shielding, resulting in a larger atomic radius.

Visual Representation:

- Graph of Covalent Radius vs. Atomic Number: Shows a decrease in atomic radius across a period and an increase down a group.
- Figures:
 - Figure 1: Shows the measurement of atomic radius.
 - Figure 2: Covalent radius plotted against atomic number, illustrating periodic trends.
 - Figure 3: Electronic structures of elements (e.g., sodium to chlorine) explaining why atomic radius decreases across a period.

TREND IN IONISATION ENERGY ACROSS PERIOD 3

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EXPLANATION OF IONISATION ENERGIES

1. Increase Across a Period:

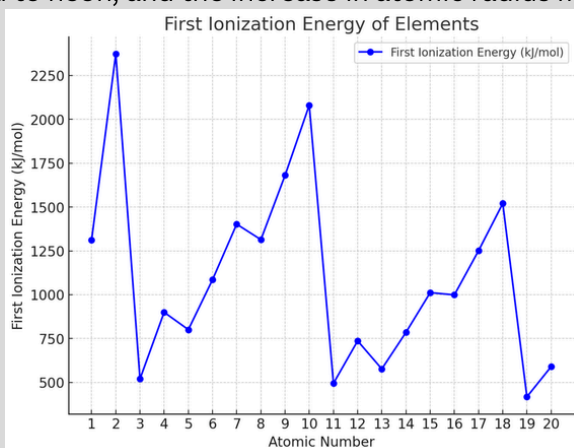
- Reason: As you move from left to right across a period, the number of protons in the nucleus increases. This leads to a higher positive charge in the nucleus, which attracts electrons more strongly.
- Effect: The electrons are added to the same energy level (shell), but the increased nuclear charge pulls these electrons closer to the nucleus. Consequently, it becomes more difficult to remove an electron, leading to higher ionisation energy.

2. Decrease Down a Group:

- Reason: As you move down a group, additional electron shells are added, which increases the distance between the nucleus and the outermost electrons. The increased number of inner electron shells also provides more shielding.
- Effect: The outer electrons are further from the nucleus and experience less attraction due to increased shielding. Therefore, it is easier to remove an outer electron, resulting in lower ionisation energy.

3. Drop Between Periods:

- Reason: There is a significant drop in ionisation energy when moving from one period to the next. For example, moving from neon (Period 0) to sodium (Period 1) shows a sharp decrease.
- Effect: This drop occurs because a new main energy level starts in sodium. The outer electron is further from the nucleus compared to neon, and the increase in atomic radius means the outer electron is less strongly attracted and easier to remove.



IONISATION ENERGY ANOMALIES

1. Drop in Ionisation Energy Between Groups:

- Between Group 2 and Group 3:
 - Magnesium (Group 2) has the electron configuration $1s^2 2s^2 2p^6 3s^2$.
 - Aluminium (Group 3) has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^1$.
 - Explanation: Aluminium loses a 3p electron, which is in a higher energy level compared to the 3s electron removed from magnesium. Consequently, the 3p electron is easier to remove, leading to a lower ionisation energy for aluminium.
- Between Group 5 and Group 6:
 - Phosphorus (Group 5) has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^3$, with unpaired electrons in the p-orbitals.
 - Sulfur (Group 6) has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^4$, with paired electrons in the p-orbitals.
 - Explanation: In sulfur, the paired p-electrons experience electron-electron repulsion, making them easier to remove compared to the unpaired p-electrons in phosphorus.

2. Successive Ionisation Energies:

- Trend: Each successive electron is harder to remove due to increased positive charge on the nucleus.
 - For Sodium ($1s^2 2s^2 2p^6 3s^1$): The first electron (from the outermost 3s orbital) is the easiest to remove. A sharp increase in ionisation energy occurs after removing the first electron, followed by a gradual increase with each subsequent electron removed. This pattern is due to removing electrons from more stable, inner shells after the outermost one is removed.



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 - For Aluminium ($1s^2 2s^2 2p^6 3s^2 3p^1$): Similar to sodium, the first few electrons removed are from the outermost shell, followed by a sharp increase in ionisation energy when removing electrons from a more stable, inner shell.
 - For Chlorine ($1s^2 2s^2 2p^5$): The first seven electrons are relatively easy to remove compared to the next set, reflecting the number of outer shell electrons which align with its group number in the Periodic Table.

IONISATION ENERGY ANOMALIES

Group 2 Elements:

Also known as the alkaline earth metals, this group includes:

- Magnesium (Mg)
- Calcium (Ca)
- Strontium (Sr)
- Barium (Ba)
- Radium (Ra)

Key Trends and Properties:

1. Electron Arrangement:

- All Group 2 elements have two electrons in their outer s-orbital. As you move down the group, this s-orbital is increasingly farther from the nucleus due to additional filled electron levels.

2. Atomic Size:

- Trend: The atomic radius increases as you go down the group. Each successive element has an additional filled electron shell, leading to a larger atomic size.

3. Melting Points:

- Trend: Group 2 elements have high melting points due to their giant metallic structures. However, the melting points decrease slightly as you move down the group. This decrease is because the delocalised electrons are further from the positively charged nuclei, weakening the metallic bonds.
- Anomaly: Magnesium has a lower melting point compared to other Group 2 elements, but this anomaly doesn't fit the general trend and lacks a straightforward explanation.

4. Ionisation Energies:

- Trend: Both the first and second ionisation energies decrease as you move down the group. This decrease occurs because the outer electrons are further from the nucleus and experience less attraction due to increased shielding from inner electron shells.
- Ionisation Process: Group 2 elements lose their two outer electrons to form M^{2+} ions. The energy required for complete ionisation is the sum of the first and second ionisation energies.

CHEMICAL REACTIONS OF GROUP 2 ELEMENTS

Reaction with Water:

Metals get more reactive going down the group. These are also redox reactions. The basic reaction is as follows, where M is any Group 2 metal:

- $M(s) + 2H_2O(l) \rightarrow M(OH)_2(aq) + H_2(g)$

Specific Reactions:

• Magnesium:

- Magnesium reacts very slowly with cold water but more rapidly with steam. The reactions are:

- With cold water: $Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(aq) + H_2(g)$
- With steam: $Mg(s) + 2H_2O(g) \rightarrow MgO(s) + H_2(g)$

• Calcium:

- Calcium reacts more vigorously with water compared to magnesium. The reaction is:
 - $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

• Strontium and Barium:

- Strontium and barium react even more vigorously with water than calcium. They follow the same pattern as calcium in their reactions.

Uses of Group 2 Compounds:

• Magnesium Hydroxide:

- Known as milk of magnesia, used to neutralize excess stomach acid which causes heartburn, indigestion, and wind.

• Calcium Hydroxide:

- Also known as slaked lime, used to treat acidic soils. This helps improve the pH of the soil to support plant growth. For example, grass thrives at a pH of around 6. If soil pH is much below this, crops like wheat, corn, oats, and barley will not grow as well.



SOLUBILITIES OF HYDROXIDES AND SULFATES (GROUP 2)

Hydroxides

There is a clear trend in the solubilities of the hydroxides—going down the group, they become more soluble. The hydroxides are all white solids.

- Magnesium Hydroxide:
 - Magnesium hydroxide ($\text{Mg}(\text{OH})_2$), also known as milk of magnesia, is almost insoluble. It is sold as a suspension in water, rather than a solution.
- Calcium Hydroxide:
 - Calcium hydroxide ($\text{Ca}(\text{OH})_2$) is sparingly soluble and a solution is used as lime water.
- Strontium Hydroxide:
 - Strontium hydroxide ($\text{Sr}(\text{OH})_2$) is more soluble than calcium hydroxide.
- Barium Hydroxide:
 - Barium hydroxide ($\text{Ba}(\text{OH})_2$) dissolves to produce a strongly alkaline solution:
 - $\text{Ba}(\text{OH})_2(\text{s}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$

Sulfates

The solubility trend in the sulfates is the opposite—they become less soluble going down the group. Therefore, barium sulfate is virtually insoluble. This makes it useful in medical X-rays, where it is taken by mouth as a barium meal to outline the gut. The heavy barium atom absorbs X-rays effectively. This test is safe despite the toxicity of barium compounds because barium sulfate is so insoluble.

- Test for Sulfate Ions:
 - The insolubility of barium sulfate is also used in a simple test for sulfate ions in solution. First, acidify the solution with nitric or hydrochloric acid. Then add barium chloride solution. If sulfate ions are present, a white precipitate of barium sulfate is formed:
 - $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$
 - The addition of acid removes carbonate ions as carbon dioxide. (Barium carbonate is also a white insoluble solid, which would be indistinguishable from barium sulfate.)



PHYSICAL PROPERTIES OF THE HALOGENS (GROUP 7))

The gaseous halogens vary in appearance:

- Fluorine: At room temperature, fluorine is a pale yellow gas.
- Chlorine: Chlorine is a greenish gas.
- Bromine: Bromine is a red-brown liquid.
- Iodine: Iodine is a black solid.

As you move down the group, the halogens get darker and denser.

All halogens have a characteristic 'swimming-bath' smell.

Fluorine exhibits a number of untypical properties:

- Many of these unusual properties are due to the fact that the F-F bond is unexpectedly weak compared to other halogens.
- The small size of the fluorine atom results in significant repulsion between non-bonding electrons because they are so close together.

ELECTRONEGATIVITY, MELTING AND BOILING POINTS OF GROUP 7 ELEMENTS

Size of Atoms

- The size of atoms increases as you move down the group.
- Each successive element has an additional filled main electron level compared to the element above it.

Electronegativity

- Definition: Electronegativity measures an atom's ability to attract electrons within a covalent bond.
- Factors Affecting Electronegativity:
 - Nuclear Charge: The number of protons in the nucleus.
 - Distance: The distance between the nucleus and the bonding electrons.
 - Shielding Effect: The influence of inner electron shells that reduce the effective nuclear charge experienced by bonding electrons.
- Trend: Electronegativity decreases as you move down the group.
 - Reason: The shared electrons in the H-X bond (in hydrogen halides) are further from the nucleus and experience increased shielding by additional inner electron shells, making it harder for the nucleus to attract the bonding electrons.

Melting and Boiling Points

- Trend: Melting and boiling points increase as you move down the group.
- Reason: Larger atoms have more electrons, which strengthens the van der Waals forces between molecules.
 - Volatility: Elements with lower boiling points are more volatile. For example, chlorine (a gas at room temperature) is more volatile than iodine (a solid).



TRENDS IN OXIDISING ABILITY OF THE HALOGENS, DISPLACEMENT REACTIONS

Trends in Oxidizing Ability

- Halogens typically gain electrons to become negative ions with a charge of -1. These reactions are redox reactions where halogens act as oxidizing agents and are themselves reduced.
- General Reaction:
 - For chlorine: $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$
- Trend: The oxidizing ability of halogens increases as you move up the group.
 - Fluorine is one of the most powerful oxidizing agents known.
- Oxidizing Power (Increasing up the group):
 - Fluorine > Chlorine > Bromine > Iodine

Displacement Reactions

- Definition: Halogens can react with metal halides in solution where a more reactive halogen displaces the less reactive halide from the compound. This type of reaction is known as a displacement reaction.
- Example:
 - Chlorine will displace bromide ions from sodium bromide solution, but iodine will not displace bromide ions.
- Reaction:
 - $\text{Cl}_2(\text{aq}) + 2\text{NaBr}(\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{NaCl}(\text{aq})$
- Ionic Equation:
 - $\text{Cl}_2 + 2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{Cl}^-$
- Observation: The two colorless starting materials react to produce the red-brown color of bromine.
- Redox Reaction Details:
 - In this reaction, chlorine acts as an oxidizing agent by removing electrons from bromide ions, oxidizing 2Br^- to Br_2 . This increases the oxidation number of bromine from -1 to 0.
- General Rule: A halogen will always displace the ion of a halogen below it in the Periodic Table.

REACTIONS OF HALIDE IONS- HALIDE IONS AS REDUCING AGENTS

- **General Trend:** Halide ions can act as reducing agents by donating electrons to become halogen molecules. The reducing ability increases as you move down the group, linked to the size of the ions.
 - Reason: Larger ions lose electrons more easily because the outer electron is further from the nucleus, resulting in a weaker attraction.
- **Reducing Power (Increasing down the group):**
 - Ionic Radii:
 - Fluoride ion: 0.133 nm
 - Chloride ion: 0.180 nm
 - Bromide ion: 0.195 nm
 - Iodide ion: 0.215 nm

Reactions of Sodium Halides with Concentrated Sulfuric Acid

- **Sodium Chloride (solid):**
 - Reaction: $\text{NaCl}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HCl}(\text{g})$
 - Observation: Steamy fumes of hydrogen chloride are seen.
 - Type: Acid-base reaction (not redox) because chloride ions are not strong enough reducing agents to reduce sulfuric acid.
- **Sodium Fluoride (solid):**
 - Similar reaction to sodium chloride: $\text{NaF}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HF}(\text{g})$
 - Note: Hydrogen fluoride is an extremely dangerous gas that etches glass. Fluoride ions are weaker reducing agents compared to chloride ions.
- **Sodium Bromide (solid):**
 - First Reaction: $\text{NaBr}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HBr}(\text{g})$
 - Second Reaction: $2\text{HBr}(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{SO}_2(\text{g}) + \text{Br}_2(\text{l}) + 2\text{H}_2\text{O}(\text{l})$
 - Observation: Steamy fumes of hydrogen bromide, brown fumes of bromine, and colorless sulfur dioxide are produced.
 - Type: Redox reaction. Bromide ions are strong reducing agents and reduce sulfuric acid to sulfur dioxide (sulfur's oxidation state changes from +6 to +4).
- **Sodium Iodide (solid):**
 - First Reaction: $\text{NaI}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HI}(\text{g})$
 - Further Reactions: $6\text{HI}(\text{g}) + \text{SO}_2(\text{l}) \rightarrow \text{H}_2\text{S}(\text{g}) + 3\text{I}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$ and $6\text{HI}(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow 3\text{I}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{S}(\text{g})$
 - Observation: Steamy fumes of hydrogen iodide, black solid iodine, and the bad egg smell of hydrogen sulfide gas are present. Yellow solid sulfur may also be observed.
 - Type: Redox reaction. Iodide ions are stronger reducing agents than bromide ions and reduce sulfur in sulfuric acid further, producing sulfur dioxide, sulfur, and hydrogen sulfide gas. The sulfur undergoes multiple oxidation states from +6 to -2.



IDENTIFYING METAL HALIDES WITH SILVER IONS

To identify metal halides, a common method involves reacting them with silver ions in aqueous solution, typically from silver nitrate. This reaction forms an insoluble silver halide precipitate. Here's how the process works:

1. Preparation:

- Add Dilute Nitric Acid: Before testing with silver nitrate, dilute nitric acid (HNO_3) is added to the halide solution to remove any interfering substances like soluble carbonates or hydroxides:
 - Carbonate Reaction:

$$\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$$
 - Hydroxide Reaction:

$$\text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$$
- These reactions prevent interference by removing any substances that could form insoluble silver carbonate or silver hydroxide:
 - Silver Carbonate:

$$2\text{Ag}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{Ag}_2\text{CO}_3(\text{s})$$
 - Silver Hydroxide:

$$\text{Ag}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{AgOH}(\text{s})$$

2. Add Silver Nitrate:

- After the solution is prepared, a few drops of silver nitrate solution are added. This forms a precipitate of the insoluble silver halide:
 - Example Reaction:

$$\text{Cl}^-(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{AgCl}(\text{s})$$

3. Observing the Precipitate:

- The color of the precipitate indicates which halide is present:
 - Silver Fluoride: No precipitate (soluble in water).
 - Silver Chloride: White precipitate.
 - Silver Bromide: Cream precipitate.
 - Silver Iodide: Pale yellow precipitate.

4. Confirming the Results:

- For Silver Bromide and Silver Iodide: To differentiate between silver bromide and silver iodide, add a few drops of concentrated ammonia solution:
 - Silver Bromide: Dissolves in concentrated ammonia.
 - Silver Iodide: Remains insoluble in concentrated ammonia.

Halide	Precipitate Color	Solubility in Ammonia
Silver Fluoride	No precipitate	-
Silver Chloride	White	-
Silver Bromide	Cream	Dissolves in concentrated ammonia
Silver Iodide	Pale yellow	Insoluble in concentrated ammonia

REACTIONS OF HALOGENS

Reaction with Water

- Chlorine Reaction:
 - Equation: $\text{Cl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HClO}(\text{aq}) + \text{HCl}(\text{aq})$
 - Oxidation States: Chlorine undergoes disproportionation, where one chlorine atom is oxidized (+1) and the other is reduced (-1).
 - Uses:
 - Purifies drinking water and swimming pools.
 - Chloric(I) acid is a disinfectant and bleach.
- In Sunlight:
 - Chlorine degrades quickly, so pools often use sodium chlorate(III), which forms chloric(I) acid when dissolved.

Reaction with Alkali

- Chlorine Reaction:
 - Equation: $\text{Cl}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{NaClO}(\text{aq}) + \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 - Oxidation States: This is also a disproportionation reaction.
 - Uses: Sodium chlorate(III) is used in household bleach.



AN INTRO TO ORGANIC CHEMISTRY

Carbon Bonding:

- Carbon atoms have four outer shell electrons, allowing for the formation of four covalent bonds.
- Carbon-carbon bonds are strong (347 kJ mol^{-1}) and non-polar.
- Carbon-hydrogen bonds are also strong (413 kJ mol^{-1}) and relatively non-polar.
- Hydrocarbon chains form the backbone of most organic compounds.

Bonding in Carbon Compounds:

- Single Bonds: Methane (CH_4)
- Double Bonds: Ethene (C_2H_4)
- Triple Bonds: Ethyne (C_2H_2)
- $\text{H} - \text{C} \equiv \text{C} - \text{H}$

Formulae of Carbon Compounds:

Empirical Formula:

- Represents the simplest ratio of atoms.
- Example: Ethane (C_2H_6)
 - Given: 3.00 g of ethane contains 2.40 g of carbon and 0.60 g of hydrogen.
 - Moles of carbon = $2.40 \text{ g} / 12.0 \text{ g/mol} = 0.20 \text{ mol}$
 - Moles of hydrogen = $0.60 \text{ g} / 1.0 \text{ g/mol} = 0.60 \text{ mol}$
 - Empirical formula = CH_3

Molecular Formula:

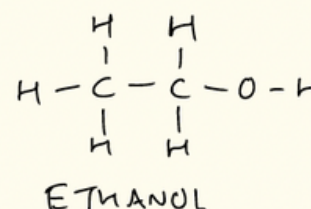
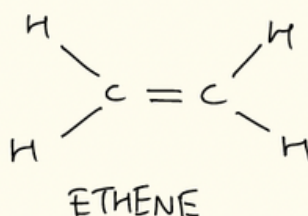
- Shows the actual number of atoms in a molecule.
- Ethane's empirical formula is CH_3 . The molecular mass of ethane is 30.0 (2×15.0).
- Molecular formula = C_2H_6

AN INTRO TO ORGANIC CHEMISTRY

Displayed Formula

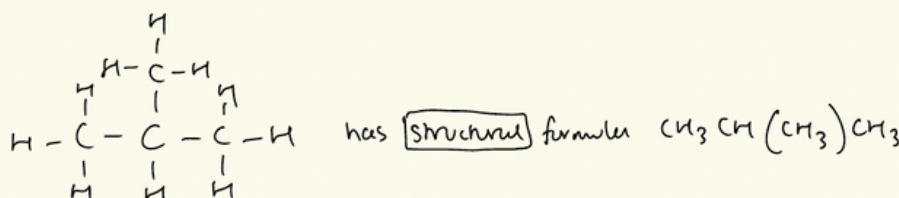
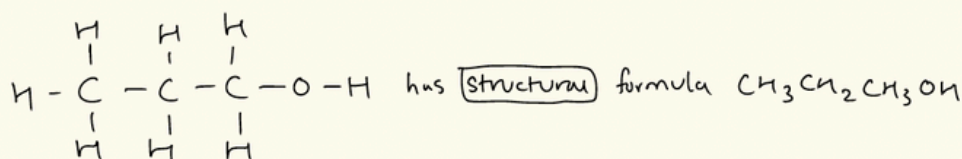
- Shows every atom and every bond in the molecule

$-$ is a single bond
 $=$ is a double bond
 $\equiv$ is a triple bond



Structural Formula

- Shows arrangement of atoms in a molecule in a form that is simplified - does not show all the bonds



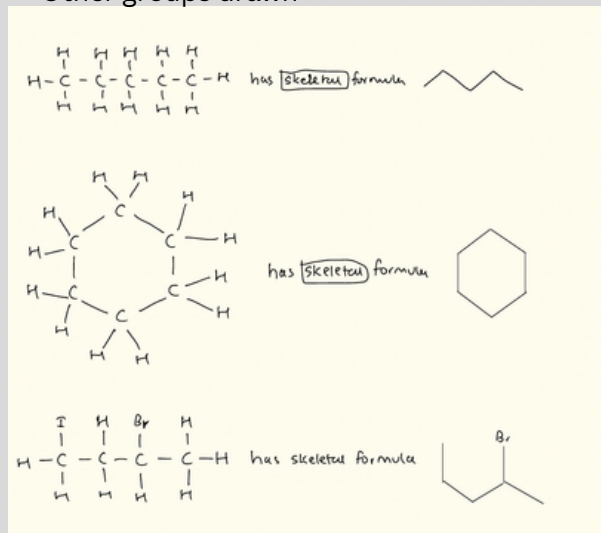
03-CHEM-1

INTRO TO ORGANIC CHEMISTRY



Skeletal Formula

- Carbon atoms not drawn at all, H atoms not drawn, C-H bonds not drawn
- Other groups drawn



3D Formula

- Bonds coming out of the paper are shown by wedges
- Bonds going into the paper are shown by dotted lines

Reaction Mechanisms:

- Curly Arrows:**
 - Indicate the movement of electron pairs.
 - Example: Electron pair moves from a lone pair to form a bond.
- Free Radicals:**
 - Molecules with unpaired electrons, making them highly reactive.

Examples:

Reaction of Sodium Chloride with Silver Nitrate:

- $\text{Cl}^-(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{AgCl}(\text{s})$

Reaction of Sodium Bromide with Concentrated Sulfuric Acid:

- $\text{NaBr}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HBr}(\text{g})$
- $\text{HBr}(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g}) + \text{Br}_2(\text{l})$

Reaction of Sodium Iodide with Concentrated Sulfuric Acid:

- $\text{NaI}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HI}(\text{g})$
- $\text{HI}(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g}) + \text{I}_2(\text{s}) + \text{H}_2\text{S}(\text{g})$

SYSTEMATIC NAMING OF ORGANIC COMPOUNDS

Root Names:

- The root indicates the longest unbranched chain or ring.
- Table 1: Root Names for Organic Compounds

SUFFIXES AND MORE NAMING

Suffixes:

- Indicate the type of bonding in the molecule.
- ane: No double bonds (alkanes)
 - Example: Ethane
 - mathematica
 - Copy code
 - $\text{H} \quad \text{H} \quad | \quad \text{H} - \text{C} - \text{C} - \text{H} \quad | \quad \text{H} \quad \text{H}$
- ene: Contains at least one double bond (alkenes)
 - Example: Ethene
 - mathematica
 - Copy code
 - $\text{H} \quad \text{H} \quad | \quad \text{H} - \text{C} = \text{C} - \text{H} \quad | \quad \text{H} \quad \text{H}$

Prefixes:

- Indicate the presence of side chains and their length.
 - methyl: 1 carbon
 - ethyl: 2 carbons
 - propyl: 3 carbons
 - butyl: 4 carbons
 - Example: Methylbutane
 - mathematica
 - Copy code
 - $\text{H} \quad \text{H} \quad \text{H} \quad | \quad | \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \quad | \quad \text{CH}_3$

Number of Carbons	Root
1	meth
2	eth
3	prop
4	but
5	pent
6	hex

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INTRO TO ORGANIC CHEMISTRY



FUNCTIONAL GROUPS AND SUFFIXES

Functional Groups and Suffixes:

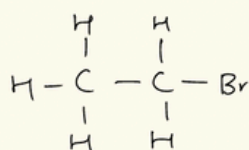
- Functional groups are reactive groups attached to the hydrocarbon chain.
- The suffix or prefix of the functional group is used to name the compound.

Hydrocarbon rings use the prefix **cyclo**.

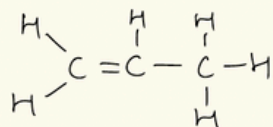
- Example: Cyclohexane
- mathematica
- Copy code
- C_6H_{12}

Functional Group	General Formula	Suffix	Example
Alkanes (no double bonds)	C_nH_{2n+2}	-ane	Ethane (C_2H_6)
Alkenes (one or more double bonds)	$R-CH=CH-R$	-ene	Propene (C_3H_6)
Halogenoalkanes (with halogen)	$R-X$ ($X = F, Cl, Br, I$)	none	Chloromethane (CH_3Cl)
Alcohols (with -OH)	$R-OH$	-ol	Ethanol (C_2H_5OH)
Aldehydes (with -CHO)	$R-CHO$	-al	Ethanal (CH_3CHO)
Ketones (with -CO- group)	$R-CO-R'$	-one	Propanone (CH_3COCH_3)
Carboxylic Acids (with -COOH)	$R-COOH$	-oic acid	Ethanoic Acid (CH_3COOH)

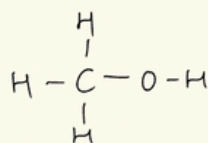
MORE NAMING



Bromoethane

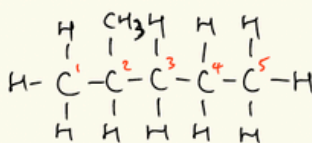


PROPENE
3 C atoms → Double Bond

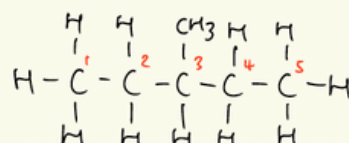


METHANOL
1 C atom → OH alcohol group

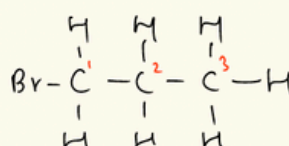
CHAIN AND POSITION ISOMERISM



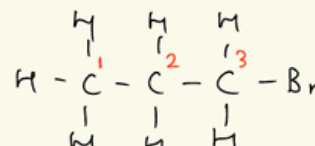
2-METHYLPENTANE



3-METHYLPENTANE



1-BROMOPROPANE

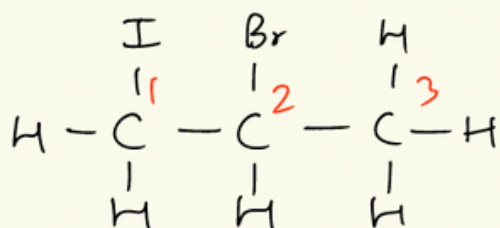


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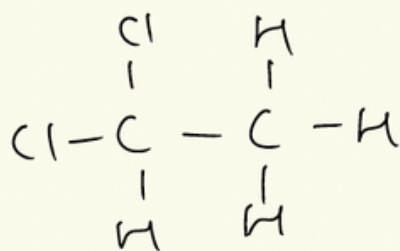
INTRO TO ORGANIC CHEMISTRY



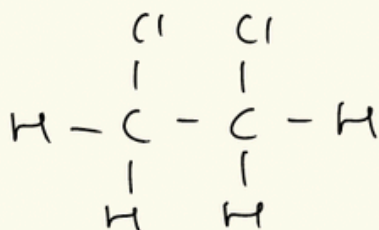
MOLECULES WITH MORE THAN ONE FUNCTIONAL GROUP OR SIDE CHAIN



2-BROMO - 1-IODOPROPANE
Alphabetical order



1,1-DICHLOROETHANE



1,2-DICHLOROETHANE

HOMOLOGOUS SERIES

Definition: A homologous series is a family of organic compounds with the same functional group but different carbon chain lengths.

Characteristics:

- **General Formula:**
 - Alkanes: $\text{C}_n\text{H}_{2n+2}$
 - Alkenes (with one double bond): C_nH_{2n}
- **Differences Between Members:**
 - Each member differs from the next by a $-\text{CH}_2-$ unit.
- **Chemical Reactivity:**
 - The length of the carbon chain has minimal effect on the chemical reactivity of the functional group.
- **Physical Properties:**
 - Melting and Boiling Points: Increase with the number of carbon atoms due to stronger intermolecular forces.
 - State of Matter: Smaller molecules are typically gases, while larger ones are liquids or solids.
 - Chain Branching: Reduces melting points as branched molecules pack less efficiently.



STRUCTURAL ISOMERS

Isomers are molecules that have the same molecular formula but differ in the arrangement of their atoms. There are two primary types of isomerism in organic chemistry:

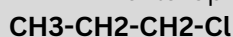
1. Structural Isomerism
2. Stereoisomerism

1. Structural Isomerism

Structural isomers have the same molecular formula but different structural formulae. This type of isomerism can be further divided into three subcategories:

A. Positional Isomerism

- Definition: The functional group is attached to different positions on the main carbon chain.
- Example: The molecular formula C_3H_7Cl can represent:
 - 1-chloropropane:



- 2-chloropropane:



B. Functional Group Isomerism

- Definition: Isomers have different functional groups.
- Example: The molecular formula C_2H_6O can represent:
 - Ethanol (an alcohol):
 - CH_3-CH_2-OH
 - Methoxymethane (an ether):
 - CH_3-O-CH_3

C. Chain Isomerism

- Definition: The arrangement of the hydrocarbon chain differs, leading to branching.
- Example: The molecular formula $C_4H_{10}O$ can represent:
 - Butan-1-ol: $CH_3-CH_2-CH_2-CH_2-OH$
 - 2-Methylpropan-1-ol: $CH_3-CH(CH_3)-CH_2-OH$

STRUCTURAL ISOMERS

Stereoisomerism occurs when two (or more) compounds have the same structural formula but differ in the arrangement of the bonds in space. There are two primary types of

stereoisomerism:

1. E-Z Isomerism
2. Optical Isomerism

1. E-Z Isomerism

Definition

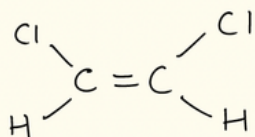
E-Z isomerism describes the different spatial arrangements of substituents around a carbon-carbon double bond ($C=C$). The prefixes E and Z denote the relative positions of the substituents.

Characteristics

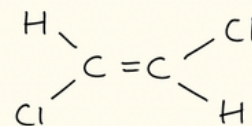
- Z Isomer (cis): Substituents are on the same side of the double bond.
- E Isomer (trans): Substituents are on opposite sides of the double bond.

Example

- Z-1,2-Dichloroethene:



Z-1,2-DICHLOROETHENE



E-1,2-DICHLOROETHENE

Importance

- Substituted groups connected by single bonds can rotate around the bond, which prevents the formation of isomers. However, rotation is restricted around double bonds, resulting in the existence of distinct E and Z isomers. These isomers cannot easily convert from one form to another due to the rigidity of the double bond.

Origin of Terms

- E comes from the German word "Entgegen," meaning opposite (trans).
- Z comes from the German word "Zusammen," meaning together (cis).

03-CHEM-2

ALKANES



ALKANES- INTRO

Alkanes are saturated hydrocarbons, meaning they contain only carbon-carbon (C-C) and carbon-hydrogen (C-H) single bonds. They are among the least reactive organic compounds and play a significant role in various industries, serving as fuels, lubricants, and starting materials for the synthesis of other compounds. The main source of alkanes is crude oil.

General Formula

The general formula for all chain alkanes is C_nH_{2n+2} . Hydrocarbons can exist in three structural forms:

1. Unbranched chains
2. Branched chains
3. Rings

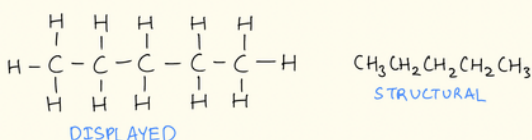
1. Unbranched Chains

- **Definition:** Unbranched chains are often referred to as straight chains.
- **Bond Angle:** The C-C-C bond angle in unbranched alkanes is approximately 109.5° , indicating that the chains are not perfectly straight.
- **Hydrogen Atoms:** In an unbranched alkane, each carbon atom is bonded to two hydrogen atoms, except for the terminal (end) carbon atoms, which are bonded to three hydrogen atoms.

EXAMPLES

Pentane (C_5H_{12})

- Molecular Formula: (C_5H_{12})
- Displayed and Structural Formula:



Branched Chains

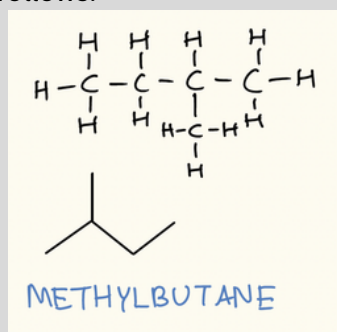
Branched chains are hydrocarbons where one or more branches extend from the main carbon chain. This results in structural isomers with the same molecular formula but different arrangements.

Example: Methylbutane

- Isomer of Pentane: Methylbutane is a structural isomer of pentane, sharing the same molecular formula (C_5H_{12}) but differing in structure.
- Molecular Formula: C_5H_{12}

Displayed Structural Formula

The displayed structural formula for methylbutane can be represented as follows:



Characteristics of Methylbutane

- Branches: The structure contains a branch (methyl group) attached to the main carbon chain, demonstrating structural isomerism.
- Importance: Understanding branched alkanes is essential in organic chemistry as they exhibit different physical and chemical properties compared to their straight-chain counterparts.

Ring alkanes are hydrocarbons in which carbon atoms are arranged in a closed loop, forming a cyclic structure.

General Molecular Formula

- The general molecular formula for ring alkanes is C_nH_{2n} , where n is the number of carbon atoms. This reflects that the end hydrogens are not required due to the ring structure.

Key Points

- Saturation: Ring alkanes are saturated, containing only single bonds between carbon atoms.
- Reactivity: Although generally less reactive than other functional groups, ring alkanes can participate in reactions such as combustion and substitution.

Example of a Ring Alkane

A common example of a ring alkane is cyclohexane, which has the molecular formula C_6H_{12} .

03-CHEM-2

ALKANES



NAMING ALKANES, AND WHAT ARE ALKANES?

Feature	Description
Definition	Saturated hydrocarbons containing only carbon-carbon (C-C) and carbon-hydrogen (C-H) single bonds.
General Formula	$C_nH_{(2n+2)}$
Examples of Alkanes	Methane: CH_4 Ethane: C_2H_6 Propane: C_3H_8 Butane: C_4H_{10} Pentane: C_5H_{12} Hexane: C_6H_{14}
Naming Alkanes	
Root Name	Indicates the number of carbon atoms in the longest chain (e.g., "pent" for 5 carbons).
Suffix	The suffix -ane denotes an alkane.
Branched Chain Naming	1. Identify the longest unbranched chain. 2. Name branches as prefixes (e.g., methyl-, ethyl-). 3. Number to show attachment points.
Example of 3-Methylpentane	Longest chain: pentane (5 carbons) Side chain: methyl- at carbon 3 Full name: 3-methylpentane
Structural Isomerism	Molecules with the same molecular formula but different structural arrangements.
Isomer Examples	- Butane (C_4H_{10}): 2 isomers - Pentane (C_5H_{12}): 3 isomers - Decane ($C_{10}H_{22}$): 75 isomers - $C_{30}H_{60}$: Over 4 billion isomers

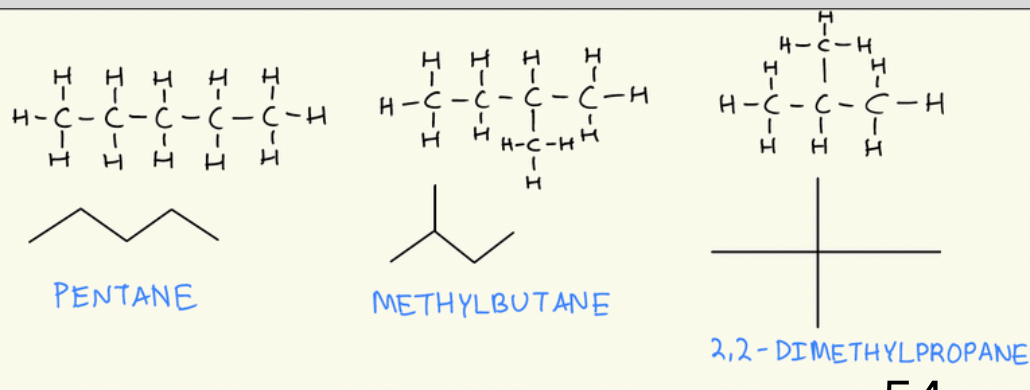
STRUCTURAL ISOMERS

- Isomers: Molecules with the same molecular formula but different structural arrangements.
- No Isomers: Methane (C_4H_4), ethane (C_2H_6), and propane (C_3H_8) do not have isomers.
- Isomers in Alkanes:
 - Butane (C_4H_{10}) has two isomers:
 - n-Butane
 - Isobutane (methylpropane)

- Pentane (C_5H_{12}) has three isomers:
 - n-Pentane
 - 2-Methylbutane
 - 2,2-Dimethylpropane

Structural Representation of Isomers

- Pentane (C_5H_{12}):



03-CHEM-2

ALKANES



PHYSICAL PROPERTIES

Property	Description
Polarity	Alkanes are almost non-polar due to similar electronegativities of carbon (2.5) and hydrogen (2.1). The only intermolecular forces are weak van der Waals forces.
Boiling Points	- Boiling points increase with chain length due to stronger van der Waals forces. - Short-chain alkanes are gases at room temperature. - Pentane (C ₅ H ₁₂) is a liquid.
Effect of Branching	Branched alkanes have lower boiling points than their straight-chain isomers because they cannot pack closely together, reducing van der Waals interactions.
Solubility	Alkanes are insoluble in water due to strong hydrogen bonds in water. However, they mix with non-polar liquids because of van der Waals forces.
Reactivity	- Alkanes are unreactive due to strong C-C and C-H bonds. - They do not react with acids, bases, or oxidizing/reducing agents. - They burn in oxygen.
Combustion	- Complete combustion in oxygen forms carbon dioxide and water. - Incomplete combustion forms carbon monoxide or carbon (soot).

INTRO TO FRACTIONAL DISTILLATION OF CRUDE OIL

Fraction	Approximate Boiling Temperature (K)	Chain Length	Percentage (%)
Gases	310	1-5	2
Petrol	310-450	5-10	10
Naphtha	400-490	8-12	14
Kerosene	430-523	11-16	21
Gas Oil	590-620	16-24	45
Fuel Oil & Wax	Above 620	25+	—

- Crude oil is a **mixture of hydrocarbons, mainly alkanes**.
- Its composition varies depending on the source of the oil.
- Crude oil contains small amounts of sulfur compounds. When these are burned, they produce sulfur dioxide (SO₂), a contributor to acid rain.

03-CHEM-2

ALKANES

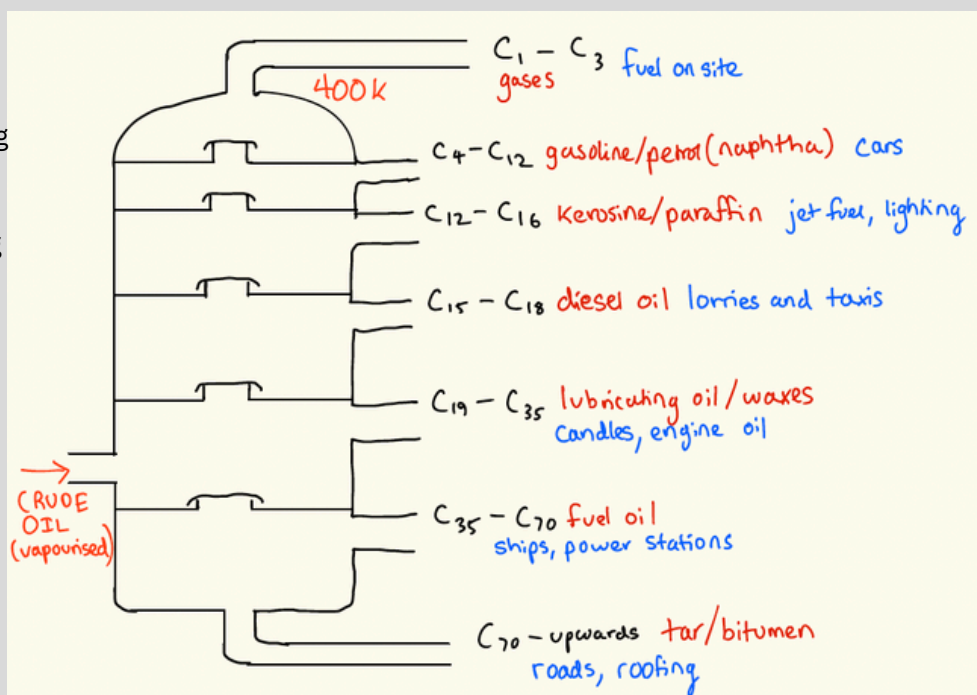


PROCESS OF FRACTIONAL DISTILLATION

Fractional distillation is the process used to separate crude oil into its useful components, called fractions. Each fraction contains hydrocarbons with similar chain lengths and boiling points.

Steps in Fractional Distillation:

1. **Heating Crude Oil:**
 - Crude oil is heated in a furnace, causing it to vaporize.
2. **Entry into Fractionating Tower:**
 - The vaporized oil enters a fractionating tower, which is hotter at the bottom and cooler at the top.
3. **Rising Vapours:**
 - As the vapours rise, they pass through trays with bubble caps. The temperature decreases as the vapours move upwards.
4. **Condensation on Trays:**
 - When vapours reach a tray where the temperature is lower than their boiling point, they condense into liquids.
5. **Piping off Fractions:**
 - The liquids on each tray, which are mixtures of hydrocarbons with similar boiling points, are piped off.
6. **Shorter Chains at the Top:**
 - Hydrocarbons with shorter chains and lower boiling points condense at the top of the tower, where it's cooler.
7. **Residue Collection:**
 - The residue at the bottom is called tar or bitumen. It can be used for road surfacing, but sometimes it is further processed for more valuable products.



Key Points:

- Shorter-chain hydrocarbons (like gases and petrol) condense near the top of the tower.
- Longer-chain hydrocarbons (like gas oil) condense near the bottom.
- The thick residue (bitumen) is collected at the base of the tower.

Fractional distillation allows for the efficient separation of crude oil into useful fractions such as petrol, diesel, kerosene, and lubricating oils, which are essential for various industries.

03-CHEM-2

ALKANES



FRACKING

Natural gas, particularly methane, is a major source of electricity in the UK, generating nearly half of the country's supply. Historically, much of this gas has come from the North Sea, but as those reserves are being depleted, the UK is increasingly importing gas from Europe through pipelines.

Shale Gas Resources:

- In addition to offshore gas, the UK has shale gas resources.
- Unlike the North Sea reserves trapped under impervious rock layers, shale gas is contained within shale rock, similar to water held in a sponge.

Hydraulic Fracturing (Fracking) Process:

- Fracking is used to extract shale gas.
 - A well is drilled into the shale.
 - Pressurized water, mixed with sand, is forced into the shale rock.
 - The pressure fractures the soft shale, releasing the trapped gas.

Chemicals in Fracking:

- Chemicals are added to assist the process:
 - Hydrochloric acid is used to help break down the rock.
 - Methanol is added to prevent corrosion in the system.

This method of gas extraction has generated significant interest, as it offers an additional domestic energy source. However, fracking has also raised concerns about environmental impact, including possible groundwater contamination and seismic activity.

CRACKING- THERMAL AND CATALYTIC CRACKING,, AN INTRO

Cracking is a process used to **break down long-chain hydrocarbons into shorter, more useful ones**, such as those found in petrol. This process is essential because most crude oil contains more long-chain hydrocarbons than are needed, whereas there is a higher demand for shorter chain hydrocarbons like those in the naphtha fraction.

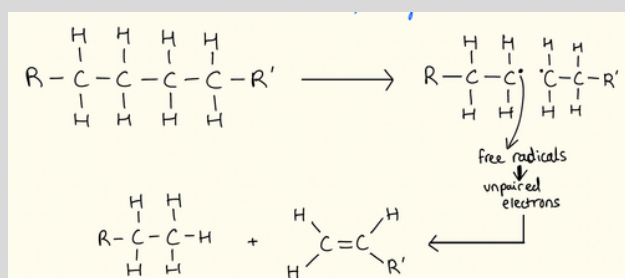
Benefits of Cracking:

- Shorter chains (especially petrol) are produced, which are economically valuable.
- Alkenes are formed, which are more reactive and serve as chemical feedstock for producing polymers and other products.

Types of Cracking:

1. Thermal Cracking:

- Involves heating long-chain alkanes to very high temperatures (700-1200 K) under high pressure (up to 7000 kPa).
- Carbon-carbon bonds break in such a way that free radicals (highly reactive fragments) are formed.
- Reaction Example:



Free Radicals have unpaired electrons and can react in various ways to form shorter chain molecules.

- Since there aren't enough hydrogen atoms to form two alkanes, at least one of the products is an alkene.
 - Cracking produces a high proportion of alkenes, such as ethene, a vital starting material for plastics like poly(ethene) (polythene).
- **Time Control:** To prevent excessive decomposition of alkanes into carbon and hydrogen, the alkanes are kept under thermal cracking conditions for a short time (typically around 1 second).

03-CHEM-2

ALKANES

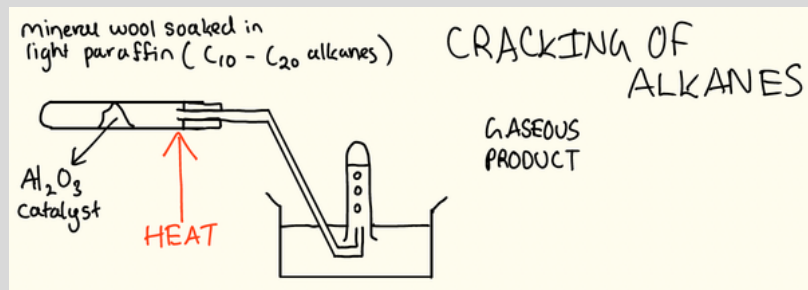


CATALYTIC CRACKING

Catalytic cracking is a process where longer-chain hydrocarbons are broken down at lower temperatures (~720 K) and moderate pressures using a zeolite catalyst. The catalyst consists of silicon dioxide and aluminium oxide (aluminosilicates) and has a honeycomb structure, providing a large surface area. Zeolites are also acidic, which enhances their catalytic activity.

Key Points:

- **Temperature:** ~720 K (lower than thermal cracking)
- **Catalyst:** Zeolite (silicon dioxide and aluminium oxide)
- **Main Products:**
 - Branched alkanes
 - Cycloalkanes (ring structures)
 - Aromatic compounds



This form of cracking is primarily used to produce motor fuels, which include branched hydrocarbons that burn more efficiently in engines.

Laboratory Catalytic Cracking:

In the lab, catalytic cracking can be demonstrated using aluminium oxide as a catalyst and mineral wool soaked in light paraffin (a mixture of alkanes, C10 to C20). The setup involves heating the catalyst and observing the products, which are mostly gases (indicating short-chain hydrocarbons). The gaseous products often include alkenes, as indicated by the decolorisation of bromine solution, which is a test for the presence of carbon-carbon double bonds.

COMBUSTION- AN INTRO

Combustion of Alkanes

Alkanes are relatively unreactive but burn readily in a plentiful supply of oxygen to produce carbon dioxide and water. These reactions release large amounts of heat and have large negative enthalpies of combustion, making alkanes important fuels.

Example Combustion Reactions:

- Methane combustion: $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ $\Delta H = -890 \text{ kJ mol}^{-1}$
- Ethane combustion: $\text{C}_2\text{H}_6(\text{g}) + 3.5\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$ $\Delta H = -1559.7 \text{ kJ mol}^{-1}$

The heat output increases with the number of carbon atoms in the alkane chain. Alkanes are used as fuels because:

- They release large amounts of heat energy when they burn.
- They have a high energy density, meaning they store a significant amount of energy per unit mass.

Examples of Alkane Fuels:

- **Methane:** The main component of natural gas.
- **Propane:** Used in camping gas.
- **Butane:** Found in Calor gas.
- **Petrol:** A mixture of hydrocarbons with chain lengths around C8.
- **Paraffin:** A mixture of hydrocarbons with chain lengths ranging from C10 to C18.

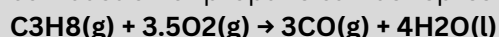
These fuels are widely used due to their efficient energy release during combustion. Octane, for example, produces about 48 kJ of energy per gram, which is nearly double that of coal.



INCOMPLETE COMBUSTION AND ATMOSPHERIC POLLUTION

Incomplete Combustion

In a limited supply of oxygen, incomplete combustion occurs, producing carbon monoxide (CO), a poisonous gas. For example, the incomplete combustion of propane can be represented by:



With even less oxygen, carbon (soot) is produced, which can be observed as a yellow flame and sooty deposits on apparatus, such as when using a Bunsen burner with the air hole closed. Longer chain hydrocarbons are more prone to incomplete combustion because they require more oxygen to burn than shorter chains.

Pollutants from Burning Hydrocarbons

When hydrocarbon-based fuels derived from crude oil burn, they may produce harmful pollutants, including:

- **Carbon monoxide (CO):** A poisonous gas formed during incomplete combustion. It interferes with the transport of oxygen in the blood.
- **Nitrogen oxides (NO, NO₂, N₂O₄):** Formed when nitrogen and oxygen in the air react under the high temperatures found in petrol engines: $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$. Nitrogen oxides can react with water vapour and oxygen in the air to form nitric acid, contributing to acid rain and photochemical smog.
- **Sulfur dioxide (SO₂):** Produced from sulfur impurities in crude oil. It reacts with water vapour and oxygen in the air to form sulfuric acid, contributing to acid rain.
- **Carbon particles (particulates):** Can exacerbate asthma and cause cancer.
- **Unburnt hydrocarbons:** These are significant greenhouse gases and contribute to photochemical smog, leading to health problems such as respiratory issues.
- **Carbon dioxide (CO₂):** A greenhouse gas always produced during combustion. While necessary in the atmosphere, rising CO₂ levels are contributing to global warming and climate change.
- **Water vapour:** Also a greenhouse gas produced during combustion, though it has a lesser impact compared to carbon dioxide.

FLUE GAS DESULFURISATION (FGD)

Flue gas desulfurisation (FGD) is a crucial process for removing sulfur dioxide (SO₂) from flue gases produced by burning fossil fuels. **Here's a structured overview:**

- **Importance of FGD:**
 - Sulfur dioxide contributes to acid rain.
 - Acid rain forms when SO₂ reacts with oxygen and water, producing sulfuric acid (H₂SO₄):
 - $\text{SO}_2(\text{g}) + 0.5 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{l})$
- **Flue Gases:**
 - The gases emitted from power stations are called flue gases.
 - FGD aims to remove SO₂ to reduce environmental impact.

Method 1: Using Calcium Oxide (Lime)

- **Process:**
 - A slurry of calcium oxide (CaO) and water is sprayed into the flue gases.
 - Reaction with sulfur dioxide and water produces calcium sulfite:
 - $\text{CaO}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g}) + 0.5 \text{O}_2(\text{g}) \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$
 - By-Product:
 - Calcium sulfate dihydrate (gypsum) is produced, which is valuable for:
 - Builders' plaster
 - Plasterboard

Method 2: Using Calcium Carbonate (Limestone)

- **Process:**
 - This method uses calcium carbonate (CaCO₃).
 - Reaction with sulfur dioxide and oxygen yields calcium sulfate and carbon dioxide:
 - $\text{CaCO}_3(\text{s}) + 0.5 \text{O}_2(\text{g}) + \text{SO}_2(\text{g}) \rightarrow \text{CaSO}_4(\text{s}) + \text{CO}_2(\text{g})$
- **Benefits:**
 - Both methods effectively remove sulfur dioxide from flue gases.
 - They prevent SO₂ from contributing to acid rain.
 - Valuable by-products, such as gypsum, are produced.

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ALKANES



CATALYTIC CONVERTERS

Catalytic converters are essential components in the exhaust systems of modern internal combustion engines. They help reduce harmful emissions and pollutants. Here's an overview of their function and impact:

- **Pollutants Addressed:**
 - Carbon monoxide (CO)
 - Nitrogen oxides (NO_x)
 - Unburnt hydrocarbons (HC)
- **Construction:**
 - Composed of a honeycomb structure made from ceramic materials.
 - Coated with platinum and rhodium metals, which serve as catalysts.
 - The honeycomb design provides a large surface area for reactions, allowing minimal amounts of these expensive metals to be effective.
- **Reactions in Catalytic Converters:**
 - As exhaust gases pass over the catalyst, they undergo several reactions to form less harmful products:
 - **Reaction 1:**
 - $2\text{CO(g)} + 2\text{NO(g)} \rightarrow \text{N}_2\text{(g)} + 2\text{CO}_2\text{(g)}$
 - Carbon monoxide reacts with nitrogen oxide to produce nitrogen and carbon dioxide.
 - **Reaction 2:**
 - Hydrocarbons + nitrogen oxide → nitrogen + carbon dioxide + water
 - For example:
 - $\text{C}_8\text{H}_{18} + 25\text{NO} \rightarrow 8\text{N}_2 + 9\text{CO}_2 + 9\text{H}_2\text{O}$
 - Alkanes react with nitrogen oxides, yielding nitrogen, carbon dioxide, and water.

GLOBAL WARMING AND THE GREENHOUSE EFFECT

- **Greenhouse Effect:**
 - Greenhouses retain heat because visible sunlight penetrates the glass and is re-radiated as infrared radiation, which cannot escape.
 - Carbon dioxide (CO₂) behaves similarly, trapping infrared radiation in the Earth's atmosphere, leading to warming.
 - Other greenhouse gases: Water vapour and methane are also significant, with methane being more effective than CO₂ in trapping heat.
- **Impact of Fossil Fuels:**
 - The industrial revolution marked an increase in fossil fuel consumption, leading to higher levels of CO₂ in the atmosphere.
 - There is a consensus among scientists that the rising CO₂ levels contribute to global warming.
- **Water Vapour:**
 - Water vapour is the most abundant greenhouse gas, but its concentration tends to remain stable due to equilibrium with liquid water.
 - Increased temperatures can lead to more water vapour, contributing to additional greenhouse warming.
 - The role of water vapour in climate dynamics is significant yet not fully understood.

Carbon Neutral Activities

- Concerns about Carbon Emissions:
 - Activities like air travel contribute substantially to CO₂ emissions.
 - For instance, a flight from London to Paris produces about 350 kg of CO₂ per passenger from burning hydrocarbon fuels.

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ALKANES



HALOGENATION OF ALKANES

Halogenation is a process where an alkane reacts with a halogen in the presence of ultraviolet (UV) light, resulting in the formation of a halogenoalkane (haloalkane). Here's a structured overview of the reaction:

- **Reaction Conditions:**
 - Light Source: Requires bright sunlight or a photoflood lamp, which emits ultraviolet light.
 - Temperature: The reaction does not occur in the dark at room temperature.
- **Example Reaction:**
 - Reactants: Hexane (C_6H_{14}) and liquid bromine (Br_2).
 - Observation:
 - In the dark: The mixture remains red-brown due to the presence of bromine.
 - When exposed to UV light: The mixture becomes colourless, and misty fumes of hydrogen bromide (HBr) are produced.
- **Mechanism:**
 - The ultraviolet light initiates the reaction by breaking the $Br-Br$ bond, generating bromine radicals ($Br\cdot$).
 - A substitution reaction occurs where one or more hydrogen atoms in the alkane are replaced by bromine atoms.
- **Overall Reaction:**
 - $C_6H_{14} + Br_2 \rightarrow C_6H_{13}Br + HBr$
 - Products:
 - Bromohexane ($C_6H_{13}Br$): The resulting halogenoalkane.
 - Hydrogen Bromide (HBr): A gaseous byproduct.

CHAIN REACTIONS: FREE-RADICAL SUBSTITUTION

Free-radical substitution involves a chain reaction that proceeds through three key stages: initiation, propagation, and termination. This mechanism applies to the reaction between any alkane and halogen, such as methane and chlorine.

Initiation

- The reaction begins with the breaking of the $Cl-Cl$ bond.
 - UV light provides enough energy to break the bond homolytically, meaning one electron goes to each chlorine atom
 - This creates two highly reactive chlorine free radicals, $Cl\cdot$, each with an unpaired electron.
 - UV light: $Cl_2 \rightarrow 2Cl\cdot$

Propagation

- This stage occurs in two steps, creating the chain reaction:
- **Step 1:**
 - A chlorine free radical reacts with methane (CH_4), removing a hydrogen atom to form hydrogen chloride (HCl) and leaving behind a methyl free radical ($\cdot CH_3$).
 - $Cl\cdot + CH_4 \rightarrow HCl + \cdot CH_3$
- **Step 2:**
 - The methyl free radical ($\cdot CH_3$) reacts with another chlorine molecule (Cl_2), forming chloromethane (CH_3Cl) and generating another chlorine free radical ($Cl\cdot$).
 - $\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot$
- These two steps repeat, with each new chlorine free radical continuing the chain reaction.

Termination

- The chain reaction stops when free radicals combine and form stable compounds without unpaired electrons. This can happen in three ways:
 - $Cl\cdot + Cl\cdot \rightarrow Cl_2$ (chlorine molecules)
 - $\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6$ (ethane)
 - $Cl\cdot + \cdot CH_3 \rightarrow CH_3Cl$ (chloromethane)

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HALOGENOALKANES



HALOGENOALKANES- AN INTRO

Halogenoalkanes (also known as alkyl halides) are organic compounds where one or more hydrogen atoms in an alkane skeleton are replaced by halogen atoms (fluorine, chlorine, bromine, or iodine). Though few occur naturally, halogenoalkanes form the basis of many synthetic compounds used in everyday applications, such as:

- PVC (for drainpipes)
- Teflon (non-stick coating on pans)
- Various anaesthetics and solvents

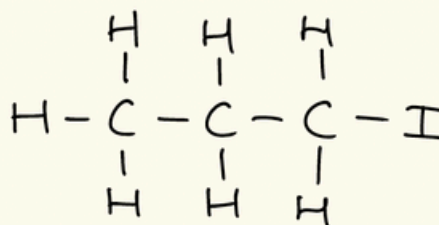
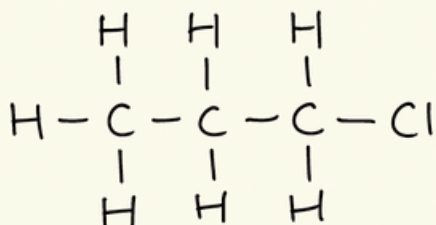
General Formula of Halogenoalkanes

- The general formula for a halogenoalkane with one halogen atom is:
- $C_nH_{2n+1}X$
- where X represents the halogen atom (e.g., F, Cl, Br, I).
- This formula is often written as R-X, where R refers to the alkyl group.

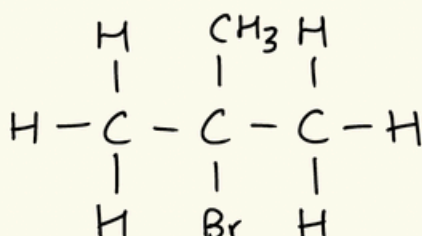
How to Name Halogenoalkanes

- **Halogen Prefixes:**
 - The halogen present is indicated by prefixes:
 - Fluoro- (F), Chloro- (Cl), Bromo- (Br), Iodo- (I)
- **Numbering the Carbon Chain:**
 - Numbers are used to show the position of the halogen atom on the carbon chain:
 - For example:
 - 1-chloropropane: Cl on the first carbon
 - 1-iodopropane: I on the first carbon
 - 2-bromo-2-methylpropane: Br on the second carbon of a branched chain
- **Multiple Halogen Atoms:**
 - When there are multiple halogen atoms, prefixes such as di-, tri-, tetra- are used:
 - For example, dichloromethane (CH_2Cl_2) has two chlorine atoms.
- **Ordering Halogens Alphabetically:**
 - When different halogens are present, they are listed in alphabetical order, not based on the position of attachment:
 - Example:
 - 3-chloro-2-iodopentane (Cl comes before I alphabetically)
 - Not 2-iodo-3-chloropentane

1-CHLOROPROPANE



1- IODOPROPANE



2-BROMO-2-METHYLPROPANE

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HALOGENOALKANES



BOND POLARITY OF HALOGENOALKANES

Bond Polarity in Halogenoalkanes

- C-X bond: Halogenoalkanes contain a polar bond ($C\delta^+ - X\delta^-$) because halogens are more electronegative than carbon.
- Electronegativity trend: As you go down the halogen group, the bonds become less polar due to decreasing electronegativity.

Physical Properties of Halogenoalkanes

Solubility:

- The C-X bonds are polar but not polar enough to make halogenoalkanes soluble in water.
- Main intermolecular forces:
 - Dipole-dipole attractions
 - Van der Waals forces
- Halogenoalkanes mix with hydrocarbons, making them useful for dry-cleaning fluids and removing oily stains (since oil is a mixture of hydrocarbons).

Boiling Point:

- Factors influencing boiling point:
 - Chain length: Boiling point increases with longer carbon chains.
 - Position in the halogen group: Boiling point increases down the group.
 - Both effects are due to increased van der Waals forces as larger molecules have more electrons, which strengthens these forces.
- Branching: Increased branching in the carbon chain tends to lower the boiling point.
- Comparison with alkanes:
 - Halogenoalkanes have higher boiling points than alkanes of similar chain length due to their higher relative molecular mass and polarity.

HOW HALOGENOALKANES REACTS

When halogenoalkanes react, it is almost always the C-X bond that breaks. Two main factors influence how readily the C-X bond reacts:

1. $C\delta^+ - X\delta^-$ bond polarity
2. C-X bond enthalpy

1. Bond Polarity

- Electronegativity: Halogens are more electronegative than carbon, leading to a polar $C\delta^+ - X\delta^-$ bond. This means the carbon atom is electron-deficient and can be attacked by nucleophiles.
- Nucleophiles: These are electron pair donors that attack electron-deficient areas (such as the carbon atom in the C-X bond).
 - The C-F bond is the most polar, with the largest positive charge on carbon, so you would expect it to be the most reactive towards nucleophiles.
 - The C-I bond is the least polar, so it should theoretically be the least reactive.

2. Bond Enthalpy

- Bond enthalpies (strengths) decrease as you go down the halogen group:
 - C-F bond is the strongest due to the small size of fluorine, meaning the shared electrons are closer to the nucleus and more strongly attracted.
 - As you move down the group, the shared electrons in the C-X bond are further from the halogen nucleus, making the bond weaker.
- Reactivity prediction based on bond enthalpy:
 - C-I bonds (iodo-compounds) have the weakest bonds and should be the most reactive.
 - C-F bonds (fluoro-compounds) are strongest and should be least reactive.

Conclusion:

- Although bond polarity suggests that C-F should be the most reactive, experiments confirm that reactivity increases down the group. This means bond enthalpy (the bond strength) is the more important factor in determining reactivity.

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HALOGENOALKANES



WHAT ARE NUCLEOPHILES

In organic chemistry, many reactions occur in a series of steps that can often be predicted by considering how electrons move. This approach not only helps to understand the reaction mechanism but also reduces the need for memorization.

Nucleophiles:

- **Definition:** A nucleophile is a species that attacks and forms bonds with positively or partially positively charged carbon atoms.
- **Characteristics:**
 - A nucleophile can be a negatively charged ion or a molecule with a δ^- atom.
 - It possesses a lone pair of electrons that it can use to form a covalent bond.
 - The lone pair is typically located on an electronegative atom (such as oxygen, nitrogen, or carbon).
- **Common Nucleophiles:**
 - Hydroxide ion: OH^-
 - Ammonia:
 - NH_3
 - Cyanide ion: CN^-

These nucleophiles are capable of replacing the halogen in a halogenoalkane, leading to nucleophilic substitution reactions.

INTRODUCTION TO NUCLEOPHILIC SUBSTITUTION

Nucleophilic Substitution Reaction Mechanism:

- In these reactions, a nucleophile replaces a halogen in a halogenoalkane.
- Mechanism: The nucleophile donates its lone pair of electrons to the electron-deficient carbon atom (attached to the halogen). This leads to the displacement of the halogen atom, which leaves as a halide ion.

Key Points:

- Nucleophiles always target electron-deficient carbon atoms.
- The reaction proceeds through a series of steps, often involving short-lived intermediates.
- These reactions are classified as nucleophilic substitutions, since the nucleophile substitutes the halogen atom in the organic compound.

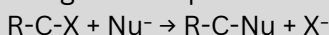


NUCLEOPHILIC SUBSTITUTION- A DETAILED OVERVIEW

In a nucleophilic substitution reaction, a nucleophile (represented as Nu^-) replaces a halogen atom (represented as X) in a halogenoalkane, forming a new compound.

General Equation:

The general equation for nucleophilic substitution can be written as:



Where:

- R is the alkyl group.
- C is the carbon atom attached to both X and Nu.
- X is the halogen atom (the leaving group).
- Nu^- is the nucleophile.

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HALOGENOALKANES



EXAMPLES OF NUCLEOPHILIC SUBSTITUTION REACTIONS- PART 1

Reaction Mechanism and Curly Arrows:

Curly arrows are used to represent the movement of electron pairs during the reaction:

- **Curly Arrow 1:** The lone pair of electrons on the nucleophile (Nu^-) is attracted to the electron-deficient carbon (C^+) attached to the halogen (X). This is shown by an arrow starting from the lone pair on Nu^- and pointing towards the C^+ atom.
- **Curly Arrow 2:** The electron pair in the C-X bond moves to the halogen atom (X), resulting in the halogen leaving as a halide ion (X^-). This is the leaving group.

The curly arrows illustrate the stepwise process:

1. Nucleophile attack: The nucleophile donates its lone pair of electrons to the partially positive carbon atom (C^+).
2. Halide departure: The halogen takes the electron pair from the C-X bond, leaving as X^- .

Effect of Halogen on Reaction Rate:

The rate of nucleophilic substitution depends on the strength of the C-X bond:

- Fluoro-compounds are unreactive due to the strength of the C-F bond.
- As you move down the halogen group (Cl, Br, I), the C-X bond strength decreases, making the reaction easier. Therefore, the reactivity increases as bond strength decreases:
 - C-I (weakest bond, most reactive)
 - C-Br
 - C-Cl
 - C-F (strongest bond, least reactive)

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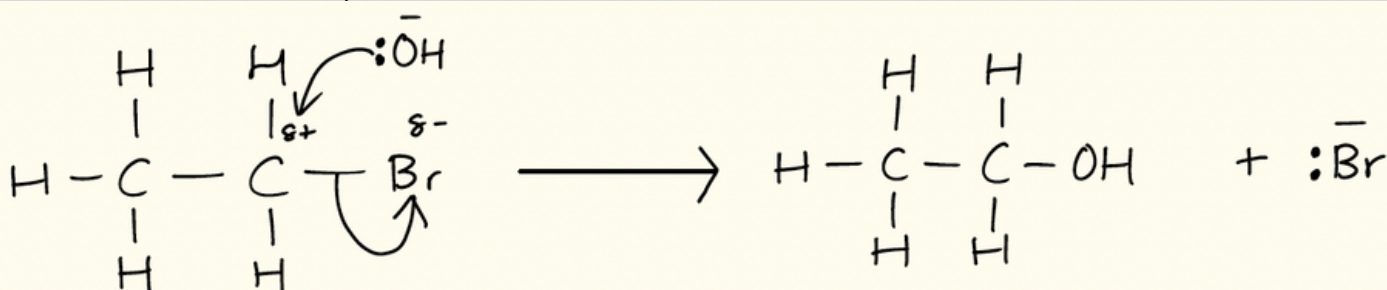
HALOGENOALKANES



EXAMPLES OF NUCLEOPHILIC SUBSTITUTION REACTIONS- PART 2

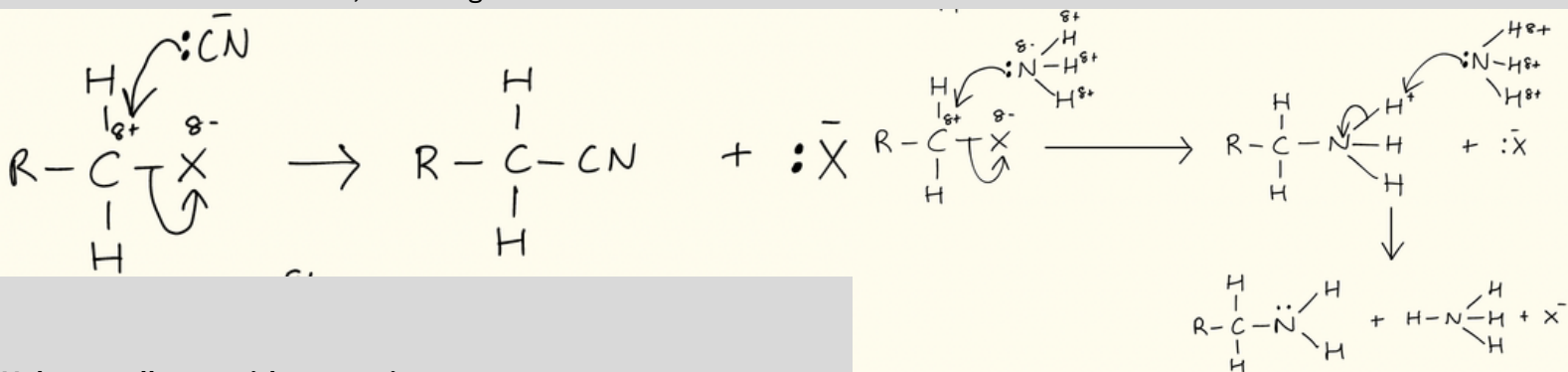
Halogenoalkanes with aqueous sodium (or potassium) hydroxide:

- Nucleophile: Hydroxide ion (OH^-)
- Conditions: Warm the mixture in ethanol as a solvent (halogenoalkanes don't mix with water).
- Overall reaction:
- $\text{R-X} + \text{OH}^- \rightarrow \text{R-OH} + \text{X}^-$
- Example: $\text{C}_2\text{H}_5\text{Br} + \text{OH}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$
- (bromoethane to ethanol)
- Mechanism:
 - a. Hydroxide ion attacks the carbon atom bonded to the halogen.
 - b. The C-X bond breaks, and a halide ion (X^-) is released.



Halogenoalkanes with cyanide ions:

- Nucleophile: Cyanide ion (CN^-)
- Conditions: Warm halogenoalkanes with an aqueous alcoholic solution of potassium cyanide.
- Overall reaction:
- $\text{R-X} + \text{CN}^- \rightarrow \text{R-CN} + \text{X}^-$
- (A nitrile is formed)
- Mechanism:
 - a. Cyanide ion attacks the carbon atom bonded to the halogen.
 - b. The C-X bond breaks, releasing the halide ion (X^-).



Halogenoalkanes with ammonia:

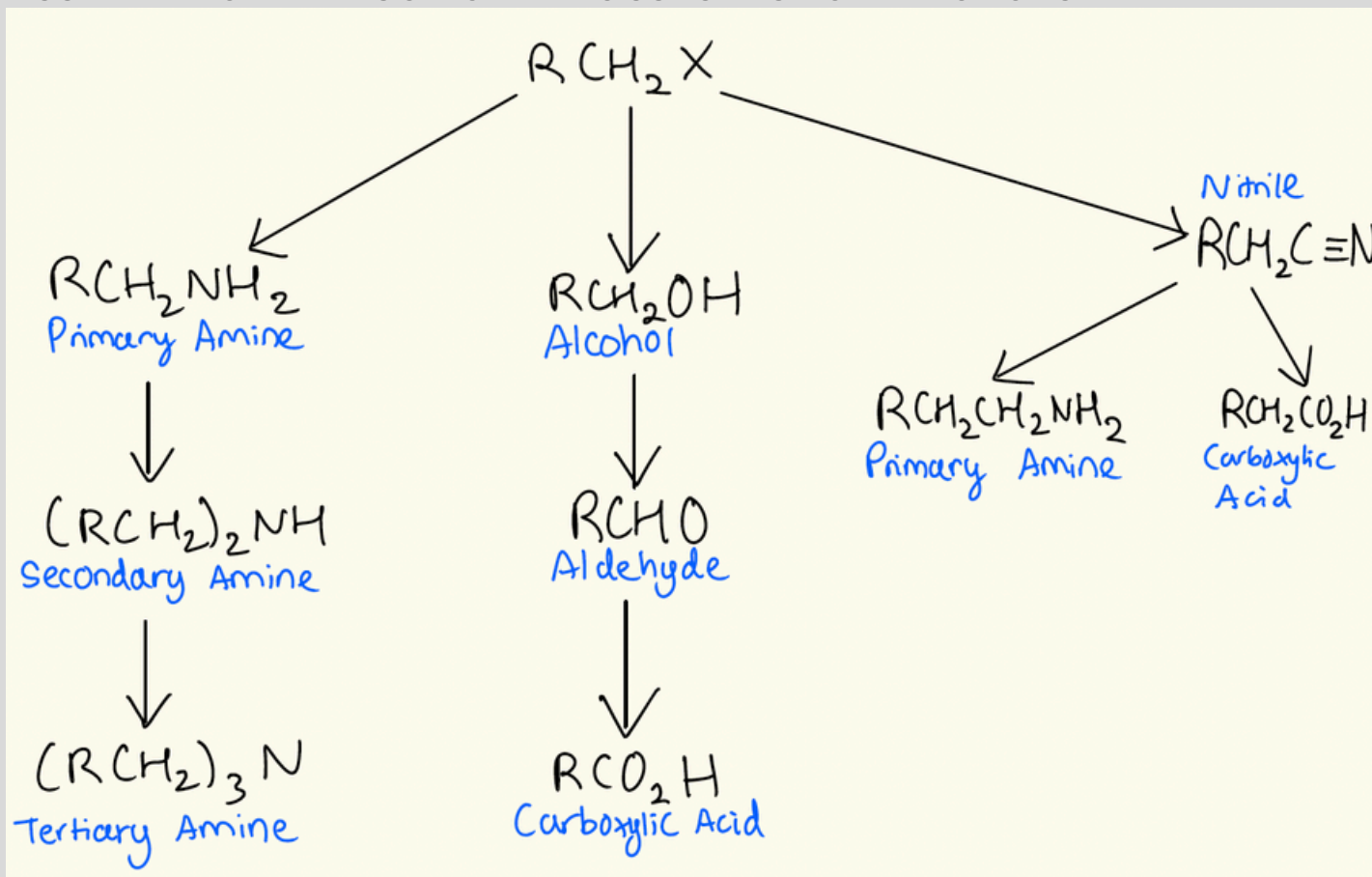
- Nucleophile: Ammonia (NH_3)
- Conditions: Excess concentrated ammonia in ethanol, carried out under pressure.
- Overall reaction:
- $\text{R-X} + 2\text{NH}_3 \rightarrow \text{R-NH}_2 + \text{NH}_4^+\text{X}^-$
- (An amine is formed)
- Mechanism:
 - a. Ammonia attacks the carbon atom bonded to the halogen.
 - b. A halide ion (X^-) is released.
 - c. Ammonia (NH_3) donates a proton (H^+) to form the final amine (R-NH_2).
 - d. The proton (H^+) reacts with a second ammonia molecule to form an ammonium ion (NH_4^+).

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HALOGENOALKANES



A SUMMARY OF THE NUCLEOPHILIC SUBSTITUTION REACTIONS



EXAMPLES OF NUCLEOPHILIC SUBSTITUTION REACTIONS- PART 1

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 - $C-I$ (weakest bond, most reactive)
 - $C-Br$
 - $C-Cl$
 - $C-F$ (strongest bond, least reactive)

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HALOGENOALKANES



INTRO TO ELIMINATION REACTIONS IN HALOGENOALKANES

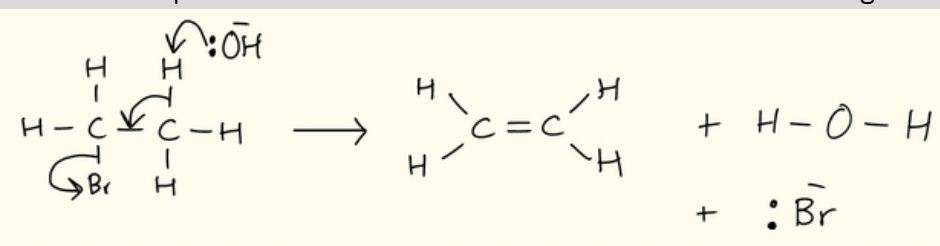
Mechanism of Elimination in Halogenoalkanes:

In an elimination reaction, hydrogen bromide (HBr) is removed from a halogenoalkane, resulting in the formation of an alkene. The following steps explain how the process works, focusing on curly arrows to show the movement of electron pairs.

Step-by-step Mechanism of Elimination:

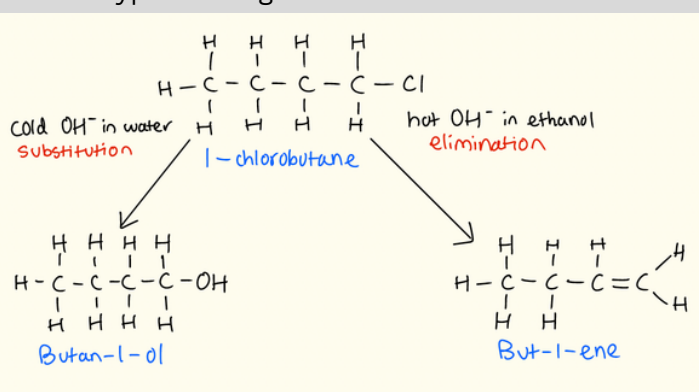
- Reaction: Bromoethane reacts with hydroxide ions, leading to the formation of ethene, water, and a bromide ion.
- Equation: $\text{CH}_3\text{CH}_2\text{Br} + \text{OH}^- \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} + \text{Br}^-$
- Curly Arrows:
 - The OH^- ion uses its lone pair of electrons to form a bond with a hydrogen atom on a carbon atom next to the C-Br bond. These hydrogen atoms have a very slight positive charge ($\text{H}^\delta+$).
 - The C-H bond breaks, and its electrons are used to form a carbon-carbon double bond ($\text{C}=\text{C}$).
 - The C-Br bond breaks, and the bromine atom takes the electrons from the bond, leaving as a bromide ion (Br^-).

This reaction produces an alkene and is a useful method for creating molecules with carbon-carbon double bonds.



Substitution or Elimination?

The hydroxide ion (OH^-) can act as either a nucleophile or a base, leading to competition between nucleophilic substitution and elimination. In many cases, a mixture of an alcohol and an alkene is produced, depending on the reaction conditions and the type of halogenoalkane.



Example: 1-Chlorobutane Reaction

- Substitution: In cold aqueous hydroxide (OH^- in water), butan-1-ol is produced:
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{Cl}^-$
- Elimination: In hot ethanolic hydroxide (OH^- in ethanol), but-1-ene is produced:
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{OH}^- \rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{H}_2\text{O} + \text{Cl}^-$

Factors Determining Substitution vs Elimination:

1. Reaction Conditions:

- Aqueous OH^- at room temperature: Favours substitution (produces an alcohol).
- Ethanolic OH^- at high temperature: Favours elimination (produces an alkene).

2. Type of Halogenoalkane:

- Primary halogenoalkanes: Tend to undergo substitution.
- Tertiary halogenoalkanes: Tend to undergo elimination.
- Secondary halogenoalkanes: Can undergo both substitution and elimination.

03-CHEM-3

HALOGENOALKANES



EXAMPLES OF NUCLEOPHILIC SUBSTITUTION REACTIONS- PART 1

Reaction Mechanism and Curly Arrows:

Curly arrows are used to represent the movement of electron pairs during the reaction:

- **Curly Arrow 1:** The lone pair of electrons on the nucleophile (Nu^-) is attracted to the electron-deficient carbon (C^+) attached to the halogen (X). This is shown by an arrow starting from the lone pair on Nu^- and pointing towards the C^+ atom.
- **Curly Arrow 2:** The electron pair in the C-X bond moves to the halogen atom (X), resulting in the halogen leaving as a halide ion (X^-). This is the leaving group.

The curly arrows illustrate the stepwise process:

1. Nucleophile attack: The nucleophile donates its lone pair of electrons to the partially positive carbon atom (C^+).
2. Halide departure: The halogen takes the electron pair from the C-X bond, leaving as X^- .

Effect of Halogen on Reaction Rate:

The rate of nucleophilic substitution depends on the strength of the C-X bond:

- Fluoro-compounds are unreactive due to the strength of the C-F bond.
- As you move down the halogen group (Cl, Br, I), the C-X bond strength decreases, making the reaction easier. Therefore, the reactivity increases as bond strength decreases:
 - C-I (weakest bond, most reactive)
 - C-Br
 - C-Cl
 - C-F (strongest bond, least reactive)

ISOMERIC PRODUCTS IN ELIMINATION REACTIONS

In certain cases of elimination reactions, multiple isomeric products can be formed. For example, when 2-chlorobutane undergoes elimination, it can produce various alkenes:

Reaction Example:

- Starting Material: 2-chlorobutane ($\text{C}_4\text{H}_9\text{Cl}$)
- Products:
 - Z-but-2-ene (cis-isomer): $\text{CH}_3\text{-CH=CH-CH}_3$
 - E-but-2-ene (trans-isomer): $\text{CH}_3\text{-CH=CH-CH}_3$
 - But-1-ene: $\text{CH}_2\text{=CH-CH}_2\text{-CH}_3$

These different products arise due to the positional and geometric isomerism that can occur during the elimination process.

Halogenoalkanes and the Environment

Chlorofluorocarbons (CFCs)

- **Definition:** CFCs are halogenoalkanes containing chlorine and fluorine atoms, but no hydrogen. An example is trichlorofluoromethane (CCl_3F).
- **Properties:**
 - Very unreactive under normal conditions.
 - Short-chain CFCs are gases used as aerosol propellants, refrigerants, and blowing agents for foams (like expanded polystyrene).
 - Longer-chain CFCs are utilized as dry cleaning and degreasing solvents.

Environmental Impact:

- **Ozone Depletion:** CFC gases eventually reach the atmosphere, where they decompose and release chlorine atoms. These chlorine atoms can decompose ozone (O_3) in the stratosphere, contributing to the depletion of the ozone layer.
- **Scientific Research:** Research in both the atmosphere and laboratories demonstrated how ozone is broken down, leading to international agreements to phase out CFCs.

03-CHEM-3

HALOGENOALKANES



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 - But-1-ene: $CH_2=CH-CH_2-CH_3$

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ALTERNATIVES TO CFCs

Alternatives to CFCs

- **Hydrochlorofluorocarbons (HCFCs):**
 - Contain hydrogen, carbon, fluorine, and chlorine (e.g., $CHFCl_2$).
 - Decompose more easily than CFCs due to their C-H bonds, releasing chlorine atoms lower in the atmosphere, where they are less harmful to the ozone layer.
- **Hydrofluorocarbons (HFCs):**
 - Second-generation replacements that contain no chlorine (e.g., CHF_3).
 - Do not harm the ozone layer but may still pose other environmental challenges.
- **Future Developments:** Chemists are exploring third-generation compounds and considering the revival of older refrigerants like ammonia, which were used prior to CFCs.

03-CHEM-3

HALOGENOALKANES



ALTERNATIVES TO CFCs

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03-CHEM-4

ALKENES



ALKENES- AN INTRO

- Definition:** Alkenes are unsaturated hydrocarbons composed of carbon and hydrogen, characterized by one or more carbon-carbon double bonds (C=C). This double bond results in fewer hydrogen atoms compared to alkanes, which are saturated.
- Reactivity:** Alkenes are more reactive than alkanes due to the high electron density at the double bond, which makes them susceptible to chemical reactions.

General Formula

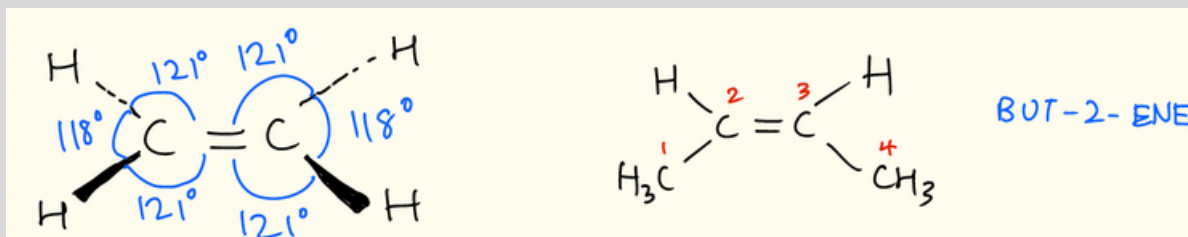
- The general formula for the homologous series of alkenes with one double bond is:
 - C_nH_{2n}

Naming Alkenes

- The simplest alkene is ethene (C₂H₄), represented as:
 - C₂H₄: H₂C=CH₂
- The next alkene is propene (C₃H₆):
 - C₃H₆: H₃C-CH=CH₂

Structure of Alkenes

- Planar Structure: Alkenes, such as ethene, are planar molecules with bond angles of approximately 120°.
 - Ethene Structure:



- Restricted Rotation:** Unlike alkanes, alkenes cannot rotate around the double bond. This is due to the presence of pi (π) orbitals formed from overlapping p-orbitals on each carbon atom.

Why a Double Bond Cannot Rotate

- Orbital Overlap:** Each carbon in the double bond has one p-orbital containing a single electron. When these p-orbitals overlap, they form a π-orbital, which creates an electron cloud above and below the bond.
- Restricted Rotation:** The presence of this π-orbital means that rotation around the double bond is restricted, maintaining the geometry of the molecule.

ISOMERS OF ALKENES- INTRO AND POSITION ISOMERS

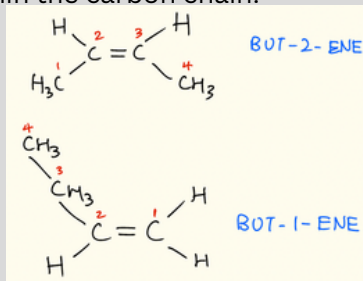
Alkenes with more than three carbon atoms can form different types of isomers. They are named according to the IUPAC system, with the suffix -ene indicating a double bond. The two main types of isomers for alkenes are:

1. Position Isomers
2. Geometrical Isomers

1. Position Isomers

- Definition:** Position isomers are alkenes that have the same molecular formula but differ in the position of the double bond within the carbon chain.

- Example:**



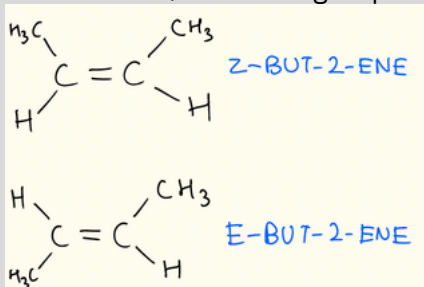
Note: As the carbon chain length increases, the number of possible position isomers also increases.



ISOMERS OF ALKENES- GEOMETRICAL ISOMERISM

2. Geometrical Isomers

- Definition: Geometrical isomers are a type of stereoisomerism where compounds have the same structural formula but differ in the spatial arrangement of atoms around the double bond. This type occurs only around C=C double bonds.
- Example: But-2-ene can exist as two geometrical isomers:
 - Z-but-2-ene (both -CH₃ groups on the same side):

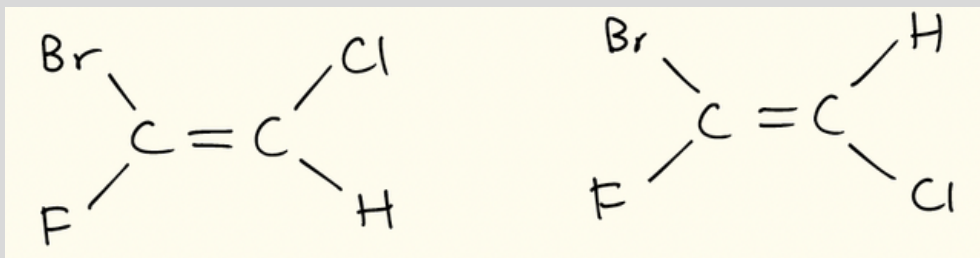


E-Z ISOMERISM- THE CAHN-INGOLD-PRELOG (CIP) NOTATION

- Importance: As the number of known organic compounds increases, a standardized naming system is essential for clarity and communication in chemistry.
- Historical Context:
 - E-Z notation replaced the older cis-trans terminology. For example:
 - Z-but-2-ene was previously known as cis-but-2-ene.
 - E-but-2-ene was previously known as trans-but-2-ene.
- Reason for Change: The cis-trans notation is limited when there are more than two different substituents around a double bond. The E-Z notation provides a more comprehensive system for naming isomers.
- Understanding E-Z Notation:
 - The E-Z notation is based on atomic numbers of the groups attached to the double bond carbons.
 - If the two atoms of higher atomic number are on the same side of the double bond, the isomer is designated Z (from the German word "zusammen," meaning together).
 - If they are on opposite sides, it is designated E (from the German word "entgegen," meaning opposite).

Example of E-Z Isomerism

- Consider the following isomers:



PHYSICAL PROPERTIES OF ALKENES AND HOW THEY REACT

Physical Properties of Alkenes

- **Boiling and Melting Points:**
 - The presence of a double bond in alkenes does not significantly affect their physical properties such as boiling and melting points.
 - The boiling and melting points increase with the number of carbon atoms present in the alkene.
- **Intermolecular Forces:**
 - The only intermolecular forces acting between alkene molecules are van der Waals forces.
 - As a result, the physical properties of alkenes are very similar to those of alkanes.
- **Solubility:**
 - Alkenes are not soluble in water due to their non-polar nature.



PHYSICAL PROPERTIES OF ALKENES AND HOW THEY REACT

Reactivity of Alkenes

- **Comparison with Alkanes:**
 - While the bond enthalpy of a C-C single bond is 347 kJ mol^{-1} and that of a C=C double bond is 612 kJ mol^{-1} , suggesting that alkenes might be less reactive, the opposite is true: alkenes are more reactive than alkanes.
- **Reason for Increased Reactivity:**
 - The C=C double bond creates an electron-rich area in the molecule, which can be easily attacked by positively charged reagents, known as electrophiles (electron-loving).
- **Electrophiles:**
 - Electrophiles are electron pair acceptors. A common example of a strong electrophile is the H^+ ion.
- **Addition Reactions:**
 - Due to their unsaturated nature, alkenes readily undergo addition reactions.
 - The majority of reactions involving alkenes are classified as electrophilic addition reactions, where electrophiles react with the double bond.

REACTIVITY OF ALKENES

Combustion of Alkenes

- **General Reaction:**
 - Alkenes can combust in the presence of air, producing carbon dioxide and water. For example, the combustion of ethene can be represented as:
- $\text{C}_2\text{H}_4 (\text{g}) + 3 \text{O}_2 (\text{g}) \rightarrow 2 \text{CO}_2 (\text{g}) + 2 \text{H}_2\text{O} (\text{l})$
- **Fuel Usage:**
 - Despite their ability to combust, alkenes are not used as fuels due to their high reactivity, which makes them valuable for other chemical reactions rather than simply burning for energy.

Electrophilic Addition Reactions

- **Nature of Reactions:**
 - Alkenes predominantly undergo electrophilic addition reactions due to the presence of a carbon-carbon double bond (C=C) that contains four electrons. This double bond creates a region of high electron density, attracting electrophiles.
- **Mechanism Overview:**
 - a. **Electrophile Attraction:** The electrophile approaches and is attracted to the double bond.
 - b. **Electron Pair Donation:** The electrophile (which can be a positively charged ion or have a positively charged area) accepts a pair of electrons from the double bond.
 - c. **Formation of Carbocation:** This leads to the formation of a positively charged ion known as a carbocation.
 - d. **Bond Formation:** A negatively charged ion then forms a bond with the carbocation, completing the addition reaction.

Example: Reaction with Hydrogen Halides

- **Reaction with HBr:**
 - Hydrogen halides, such as HCl, HBr, and HI, add across the double bond to form halogenoalkanes. For instance, the reaction of ethene with hydrogen bromide can be represented as:
- $\text{C}_2\text{H}_4 + \text{HBr} \rightarrow \text{C}_2\text{H}_5\text{Br}$
- **Polarity of HBr:**
 - The hydrogen bromide molecule is polar due to the difference in electronegativity between hydrogen and bromine, resulting in:
 $\text{H}\delta^+ - \text{Br}\delta^-$
- **Mechanism Specifics:**
 - The electrophile is the H^+ ion from HBr.
 - The H^+ ion is attracted to the C=C bond because of its high electron density.
 - One pair of electrons from the double bond forms a bond with H^+ , resulting in the formation of a carbocation (positively charged ion).
 - At the same time, the bond between H and Br breaks heterolytically, with both electrons moving towards the bromine atom due to its higher electronegativity, forming a Br^- ion.
 - The Br^- ion then attaches to the positively charged carbon of the carbocation, completing the reaction:
- $\text{C}_2\text{H}_5^+ + \text{Br}^- \rightarrow \text{C}_2\text{H}_5\text{Br}$

03-CHEM-4

ALKENES



PHYSICAL PROPERTIES OF ALKENES AND HOW THEY REACT

Reactivity of Alkenes

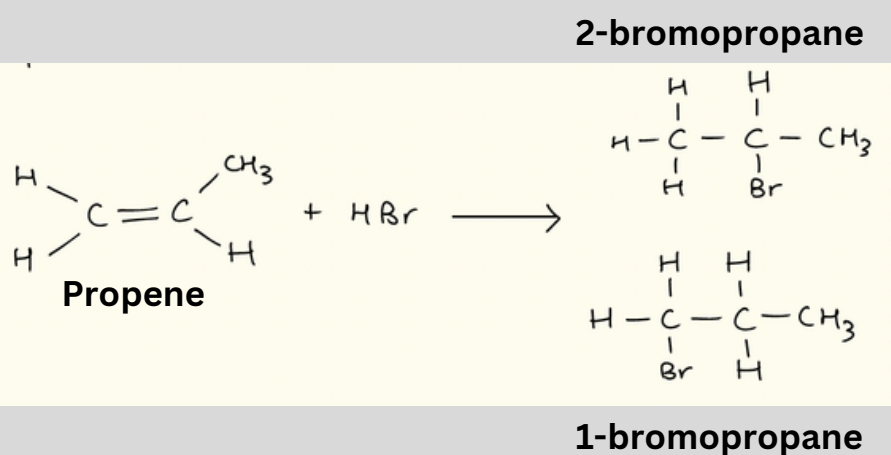
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ASSYMETRICAL ALKENES

- When hydrogen bromide (HBr) adds to ethene, there is only one possible product, bromoethane. However, for asymmetrical alkenes like propene, two possible products can form because the double bond is not exactly in the middle of the chain. This means the bromine from the HBr could attach to either of the two carbon atoms in the double bond.

Example: Addition to Propene

- The reaction of propene (C_3H_6) with HBr could theoretically yield two different products:



Carbocation Stability: The Positive Inductive Effect

- To explain this outcome, we need to understand the positive inductive effect. Alkyl groups (such as $-\text{CH}_3$ or $-\text{C}_2\text{H}_5$) have a tendency to release electrons towards the positively charged carbon atom in the intermediate carbocation. This electron-releasing effect helps to stabilise the carbocation.
- The more alkyl groups attached to the positively charged carbon, the more stable the carbocation is:
 - **Tertiary carbocation (3 alkyl groups) is the most stable.**
 - **Secondary carbocation (2 alkyl groups) is less stable.**
 - **Primary carbocation (1 alkyl group) is the least stable.**
- In the case of propene, the secondary carbocation formed in the production of 2-bromopropane is more stable than the primary carbocation that would form for 1-bromopropane.

Thus, the major product is 2-bromopropane due to the greater stability of the intermediate secondary carbocation.

REACTIONS OF ALKENES WITH HALOGENS

Alkenes react quickly with halogens like chlorine, bromine, or iodine, typically in an organic solvent, to form dihalogenoalkanes. The halogen atoms add across the double bond in a reaction that occurs via electrophilic addition.

03-CHEM-4

ALKENES



MECHANISM OF ELECTROPHILIC ADDITION- ALKENES REACTING WITH HALOGENS

1. Instantaneous Dipole Formation:

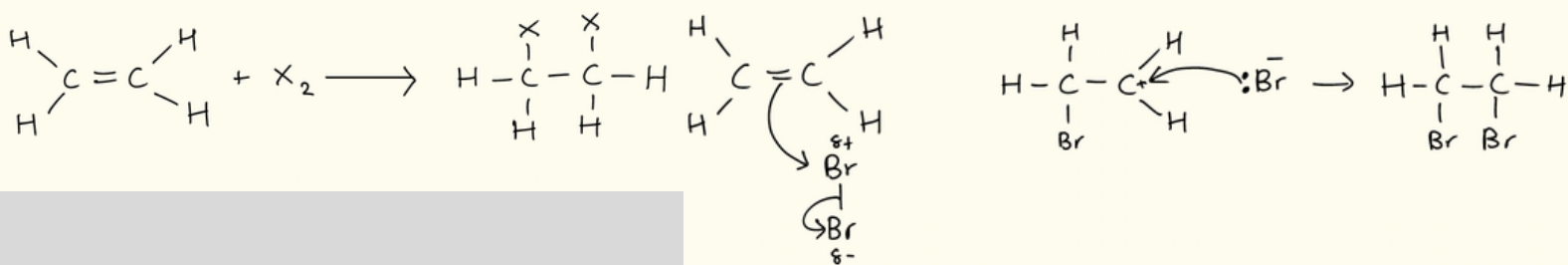
- Halogen molecules (e.g., Br₂) may momentarily have an instantaneous dipole.
- Example: Br^{δ+}—Br^{δ-} (This dipole can reverse quickly).
- The ^{δ+} end of the dipole is attracted to the electron-rich double bond of the alkene, making the bromine molecule an electrophile.

2. Interaction with the Double Bond:

- The electrons from the double bond are attracted to the Br^{δ+} end of the bromine molecule, causing the bromine molecule's dipole to strengthen.
- Two electrons from the double bond form a bond with the Br^{δ+}, leaving behind a carbocation (positively charged carbon) and a Br⁻ ion.

3. Carbocation Formation:

- A carbocation is created at the carbon atom not bonded to bromine, with a positive charge.
- The Br⁻ ion then quickly reacts with the carbocation, forming a dihalogenoalkane.



TEST FOR CARBON-CARBON DOUBLE BOND

This electrophilic addition reaction can be used to test for the presence of a double bond. When a few drops of bromine solution (reddish-brown) are added to an alkene, the solution is decolourised as the bromine adds across the double bond, forming a colourless product.

This reaction is a qualitative test to distinguish alkenes from alkanes, which do not react with bromine in the same way.

REACTIONS OF ALKENES WITH CONCENTRATED SULFURIC ACID

Concentrated sulfuric acid adds across the double bond of alkenes, forming alkyl hydrogensulfates. This reaction is exothermic and occurs at room temperature.

Mechanism of Reaction

1. Electrophile Formation:

- The electrophile is the partially positively charged hydrogen in the sulfuric acid molecule. This can be represented as H^{δ+}—O^{δ-}—SO₃H.

2. Carbocation Formation:

- The π electrons from the double bond attack the H^{δ+} from sulfuric acid, forming a carbocation.
- Example for ethene:
- (Ethene) (Ethyl hydrogensulfate)

3. Reaction with Hydrogensulfate:

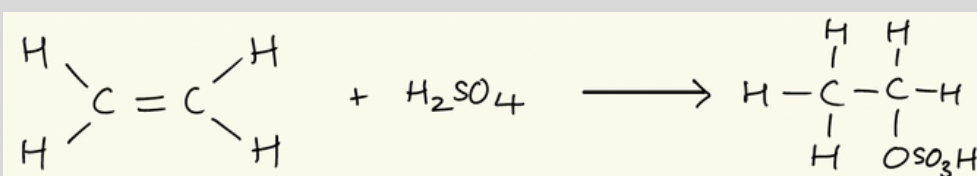
- The carbocation rapidly reacts with the hydrogensulfate ion (HSO₄⁻) to form an alkyl hydrogensulfate.

03-CHEM-4

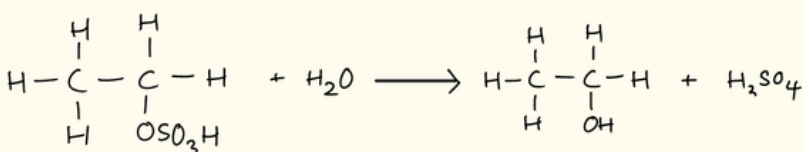
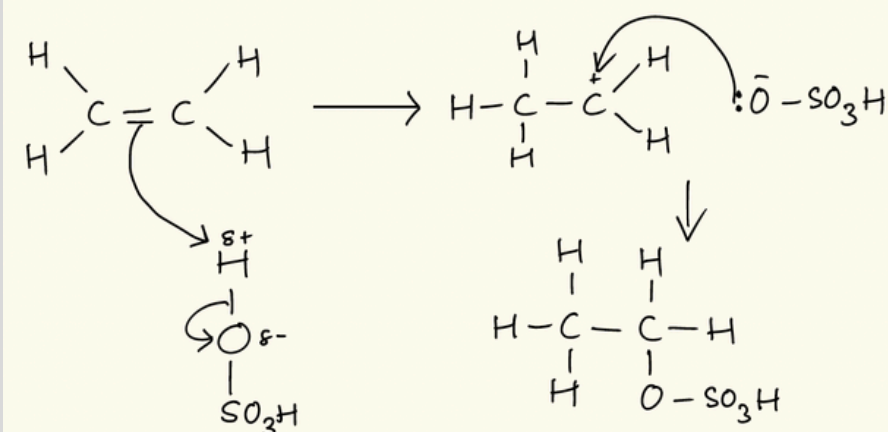
ALKENES



MECHANISM OF ACTION OF REACTION BETWEEN ETHENE AND SULFURIC ACID



ETHYL HYDROGENSULFATE



ETHYL HYDROGENSULFATE

Formation of Alcohols from Alkenes

When water is added to the alkyl hydrogensulfate, an alcohol is produced, and sulfuric acid is regenerated.

- Example for ethene:
- Ethyl hydrogensulfate + water → ethanol + sulfuric acid
- (Ethyl hydrogensulfate) (Ethanol)
- The overall reaction adds water (H-OH) across the double bond, and sulfuric acid acts as a catalyst.

Reaction with Asymmetrical Alkenes

In the case of asymmetrical alkenes like propene, the same carbocation stability principles apply as seen in reactions with hydrogen halides. The more stable carbocation leads to the major product.

Industrial Production of Alcohols from Alkenes

Water can also be added across the double bond in alkenes using steam under appropriate temperature and pressure, with an acid catalyst like phosphoric acid (H3PO4). This reaction is used industrially to produce alcohols.

- Example for ethene:
- $\text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\text{g})$
- (Ethene) (Water) (Ethanol)

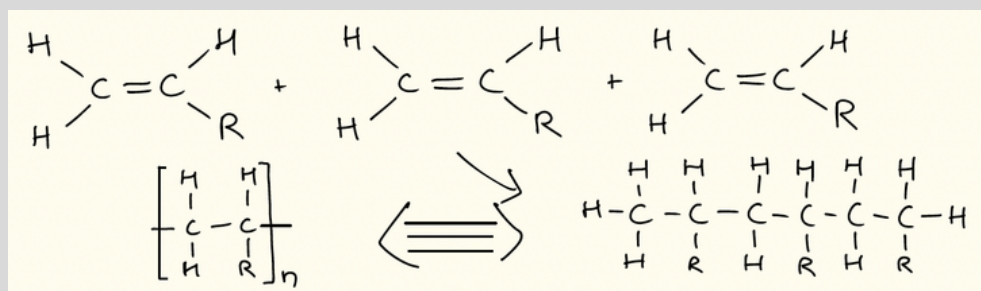
03-CHEM-4

ALKENES



INTRO TO ADDITION POLYMERS AND POLYMERISATION

- Polymers are large molecules made by joining smaller molecules called monomers.
- Addition polymers form from alkenes (molecules with a carbon-carbon double bond).
- The double bond in the alkene opens during polymerisation, allowing monomers to bond together to form a long chain.
- Monomers in addition polymers have the general structure:



- R can be a group like hydrogen or an alkyl group.
- Examples of addition polymers include:
 - Poly(ethene): Used in carrier bags, made from ethene.
 - Poly(propene): Found in yoghurt containers and car bumpers, made from propene.
 - Poly(chloroethene) (PVC): Used in drainpipes and aprons, made from chloroethene.

Key Process:

- Double bond in the monomer breaks.
- Monomers add together to form a polymer chain without losing any atoms.

This process is called addition polymerisation.

Monomer Structure	Polymer Name	Common Name	Applications
$\text{H}_2\text{C}=\text{CH}_2$	Poly(ethene)	Polythene	Carrier bags, washing-up bowls
$\text{CH}_3\text{CH}=\text{CH}_2$	Poly(propene)	Polypropylene	Yoghurt containers, car bumpers
$\text{ClCH}=\text{CH}_2$	Poly(chloroethene)	PVC (Polyvinyl chloride)	Aprons, 'vinyl' records, drainpipes
$\text{CNCH}=\text{CH}_2$	Poly(propenenitrile)	Acrylic (Acrilan, Courtelle)	Clothing fabrics
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	Poly(phenylethene)	Polystyrene	Packing materials, electrical insulation

Identifying the Addition Polymer from the Monomer

- Addition polymers are formed from monomers with carbon-carbon double bonds.
- During polymerisation, the double bond opens and forms a single bond, creating a repeating unit.

Steps to Identify the Monomer:

1. Look for a backbone of carbon atoms in the polymer.
2. The monomer must contain at least two carbon atoms to form a carbon-carbon double bond.
3. If the polymer has substituents (side groups attached to the carbon chain), the monomer must also have these substituents.

03-CHEM-4

ALKENES



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- Example for ethene:
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3. Reaction with Hydrogensulfate:

- The carbocation rapidly reacts with the hydrogensulfate ion (HSO_4^-) to form an alkyl hydrogensulfate.

BIODEGRABILITY

- Polyalkenes have a saturated alkane backbone with non-polar C-C and C-H bonds.
- These bonds are very strong and make polyalkenes unreactive.
- As a result, they are not biodegradable and cannot be broken down by biological agents like enzymes.
- This is a growing environmental problem because it makes plastic waste disposal difficult.

High-Density vs Low-Density Poly(ethene)

- **Low-density poly(ethene) is made at high temperature and pressure using a free-radical mechanism.**
 - Produces branched chains that do not pack tightly.
 - Results in a flexible, stretchable, and low-density material.
 - Used in plastic bags, sheeting, and insulation for cables.
- **High-density poly(ethene) is made at lower temperatures and pressures using a Ziegler-Natta catalyst.**
 - Has fewer branches, allowing chains to pack tightly.
 - Results in a higher density and higher melting temperature material.
 - Used in milk crates, buckets, and bottles.

Solutions to Plastic Pollution

- Reduce and recycle to manage plastic waste.

1. Mechanical Recycling:

- Plastics are sorted, washed, and ground into pellets.
- Pellets are melted and remoulded into new products (e.g. PET bottles recycled into fleece clothing).

2. Feedstock Recycling:

- Plastics are heated to break polymer bonds and produce monomers for new plastics.
- Poly(propene), a thermoplastic, can be recycled but with limited reuses because the chains degrade after repeated heating.

PLASTICISERS

- Additives are used to modify the properties of polymers to suit different applications.
- Plasticisers are small molecules that:
 - Insert themselves between polymer chains.
 - Allow the chains to slide more easily past one another.
 - Make the polymer more flexible.
- Example: Poly(chloroethene), also known as polyvinyl chloride (PVC):
 - Without plasticisers, PVC is rigid, suitable for products like drainpipes.
 - With plasticisers, PVC becomes flexible, making it ideal for products like plastic aprons

03-CHEM-4

ALKENES



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03-CHEM-5

ALCOHOLS



INTRO TO ALCOHOLS

Overview of Ethanol

- Ethanol is one of the oldest social drugs, derived from the fermentation of sugars in fruits.
- It is the active ingredient in alcoholic drinks and acts as a nervous system depressant, affecting nerve impulse transmission.

Effects of Ethanol

- Moderate consumption may promote:
 - A feeling of well-being.
 - Reduced inhibitions.
- Excessive consumption can lead to:
 - Loss of balance.
 - Poor hand-eye coordination.
 - Impaired vision.
 - Inability to judge speed.
 - Potentially fatal in large amounts.
 - Long-term use can result in addiction (alcoholism).

Absorption and Elimination

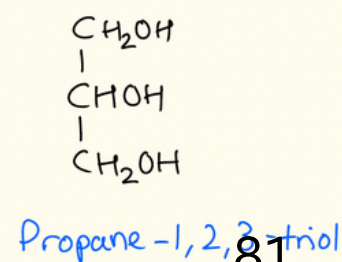
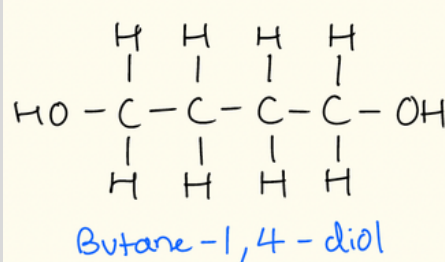
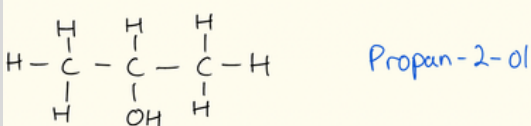
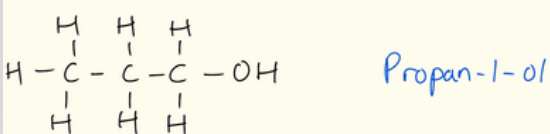
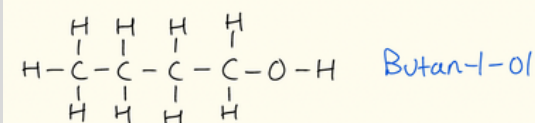
- Ethanol is absorbed through the walls of the:
 - Stomach
 - Small intestine into the bloodstream.
- It is eliminated through:
 - Urine.
 - Breath.
- The liver metabolises the remainder, with an average person eliminating about 10 cm³ of ethanol per hour. This equates to:
 - Half a pint of beer
 - Small glass of wine (125 ml)
 - Shot of spirits (25 ml).

General Formula of Alcohols

- Alcohols have the functional group -OH (hydroxyl group) attached to a hydrocarbon chain.
- The general formula for alcohols is C_nH_{2n+1}OH, often simplified to ROH.

Naming Alcohols

- The functional group -OH is indicated by the suffix -ol.
- If other functional groups are present, the prefix hydroxy- is used.



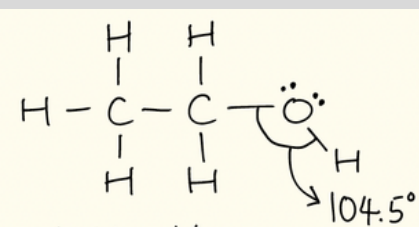
03-CHEM-5

ALCOHOLS



SHAPE OF ALCOHOLS

- **Molecular Geometry:** In alcohols, the oxygen atom has:
 - Two bonding pairs of electrons (from C-O bonds).
 - Two lone pairs of electrons.
- **Bond Angle:**
 - The C-O-H bond angle is approximately 105° .
 - This angle is reduced from the ideal tetrahedral angle of 109.5° due to the presence of lone pairs.
- **Effect of Lone Pairs:**
 - The two lone pairs on the oxygen atom repel each other more strongly than the bonding pairs.
 - This greater repulsion causes the bonding pairs to be pushed closer together, resulting in a smaller bond angle.



SHAPE OF ALCOHOLS

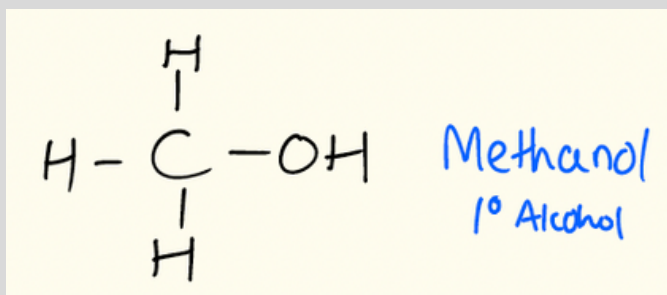
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CLASSIFICATION OF ALCOHOLS

Alcohols can be classified as primary (1°), secondary (2°), or tertiary (3°) based on the number of other carbon groups (R) bonded to the carbon atom that has the -OH (hydroxyl) group.

1. Primary Alcohols (1°)

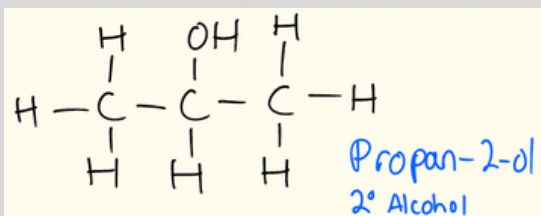
- **Definition:** The carbon with the -OH group is attached to one R group and has two hydrogen atoms.
- **Example:**
 - **Methanol:** The carbon with the -OH group has no R groups (only hydrogen atoms), still classified as primary.



- **Location:** The -OH group is at the end of the carbon chain.

2. Secondary Alcohols (2°)

- **Definition:** The carbon with the -OH group is attached to two R groups and has one hydrogen atom.
- **Example:**
 - **Propan-2-ol:**



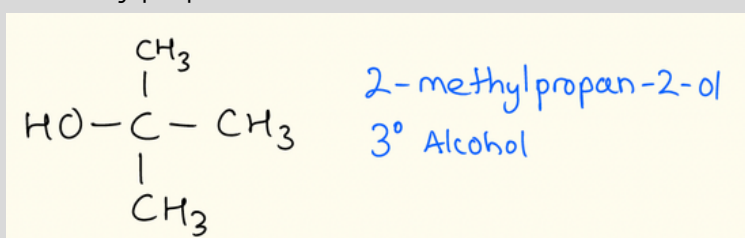
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ALCOHOLS



TERTIARY ALCOHOLS

- Definition: The carbon with the -OH group is attached to three R groups and has no hydrogen atoms.
- Example:
 - 2-Methylpropan-2-ol:



- Location: The -OH group is at a branch in the carbon chain.

PHYSICAL PROPERTIES OF ALCOHOLS

- **Hydrogen Bonding:**
 - The presence of the -OH group allows alcohol molecules to form hydrogen bonds with each other.
 - This results in higher melting and boiling points compared to alkanes of similar relative molecular mass.
- **Solubility in Water:**
 - The -OH group can hydrogen bond with water molecules, enhancing solubility.
- **Short-chain Alcohols:**
 - Generally soluble in water due to the predominance of hydrogen bonding between the -OH group and water.
- **Long-chain Alcohols:**
 - As the hydrocarbon chain length increases, the non-polar hydrocarbon part becomes more dominant.
 - This leads to decreased solubility in water, making longer-chain alcohols insoluble.

INDUSTRIAL CHEMISTRY OF ALCOHOLS

Importance of Alcohols:

- Alcohols are crucial in industrial chemistry due to their role as intermediates.
- They are easily produced and converted into other compounds.

Key Alcohols

1. Methanol:

- Produced from methane (natural gas).
- Used as a starting material for other organic chemicals.

2. Ethanol (C₂H₅OH):

- The most important alcohol used as an intermediate in organic chemical production.
- Commonly found as a solvent in cosmetics (e.g., aftershave, perfumes) and in the manufacture of drugs, detergents, inks, and coatings.
- Produced through:
 - Hydration of ethene (from cracking crude oil) with steam and a phosphoric acid catalyst.
 - Fermentation of sugars from crops like sugar cane and sugar beet.

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ALCOHOLS



PRODUCTION OF ETHANOL

1. Fermentation:

- **Process:**
 - Carbohydrates from plants are broken down into sugars, then converted into ethanol via anaerobic respiration using yeast enzymes.
- **Chemical Equation:**
 - $C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$
- **Conditions:**
 - Temperature is crucial; an optimal temperature of around 35°C is used.
 - Oxygen is excluded to prevent ethanol oxidation to ethanoic acid (vinegar).
 - Fermentation halts when ethanol concentration reaches about 15%; ethanol is then distilled out (boiling point 78°C).

2. From Crude Oil:

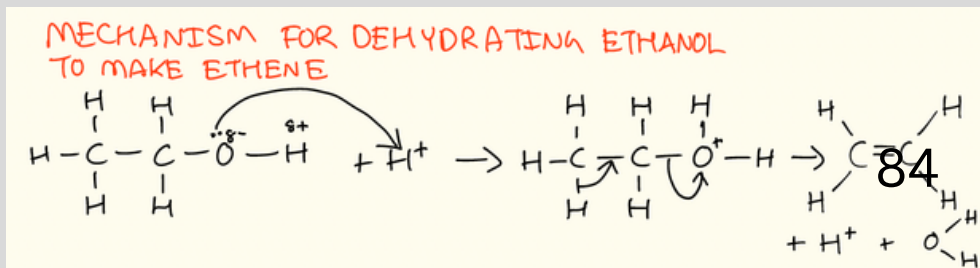
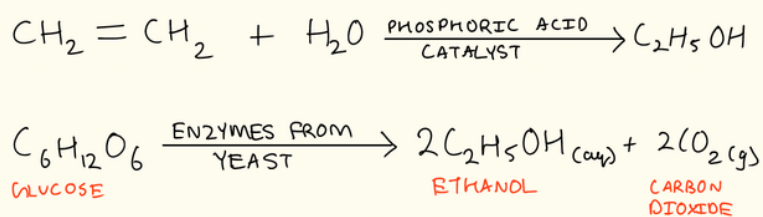
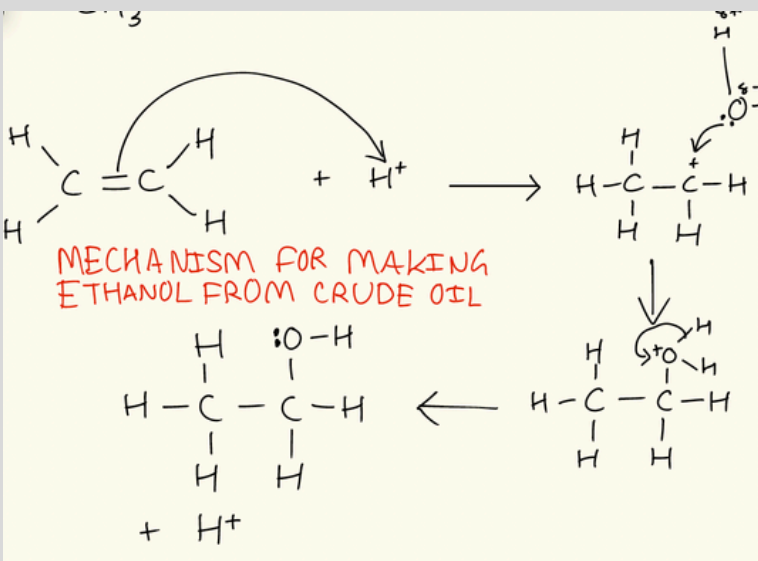
- Ethene is produced by cracking crude oil.
- Ethene can be converted back to ethanol through hydration.

Renewable Source of Ethene

- Ethene is vital for producing poly(ethene) and other chemicals.
- Ethene can be generated by dehydrating ethanol obtained from fermentation, providing a renewable source.

Environmental Considerations

- **Ethanol as a Fuel:**
 - Many petrol engines can operate on ethanol or ethanol-petrol mixtures (currently, UK petrol often contains 5-10% ethanol).
- **Renewability:**
 - Ethanol from fermentation is renewable due to the use of annually grown crops.
 - In contrast, ethanol derived from ethene (from crude oil) is not renewable.



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ALCOHOLS



COMBUSTION OF ALCOHOLS

Complete Combustion:

- Alcohols burn completely in the presence of sufficient oxygen, producing carbon dioxide and water.
- The equation for the complete combustion of ethanol (C_2H_5OH) is:
- $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

Incomplete Combustion:

- In limited oxygen conditions, alcohols undergo incomplete combustion, producing carbon monoxide (CO) or carbon (soot) instead of carbon dioxide.

Ethanol as Fuel

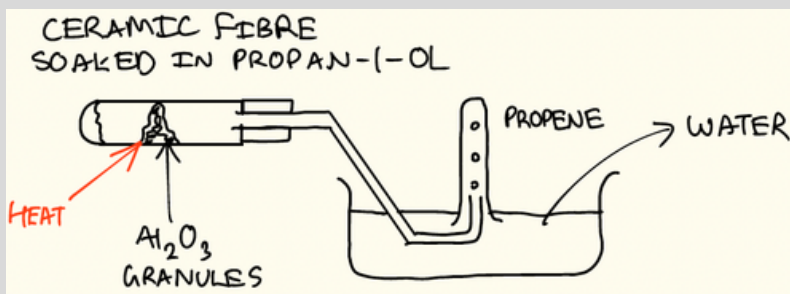
- Ethanol is commonly used as a fuel in applications such as picnic stoves that burn methylated spirits.
- Methylated Spirits: This is ethanol with a small percentage of methanol added to render it undrinkable and exempt from alcoholic beverage taxes. A purple dye is also included to indicate that it should not be consumed.

ELIMINATION REACTIONS OF ALCOHOLS

- Definition:** Elimination reactions involve the removal of a small molecule from a parent molecule. In the case of alcohols, the small molecule is always water.
- Dehydration:** The elimination of water from alcohols is specifically referred to as dehydration.
 - The water is formed from the hydroxyl (-OH) group and a hydrogen atom from an adjacent carbon atom.

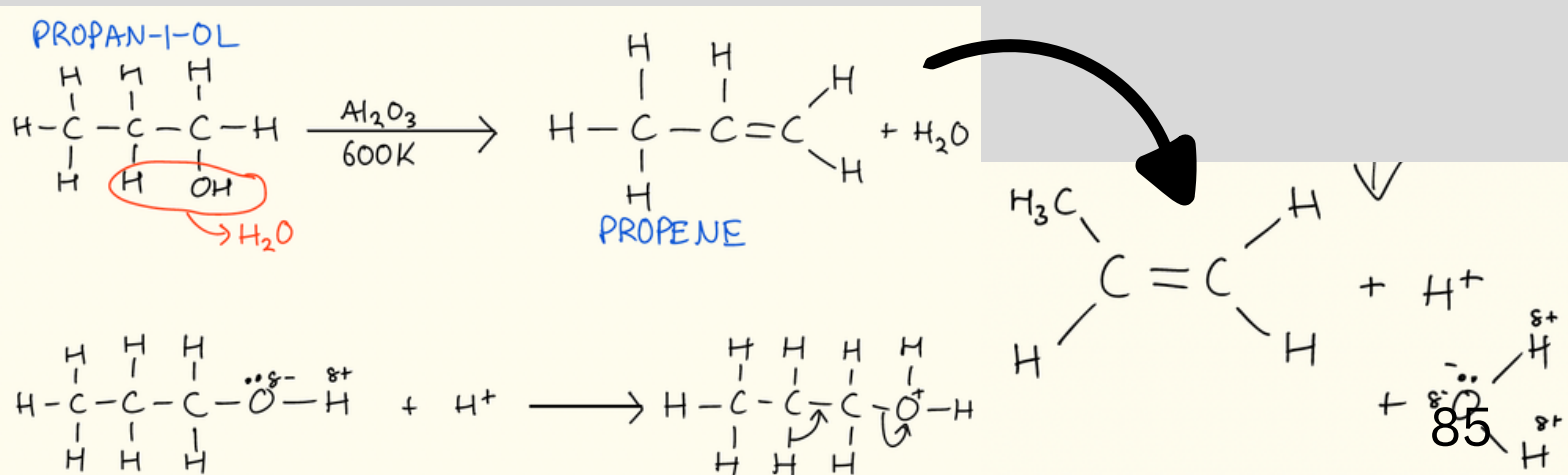
Dehydration of Alcohols

- Alcohols can be dehydrated using:
 - Excess hot concentrated sulfuric acid
 - Heated aluminium oxide (Al_2O_3)
- An alkene is produced from the dehydration process.



Example Reaction

- Propan-1-ol to Propene:**
 - When propan-1-ol undergoes dehydration, propene (C_3H_6) is formed.
- Chemical Equation:**
 - C_3H_8O (propan-1-ol) $\rightarrow$ C_3H_6 (propene) + H_2O (water)
- Alternative Dehydrating Agent:** Phosphoric(V) acid can also be used for dehydration.





OXIDATION OF ALCOHOLS

General Overview:

- Alcohols can undergo oxidation, which involves the loss of hydrogen or the addition of oxygen.
- Oxidation can occur gently and in stages, leading to different products depending on the type of alcohol.

Types of Alcohols and Their Oxidation Products

1. Primary Alcohols

- Oxidation Reaction: Primary alcohols ($RCHOH$) are oxidized to aldehydes ($RCHO$).
- Further Oxidation: Aldehydes can be further oxidized to carboxylic acids ($RCOOH$).

Example:

- Ethanol (C_2H_5OH) oxidizes to ethanal (CH_3CHO) and can further oxidize to ethanoic acid (CH_3COOH).

Chemical Equations:

- Oxidation of ethanol to ethanal:**
 - $C_2H_5OH + [O] \rightarrow CH_3CHO + H_2O$
- Further oxidation to ethanoic acid:**
 - $CH_3CHO + [O] \rightarrow CH_3COOH$

2. Secondary Alcohols

- Oxidation Reaction: Secondary alcohols (R_2CHOH) are oxidized to ketones (R_2CO).
- Note: Ketones are not oxidized further under typical conditions because breaking a C-C bond is required.

Example:

- Propan-2-ol (C_3H_8O) oxidizes to propanone (C_3H_6O).

Chemical Equation:

- $C_3H_8O + [O] \rightarrow C_3H_6O + H_2O$

3. Tertiary Alcohols

- Tertiary alcohols (R_3COH) are not easily oxidized because oxidation would require breaking a C-C bond instead of a C-H bond.
- Therefore, tertiary alcohols do not have oxidation products like aldehydes or ketones.

Characteristics of Aldehydes and Ketones

- Many aldehydes and ketones possess pleasant smells, making them valuable in the fragrance and flavor industries.

Summary

- Primary Alcohols: Oxidized to aldehydes and further to carboxylic acids.
- Secondary Alcohols: Oxidized to ketones, which do not undergo further oxidation.
- Tertiary Alcohols: Resistant to oxidation due to the structural requirements for the reaction.
- The oxidation of alcohols is an essential reaction in organic chemistry, leading to a variety of functional groups with distinct properties

OXIDATION OF ETHANOL- THE
EXPERIMENTAL DETAILS

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ALCOHOLS



OXIDATION OF ETHANOL- THE EXPERIMENTAL DETAILS

Overview: Potassium dichromate, acidified with dilute sulfuric acid, serves as the oxidizing agent to convert alcohols into aldehydes or carboxylic acids. During this process, the orange dichromate(VI) ions are reduced to green chromium(III) ions.

1. Oxidation of Ethanol (1° Alcohol) to Ethanal (Aldehyde)

Conditions:

- Use dilute sulfuric acid and less potassium dichromate(VI) than required for complete oxidation to the carboxylic acid.
- Apparatus Setup: The mixture is heated gently in a flask, with the receiver cooled in ice to minimize evaporation of the product.

Process:

- Ethanol vaporizes immediately upon formation, allowing for its distillation without further oxidation to ethanoic acid.

Chemical Equation:

- $\text{C}_2\text{H}_5\text{OH}(\text{l}) + [\text{O}] \rightarrow \text{CH}_3\text{CHO}(\text{g}) + \text{H}_2\text{O}(\text{l})$

Key Points:

- Ethanol is oxidized to ethanal.
- Unreacted ethanol remains in the flask, while ethanal distills off as it forms.

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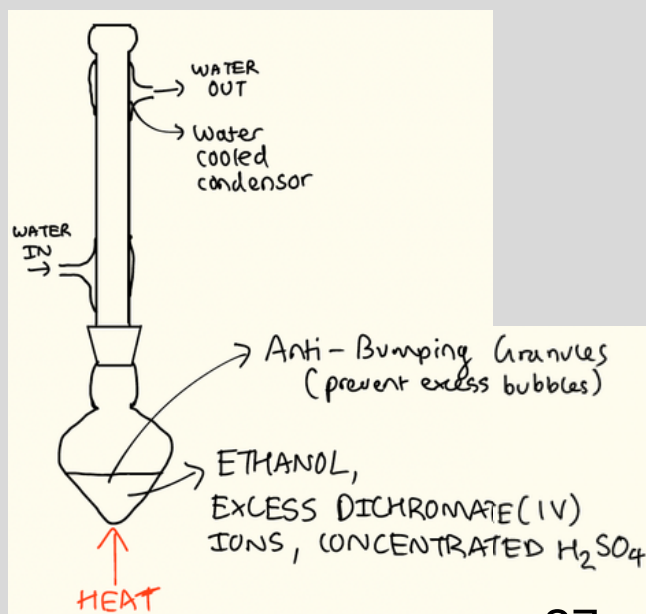
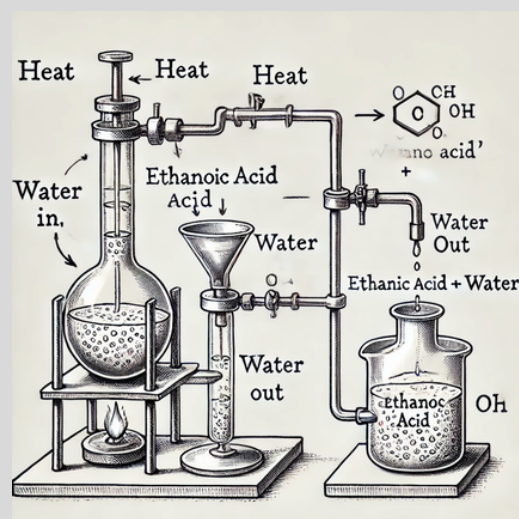
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ALCOHOLS



OXIDATION OF ETHANOL- THE EXPERIMENTAL DETAILS

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- $\text{C}_2\text{H}_5\text{OH}(\text{l}) + [\text{O}] \rightarrow \text{CH}_3\text{CHO}(\text{g}) + \text{H}_2\text{O}(\text{l})$

Key Points:

- Ethanol is oxidized to ethanal.
- Unreacted ethanol remains in the flask, while ethanal distills off as it forms.

OXIDATION OF A SECONDARY ALCOHOL TO A KETONE

Overview: Secondary alcohols are oxidized to ketones using acidified dichromate. Unlike aldehydes, ketones do not undergo further oxidation under these conditions.

Chemical Reaction:

- Secondary Alcohol to Ketone:
- $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + [\text{O}] \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}$
- (propan-2-ol to propanone)

Structure of Aldehydes and Ketones

- Carbonyl Group ($\text{C}=\text{O}$):
 - Present in both aldehydes and ketones.
- Aldehydes:
 - The carbonyl group is at the end of the hydrocarbon chain.
 - General structure: RCHO
 - Example: Ethanal (CH_3CHO)
- Ketones:
 - The carbonyl group is located within the hydrocarbon chain.
 - General structure: RCOR'
 - Example: Propanone (CH_3COCH_3)

Naming Conventions

- Aldehydes are typically named with the suffix -al.
- Ketones are named with the suffix -one.
- Examples:
 - Ethanal (2 carbons): CH_3CHO
 - Propanone (3 carbons): CH_3COCH_3



TEST FOR ALDEHYDES AND KETONES

Both aldehydes and ketones exhibit similar physical properties, but they can be differentiated using specific tests that involve gentle oxidation.

1. Oxidation Reaction:

- Aldehydes can be oxidised to carboxylic acids:
 - $\text{RCHO} + [\text{O}] \rightarrow \text{RCOOH}$
- Ketones are not oxidized under gentle conditions.

2. Tollens' Test (Silver Mirror Test):

- **Reagent:** Tollens' reagent (silver nitrate in aqueous ammonia).
- **Reaction:**
 - Aldehydes are oxidised, producing metallic silver.
 - No reaction occurs with ketones.
- **Observation:**
 - Upon warming an aldehyde with Tollens' reagent, a deposit of metallic silver forms, creating a "silver mirror" on the inside of the test tube.

3. Fehling's Test:

- **Reagent:** Fehling's solution (contains blue copper(II) complex ions).
- **Reaction:**
 - Aldehydes oxidize, causing the blue solution to change to brick red due to the formation of copper(I) oxide.
 - No reaction occurs with ketones.
- **Observation:**
 - When warming an aldehyde with blue Fehling's solution, a gradual formation of a brick red precipitate indicates a positive test.

CHEMICAL TESTS FOR FUNCTIONAL GROUPS

Functional Group	Test	Expected Result
Alkene	Shake with bromine water	Orange colour disappears (decolourization)
Haloalkane (R-X)	1. Add NaOH(aq) and warm 2. Acidify with HNO ₃ . Add AgNO ₃ (aq)	Precipitate of AgX; solubility in ammonia indicates halogen type
Alcohol (R-OH)	Add acidified K ₂ Cr ₂ O ₇	Orange colour turns green (for primary and secondary alcohols, also aldehydes)
Aldehyde (R-CHO)	Warm with Fehling's solution or Warm with Tollens' solution	Blue colour turns red precipitate (Fehling's); silver mirror forms (Tollens')
Carboxylic Acid (R-COOH)	Add NaHCO ₃ (aq)	CO ₂ gas given off (bubbles/fizzing)

Notes:

- The presence of halogen (X) can be confirmed by the solubility of the precipitate of AgX in ammonia.
- The tests for alcohols can also detect aldehydes since they react similarly with acidified potassium dichromate.
- The reaction results provide a visual indication of the presence of specific functional groups, which is useful for identifying organic compounds.

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ORGANIC ANALYSIS



MASS SPECTROMETRY

Overview:

- Purpose: Mass spectrometry is primarily used to determine the relative molecular mass of organic compounds.
- Process: The compound is ionized in solution and positive ions are accelerated through the mass spectrometer.
- Measurement: The time of flight of these ions is recorded, which correlates to their mass-to-charge ratio (m/z).
- Output: The results are presented as a mass spectrum, showing relative abundance (vertical axis) against mass/charge ratio (horizontal axis). Since the charge is usually +1, the horizontal axis represents relative mass.

High-Resolution Mass Spectrometry

- Precision: While typical mass spectra show masses as whole numbers, high-resolution mass spectrometry can measure masses to three or four decimal places.
- Isotope Considerations: This precision allows for distinguishing between isotopes, as they do not always have whole number atomic masses (e.g., $^{16}\text{O} = 15.99491$, $^1\text{H} = 1.007829$).

Example Calculation:

- A parent ion with a mass of 200 (to the nearest whole number) could correspond to several molecular formulas:
 - $\text{C}_{10}\text{H}_{16}\text{O}_4$ (molecular mass: 200.1049)
 - $\text{C}_8\text{H}_{14}\text{O}_4$ (molecular mass: 200.0110)
 - $\text{C}_{11}\text{H}_{20}\text{O}_3$ (molecular mass: 200.1413)

Distinguishing Molecular Formulas

- Method: By adding up the accurate atomic masses, high-resolution mass spectrometry can distinguish between these potential formulas.
- Identification: A computer database can match the accurate relative molecular mass with known molecular formulas, facilitating compound identification.

Key Takeaways:

- Mass spectrometry is a vital tool in organic chemistry for determining molecular weights and structures.
- High-resolution capabilities enhance the ability to differentiate between closely related compounds based on precise mass measurements.
- The integration of databases allows for efficient identification of compounds based on their mass spectrometric data.

INFRARED SPECTROSCOPY

Overview

Infrared spectroscopy is a powerful analytical technique used to identify functional groups in organic compounds by measuring the absorption of infrared radiation by molecular bonds.

How It Works

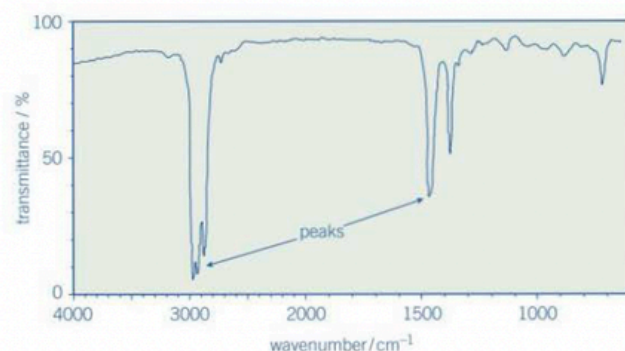
1. **Vibrational Motion:** Atoms in a molecule are always vibrating, akin to two balls connected by a spring. The frequency of this vibration depends on the strength of the bond and the mass of the atoms.
2. **Absorption of Radiation:** When infrared radiation is passed through a sample, bonds in the sample can absorb energy if the frequency of the radiation matches the bond's natural frequency.
3. **Transmission Measurement:** The emerging radiation from the sample is recorded, and the frequencies that correspond to the absorbed bonds are missing.
4. **Spectrum Generation:** The instrument plots a graph of the intensity of transmitted radiation (transmittance) against the wavenumber (cm^{-1}). Dips in the graph indicate the presence of specific bonds.

Interpretation of Infrared Spectra

- **Peaks and Dips:** The graph produced is called an infrared spectrum, where dips (often referred to as peaks) indicate particular functional groups.
- **Characteristic Absorptions:** Different bonds absorb infrared radiation at characteristic frequencies, allowing for the identification of functional groups.

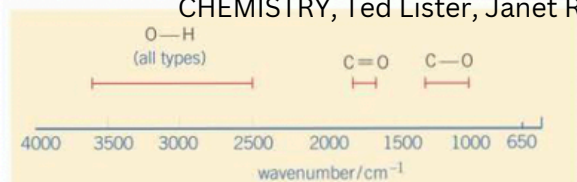
KEY ABSORPTIONS FOR COMMON FUNCTIONAL GROUPS

Bond	Wavenumber (cm ⁻¹)	Functional Group
O-H (broad)	3230-3550	Alcohols (ROH)
O-H (very broad)	2500-3000	Carboxylic acids (RCOOH)
C=O	1680-1750	Aldehydes (RCHO), Ketones (R ₂ CO), Carboxylic acids (RCOOH)
C-O	1000-1300	Alcohols, Esters
N-H	3100-3500	Primary amines



▲ **Figure 2** A typical infrared spectrum. Note that wavenumber gets smaller going from left to right

SOURCE: AQA A LEVEL STUDENT BOOK CHEMISTRY, Ted Lister, Janet Renshaw



▲ **Figure 3** The ranges of wavenumbers at which some bonds absorb infrared radiation

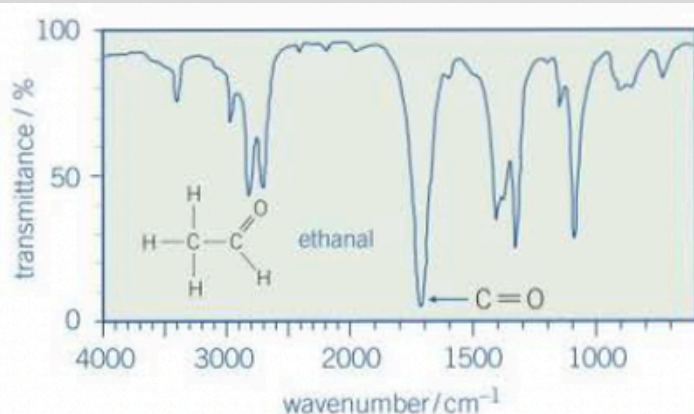
WHAT IS THE FINGERPRINT REGION?

Overview

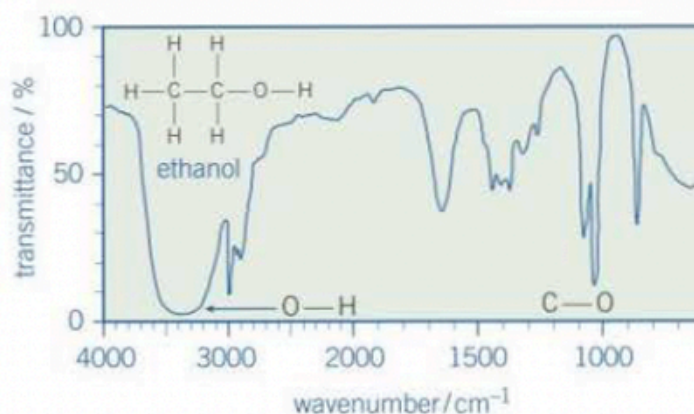
The fingerprint region of an infrared (IR) spectrum refers to the area below approximately 1500 cm⁻¹. This region contains many peaks resulting from complex vibrations of the entire molecule, creating a unique pattern for each substance.

Importance of the Fingerprint Region

- **Unique Identification:** The fingerprint region acts like a chemical "fingerprint," allowing for the identification of specific compounds. Just as individuals can be identified by their unique fingerprints, substances can be matched based on their IR spectra.
- **Database Comparison:** Chemists can use computer software to compare the fingerprint region of an unknown sample with a database of known compounds. An exact match in this region confirms the identity of the sample.



▲ **Figure 4** Infrared spectrum of ethanal



▲ **Figure 5** Infrared spectrum of ethanol

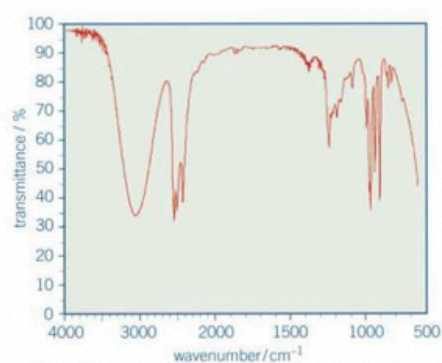
EXAMPLES OF INFRARED SPECTRA

Example: Propan-1-ol vs. Propan-2-ol

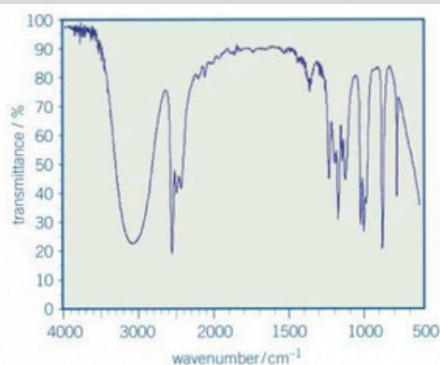
- Similarities: The overall IR spectra of propan-1-ol and propan-2-ol are very similar due to their related structures.
- Distinct Fingerprint Regions: Despite their similarities, the fingerprint regions of these two alcohols differ significantly. This distinction is essential for accurate identification.

Visual Representation

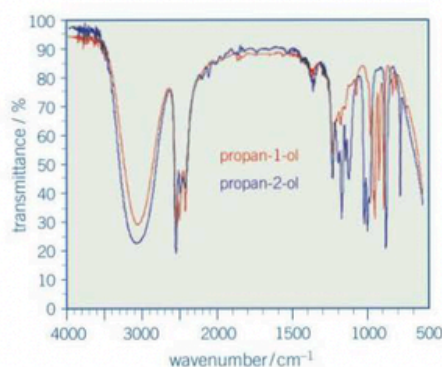
- Figures 1 and 2: Show the IR spectra of propan-1-ol and propan-2-ol.
- Figure 3: Illustrates the superimposed spectra, highlighting the similarity in overall shape but distinct differences in the fingerprint regions.
- Figure 4: Provides an enlarged view of the fingerprint region, making the differences between the two compounds more apparent.



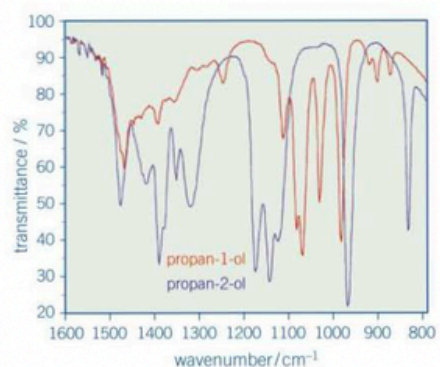
▲ Figure 7 Infrared spectrum of propan-1-ol



▲ Figure 8 Infrared spectrum of propan-2-ol



▲ Figure 9 Infrared spectra of propan-1-ol superimposed on propan-2-ol



▲ Figure 10 The fingerprint region of the infrared spectra of propan-1-ol superimposed on propan-2-ol enlarged

SOURCE: AQA A LEVEL STUDENT BOOK CHEMISTRY, Ted Lister, Janet Renshaw



DEFINITION OF TERMS

1. **Standard Enthalpy of Formation ($\Delta_f H^\circ$)**
2. The enthalpy change when **1 mole of a compound is formed from its constituent elements**, with all substances in their standard states under standard conditions (298 K, 100 kPa).
3. **Standard Enthalpy of Combustion ($\Delta_c H^\circ$)**
4. The enthalpy change when **1 mole of a substance is completely burned in oxygen** under standard conditions, with all reactants and products in their standard states.
5. **Standard Enthalpy of Atomisation ($\Delta_a H^\circ$)**
6. The enthalpy change when **1 mole of gaseous atoms is formed** from the element in its standard state under standard conditions.
7. **First Ionisation Energy ($\Delta_i H^\circ$)**
8. The enthalpy change when **1 mole of gaseous atoms loses 1 electron** to form 1 mole of gaseous ions with a single positive charge.
9. **Second Ionisation Energy (Second IE)**
10. The enthalpy change when **1 mole of gaseous singly positively charged ions loses 1 electron** to form 1 mole of gaseous ions with a 2+ charge.
11. **First Electron Affinity ($\Delta_{ea} H^\circ$)**
12. The enthalpy change when **1 mole of gaseous atoms gains 1 electron** to form 1 mole of gaseous ions with a single negative charge.
13. **Second Electron Affinity (Second EA)**
14. The enthalpy change when **1 mole of gaseous singly negatively charged ions gain 1 electron** to form 1 mole of gaseous ions with a 2- charge.
15. **Lattice Enthalpy of Formation ($\Delta_{latt} H^\circ$)**
16. The enthalpy change when **1 mole of an ionic compound is formed from its gaseous ions** under standard conditions.
17. **Lattice Enthalpy of Dissociation**
18. The enthalpy change when **1 mole of an ionic compound dissociates into its gaseous ions** under standard conditions.
19. **Enthalpy of Hydration ($\Delta_{hyd} H^\circ$)**
20. The enthalpy change when **1 mole of gaseous ions becomes hydrated** to form aqueous ions under standard conditions.
21. **Enthalpy of Solution ($\Delta_{sol} H^\circ$)**
22. The enthalpy change when **1 mole of solute dissolves completely in sufficient solvent** to form a solution in which the molecules or ions are far enough apart not to interact with each other.
23. **Mean Bond Enthalpy**
24. The average enthalpy change when **1 mole of a given type of bond in a gaseous molecule is broken**, averaged over a range of different compounds.

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THERMODYNAMICS



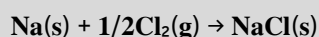
MORE ENTHALPY CHANGES

Ionic Bonding

In a simple model of ionic bonding, **electrons are transferred from metal atoms to non-metal atoms**, forming positively charged metal ions and negatively charged non-metal ions, each with stable outer shells. These ions arrange in a lattice where opposite charges are adjacent.

Enthalpy changes in forming ionic compounds

When sodium reacts with chlorine, the exothermic formation of sodium chloride occurs:



$$\Delta H = -411 \text{ kJ mol}^{-1}$$

This reaction occurs in multiple steps, involving the atomisation of sodium and chlorine, ionisation of sodium, electron affinity of chlorine, and the lattice formation:

1. **Atomisation of Na:**
2. $\text{Na(s)} \rightarrow \text{Na(g)}$
3. $\Delta H_a = +108 \text{ kJ mol}^{-1}$
4. **Atomisation of Cl_2 :**
5. $\frac{1}{2}\text{Cl}_2\text{(g)} \rightarrow \text{Cl(g)}$
6. $\Delta H_a = +122 \text{ kJ mol}^{-1}$
7. **First ionisation energy (Na):**
8. $\text{Na(g)} \rightarrow \text{Na}^+\text{(g)} + \text{e}^-$
9. $\Delta H_{\text{ie}} = +496 \text{ kJ mol}^{-1}$
10. **Electron affinity (Cl):**
11. $\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-\text{(g)}$
12. $\Delta H_{\text{ea}} = -349 \text{ kJ mol}^{-1}$
13. **Lattice formation (NaCl):**
14. $\text{Na}^+\text{(g)} + \text{Cl}^-\text{(g)} \rightarrow \text{NaCl(s)}$
15. $\Delta H_{\text{latt}} = -788 \text{ kJ mol}^{-1}$

Born-Haber cycle

Using Hess's Law, the total energy change for forming NaCl(s) from its elements is calculated by summing the above steps. The **Born-Haber** cycle allows calculation of any unknown value if all other enthalpies are known.

BORN-HABER CYCLE

The Born-Haber Cycle for Sodium Chloride

The Born-Haber cycle helps calculate the lattice formation enthalpy ($\Delta H_{\text{L}}^\circ$) of an ionic compound. Here's how to use the cycle for sodium chloride (NaCl):

Steps in the Born-Haber Cycle

1. Start with Elements in Their Standard States:

- Na(s) and $\text{Cl}_2\text{(g)}$
- This is the reference energy level (zero).

2. Atomisation of Sodium ($\Delta H_{\text{at}}^\circ$):

- Convert sodium from solid to gaseous atoms.
- Equation: $\text{Na(s)} \rightarrow \text{Na(g)}$
- Enthalpy Change: $+108 \text{ kJ mol}^{-1}$

3. Atomisation of Chlorine ($\Delta H_{\text{at}}^\circ$):

- Convert chlorine from diatomic gas to gaseous atoms.
- Equation: $\text{Cl}_2\text{(g)} \rightarrow 2 \text{Cl(g)}$
- Enthalpy Change: $+122 \text{ kJ mol}^{-1}$

4. Ionisation of Sodium ($\Delta H_{\text{IE1}}^\circ$):

- Remove an electron from gaseous sodium atoms to form sodium ions.
- Equation: $\text{Na(g)} \rightarrow \text{Na}^+\text{(g)} + \text{e}^-$
- Enthalpy Change: $+496 \text{ kJ mol}^{-1}$

5. Electron Affinity of Chlorine ($\Delta H_{\text{EA1}}^\circ$):

- Add an electron to gaseous chlorine atoms to form chloride ions.
- Equation: $\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-\text{(g)}$
- Enthalpy Change: -349 kJ mol^{-1}

6. Formation of Sodium Chloride ($\Delta H_{\text{f}}^\circ$):

- Combine gaseous sodium ions and chloride ions to form solid sodium chloride.
- Equation: $\text{Na}^+\text{(g)} + \text{Cl}^-\text{(g)} \rightarrow \text{NaCl(s)}$
- Enthalpy Change: -411 kJ mol^{-1}

7. Calculate Lattice Formation Enthalpy ($\Delta H_{\text{L}}^\circ$):

- Lattice Formation Enthalpy: The energy released when the lattice forms from gaseous ions.
- Enthalpy Change: -788 kJ mol^{-1}

2. Drawing the Born-Haber Cycle

- **Energy Zero:** Start with elements in their standard states as the baseline (zero energy).
- **Positive Enthalpy Changes:** Draw upwards. Includes atomisation and ionisation.
- **Negative Enthalpy Changes:** Draw downwards. Includes electron affinity and lattice formation.
- **Final Calculation:** The lattice formation enthalpy is calculated by summing all the other enthalpy changes and solving for the unknown value.

Tips for Drawing

- **Use a Scale:** For accuracy, use a rough scale (e.g., 1 line = 100 kJ mol^{-1}).
- **Plan Layout:** Arrange steps to avoid overlapping or running off the paper.
- **Label Clearly:** Indicate the sign and direction of each enthalpy change with arrows.

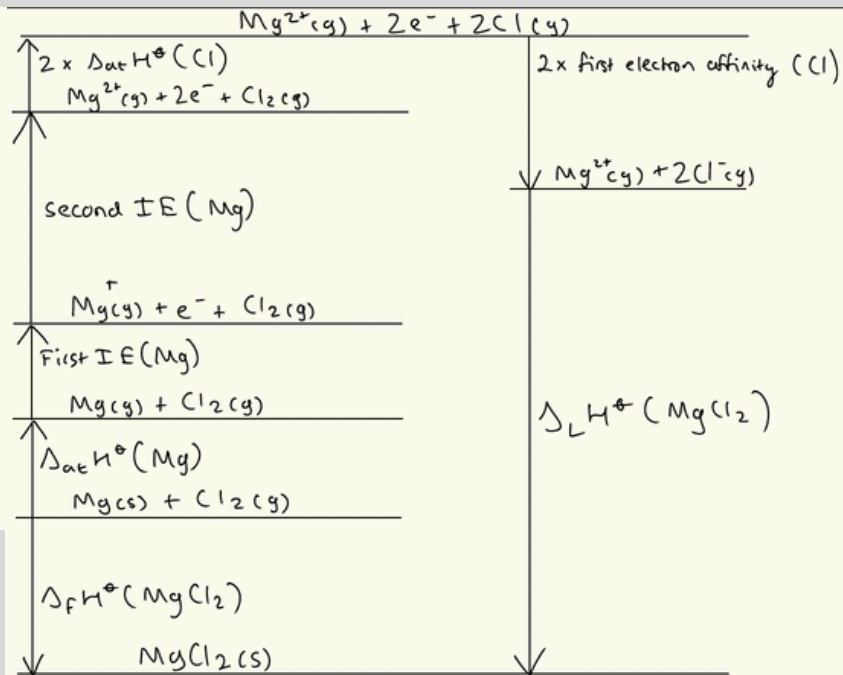
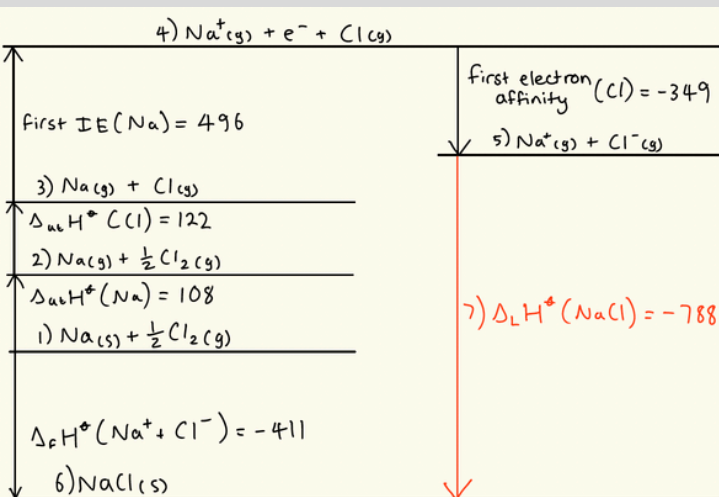
The Born-Haber cycle shows why the formation of ionic compounds like sodium chloride is typically exothermic, primarily due to the significant energy released when the ionic lattice forms.

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EXAMPLES OF BORN HABER CYCLES



TRENDS IN LATTICE ENTHALPY

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic compound. Here's how lattice enthalpy trends with ion size and charge:

1. Effect of Ion Size

- Larger Ions: When the ions in an ionic compound are larger, they have a lower lattice enthalpy.
 - Reason: Larger ions are less effective at approaching each other closely, reducing the electrostatic attraction between them.
 - Result: The lattice is less stable, and less energy is released when the lattice forms.

2. Effect of Ion Charge

- Higher Charge on Ions: For ions of similar size (e.g., ions from the same group of the Periodic Table), increasing the charge on the ions increases the lattice enthalpy.
 - Reason: Ions with higher charges have stronger electrostatic attractions.
 - Result: More energy is released when these ions come together to form the lattice.

3. Comparing Ions of Similar Size

- Example: Comparing ions with the same size but different charges (e.g., Na^+ vs. Mg^{2+}).
 - Trend: The lattice enthalpy increases with the charge of the ions.
 - Explanation: Ions with double the charge (e.g., Mg^{2+}) give out approximately twice as much energy when forming the lattice compared to ions with a single charge (e.g., Na^+).

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ENTHALPY OF SOLUTION/HYDRATION

When an ionic compound dissolves in water, the process involves several steps, each associated with energy changes. Here's a step-by-step breakdown:

1. Breaking the Ionic Lattice

- Process: Solid ionic compound (e.g., NaCl) is broken into gaseous ions.
- Energy Change: This requires energy input, known as the lattice dissociation enthalpy.
- Example: For NaCl : $\text{NaCl(s)} \rightarrow \text{Na}^{\text{+}}(\text{g}) + \text{Cl}^{\text{-}}(\text{g})$
 - Lattice Dissociation Enthalpy (Δ_{LatticeH}): +788 kJ/mol

2. Hydrating the Positive Ions

- Process: The positive ions (cations) are surrounded by water molecules.
- Energy Change: Energy is released, called the enthalpy of hydration.
- Example: $\text{Na}^{\text{+}}(\text{g}) + \text{aq} \rightarrow \text{Na}^{\text{+}}(\text{aq})$
 - Enthalpy of Hydration (Δ_{HydH}) for $\text{Na}^{\text{+}}$: -406 kJ/mol

3. Hydrating the Negative Ions

- Process: The negative ions (anions) are surrounded by water molecules.
- Energy Change: Energy is also released here.
- Example: $\text{Cl}^{\text{-}}(\text{g}) + \text{aq} \rightarrow \text{Cl}^{\text{-}}(\text{aq})$
 - Enthalpy of Hydration (Δ_{HydH}) for $\text{Cl}^{\text{-}}$: -363 kJ/mol

4. Enthalpy of Solution

- Process: Combining all steps to find the overall enthalpy change when the ionic compound dissolves.
- Example: $\text{NaCl(s)} + \text{aq} \rightarrow \text{Na}^{\text{+}}(\text{aq}) + \text{Cl}^{\text{-}}(\text{aq})$
 - Enthalpy of Solution (Δ_{SolH}): $\Delta_{\text{LatticeH}} + \Delta_{\text{HydH}}(\text{for Na}^{\text{+}}) + \Delta_{\text{HydH}}(\text{for Cl}^{\text{-}})$
 - Calculation: $\Delta_{\text{SolH}} = +788 \text{ kJ/mol (lattice dissociation)} - 406 \text{ kJ/mol (hydration of Na}^{\text{+}}) - 363 \text{ kJ/mol (hydration of Cl}^{\text{-}}) = +19 \text{ kJ/mol}$

Trends in Hydration

- Highly Charged Ions: Have more negative enthalpies of hydration because they attract water molecules more strongly.
- Larger Ions: Have less negative enthalpies of hydration due to weaker interactions with water.

Theoretical vs. Experimental Lattice Enthalpy

- Theoretical Value: Calculated based on ideal ionic models.
- Experimental Value: Measured in the lab.

For many ionic compounds, experimental and theoretical values agree well, confirming the ionic model. However, discrepancies suggest some covalent character.

Example: Zinc Selenide (ZnSe)

- Experimental Lattice Enthalpy: -3611 kJ/mol
- Theoretical Lattice Enthalpy: -3305 kJ/mol
- Reason for Discrepancy: Zn^{2+} can polarize the large Se^{2-} ion, leading to extra bonding beyond pure ionic interaction.

Factors Increasing Polarization:

- Cation: Small size, high charge
- Anion: Large size, high charge

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THERMODYNAMICS



WHY DO CHEMICAL REACTIONS HAPPEN? ENTROPY

Chemists describe reactions that occur on their own as "feasible" or "spontaneous." These terms indicate that a reaction can happen without external input. However, they do not consider how quickly the reaction happens, which could be very slow or not measurable at room temperature.

Exothermic Reactions

- **Definition:** Exothermic reactions release heat (ΔH is negative).
- **Example:** Magnesium reacting with copper sulfate. The solution heats up as copper and magnesium sulfate are formed.

Endothermic Reactions

- **Definition:** Endothermic reactions absorb heat (ΔH is positive).
- **Examples:**
 - Ice melting absorbs heat but occurs spontaneously at room temperature.
 - Dissolving certain salts in water can be endothermic.

Factors Affecting Spontaneity

While exothermic reactions often occur spontaneously, this is not always the case. Some endothermic reactions can also be spontaneous. To understand why, we need to consider entropy.

Entropy (S) and Disorder

- **Definition:** Entropy is a measure of the disorder or randomness in a system.
- **Observation:** Processes that increase disorder or randomness are more likely to be spontaneous. For example:
 - Gases are more disordered than liquids.
 - Liquids are more disordered than solids.
 - Mixing liquids or gases increases entropy.

Entropy Change (ΔS)

- **Definition:** The change in entropy during a reaction.
- **Significance:** A reaction is more likely to be spontaneous if it increases the entropy of the system. For example, when solids dissolve or gases mix, the entropy increases.

Standard Conditions

- **Standard Conditions:** Entropies are typically measured at 298 K and 100 kPa.
- **Reference:** Tables of standard entropy values are used to find the entropy change for specific reactions.

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THE GIBBS FREE ENERGY CHANGE AND CALCULATION OF ENTROPY

To find the entropy change (ΔS) for a reaction, use the following approach:

1. Add the entropies of the products.
2. Subtract the sum of the entropies of the reactants.

Example Calculation:

For the reaction:

- Calcium carbonate (CaCO_3) decomposes into calcium oxide (CaO) and carbon dioxide (CO_2).

Using entropy values:

- Entropy of CaO (s) = 40 J/K·mol
- Entropy of CO_2 (g) = 214 J/K·mol

So, the total entropy of the products is: $40 + 214 = 254$ J/K·mol

- Entropy of CaCO_3 (s) = 93 J/K·mol

The entropy change (ΔS) is calculated as: $254 - 93 = 161$ J/K·mol

A positive value for ΔS indicates an increase in disorder, such as when a gas is formed from a solid.

Gibbs Free Energy (ΔG)

To determine if a reaction is feasible, consider both enthalpy change (ΔH) and entropy change (ΔS) using Gibbs Free Energy (ΔG):

- If ΔG is negative, the reaction is feasible.
- If ΔG is positive, the reaction is not feasible.

The formula to calculate ΔG is: $\Delta G = \Delta H - T \times \Delta S$

Where:

- ΔH is the enthalpy change
- T is the temperature in Kelvin
- ΔS is the entropy change

Effect of Temperature:

The feasibility of a reaction depends on temperature because of the $T \times \Delta S$ term. An endothermic reaction (where ΔH is positive) can become feasible at higher temperatures if ΔS is positive enough.

Example Calculation:

For a reaction with:

- $\Delta H = +178$ kJ/mol
- $\Delta S = +161$ J/K·mol (or 0.161 kJ/K·mol)

At Room Temperature (298 K): $\Delta G = \Delta H - (T \times \Delta S)$ $\Delta G = 178 - (298 \times 0.161)$ $\Delta G = 178 - 48$ $\Delta G = +130$ kJ/mol

A positive ΔG means the reaction is not feasible at room temperature.

At 1500 K: $\Delta G = \Delta H - (T \times \Delta S)$ $\Delta G = 178 - (1500 \times 0.161)$ $\Delta G = 178 - 242$ $\Delta G = -64$ kJ/mol

A negative ΔG means the reaction is feasible at this higher temperature.

Finding the Temperature for Feasibility:

To find the temperature at which ΔG is zero (indicating the reaction is just feasible):

$$\Delta G = \Delta H - T \times \Delta S \quad 0 = \Delta H - T \times \Delta S \quad T = \Delta H / \Delta S$$

For:

- $\Delta H = +178$ kJ/mol
- $\Delta S = 0.161$ kJ/K·mol

$$T = 178 / 0.161 \quad T \approx 1105.6 \text{ K}$$

At this temperature, the reaction is at equilibrium with both reactants and products present.



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THE GIBBS FREE ENERGY CHANGE AND CALCULATION OF ENTROPY

To find the entropy change (ΔS) using the temperature where $\Delta G = 0$, follow these steps:

1. At the melting point, $\Delta G = 0$, so use the equation: $\Delta G = \Delta H - T \times \Delta S$ $\Delta G = \Delta H - T \times \Delta S$
2. Rearranging for ΔS gives: $\Delta S = \Delta H / T$ $\Delta S = \Delta H / T$

Example: Melting of Ice

- Melting point of ice: 273 K
- Enthalpy change for melting: 6.0 kJ/mol

Calculate ΔS : $\Delta S = 6.0 / 273$ $\Delta S = 0.022 \text{ kJ/K} \cdot \text{mol}$ $\Delta S = 0.022 \text{ kJ/K} \cdot \text{mol}$

$\Delta S = 22 \text{ J/K} \cdot \text{mol}$ $\Delta S = 22 \text{ J/K} \cdot \text{mol}$

This positive ΔS reflects the increase in disorder when ice melts into water.

KINETIC FACTORS AFFECTING GIBBS FREE ENERGY CHANGE

Neither enthalpy changes nor entropy changes tell us anything about how quickly or slowly a reaction is likely to occur. You might predict that a certain reaction should occur spontaneously due to these factors, but in practice, the reaction might proceed so slowly that it does not seem to happen at all. This is because there is often a large activation energy barrier.

Example: Carbon Reaction $\text{C(s, graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

$\Delta H = -393.5 \text{ kJ mol}^{-1}$

This reaction is **exothermic**, and you can calculate the actual value of ΔS (entropy change) and find ΔG (Gibbs free energy change).

Calculating ΔS (Entropy Change):

ΔS for the reaction is the sum of the entropies of the products minus the sum of the entropies of the reactants.

$\text{C(s, graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

$S(\text{C, graphite}) = 5.7 \text{ J K}^{-1} \text{ mol}^{-1}$

$S(\text{O}_2, \text{gas}) = 205.0 \text{ J K}^{-1} \text{ mol}^{-1}$

$S(\text{CO}_2, \text{gas}) = 213.6 \text{ J K}^{-1} \text{ mol}^{-1}$

So,

$\Delta S = 213.6 - (5.7 + 205.0)$

$\Delta S = +2.9 \text{ J K}^{-1} \text{ mol}^{-1}$ (positive as expected).

Calculating ΔG (Gibbs Free Energy Change):

$\Delta G = \Delta H - T\Delta S$

At standard conditions (approximately room temperature at 298 K),

$\Delta G = -394 - (298 \times 2.9/1000)$

(Remember to divide the entropy value by 1000 to convert from $\text{J K}^{-1} \text{ mol}^{-1}$ to $\text{kJ K}^{-1} \text{ mol}^{-1}$).

So,

$\Delta G = -394 - 0.86$

$\Delta G = -394.86 \text{ kJ mol}^{-1}$

This negative value means the reaction is feasible.

However, despite the reaction being feasible thermodynamically, graphite does not react with oxygen at room temperature because the reaction rate is extremely slow. At higher temperatures, the reaction will proceed. Therefore, graphite is said to be thermodynamically unstable but kinetically stable.

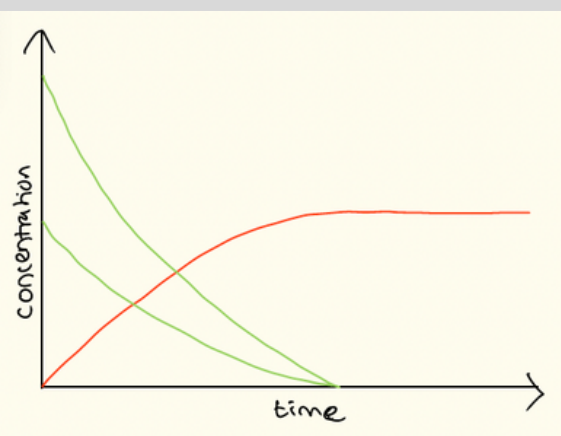
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REACTION RATES



WHAT IS A REACTION RATE?

- The rate of reaction is the change in concentration of reactants or products per unit time.
- In the reaction $A + 2B \rightarrow C$, as $[C]$ (the product) increases, $[A]$ and $[B]$ (the reactants) decrease.
- $[B]$ decreases twice as fast as $[A]$, due to the stoichiometric ratio (2:1 in the equation).
- The rate is typically measured by tracking the concentration of the product because it increases over time.



RATE OF REACTION AT ANY INSTANT

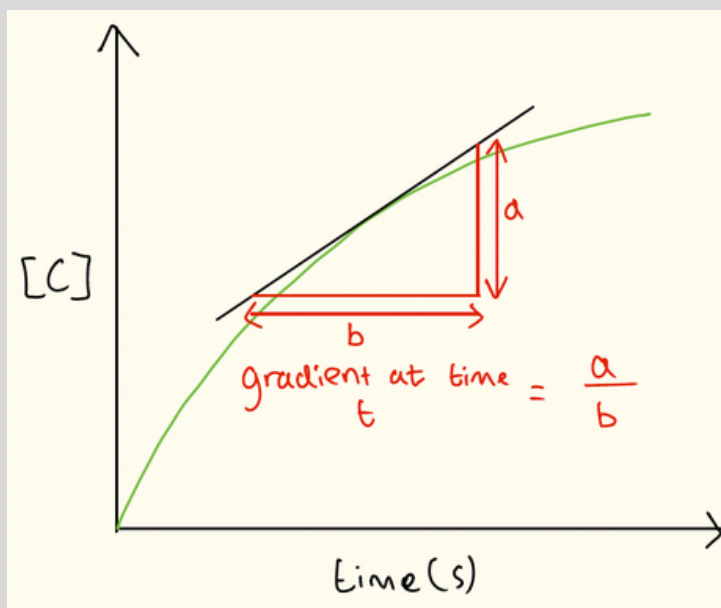
- To find the rate of reaction at a specific time, you need to calculate the instantaneous rate.
- Draw a tangent to the concentration vs. time curve at the desired point.
- The rate is the **gradient (slope) of the tangent: change in y/change in x**
- $\text{Rate} = \frac{\text{change in concentration}}{\text{change in time}}$

This method gives the rate at that particular instant.

THE RATE EXPRESSION AND THE RATE CONSTANT

- **Rate Expression:**
 - Determined through experimental investigation.
 - Describes how the rate of reaction depends on the concentration of species involved at a given temperature.
 - Some species in the chemical equation may not appear in the rate expression, meaning they don't affect the rate.
- Example:
- Reaction: $X + Y \rightarrow Z$
- Possible rate expressions:
 - $\text{rate} \propto [X][Y]$:
 - Doubling $[X]$ or $[Y]$ would double the rate.
 - Doubling both would quadruple the rate.
 - $\text{rate} \propto [X][Y]^2$:
 - Doubling $[X]$ doubles the rate.
 - Doubling $[Y]$ quadruples the rate.
- **Rate Constant (k):**
 - k removes the proportionality:
 - $\text{rate} = k[X][Y]^2$.
 - k is different for each reaction and varies with temperature.
 - If the concentrations of all species are 1 mol dm^{-3} , the reaction rate equals k .

ORDER OF A REACTION



- The order of reaction indicates how the rate depends on the concentration of each reactant.
- If the rate expression is:
- $\text{rate} = k[X][Y]^2$, then:
 - The order with respect to $[X]$ is 1.
 - The order with respect to $[Y]$ is 2 (since it's raised to the power of 2).
- Overall order of the reaction is the sum of the orders of all reactants:
 - For $\text{rate} = k[X][Y]^2$, the overall order is $1 + 2 = 3$.
 - Therefore, the reaction is:
 - First order with respect to X .
 - Second order with respect to Y .
 - Third order overall.
- **General Case:**
 - For the rate expression $\text{rate} = k[A]^m[B]^n$:
 - m and n are the orders with respect to A and B .
 - The overall order is $m + n$.



HOW IS THE CHEMICAL EQUATION RELATED TO THE RATE EXPRESSION?

- **The Chemical Equation and the Rate Expression:**

- The rate expression only includes species that affect the rate of reaction.
- Species in the chemical equation may not appear in the rate expression, and their coefficients have no impact on the rate expression.
- Catalysts, which may not appear in the chemical equation, can appear in the rate expression.

- **Example:**

- For the reaction with propanone, iodine, and a catalyst:

- Rate expression: $\text{rate} = k[\text{CH}_3\text{COCH}_3(\text{aq})][\text{H}^+(\text{aq})]$
- The reaction is:
 - First order with respect to propanone.
 - First order with respect to H^+ ions.
 - Zero order with respect to iodine.
- The overall order is 2.
- H^+ ions act as a catalyst.

For zero order reaction:

$$\text{rate} = k \rightarrow \text{units are } \text{mol dm}^{-3} \text{ s}^{-1}$$

First order reaction:

$$\text{rate} = k[A]$$

$$k = \frac{\text{Rate}}{[A]}$$

- **Units of the Rate Constant (k):**

- The units of k depend on the overall order of the reaction.

- a. **Zero Order:**

- $\text{rate} = k$
- Units of rate: $\text{mol dm}^{-3} \text{ s}^{-1}$
- Units of k : $\text{mol dm}^{-3} \text{ s}^{-1}$.

- b. **First Order:**

- $\text{rate} = k[A]$
- Units of rate: $\text{mol dm}^{-3} \text{ s}^{-1}$
- Units of $[A]$: mol dm^{-3}
- Units of k : s^{-1} (from cancelling out).

- c. **Second Order:**

- $\text{rate} = k[B][C]$
- Units of rate: $\text{mol dm}^{-3} \text{ s}^{-1}$
- Units of $[B]$ and $[C]$: mol dm^{-3}
- Units of k : $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

- d. **Third Order:**

- $\text{rate} = k[D][E]^2$
- Units of rate: $\text{mol dm}^{-3} \text{ s}^{-1}$
- Units of $[D]$: mol dm^{-3}
- Units of $[E]^2$: $(\text{mol dm}^{-3})^2$
- Units of k : $\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$.

- **Study Tip:**

- Understanding the difference between rate of reaction, order of reaction, and rate constant is essential.

For second order reaction:

$$\text{rate} = k[B][C]$$

$$k = \frac{\text{rate}}{[B][C]}$$

units of k :

$$k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3} \text{ mol dm}^{-3}}$$

$$\Rightarrow \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

For third order reaction:

$$\text{rate} = k[D][E]^2$$

$$k = \frac{\text{rate}}{[D][E]^2}$$

FINDING THE ORDER OF A REACTION BY USING RATE-CONCENTRATION GRAPHS

- **Order of a Reaction:**

- The order with respect to a reagent is found experimentally by investigating how the rate changes with concentration.

- **Zero Order:**

- If the rate is not affected by the concentration of a species, the reaction is zero order with respect to that species.
- This species does not appear in the rate expression.

- **First Order:**

- If the rate is directly proportional to the concentration of the species, the reaction is first order with respect to that species.

- **Second Order:**

- If the rate is proportional to the square of the concentration, the reaction is second order.

- **Rate-Concentration Graphs:**

- To determine the order of a reaction with respect to a species, A, plot graphs of rate against concentration:

- i. **Zero Order:**

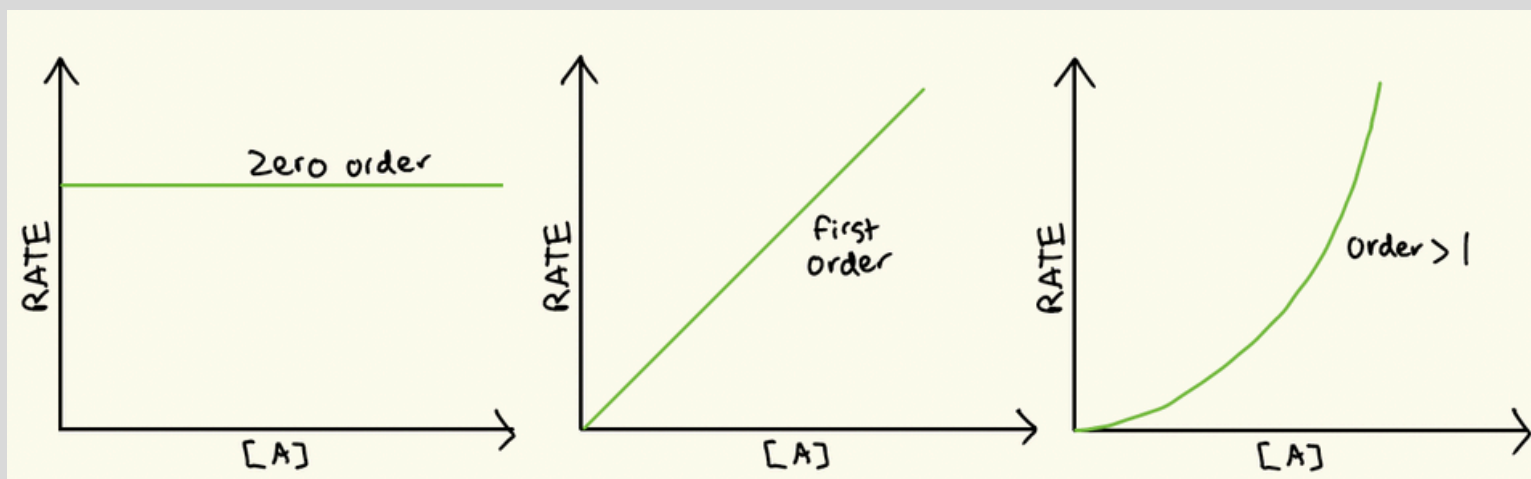
- The graph is a horizontal line (Figure 2a), showing the rate is unaffected by concentration.

- ii. **First Order:**

- The graph is a straight sloping line through the origin (Figure 2b), indicating the rate is proportional to $[A]^1$.

- iii. **Second Order:**

- If the graph is curved (Figure 2c), try plotting rate vs. $[A]^2$. If this gives a straight line, the reaction is second order.



04-CHEM-2

REACTION RATES



INITIAL RATE METHOD, WORKED EXAMPLE

Experiment Number	[NO] (mol dm ⁻³)	[O ₂] (mol dm ⁻³)	Initial Rate (mol dm ⁻³ s ⁻¹)	Comparison	Rate Analysis
1	1.0 × 10 ⁻³	1.0 × 10 ⁻³	7.0 × 10 ⁻⁴	Base Case	-
2	2.0 × 10 ⁻³	1.0 × 10 ⁻³	28.0 × 10 ⁻⁴	Compare to 1: [NO] doubled	Rate quadruples (4x) → Second order with respect to NO
3	3.0 × 10 ⁻³	1.0 × 10 ⁻³	63.0 × 10 ⁻⁴	Compare to 1: [NO] tripled	Rate increases ninefold (9x) → Confirms second order with respect to NO
4	2.0 × 10 ⁻³	2.0 × 10 ⁻³	56.0 × 10 ⁻⁴	Compare to 2: [O ₂] doubled	Rate doubles (2x) → First order with respect to O ₂
5	3.0 × 10 ⁻³	3.0 × 10 ⁻³	189.0 × 10 ⁻⁴	Compare to 3: [O ₂] tripled	Rate triples (3x) → Confirms first order with respect to O ₂

EXAMPLE CALCULATION: FINDING THE RATE CONSTANT

1. Rate Expression: The rate expression for the reaction is:
2. $\text{rate} = k [\text{NO}]^2 [\text{O}_2]$
3. Substituting Values (using Experiment 2):
 - $\text{Rate} = 28.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
 - $[\text{NO}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$
 - $[\text{O}_2] = 1 \times 10^{-3} \text{ mol dm}^{-3}$
4. Substituting these into the rate expression:
5. $28.0 \times 10^{-4} = k (2 \times 10^{-3})^2 \times (1 \times 10^{-3})$
6. Simplifying:
7. $28.0 \times 10^{-4} = k \times 4 \times 10^{-9}$
8. Solving for k:
9. $k = (28.0 \times 10^5) / 4$
10. $k = 7.0 \times 10^5 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
11. Units of k:
 - Rate units = $\text{mol dm}^{-3} \text{ s}^{-1}$
 - Concentration units = mol dm^{-3}
12. Rearranging and cancelling units:
13. $k = (\text{mol dm}^{-3} \text{ s}^{-1}) / (\text{mol dm}^{-3})^3$
14. $k = \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
15. Effect of Temperature on k:
 - Temperature Impact: Increasing temperature increases the rate constant (k), as more particles have energy greater than the activation energy (E_a).
 - Rule of Thumb: For every 10 K increase in temperature, the reaction rate approximately doubles.
 - Activation Energy: The higher the proportion of molecules with energy greater than E_a, the faster the reaction.

- The reaction is second order with respect to NO and first order with respect to O₂.
- Rate Expression:
- $\text{rate} = k[\text{NO}]^2[\text{O}_2]^1$
- Overall Order: 3 (second order in NO + first order in O₂).

04-CHEM-2

REACTION RATES



EXAMPLE CALCULATION: FINDING THE RATE CONSTANT

1. Introducing the Arrhenius Equation

The rates of chemical reactions increase significantly with relatively small rises in temperature. This happens because as the temperature rises, not only does the number of collisions between reactant molecules increase, but more importantly, the number of collisions with energy greater than the activation energy increases.

1. **Energy Distribution:** The Maxwell-Boltzmann distribution curve shows how the distribution of energies among reactant molecules varies with temperature.

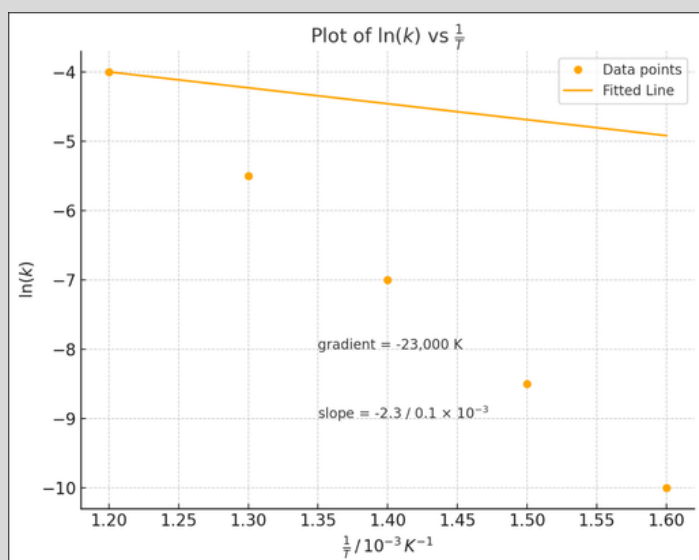
2. **Activation Energy:** The fraction of molecules with energy greater than the activation energy can be expressed as e raised to the power of $(-E_a/RT)$. Here:

1. E_a is the activation energy in J mol^{-1} .
2. R is the gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$).
3. T is the temperature in Kelvin (K).

The activation energy is linked to the rate constant using the **Arrhenius equation**:

1. $k = A \cdot e$ raised to the power of $(-E_a/RT)$

1. k is the rate constant, which is proportional to the reaction rate.
2. A is the pre-exponential factor, representing the frequency of collisions between reactant molecules.
3. e raised to $(-E_a/RT)$ represents the fraction of collisions that have enough energy to result in a reaction.



THE ARRHENIUS EQUATION

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For a reaction with **activation energy** of 50 kJ mol^{-1} ($50,000 \text{ J mol}^{-1}$):

- At 300 K:
- The fraction of molecules with energy $> 50 \text{ kJ mol}^{-1} = 19 \times 10^{-10}$.
- (Only 19 molecules out of every 10^{10} can react.)
- At 310 K (10 K higher):
- The fraction $= 36 \times 10^{-10}$.
- (Now 36 molecules out of every 10^{10} can react.)

Key Point

A 10 K increase nearly doubles the number of reacting molecules, and the rate almost doubles. This is a general rule for reactions around room temperature with activation energies near 50 kJ mol^{-1} .

04-CHEM-2

REACTION RATES



EXAMPLE CALCULATION: FINDING THE RATE CONSTANT

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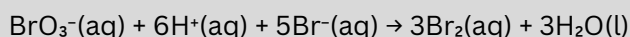
2. A is the pre-exponential factor, representing the frequency of collisions between reactant molecules.

3. e raised to $(-E_a/RT)$ represents the fraction of collisions that have enough energy to result in a reaction.

THE RATE DETERMINING STEP

Reactions usually occur in multiple steps, called the reaction mechanism.

For example:



This reaction happens in steps because it's unlikely that 12 ions will all collide simultaneously. Each step may produce short-lived intermediates that are difficult to isolate.

Rate-Determining Step (RDS)

- In multi-step reactions, the slowest step determines the overall rate, known as the rate-determining step.
- Any steps after the RDS do not affect the rate because they are fast in comparison.
- Only species involved up to the RDS appear in the rate expression.

Example:

For the reaction $\text{A} + \text{B} + \text{C} \rightarrow \text{Y} + \text{Z}$, the steps might be:

1. $\text{A} + \text{B}$ (fast) $\rightarrow$ D (intermediate)

2. D (slow) $\rightarrow$ E (intermediate)

3. $\text{E} + \text{C}$ (fast) $\rightarrow \text{Y} + \text{Z}$

Since Step 2 is the slowest, it controls the rate. Therefore, the rate expression might be:

$\text{Rate} \propto [\text{A}][\text{B}]$ (but not C, since it appears after the RDS).

Propanone and Iodine Reaction

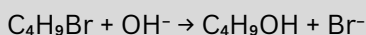
The reaction: CH_3COCH_3 (propanone) + $\text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I}$ (iodopropane) + HI

Rate expression: $\text{Rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$

The rate-determining step involves propanone and H^+ , which explains why I_2 is not in the rate expression.

DETERMINING ORDER OF A REACTION TO FIND THE RATE DETERMINING STEP

Consider the reaction of $\text{C}_4\text{H}_9\text{Br}$ with OH^- :



Two possible mechanisms are:

a. Two-Step Mechanism

1. Slow step: $\text{C}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{H}_9^+ + \text{Br}^-$

2. Fast step: $\text{C}_4\text{H}_9^+ + \text{OH}^- \rightarrow \text{C}_4\text{H}_9\text{OH}$

The slow step involves breaking the C-Br bond, followed by the fast step where oppositely charged ions react.

b. One-Step Mechanism

• Slow step: $\text{C}_4\text{H}_9\text{Br} + \text{OH}^- \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{Br}^-$

The C-Br bond breaks as the C-OH bond forms simultaneously.

Experimental Evidence and Mechanisms

• 1-bromobutane reacts via a second-order mechanism:

• $\text{Rate} = k[\text{C}_4\text{H}_9\text{Br}][\text{OH}^-]$

• This suggests a one-step mechanism (Mechanism b), where both reactants are involved in the rate-determining step.

• 2-bromo-2-methylpropane reacts via a first-order mechanism:

• $\text{Rate} = k[\text{C}_4\text{H}_9\text{Br}]$

• This supports the two-step mechanism (Mechanism a), where the C-Br bond breaking is the rate-determining step.

• 2-bromobutane reacts by a mixture of both mechanisms, resulting in a more complex rate expression.

04-CHEM-2

REACTION RATES



K_p- EQUILLIBRIUM CONSTANT FOR GASEOUS EQUILLIBRIA

In gaseous equilibria, concentrations are expressed using partial pressures instead of molar concentrations. This applies to many key industrial processes, like the Haber process (ammonia synthesis) and the Contact process (sulfuric acid production).

Partial Pressure

- Partial pressure (p) is the pressure that a gas would exert if it occupied the container alone.
- The sum of partial pressures of all gases in a mixture equals the total pressure.

For example, in air (100 kPa total pressure):

- Oxygen (20%) has a partial pressure of 20 kPa.
- Nitrogen (80%) has a partial pressure of 80 kPa.

Calculating Partial Pressure

The partial pressure of a gas is calculated using its mole fraction:
 $p_A = \text{mole fraction of A} \times \text{total pressure}$

Where:

$\text{Mole fraction of A} = \frac{\text{moles of gas A}}{\text{total moles of gas}}$
 $\text{Mole fraction of A} = \frac{\text{moles of gas A}}{\text{total moles of gas}}$

EFFECT OF CHANGING TEMPERATURE AND PRESSURE ON GASEOUS EQUILLIBRIUM

Le Chatelier's Principle applies to gaseous equilibria similarly to those in solution, but partial pressures replace concentrations.

Effect of Temperature:

- For an exothermic reaction (negative ΔH), increasing the temperature shifts the equilibrium to the left (towards reactants), as the system absorbs heat to counteract the temperature rise.
- Example:
 $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, $\Delta H = -92 \text{ kJ mol}^{-1}$
- Increasing temperature decreases the yield of ammonia, as K_p decreases.
- Effect of Pressure:
• Increasing pressure shifts the equilibrium to the side with fewer gas molecules to reduce the total pressure.
- In the Haber process, increasing pressure increases ammonia yield, as fewer gas molecules exist on the product side.
- Example:
 $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
- Here, pressure changes have no effect on equilibrium, as the number of molecules is the same on both sides.

Effect on Rate:

- Increasing pressure increases the rate of reaction due to more frequent collisions between gas molecules.
- Increasing temperature also increases the rate at which equilibrium is reached.
- Catalysts speed up the attainment of equilibrium but do not affect the equilibrium position.

04-CHEM-3

ELECTRODE POTENTIALS



HALF CELLS

When two different metals are placed in a salt solution and connected, an electric current flows from the more reactive metal (which loses electrons) to the less reactive metal. This forms the basis of batteries.

Half Cells

- A half cell is created when a metal rod is dipped into a solution containing its ions, setting up an equilibrium.
- Example:
 - $\text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$
- The electrode potential shows how readily a metal releases electrons, indicating its strength as a reducing agent. However, we can only measure the potential difference (voltage) between two half cells using a voltmeter.

Salt Bridge

- To complete the circuit, a salt bridge (often filter paper soaked in potassium nitrate) is used. It allows the flow of ions while avoiding interference from additional metal potentials.

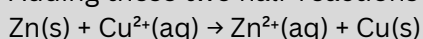
Example: Zinc and Copper Electrodes

- Connecting zinc and copper electrodes in solutions of their ions generates a potential difference of 1.10 V (at 1.00 mol dm⁻³, 298 K).
 - Zinc is more negative, meaning it loses electrons more easily (it is a better reducing agent).
- Electron flow: From zinc to copper.
 - Zinc loses electrons and forms Zn²⁺ ions.
 - Copper ions gain electrons and form solid copper.

Half Reactions:

- Zinc half-reaction:
 - $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$
- Copper half-reaction:
 - $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu(s)}$

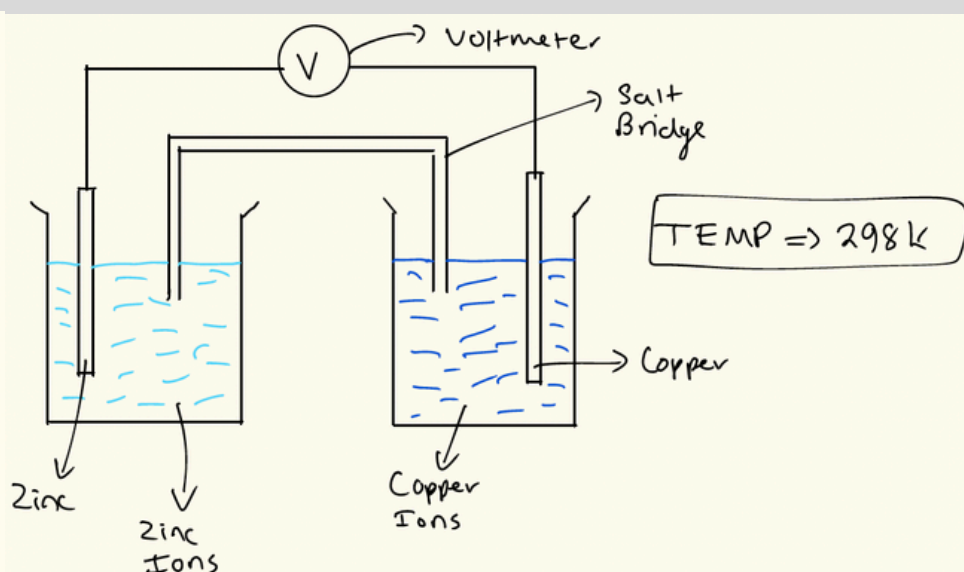
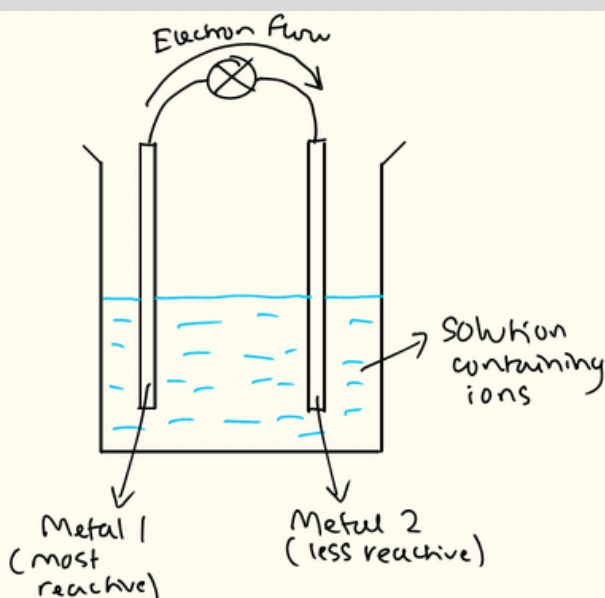
Adding these two half-reactions gives the overall redox reaction:



This is a redox reaction, with zinc being oxidized and copper ions being reduced.

Daniell Cell

- When two half cells are connected and generate electricity, they form an electrical cell, known as the Daniell cell.



04-CHEM-3

ELECTRODE POTENTIALS



THE STANDARD HYDROGEN ELECTRODE

To compare how easily different metals release electrons, a standard electrode is needed. The standard hydrogen electrode (SHE) is used for this purpose.

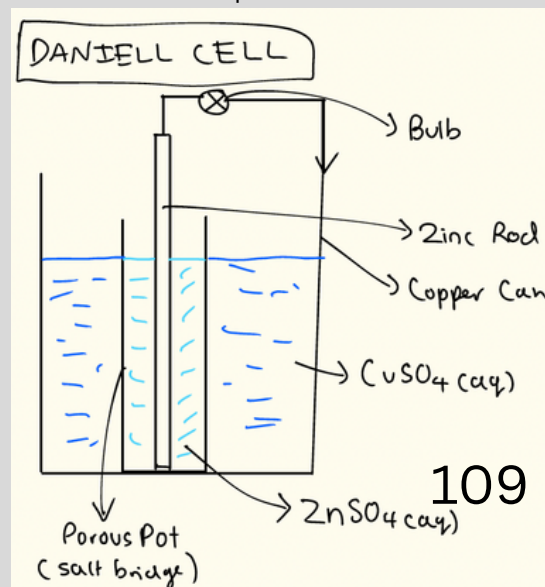
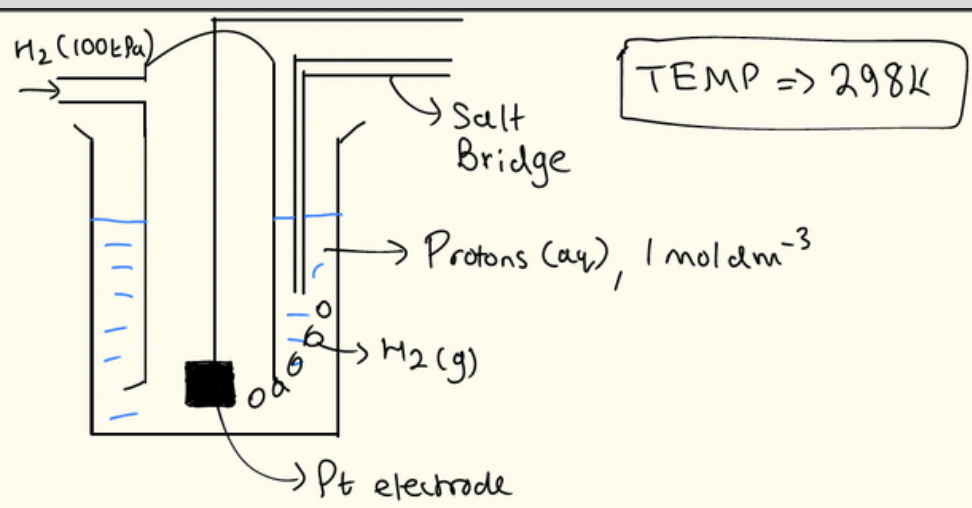
Setup:

- **Hydrogen gas (H_2) is bubbled through a solution of $H^+(aq)$ ions (1.00 mol dm^{-3}).**
 - Platinum electrode: A piece of unreactive platinum is used for electrical contact since hydrogen gas doesn't conduct.
 - The platinum is coated with finely divided platinum to increase the surface area, allowing reactions to proceed faster.
- **Standard conditions:**
 - $[H^+] = 1.00 \text{ mol dm}^{-3}$
 - Pressure = 100 kPa
 - Temperature = 298 K

This electrode is used as a reference to measure the potential of other half cells.

MORE ABOUT THE HYDROGEN ELECTRODE

- Standard Hydrogen Electrode (SHE):
- The potential of the standard hydrogen electrode is defined as zero volts.
- Electromotive Force (emf):
- When SHE is connected to another electrode, the measured voltage is known as the electromotive force (emf), denoted as E .
 - E represents the electrode potential of that cell.
- Standard Conditions:
- For accurate measurements, the second electrode should also be under standard conditions:
 - $[\text{metal ions}] = 1.00 \text{ mol dm}^{-3}$
 - Temperature = 298 K
- Electrode Potential ($E^\ominus$):
- The emf (E) measured under standard conditions is referred to as $E^\ominus$.
 - Electrodes with negative $E^\ominus$ values are better at releasing electrons (better reducing agents) compared to hydrogen.
- Effect of Changing Conditions:
- Variations in conditions, such as ion concentration or temperature, will affect the electrical potential of the electrode.



04-CHEM-3

ELECTRODE POTENTIALS



THE ELECTROCHEMICAL SERIES

The Electrochemical Series and Cell Notation

- **Electrode Potentials:** Electrode potentials (E^θ) are reduction potentials listed in the electrochemical series. They indicate the tendency of a species to gain electrons. Reduction potentials are given as reduction half-reactions with electrons on the left.
- **Electrochemical Series:** Arranges electrodes by their E^θ values, with more negative values at the top. The voltage between two electrodes is the difference in their E^θ values. For instance:
 - Connecting $\text{Al}^{3+}(\text{aq})/\text{Al}(\text{s})$ and $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ yields 2.00 V.
 - Connecting $\text{Al}^{3+}(\text{aq})/\text{Al}(\text{s})$ and $\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$ yields 1.53 V.
- **Cell Notation:** Represents electrochemical cells using standard conventions:
 - A solid vertical line (|) indicates a phase boundary.
 - A double vertical line (||) represents a salt bridge.
 - The higher oxidation state is written next to the salt bridge.
 - The emf (E^θ) value reflects the potential difference between electrodes.

Examples:

- Cell Diagram: $\text{Al}(\text{s}) | \text{Al}^{3+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}(\text{s})$, $E^\theta = +2.00 \text{ V}$
- Alternate Notation: $\text{Cu}(\text{s}) | \text{Cu}^{2+}(\text{aq}) || \text{Al}^{3+}(\text{aq}) | \text{Al}(\text{s})$, $E^\theta = -2.00 \text{ V}$
 - Note: Electrons flow from Al to Cu.

Example with Silver and Lead:

- Cell Diagram: $\text{Pb}(\text{s}) | \text{Pb}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}(\text{s})$, $E^\theta = +0.93 \text{ V}$

REPRESENTING HALF CELLS

1. **Vertical Solid Line (|):** Represents a phase boundary (e.g., between a solid and a solution).
2. **Double Vertical Line (||):** Represents a salt bridge between two half-cells.
3. **Species Order:** The species with the highest oxidation state is written next to the salt bridge.

Electromotive Force (Emf):

- When writing the emf (E^θ) value, indicate whether the right-hand electrode is positive or negative.
- General Formula for Emf:
$$E^\theta(\text{cell}) = E^\theta(\text{Right-hand electrode}) - E^\theta(\text{Left-hand electrode})$$

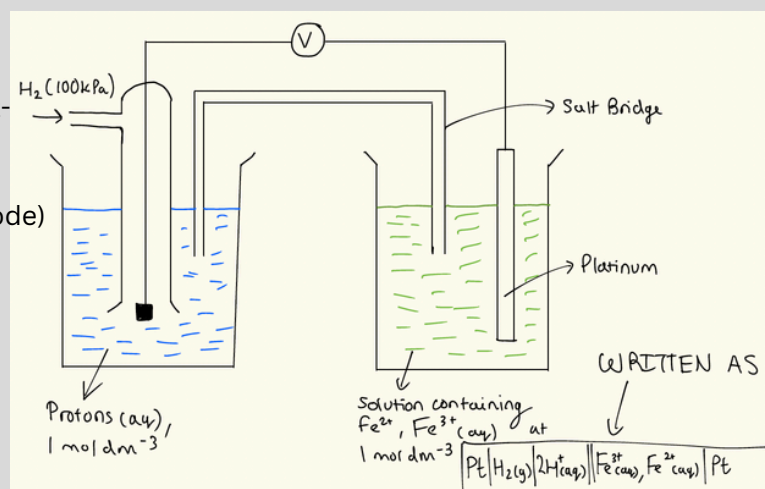
Example:

- Aluminium and Copper:
- $\text{Al}(\text{s}) | \text{Al}^{3+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}(\text{s})$, $E^\theta = +2.00 \text{ V}$
- (Electrons flow from aluminium to copper.)
- Alternate Notation:
- $\text{Cu}(\text{s}) | \text{Cu}^{2+}(\text{aq}) || \text{Al}^{3+}(\text{aq}) | \text{Al}(\text{s})$, $E^\theta = -2.00 \text{ V}$

Silver and Lead Cell:

- Cell Notation:
- $\text{Pb}(\text{s}) | \text{Pb}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}(\text{s})$, $E^\theta = +0.93 \text{ V}$

This shorthand follows standard conventions for writing electrochemical cells and allows easy interpretation of the flow of electrons.



FEASIBILITY OF REDOX REACTIONS USING STANDARD ELECTRODE POTENTIALS

- Direction of Electron Flow:
- Electrons flow from the more negative electrode to the more positive electrode.

Example:

- Zinc Half-Cell:
- $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$
- $E^\circ = -0.76 \text{ V}$
- Copper Half-Cell:
- $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$
- $E^\circ = +0.34 \text{ V}$

Direction of Reaction:

- Electrons flow from zinc to copper because zinc has a more negative potential.

Cell Diagram:

- $\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu}(\text{s})$
- $\text{emf} = E^\circ(\text{Cu}) - E^\circ(\text{Zn}) = +0.34 \text{ V} - (-0.76 \text{ V}) = +1.10 \text{ V}$

This positive emf indicates the reaction is feasible, with zinc being oxidized and copper reduced.

PREDICTING THE DIRECTION OF REDOX REACTIONS

Standard Electrode Potentials allow us to predict the feasibility of redox reactions by comparing the relative ease with which substances gain or lose electrons.

Key Concepts:

1. Electron Flow: Electrons always flow from the more negative to the more positive electrode. This helps determine the direction of the redox reaction.
2. Electrode Potential: Standard electrode potentials (E° values) show how easily a species gains electrons. A more negative E° indicates a better ability to lose electrons (better reducing agent).

Example of Zn and Cu Half Cells:

- Zinc Electrode: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$ ($E^\circ = -0.76 \text{ V}$)
- Copper Electrode: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ ($E^\circ = +0.34 \text{ V}$)

Since zinc has a more negative E° , it loses electrons (is oxidised), and copper gains electrons (is reduced).

Cell Representation:

- Zinc-Copper Cell: $\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu}(\text{s})$

EMF Calculation:

- $\text{emf} = E^\circ(\text{right-hand electrode}) - E^\circ(\text{left-hand electrode})$
- In this case:
 - $\text{emf} = +0.34 \text{ V} - (-0.76 \text{ V}) = +1.10 \text{ V}$.

Reaction:

The overall redox reaction is: $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

This reaction is feasible because the emf is positive.

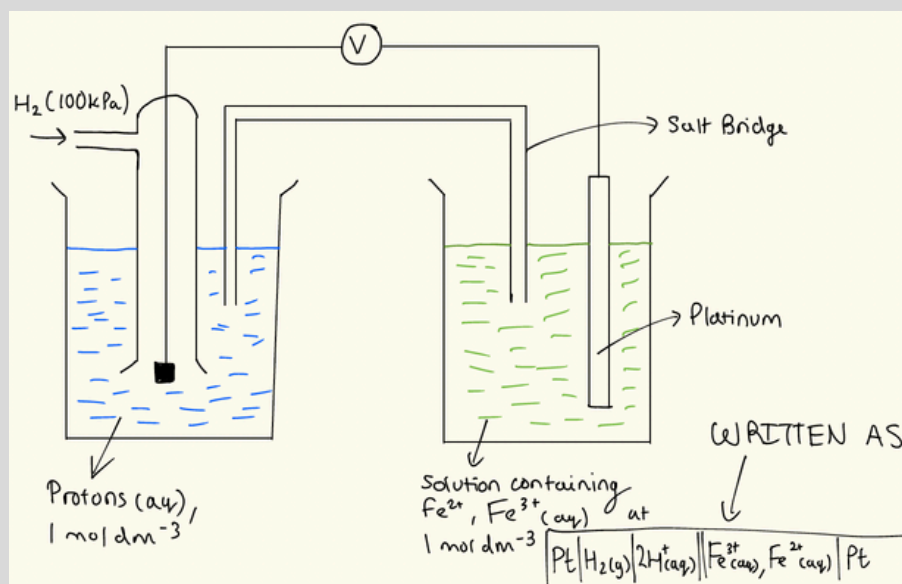
Extension:

For reactions involving ions only, like $\text{Fe}^{3+}/\text{Fe}^{2+}$, a platinum electrode is used. The more oxidised species (like Fe^{3+}) is written next to the salt bridge in the cell diagram:

- Example: $\text{Pt} \mid \text{Fe}^{2+}(\text{aq}), \text{Fe}^{3+}(\text{aq}) \parallel \text{Zn}^{2+}(\text{aq}) \mid \text{Zn}(\text{s})$

In exams, always use these steps to decide if a redox reaction is feasible.

EXAMPLE OF A CELL DIAGRAM



04-CHEM-3

ELECTRODE POTENTIALS

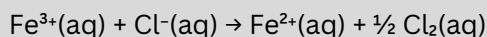


STANDARD ELECTRODE POTENTIALS FOR REDUCTION HALF EQUATIONS

Reduction Half-Equation	E° (V)
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.03
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Cr}^{2+}(\text{aq})$	-0.41
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^+(\text{aq})$	+0.15
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{I}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	+0.54
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.79
$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.07
$\text{Cl}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.70

WORKED EXAMPLE 1

Reaction to Predict:



We need to determine if this reaction is feasible by calculating the cell's emf (electromotive force).

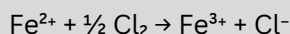
Standard Electrode Potentials:

- $\text{Fe}^{3+}/\text{Fe}^{2+}$: +0.77 V
- Cl_2/Cl^- : +1.36 V
- Hydrogen: 0.00 V (as reference)

Steps to Calculate emf:

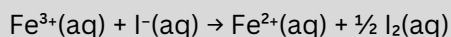
1. Identify the half-equations:
 - Oxidation: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$
 - Reduction: $\frac{1}{2} \text{Cl}_2 + \text{e}^- \rightarrow \text{Cl}^-$
2. Calculate the emf:
 - Use the formula: $\text{emf} = E^\circ (\text{right electrode}) - E^\circ (\text{left electrode})$
 - In this case: $\text{emf} = 1.36 \text{ V} - 0.77 \text{ V} = 0.59 \text{ V}$
3. Interpret the result:
 - Since the emf is positive (+0.59 V), the reaction is feasible.
 - Electrons will flow from $\text{Fe}^{2+}/\text{Fe}^{3+}$ (more negative) to Cl_2/Cl^- (more positive), meaning chlorine will oxidize Fe^{2+} to Fe^{3+} .

Final Reaction:



WORKED EXAMPLE 2

Reaction to Predict:



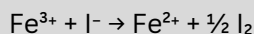
Standard Electrode Potentials:

- $\text{Fe}^{3+}/\text{Fe}^{2+}$: +0.77 V
- I_2/I^- : +0.54 V
- Hydrogen: 0.00 V (as reference)

Steps to Calculate emf:

1. Identify the half-equations:
 - Oxidation: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$
 - Reduction: $\frac{1}{2} \text{I}_2 + \text{e}^- \rightarrow \text{I}^-$
2. Calculate the emf:
 - Use the formula: $\text{emf} = E^\circ (\text{right electrode}) - E^\circ (\text{left electrode})$
 - In this case: $\text{emf} = 0.77 \text{ V} - 0.54 \text{ V} = 0.23 \text{ V}$
3. Interpret the result:
 - Since the emf is positive (+0.23 V), the reaction is feasible.
 - Electrons will flow from the I_2/I^- electrode to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ electrode, meaning iodine will reduce Fe^{3+} to Fe^{2+} .

Final Reaction:



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ELECTRODE POTENTIALS



INTRO TO ELECTROCHEMICAL CELLS AND BATTERIES- IN THE REAL WORLD

Modern devices like phones, tablets, and MP3 players rely heavily on batteries, which are based on electrochemical cells. Although a battery technically refers to multiple cells connected together, in everyday language, "battery" is used for almost any portable source of stored electricity.

In this section, we'll cover different types of cells and batteries, including both non-rechargeable and rechargeable types. For all batteries, the general principle involves a transfer of electrons from a more reactive substance to a less reactive one, which generates an emf (electromotive force). Let's explore these types of batteries and how they work.

NON RECHARGEABLE CELLS

1. Zinc/Copper Cells (Daniell Cell):

- Developed by John Daniell in the 1830s, the Daniell cell provides an emf of 1.1 V. This cell was historically used in telegraphs.
- Key principle: Electrons transfer from zinc, a more reactive metal, to copper, a less reactive metal.
- However, because the Daniell cell contains liquids, it wasn't suitable for portable devices.

2. Zinc/Carbon Cells (Leclanché Cell):

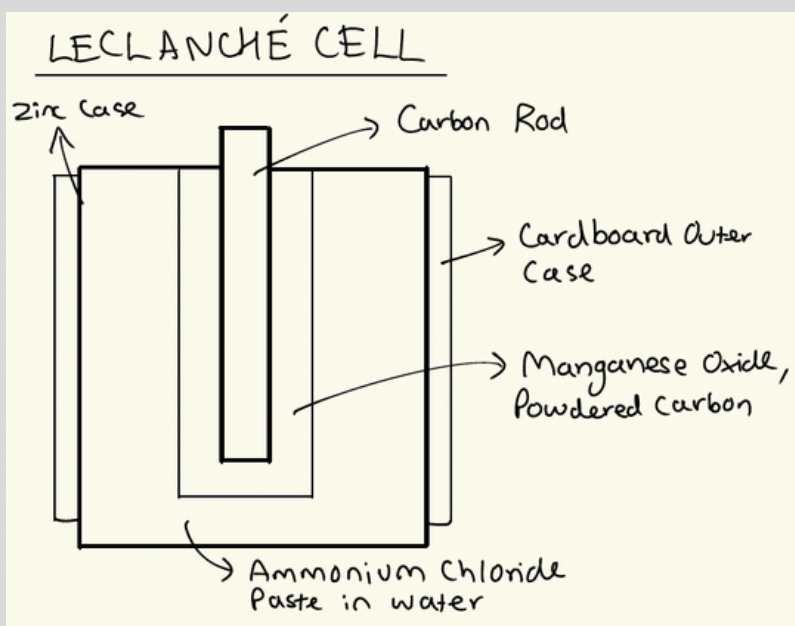
- In this type of cell, the positive electrode is made of carbon, and the electrolyte is a paste of ammonium chloride (NH_4Cl) and water.
- The commercial form of the Leclanché cell has a zinc canister as the negative electrode.
- Half-equations:
 - At the zinc electrode: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
 - At the carbon rod: $2\text{NH}_4^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{NH}_3(\text{g}) + \text{H}_2(\text{g})$
- The overall reaction when the cell discharges:
 - $2\text{NH}_4^+(\text{aq}) + \text{Zn(s)} \rightarrow 2\text{NH}_3(\text{g}) + \text{H}_2(\text{g}) + \text{Zn}^{2+}(\text{aq})$
- The emf is approximately 1.5 V, with zinc being the negative terminal.

3. Zinc Chloride Cells:

- Similar to the Leclanché cell but uses zinc chloride as the electrolyte. These cells are marketed as "extra life" batteries and are better suited for higher currents.

4. Alkaline Batteries:

- Long-life alkaline batteries use potassium hydroxide as the electrolyte. These cells provide higher currents and last longer than zinc-carbon batteries.
- Suitable for devices requiring continuous high currents, like personal stereos.



NON RECHARGEABLE CELLS

Rechargeable batteries can be reused multiple times by reversing the cell reactions. This is done by applying an external voltage higher than the cell's emf to drive electrons in the opposite direction.

Lead-Acid Batteries:

- Used in cars, lead-acid batteries are made up of six 2 V cells connected in series to give a total of 12 V.
- Components:
 - The positive plate is coated with lead(IV) oxide (PbO_2).
 - The negative plate is made of lead (Pb).
- Half-equations when discharging:
 - At the lead plate: $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$
 - At the PbO_2 -coated plate: $\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$
- The overall discharge reaction:
 - $\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq}) + \text{Pb(s)} \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$
- emf = 2 V for each cell.

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ELECTRODE POTENTIALS



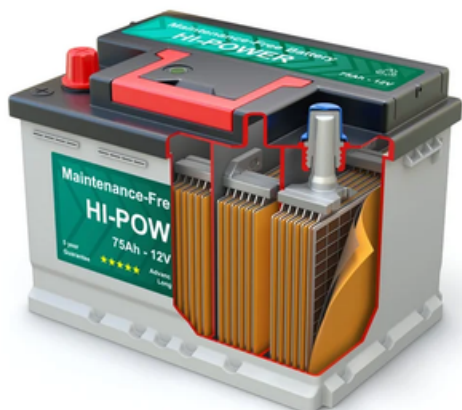
RECHARGEABLE CELLS- CONTINUED

1. Nickel/Cadmium (NiCd) Batteries:

1. These batteries are rechargeable up to 500 times and are used in standard-sized devices like radios or torches.
2. Half-equations:
 1. $\text{Cd}(\text{OH})_2(\text{s}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s}) + 2\text{OH}^-(\text{aq})$
 2. $\text{NiO}(\text{OH})(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{e}^- \rightarrow \text{Ni}(\text{OH})_2(\text{s}) + \text{OH}^-(\text{aq})$
3. Overall reaction: $2\text{NiO}(\text{OH})(\text{s}) + \text{Cd}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Ni}(\text{OH})_2(\text{s}) + \text{Cd}(\text{OH})_2(\text{s})$
4. $\text{emf} = 1.2 \text{ V}$.

2. Lithium-Ion Batteries:

1. Used in laptops, tablets, and smartphones, these batteries are lightweight and can be recharged without fully discharging.
2. The positive electrode is made of lithium cobalt oxide (LiCoO_2), while the negative electrode is made of carbon.
3. The emf ranges from 3.5 V to 4.0 V, providing higher voltage compared to other cells.



THE ALKALINE HYDROGEN-OXYGEN FUEL CELL

Fuel cells produce electricity by reacting hydrogen with oxygen. In an alkaline hydrogen-oxygen fuel cell, the following reactions occur:

1. At the negative electrode:

- $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$
- $\text{emf} = -0.83 \text{ V}$.

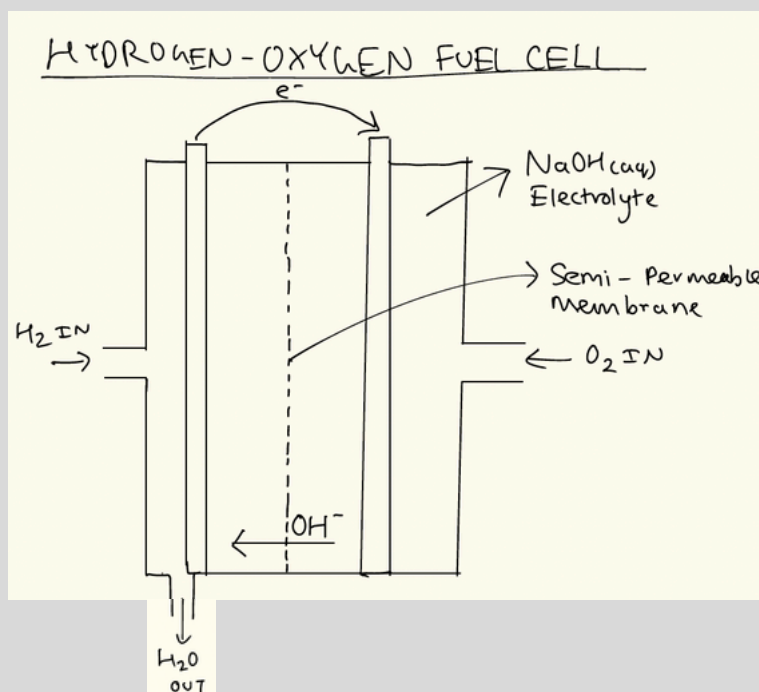
2. At the positive electrode:

- $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$
- $\text{emf} = +0.40 \text{ V}$.

The overall reaction:

- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$, with an overall emf of 1.23 V.

These cells are particularly useful because they produce only water as a by-product, making them ideal for spacecraft. However, challenges include the source of hydrogen, storage issues, and the need for an infrastructure to support hydrogen-powered vehicles.



04-CHEM-4

ACIDS AND BASES



WHAT IS AN ACID?

Here's a structured version of the Brønsted-Lowry theory of acidity and the related concepts in bullet points:

Brønsted-Lowry Theory

- **Definition:**
 - Acid: A substance that donates a proton (H^+).
 - Base: A substance that accepts a proton.

Example Reactions

- Hydrogen Chloride and Ammonia:
 - Reaction: $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
 - Roles:
 - HCl acts as an acid (donates a proton).
 - NH_3 acts as a base (accepts a proton).
- Sulfuric Acid and Nitric Acid:
 - Reaction: $H_2SO_4 + HNO_3 \rightarrow HNO_3^+ + HSO_4^-$
 - Roles:
 - H_2SO_4 donates a proton (acts as an acid).
 - HNO_3 accepts a proton (acts as a base).

Water as an Acid and Base

- Water Accepting a Proton:
 - Reaction: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$
 - H_2O acts as a base.
- Water Donating a Proton:
 - Reaction: $H_2O + NH_3 \rightarrow OH^- + NH_4^+$
 - H_2O acts as an acid.

Proton in Aqueous Solutions

- Representation:
 - In aqueous solutions, H^+ is often represented as H_3O^+ (hydronium ion).
 - H^+ ions bond with water molecules.

Ionisation of Water

- Self-Ionization:
 - Reaction: $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
 - This represents an acid-base reaction between two water molecules.

Equilibrium Expression

- Ionic Product of Water (K_w):
 - $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ mol}^2/\text{dm}^3$ at 298 K.
 - Concentration of H_3O^+ and OH^- in pure water at 298 K is $1.0 \times 10^{-7} \text{ mol}/\text{dm}^3$.



pH CALCULATIONS- INTRODUCTION

Acidity and pH

- Definition of pH:
 - $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$
 - Square brackets indicate concentration in mol/dm^3 .
- Historical Context:
 - The pH scale was introduced by Søren Sørensen in 1909 while studying brewing at Carlsberg.
 - He needed a way to express very small acid concentrations without awkward numbers.

pH Scale Characteristics

- Interpretation:
 - Smaller pH values indicate greater concentrations of $\text{H}^+(\text{aq})$.
 - A change of 1 pH unit represents a tenfold change in $[\text{H}^+]$.
- Neutral Solution:
 - At 298 K, $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1.0 \times 10^{-14} \text{ mol}^2/\text{dm}^3$.
 - In neutral solutions: $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})] = 1.0 \times 10^{-7} \text{ mol/dm}^3$.
 - pH of neutral solution at 298 K is 7.00.

Measuring pH

- Methods:
 - Indicator Paper: Changes color based on acidity.
 - pH Meter: Provides precise measurements using an electrode.

Acidity and Alkalinity

- Acidic Solution: $[\text{H}^+(\text{aq})] > [\text{OH}^-(\text{aq})]$, $\text{pH} < 7$.
- Alkaline Solution: $[\text{H}^+(\text{aq})] < [\text{OH}^-(\text{aq})]$, $\text{pH} > 7$.

Calculating $[\text{H}^+(\text{aq})]$ from pH

- Example:
 - For $\text{pH} = 3.00$:
 - $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$
 - **Rearranging gives: $[\text{H}^+(\text{aq})] = 1.0 \times 10^{-3} \text{ mol/dm}^3$.**

Calculating $[\text{OH}^-(\text{aq})]$ from pH

- Example:
 - For $\text{pH} = 10.00$:
 - $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$
 - Rearranging gives: $[\text{H}^+(\text{aq})] = 1.0 \times 10^{-10} \text{ mol/dm}^3$.
 - Using K_w :
 - $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1.0 \times 10^{-14} \text{ mol}^2/\text{dm}^3$.
 - Substitute $[\text{H}^+(\text{aq})]$ to find: $[\text{OH}^-(\text{aq})] = 1.0 \times 10^{-4} \text{ mol/dm}^3$.

pH of Strong Acid Solutions

- Strong Acids:
 - Example: HCl dissociates completely in dilute aqueous solution:
 - Reaction: $\text{HCl}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$.
- Concentration Calculations:
 - For 1.00 mol/dm^3 HCl:
 - $[\text{H}^+(\text{aq})] = 1.00 \text{ mol/dm}^3$.
 - $\text{pH} = 0.00$.
 - For 0.16 mol/dm^3 HCl:
 - $[\text{H}^+(\text{aq})] = 0.16 \text{ mol/dm}^3$.
 - $\text{pH} = -\log(0.16) \approx 0.80$ (to 2 d.p.).



pH CALCULATIONS- WORKED EXAMPLES

Worked Example: pH of Alkaline Solutions

To find the $[H^+(aq)]$ of an alkaline solution at 298 K:

1. Calculate $[OH^-(aq)]$.
2. Use the equation: $[H^+(aq)][OH^-(aq)] = 1.00 \times 10^{-14} \text{ mol}^2/\text{dm}^3$ to calculate $[H^+(aq)]$.

Example Calculation: $1.00 \text{ mol}/\text{dm}^3$ Sodium Hydroxide Solution

- Dissociation:
 - $\text{NaOH}(aq) \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq)$.
- Concentration:
 - $[OH^-(aq)] = 1.00 \text{ mol}/\text{dm}^3$.

Step 1: Calculate $[H^+(aq)]$

- Using K_w :
 - $[H^+(aq)][OH^-(aq)] = 1.00 \times 10^{-14} \text{ mol}^2/\text{dm}^3$.
 - $[H^+(aq)] \times 1.00 = 1.00 \times 10^{-14}$.
 - $[H^+(aq)] = 1.00 \times 10^{-14} \text{ mol}/\text{dm}^3$.

Step 2: Calculate pH

- $\text{pH} = -\log_{10}[H^+(aq)]$.
- $\text{pH} = -\log_{10}(1.00 \times 10^{-14}) = 14.00$.

Example Calculation: $0.100 \text{ mol}/\text{dm}^3$ Sodium Hydroxide Solution

- Concentration:
 - $[OH^-(aq)] = 0.100 \text{ mol}/\text{dm}^3$.

Step 1: Calculate $[H^+(aq)]$

- Using K_w :
 - $[H^+(aq)][OH^-(aq)] = 1.00 \times 10^{-14} \text{ mol}^2/\text{dm}^3$.
 - $[H^+(aq)] \times 0.100 = 1.00 \times 10^{-14}$.
 - $[H^+(aq)] = 1.00 \times 10^{-14} / 0.100 = 1.00 \times 10^{-13} \text{ mol}/\text{dm}^3$.

Step 2: Calculate pH

- $\text{pH} = -\log_{10}[H^+(aq)]$.
- $\text{pH} = -\log_{10}(1.00 \times 10^{-13}) = 13.00$.

WEAK/STRONG ACIDS AND BASES, AND pKa

Strong Acids and Bases

- Definition: Strong acids completely dissociate into ions in aqueous solutions.
 - Example: Hydrochloric acid (HCl) $\rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$.
- Dilution: Strong acids can be very dilute while remaining strong.
- Strong Bases: Similarly, strong bases completely dissociate in aqueous solutions.
 - Example: Sodium hydroxide (NaOH) $\rightarrow \text{Na}^+(aq) + \text{OH}^-(aq)$.

Weak Acids and Bases

- Definition: Weak acids and bases are only slightly ionized in water.
 - Example: Ethanoic acid (acetic acid) has a low degree of dissociation.
- Equilibrium Setup:
 - For ethanoic acid: $\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq)$.
- Before Dissociation:
 - 1000 molecules: 996 remain as CH_3COOH , 4 dissociate.
- Weak Acids: The degree of dissociation is low, even in high concentrations.

Acid Dissociation Constant (K_a)

- Expression: For a weak acid HA :
 - $K_a = [H^+(aq)][A^-(aq)] / [HA(aq)]$.
- Larger K_a : Indicates more dissociation, making the acid stronger.
- Units of K_a : mol/dm^3 .

Calculating the pH of Weak Acids

Example: $1.00 \text{ mol}/\text{dm}^3$ Ethanoic Acid

1. Equilibrium Expression:

- Before dissociation:
 - $[\text{CH}_3\text{COOH}] = 1.00$, $[\text{CH}_3\text{COO}^-] = 0$, $[H^+] = 0$.
- At equilibrium:
 - $[\text{CH}_3\text{COOH}] = 1.00 - x$, $[\text{CH}_3\text{COO}^-] = x$, $[H^+] = x$.

2. Set Up Equation:

- $K_a = [H^+][\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}]$.
- Using K_a for ethanoic acid: $1.70 \times 10^{-5} \text{ mol}/\text{dm}^3$.
- $1.70 \times 10^{-5} = x^2 / (1.00 - x)$.
- Approximate: $1.00 - x \approx 1.00$.
- Therefore, $1.70 \times 10^{-5} = x^2 / 1.00$.
- Solve for x : $[H^+] = 1.30 \times 10^{-3} \text{ mol}/\text{dm}^3$.

3. Calculate pH:

- $\text{pH} = -\log_{10}(1.30 \times 10^{-3}) \approx 2.89$ (to 2 d.p.).

Example: $0.100 \text{ mol}/\text{dm}^3$ Ethanoic Acid

1. Equilibrium Expression:

- $K_a = [H^+][\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}]$.
- $1.70 \times 10^{-5} = x^2 / (0.100 - x)$.
- Approximate: $0.100 - x \approx 0.100$.
- Therefore, $1.70 \times 10^{-5} = x^2 / 0.100$.
- Solve for x : $[H^+] = 1.30 \times 10^{-3} \text{ mol}/\text{dm}^3$.

2. Calculate pH:

- $\text{pH} = -\log_{10}(1.30 \times 10^{-3}) \approx 2.89$ (to 2 d.p.).

pKa

- Definition: $\text{pKa} = -\log_{10}(K_a)$.
- Utility: pKa indicates the strength of a weak acid; smaller pKa values indicate stronger acids.

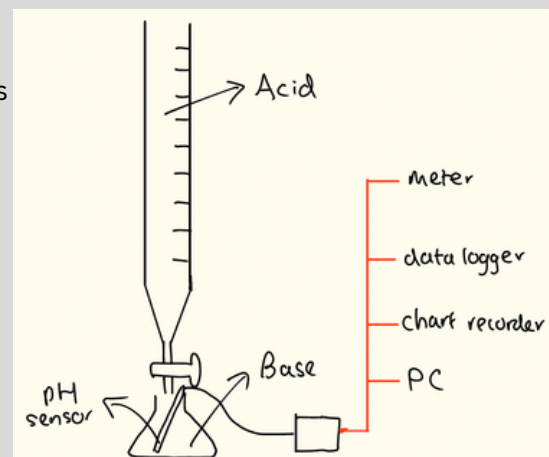
ACID-BASE TITRATIONS, AN INTRO

Overview of Acid-Base Titration

- **Definition:** A process where an acid of known concentration is added to a base (alkali) or vice versa until neutralization occurs.
- **Indicators:** Typically, an indicator shows when the reaction reaches neutralization. Alternatively, a pH meter can be used to monitor pH changes directly.
- **Calculation:** The concentration of the alkali can be calculated from the volume of acid used during titration.

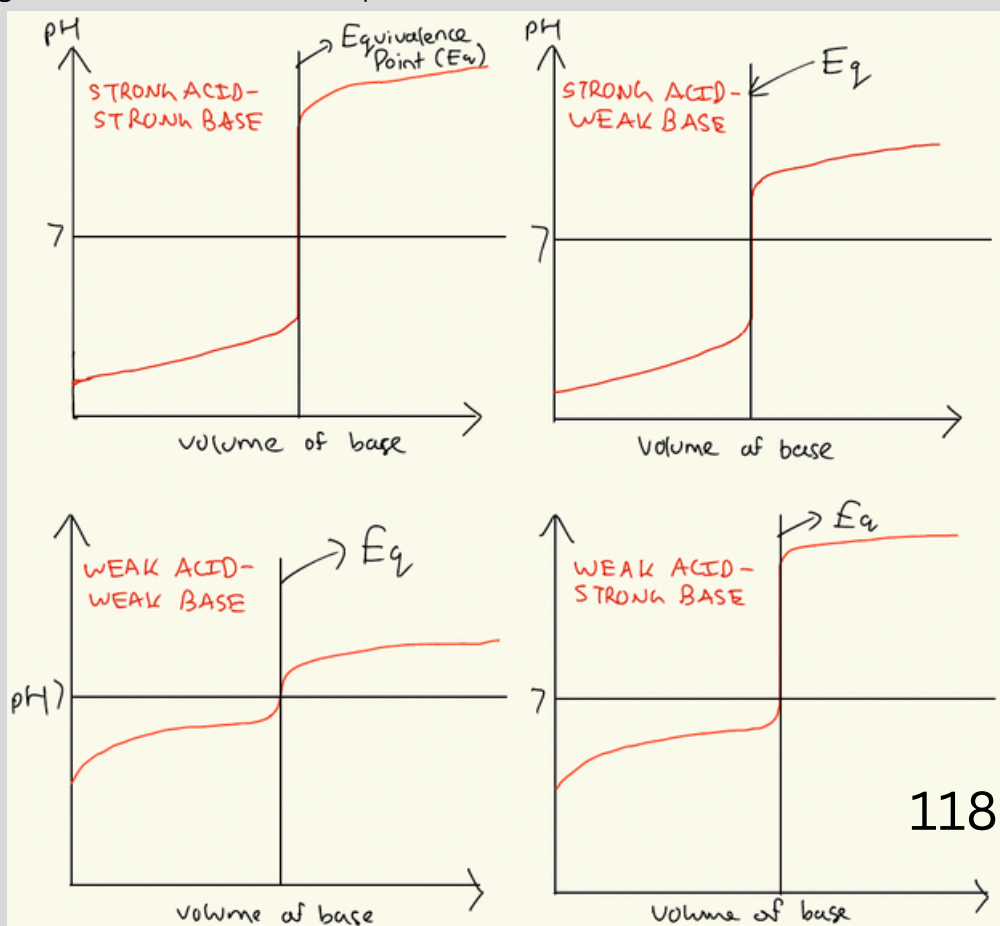
Titration Procedure

- **Apparatus:**
 - Burette filled with the acid or base.
 - Conical flask containing the other solution.
 - pH meter for measuring pH.
- **Steps:**
 - a. Preparation: Use a pipette to place 25 cm³ of the acid into a conical flask.
 - b. Addition of Base:
 - Add the base from the burette, starting with 1 cm³ increments.
 - Record the pH after each addition.
 - c. Precision in Rapid Change Areas:
 - Where the pH changes rapidly, repeat the addition by reducing increments to 0.1 cm³ for more accurate readings.
- **Calibration:**
 - The pH meter is calibrated using a buffer solution of known pH.



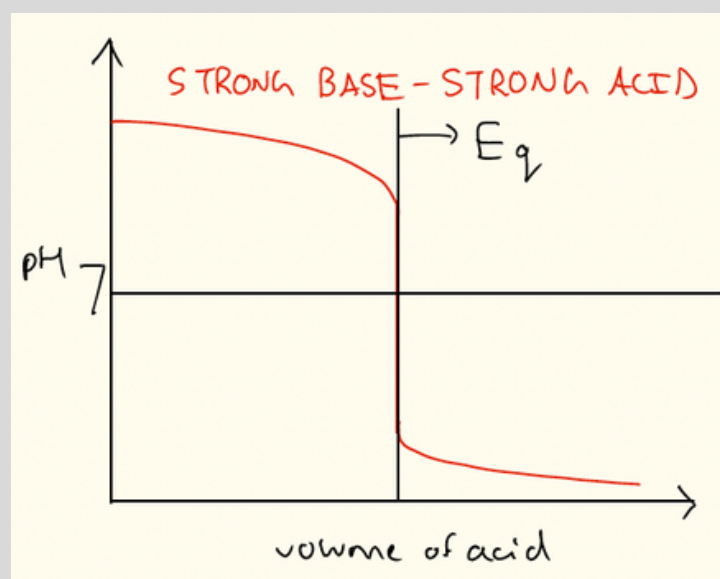
ACID-BASE TITRATIONS, AN INTRO

- **Graphing:** The resulting data can be plotted to create a titration curve, which shows how pH changes as the titrant is added.
- **Interpreting Curves:**
 - The steep part of the curve indicates a rapid change in pH, typically near the equivalence point where neutralization occurs.



OBSERVATIONS FROM TITRATION CURVES

- **Non-Linear pH Changes:**
 - The pH does not change linearly as the base is added.
 - Horizontal Sections:
 - These sections indicate that a significant amount of base can be added without a substantial change in pH.
- **Steep Portions:**
 - Each curve (except for weak acid-weak base) features a steep section where a small addition of base (like a single drop) can change the pH by several units.
- **Equivalence Point:**
 - Defined as the point at which sufficient base has been added to completely neutralize the acid (or vice versa).
 - In the titrations being discussed, the equivalence point occurs after 25.0 cm³ of base has been added.
 - pH at Equivalence Point:
 - The pH at the equivalence point is not always exactly 7.
 - There is often a significant and rapid change in pH at this point, indicated by an almost vertical curve.
- **Choice of Indicator:**
 - The rapid change in pH at the equivalence point is relevant when selecting an indicator for a specific titration.
- **Reversed Titration:**
 - When adding acid to base, the shape of the curve is flipped around the pH 7 line.
 - For example, a strong acid-strong base titration curve can illustrate this reversal.



WORKED EXAMPLE: A MONOPROTIC ACID

Example 1: Monoprotic Acid

- Titration Details:
 - Volume of NaOH = 25.00 cm³
 - Concentration of NaOH = 0.0150 mol dm⁻³
 - Volume of HCl = 15.00 cm³
- Reaction:
 - $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$
- Moles of NaOH:
 - Formula: Number of moles = $c \times (V/1000)$
 - Calculation:
 - Number of moles of NaOH = $25.00 \times 0.0150 / 1000$
 - Number of moles of NaOH = 0.000375 moles
- Moles of HCl:
 - At equivalence point, moles of HCl = moles of NaOH
 - Calculation:
 - $15.00 \times A / 1000 = 0.000375$
 - $A = 0.0250 \text{ mol dm}^{-3}$

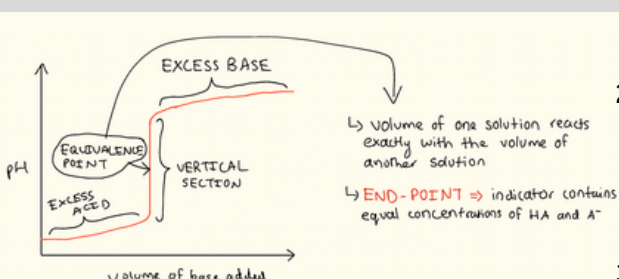
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ACIDS AND BASES



WORKED EXAMPLE: A DIPROTIC ACID

- **Titration Details:**
 - Volume of NaOH = 20.00 cm³
 - Concentration of NaOH = 0.0100 mol dm⁻³
 - Volume of H₂SO₄ = 15.00 cm³
- **Reaction:**
 - $\text{H}_2\text{SO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
- **Moles of NaOH:**
 - Calculation:
 - Number of moles of NaOH = $20.00 \times 0.0100 / 1000$
 - Number of moles of NaOH = 0.000200 moles
- **Moles of H₂SO₄:**
 - At equivalence point, moles of H₂SO₄ = 1/2 moles of NaOH
 - Calculation:
 - Number of moles of H₂SO₄ = $0.000200 / 2 = 0.000100$ moles
- **Concentration of H₂SO₄:**
 - Calculation:
 - Concentration (B) = Number of moles of H₂SO₄ / (Volume in dm³)
 - B = $0.000100 / (15.00/1000)$
 - B = 0.00667 mol dm⁻³
- **Conclusion:** The concentration of the acid (H₂SO₄) is 0.00667 mol dm⁻³.



CHOOSING AN INDICATOR FOR TITRATIONS

Key Concepts for Choosing a Suitable Indicator:

- **Equivalence Point:** The volume at which equal moles of H⁺ and OH⁻ have been added during a titration.
- **End Point:** The volume of titrant added when the indicator changes color.

Requirements for a Suitable Indicator:

1. **Sharp Colour Change:** The indicator should change color with no more than one drop of titrant. Gradual changes over several cm³ are unsuitable.
2. **Match of End Point and Equivalence Point:** The end point given by the indicator should align with the equivalence point to avoid inaccurate titration results.
3. **Distinct Colour Change:** The color change should be easily distinguishable (e.g., phenolphthalein from colorless to pink is more visible than methyl orange from red to yellow).

Examples of Indicator Suitability:

- **Phenolphthalein and methyl orange** are two common indicators used in titrations, but their suitability depends on the type of titration.
- **Phenolphthalein:** Suitable for titrations involving strong bases and weak acids (e.g., NaOH vs. CH₃COOH).
- **Methyl Orange:** Suitable for titrations involving strong acids and weak bases (e.g., HCl vs. NH₃).

WORKED EXAMPLE: A DIPROTIC ACID

1. Strong Acid-Strong Base (e.g., HCl + NaOH)

- pH curve: Large vertical section around equivalence point.
- Suitable Indicators: Both phenolphthalein and methyl orange.
 - Phenolphthalein is usually preferred due to its distinct color change (colorless to pink).

2. Weak Acid-Strong Base (e.g., CH₃COOH + NaOH)

- pH curve: Vertical section around the equivalence point, but not at pH 7.
- Suitable Indicator: Phenolphthalein.
 - Methyl orange is not suitable because it changes color too early, outside the vertical portion of the curve.

3. Strong Acid-Weak Base (e.g., HCl + NH₃)

- pH curve: Vertical portion near the equivalence point, but not at pH 7.
- Suitable Indicator: Methyl orange.
 - Phenolphthalein is not suitable because it changes color too late.

4. Weak Acid-Weak Base (e.g., CH₃COOH + NH₃)

- pH curve: No distinct vertical portion.
- Suitable Indicators: None.
 - No indicator can provide a sharp color change due to the absence of clear vertical section in the pH curve.



HALF NEUTRALISATION POINT

- **Location on the curve:** The half-neutralisation point occurs halfway between the start of the titration and the equivalence point on a titration curve.
 - This is where half of the weak acid (HA) has been converted into its conjugate base (A⁻).
 - The pH changes very little around this point, which is useful in buffer theory.
- **Significance:**
 - At the half-neutralisation point, the concentrations of the weak acid (HA) and its conjugate base (A⁻) are equal.
 - This relationship can be used to find the pK_a of the weak acid because:
 - $[HA] = [A^-]$, so the equation for the acid dissociation constant becomes: $K_a = [H^+]$
 - Therefore, $pK_a = pH$ at the half-neutralisation point.

This concept is important for understanding buffer solutions and provides a practical way to determine the pK_a of a weak acid during a titration.

WHAT ARE BUFFERS?

Buffers are solutions that resist changes in pH when small amounts of acid or alkali are added. They work by keeping the concentration of hydrogen ions (H⁺) and hydroxide ions (OH⁻) relatively constant.



HOW TO MAKE BUFFERS?

Creating Buffers

- One way to create an acidic buffer is to neutralise some of the weak acid with an alkali (e.g., sodium hydroxide). If half the acid is neutralised, the resulting buffer will have a pH equal to the pK_a of the acid because $[HA] = [A^-]$.

At half-neutralisation:

- $pH = pK_a$
- This creates a buffer that resists changes in pH from both added acid and alkali.

HOW DO BUFFERS WORK? AND SOME BUFFER EXAMPLES

- Buffers rely on an equilibrium reaction that shifts to counteract any added H⁺ or OH⁻ ions.

Acidic Buffers

Acidic buffers are made from weak acids and their salts. They maintain a pH below 7 by resisting changes in pH when small amounts of acid or alkali are added.

- Weak acid dissociation:
 - $HA \rightleftharpoons H^+ + A^-$

In an acidic buffer:

- The weak acid (HA) dissociates very little, so $[H^+]$ and $[A^-]$ are small.

Adding Alkali (OH⁻)

- If OH⁻ ions are added, they react with the weak acid:
 - $HA + OH^- \rightarrow A^- + H_2O$
 - This removes the added OH⁻ ions, preventing a significant change in pH.

Adding Acid (H⁺)

- If H⁺ ions are added, the equilibrium shifts to the left:
 - $H^+ + A^- \rightarrow HA$
 - This uses up added H⁺ ions, maintaining pH.

However, since $[A^-]$ is small, the supply of A⁻ will run out if enough acid is added. To maintain buffering capacity, a soluble salt of the acid (e.g., Na⁺ A⁻) can be added to increase $[A^-]$.

Components of an Acidic Buffer

- The weak acid (HA) removes any added OH⁻:
 - $HA + OH^- \rightarrow A^- + H_2O$
- The salt provides A⁻ ions to remove any added H⁺:
 - $A^- + H^+ \rightarrow HA$

Buffer Limitations

- Buffers don't completely prevent changes in pH, but they significantly reduce the change compared to non-buffered solutions.
- Buffers can be saturated if too much acid or alkali is added, using up all available HA or A⁻.

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ACIDS AND BASES



BASIC BUFFERS

Basic buffers resist changes in pH but maintain a pH above 7. They are made from a mixture of a weak base and a salt of that base.

Example: Aqueous Ammonia and Ammonium Chloride Buffer

In a mixture of aqueous ammonia (NH_3) and ammonium chloride ($\text{NH}_4^+ \text{Cl}^-$), the buffer works as follows:

- Ammonia (NH_3) removes any added H^+ ions:
 - $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$
- Ammonium ion (NH_4^+) removes any added OH^- ions:
 - $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$

Buffer Systems in Blood

One important buffer system in the body is found in blood, which maintains a pH of 7.4. A small change of as little as 0.5 pH units can be fatal.

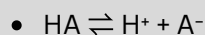
- The main buffer system in blood involves the following equilibrium:
 - $\text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O}$
- If H^+ ions are added, the equilibrium shifts to the right, removing H^+ by forming water and CO_2 .
- If OH^- ions are added, the equilibrium shifts to the left, releasing H^+ to neutralise the OH^- ions.

Buffers in Everyday Products

Buffers are commonly used in products like detergents and shampoos to maintain a consistent pH and prevent damage to fabric or skin/hair.

Buffer Calculations

Different buffers can be formulated to maintain different pH values. The dissociation of a weak acid can be represented as:



The equilibrium expression for this reaction is:

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

This expression can be used to calculate the pH of a buffer solution by rearranging the terms.

WORKED EXAMPLE 1

A buffer consists of $0.100 \text{ mol dm}^{-3}$ ethanoic acid and $0.100 \text{ mol dm}^{-3}$ sodium ethanoate. What is the pH of the buffer? Given:

- K_a for ethanoic acid = 1.7×10^{-5}
- $\text{p}K_a = 4.77$

Step 1: Use the equation for K_a

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

Since sodium ethanoate is fully dissociated, $[\text{A}^-] = 0.100 \text{ mol dm}^{-3}$, and ethanoic acid is almost undissociated, so $[\text{HA}] \approx 0.100 \text{ mol dm}^{-3}$.

$$1.7 \times 10^{-5} = \frac{[\text{H}^+] \times 0.100}{0.100}$$

Step 2: Solve for $[\text{H}^+]$

$$[\text{H}^+] = 1.7 \times 10^{-5}$$

Step 3: Calculate the pH

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}(1.7 \times 10^{-5}) = 4.77$$

Conclusion:

When you have equal concentrations of acid and salt, the pH of the buffer is equal to the $\text{p}K_a$ of the acid used, which is 4.77 in this case. This is also the same situation as the half-neutralisation point.

WORKED EXAMPLE 2

Calculate the pH of the buffer formed when 500 cm^3 of $0.400 \text{ mol dm}^{-3}$ NaOH is added to 500 cm^3 of 1.00 mol dm^{-3} HA. Given:

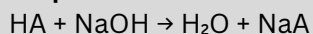
- $K_a = 6.25 \times 10^{-5}$

Step 1: Calculate moles of HA and NaOH

$$\text{Moles of HA} = c \times V / 1000 = 1.00 \times 500 / 1000 = 0.500 \text{ mol}$$

$$\text{Moles of NaOH} = \text{Moles of OH}^- = 0.400 \times 500 / 1000 = 0.200 \text{ mol}$$

Step 2: Write the reaction



- Initially: 0.500 mol HA , 0.200 mol NaOH
- Finally: 0.300 mol HA , 0 mol NaOH , and 0.200 mol A^-

Step 3: Calculate concentrations of HA and A^-

Since the final volume is 1000 cm^3 :

$$[\text{HA}] = 0.300 \text{ mol} / 1 \text{ dm}^3 = 0.300 \text{ mol dm}^{-3}$$

$$[\text{A}^-] = 0.200 \text{ mol} / 1 \text{ dm}^3 = 0.200 \text{ mol dm}^{-3}$$

Step 4: Use the K_a expression

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

Substitute the values:

$$6.25 \times 10^{-5} = \frac{[\text{H}^+] \times 0.200}{0.300}$$

Step 5: Solve for $[\text{H}^+]$

$$[\text{H}^+] = (6.25 \times 10^{-5}) \times (0.300 / 0.200) = 9.375 \times 10^{-5}$$

Step 6: Calculate the pH

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}(9.375 \times 10^{-5}) = 4.03$$

Conclusion:

The pH of the buffer solution is 4.03.

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ACIDS AND BASES



WHAT HAPPENS TO pH WHEN ACID IS PUT INTO A BUFFER?

Let's calculate how the pH changes when acid is added to a buffer.

Suppose you start with 1.00 dm^3 of a buffer solution made of:

- 0.10 mol dm^{-3} ethanoic acid
- 0.10 mol dm^{-3} sodium ethanoate

The given K_a is 1.7×10^{-5} . The buffer initially has a pH of 4.77.

Step 1: Add Hydrochloric Acid

Now, 10.0 cm^3 of 1.00 mol dm^{-3} HCl is added to this buffer. Virtually all the added H^+ ions will react with the ethanoate ions (A^-), forming ethanoic acid (HA).

Step 2: Moles Before Adding Acid

Before adding the acid:

- Number of moles of ethanoic acid (HA) = 0.10 mol
- Number of moles of sodium ethanoate (A^-) = 0.10 mol

Step 3: Calculate Moles of Hydrochloric Acid Added

Moles of HCl added = $c \times V / 1000$

= $1.00 \text{ mol dm}^{-3} \times 10.0 \text{ cm}^3 / 1000$

= 0.010 mol HCl

Step 4: Moles After Adding Acid

After adding the HCl:

- The amount of ethanoic acid increases by 0.010 mol to 0.110 mol .
- The amount of sodium ethanoate decreases by 0.010 mol to 0.090 mol .

Step 5: Calculate New Concentrations

- $[\text{HA}] = 0.110 \text{ mol dm}^{-3}$
- $[\text{A}^-] = 0.090 \text{ mol dm}^{-3}$

(The small volume change from adding 10 cm^3 of HCl to 1000 cm^3 is ignored, as it only causes a 1% change.)

Step 6: Use the K_a Expression

$K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$

Substitute the values:

$1.7 \times 10^{-5} = [\text{H}^+] \times 0.090 / 0.110$

Step 7: Solve for $[\text{H}^+]$

$[\text{H}^+] = (1.7 \times 10^{-5}) \times (0.110 / 0.090)$

= $2.08 \times 10^{-5} \text{ mol dm}^{-3}$

Step 8: Calculate the pH

$\text{pH} = -\log_{10}[\text{H}^+]$

= $-\log_{10}(2.08 \times 10^{-5})$

= 4.68

Conclusion:

The pH changes from 4.77 to 4.68. Notice how small the pH change is, thanks to the buffer!

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ACIDS AND BASES



WHAT HAPPENS TO pH WHEN BASE IS PUT INTO A BUFFER?

Let's calculate how the pH changes when sodium hydroxide (NaOH) is added to the same buffer solution.

Starting with 1.00 dm³ of a buffer containing:

- 0.10 mol dm⁻³ ethanoic acid
- 0.10 mol dm⁻³ sodium ethanoate

The K_a of ethanoic acid is 1.7×10^{-5} . The initial pH of the buffer is 4.77.

Step 1: Add Sodium Hydroxide

Now, add 10.0 cm³ of 1.00 mol dm⁻³ NaOH to this buffer. The OH⁻ ions from the NaOH will react with H⁺ ions, and more HA (ethanoic acid) will ionise.

Step 2: Moles of Sodium Hydroxide Added

Moles of NaOH added = $c \times V / 1000$
= $1.00 \text{ mol dm}^{-3} \times 10.0 \text{ cm}^3 / 1000$
= 0.010 mol NaOH

Step 3: Moles After Adding Base

After adding NaOH:

- The amount of ethanoic acid (HA) decreases by 0.010 mol to 0.090 mol.
- The amount of sodium ethanoate (A⁻) increases by 0.010 mol to 0.110 mol.

Step 4: Calculate New Concentrations

- [HA] = 0.090 mol dm⁻³
- [A⁻] = 0.110 mol dm⁻³

Step 5: Use the K_a Expression

$K_a = [H^+][A^-] / [HA]$

Substitute the values:

$1.7 \times 10^{-5} = [H^+] \times 0.110 / 0.090$

Step 6: Solve for [H⁺]

$[H^+] = (1.7 \times 10^{-5}) \times (0.090 / 0.110)$
= $1.39 \times 10^{-5} \text{ mol dm}^{-3}$

Step 7: Calculate the pH

pH = $-\log_{10}[H^+]$
= $-\log_{10}(1.39 \times 10^{-5})$
= 4.89

Conclusion:

The pH changes from 4.77 to 4.89, again a very small change due to the buffer!



PHYSICAL TRENDS IN ELEMENTS OF PERIOD 3

- Metals on the left and non-metals on the right:
 - Sodium (Na), Magnesium (Mg), Aluminium (Al):**
 - Metallic elements
 - Shiny when freshly exposed to air
 - Conduct electricity
 - React with dilute acids to produce hydrogen and salts
 - Silicon (Si):**
 - A semi-metal (metalloid)
 - Conducts electricity to some extent
 - Useful for making semiconductors
 - Phosphorus (P), Sulfur (S), Chlorine (Cl):**
 - Non-metals
 - Do not conduct electricity
 - Have low melting and boiling points
 - Argon (Ar):**
 - A noble gas
 - Chemically unreactive
 - Exists as separate atoms



KEY TRENDS IN PHYSICAL PROPERTIES

Key Trends:

- Melting points decrease from left to right across the period due to a shift from giant ionic or covalent structures to molecular structures with weaker intermolecular forces.
- Ionic compounds (Na_2O , MgO , Al_2O_3) have higher melting points than covalent molecules (P_4O_{10} , SO_3 , SO_2).

For molecular compounds, larger molecules (like P_4O_{10}) have higher melting points due to stronger intermolecular forces (more electrons--> stronger van der Waals forces)

REDOX REACTIONS OF PERIOD 3 ELEMENTS

- All reactions involving Period 3 elements are redox reactions.
- The elements begin with an oxidation state of zero.
- Through reactions, they either gain or lose electrons, changing their oxidation states.

OXIDES OF ELEMENTS IN PERIOD 3

Metal Oxides (Sodium, Magnesium, Aluminium)

- Sodium Oxide (Na_2O), Magnesium Oxide (MgO), and Aluminium Oxide (Al_2O_3) form giant ionic lattices.
 - Ionic bonding extends throughout the structure, resulting in high melting points due to strong electrostatic forces between oppositely charged ions.
 - Aluminium oxide (Al_2O_3) has some covalent character (**amphoteric**) due to the small, highly charged aluminium ion (Al^{3+}) distorting the electron cloud of the O^{2-} ion. This introduces covalent character, making the bond less purely ionic.

Non-metal Oxides (Silicon, Phosphorus, Sulfur)

- Silicon Dioxide (SiO_2):**
 - Has a giant covalent (macromolecular) structure.
 - The strong covalent bonds extend throughout the structure, making the melting point very high since many covalent bonds must be broken to melt it.
- Phosphorus Oxides (P_4O_{10}):**
 - Phosphorus forms molecular compounds.
 - These exist as covalently bonded molecules with weak intermolecular forces (van der Waals and dipole-dipole interactions).
 - The melting points are relatively low compared to giant structures.
- Sulfur Dioxide (SO_2) and Sulfur Trioxide (SO_3):**
 - Both are molecular compounds.
 - SO_2 and SO_3 exist as gases at 298 K due to weak intermolecular forces.
 - Sulfur trioxide (SO_3) has a higher melting point than SO_2 due to the increase in molecular size and resulting stronger van der Waals forces.

Compound	Melting Point (K)	Bonding	Structure Type
Na_2O	1548	Ionic	Giant ionic
MgO	3125	Ionic	Giant ionic
Al_2O_3	2345	Ionic/Covalent	Giant ionic
SiO_2	1883	Covalent	Giant covalent
P_4O_{10}	573	Covalent	Molecular
SO_3	290	Covalent	Molecular
SO_2	200	Covalent	Molecular



REACTIONS OF PERIOD 3 ELEMENTS WITH WATER

- **Sodium (Na):**

- Reacts vigorously with cold water, forming sodium hydroxide and hydrogen gas.
- Sodium floats and fizzes on water, releasing heat.
- The resulting solution is strongly alkaline with a pH of 13-14.
- Equation:
- $2\text{Na(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{NaOH(aq)} + \text{H}_2\text{(g)}$

- **Magnesium (Mg):**

- Reacts very slowly with cold water, producing magnesium hydroxide and hydrogen gas.
- The solution is weakly alkaline with a pH around 10 because magnesium hydroxide is only sparingly soluble.
- Equation:
- $\text{Mg(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Mg(OH)}_2\text{(s)} + \text{H}_2\text{(g)}$
- The reaction is much faster with steam, forming magnesium oxide instead of hydroxide:
- Equation (with steam):
- $\text{Mg(s)} + \text{H}_2\text{O(g)} \rightarrow \text{MgO(s)} + \text{H}_2\text{(g)}$

- **Chlorine (Cl):**

- The only non-metal in Period 3 that reacts with water, forming hydrochloric acid and hypochlorous acid.

Reactions with Oxygen

- **Sodium (Na):**

- Burns in air with a yellow flame, producing sodium oxide.
- Equation:
- $4\text{Na(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{Na}_2\text{O(s)}$

- **Magnesium (Mg):**

- Burns in air with a bright white flame, forming magnesium oxide.
- Equation:
- $2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$

- **Aluminium (Al):**

- Burns brightly in oxygen, producing aluminium oxide.
- Aluminium forms a protective oxide layer that prevents further reaction.
- Equation:
- $4\text{Al(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Al}_2\text{O}_3\text{(s)}$

- **Silicon (Si):**

- Burns when strongly heated in oxygen, forming silicon dioxide.
- Equation:
- $\text{Si(s)} + \text{O}_2\text{(g)} \rightarrow \text{SiO}_2\text{(s)}$

- **Phosphorus (P):**

- Red phosphorus needs to be heated to react with oxygen, forming phosphorus pentoxide.
- White phosphorus ignites spontaneously in air.
- Equation:
- $4\text{P(s)} + 5\text{O}_2\text{(g)} \rightarrow \text{P}_4\text{O}_{10}\text{(s)}$
- If oxygen is limited, phosphorus trioxide (P_2O_3) may also form.

- **Sulfur (S):**

- Burns with a blue flame to form sulfur dioxide and small amounts of sulfur trioxide.
- Equation:
- $\text{S(s)} + \text{O}_2\text{(g)} \rightarrow \text{SO}_2\text{(g)}$

Redox Reactions

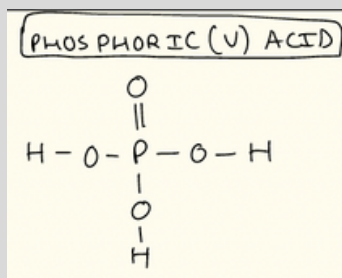
- In all these reactions, the oxidation state of the Period 3 element increases, while the oxidation state of oxygen decreases to -2.
- Moving from left to right across Period 3, the oxidation number of the elements in their oxides increases.



STRUCTURES OF OXO-ACIDS AND THEIR ANIONS

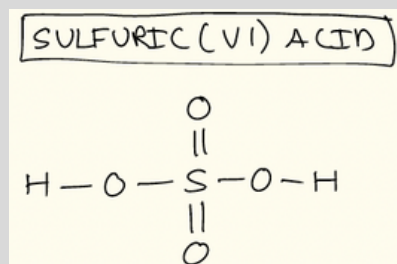
Phosphoric(V) Acid (H_3PO_4):

- Phosphorus (P) has 5 valence electrons.
- In phosphoric(V) acid, phosphorus forms 4 bonds with oxygen atoms, where one of the oxygen atoms is double bonded to phosphorus.
- However, due to delocalisation, the bonding electrons are spread equally over all the phosphorus-oxygen bonds, making them the same length.
- Shape: The phosphate(V) ion (PO_4^{3-}), formed after all hydrogens are lost as protons (H^+), has a perfect tetrahedral structure due to the equal distribution of bonding electrons.
- Bond angle in a perfect tetrahedron: 109.5° .



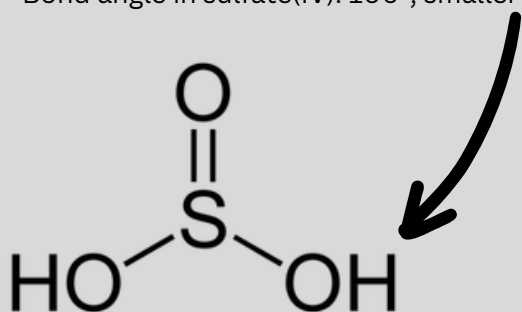
Sulfuric(VI) Acid (H_2SO_4):

- Sulfur (S) has 6 valence electrons.
- In sulfuric(VI) acid, sulfur forms 6 bonds with oxygen atoms, with two of the oxygen atoms double bonded to sulfur and the other two single bonded to hydroxyl groups ($-\text{OH}$).
- Similar to phosphate(V), delocalisation spreads the bonding electrons equally, giving the sulfate(VI) anion (SO_4^{2-}) a perfect tetrahedral structure.
- The sulfate(VI) anion has all four S-O bonds of the same length due to delocalisation.

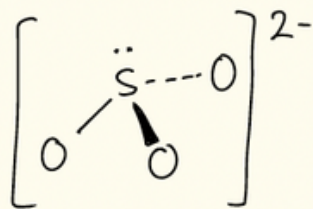


Sulfuric(IV) Acid (H_2SO_3):

- In sulfuric(IV) acid (also known as sulfurous acid), sulfur forms bonds with three oxygen atoms.
- The sulfate(IV) anion (SO_3^{2-}) has three S-O bonds, but due to delocalisation, the bonds are of equal length.
- Shape: The bonding in the sulfate(IV) ion is trigonal pyramidal due to the presence of a lone pair of electrons on the sulfur atom.
- Bond angle in sulfate(IV): 106° , smaller than the 109.5° of a perfect tetrahedron, due to the lone pair of electrons.



SULFATE (IV) ANION



REACTIONS OF OXIDES WITH WATER- BASIC OXIDES

Basic Oxides:

- Sodium Oxide (Na_2O):**
 - Reacts with water to form sodium hydroxide (NaOH), a strongly alkaline solution.
 - Equation: $\text{Na}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}^+(\text{aq}) + 2\text{OH}^-(\text{aq})$
 - pH of solution: ~ 14 (highly alkaline).
- Magnesium Oxide (MgO):**
 - Reacts with water to form magnesium hydroxide ($\text{Mg}(\text{OH})_2$), which is sparingly soluble in water and produces a mildly alkaline solution.
 - Equation: $\text{MgO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$
 - pH of solution: ~ 9 (moderately alkaline).



REACTIONS OF OXIDES WITH WATER- INSOLUBLE OXIDES AND ACIDIC OXIDES

Insoluble Oxides:

- Aluminium Oxide (Al_2O_3):
 - Insoluble in water, does not react.
- Silicon Dioxide (SiO_2):
 - Insoluble in water, does not react.

Acidic Oxides:

- Phosphorus Pentoxide (P_4O_{10}):
 - Reacts violently with water to produce phosphoric(V) acid (H_3PO_4), which ionises to form acidic solutions.
 - Equation:
 - $\text{P}_4\text{O}_{10}(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{H}_3\text{PO}_4(\text{aq})$
 - Ionisation (first stage):
 - $\text{H}_3\text{PO}_4(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq})$

Sulfur Dioxide (SO_2):

- Reacts with water to form sulfurous acid (H_2SO_3), which partially dissociates to give H^+ ions (acidic solution).
- Equation:
- $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_3(\text{aq})$
 - Ionisation:
 - $\text{H}_2\text{SO}_3(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HSO}_3^-(\text{aq})$

Sulfur Trioxide (SO_3):

- Reacts violently with water to produce sulfuric acid (H_2SO_4).
- Equation:
- $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$
 - Ionisation:
 - $\text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{HSO}_4^-(\text{aq})$

REACTIONS OF OXIDES WITH WATER- INSOLUBLE OXIDES AND ACIDIC OXIDES

Insoluble Oxides:

- Aluminium Oxide (Al_2O_3):
 - Insoluble in water, does not react.
- Silicon Dioxide (SiO_2):
 - Insoluble in water, does not react.

Acidic Oxides:

- Phosphorus Pentoxide (P_4O_{10}):
 - Reacts violently with water to produce phosphoric(V) acid (H_3PO_4), which ionises to form acidic solutions.
 - Equation:
 - $\text{P}_4\text{O}_{10}(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{H}_3\text{PO}_4(\text{aq})$
 - Ionisation (first stage):
 - $\text{H}_3\text{PO}_4(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq})$

SUMMARY OF TRENDS IN PERIOD 3

- Metal oxides (e.g., sodium, magnesium) on the left of Period 3 form alkaline solutions in water.
- Non-metal oxides (e.g., phosphorus, sulfur) on the right form acidic solutions.
- Oxides in the middle (e.g., aluminium, silicon) are typically insoluble in water and do not react.





EXPLANATION OF THE REACTION OF PERIOD 3 OXIDES WITH WATER

Oxide	Bonding	pH After Reaction with Water	Ions Present	Acidity/Alkalinity
Na ₂ O	Ionic	13-14	Na ⁺ (aq), OH ⁻ (aq)	Strongly alkaline
MgO	Ionic	~10	Mg ²⁺ (aq), OH ⁻ (aq)	Somewhat alkaline
Al ₂ O ₃	Covalent/Ionic	Insoluble	-	Neutral (pH ~7)
SiO ₂	Covalent	Insoluble	-	Neutral (pH ~7)
P ₄ O ₁₀	Covalent	1-2	H ⁺ (aq), H ₂ PO ₄ ⁻ (aq)	Fairly strong acid
SO ₂	Covalent	2-3	H ⁺ (aq), HSO ₃ ⁻ (aq)	Weak acid
SO ₃	Covalent	~0-1	H ⁺ (aq), HSO ₄ ⁻ (aq)	Strong acid

REACTIONS OF PERIOD 3 ELEMENTS WITH ACIDS AND BASES

Reactions of Period 3 Oxides with Acids and Bases

1. Sodium and Magnesium Oxides:

- Both sodium oxide (Na₂O) and magnesium oxide (MgO) are basic oxides and react with acids to form salt and water.
- Sodium Oxide + Sulfuric Acid:
 - Reaction: Na₂O(s) + H₂SO₄(aq) → Na₂SO₄(aq) + H₂O(l)
- Magnesium Oxide + Hydrochloric Acid:
 - Reaction: MgO(s) + 2HCl(aq) → MgCl₂(aq) + H₂O(l)

2. Aluminium Oxide (Al₂O₃):

- Amphoteric Oxide: Reacts with both acids and alkalis.
- Reaction with Acid (Hydrochloric Acid):
 - Reaction: Al₂O₃(s) + 6HCl(aq) → 2AlCl₃(aq) + 3H₂O(l)
- Reaction with Base (Hot, Concentrated Sodium Hydroxide):
 - Reaction: Al₂O₃(s) + 2NaOH(aq) + 3H₂O(l) → 2NaAl(OH)₄(aq)
 - (Sodium aluminate is formed)

KEY POINTS

- Sodium Oxide (Na₂O):**
 - Bonding: Ionic
 - Reactivity: Produces a strongly alkaline solution when dissolved in water, forming hydroxide ions (OH⁻).
 - Reaction: Na₂O + H₂O → 2Na⁺(aq) + 2OH⁻(aq)
- Magnesium Oxide (MgO):**
 - Bonding: Ionic
 - Reactivity: Produces a somewhat alkaline solution, less soluble than Na₂O, leading to fewer hydroxide ions in solution.
 - Reaction: MgO + H₂O → Mg²⁺(aq) + 2OH⁻(aq)
- Aluminium Oxide (Al₂O₃):**
 - Bonding: Both ionic and covalent
 - Reactivity: Insoluble in water due to strong bonding, so no reaction with water.
- Silicon Dioxide (SiO₂):**
 - Bonding: Covalent, macromolecular structure
 - Reactivity: Insoluble in water, does not react.
- Phosphorus Pentoxide (P₄O₁₀):**
 - Bonding: Covalent
 - Reactivity: Reacts with water to form phosphoric acid (H₃PO₄), which is a fairly strong acid.
 - Reaction: P₄O₁₀ + 6H₂O → 4H₃PO₄
- Sulfur Dioxide (SO₂):**
 - Bonding: Covalent
 - Reactivity: Forms sulfurous acid (H₂SO₃) in water, which dissociates to give a weak acidic solution.
 - Reaction: SO₂ + H₂O → H₂SO₃
- Sulfur Trioxide (SO₃):**
 - Bonding: Covalent
 - Reactivity: Reacts violently with water to form sulfuric acid (H₂SO₄), a strong acid.
 - Reaction: SO₃ + H₂O → H₂SO₄

General Trend:

- As you move from left to right across Period 3, the solutions of the oxides change from alkaline (basic) to acidic, with the oxides in the middle (Al₂O₃, SiO₂) being insoluble and not reacting with water.

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PERIOD 3/TRANSITION METALS



REACTIONS OF PERIOD 3 ELEMENTS WITH ACIDS AND BASES CONTINUED

1. Silicon Dioxide (SiO₂):

- Weakly Acidic Oxide: Reacts with strong bases.
- Reaction with Sodium Hydroxide (Hot, Concentrated):
 - Reaction:
 - $\text{SiO}_2(\text{s}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SiO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 - (Sodium silicate is formed)
- Reaction with Calcium Oxide (High temperatures in a blast furnace):
 - Reaction:
 - $\text{SiO}_2(\text{s}) + \text{CaO}(\text{l}) \rightarrow \text{CaSiO}_3(\text{l})$
 - (Forms calcium silicate, used as slag in iron production)

2. Phosphorus Pentoxide (P₄O₁₀):

- Reacts with water to form phosphoric(V) acid (H₃PO₄), which then reacts with bases like sodium hydroxide in three stages.
- Overall Reaction with Sodium Hydroxide:
 - Reaction:
 - $3\text{NaOH}(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq}) \rightarrow \text{Na}_3\text{PO}_4(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$

3. Sulfur Dioxide (SO₂):

- Reacts with bases to form sulfites.
- Reaction with Sodium Hydroxide:
 - Reaction (Step 1):
 - $\text{SO}_2(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaHSO}_3(\text{aq})$
 - (Sodium hydrogen sulfite is formed)
 - Reaction (Step 2):
 - $\text{NaHSO}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 - (Sodium sulfite is formed)
- Reaction with Calcium Oxide (for flue gas desulfurization in power stations):
 - Reaction:
 - $\text{CaO}(\text{s}) + \text{SO}_2(\text{g}) \rightarrow \text{CaSO}_3(\text{s})$
 - (Calcium sulfite is formed, which is then converted to calcium sulfate or gypsum used in plastering)

D BLOCK ELEMENTS- TRANSITION METALS- ELECTRON CONFIGURATION

General Properties of d-Block Elements (Titanium to Copper)

1. Metals: All elements from titanium to copper are metals.
2. Physical Properties:
 1. Good conductors of heat and electricity.
 2. Hard, strong, shiny.
 3. High melting and boiling points.
3. Applications:
 1. Iron (and steel alloys) for vehicle bodies and reinforcing concrete.
 2. Copper for water pipes.
 3. Titanium for jet engine parts due to its ability to withstand high temperatures.

Electronic Configurations of d-Block Elements

1. Electron Filling: Across the first row of the d-block, electrons are added to the 3d sub-level (3d in the case of elements like titanium to copper).
2. Outer Electrons: Typically, these elements have two outer 4s electrons.
 1. As you move across the period, electrons are added to the 3d sub-level, which lies below the outer 4s sub-level in terms of energy.

05-CHEM-2

TRANSITION METALS



COPPER AND CHROMIUM EXCEPTIONS

1. The electronic configurations of chromium and copper deviate from the expected pattern:

1. Chromium (Cr): $3d^5 4s^1$ (instead of $3d^4 4s^2$)
2. Copper (Cu): $3d^{10} 4s^1$ (instead of $3d^9 4s^2$)

2. Reason for Deviations: These deviations occur because a half-filled ($3d^5$) or fully filled ($3d^{10}$) d-sub-level provides additional stability to the atom. This is similar to the stability provided by a full outer main level in noble gases.

Electron Configurations of Ions in d-Block Elements

1. To determine the electron configuration of a d-block ion:

1. Start with the neutral atom's electron configuration, based on its position in the periodic table.
2. Remove electrons from the 4s sub-level first (before removing from 3d), as the 4s electrons are higher in energy once the 3d sub-level starts to fill.

Example: Iron (Fe)

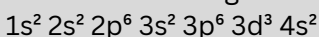
- Neutral Fe Atom: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
- Fe^{2+} Ion: Remove two electrons from the 4s sub-level first.
 - Electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
 - (No 4s electrons)

WORKED EXAMPLES

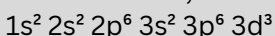
Worked example: Electron configuration of V^{2+} (Vanadium ion)

Vanadium (V) has an atomic number of 23.

Its electron configuration is:



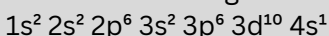
For the V^{2+} ion, it loses the two 4s electrons:



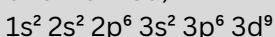
Worked example: Electron configuration of Cu^{2+} (Copper ion)

Copper (Cu) has an atomic number of 29.

Its electron configuration is:



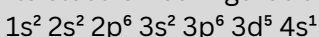
For the Cu^{2+} ion, it loses two electrons (one from 4s and one from 3d):



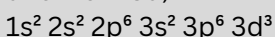
Worked example: Electron configuration of Cr^{3+} (Chromium ion)

Chromium (Cr) has an atomic number of 24.

Its electron configuration is:



For the Cr^{3+} ion, it loses three electrons (one from 4s and two from 3d):



WHAT IS THE DEFINITION OF A TRANSITION ELEMENT AND WHAT ARE ITS CHEMICAL PROPERTIES?

The Definition of a Transition Element

A transition element is defined as one that forms at least one stable ion with a partially filled d-shell of electrons.

- Scandium (Sc) only forms the Sc^{3+} ion with the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^0$, so it does not have a partially filled d-shell.
- Zinc (Zn) only forms the Zn^{2+} ion with the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$, which has a full d-shell.
- As a result, Scandium and Zinc are d-block elements but not considered transition elements.

Chemical Properties of Transition Metals

Transition metals share four key chemical features:

1. Variable Oxidation States:

- Transition metals can exist in more than one oxidation state. For example, copper can form Cu^+ and Cu^{2+} ions, which makes them versatile in redox reactions.

2. Colour:

- Transition metal ions are often coloured due to d-d electron transitions. For instance, $Cu^{2+}(aq)$ is blue in solution.

3. Catalysis:

- Transition metals and their compounds often act as catalysts. Examples include:
 - Iron (Fe) in the Haber process.
 - Vanadium(V) oxide (V_2O_5) in the Contact process for sulfuric acid production.
 - Manganese(IV) oxide (MnO_2) in the decomposition of hydrogen peroxide.

4. Complex Ion Formation:

- Transition metals form complex ions by coordinating with ligands via co-ordinate (dative covalent) bonds. An example is $[Cu(H_2O)_6]^{2+}$, which is formed when copper sulfate dissolves in water.

05-CHEM-2

TRANSITION METALS



FORMATION OF COMPLEX IONS

Complex ions are formed when transition metal ions accept electron pairs from other ions or molecules to form co-ordinate (dative) bonds. Molecules or ions with lone pairs that form these bonds are called ligands.

Common ligands include:

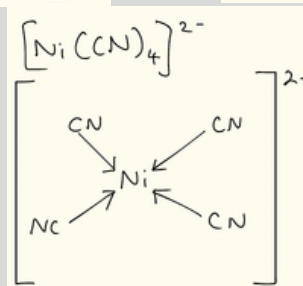
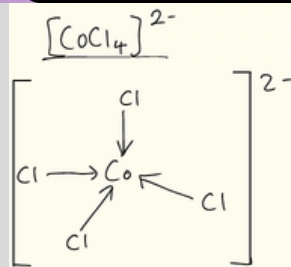
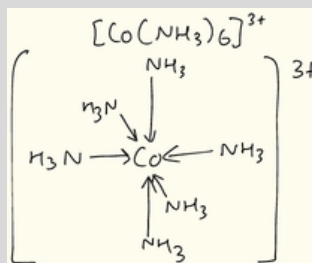
- H_2O
- NH_3
- Cl^-
- CN^-

Key Concepts in Complex Ion Formation:

- Ligands bond to the metal ion via co-ordinate bonds.
- The coordination number is the number of co-ordinate bonds formed between the metal ion and ligands.

Examples of Co-ordination Numbers:

1. Co-ordination number six:
 - These complexes usually form octahedral shapes.
 - Example: $[\text{Co}(\text{NH}_3)_6]^{3+}$
2. Co-ordination number four:
 - These complexes are generally tetrahedral.
 - Example: $[\text{CoCl}_4]^{2-}$
 - Some can also be square planar, depending on the metal ion.
 - Example: $[\text{Ni}(\text{CN})_4]^{2-}$



AQUA IONS

When a transition metal salt, such as copper sulfate, dissolves in water, the metal ion becomes surrounded by water molecules acting as ligands. Normally, there are six water molecules in an octahedral arrangement, forming aqua ions.

FORMATION OF COMPLEX IONS

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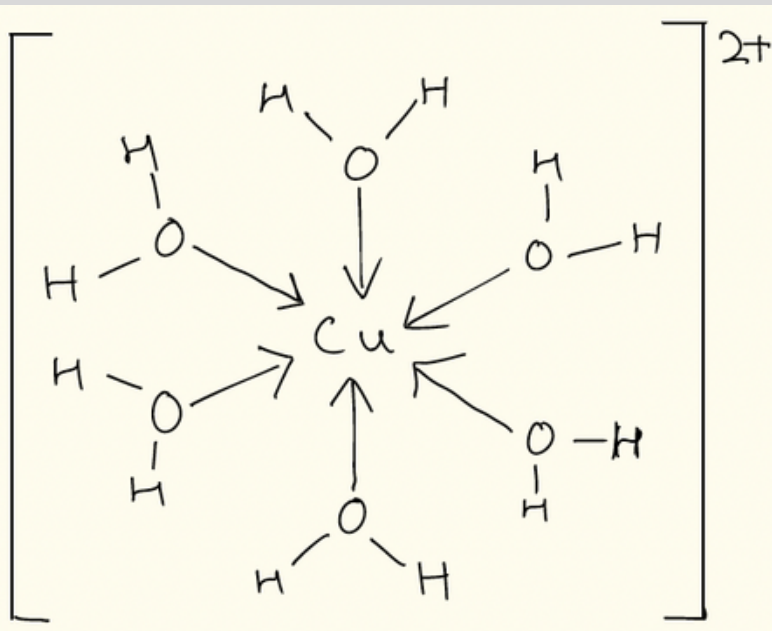
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05-CHEM-2

TRANSITION METALS



CHELATION- THE FORMATION OF MULTIDENTATE LIGANDS

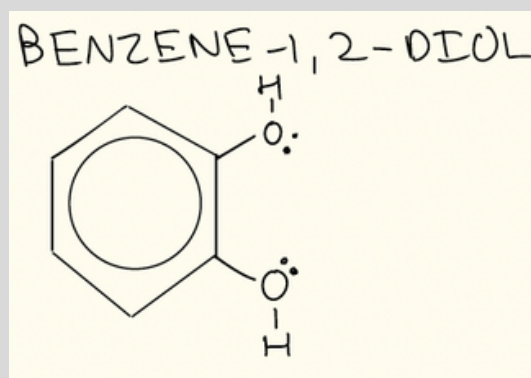
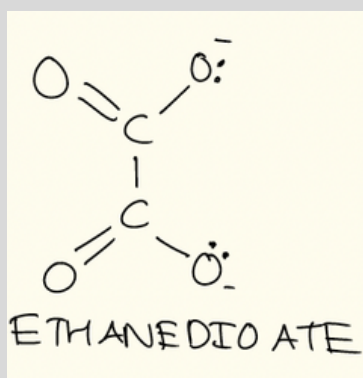
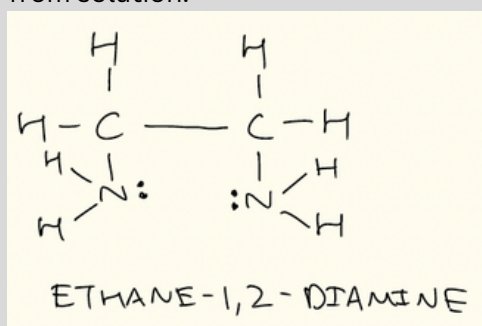
Some molecules or ions, called multidentate ligands, have more than one atom with a lone pair of electrons that can bond to a transition metal ion.

Bidentate ligands include:

- **Ethane-1,2-diamine** (often abbreviated to en), also known as 1,2-diaminoethane. Each nitrogen atom has a lone pair that can form a co-ordinate bond with the metal ion. For example, in the complex ion $[\text{Cr}(\text{en})_3]^{3+}$, the chromium ion has a 3+ charge, so the complex ion also has a 3+ charge.
- **Ethanedioate ion (oxalate ion, $\text{C}_2\text{O}_4^{2-}$)**.
- **Benzene-1,2-diol (1,2-dihydroxybenzene)**, which is also a neutral ligand.

An important multidentate ligand is ethylenediaminetetraacetate (EDTA^{4-}), which can act as a hexadentate ligand using lone pairs on four oxygen atoms and both nitrogen atoms.

Complex ions with polydentate ligands are called chelates. Chelates can be used to effectively remove d-block metal ions from solution.



THE CHELATE EFFECT

When you add a **hexadentate ligand** such as EDTA^{4-} to a solution of a transition metal salt, the EDTA can replace all six water ligands in the aqua ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, as shown in the following equation:



In this reaction, one complex ion is replaced by another, resulting in a total increase from two species to seven. This increase in the number of particles leads to a significant increase in entropy (the measure of disorder), which drives the reaction to the right.

For this reason, chelate complexes with polydentate ligands are favored over complexes with monodentate ligands. This phenomenon is known as the chelate effect.

HAEMOGLOBIN AND ITS STRUCTURE

Haemoglobin is the red pigment in blood responsible for carrying oxygen from the lungs to the body's cells. The central component of haemoglobin is an Fe^{2+} ion, with a co-ordination number of six. The structure around the iron ion is as follows:

- Four of the co-ordination sites are occupied by a ring system known as porphyrin, which acts as a tetradentate ligand. This forms the complex called haem.
- Below the plane of the porphyrin ring, a fifth nitrogen atom from a protein molecule called globin acts as a ligand.
- The sixth site on the Fe^{2+} ion can bind to an oxygen molecule (O_2) as a ligand.

Oxygen Binding and Release:

- The Fe^{2+} to O_2 bond is relatively weak, as O_2 is not a strong ligand, making it easy for oxygen to be released to the cells where it is needed.

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PERIOD 3



MORE ABOUT HAEMOGLOBIN

The Poisonous Effect of Carbon Monoxide:

- Carbon monoxide (CO) is a much better ligand than oxygen and can irreversibly bind to Fe^{2+} , preventing oxygen from binding. This blocks haemoglobin's oxygen-carrying capacity, leading to suffocation, even if oxygen is available. Carbon monoxide poisoning often occurs due to incomplete combustion, such as from faulty gas heaters.

Anaemia:

- Anaemia is a condition caused by a shortage of haemoglobin, leading to insufficient oxygen in the body. Symptoms include fatigue, breathlessness, and pale skin.
- Causes of anaemia may include blood loss or iron deficiency. Iron deficiency can be treated by taking iron(II) sulfate tablets, which help restore the iron levels needed for haemoglobin production.

SHAPES OF COMPLEX IONS

1. Octahedral Complexes:

- Example: $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Co^{3+} ion has a charge of +3, and since the ligands (NH_3) are neutral, the complex ion also has an overall charge of +3.
- An octahedron has six points and eight faces.

2. Tetrahedral Complexes:

- Example: $[\text{CoCl}_4]^{2-}$
- Co^{2+} ion has a charge of +2, and the four chloride ligands (Cl^-) each have a charge of -1, resulting in an overall charge of -2 for the complex ion.
- The larger size of the chloride ion compared to ammonia limits the number of ligands that can surround the metal ion.

3. Square Planar Complexes:

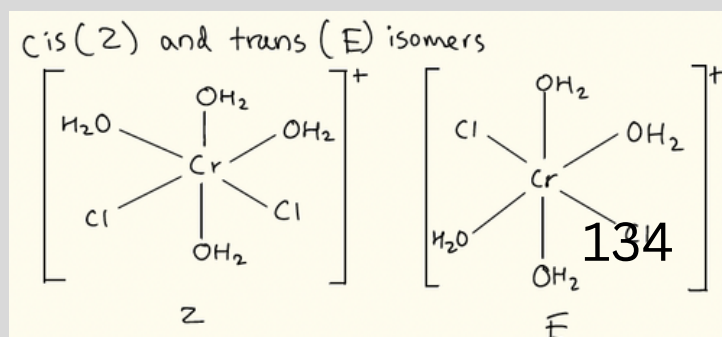
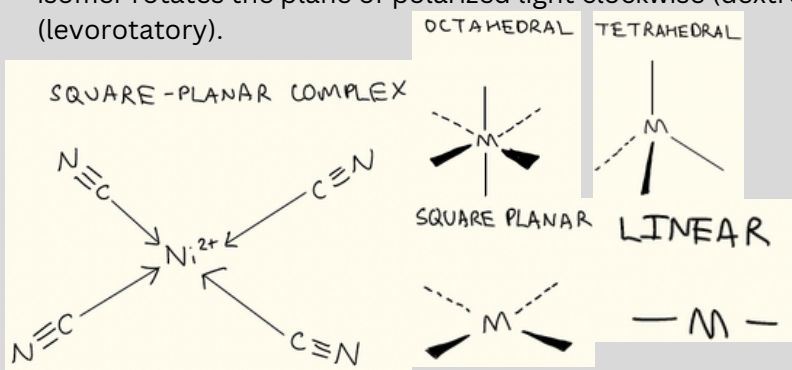
- Some complexes with a co-ordination number of four adopt a square planar geometry.

4. Linear Complexes:

- Example: $[\text{Ag}(\text{NH}_3)_2]^+$
- This complex is known as Tollens' reagent, used in organic chemistry to differentiate between aldehydes and ketones.
- Aldehydes reduce the $[\text{Ag}(\text{NH}_3)_2]^+$ complex to metallic silver (Ag), forming a mirror on the test tube, which is the basis for the silver mirror test.

Optical Isomerism

- Optical isomers are non-superimposable mirror images of each other, occurring in transition metal complexes with two or more bidentate ligands.
- Example: When visualizing two complexes, rotating one around a vertical axis shows that the end ligands do not match, confirming they are distinct isomers.
- Optical isomers are termed chiral and have identical chemical properties but affect polarized light differently. One isomer rotates the plane of polarized light clockwise (dextrorotatory), while the other rotates it counterclockwise (levorotatory).





COLOURS OF TRANSITION METAL COMPLEXES

Color of Transition Metal Complexes

1. Color Origin:

- Transition metal compounds are typically colored due to their ability to absorb specific wavelengths of visible light.
- For instance, if a solution appears purple, it absorbs all wavelengths except red and blue light, which are transmitted through.

2. Reasons for Color:

- Part-Filled d-Orbitals:** Transition metal compounds have partially filled d-orbitals, allowing electrons to move between them.
- Energy Levels:** In an isolated transition metal atom, all d-orbitals are of the same energy. However, in a compound, nearby atoms cause the d-orbitals to have slightly different energy levels.
- Excitation of Electrons:** When electrons move from a lower energy d-orbital to a higher energy d-orbital (excited state), they absorb energy corresponding to the visible light spectrum. This absorbed energy results in the specific color not being seen.

3. Relationship Between Energy and Light:

- The energy difference between the levels (ΔE) can be described by the equation $\Delta E = h\nu$, where:
 - ΔE = energy difference
 - h = Planck's constant
 - ν = frequency of light
- Violet light has high energy and frequency, while red light has low energy and frequency.

4. Factors Affecting Color:

- The color of a transition metal complex depends on the energy gap (ΔE), which is influenced by:
 - The oxidation state of the metal.
 - The ligands surrounding the metal (which affect the shape of the complex ion).

5. Examples of Colors by Oxidation State:

- The following table illustrates how different oxidation states of vanadium affect the color of its species:

Oxidation Number	Species	Color
5	$\text{VO}_4^{3-} (\text{aq})$	Yellow
4	$\text{VO}_2^+ (\text{aq})$	Blue
3	$\text{V}^{3+} (\text{aq})$	Green
2	$\text{V}^{2+} (\text{aq})$	Violet

Metal	Oxidation State	Complex Ion	Color
Iron	2	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	Green
Iron	3	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	Pale Brown
Chromium	2	$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	Blue
Chromium	3	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	Red-Violet
Cobalt	2	$[\text{Co}(\text{NH}_3)_6]^{2+}$	Brown
Cobalt	3	$[\text{Co}(\text{NH}_3)_6]^{3+}$	Yellow



COLORIMETRY

- Principle: A colorimeter measures the amount of light that passes through a colored solution at a specific wavelength. The intensity of transmitted light decreases as the concentration of the solution increases.
- How it works:
 - A light source shines light through the solution.
 - A detector measures how much light passes through the solution.
 - The amount of light absorbed by the solution correlates with the concentration of the transition metal compound.
- Application:
 - Used to measure the concentration of solutions containing colored transition metal compounds.
 - A calibration graph is created using known concentrations, allowing the concentration of unknown solutions to be determined from the colorimeter readings.

VARIABLE OXIDATION STATES OF TRANSITION ELEMENTS AND REDOX REACTIONS

Group 1 metals lose their outer electron to form +1 ions, and **Group 2 metals** lose their outer two electrons to form +2 ions in compounds. Transition metals can use their 3d-electrons in addition to their 4s-electrons for bonding, which allows them to have a variety of oxidation states.

For example:

- Nickel (Ni) has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$. When it forms a Ni^{2+} ion, it loses the two 4s electrons, resulting in $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$.
- Iron (Fe) has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. When it forms a Fe^{2+} ion, the electron configuration becomes $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.

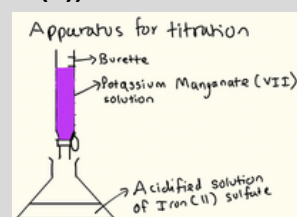
In **redox reactions**, iron can exist in two stable oxidation states— Fe^{2+} and Fe^{3+} . For example, Fe^{2+} can be oxidized to Fe^{3+} by oxygen in the air or chlorine, as shown in the reaction: $2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$

Here, the iron is oxidized (loses electrons) from Fe^{2+} to Fe^{3+} , and chlorine is reduced (gains electrons) from 0 to Cl^- .

HALF EQUATIONS FOR TRANSITION METAL REDOX REACTIONS

Reduction Half-Equation (Manganate(VII) to Manganese(II)):

1. Start with the manganese species:
2. $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$
3. Balance the oxygen by adding water molecules:
4. $MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
5. Balance the hydrogen atoms by adding H^+ ions:
6. $MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
7. Balance the charge by adding electrons (MnO_4^- gains 5 electrons):
8. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$



Oxidation Half-Equation (Iron(II) to Iron(III)):

1. $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

Combining the Half-Equations:

1. Multiply the iron half-equation by 5 so that the number of electrons matches:
2. $5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$
3. Add the two half-equations together:
4. $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

This is the balanced equation for the reaction between potassium manganate(VII) and Fe^{2+} ions in acidic solution.

Redox Titrations and the Role of Acid:

In a redox titration using potassium manganate(VII), you add $MnO_4^-(aq)$ to $Fe^{2+}(aq)$ in an acidic solution. The purple MnO_4^- ions are reduced to the nearly colorless Mn^{2+} , which changes the solution's color as the titration proceeds. Once all Fe^{2+} ions are oxidized to Fe^{3+} , any excess MnO_4^- will give the solution a purple tint, marking the end point of the titration.

Why Sulfuric Acid (H_2SO_4) Is Used:

- Sulfuric acid provides H^+ ions without reacting with MnO_4^- .
- Hydrochloric acid (HCl) contains Cl^- ions, which can also be oxidized by MnO_4^- , leading to unwanted side reactions.

Electrode Potentials for the Half-Reactions:

- $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$, $E^\circ = +1.51 V$
- $Cl_2(aq) + e^- \rightarrow 2Cl^-(aq)$, $E^\circ = +1.36 V$

The reaction between MnO_4^- and Cl^- is thermodynamically feasible ($E^\circ = +0.15 V$), which means Cl^- ions will be oxidized by MnO_4^- . This would interfere with the titration because the MnO_4^- is supposed to only oxidize Fe^{2+} , not Cl^- . Thus, sulfuric acid is used to avoid the oxidation of Cl^- ions.



WORKED EXAMPLE FOR TRANSITION METAL REDOX REACTIONS

Problem:

A brand of iron tablets claims each tablet contains 0.200 g of iron(II) sulfate (FeSO_4). The tablet is dissolved in excess sulfuric acid and diluted to 250 cm^3 . A 25.00 cm^3 aliquot of this solution is titrated with $0.00100 \text{ mol dm}^{-3}$ potassium manganate(VII) solution. The average volume of potassium manganate(VII) used is 26.30 cm^3 .

Solution:

Step 1: Calculate moles of potassium manganate(VII)

Use the formula:

Number of moles of potassium manganate(VII) = concentration (mol dm^{-3}) $\times$ volume (cm^3) $\div 1000$

- Concentration of potassium manganate(VII) = $0.00100 \text{ mol dm}^{-3}$
- Volume of potassium manganate(VII) used = 26.30 cm^3

Number of moles of potassium manganate(VII) = $0.00100 \times 26.30 \div 1000 = 2.63 \times 10^{-5} \text{ mol}$

Step 2: Determine moles of Fe^{2+}

From the balanced equation: $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$

For every 1 mole of MnO_4^- , 5 moles of Fe^{2+} react.

Number of moles of $\text{Fe}^{2+} = 5 \times 2.63 \times 10^{-5} = 1.315 \times 10^{-4} \text{ mol}$

Step 3: Scale up to the whole solution

The titration was done with a 25.00 cm^3 sample, but the total volume of the solution was 250 cm^3 .

So, the number of moles of Fe^{2+} in the entire solution = $1.315 \times 10^{-4} \times (250 \div 25) = 1.315 \times 10^{-3} \text{ mol}$

Step 4: Calculate the mass of FeSO_4 in the tablet

The relative formula mass of $\text{FeSO}_4 = 151.9 \text{ g mol}^{-1}$.

Mass of $\text{FeSO}_4 = \text{number of moles} \times \text{molar mass}$

Mass of $\text{FeSO}_4 = 1.315 \times 10^{-3} \times 151.9 = 0.200 \text{ g}$

OXIDATION OF TRANSITION METALS IN ALKALINE SOLUTION- THE EQUATIONS

In acidic solutions, high oxidation states of metals, such as Mn(VII) and Cr(VI), are reduced.

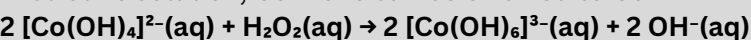
- Oxidation of lower oxidation states of transition metal ions typically occurs in alkaline solutions because there is a tendency to form negative ions, making electron loss (oxidation) easier from these negatively charged species.

Examples of typical transition metal species:

- Acid solution: $\text{M}(\text{H}_2\text{O})_6^{2+}$ (positively charged)
- Neutral solution: $\text{M}(\text{H}_2\text{O})_4(\text{OH})_2$ (neutral)
- Alkaline solution: $\text{M}(\text{H}_2\text{O})_2(\text{OH})_4^{2-}$ (negatively charged)

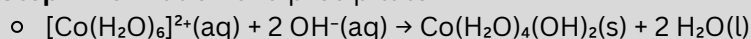
Example – Cobalt Chemistry:

In alkaline solution, Co^{2+} ions can be oxidized to Co^{3+} :

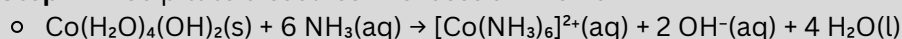


1. In an ammoniacal solution, Co^{2+} ions are oxidized by oxygen in the air.

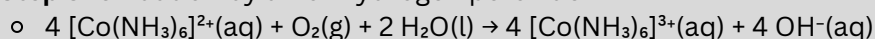
2. **Step 1:** Formation of a precipitate:



3. **Step 2:** Precipitate dissolves in excess ammonia:



4. **Step 3:** Oxidation by air or hydrogen peroxide:





WHAT IS CATALYSIS? THE IMPORTANCE OF CATALYSIS IN INDUSTRY

Catalysts affect the rate of reaction without being chemically changed at the end of the reaction. They are crucial in industrial processes because they allow reactions to occur at lower temperatures and pressures, saving valuable resources.

Example:

Modern cars use catalytic converters made from platinum and rhodium. These metals catalyse the conversion of harmful substances in exhaust gases, such as carbon monoxide, nitrogen oxides, and unburnt petrol, into carbon dioxide, nitrogen, and water.

TYPES OF CATALYSTS

Heterogeneous Catalysts

These catalysts are present in a different phase from the reactants (e.g., a solid catalyst with gas or liquid reactants). The reaction occurs on the surface of the solid catalyst, and the catalyst remains in place, so it does not need to be separated from the products.

Homogeneous Catalysts

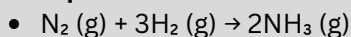
These catalysts exist in the same phase as the reactants, typically in a solution.

SOME IMPORTANT EXAMPLES OF HETEROGENOUS CATALYSTS

1. The Haber Process

The Haber process is used to make ammonia (NH_3) by reacting nitrogen (N_2) with hydrogen (H_2). The catalyst used in this process is iron, typically present as pea-sized lumps to maximize the surface area.

- **Equation:**



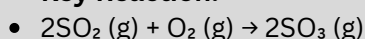
- Iron catalyst lifespan:

- The iron catalyst lasts about five years before it becomes poisoned by sulfur compounds and other impurities in the gas stream, after which it needs to be replaced.

2. The Contact Process

The Contact process is used to produce sulfuric acid, a crucial industrial chemical. The key step involves the oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3), catalysed by vanadium(V) oxide (V_2O_5).

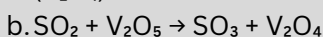
- **Key Reaction:**



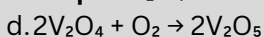
- Catalysed by vanadium(V) oxide (V_2O_5).

- Mechanism in two steps:

- a. **Step 1:** V_2O_5 oxidises SO_2 to SO_3 and is itself reduced to vanadium(IV) oxide (V_2O_4):



- c. **Step 2:** V_2O_4 is then oxidised back to V_2O_5 by oxygen:



The vanadium(V) oxide is regenerated and remains unchanged at the end of the reaction. This process benefits from the variable oxidation states of transition metals, which help lower the activation energy, making the reaction faster.

IMPROVING THE EFFICIENCY OF HETEROGENOUS CATALYSTS

Since heterogeneous catalysts operate on the surface, there are ways to improve their efficiency:

- Increase surface area:
- The larger the surface area, the more efficient the catalyst.
- Support medium:
- The catalyst can be spread onto an inert support medium or impregnated into one, increasing the surface-to-mass ratio. For instance, in car catalytic converters, finely divided rhodium and platinum are supported on a ceramic material.

LIMITATIONS OF CATALYSTS

- Catalyst Poisoning:
- Over time, the catalyst surface can become coated with unwanted impurities, known as poisoning. For example, catalytic converters in cars were poisoned by lead-based additives in petrol, which is why leaded fuel cannot be used in cars with converters.
- Catalyst Loss:
- The finely divided catalyst may gradually be lost from its support medium, reducing its effectiveness over time.

05-CHEM-2

TRANSITION METALS



THE MANUFACTURE OF METHANOL

3. Synthesis Gas and Methanol Production

Synthesis gas is a mixture of carbon monoxide (CO) and hydrogen (H₂), made by reacting methane (CH₄) with steam. It is used to make methanol (CH₃OH).

- **Reaction:**
- $\text{CO (g)} + 2\text{H}_2 \text{ (g)} \rightarrow \text{CH}_3\text{OH (g)}$
- Initially, this reaction was catalysed by chromium oxide (CrO₃), but today, the most common catalyst is a mixture of copper, zinc oxide, and aluminium oxide.
- **Methanol importance:**
- Over 30 million tonnes of methanol are produced annually. It serves as a starting material for the production of plastics like Bakelite, Terylene, and Perspex.

HOMOGENOUS CATALYSTS

When a catalyst is in the same phase as the reactants, it forms an intermediate species during the reaction. A well-known example is the destruction of the ozone layer by chlorine free radicals (Cl·), where the intermediate species is the ClO· free radical.

HOMOGENOUS CATALYSIS BY TRANSITION METALS: AN EXAMPLE

The oxidation of iodide ions (I⁻) to iodine (I₂) by peroxodisulfate ions (S₂O₈²⁻) is an example of a reaction catalysed by iron(II) ions (Fe²⁺).

- Overall Reaction: $\text{S}_2\text{O}_8^{2-} \text{ (aq)} + 2\text{I}^- \text{ (aq)} \rightarrow 2\text{SO}_4^{2-} \text{ (aq)} + \text{I}_2 \text{ (aq)}$

Catalysed Reaction

The catalysed reaction occurs in two steps:

1. Step 1: The peroxodisulfate ions oxidise iron(II) ions (Fe²⁺) to iron(III) ions (Fe³⁺):
 $\text{S}_2\text{O}_8^{2-} \text{ (aq)} + 2\text{Fe}^{2+} \text{ (aq)} \rightarrow 2\text{SO}_4^{2-} \text{ (aq)} + 2\text{Fe}^{3+} \text{ (aq)}$
2. Step 2: The iron(III) ions (Fe³⁺) then oxidise the iodide ions (I⁻) to iodine (I₂), regenerating the iron(II) ions (Fe²⁺):
 $2\text{Fe}^{3+} \text{ (aq)} + 2\text{I}^- \text{ (aq)} \rightarrow 2\text{Fe}^{2+} \text{ (aq)} + \text{I}_2 \text{ (aq)}$

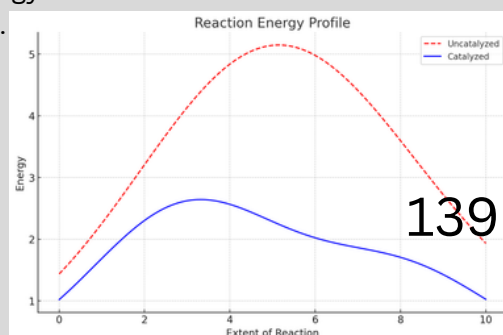
In this mechanism, Fe²⁺ acts as a catalyst by first giving an electron to the peroxodisulfate, and then taking an electron back from the iodide ions.

Explanation of Rate Increase:

- The uncatalysed reaction occurs between two ions with the same charge (both negatively charged), which results in electrostatic repulsion and gives the reaction a high activation energy.
- In the catalysed reaction, both steps involve ions with opposite charges, which reduces repulsion and lowers the activation energy.

Reaction Profile:

- Even though the catalysed reaction has two steps, the overall activation energy is still lower than that of the uncatalysed reaction. This explains why the catalysed reaction occurs faster.





AUTOCATALYSIS

Autocatalysis occurs when one of the products of a reaction acts as a catalyst for the same reaction. This leads to a unique behavior where:

- The reaction starts slowly at the uncatalysed rate.
- As the concentration of the product-catalyst increases, the reaction speeds up to the catalysed rate.
- Eventually, the reaction slows down as the reactants are used up, similar to a typical catalysed reaction.

This results in an unusual rate curve, which initially rises slowly, accelerates, and then gradually tapers off as reactants deplete.

EXAMPLE: OXIDATION OF ETHANEDIOIC ACID BY MANGANATE (VII) IONS

One notable example of autocatalysis is the reaction between ethanedioic acid (oxalic acid) and acidified potassium manganate(VII) solution. This reaction is often used as a titration to determine the concentration of potassium manganate(VII).

Overall Reaction: $2\text{MnO}_4^- (\text{aq}) + 16\text{H}^+ (\text{aq}) + 5\text{C}_2\text{O}_4^{2-} (\text{aq}) \rightarrow 2\text{Mn}^{2+} (\text{aq}) + 8\text{H}_2\text{O} (\text{l}) + 10\text{CO}_2 (\text{g})$

- MnO_4^- ions (manganate(VII)) are reduced to Mn^{2+} ions (manganese(II)).
- $\text{C}_2\text{O}_4^{2-}$ ions (oxalate) are oxidised to CO_2 (carbon dioxide).

Autocatalysis Mechanism:

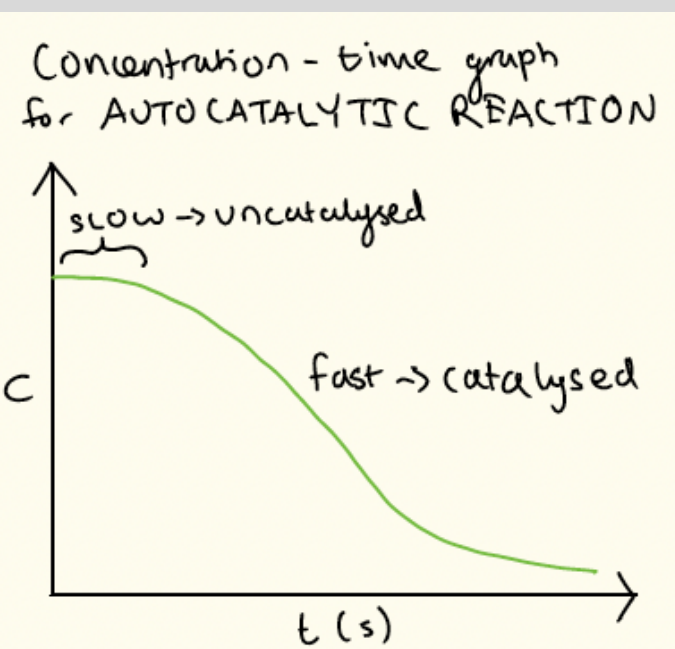
In this reaction, Mn^{2+} ions act as the catalyst. Initially, there are no Mn^{2+} ions, but once some Mn^{2+} ions are formed, they catalyse the reaction by:

1. **Step 1:** The Mn^{2+} ions react with MnO_4^- ions to form Mn^{3+} ions:
2. $4\text{Mn}^{2+} (\text{aq}) + \text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) \rightarrow 5\text{Mn}^{3+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l})$
3. **Step 2:** The Mn^{3+} ions then react with $\text{C}_2\text{O}_4^{2-}$ ions (oxalate), regenerating Mn^{2+} ions:
4. $2\text{Mn}^{3+} (\text{aq}) + \text{C}_2\text{O}_4^{2-} (\text{aq}) \rightarrow 2\text{CO}_2 (\text{g}) + 2\text{Mn}^{2+} (\text{aq})$

This process accelerates the reaction as more Mn^{2+} ions are produced, further catalysing the reaction.

Monitoring the Reaction:

The reaction can be followed using a colorimeter, as MnO_4^- ions are purple, and their concentration decreases over time as they are reduced. The rate curve for this autocatalytic reaction starts slowly, speeds up, and eventually levels off



05-CHEM-3

REACTIONS OF INORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS



ACID-BASE CHEMISTRY OF AQUEOUS TRANSITION METAL IONS

When **salts of transition metals**, such as **iron(II) nitrate ($\text{Fe}(\text{NO}_3)_2$)**, are dissolved in water, the metal ion forms a complex ion with water molecules. This involves the water molecules acting as ligands, using their lone pairs of electrons to form coordinate (dative) bonds with the metal ion.

Formation of Aqua Ions

- Iron(II) nitrate dissolves to form $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, an octahedral complex ion with six water ligands.
- Each water molecule forms a coordinate bond with the Fe^{2+} ion, donating a lone pair of electrons.
- Similarly, when iron(III) salts dissolve, they form $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

Acidity of Aqua Ions

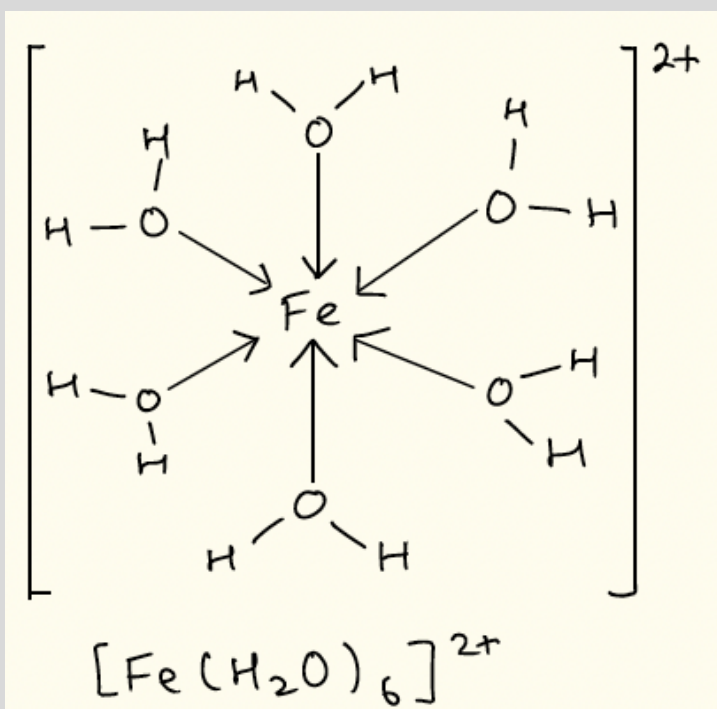
- Fe^{2+} complexes are not noticeably acidic, but Fe^{3+} complexes are more acidic, with a pK_a of 2.2.
- Fe^{3+} has a higher charge density than Fe^{2+} , as it is smaller and more highly charged.
- This greater polarising power of Fe^{3+} means it strongly attracts electrons from the water ligands, weakening the O-H bonds.

Hydrolysis Reaction

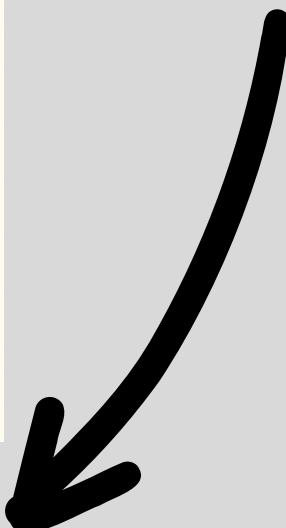
- The $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ complex ion readily loses an H^+ ion to form $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$:
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) \rightarrow [\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{aq}) + \text{H}^+(\text{aq})$.
- This process is called hydrolysis, as the water molecules undergo ionisation.
- This explains the acidity of Fe^{3+} compared to Fe^{2+} , as Fe^{2+} is less polarising and does not weaken the O-H bonds to the same extent.

General Rule for Transition Metals

- M^{3+} aqua ions are significantly more acidic than M^{2+} aqua ions due to their higher charge density and stronger ability to attract electrons from ligands.
- Aluminium(III) (Al^{3+}), though not a transition metal, shows similar behaviour to Fe^{3+} .



ACID BASE REACTIONS OF
TRANSITION METAL
AQUEOUS IONS WITH BASES



05-CHEM-3

REACTIONS OF INORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS



ACID-BASE REACTIONS OF TRANSITION METAL AQUEOUS IONS WITH BASE OH⁻

When you add a base, such as OH⁻ ions, to solutions containing transition metal ions, protons (H⁺) are removed in a series of steps.

For M³⁺(aq) Ions:

1. The first step involves the reaction of the aqueous complex: $[M(H_2O)_6]^{3+}(aq) + OH^-(aq) \rightarrow [M(H_2O)_5(OH)]^{2+}(aq) + H_2O(l)$
2. The second step continues the reaction: $[M(H_2O)_5(OH)]^{2+}(aq) + OH^-(aq) \rightarrow [M(H_2O)_4(OH)_2]^+(aq) + H_2O(l)$
3. The third step results in the formation of the precipitate: $[M(H_2O)_4(OH)_2]^+(aq) + OH^-(aq) \rightarrow M(H_2O)_3(OH)_3(s) + H_2O(l)$

The neutral metal (III) hydroxide, M(H₂O)₃(OH)₃, is effectively M(OH)₃, which is uncharged and insoluble, forming a precipitate.

For M²⁺(aq) Ions:

1. The first step is: $[M(H_2O)_6]^{2+}(aq) + OH^-(aq) \rightarrow [M(H_2O)_5(OH)]^+(aq) + H_2O(l)$
2. The second step continues: $[M(H_2O)_5(OH)]^+(aq) + OH^-(aq) \rightarrow M(H_2O)_4(OH)_2 + H_2O(l)$

The neutral metal (II) hydroxide, M(H₂O)₄(OH)₂, is effectively M(OH)₂, which is uncharged and insoluble, also forming a precipitate.

Ammonia as a Base:

Ammonia (NH₃), which is basic, has the same effect as OH⁻ ions in removing protons:

For M³⁺ ions: $[M(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \rightarrow M(H_2O)_3(OH)_3(s) + 3NH_4^+(aq)$

For M²⁺ ions: $[M(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightarrow M(H_2O)_4(OH)_2(s) + 2NH_4^+(aq)$

ACID-BASE REACTIONS OF TRANSITION METAL AQUEOUS IONS WITH BASE (CO₃)²⁻

The greater acidity of the aqueous Fe³⁺ ion explains why iron(III) carbonate does not exist, while iron(II) carbonate does. The carbonate ion is able to remove protons from [Fe(H₂O)₆]³⁺(aq) to form hydrated iron(III) hydroxide, but it cannot do so from [Fe(H₂O)₆]²⁺(aq).

The reaction can be represented as follows: $2[Fe(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow 2Fe(OH)_3 + 3HCO_3^-(aq)$

The overall reaction is: $2[Fe(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow 2Fe(OH)_3 + 3CO_2(g) + 3H_2O(l)$

This can be derived from: $2H_2O(l) + CO_3^{2-}(aq) \rightarrow 3H_2O(l) + CO_2(g)$

This occurs with the removal of HCO₃⁻, displacing the hydrolysis equilibrium: $[Fe(H_2O)_6]^{3+}(aq) + 3H_2O(l) \rightarrow Fe(H_2O)_3(OH)_3 + 3H_3O^+(aq)$

In the case of the aqueous Fe²⁺ ion, which is less acidic than Fe³⁺(aq), insoluble iron(II) carbonate is formed: $[Fe(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow FeCO_3(s) + 6H_2O(l)$

In general, carbonates of transition metal ions in the +2 oxidation state exist, while those of ions in the +3 state do not.

Distinguishing Iron Ions

Both Fe²⁺ and Fe³⁺ exist in aqueous solution as octahedral hexa-aqua ions. [Fe(H₂O)₆]²⁺ is pale green, and [Fe(H₂O)₆]³⁺ is pale brown; thus, dilute solutions are hard to distinguish. A simple test to differentiate the two is to add dilute alkali, which precipitates the hydroxides whose colours are more obviously different:

1. $[Fe(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s) + 3H_2O(l)$ (iron(III) hydroxide - brown)
2. $[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(H_2O)_4(OH)_2(s) + 2H_2O(l)$ (iron(II) hydroxide - green)

05-CHEM-3

REACTIONS OF INORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS



EVOLUTION OF ACID-BASE REACTION THEORIES

Throughout history, various theories of acidity have been proposed, evolving with new scientific discoveries. These theories aim to explain the characteristics of acids, such as their ability to neutralise bases, react with metals, and release carbon dioxide from carbonates. Below is a structured summary of the key theories, highlighting how scientific understanding has progressed.

1. Lavoisier's Theory (1777)

- Key Idea: All acids contain oxygen.
- Examples: Nitric acid (HNO_3), sulfuric acid (H_2SO_4), and ethanoic acid (CH_3COOH) fit this theory.
- Limitations: Once hydrochloric acid (HCl) was identified, it became clear that this theory was incorrect because HCl contains no oxygen.

2. Davy's Theory (1816)

- Key Idea: All acids contain hydrogen.
- Strengths: This theory includes HCl , solving the issue with Lavoisier's theory.
- Limitations: It doesn't explain why hydrogen is important or why not all hydrogen-containing compounds (like ammonia (NH_3)) are acidic.

3. Liebig's Theory (1838)

- Key Idea: Acids contain hydrogen, which can be replaced by a metal.
- Strengths: This explains why ammonia (NH_3) is not acidic – its hydrogen cannot be easily replaced by a metal.
- Relevance: This theory aligns closely with modern understanding but doesn't fully explain the nature of hydrogen ions.

4. Arrhenius' Theory (1887)

- Key Idea: Acids produce hydrogen ions (H^+) in solution.
- Strengths: This builds on Liebig's theory by identifying what makes the hydrogen important – it must be able to become an H^+ ion.

5. Bronsted-Lowry Theory (1923)

- Key Idea: Acids donate protons (H^+), and bases accept protons.
- Strengths: This is the most widely used modern theory and applies to a broad range of reactions.
- Limitations: It struggles to explain acids that do not contain hydrogen, such as aluminium chloride (AlCl_3) and boron trifluoride (BF_3).

6. Lewis Theory

- Key Idea: Acids accept electron pairs, and bases donate electron pairs to form co-ordinate covalent bonds.
- Strengths: This theory accounts for acids that do not contain hydrogen, such as AlCl_3 and BF_3 .

05-CHEM-3

REACTIONS OF INORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS



REPLACING WATER AS A LIGAND IN METAL AQUA IONS

The water molecules that act as ligands in metal aqua ions can be replaced by other ligands, either because the other ligands form stronger coordinate bonds or because they are present in higher concentration, displacing the equilibrium.

Possibilities for Replacing Water as a Ligand:

- The water molecules may be replaced by other neutral ligands, such as ammonia.
- The water molecules may be replaced by negatively charged ligands, such as chloride ions.
- The water molecules may be replaced by bi- or multidentate ligands, a process known as chelation.
- Replacement of the water ligands may be complete or partial.

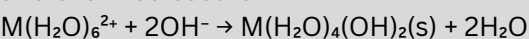
Replacement by Neutral Ligands - No Change in Coordination Number

For an M^{2+} ion, water molecules may be replaced one at a time by ammonia. Both ligands are uncharged and similar in size, so there is no change in coordination number or charge on the ion:

1. $M(H_2O)_6^{2+} + NH_3 \rightarrow [M(NH_3)(H_2O)]^{2+} + H_2O$
2. $[M(NH_3)(H_2O)]^{2+} + NH_3 \rightarrow [M(NH_3)_2(H_2O)_4]^{2+} + H_2O$
3. $[M(NH_3)_2(H_2O)_4]^{2+} + NH_3 \rightarrow [M(NH_3)_3(H_2O)_3]^{2+} + H_2O$
4. $[M(NH_3)_3(H_2O)_3]^{2+} + NH_3 \rightarrow [M(NH_3)_4(H_2O)_2]^{2+} + H_2O$
5. $[M(NH_3)_4(H_2O)_2]^{2+} + NH_3 \rightarrow [M(NH_3)_5(H_2O)]^{2+} + H_2O$
6. $[M(NH_3)_5(H_2O)]^{2+} + NH_3 \rightarrow [M(NH_3)_6]^{2+} + H_2O$

Overall: $M(H_2O)_6^{2+} + 6NH_3 \rightarrow [M(NH_3)_6]^{2+} + 6H_2O$

There is a complication because ammonia is a base as well as a ligand. When OH^- ions are present, a precipitate may form and then redissolve:



COBALT (II) EXAMPLE

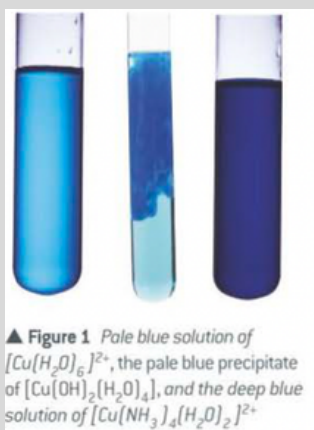
When the metal is cobalt (Co), the first step is the formation of a blue precipitate of hydrated cobalt(II) hydroxide when ammonia (NH_3) is added. This occurs due to the loss of a proton from each of two of the six water molecules coordinated to the Co^{2+} ion: **$Co(H_2O)_6^{2+}(aq) + 2NH_3(aq) \rightarrow Co(OH)_2(H_2O)_4 + 2NH_4^+(aq)$**

Here, ammonia is acting as a base. If more concentrated ammonia is added, both OH^- and all four water ligands are replaced by ammonia due to **two reasons**:

1. Ammonia is a better ligand than water.
2. The high concentration of ammonia shifts equilibria to the right, displacing water and OH^- .

Overall: $Co(H_2O)_4(OH)_2 + 6NH_3(aq) \rightarrow [Co(NH_3)_6]^{2+}(aq) + 4H_2O(l) + 2OH^-(aq)$

The blue precipitate dissolves to form a pale yellow solution, which can be oxidized by oxygen in air to produce a brown mixture containing Co(III).



05-CHEM-3

REACTIONS OF INORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS



COPPER REACTIONS WITH AMMONIA

- **Partial Ligand Replacement:**
 - When aqueous copper ions (Cu^{2+}) react with ammonia, only four water ligands are replaced.
 - Overall Reaction:
 - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 4\text{H}_2\text{O}$
- **Color Change:**
 - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is pale blue.
 - $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is a deep blue.
- **Initial Reaction:**
 - Ammonia acts as a base, removing protons from two water molecules in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.
 - This forms $\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4$, resulting in a pale blue precipitate of copper hydroxide.
- **Further Reaction:**
 - With more concentrated ammonia, the precipitate dissolves:
 - $\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4 + 4\text{NH}_3(\text{aq}) \rightarrow [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{OH}^-(\text{aq})$

Shape of the $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ Ion

- **Coordination:**
 - The $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ ion is octahedral, as expected for a six-coordinate ion.
 - Four ammonia molecules are arranged in a square-planar configuration around the metal ion, with two water molecules above and below.
- **Bonding:**
 - Cu-O bonds are longer and weaker than Cu-N bonds, since water is a poorer ligand than ammonia.
 - The octahedron is slightly distorted.

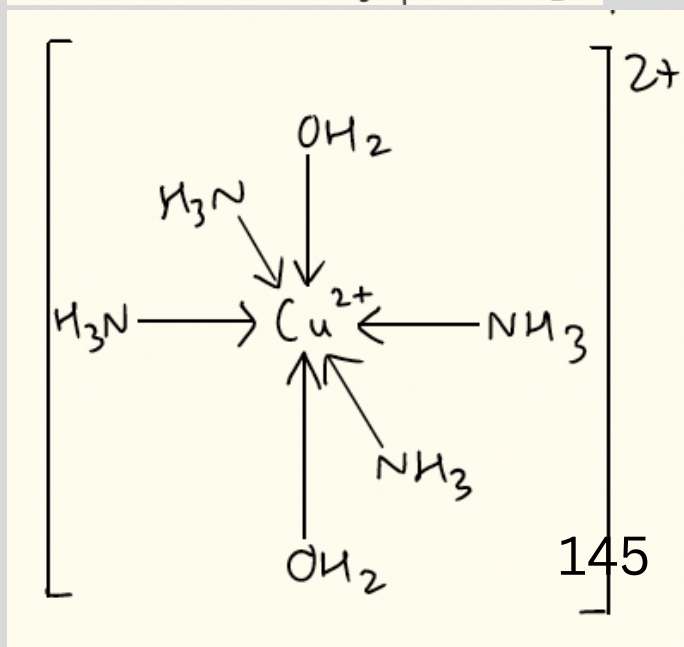
REPLACEMENT BY CHLORIDE IONS- CHANGE IN COORDINATION NUMBER

- **Reaction with Hydrochloric Acid:**
 - Concentrated hydrochloric acid provides a high concentration of Cl^- ligands.
 - Overall Reaction:
 - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$
- **Colour Change:**
 - The pale blue color of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is replaced by yellow $[\text{CuCl}_4]^{2-}$ (solution may appear green due to remaining $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$).
- **Coordination Change:**
 - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is six-coordinate; $[\text{CuCl}_4]^{2-}$ is four-coordinate due to larger Cl^- ions.

Chelation

- **Definition:**
 - Chelation is the formation of complexes with multidentate ligands (ligands with more than one lone pair).
- **Examples of Multidentate Ligands:**
 - Ethylene diamine (en), benzene-1,2-diol, and EDTA^{4-} .
- **Increased Stability:**
 - Chelates are usually more stable than those with monodentate ligands due to entropy changes.

SHAPE OF $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$



05-CHEM-3

REACTIONS OF INORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS



EXAMPLES OF CHELATOR IONS

Ethylene Diamine (en)

- Bidentate Ligand:
 - Ethylene diamine can be thought of as two ammonia ligands linked by a short hydrocarbon chain.
- Replacement Reaction:
 - Overall Reaction:
 - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 3\text{en} \rightarrow [\text{Cu}(\text{en})_3]^{2+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$
 - Three molecules of ethylene diamine release six water molecules, favoring the reaction due to significant entropy increase.

EDTA⁴⁻

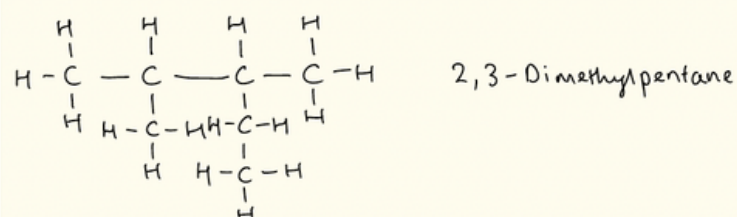
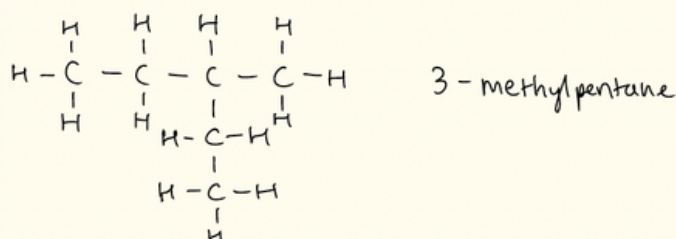
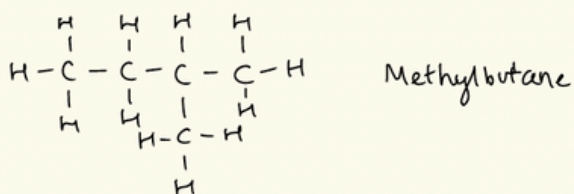
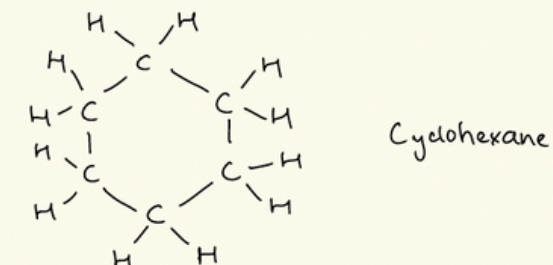
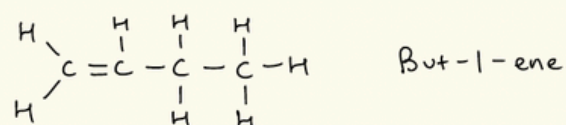
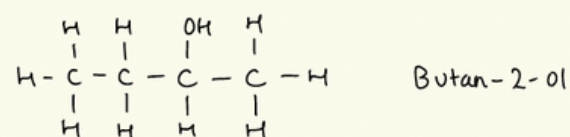
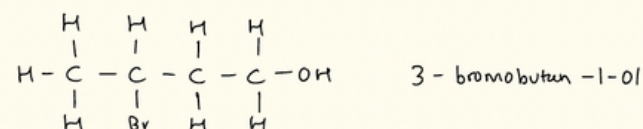
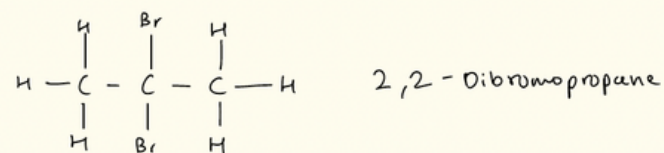
- Hexadentate Ligand:
 - EDTA⁴⁻ can displace all six water ligands from $[\text{M}(\text{H}_2\text{O})_6]^{2+}$.
- Replacement Reaction:
 - Overall Reaction:
 - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + \text{EDTA}^{4-}(\text{aq}) \rightarrow [\text{CuEDTA}]^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$
 - This reaction also results in an entropy increase, favoring chelate formation.

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NOMENCLATURE AND ISOMERISM



HOW TO NAME ORGANIC COMPOUNDS



HOW TO NAME COMPOUNDS WITH FUNCTIONAL GROUPS

Key Concepts:

- Functional Groups: Specific groups of atoms within molecules that determine their chemical properties and reactions.
- Suffixes: Indicate the type of functional group present in the molecule.
- Prefixes: Provide additional information about substituents in the molecule, including halogens and functional groups.



06-CHEM-1

NOMENCLATURE AND ISOMERISM



HOW TO NAME ORGANIC COMPOUNDS WITH FUNCTIONAL GROUPS- EXAMPLES

Family	Formula	Suffix	Prefix	Example
Alkenes	$\text{RCH}=\text{CH}_2$	-ene		Propene ($\text{CH}_3\text{CH}=\text{CH}_2$)
Alkynes	$\text{RC}\equiv\text{CH}$	-yne		Propyne ($\text{CH}_3\text{C}\equiv\text{CH}$)
Halogenoalkanes	R-X (X = F, Cl, Br, I)	halo-	fluoro-, chloro-, bromo-, iodo-	Chloromethane (CH_3Cl)
Carboxylic Acids	RCOOH	-oic acid		Ethanoic Acid (CH_3COOH)
Anhydrides	$\text{RCOOCOR}'$	-anhydride		Ethanoic Anhydride ($\text{CH}_3\text{COOCOCH}_3$)
Esters	RCOOR'	-oate		Propyl Ethanoate ($\text{CH}_3\text{COOC}_3\text{H}_7$)
Acyl Chlorides	RCOCl	-oyl chloride		Ethanoyl Chloride (CH_3COCl)
Amides	RCONH_2	-amide		Ethanamide (CH_3CONH_2)
Nitriles	$\text{RC}\equiv\text{N}$	-nitrile		Ethanenitrile ($\text{CH}_3\text{C}\equiv\text{N}$)
Aldehydes	RCHO	-al		Ethanal (CH_3CHO)
Ketones	RCOR'	-one		Propanone (CH_3COCH_3)
Alcohols	ROH	-ol	hydroxy-	Ethanol ($\text{C}_2\text{H}_5\text{OH}$), 2-Hydroxyethanal (HOCH_2CHO)
Amines	RNH_2	-amine	amino-	Aminoethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$)
Arenes	$\text{C}_6\text{H}_5\text{R}$			Methylbenzene ($\text{C}_6\text{H}_5\text{CH}_3$)

ISOMERISM- OPTICAL ISOMERISM

Isomers: Compounds with the same molecular formula but different molecular structures or arrangements of atoms in space.

Types of Isomerism

1. Structural Isomers:

- Different Functional Groups: Isomers can have entirely different functional groups.
- Functional Groups Attached Differently:
 - Isomers may have functional groups attached to different points on the main carbon chain.
- Different Carbon Skeleton Arrangements:
 - Isomers can have distinct arrangements of carbon atoms in the molecule.

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NOMENCLATURE AND ISOMERISM



ISOMERISM- OPTICAL ISOMERISM CONTINUED

2. Stereoisomerism:

- Compounds have the same structural formula but differ in the spatial arrangement of their bonds.
- Types of Stereoisomerism:
 - E-Z Isomerism: Variations in the arrangement of groups around a double bond.
 - Optical Isomerism:
 - Occurs when there are four different substituents attached to a single carbon atom.
 - Results in two non-superimposable mirror images.

Example: Optical Isomers

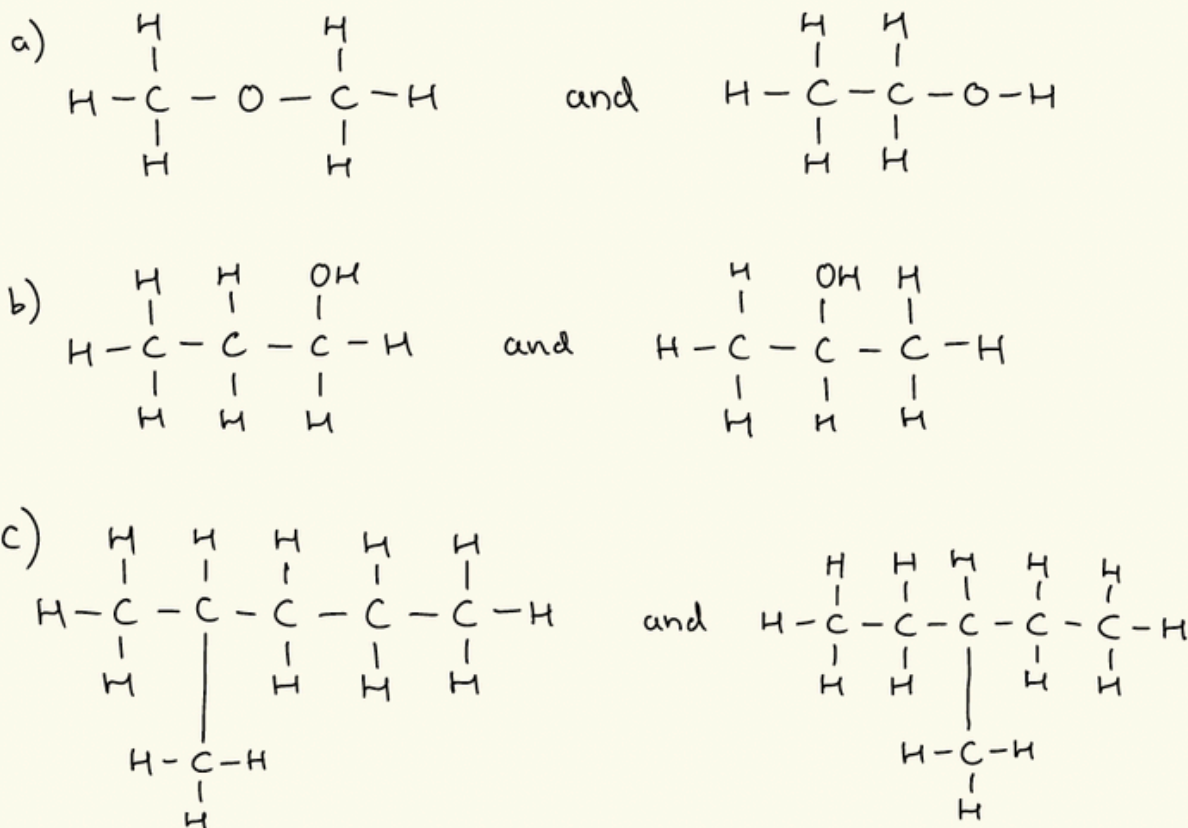
- Bromochlorofluoromethane:
 - Exists in two mirror image forms.
 - Visual aids, like ball and stick models, illustrate that these forms are not identical.
 - Rotating one molecule around the carbon-chlorine bond shows that the positions of bromine, hydrogen, and fluorine will not align perfectly, confirming that one cannot superimpose one molecule onto the other.

Analogy

- Optical isomers can be compared to a pair of shoes:
 - A left shoe and a right shoe are mirror images but not identical.
 - They cannot be superimposed.

Light Rotation

- Optical Isomers differ in how they rotate the plane of polarised light:
 - (+)-Isomer: Rotates plane polarised light clockwise.
 - (-)-Isomer: Rotates light plane polarised anticlockwise.



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NOMENCLATURE AND ISOMERISM



CHIRALITY

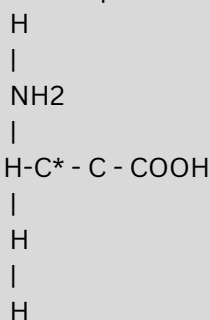
Chirality

- **Optical Isomers:**
 - Are classified as chiral compounds.
 - The two isomers are referred to as a pair of enantiomers.
- **Chiral Centre:**
 - The carbon atom bonded to four different groups is called the chiral centre or asymmetric carbon atom.
 - This carbon is often indicated in structural formulae with an asterisk (*).
 - A chiral molecule must contain at least one carbon atom that has four different groups attached.

Examples of Chiral Molecules

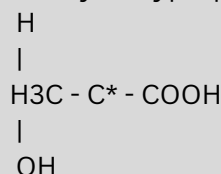
1. Alpha-Amino Acids:

- All alpha-amino acids, except aminoethanoic acid (glycine), possess a chiral centre.
- Alpha-Aminopropanoic Acid (2-aminopropanoic acid):



2-Hydroxypropanoic Acid:

- Commonly known as lactic acid (non-systematic name), this compound is also chiral.
- 2-Hydroxypropanoic Acid:



Representation of Optical Isomerism

- Three-Dimensional Structures:
 - Optical isomerism arises due to the three-dimensional structures of the isomers.
 - This can only be accurately represented using three-dimensional models or representations.

INVESTIGATING Optical Activity

- **Definition:**
 - Light consists of vibrating electric and magnetic fields, which can be visualized as waves with vibrations occurring in all directions perpendicular to the direction of the light wave's motion.
- **Polarisation:**
 - When light passes through a special filter called a polaroid (as in polaroid sunglasses), all vibrations are eliminated except those in one plane (e.g., the vertical plane).
 - The resulting light is termed vertically polarised.
- **Interaction with Optical Isomers:**
 - Vertically polarised light is affected differently by different optical isomers of the same substance.
 - Optical Rotation can be measured using a polarimeter.

Measuring Optical Rotation

1. Procedure:

- Polarised light is passed through two solutions of the same concentration, each containing a different optical isomer of the same substance.

2. Observation:

- One solution will rotate the plane of polarisation through a specific angle, clockwise. This is the (+)-isomer.
- The other solution will rotate the plane of polarisation by the same angle, anticlockwise. This is the (-)-isomer.

Notation for Isomers

- Different systems may be used to distinguish pairs of isomers, including:
 - (+) and (-)
 - R and S
 - D and L
 - d and l

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NOMENCLATURE AND ISOMERISM



SYNTHESIS OF OPTICALLY ACTIVE COMPOUNDS- LACTIC ACID

Racemic Mixtures

- **Definition:**

- Many reactions used in organic synthesis to produce optically active compounds yield a 50:50 mixture of two optical isomers.
- This mixture is called a racemic mixture or racemate and is not optically active because the effects of the two isomers cancel out.

Example: Synthesis of 2-Hydroxypropanoic Acid (Lactic Acid)

- **Chiral Centre:**

- 2-hydroxypropanoic acid (lactic acid) contains a chiral centre, indicated by an asterisk (*) in its structure.

- **Synthesis Process:**

- The synthesis of 2-hydroxypropanoic acid can be performed in two stages, starting from ethanal(acetaldehyde).

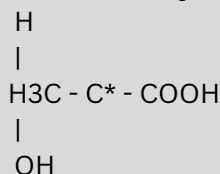
- **Stage 1:**

- The reaction of ethanal with a suitable reagent leads to the formation of an intermediate compound that can produce both optical isomers.

- **Stage 2:**

- This intermediate is then converted into 2-hydroxypropanoic acid, resulting in a racemic mixture of optical isomers.

Structure of 2-Hydroxypropanoic Acid



SYNTHESIS OF LACTIC ACID- IN DETAIL

Stage 1: Nucleophilic Addition Reaction

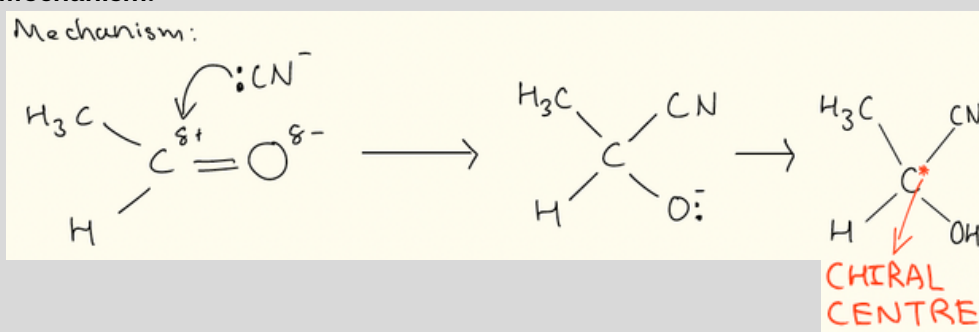
- **Reaction Overview:**

- Hydrogen cyanide (HCN) is added across the C=O bond of ethanal to form 2-hydroxypropanenitrile.
- This reaction is a nucleophilic addition reaction, where the nucleophile is the CN^- ion.

- **Chiral Centre:**

- 2-hydroxypropanenitrile has a chiral centre at the starred carbon, which is bonded to four different groups: $-\text{CH}_3$, $-\text{H}$, $-\text{OH}$, and $-\text{CN}$.
- The addition of the $-\text{CN}$ group occurs with equal probability from above or below the planar CH_3CHO , resulting in a racemic mixture of optical isomers.

- **Mechanism:**



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NOMENCLATURE AND ISOMERISM



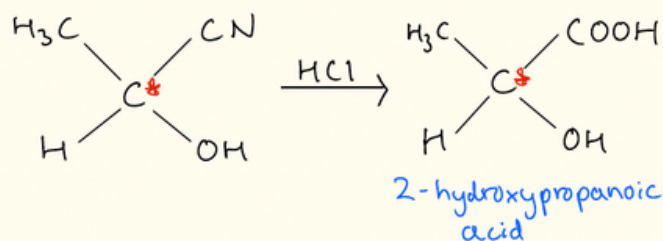
SYNTHESIS OF LACTIC ACID- IN DETAIL

Stage 2: Hydrolysis Reaction

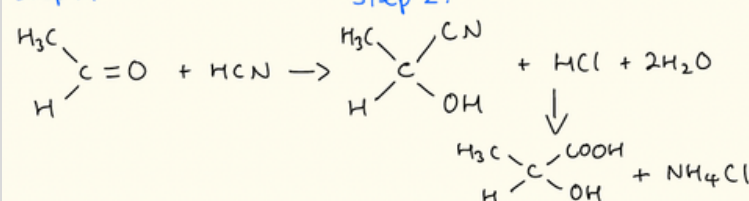
- Conversion to Carboxylic Acid:
 - 2-hydroxypropanenitrile is reacted with water acidified with dilute hydrochloric acid (HCl), leading to hydrolysis.
- **Result:**
 - The product, 2-hydroxypropanoic acid, retains the chiral centre; therefore, a racemic mixture of two optical isomers is produced.

Reaction Overview:

SYNTHESIS OF LACTIC ACID:



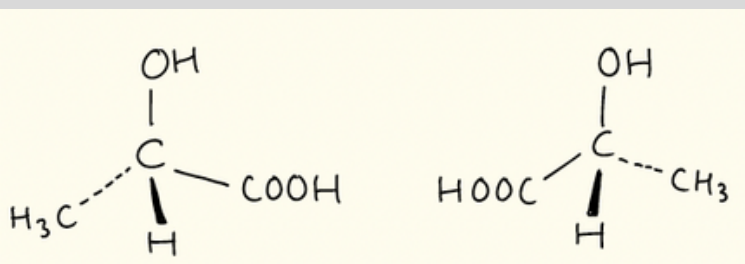
Step 1:



Natural Occurrence of Optical Isomers

- In synthetic processes, molecules with a chiral centre often result in a mixture of optical isomers.
- In contrast, naturally occurring molecules, such as amino acids, typically exist as only one optical isomer.
- Most naturally occurring amino acids (except aminoethanoic acid or glycine) are chiral, but only one isomer is produced in nature due to the action of enzyme catalysts, which preferentially synthesize one optical isomer.

EXAMPLES OF OPTICAL ISOMERS OF 2-HYDROXYPROPANOIC ACID



HOW ARE OPTICAL ISOMERS USED IN THE DRUG INDUSTRY?

Importance of Optical Isomers

- **Optically Active Molecules:** Some drugs are optically active, meaning they exist as pairs of optical isomers (enantiomers).
- **Racemic Mixture:** For certain applications, a racemic mixture of both optical isomers may be sufficient. However, for other uses, only one specific isomer is required.

Mechanism of Action

- **Receptors and Active Sites:**
 - Drugs often interact with receptors or the active sites of enzymes. This interaction resembles fitting a piece into a jigsaw puzzle.
 - Due to the three-dimensional structure of receptors, only one optical isomer can effectively bind to the target site.

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NOMENCLATURE AND ISOMERISM/COMPOUNDS CONTAINING THE CARBONYL GROUP



OPTICAL ISOMERS IN THE DRUG INDUSTRY CONTINUED

Challenges with Optical Isomers

- Active vs. Inactive Isomers:
 - In some cases, one optical isomer may be an effective drug, while the other is inactive. This situation poses several challenges:
- 1. Separation of Isomers:
 - Separating the two isomers can be difficult and expensive due to their similar properties.
- 2. Selling the Mixture:
 - Marketing the racemic mixture is wasteful since half of it may consist of the inactive isomer.
- 3. Alternative Synthesis:
 - Designing a synthetic route that selectively produces only the desired isomer can be a more efficient solution.

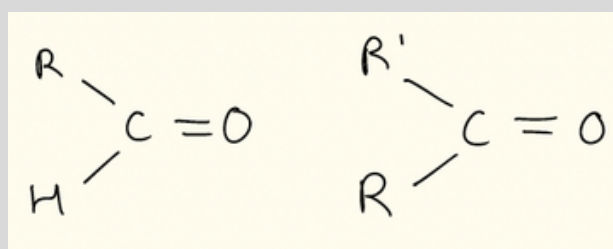
Example: Ibuprofen

- Ibuprofen (commercially known as Nurofen and Calprofen) is an example of a drug that highlights these concepts:
 - It exists as optical isomers, but only one isomer is therapeutically active.

ALDEHYDES AND KETONES- AN INTRO

Carbonyl Group

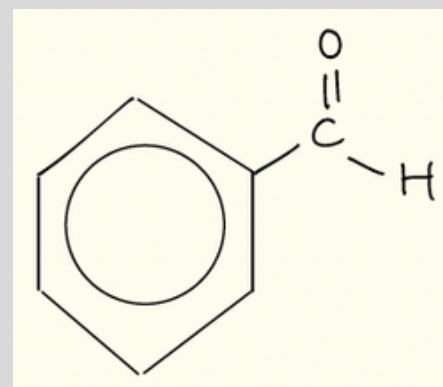
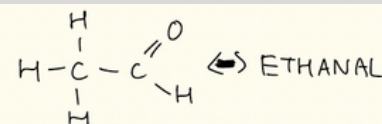
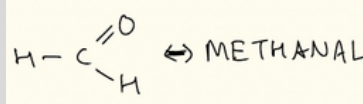
- The carbonyl group consists of a carbon-oxygen double bond (C=O).
- It is present in aldehydes and ketones:
 - Aldehydes: The carbonyl carbon has at least one hydrogen atom bonded to it. The general formula is RCHO.
 - Ketones: The carbonyl carbon is bonded to two organic groups, represented as R and R'. The formula is R'CO-R.



Naming Aldehydes and Ketones

Aldehydes

- Named using the suffix -al.
- The carbon of the aldehyde functional group is included in the carbon chain.
- Example names:
 - HCHO is called methanal.
 - CH₃CHO is called ethanal.
- The aldehyde group can only occur at the end of the carbon chain, so a numbering system is not necessary.
- Example: C₆H₅CHO is a derivative of benzene, known as benzenecarbaldehyde (often referred to as benzaldehyde).



Ketones

- Named using the suffix -one.
- The carbon atom of the ketone functional group is included in the carbon chain.
- The simplest ketone:
 - CH₃COCH₃ is called propanone.
- No ketone with fewer than three carbon atoms is possible.
- Example: Butanone can be represented as:
 - CH₃COCH₂CH₃ (butan-2-one).
- For larger carbon chains, numbers are required to locate the carbonyl group:
 - Example: Pentanone can be named as pentan-3-one (CH₃CH₂COCH₂CH₃) or pentan-2-one (CH₃COCH₂CH₂CH₃).

06-CHEM-2

COMPOUNDS CONTAINING THE CARBONYL GROUP



PROPERTIES (PHYSICAL) OF CARBONYL COMPOUNDS

- The carbonyl group ($C=O$) is strongly polar, resulting in permanent dipole-dipole forces between molecules.
- Boiling Points:**
 - Carbonyl compounds have higher boiling points than alkanes with comparable relative molecular mass due to these dipole-dipole interactions.
 - However, their boiling points are lower than those of alcohols, which can form hydrogen bonds.

Solubility in Water

- Short-chain aldehydes and ketones are completely miscible with water because hydrogen bonds form between the oxygen of the carbonyl compound and water molecules.
- As the length of the carbon chain increases, the solubility in water decreases.

Examples of Carbonyl Compounds:

- Methanal ($HCHO$): A gas at room temperature.
- Short-chain aldehydes and ketones: Typically liquids with characteristic smells.
 - Propanone (acetone): Commonly found in nail varnish remover.
 - Benzenecarbaldehyde: Has an almond scent and is used in soaps and food flavoring.

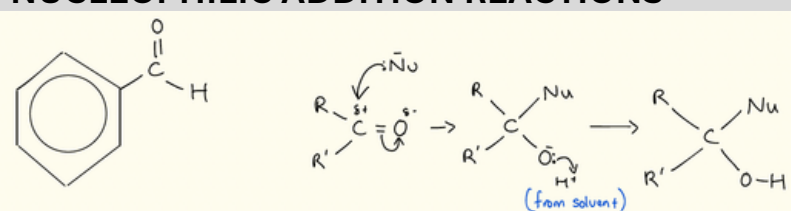
Reactivity of Carbonyl Compounds

- The $C=O$ bond in carbonyl compounds is strong, which might suggest low reactivity.
- However, nearly all reactions of carbonyl compounds involve the $C=O$ bond due to:
 - A significant difference in electronegativity between carbon and oxygen, making the bond strongly polar ($C\delta+-O\delta-$)
 - This polarity allows nucleophilic reagents to attack the carbonyl carbon.
- Since carbonyl compounds contain a double bond, they are classified as unsaturated, allowing for addition reactions.

Typical Reactions:

- The most common reactions involving the carbonyl group are nucleophilic addition reactions.

NUCLEOPHILIC ADDITION REACTIONS



Addition of Hydrogen Cyanide to Carbonyl Compounds

- Reagents Used:**
 - Sodium cyanide ($NaCN$) or potassium cyanide (KCN) is employed as a source of cyanide ions (CN^-).
 - The reaction is followed by the addition of dilute hydrochloric acid (HCl).
- Safety Note:**
 - This reaction is not performed in the laboratory due to the toxic nature of cyanide ions.
- Products:**
 - The resulting compounds from this reaction are called hydroxynitriles.

Importance of Hydroxynitriles

- Hydroxynitriles are significant in organic synthesis because:
 - They contain both the hydroxyl group ($-OH$) and the nitrile group ($-CN$), which are reactive and can be transformed into other functional groups.

Reaction Overview

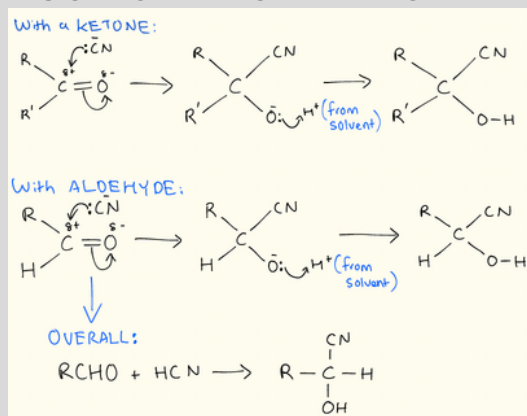
- The nucleophile in this reaction is the cyanide ion (CN^-), which attacks the electrophilic carbon atom of the carbonyl group ($C=O$), leading to the formation of the hydroxynitrile.

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COMPOUNDS CONTAINING THE CARBONYL GROUP



NUCLEOPHILIC ADDITION REACTIONS: THE MECHANISMS



REDOX REACTIONS OF CARBONYL COMPOUNDS- OXIDATION

Oxidation of Aldehydes

- Aldehyde Oxidation:
 - Aldehydes can be oxidised to carboxylic acids.
 - The oxidising agent is often represented as [O].
 - A commonly used oxidising agent is acidified potassium dichromate(VI) ($\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$).
- Ketone Stability:
 - Ketones are not easily oxidised to carboxylic acids.
 - This is because breaking a C-C bond is necessary, which requires stronger oxidising agents.
 - Stronger oxidising agents may break the hydrocarbon chain, resulting in shorter-chain molecules, carbon dioxide (CO_2), and water (H_2O).

Distinguishing Aldehydes from Ketones

- Weak oxidising agents can oxidise aldehydes but not ketones. This distinction is the basis for two common tests:

1. Fehling's Test:

- Composition:
 - Fehling's solution is a mixture of two solutions:
 - Fehling's A (contains Cu^{2+} ions, blue in colour)
 - Fehling's B (contains an alkali and a complexing agent).
- Reaction:
 - When an aldehyde is warmed with Fehling's solution:
 - A brick-red precipitate of copper(I) oxide (Cu_2O) is formed.
 - The copper(II) ion (Cu^{2+}) is reduced, while the aldehyde is oxidised to a carboxylic acid.
 - Result: Aldehydes yield a positive result, while ketones do not react.

2. Tollens' Test:

- Composition:
 - Tollens' reagent contains the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$, formed when aqueous ammonia is added to silver nitrate.
- Reaction:
 - When an aldehyde is warmed with Tollens' reagent:
 - Metallic silver is formed.
 - Aldehydes are oxidised to carboxylic acids, while silver ions (Ag^+) are reduced to metallic silver.
 - A silver mirror forms on the inside of a spotlessly clean test tube.
 - Result: Aldehydes yield a positive result, while ketones do not react.

Summary of Reactions

- General Equation for Aldehyde Oxidation:
 - $\text{RCHO} + [\text{O}] \rightarrow \text{RCOOH}$ (Aldehyde to Carboxylic Acid)
- General Equation for Tollens' Test:
 - $[\text{Ag}(\text{NH}_3)_2]^+ + \text{e}^- \rightarrow \text{Ag} + 2\text{NH}_3$ (Reduction of Silver Ion)

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COMPOUNDS CONTAINING THE CARBONYL GROUP



REDOX REACTIONS OF CARBONYL COMPOUNDS- REDUCTION

General Overview

- Many reducing agents can reduce both aldehydes and ketones to alcohols.
- A commonly used reducing agent is sodium tetrahydridoborate(III) (NaBH_4) in aqueous solution.
- This compound generates the nucleophile H^- (hydride ion), which is attracted to the carbonyl carbon ($\text{C}=\text{O}$) due to its partial positive charge (C^+).

Mechanism of Reduction

- H^- interacts with $\text{C}=\text{O}$, but not with $\text{C}=\text{C}$ bonds, as the latter is repelled by the high electron density in the double bond.

Reducing an Aldehyde

- Aldehydes are reduced to primary alcohols through the following nucleophilic addition mechanism:
 - Reaction:
 - $\text{RCHO} + \text{H}^- \rightarrow \text{RCH}_2\text{OH}$
- The overall reaction can be represented as:
 - $\text{RCHO} + [\text{H}] \rightarrow \text{RCH}_2\text{OH}$ (primary alcohol)

Reducing a Ketone

- Ketones are reduced to secondary alcohols similarly:
 - Reaction:
 - $\text{R}'\text{CO} + 2[\text{H}] \rightarrow \text{R}'\text{CHOH}$
- The overall reaction can be represented as:
 - $\text{R}'\text{CO} + [\text{H}] \rightarrow \text{R}'\text{CH}(\text{OH})\text{R}$ (secondary alcohol)

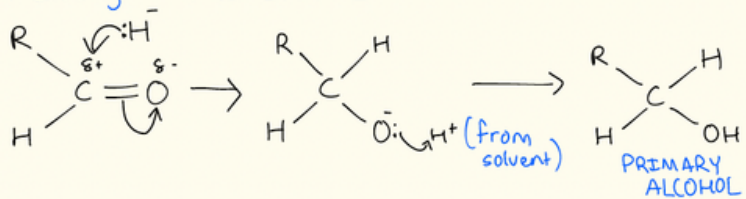
Summary of Reduction Reactions

- Aldehyde Reduction:
 - $\text{RCHO} + [\text{H}] \rightarrow \text{RCH}_2\text{OH}$ (Primary Alcohol)
- Ketone Reduction:
 - $\text{R}'\text{CO} + [\text{H}] \rightarrow \text{R}'\text{CHOH}$ (Secondary Alcohol)

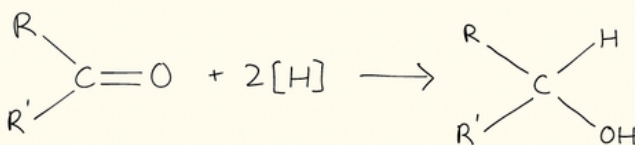
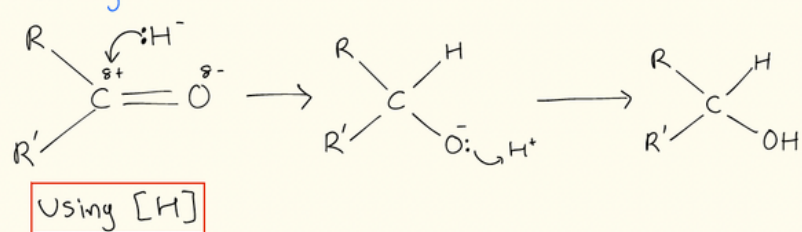
Notes

- These reactions are classified as nucleophilic addition reactions, where the hydride ion (H^-) acts as the nucleophile.

Reducing an ALDEHYDE:



Reducing a KETONE:



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COMPOUNDS CONTAINING THE CARBONYL GROUP



CARBOXYLIC ACIDS

Functional Group

- The carboxylic acid functional group is represented as -COOH or -C(=O)OH .
- This functional group can only occur at the end of a carbon chain.

Structure

- Carboxylic acids contain two functional groups:
 - The carbonyl group (C=O), which is also found in aldehydes and ketones.
 - The hydroxy group (-OH), which is found in alcohols.

Properties

- The presence of both the carbonyl and hydroxy groups on the same carbon atom significantly changes the properties of each group:
 - The -OH group in carboxylic acids is much more acidic compared to the -OH group in alcohols.
 - This increased acidity is due to the ability of carboxylic acids to donate a proton (H^+) more readily.

Example

- A well-known example of a carboxylic acid is ethanoic acid (also known as acetic acid), which is commonly found in vinegar.

NAMING CARBOXYLIC ACIDS

General Naming Rules

- Carboxylic acids are named using the suffix -oic acid .
- The carbon atom of the carboxylic acid functional group is counted as part of the carbon chain when determining the root name.

Examples

- Methanoic acid: HCOOH
- Ethanoic acid: CH_3COOH

Naming with Substituents

- When there are substituents or side chains on the carbon chain:
 - Number the carbon atoms starting from the carboxylic acid carbon (carbon number one).

Examples:

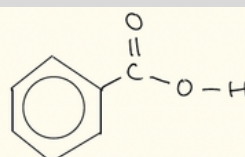
- 2-Bromopropanoic acid: $\text{CH}_3\text{CHBrCOOH}$
- 3-Methylbutanoic acid: $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH}$

Naming Aromatic Carboxylic Acids

- When the functional group is attached to a benzene ring, the suffix -carboxylic acid is used, and the carbon of the carboxylic acid functional group is not counted as part of the root.

Example:

- Benzenecarboxylic acid: $\text{C}_6\text{H}_5\text{COOH}$ (also commonly referred to as benzoic acid).



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BENZENE CARBOXYLIC ACID
(BENZOIC ACID)

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COMPOUNDS CONTAINING THE CARBONYL GROUP



PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

Solubility in Water

- Carboxylic acids can form hydrogen bonds with water molecules, which enhances their solubility.
- Solubility: Carboxylic acids with up to four carbon atoms (including butanoic acid) are completely soluble in water.

Melting Points

- Carboxylic acids also form hydrogen bonds with each other in the solid state, leading to higher melting points compared to alkanes of similar molecular mass.
- Example:
 - Ethanoic acid ($M_r = 60$) melts at 290 K.
 - Butane ($M_r = 58$) melts at 135 K.
- Melting Point Determination:
 - The melting point of a carboxylic acid can be measured using a Thiele tube or electrically and compared with known melting point tables to identify the acid.

Freezing Point

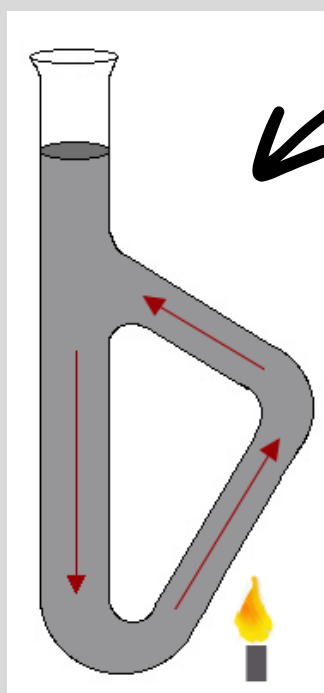
- Pure ethanoic acid is often referred to as glacial ethanoic acid because it may freeze on a cold day, with a freezing point of 13 °C (260 K).

Odour Characteristics

- Carboxylic acids have distinctive smells:
 - Ethanoic acid has a vinegar-like smell.
 - Butanoic acid is associated with the smell of rancid butter.

Non-Systematic Names

- Carboxylic acids with longer carbon chains also have common names:
 - Hexanoic acid is known as caproic acid.
 - Octanoic acid is known as caprylic acid.
- These names are derived from their presence in goat fat, contributing to its unpleasant smell.



**MELTING POINT
MEASURING
APPARATUS- THE
THIELE TUBE**

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COMPOUNDS CONTAINING THE CARBONYL GROUP



ESTERS AND HOW TO NAME ESTERS

Structure and General Formula

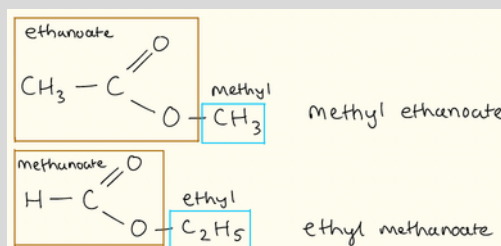
- Definition: Esters are compounds derived from carboxylic acids, formed when the hydrogen from the -OH group of the acid is replaced by a hydrocarbon group (an alkyl or aryl group).
- General Formula: The structure of esters can be represented as RCOOR' , where:
 - R is the alkyl or aryl group derived from the acid.
 - R' is the hydrocarbon group that replaces the hydrogen atom.

Naming Esters

- Naming Convention: The names of esters are based on the parent carboxylic acid, with the name always starting with the alkyl or aryl group that replaces the hydrogen atom from the acid.
- Examples:
 - Methyl Ethanoate: Derived from ethanoic acid, it is represented as $\text{CH}_3\text{COOCH}_3$.
 - Ethyl Methanoate: Derived from methanoic acid, it is represented as $\text{C}_2\text{H}_5\text{COOCH}_3$.

Properties and Uses

- Volatility and Odour: Short-chain esters are typically volatile and possess pleasant fruity smells, making them popular in flavourings and perfumes.
 - Examples of Fruity Smells:
 - 3-Methylbutyl Ethanoate: Smells like pear drops.
 - Octyl Ethanoate: Has an orange flavour.
 - Pentyl Pentanoate: Smells and tastes of apples.
- Applications:
 - Esters are widely used as solvents and plasticisers.
 - Fats and oils are also classified as esters, typically having longer carbon chains.



REACTIONS OF CARBOXYLIC ACIDS

Polarisation of the Carboxylic Acid Group

- The carboxylic acid group ($-\text{COOH}$) is polarized, with a positive charge (δ^+) on the hydrogen and a negative charge (δ^-) on the oxygen.
- The carbon atom (C) is electrophilic, making it open to attack from nucleophiles.
- The carbonyl oxygen ($\text{C}=\text{O}$) can also be attacked by positively charged species (such as H^+), a process known as protonation.

Loss of Proton

- When the hydrogen from the -OH group is lost, a negative ion known as a carboxylate ion is formed:
 - $\text{R}-\text{C}(=\text{O})\text{O}^-$ (carboxylate ion)
- The negative charge is delocalized over the carboxylate group, which stabilizes the resulting ion.
- Carboxylic acids are classified as weak acids, meaning that the equilibrium lies to the left, but they are sufficiently strong to react with sodium hydrogencarbonate (NaHCO_3), producing carbon dioxide, which distinguishes them from other organic compounds containing -OH groups (like alcohols).

Reactions of Carboxylic Acids

- Carboxylic acids act as proton donors and exhibit typical acid reactions. They can form ionic salts with more reactive metals, alkalis, metal oxides, or metal carbonates, producing compounds known as carboxylates.
- Examples of carboxylate formation:
 - Methanoic acid produces methanoates.
 - Ethanoic acid produces ethanoates.
 - Propanoic acid produces propanoates.

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COMPOUNDS CONTAINING THE CARBONYL GROUP



REACTIONS OF CARBOXYLIC ACIDS--> CONTINUED (EXAMPLES)

Example Reactions

1. Reaction with Sodium Hydroxide:

- Ethanoic acid reacts with aqueous sodium hydroxide:
- Ethanoic acid (CH_3COOH) + Sodium hydroxide (NaOH) $\rightarrow$ Sodium ethanoate (CH_3COONa) + Water (H_2O)

2. Reaction with Sodium Carbonate:

- Ethanoic acid reacts with aqueous sodium carbonate:
- 2 Ethanoic acid (CH_3COOH) + Sodium carbonate (Na_2CO_3) $\rightarrow$ 2 Sodium ethanoate (CH_3COONa) + Water (H_2O) + Carbon dioxide (CO_2)

ESTERS

Formation of Esters

- Esters are derivatives of carboxylic acids with the general formula RCOOR' .
- The formation of esters occurs when carboxylic acids react with alcohols, typically in the presence of a strong acid catalyst.
- This reaction is reversible, leading to an equilibrium mixture of reactants and products.
- Example Reaction:
 - Ethanoic acid (CH_3COOH) + Ethanol ($\text{C}_2\text{H}_5\text{OH}$) $\rightleftharpoons$ Ethyl ethanoate ($\text{CH}_3\text{COOC}_2\text{H}_5$) + Water (H_2O)

Hydrolysis of Esters

- The carbonyl carbon atom in an ester carries a partial positive charge (δ^+), making it susceptible to attack by water acting as a weak nucleophile. This reaction is the reverse of ester formation.
- The hydrolysis of esters does not proceed to completion and establishes an equilibrium mixture that includes the ester, water, carboxylic acid, and alcohol. The acid acts as a catalyst, influencing the rate of reaching equilibrium but not the equilibrium composition.
- Hydrolysis Reaction:
 - Ester (RCOOR') + Water (H_2O) $\rightleftharpoons$ Carboxylic acid (RCOOH) + Alcohol ($\text{R}'\text{OH}$)

Acid-Catalyzed Hydrolysis Example

- The balanced equation for the acid-catalyzed hydrolysis of ethyl ethanoate is:
 - Ethyl ethanoate ($\text{CH}_3\text{COOC}_2\text{H}_5$) + Water (H_2O) $\rightleftharpoons$ Ethanoic acid (CH_3COOH) + Ethanol ($\text{C}_2\text{H}_5\text{OH}$)

Base-Catalyzed Hydrolysis

- Bases can also catalyze the hydrolysis of esters. In this case, the salt of the acid is produced rather than the acid itself.
- The base removes the acid from the reaction mixture, preventing the establishment of equilibrium, which allows the reaction to proceed to completion.
- Base-Catalyzed Hydrolysis Reaction:
 - Ethyl ethanoate ($\text{CH}_3\text{COOC}_2\text{H}_5$) + Sodium hydroxide (NaOH) + Water (H_2O) $\rightarrow$ Sodium ethanoate (CH_3COONa) + Ethanol ($\text{C}_2\text{H}_5\text{OH}$)

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COMPOUNDS CONTAINING THE CARBONYL GROUP



SOME EXAMPLES OF COMMON FATTY ACIDS

Name	Formula	Details
Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$	Present in most animal fats
Palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$	Used in making soaps
Oleic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	Monounsaturated; has one double bond, present in most fats and in olive oil
Linoleic acid	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{CO}_2\text{H}$	Polyunsaturated; present in many vegetable oils

Glycerol (Propane-1,2,3-triol)

- **Glycerol** contains **three -OH (hydroxyl) groups**, allowing it to form hydrogen bonds, making it highly soluble in water.
- It is an important chemical used in various industries with a wide range of applications:
 - **Pharmaceutical and Cosmetic Preparations:** Used to prevent ointments and creams from drying out due to its hygroscopic nature (water-attracting).
 - **Solvent in Medicines:** Acts as a solvent for many medicinal compounds.
 - **Food Industry:** Used as a solvent for food colorings and other ingredients.
 - **Plasticiser:** Utilised to plasticise materials like sheets, gaskets, cellophane, and special quality papers. Plasticisers, such as esters of hexanedioic acid, are added to polymers to improve flexibility and smoothness. For example, PVC can contain up to 50% plasticiser, but over time, the plasticiser may leak out, leading to brittleness and inflexibility.

Biodiesel as a Renewable Fuel

- **Definition:** Biodiesel is a renewable fuel produced from oils derived from crops, such as rape seed.
- **Source:**
 - Rape seed oil is a triglyceride ester.
- **Production Process:**
 - Reactants: Rape seed oil and methanol.
 - Catalyst: A strong alkali is used as a catalyst.
 - Reaction: The reaction generates a mixture of methyl esters suitable for diesel vehicles.
- **Advantages:**
 - Can be used in diesel vehicles with little or no modifications.
 - The production process is relatively simple, allowing individuals to make biodiesel at home (e.g., using used cooking oil).
- **Commercial Availability:**
 - Germany has thousands of filling stations supplying biodiesel, often at a lower cost than ordinary diesel fuel.
 - In France, all fossil diesel fuel contains between 2% and 5% biodiesel, promoting sustainability.

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COMPOUNDS CONTAINING THE CARBONYL GROUP



ACYLATION AND ACID DERIVATIVES

- **Definition:**
 - Acylation is the process of introducing an acyl group into another molecule.
 - The acyl group has the general structure:
 - O
 - ||
 - R-C-
- **Acid Derivatives:**
 - A group of compounds known as acid derivatives contain the acyl group as part of their structure.
 - They are derived from carboxylic acids and have the general formula:
 - O
 - ||
 - R-C-Z
 - Z can be a variety of groups.

Name of Acid Derivative	General Formula	Example
Ester	RCOOR'	Ethyl ethanoate (CH ₃ COOC ₂ H ₅)
Acid Chloride	RCOCl	Ethanoyl chloride (CH ₃ COCl)
Acid Anhydride	RCOOCOR'	Ethanoic anhydride (CH ₃ COOCOCH ₃)

REACTIVITY OF ACID DERIVATIVES

- **Polarisation of Carbonyl Group:**
 - The carbonyl group of an acid derivative is polarised, making the carbon more positive:
 - O δ^-
 - ||
 - R-C-Z
- **Nucleophilic Attack:**
 - The carbon atom (C δ^+) is attacked by nucleophiles, which replace the Z group, resulting in the nucleophile acquiring an acyl group:
 - General reaction:
 - Nu⁻ + R-C-Z $\rightarrow$ R-C-Nu + Z
- **Factors Affecting Reactivity:**
 - Magnitude of δ^+ Charge:
 - Depends on the electron-releasing or attracting power of Z.
 - Leaving Group Ability:
 - How easily Z is lost (Z is the leaving group).
 - Nucleophile Quality:
 - The effectiveness of the nucleophile in the reaction.
- **Reactivity of Acid Derivatives:**
 - Acid chlorides and acid anhydrides withdraw electrons from the carbonyl carbon, making it more positive and reactive towards nucleophiles.
 - Both are good acylating agents, with acid chlorides being somewhat more reactive than acid anhydrides

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COMPOUNDS CONTAINING THE CARBONYL GROUP



NUCLEOPHILES

- **Definition of Nucleophiles:**

- Nucleophiles are species that have a lone pair of electrons, which they use to attack electron-deficient carbon atoms ($C\delta^+$).
- The best nucleophiles are those that are most effective at donating their lone pairs.

Reactivity of Common Nucleophiles

- Acyl chlorides and acid anhydrides will react with various nucleophiles in the following order of reactivity:

1. Primary Amine ($R-NH_2$)
2. Ammonia (NH_3)
3. Alcohol ($R-OH$)
4. Water (H_2O)

Reaction Overview

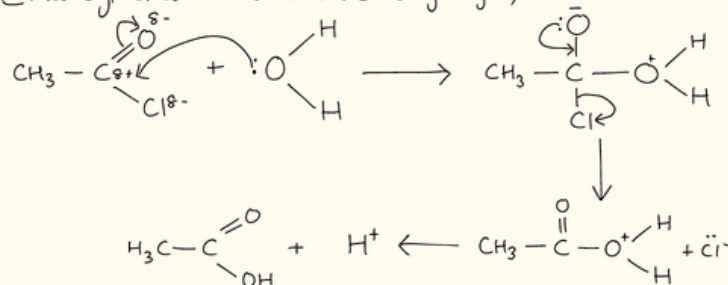
- The reactions of these nucleophiles with acyl chlorides and acid anhydrides are classified as addition-elimination reactions.
- Since these nucleophiles are neutral, they must lose a hydrogen ion during the reaction.
- Conceptually, one can view these reactions as the replacement of a hydrogen atom (the "active hydrogen") of the nucleophile by an acyl group.

Products of Reactions

- The products formed from these reactions are as follows:

1. With Ammonia (NH_3):
 - Product: Amide
 - Structure:
 $R-C(=O)-NH_2$
2. With Primary Amine ($R-NH_2$):
 - Product: N-Substituted Amide
 - Structure:
 $R-C(=O)-NHR$
3. With Alcohol ($R-OH$):
 - Product: Ester
 - Structure:
 $R-C(=O)-OR'$
4. With Water (H_2O):
 - Product: Carboxylic Acid
 - Structure:
 $R-C(=O)-OH$

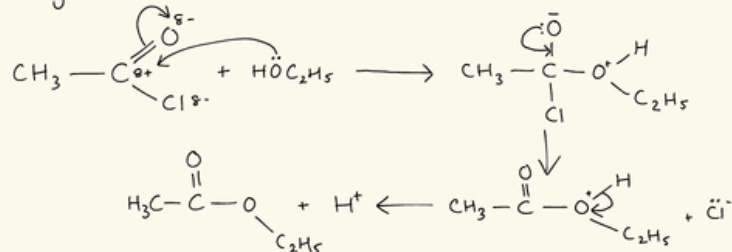
1) Ethanoyl Chloride and water (Hydrolysis)



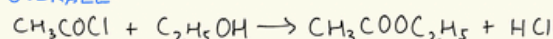
OVERALL:



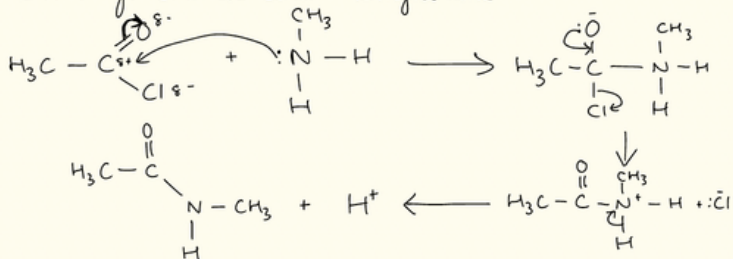
2) Ethanoyl Chloride and Ethanol



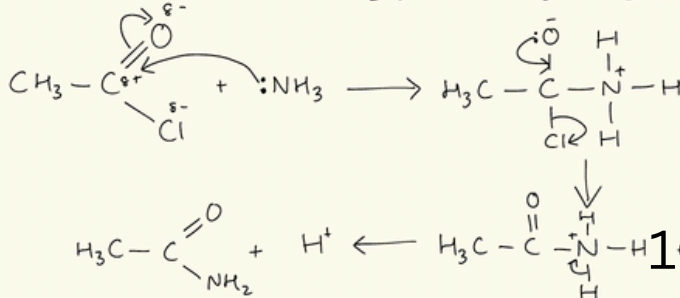
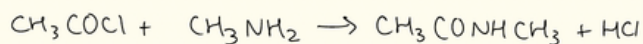
OVERALL:



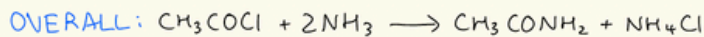
3) Ethanoyl Chloride and Methylamine



OVERALL:



OVERALL:



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COMPOUNDS CONTAINING THE CARBONYL GROUP



USE OF ACYLATION REACTIONS

Definition:

- Acylation is the process of introducing an acyl group ($R-C=O$) into another molecule.

Acid Derivatives:

- Compounds that contain the acyl group are known as acid derivatives. Two important types of acid derivatives are:
 - Acid chlorides ($RCOCl$)
 - Acid anhydrides ($RCOOCOR'$)

Structure of Acid Derivatives

- The general formula for acid derivatives is $RCOZ$, where Z can be various groups.

Name of Acid Derivative	General Formula	Example
Ester	$RCOOR'$	Ethyl ethanoate ($CH_3COOC_2H_5$)
Acid Chloride	$RCOCl$	Ethanoyl chloride (CH_3COCl)
Acid Anhydride	$RCOOCOR'$	Ethanoic anhydride ($CH_3COOCOCH_3$)

Reactivity of Acid Derivatives

- The carbonyl carbon atom in acid derivatives has a partial positive charge ($C\delta^+$). This makes it susceptible to attack by nucleophiles, which are species that can donate a pair of electrons to form a new bond.

Factors Affecting Reactivity

- Polarity of the Carbonyl Group:** The magnitude of the positive charge on the carbonyl carbon is influenced by the electron-releasing or withdrawing ability of Z .
- Leaving Group Ability:** How easily Z can leave during the reaction. Good leaving groups form stable negative ions.
- Nucleophile Strength:** The better the nucleophile can donate its electrons, the more reactive it will be.

Common Nucleophiles

Acyl chlorides and acid anhydrides react with various nucleophiles, which can be ranked in terms of reactivity:

- Primary amine
- Ammonia
- Alcohol
- Water

Reaction Types

- The reactions of nucleophiles with acyl chlorides and acid anhydrides are known as addition-elimination reactions. During these reactions, the nucleophile loses a hydrogen ion (H^+), replacing the "active hydrogen" with an acyl group.

Products from Reactions with Nucleophiles:

- Ammonia $\rightarrow$ Forms an amide ($R-C(=O)-NH_2$).
- Primary Amine $\rightarrow$ Forms an N-substituted amide ($R-C(=O)-N-R'$).
- Alcohol ($-OH$) $\rightarrow$ Forms an ester ($R-C(=O)-O-R'$).
- Water $\rightarrow$ Forms a carboxylic acid ($R-C(=O)-OH$).

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COMPOUNDS CONTAINING THE CARBONYL GROUP/AROMATIC CHEMISTRY



USE OF ACYLATION REACTIONS

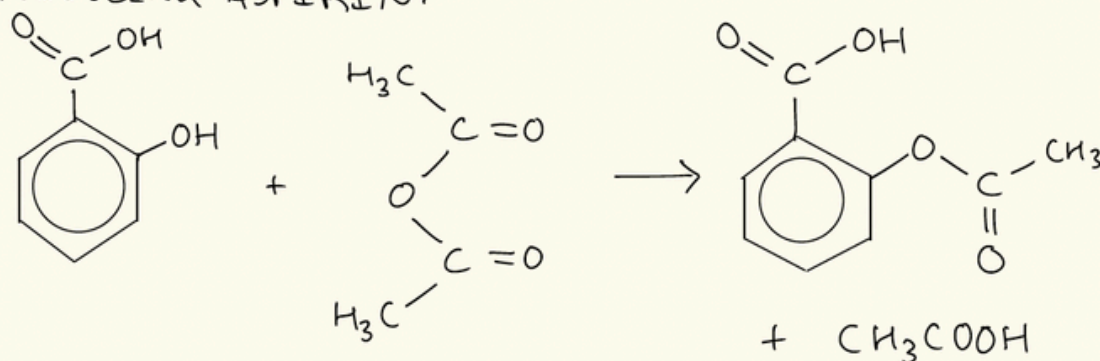
Uses of Acylation Reactions

- Ethanoic Anhydride:
 - Manufactured on a large scale due to its advantages over ethanoyl chloride:
 - Cost: Cheaper
 - Corrosiveness: Less corrosive
 - Water Reactivity: Does not react with water as readily
 - Safety: Produces ethanoic acid (a mild acid) as a by-product instead of hydrogen chloride (which is corrosive).

Example: Production of Aspirin

- Aspirin, scientifically known as 2-ethanoyloxybenzenecarboxylic acid, is a widely used medication for treating pain and reducing fever.
- Historical Context:
 - Originally derived from willow bark, its use can be traced back to ancient remedies.
 - In 1890, Felix Hofmann synthesised aspirin from salicylic acid, an extract of willow bark, to treat his father's rheumatism.

PRODUCING ASPIRIN:



INTRO TO AROMATIC CHEMISTRY- ARENES

- **Definition:** Arenes are hydrocarbons based on benzene (C_6H_6), which is the simplest aromatic compound.
- **Structure:**
 - Benzene: Benzene has a hexagonal (six-sided) ring structure that is stabilised by a special type of bonding known as resonance.
 - Bonding: Despite being unsaturated, benzene is very stable due to the delocalisation of π electrons across the ring. This gives rise to its characteristic stability compared to alkenes.
 - Skeletal Formula: Benzene is represented by a skeletal formula that shows the hexagon with a circle inside, indicating the delocalised electrons. Each vertex of the hexagon represents a carbon atom bonded to a hydrogen atom.
- **History:**
 - The term "aromatic" originally derived from the isolation of these compounds from sweet-smelling oils, such as balsam. Today, "aromatic" refers to the structure and properties of these compounds rather than their smell.
- **Substituents:**
 - Arenes can have functional groups (substituents) that replace one or more of the hydrogen atoms in the benzene ring. This leads to a wide variety of aromatic compounds with different properties and reactivities.

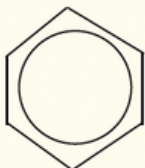


BONDING AND STRUCTURE OF BENZENE

- **Molecular Formula:** Benzene has the formula C_6H_6 .
- **Challenges in Understanding:**
 - **Unsaturation:** Although benzene is unsaturated, it does not readily undergo addition reactions, which is typical for unsaturated compounds.
 - **Bond Equivalence:** All carbon atoms in benzene are equivalent, indicating that all carbon-carbon bonds are the same.
- **Structure:**
 - **Geometry:** Benzene consists of a flat, regular hexagon of carbon atoms, with each carbon bonded to one hydrogen atom. This flat structure differs from the puckered structure of cyclohexane.
- **Bond Lengths:**
- The carbon-carbon bond lengths in benzene are intermediate between those expected for a single bond and a double bond, indicating that each bond is a resonance hybrid. This is often represented with a symbol ($-C=C-$), suggesting bond character between single and double.

Delocalisation:

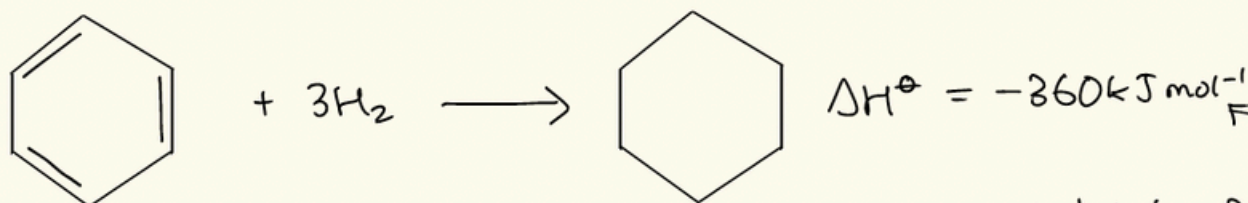
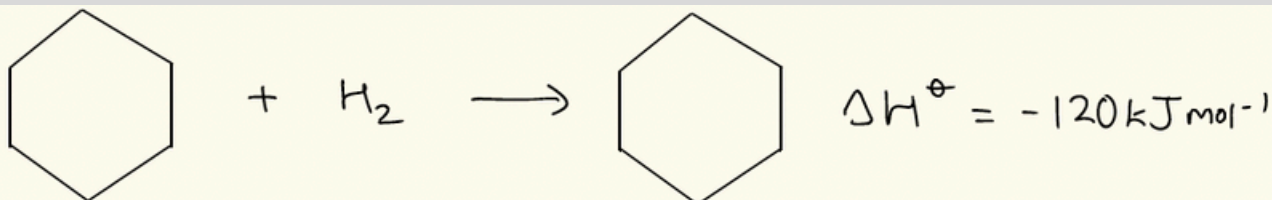
- **Electrons:** In benzene, the electrons are delocalised across the six carbon atoms, meaning they are spread over more than two atoms.
- **Covalent Bonds:** Each carbon atom forms three covalent bonds—one with a hydrogen atom and two with adjacent carbon atoms.
- **P-Orbitals:** The fourth electron of each carbon atom resides in a p-orbital. The six p-orbitals overlap, leading to delocalisation and forming a region of electron density above and below the ring.
- **Stability:**
 - The delocalised system of electrons contributes significantly to the stability of benzene, known as aromatic stability. This unique stability is crucial for understanding the chemistry of benzene and its derivatives.

The symbol  is used to represent this

The bonding and stability of benzene can be understood through the concept of delocalisation of electrons:

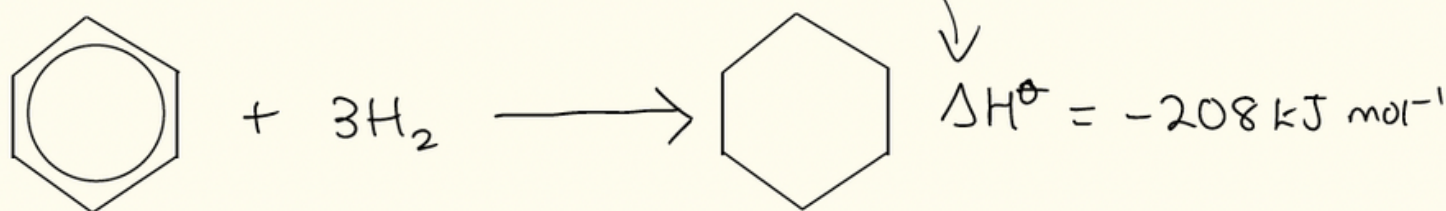
- **Delocalisation:** In benzene, some of the electrons are delocalised, meaning they are shared over more than just two atoms. In this case, the six carbon atoms in the benzene ring share these electrons.
- **Covalent Bonds:** Each carbon atom in benzene forms:
 - Three covalent bonds:
 - i. One bond with a hydrogen atom.
 - ii. Two bonds with adjacent carbon atoms.
- **P-Orbitals and Delocalised Electrons:**
 - Each carbon atom has a fourth electron that occupies a p-orbital.
 - The six p-orbitals (one on each carbon) overlap, and the electrons in these orbitals become delocalised, creating a region of electron density above and below the carbon ring.
- **Bonding:** Due to this delocalisation, the carbon-carbon bonds in benzene are intermediate between single and double bonds, contributing to its unique structure and properties.
- **Aromatic Stability:**
 - The delocalised system makes benzene unusually stable, a feature referred to as aromatic stability. This stability is central to benzene's chemistry and is shared by many of its derivatives.

THERMOCHEMICAL EVIDENCE FOR THE STABILITY OF BENZENE



Hydrogenation of a ring with alternate double bonds would be expected to be $3 \times (-120)$

BUT enthalpy change for BENZENE is lower



PHYSICAL PROPERTIES OF ARENES

- **Benzene is a colourless liquid at room temperature.**
 - Boiling point: 353 K (similar to hexane's boiling point of 354 K).
 - Freezing point: 279 K (much higher than hexane's freezing point of 178 K).
 - Benzene's higher freezing point is due to its flat, hexagonal molecules packing together tightly in the solid state, making them harder to separate during melting.
- **Solubility:**
 - Non-polar arenes do not mix with water but dissolve in other hydrocarbons and non-polar solvents.

Naming Aromatic Compounds:

- Substituted arenes are named as derivatives of benzene, where benzene forms the root of the name.

Reactivity of Aromatic Compounds:

Two key factors affect the reactivity of arenes:

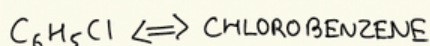
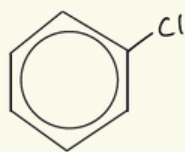
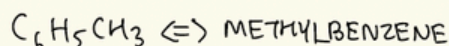
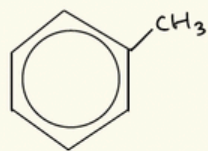
- High electron density:
 - The aromatic ring contains delocalised electrons, making it a region of high electron density.
 - This high electron density attracts electrophiles (electron-seeking species).
- Aromatic stability:
 - The aromatic ring is very stable due to delocalisation energy.
 - Delocalisation energy is the energy required to break the stable ring structure. As a result, the ring typically remains intact during chemical reactions.

06-CHEM-3

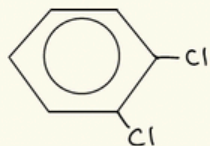
AROMATIC CHEMISTRY



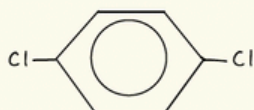
EXAMPLES OF NAMING ARENES



If there is more than 1 substituent then the ring is numbered:



1,2-dichlorobenzene



1,4-dichlorobenzene

REACTIONS OF ARENES

Combustion of Arenes:

- Arenes burn in air with smoky flames.
 - This is due to their high carbon-to-hydrogen ratio, compared to alkanes.
 - The incomplete combustion of arenes leaves unburnt carbon which produces soot.
 - A smoky flame often indicates the presence of an aromatic compound.

Electrophilic Substitution Reactions:

- Although benzene is unsaturated, it does not react like alkenes.
- The typical reaction for benzene is electrophilic substitution, where:
 - The aromatic system remains unchanged.
 - Addition reactions are not favoured because they would require the input of delocalisation energy to disrupt the aromatic system.

Mechanism of Electrophilic Substitution:

- The delocalised electrons in the aromatic ring create a region of high electron density that attracts electrophiles (E^+).
- The electrons in the ring are also attracted towards the electrophile.

1. Formation of the bond:

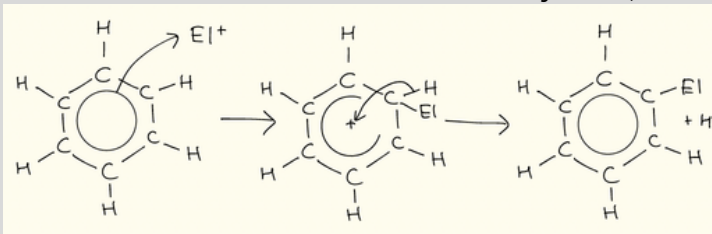
- A bond forms between one of the carbon atoms in the ring and the electrophile.
- To form this bond, the carbon atom must use electrons from the delocalised system, temporarily destroying the aromatic system.

2. Restoration of the aromatic system:

- To restore the stability of the aromatic system, the carbon atom loses a H^+ ion.
- The electron from the $C-H$ bond returns to the delocalised system, re-establishing aromatic stability.
- This overall process involves the substitution of a H^+ ion with an electrophile (E^+).

Examples:

- The same mechanism applies in reactions like nitration and Friedel-Crafts acylation, which are key electrophilic substitution reactions for arenes.





ELECTROPHILIC SUBSTITUTION- NITRATION

Nitration of Arenes:

- Nitration is the substitution of a NO_2 group for a hydrogen atom on an arene ring.

Generation of the Electrophile (NO_2^+):

- The electrophile NO_2^+ (nitronium ion) is generated using a mixture of concentrated nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4).
 - Sulfuric acid acts as a stronger acid and donates a proton (H^+) to nitric acid:
 - $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$
 - The H_2NO_3^+ then loses a water molecule to produce the NO_2^+ (nitronium ion):
 - $\text{H}_2\text{NO}_3^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}$
 - Overall equation for the generation of NO_2^+ :
 - $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$

Mechanism of Nitration:

- Electrophilic attack:
 - The NO_2^+ ion acts as the electrophile and attacks the electron-rich benzene ring.
- Intermediate formation:
 - A bond forms between the benzene ring and the NO_2^+ ion, temporarily disrupting the delocalised system.
- Restoration of aromaticity:
 - The H^+ ion is lost, and the electron from the C-H bond returns to the delocalised system, restoring aromatic stability.
 - The H^+ ion then reacts with HSO_4^- to regenerate H_2SO_4 , making sulfuric acid a catalyst in the reaction.

Overall Reaction:

- The product of the nitration reaction is nitrobenzene:
 - $\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$

Uses of Nitrated Arenes:

- Nitration is an important step in:
 - The production of explosives such as TNT (trinitrotoluene).
 - The synthesis of aromatic amines, which are used to produce industrial dyes.

TNT

TNT (Trinitrotoluene)

- TNT stands for 2,4,6-trinitrotoluene and is made by nitrating methylbenzene (toluene).
- TNT is a significant high explosive with various applications, both in military operations and peaceful uses.

Properties of TNT:

- TNT is a solid with a low melting point, making it useful for filling shells.
- Bomb disposal teams often use steam to safely remove TNT from unexploded bombs due to its low melting point.

Explosion of TNT:

- The explosion of TNT can be represented by the following equation:
 - $\text{C}_7\text{H}_5\text{N}_3\text{O}_6 \rightarrow 7 \text{CO} + 7 \text{CO}_2 + 2.5 \text{N}_2 + 2.5 \text{H}_2\text{O}$
- The reaction is highly exothermic, producing large amounts of gas and heat. This rapid release of gas and energy leads to the destructive force of the explosion.

Other Explosive Compounds:

- Compounds containing several nitrogen atoms are often explosive.
- An example is 2,4,6-trinitrophenol, which is used as a detonator due to its ability to explode on impact and set off other explosives

FRIEDEL-CRAFTS ACYLATION REACTIONS

- Friedel-Crafts acylation reactions involve the substitution of an RCO group (acyl group) onto an aromatic ring.
- This process uses aluminium chloride (AlCl_3) as a catalyst.
- These reactions were developed by Charles Friedel and James Crafts.

Mechanism of Acylation:

1. Acylium ion (RCO^+) formation:

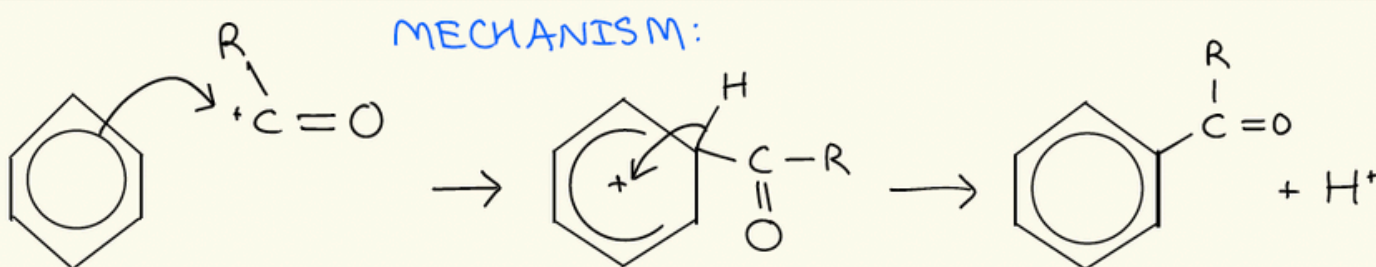
- The acyl chloride (RCOCl) reacts with AlCl_3 , which accepts a lone pair from the chlorine atom of the acyl chloride.
- This results in the formation of the acylium ion, RCO^+ , which is a strong electrophile:
 - $\text{RCOCl} + \text{AlCl}_3 \rightarrow \text{RCO}^+ + \text{AlCl}_4^-$

2. Electrophilic Substitution:

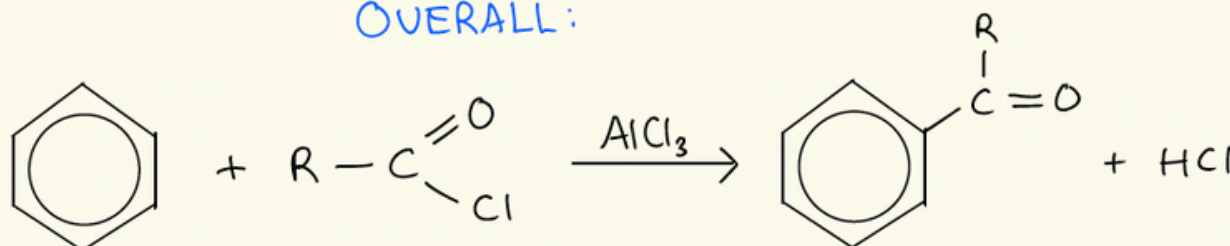
- The RCO^+ electrophile is attacked by the delocalised π -electrons of the benzene ring.
- This results in the substitution of a hydrogen atom on the aromatic ring by the RCO group.

3. Catalyst Regeneration:

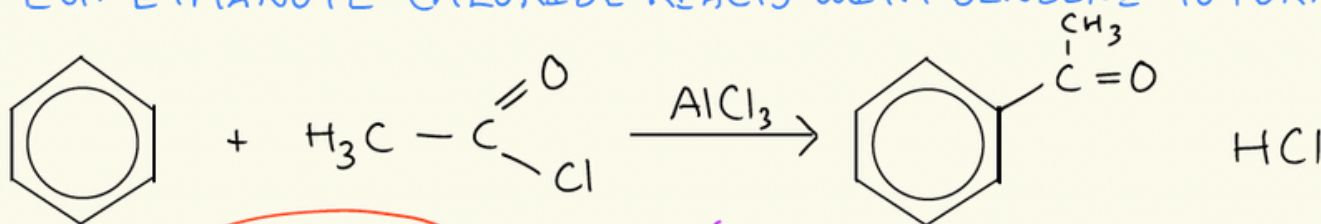
- The AlCl_4^- ion reacts with the proton (H^+) removed from the ring to regenerate the AlCl_3 catalyst:
 - $\text{AlCl}_4^- + \text{H}^+ \rightarrow \text{AlCl}_3 + \text{HCl}$



OVERALL:



EG: ETHANOYL CHLORIDE REACTS WITH BENZENE TO FORM:



06-CHEM-4

AMINES



INTRO TO AMINES

Amines are organic compounds derived from ammonia (NH_3), where one or more of the hydrogen atoms in ammonia are replaced by alkyl (R) or aryl groups. These are classified based on the number of groups attached to the nitrogen atom.

- Ammonia: NH_3 has three hydrogen atoms bonded to the nitrogen.
- Primary amines (1°): One hydrogen atom in ammonia is replaced by an alkyl or aryl group (R-NH_2).
- Secondary amines (2°): Two hydrogen atoms are replaced by alkyl or aryl groups (R_2NH).
- Tertiary amines (3°): All three hydrogen atoms are replaced by alkyl or aryl groups (R_3N).

Key point: The terms primary, secondary, and tertiary in amines refer to the number of alkyl or aryl groups attached to the nitrogen atom, unlike in alcohols where they refer to the number of alkyl groups attached to the carbon bonded to the hydroxyl ($-\text{OH}$) group.

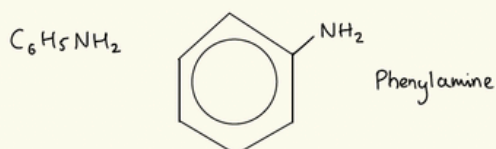
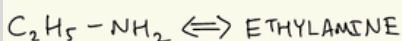
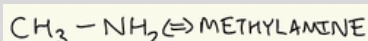
Structure:

- Ammonia: NH_3
 - H-N-H
 - H
- Primary amine (1°): R-NH_2
 - R-N-H
 - H
- Secondary amine (2°): R_2NH
 - $\text{R-N-R}'$
 - H
- Tertiary amine (3°): R_3N
 - $\text{R-N-R}'$
 - R''

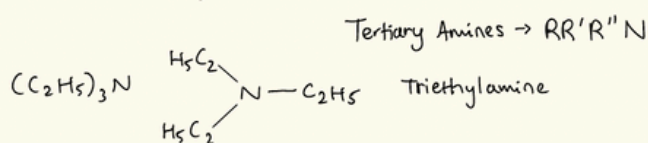
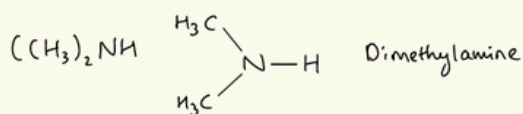
Applications:

Amines are highly reactive compounds, making them important intermediates in the synthesis of new molecules. They are used in the production of dyes, pharmaceuticals, and polymers.

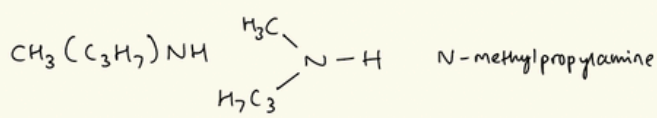
NAMING AMINES



Secondary amines have the general formula $\text{RR}'\text{NH}$, for example:



Different substituents are written in alphabetical order:





PROPERTIES AND REACTIVITY OF AMINES

Shape

- Amines have a pyramidal shape similar to ammonia (NH_3).
- The bond angles in ammonia are approximately 107° , which is slightly less than the tetrahedral angle of 109.5° . This is due to the lone pair of electrons on nitrogen, which repels more strongly than the bonding pairs in the N-H bonds.
- Primary amines maintain this basic shape due to the similar bonding structure.

Boiling Points

- Amines are polar molecules, with hydrogen bonding possible between their $-\text{NH}_2$ groups.
- The hydrogen bonds in amines are not as strong as in alcohols, because nitrogen is less electronegative than oxygen ($\text{N} = 3.0$, $\text{O} = 3.5$ on the electronegativity scale).
- As a result, the boiling points of amines are lower than those of comparable alcohols. For example:
 - Methylamine ($\text{CH}_3\text{-NH}_2$, $\text{Mr} = 31$) has a boiling point of 267 K .
 - Methanol ($\text{CH}_3\text{-OH}$, $\text{Mr} = 32$) has a boiling point of 338 K .
- Shorter chain amines (e.g., methylamine, ethylamine) are gases at room temperature, while slightly longer chain amines are volatile liquids.
- Amines have fishy smells, and diamines and triamines are responsible for the smell of rotting fish and animal flesh as they are produced during the decomposition of proteins.

Solubility

- Primary amines with chains up to four carbon atoms are very soluble in water and alcohols because they can form hydrogen bonds with the solvents.
- Phenylamine ($\text{C}_6\text{H}_5\text{NH}_2$), due to the non-polar benzene ring, is less soluble in water, as the ring cannot form hydrogen bonds.
- Most amines are also soluble in less polar solvents.

Reactivity of Amines

- Amines have a lone pair of electrons on the nitrogen atom, which is important for their reactivity.
- The lone pair can be used to form a bond with:
 - H^+ ion: When the amine acts as a base.
 - Electron-deficient carbon atom: When the amine acts as a nucleophile.

These properties make amines versatile in chemical reactions and valuable intermediates in synthesis.



AMINE MECHANISM OF REACTION



AMINES AS BASES AND THE REACTIONS INVOLVED

Brønsted-Lowry Bases

- Amines can accept a proton (H^+ ion), which classifies them as Brønsted-Lowry bases.
- For example, phenylamine reacts with H^+ to form phenylammonium chloride, an ionic, water-soluble salt:
 - $C_6H_5NH_2 + H^+ + Cl^- \rightarrow C_6H_5NH_3^+ + Cl^-$
 - Phenylamine $\rightarrow$ Phenylammonium chloride

Reaction as Bases

- Amines react with acids to form salts. For instance, ethylamine reacts with dilute hydrochloric acid to produce ethylammonium chloride:
 - $C_2H_5NH_2 + H^+ + Cl^- \rightarrow C_2H_5NH_3^+ + Cl^-$
 - Ethylamine $\rightarrow$ Ethylammonium chloride
- The products are ionic compounds that can crystallize as the water evaporates.

Solubility of Amines

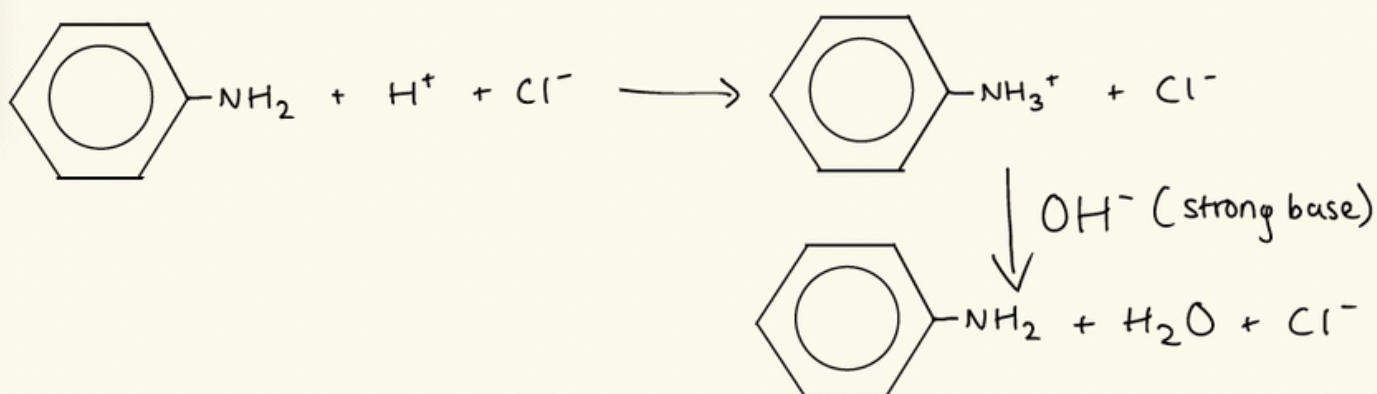
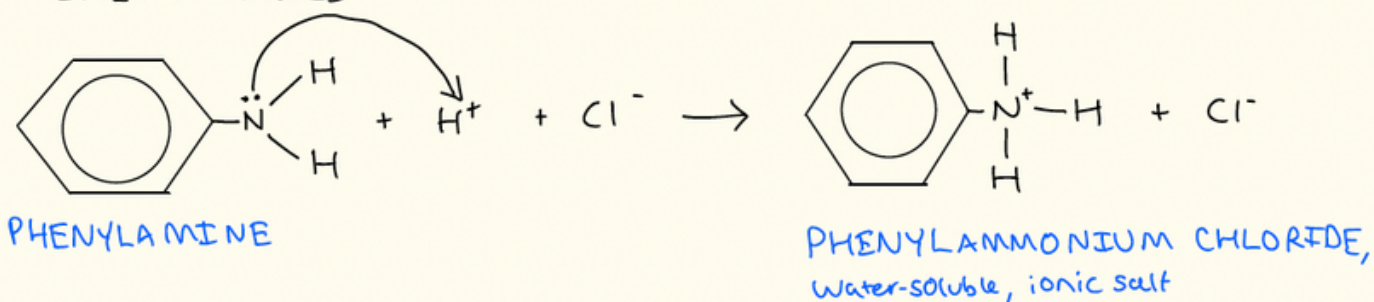
- Phenylamine (an arylamine) is relatively insoluble in water, but it becomes soluble when reacted with excess hydrochloric acid due to the formation of a soluble ionic salt, phenylammonium chloride.

Regenerating the Amine

- If a strong base, such as sodium hydroxide, is added to the solution, it removes the proton from the ionic salt and regenerates the insoluble amine:
 - $C_6H_5NH_3^+ + OH^- \rightarrow C_6H_5NH_2 + H_2O$
 - Phenylammonium chloride $\rightarrow$ Phenylamine

This shows the basic properties of amines and their ability to react with acids to form salts, which can be reversed by strong bases.

AMINES AS BASES





AMINES AS BASES AND THE REACTIONS INVOLVED

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COMPARING THE AMINE BASE STRENGTHS

The base strength of amines and ammonia depends on how readily they accept a proton (H^+), which is influenced by the electron density on the nitrogen atom. Here's how different groups attached to nitrogen affect base strength:

Alkylamines (Inductive Effect)

- Alkyl groups push electron density towards the nitrogen atom, increasing its electron density. This effect is called the inductive effect, which makes the nitrogen atom a better electron pair donor and, thus, more likely to accept a proton (H^+).
- Primary alkylamines (one alkyl group) are stronger bases than ammonia because of the inductive effect.
- Secondary alkylamines (two alkyl groups) have two inductive effects, making them even stronger bases than primary alkylamines.
- Tertiary alkylamines (three alkyl groups) would theoretically be stronger bases, but they are less soluble in water, which reduces their basic strength compared to secondary alkylamines.

Aryl Amines (Electron Withdrawal)

- Aryl groups (such as in phenylamine) withdraw electron density from the nitrogen atom because the nitrogen's lone pair overlaps with the delocalised system of the benzene ring. This makes nitrogen a weaker electron pair donor.
- As a result, arylamines are weaker bases than ammonia, as they are less likely to attract protons.

Base Strength Comparison

- Ethylamine > Ammonia > Phenylamine
- Strongest to weakest base



REACTIONS OF AMMONIA WITH HALOGENOALKANES

Reaction of Ammonia with Halogenoalkanes

Overview: When ammonia reacts with a halogenoalkane, a nucleophilic substitution reaction occurs. The halide (X^-) is replaced by an amine group ($-NH_2$), forming a primary amine.

Primary Amine Formation

Ammonia, NH_3 , acts as a nucleophile because of its lone pair of electrons on nitrogen. It attacks the carbon atom attached to the halogen in the halogenoalkane (RX), leading to the following steps:

1. Ammonia + Halogenoalkane $\rightarrow$ [Alkylammonium ion] + Halide ion
2. $NH_3 + RX \rightarrow [RNH_3]^+ + X^-$
3. The alkylammonium ion loses a proton (H^+) to another ammonia molecule, forming a primary amine: $[RNH_3]^+ + NH_3 \rightarrow RNH_2 + [NH_4]^+$

Explanation:

- NH_3 acts as a nucleophile and substitutes the halogen atom (X^-) on the halogenoalkane.
- The result is a primary amine (RNH_2) and ammonium ion ($[NH_4]^+$).

Formation of Secondary and Tertiary Amines

Primary amines can also act as nucleophiles, and they can further react with additional halogenoalkane molecules. This leads to the formation of secondary and tertiary amines through similar nucleophilic substitution.

1. Primary amine + Halogenoalkane $\rightarrow$ [Dialkylammonium ion] + Halide ion
2. $RNH_2 + RX \rightarrow [R_2NH_2]^+ + X^-$
3. The dialkylammonium ion loses a proton to form a secondary amine: $[R_2NH_2]^+ + NH_3 \rightarrow R_2NH + [NH_4]^+$
4. Secondary amine + Halogenoalkane $\rightarrow$ [Trialkylammonium ion] + Halide ion
5. $R_2NH + RX \rightarrow [R_3NH]^+ + X^-$
6. The trialkylammonium ion loses a proton to form a tertiary amine: $[R_3NH]^+ + NH_3 \rightarrow R_3N + [NH_4]^+$

Quaternary Ammonium Salt Formation

If the tertiary amine reacts with another halogenoalkane, a quaternary ammonium salt forms. In this case, there are no protons to lose:

1. Tertiary amine + Halogenoalkane $\rightarrow$ Quaternary ammonium salt
2. $R_3N + RX \rightarrow [R_4N]^+X^-$

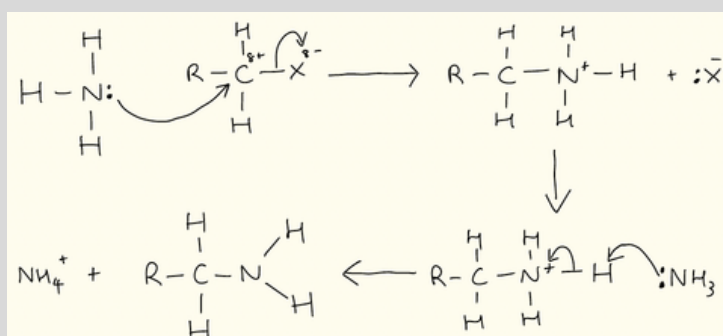
Summary of Products:

- Primary amine: RNH_2
- Secondary amine: R_2NH
- Tertiary amine: R_3N
- Quaternary ammonium salt: $[R_4N]^+X^-$

Key OCR Mark Scheme Points:

- The reaction involves nucleophilic substitution.
- Ammonia and primary amines act as nucleophiles.
- The halogen atom (X^-) is substituted by the amine group.
- A primary amine is formed when ammonia reacts with halogenoalkane.
- Secondary and tertiary amines can form when the primary amine reacts with more halogenoalkane.
- A quaternary ammonium salt forms when a tertiary amine reacts with a halogenoalkane.

By using an excess of ammonia, the yield of primary amines is maximized. Without this excess, you will obtain a mixture of primary, secondary, and tertiary amines along with quaternary ammonium salts.



06-CHEM-4

AMINES



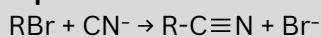
PREPARATION OF AMINES: PRIMARY AMINES VS REDUCTION OF NITRILES

Primary amines can be prepared in a two-step process starting from halogenoalkanes. This method involves the conversion of the halogenoalkane into a nitrile followed by the reduction of the nitrile to a primary amine. This process is often preferred over the direct reaction of halogenoalkanes with ammonia, as it produces a purer product, with only primary amines formed.

Step 1: Formation of Nitriles (Nucleophilic Substitution)

- Halogenoalkanes react with the cyanide ion (CN^-) in aqueous ethanol.
- The cyanide ion acts as a nucleophile and substitutes the halide ion (Br^-) in the halogenoalkane to form a nitrile ($\text{R}-\text{C}\equiv\text{N}$).

Equation



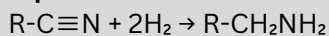
(Where R is the alkyl group and Br^- is the bromide ion)

- The nitrile ($\text{R}-\text{C}\equiv\text{N}$) contains the cyano group ($-\text{C}\equiv\text{N}$), and it will be reduced in the next step.

Step 2: Reduction of Nitriles

- The nitrile is reduced to a primary amine using hydrogen (H_2) and a nickel catalyst. This process adds hydrogen to the carbon and nitrogen atoms of the nitrile group, converting it into a primary amine.

Equation



(Where R is the alkyl group, and H_2 is hydrogen gas)

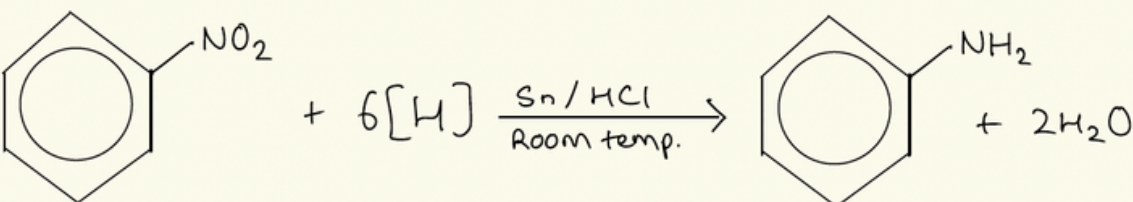
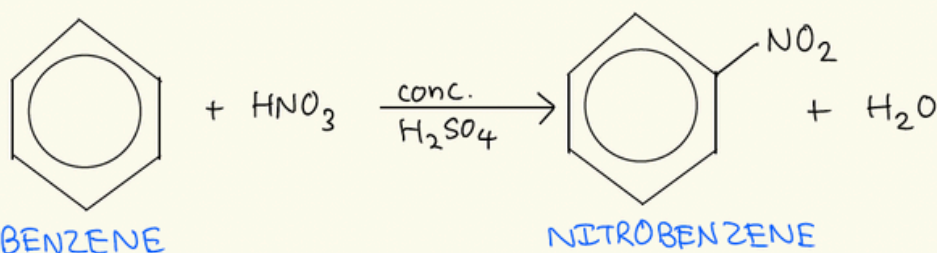
Summary of the Process:

- Nucleophilic substitution of the halogenoalkane by cyanide ion produces a nitrile ($\text{R}-\text{C}\equiv\text{N}$).
- Reduction of the nitrile with hydrogen and a nickel catalyst produces a primary amine ($\text{R}-\text{CH}_2\text{NH}_2$).

Advantages:

- This method produces only primary amines, unlike the reaction of halogenoalkanes with ammonia, which can result in a mixture of primary, secondary, and tertiary amines.
- The carbon chain of the product is one carbon atom longer than the original halogenoalkane, due to the incorporation of the cyanide ion.

SYNTHESIS OF PHENYLALAMINE





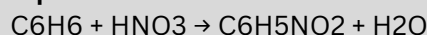
SYNTHESIS OF PHENYLALANINE

Phenylamine (C₆H₅NH₂) is the simplest arylamine and serves as an important chemical intermediate in the synthesis of dyes, pharmaceuticals, and other compounds. It is typically produced on an industrial scale using benzene, a compound derived from crude oil.

Step 1: Formation of Nitrobenzene (Nitration of Benzene)

- Benzene is first converted into nitrobenzene (C₆H₅NO₂) by reacting it with a mixture of concentrated nitric acid (HNO₃) and concentrated sulfuric acid (H₂SO₄). This is an example of an electrophilic substitution reaction where a nitro group (-NO₂) replaces one of the hydrogen atoms on the benzene ring.

Equation:



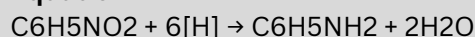
(Where C₆H₆ is benzene, HNO₃ is nitric acid, and C₆H₅NO₂ is nitrobenzene)

- Sulfuric acid acts as a catalyst in this reaction, helping to generate the nitronium ion (NO₂⁺), which is the actual electrophile that reacts with benzene.

Step 2: Reduction of Nitrobenzene to Phenylamine

- The nitrobenzene (C₆H₅NO₂) is then reduced to phenylamine (C₆H₅NH₂) using tin (Sn) and hydrochloric acid (HCl) as the reducing agents. During the reaction, tin reacts with hydrochloric acid to produce hydrogen (H₂), which reduces the nitro group (-NO₂) to an amine group (-NH₂).

Equation:



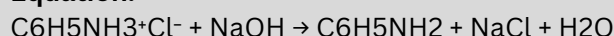
(Where C₆H₅NO₂ is nitrobenzene, 6[H] represents the reducing hydrogen, C₆H₅NH₂ is phenylamine, and H₂O is water)

- Since the reaction occurs in an acidic medium, the product is not phenylamine directly but its salt form, phenylammonium chloride (C₆H₅NH₃⁺Cl⁻).

Step 3: Liberation of Free Phenylamine

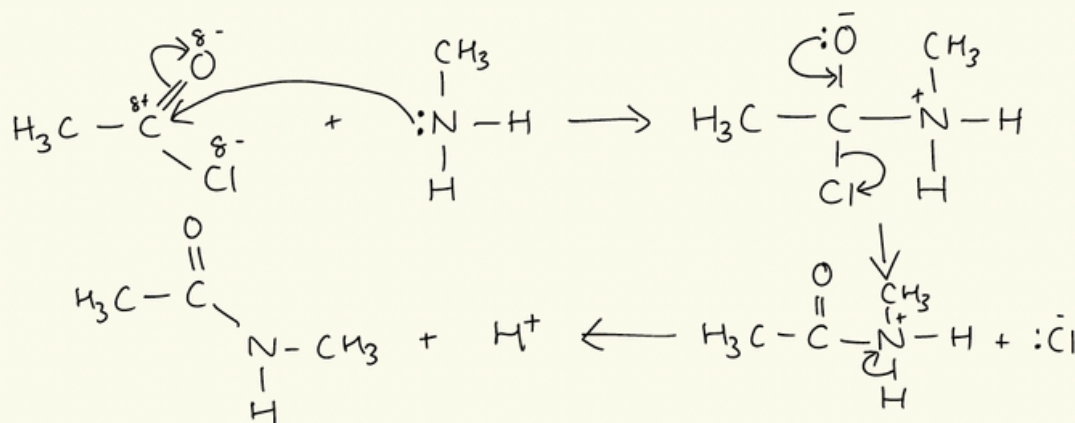
- The final step involves treating the phenylammonium chloride (C₆H₅NH₃⁺Cl⁻) with sodium hydroxide (NaOH). This removes the proton (H⁺) from the amine group, regenerating the free phenylamine (C₆H₅NH₂).

Equation:



(Where C₆H₅NH₃⁺Cl⁻ is phenylammonium chloride, NaOH is sodium hydroxide, C₆H₅NH₂ is phenylamine, NaCl is sodium chloride, and H₂O is water)

FORMATION OF AMIDES





FORMATION OF AMIDES FROM AMINES

Amides are a class of compounds formed when amines react with **acid chlorides** or **acid anhydrides**. This reaction involves nucleophilic substitution, sometimes referred to as addition-elimination reactions. The resulting products are N-substituted amides.

Mechanism of Amide Formation

1. Nucleophilic Attack:

- The amine (RNH_2) acts as a nucleophile and attacks the electrophilic carbon atom of the acid chloride (RCOCl) or acid anhydride.
- This step forms a tetrahedral intermediate.

2. Example Reaction:

- For acid chloride:
- $\text{RCOCl} + \text{RNH}_2 \rightarrow \text{RCONHR} + \text{HCl}$
- Where:
 - RCOCl is the acid chloride,
 - RNH_2 is the amine,
 - RCONHR is the N-substituted amide,
 - HCl is hydrochloric acid released during the reaction.

3. Elimination of HCl:

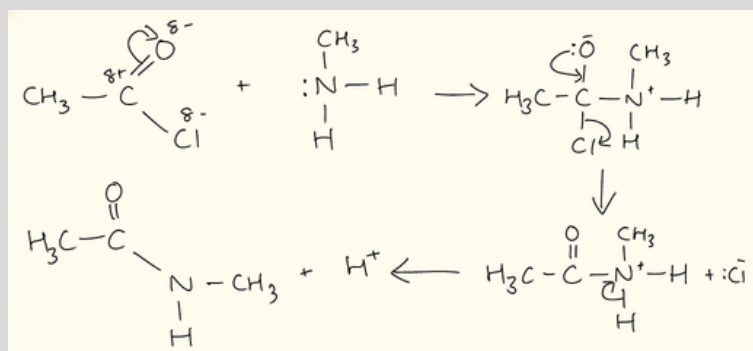
- The tetrahedral intermediate collapses, leading to the elimination of hydrochloric acid (HCl), resulting in the formation of the amide.

4. Overall Reaction:

- $\text{RCOCl} + \text{RNH}_2 \rightarrow \text{RCONHR} + \text{HCl}$

5. Polymers:

- This reaction is particularly useful in the synthesis of polymers such as nylon, where long chains of amides are formed through repeated reactions between diacid chlorides and diamines.



ECONOMIC IMPORTANCE OF AMINES

Amines are versatile compounds widely utilized in the production of various synthetic materials, including:

1. Nylon and Polyurethane:

- Amines are key building blocks in the synthesis of nylon, a type of polyamide formed through condensation reactions involving diamines and dicarboxylic acids.
- Polyurethanes are produced by reacting isocyanates with polyols, where amines can play a role in modifying the properties of the resulting polymer.

2. Dyes:

- Many dyes contain amine functional groups, which enhance their reactivity and ability to bond with fibers, making them effective coloring agents in textiles.

3. Pharmaceuticals:

- Amines are integral to the structure of many drugs, contributing to their biological activity. They often serve as functional groups that interact with biological targets.



ECONOMIC IMPORTANCE OF AMINES- CONTINUED

Quaternary Ammonium Compounds

Quaternary ammonium compounds (quats) are a specific category of amines used extensively in industrial applications, particularly in hair and fabric conditioners. Key features include:

- **Structure:**
 - Quats consist of a long hydrocarbon chain attached to a positively charged organic group. This results in a cationic nature that enhances their effectiveness as surfactants.
- **Functionality:**
 - Cationic Surfactants: In aqueous solutions, quaternary ammonium compounds behave as cationic surfactants. Their positively charged ends attract negatively charged surfaces, such as wet fabric and hair.
 - Static Electricity Reduction:
 - The positive charges of the cations bond to the negatively charged surfaces of wet fabrics and hair, forming a protective coating.
 - This coating helps prevent the build-up of static electricity, maintaining a smooth texture in fabrics and reducing flyaway hair in hair conditioners.

Mechanism of Action

- When used in fabric and hair conditioners, quaternary ammonium compounds:
 - Adsorb onto surfaces: The positively charged cationic groups adhere to the wet surfaces, creating a barrier.
 - Disperse in water: In aqueous solutions, quats cluster with their charged ends in water while their hydrocarbon tails orient toward the surface, enhancing the smoothness and feel of fabrics and hair.



CONDENSATION REACTIONS AND CONDENSATION POLYMERS

Condensation Reaction: A condensation reaction occurs when two molecules react together, resulting in the elimination of a small molecule, often water (H₂O) or hydrogen chloride (HCl).

Example of a Condensation Reaction

- Formation of Esters:
 - Esters are formed when carboxylic acids react with alcohols.
 - During this reaction, water is eliminated. The hydrogen from the alcohol combines with the hydroxyl (-OH) group from the carboxylic acid, forming an ester.
 - Equation:
 - Carboxylic Acid + Alcohol → Ester + Water
 - $R-C(=O)OH + R'-OH \rightarrow R-C(=O)OR' + H_2O$

Condensation Polymers

Condensation Polymers are formed from two different monomers, each containing two functional groups. These functional groups can react with one another, leading to the formation of long-chain polymers. Examples include:

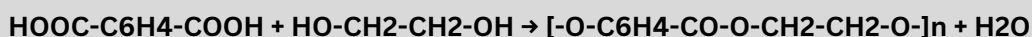
1. Polyesters
2. Polyamides
3. Polypeptides

Structure of Polyesters

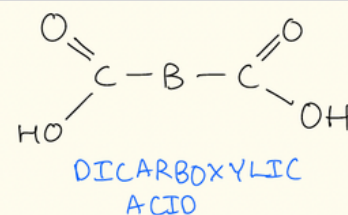
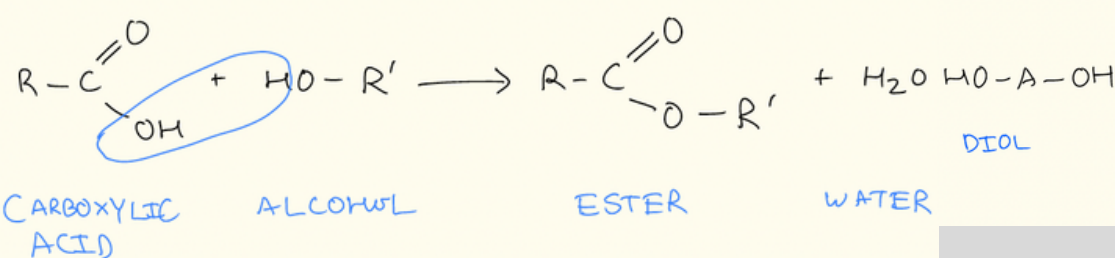
- A polyester features the ester linkage (-COO-) repeated throughout its structure.
- To synthesize a polyester, diols (which have two -OH groups) and dicarboxylic acids (which have two -COOH groups) are used.
- Example of Polymer Formation:
 - When diols and dicarboxylic acids react, they form a polyester and eliminate water molecules in the process.
 - Equation:
 - Diol + Dicarboxylic Acid → Polyester + Water
 - $HO-R-OH + HOOC-R'-COOH \rightarrow -O-R-O-C(=O)-R'- + H_2O$

Terylene: A Specific Polyester

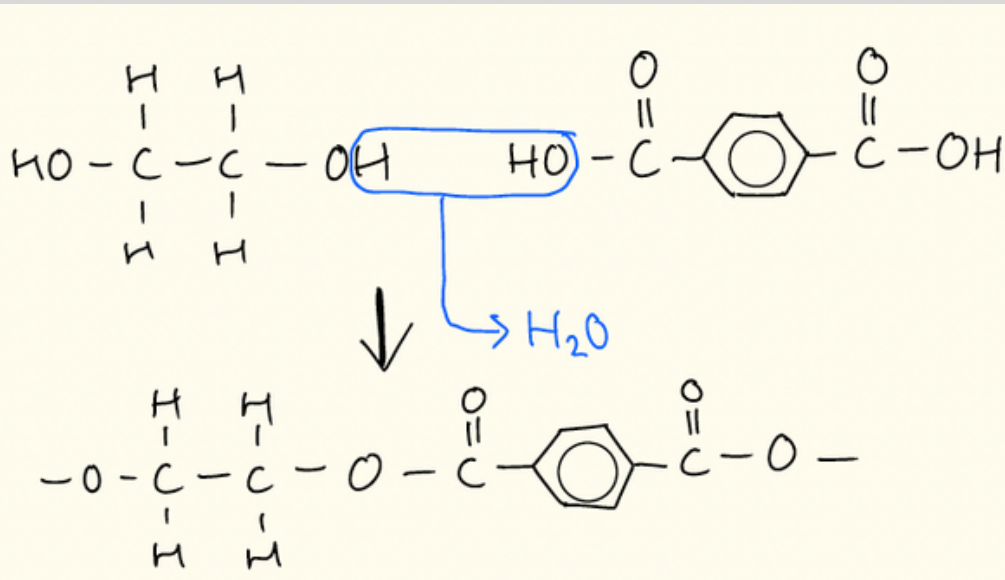
- Terylene is a well-known polyester produced from the reaction of benzene-1,4-dicarboxylic acid and ethane-1,2-diol.
- Structure of Terylene:
 - The reaction involves alternating C-O bonds to create a long-chain structure:



- Illustration of Terylene:
 - Notice how the ester linkages (-O-) alternate in orientation between the carbonyl groups (C=O)



MAKING TERYLENE- THE MECHANISM



FORMATION OF AMIDES AND POLYAMIDES

Amides are formed when a carboxylic acid reacts with an amine. This reaction involves the condensation of these two functional groups, resulting in the formation of an amide and the elimination of water (H₂O).

Formation of Amides

- General Reaction:
 - Carboxylic Acid + Amine → Amide + Water
 - Equation:
 - $R'-C(=O)OH + N-R \rightarrow R'-C(=O)N-R + H_2O$

Polyamides

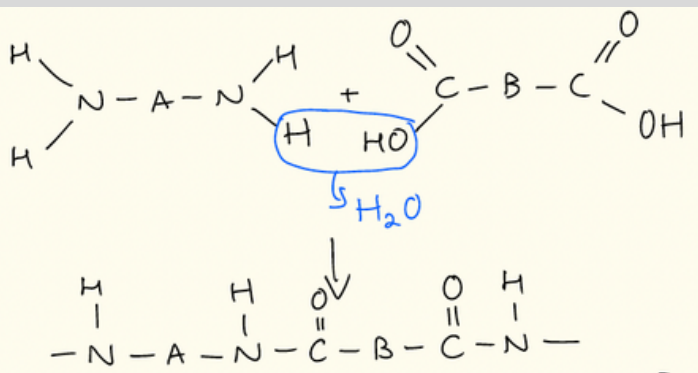
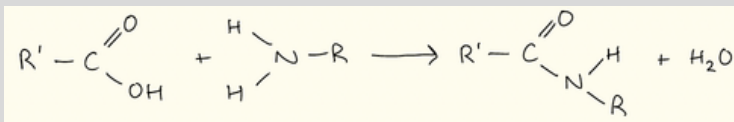
Polyamides are a type of condensation polymer that contains the amide linkage (-CONH-) repeated throughout their structure. They can be synthesized from two different monomers:

1. Diaminoalkane: This compound has two amine groups (-NH₂).
2. Dicarboxylic Acid: This compound has two carboxylic acid groups (-COOH).

Formation of Polyamides

- When a diaminoalkane reacts with a dicarboxylic acid, they undergo a condensation reaction, resulting in the formation of a polyamide and the elimination of water.

- General Reaction:
 - Diaminoalkane + Dicarboxylic Acid → Polyamide + Water
 - Equation:
 - $H_2N-R-NH_2 + HOOC-R'-COOH \rightarrow [-CONH-R-NH-CO-]_n + H_2O$





FORMATION OF AMIDES AND POLYAMIDES

Amides are formed when a carboxylic acid reacts with an amine. This reaction involves the condensation of these two functional groups, resulting in the formation of an amide and the elimination of water (H₂O).

Formation of Amides

- General Reaction:
 - Carboxylic Acid + Amine → Amide + Water
 - Equation:
 - $R'-C(=O)OH + N-R \rightarrow R'-C(=O)N-R + H_2O$

Polyamides

Polyamides are a type of condensation polymer that contains the amide linkage (-CONH-) repeated throughout their structure. They can be synthesized from two different monomers:

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 - Diaminoalkane + Dicarboxylic Acid → Polyamide + Water
 - Equation:
 - $H_2N-R-NH_2 + HOOC-R'-COOH \rightarrow [-CONH-R-NH-CO-]_n + H_2O$

NYLON: FORMATION AND STRUCTURE

Nylon is a type of synthetic polymer known as a **polyamide**. One of the most common types of Nylon produced industrially is Nylon-6,6, which is synthesized from **1,6-diaminohexane** and **hexane-1,6-dicarboxylic acid**.

Industrial Synthesis of Nylon-6,6

- Monomers:
 - 1,6-Diaminohexane: $H_2N-(CH_2)_6-NH_2$
 - Hexane-1,6-dicarboxylic acid: $HOOC-(CH_2)_6-COOH$
- General Reaction:
 - The reaction between 1,6-diaminohexane and hexane-1,6-dicarboxylic acid forms Nylon-6,6 and water as a byproduct:
 - Equation:
 - $H_2N-(CH_2)_6-NH_2 + HOOC-(CH_2)_6-COOH \rightarrow [-CONH-(CH_2)_6-NH-CO-]_n + H_2O$

Alternative Laboratory Synthesis

In a laboratory setting, the reaction can be accelerated by using a diacid chloride instead of a dicarboxylic acid. In this case, hydrogen chloride (HCl) is eliminated during the reaction.

- Example Reaction:
 - Using hexane-1,6-diacid chloride:
 - Equation:
 - $H_2N-(CH_2)_6-NH_2 + ClOC-(CH_2)_6-COCl \rightarrow [-CONH-(CH_2)_6-NH-CO-]_n + 2 HCl$

Nylon-6,10

Another variant, Nylon-6,10, is produced using 1,6-diaminohexane and decanedioic acid (1,10-dicarboxylic acid). This results in different properties due to the length and composition of the polymer chains.

Summary

- Polyamide Formation: Explain the synthesis of Nylon-6,6 and Nylon-6,10, including the use of diaminoalkanes and dicarboxylic acids (or diacid chlorides).
- Chemical Equations: Provide clear equations for both industrial and laboratory syntheses.
- Properties of Nylons: Mention that different Nylons have unique properties based on their monomer compositions.

06-CHEM-5

POLYMERISATION



KEVLAR

Kevlar is a high-performance synthetic polymer classified as a polyamide. It is renowned for its exceptional strength and durability, making it suitable for various applications, including bulletproof vests and anti-stab clothing.

Formation of Kevlar

- Monomers:
 - Benzene-1,4-diamine: $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$
 - Benzene-1,4-dicarboxylic acid: $\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$
- General Reaction:
 - The reaction between benzene-1,4-diamine and benzene-1,4-dicarboxylic acid forms Kevlar, with water as a byproduct:
 - Equation:
 - $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2 + \text{HOOC}-\text{C}_6\text{H}_4-\text{COOH} \rightarrow [-\text{N}-\text{C}_6\text{H}_4-\text{N}-\text{CO}]_n + \text{H}_2\text{O}$

Properties of Kevlar

- Strength: Kevlar's strength is attributed to:
 - Rigid Chains: The polymer chains are rigid due to the presence of amide groups linking the benzene rings.
 - Flat Aromatic Rings: The flat structure of the aromatic rings allows them to pack closely together, which enhances intermolecular forces (e.g., van der Waals forces).
- Applications:
 - Kevlar is widely used in personal protective equipment, such as:
 - Bulletproof Vests: Protects against firearms.
 - Anti-Stab Clothing: Safeguards against sharp objects.
 - Other Uses: Kevlar is also found in various household items, such as oven gloves, due to its heat-resistant properties.

POLYPEPTIDES AND PROTEINS

Polypeptides are polymers that are classified as polyamides and are formed from amino acid monomers. They can be composed of either a single type of amino acid or a combination of various amino acids. Each amino acid contains both an amine group ($-\text{NH}_2$) and a carboxylic acid group ($-\text{COOH}$), allowing them to participate in condensation reactions.

Formation of Polypeptides

- Condensation Reaction: The amine group of one amino acid reacts with the carboxylic acid group of another, resulting in the formation of a peptide bond ($-\text{C}(=\text{O})\text{N}-$). During this reaction, a molecule of water (H_2O) is eliminated:
 - Equation:
 - $\text{H}_2\text{N}-\text{R}_1-\text{COOH} + \text{H}_2\text{N}-\text{R}_2-\text{COOH} \rightarrow \text{H}_2\text{N}-\text{R}_1-\text{C}(=\text{O})-\text{N}-\text{R}_2 + \text{H}_2\text{O}$
 - This process continues, linking amino acids together to form a polypeptide chain.

Key Differences Between Polypeptides and Other Polymers

- Monomers:
 - Polypeptides: Each monomer is an amino acid, having one amine group and one carboxylic acid group (general formula $\text{H}_2\text{N}-\text{CHR}-\text{COOH}$).
 - Nylon-6,6: Formed from two distinct monomers—1,6-diaminohexane ($\text{H}_2\text{N}-\text{X}-\text{NH}_2$) and hexane-1,6-dicarboxylic acid ($\text{HOOC}-\text{Y}-\text{COOH}$).
- Amino Acids: There are 20 naturally occurring varieties of amino acids, each with different side chains (R groups) that contribute to the unique properties of the resulting polypeptide.

Identifying the Repeat Unit of a Condensation Polymer

- The repeat unit of a condensation polymer can be identified by:
 - Starting at any point in the polymer chain and observing the pattern of atoms.
 - Stopping when the same pattern of atoms begins to repeat.

06-CHEM-5

POLYMERISATION



IDENTIFYING THE MONOMERS(S) OF A CONDENSATION POLYMER

Repeat Unit of a Condensation Polymer

- The repeat unit of a condensation polymer can be determined by starting at any point in the polymer chain and stopping when the same pattern of atoms appears again. This allows for the identification of the basic structural unit that repeats throughout the polymer.

Identifying the Monomers of a Condensation Polymer To find the monomer(s) of a condensation polymer, follow these steps:

- Start with the Repeat Unit: Identify the repeat unit, which is often enclosed in brackets.
- Recognize Links Formed by Functional Groups: Familiarize yourself with the common functional groups that form the links in condensation polymers. Use the following examples to identify monomers based on their repeat units.

Monomer 1	Monomer 2	Polymer
HO-B-OH	HO-C-A-C-OH	-O-C-A-O-B-O-
(diol)	(dicarboxylic acid)	
H	H	
I	I	
II	II	
HO-C-A-C-OH	H-N-B-N-H	-A-N-B-N-A-
(dicarboxylic acid)	(diamines)	
HO-C-C-N-H	R	-C-C-N-R-
(amino acid)		

Steps to Identify Monomers

- Break the Linkage:
 - For polyesters, break at the C-O bond.
 - For polyamides, break at the C-N bond.
- Add Back Components of Water: For each ester or amide linkage formed during the polymerization, add back the components of water (H₂O) to deduce the original monomers.
- Hydrolysis Process: This method mirrors the process of hydrolysis of condensation polymers, where the polymer is broken down into its monomeric components by the addition of water.



HOW TO DISPOSE OF POLYMERS

Non-Biodegradable Polymers

- Poly(ethene) and poly(propene) are non-biodegradable because they are composed of long-chain alkane molecules.
- Alkanes are unreactive due to the presence of only strong, non-polar C-H and C-C bonds, making them resistant to breakdown by natural processes.
- These polymers can persist in the environment for many years and are usually disposed of through:
 - Landfill sites: Common disposal method, contributing to waste accumulation.
 - Incineration: Burning them can generate energy, but incomplete combustion can lead to the release of toxic carbon monoxide (CO) if there is insufficient oxygen.

Energy Production

- Poly(alkenes) can be combusted to produce carbon dioxide (CO₂) and water (H₂O), generating energy:
 - Example reaction:
 - $n(C_2H_4) + nO_2 \rightarrow nCO_2 + nH_2O$
- However, this process contributes to the increase in atmospheric CO₂ levels, which is a significant concern regarding climate change.

Toxic Byproducts

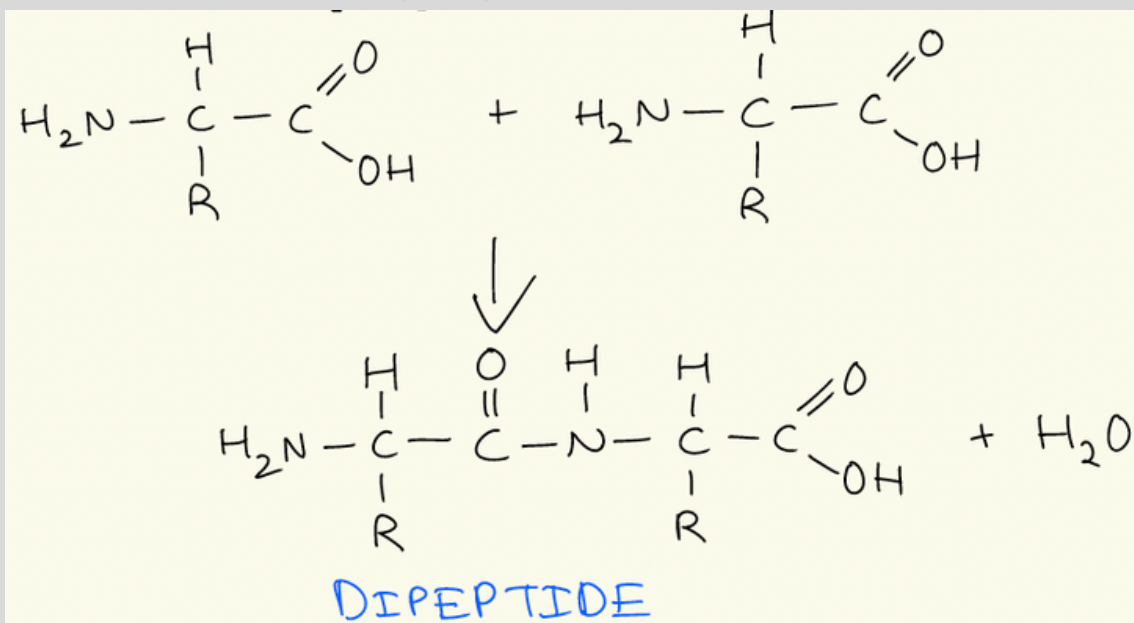
- Other addition polymers, such as polystyrene, may release toxic products upon burning.
 - Complete combustion of polystyrene (a hydrocarbon) produces CO₂ and H₂O only, but under certain conditions, it can depolymerise to release toxic styrene vapour.
 - Incomplete combustion can generate carbon monoxide and unburnt carbon particles, resulting in black smoke.

Biodegradable Polymers

- Condensation polymers, such as polyesters and polyamides, can potentially be broken down through hydrolysis, allowing them to be biodegradable by reversing the polymerisation reaction that formed them.
 - For example, the hydrolysis of a polyamide like nylon can be represented as:
 - $\text{Polyamide} + nH_2O \rightarrow n\text{Amino Acids}$
 - This reaction occurs when the N-C bond within the polymer is broken.

Slow Hydrolysis

- The hydrolysis reaction for polyamides is notably slow under everyday conditions, so there is minimal concern about items like nylon umbrellas degrading in rain.



06-CHEM-6

AMINO ACIDS, PROTEINS, DNA



AMINO ACIDS AND PEPTIDE LINKS

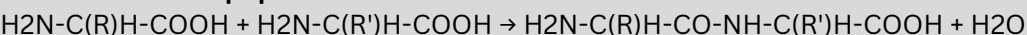
Functional Groups of Amino Acids

- An amide has the functional group -CONH_2 or $\text{-C}=\text{NH}_2$.
- The amine group of one amino acid can react with the carboxylic acid group of another amino acid, resulting in the formation of an amide linkage known as a peptide linkage (-CONH-).

Formation of Peptides

- Compounds formed by the linkage of amino acids are called peptides.
- A dipeptide consists of two amino acids linked together. The formation process is illustrated in the following reaction:

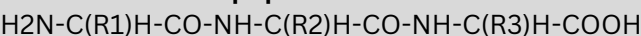
Formation of a Dipeptide:



In this reaction:

- R and R' are variable side chains.
- Water (H_2O) is eliminated as a result of the reaction.
- A dipeptide still retains the -NH_2 and -COOH groups, allowing it to undergo further reactions to form tri-peptides and tetra-peptides, as shown below:

Formation of a Tripeptide:



Protein Structure

- A particular protein has a fixed sequence of amino acids in its chain, known as the primary structure of the protein.
- For example, a short sequence from the protein insulin (which regulates sugar metabolism) is as follows:
 - $\text{-ala-glu-ala-leu-tyr-}$

Polypeptides and Proteins

- Polypeptides and proteins are classified as condensation polymers because a small molecule (water) is eliminated during the formation of each linkage in the chain.

06-CHEM-6

AMINO ACIDS, PROTEINS, DNA



AMINO ACIDS AND PEPTIDE LINKS

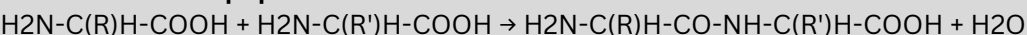
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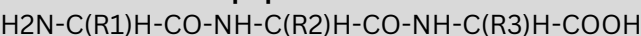
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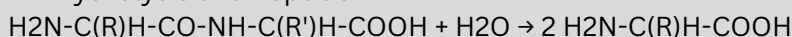
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HYDROLYSIS OF PROTEINS AND PEPTIDES

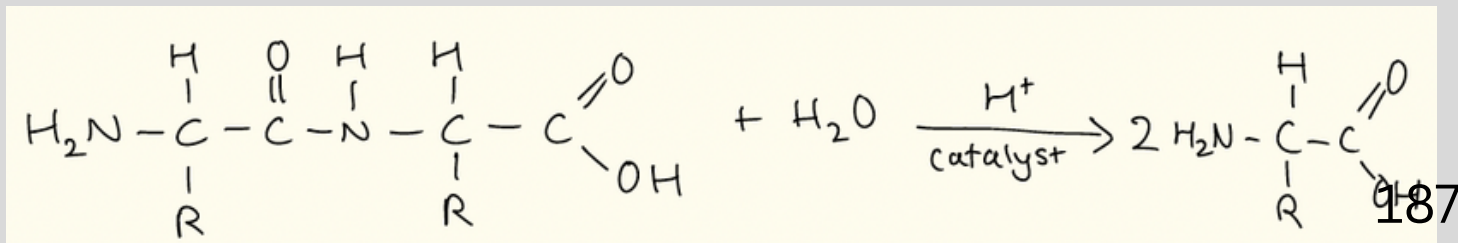
Hydrolysis Process

- When a protein or a peptide is boiled with hydrochloric acid (6 mol dm^{-3}) for approximately 24 hours, it undergoes hydrolysis, breaking down into a mixture of the amino acids that originally composed it.
- The peptide linkages ($-\text{CONH}-$) are hydrolysed by the acid, as illustrated in the following reaction:
- Hydrolysis of a Peptide:



- **In this reaction:**

- Water (H_2O) is used to break the peptide bond.
- The resulting products are the individual amino acids.



06-CHEM-6

AMINO ACIDS, PROTEINS, DNA



STRUCTURE OF PROTEINS

Complex Shapes

- Proteins have complex three-dimensional shapes that are crucial for their functions, such as acting as enzymes or providing structural support in living organisms.
- The structure of proteins is stabilized by:
 - Hydrogen bonds
 - Intermolecular forces
 - Disulfide bonds (sulfur-sulfur bonds)

Common Protein Configurations

- **Helical Structures:** Many proteins adopt a helical (spiral) shape. The helical structure is maintained by hydrogen bonding between amino acid residues.
- **Pleated Sheets:** Another common arrangement is known as pleating, where the protein forms a pleated sheet configuration, again stabilized by hydrogen bonds.

Visual Representation

- Figures that illustrate these structures should show:
 - The hydrogen bonding within the helical and pleated structures.
 - The overall arrangement of the protein chain in three-dimensional space.

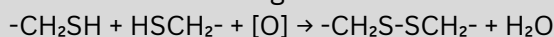
STRETCHINESS OF WOOL- EXPLAINED

- **Wool as a Protein Fibre:** Wool is a protein fibre characterized by a helical structure maintained by hydrogen bonds.
- **Stretching Mechanism:**
 - When wool is gently stretched, the hydrogen bonds stretch, allowing the fibre to extend.
 - Upon releasing the tension, the hydrogen bonds return to their original length, and the fibre reverts to its initial shape.
 - However, washing wool at high temperatures can permanently break these hydrogen bonds, causing the garment to lose its shape.

Bonding Between Amino Acids

Amino acids within a protein chain can bond in various ways, contributing to the protein's structure and stability:

- **Hydrogen Bonding:**
 - Occurs between C=O groups and -N-H groups.
 - Example: C=O...H-N interactions stabilize the protein structure.
- **Ionic Attractions:**
 - Occur between charged side chains of amino acids, such as -COO⁻ (found in glutamic acid) and -NH₃⁺ (found in lysine).
- **Disulfide Bonds:**
 - Formed between cysteine residues, which contain -CH₂SH side chains.
 - Under oxidative conditions, two cysteine molecules can bond to form cystine, a double amino acid linked by a disulfide bridge:



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AMINO ACIDS, PROTEINS, DNA



LEVELS OF PROTEIN STRUCTURE

Proteins exhibit three primary levels of structure:

1. Primary Structure:

- Defined by the sequence of amino acids in the protein chain.
- Represented by the three-letter codes of amino acids, e.g., gly-ala-ala-val-leu.
- Held together by covalent bonds, making this structure relatively stable and resistant to disruption.

2. Secondary Structure:

- Involves the formation of helical (α -helix) or pleated sheet (β -pleated sheet) structures.
- Stabilized by hydrogen bonds between C=O and -N-H groups.
- More susceptible to disruption through gentle heating or changes in pH due to the weaker nature of hydrogen bonds.

3. Tertiary Structure:

- The α -helix or β -pleated sheet folds into a three-dimensional shape.
- Stabilized by a combination of hydrogen bonds, ionic interactions, disulfide bonds, and van der Waals forces.
- Many proteins assume globular shapes, which are crucial for their functions, especially as enzymes.

DETERMINING PROTEIN STRUCTURE

Understanding protein structures is essential for comprehending their functions:

- Techniques for Structure Determination: Various methods, including X-ray diffraction, can be used to ascertain the secondary and tertiary structures of proteins, although these techniques are advanced and not covered in this context.
- Hydrolysis for Primary Structure:
 - The first step in determining the primary structure is to identify the quantity of each amino acid present in the protein.
 - This involves refluxing the protein with hydrochloric acid (6 mol dm^{-3}), which hydrolyses the amide bonds between amino acids, yielding a mixture of individual amino acids.

P-CHEM-2

THIN LAYER CHROMATOGRAPHY (TLC)



PRACTICAL- TLC

Process Overview:

1. Preparation of the TLC Plate:

- A small spot containing the amino acid mixture is applied approximately 1 cm above the baseline on the TLC plate.
- The plate is then placed in a tank with a suitable solvent, ensuring the solvent depth is around 0.5 cm.
- The baseline must remain above the initial level of the solvent.

2. Development of the Chromatogram:

- A lid is placed on the tank to saturate the environment with solvent vapour, allowing the solvent to rise along the plate.
- As the solvent ascends, it carries the amino acids with it. The distance each amino acid travels depends on its affinity for the solvent versus the stationary phase:
 - Strong affinity for solvent: Amino acid moves closer to the solvent front.
 - Strong affinity for stationary phase: Amino acid lags behind.

3. Visualization of Amino Acids:

- Once the solvent approaches the top of the plate, the plate is removed, and the solvent front is marked.
- Since amino acids are colourless, visualization is achieved by spraying the plate with a developing agent (e.g., ninhydrin) or exposing it to ultraviolet (UV) light.
 - Ninhydrin Reaction: Reacts with amino acids to produce a purple compound.

4. Calculating R_f Values:

- The R_f (retention factor) value is calculated for each amino acid spot using the formula:
 - $R_f = (\text{distance moved by the spot}) / (\text{distance moved by the solvent})$
- For example, if a red spot travels 8.0 cm and the solvent front reaches 12.0 cm, the calculation would be:
 - $R_f = 8.0 \text{ cm} / 12.0 \text{ cm} = 0.67$

5. Identification of Amino Acids:

- The R_f values obtained for the separated amino acids can be compared to known R_f values of pure amino acids run under the same conditions. This allows for the identification of the amino acids present in the original mixture.

06-CHEM-6

AMINO ACIDS, PROTEINS, DNA



WHAT ARE ENZYMES?

- **Definition:** Enzymes are protein-based catalysts found in living organisms. They significantly speed up chemical reactions, enhancing their rates by factors of up to 10^{10} . For example, a reaction that would typically take 300 years can occur in just one second when catalyzed by an enzyme.
- **Reaction Rate:**
 - A single enzyme molecule can catalyse the transformation of up to 500,000 substrate molecules per second.
 - This extraordinary efficiency highlights the critical role of enzymes in biological processes.
- **Specificity:**
 - Enzymes are highly specific, with each one optimized to catalyse only one particular reaction. This specificity is crucial for maintaining metabolic pathways and processes within cells.

Structure of Enzymes

- **Globular Proteins:** Enzymes typically have a globular structure, which is essential for their function.
- **Active Site:**
 - The enzyme's structure features a distinct area called the active site. This site has a specific shape and chemical environment conducive to the reaction.
 - The reacting molecules, known as substrates, fit into the active site, much like a key fits into a lock. This analogy is known as the lock and key hypothesis.
- **Complexity of Binding:**
 - While the lock and key model provides a basic understanding, the reality is more nuanced. The substrate must not only fit into the active site but also bind to it temporarily through intermolecular forces.
 - These interactions are critical because they facilitate the movement of electrons within the substrate, effectively lowering the activation energy required for the reaction to occur.

STEREOSPECIFICITY AND ENZYME SPECIFICITY

Stereospecificity

- **Definition:** The active site of an enzyme is often highly selective for the shape of its substrate. As a result, many enzymes can only catalyse reactions involving one enantiomer of a pair of stereoisomers.
- **Implication:** This selectivity means that enzymes are described as stereospecific, highlighting their ability to differentiate between molecules that are mirror images of each other.

Enzyme Inhibition

- **Role of Enzymes:** Enzymes are crucial for controlling the majority of chemical reactions in living organisms, from human metabolism to microbial processes.
- **Drug Design:**
 - Drugs can be engineered to influence enzyme activity. For example, if a drug blocks an enzyme responsible for catalyzing a harmful reaction, it can effectively halt that reaction.
- **Denaturation:**
 - Enzymes can be denatured (i.e., their three-dimensional structure altered) by changes in temperature and pH. However, physiological conditions in the human body typically prevent this from occurring to an extent that would impair enzyme function.
- **Competitive Inhibition:**
 - One mechanism of enzyme inhibition involves creating a molecule that mimics the shape of the substrate. This inhibitor binds to the active site of the enzyme, effectively blocking substrate access (Figure 3).
 - An example of this is penicillin, which inhibits the enzymes responsible for synthesizing bacterial cell walls.

Computer Modelling in Enzyme Research

- **Advancements in Chemistry:**
 - Chemists are increasingly utilizing advanced computer modelling techniques to understand the structural factors that determine the shapes of complex molecules like proteins.
- **Predicting Protein Shapes:**
 - By predicting the three-dimensional structures of proteins before they are synthesized, researchers can infer their properties and functionalities. This predictive capability is instrumental in designing new drugs

06-CHEM-6

AMINO ACIDS, PROTEINS, DNA



DNA: STRUCTURE AND FUNCTION

What is DNA?

- Definition: DNA (deoxyribonucleic acid) is a molecule found in all living cells, containing the genetic blueprint for the development and function of organisms. Each organism possesses its unique DNA, leading to an immense diversity of life.

Structure of DNA

- Polymers and Monomers:
 - Single Strand: DNA is a polymer composed of smaller units called nucleotides.
 - Nucleotides: Each nucleotide consists of three components:
 - i. Phosphate Group
 - ii. Sugar (specifically deoxyribose)
 - iii. Nitrogenous Base: There are four different bases:
 - Cytosine (C)
 - Thymine (T)
 - Adenine (A)
 - Guanine (G)

Polymerisation Process

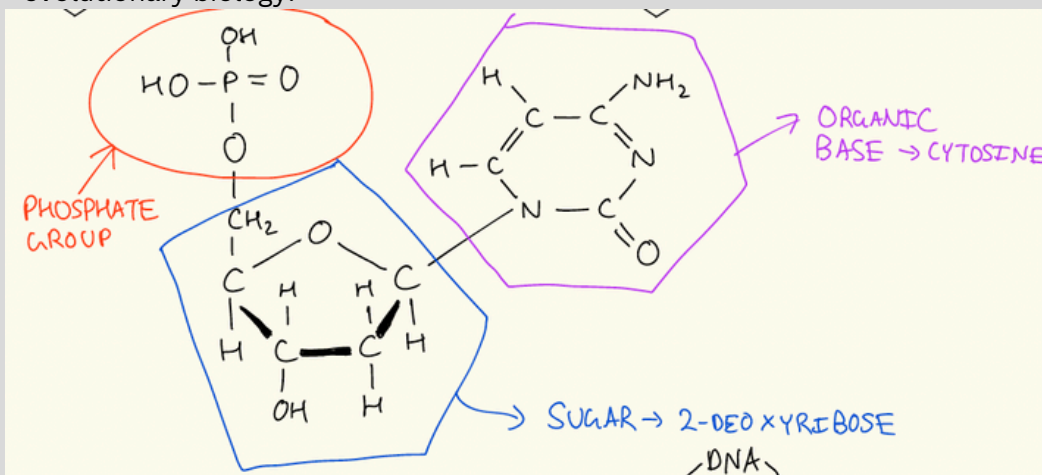
- Linking Nucleotides:
 - Nucleotides connect through a condensation reaction:
 - The -OH group of the phosphate on one nucleotide reacts with the -OH group on the sugar of another nucleotide, resulting in the elimination of a water molecule (H₂O).
 - This reaction creates a phosphodiester bond, forming a polymer chain with a backbone made of alternating phosphate and sugar molecules, to which the bases are attached.

Genetic Information

- Base Sequence:
 - The order of the nitrogenous bases along the DNA strand encodes genetic information, analogous to a four-letter code (e.g., CCAAGTTCAGGCTT).
 - This sequence is crucial as it contains the instructions for synthesizing proteins and determining the traits of an organism.

DNA Sequencing

- Definition: The process of determining the exact sequence of bases in a DNA molecule.
- Significance: Advances in DNA sequencing technologies allow scientists to read and analyze the genetic information from various living organisms, including humans, enabling research in genetics, medicine, and evolutionary biology.



06-CHEM-6

AMINO ACIDS, PROTEINS, DNA



DNA: THE DOUBLE HELIX

Complementary Base Pairing

- Strands of DNA:
 - DNA consists of two strands that run in opposite directions and are held together by hydrogen bonds between their nitrogenous bases.
- Base Pairing:
 - The bases pair specifically:
 - Adenine (A) forms hydrogen bonds with Thymine (T).
 - Guanine (G) forms hydrogen bonds with Cytosine (C).
 - This specificity ensures that only these pairs can effectively bond, resulting in the formation of complementary base pairs.

DNA REPLICATION AND CELL DIVISION

Role of DNA:

- DNA contains the genetic instructions required to create and maintain an organism.
- These instructions are present in every cell and must be precisely copied during cell division.

Hydrogen Bonds and Replication

- Breaking Hydrogen Bonds:
 - DNA strands are held together by hydrogen bonds, which are much weaker than covalent bonds, being only about 10% the strength of covalent bonds.
 - During cell division, these hydrogen bonds break, allowing the two strands of the DNA double helix to separate. However, the covalent bonds in the DNA backbone (between sugar and phosphate groups) remain intact, preserving the sequence of bases.

The Process of DNA Replication

1. Strand Separation:
 - The two strands of the DNA double helix unravel after the hydrogen bonds between the bases break.
2. Pairing with Nucleotides:
 - The cell contains a mixture of nucleotides (the building blocks of DNA).
 - These nucleotides pair up with the exposed bases on the separated DNA strands:
 - Adenine (A) pairs with Thymine (T).
 - Cytosine (C) pairs with Guanine (G).
3. Formation of New Strands:
 - The new nucleotides are linked together by phosphate-sugar bonds, forming two new strands.
 - As a result, two identical DNA molecules are formed, each consisting of one original and one new strand.

The Importance of Replication

- Ensuring Accuracy:
 - This process of DNA replication ensures that each new cell has an exact copy of the original DNA, preserving the organism's genetic information.

Using DNA Information: Protein Synthesis

- DNA as a Blueprint:
 - The information in DNA is used as a blueprint to make proteins, which are essential for the structure and function of living organisms.
 - Proteins include structural materials (such as muscle tissue) and enzymes, which control the biochemical reactions in the body.

Summary

- Replication Process:
 - Explain the breaking of hydrogen bonds during DNA replication, the pairing of nucleotides, and the formation of two identical DNA strands.
- Protein Synthesis:
 - Mention that DNA holds the instructions for making proteins, which are crucial for the organism's structure and function.

06-CHEM-6

AMINO ACIDS, PROTEINS, DNA



CISPLATIN: AN ANTICANCER DRUG

Cancer Overview:

- Cancer refers to a group of diseases characterized by uncontrolled cell growth.
- Cancer cells divide and replicate much faster than normal cells, making them a target for treatments that inhibit replication.

Cisplatin Structure:

- Cisplatin is a square planar complex with the chemical formula $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.
- It consists of:
 - Two ammonia (NH_3) ligands.
 - Two chloride (Cl^-) ligands.

Mechanism of Action:

1. Binding to DNA:

- Cisplatin works by bonding to the nitrogen atoms on two adjacent guanine bases in DNA. These nitrogen atoms have lone pairs of electrons that can form dative covalent bonds with the platinum atom in cisplatin.

2. Ligand Substitution Reaction:

- Initially, the chloride ions in cisplatin are displaced by water ligands when the drug enters the cell (a process called aquation).
- The water ligands are subsequently displaced by the nitrogen atoms on the guanine bases, which are better ligands than water. This process is a classic example of a ligand substitution reaction.

3. DNA Distortion:

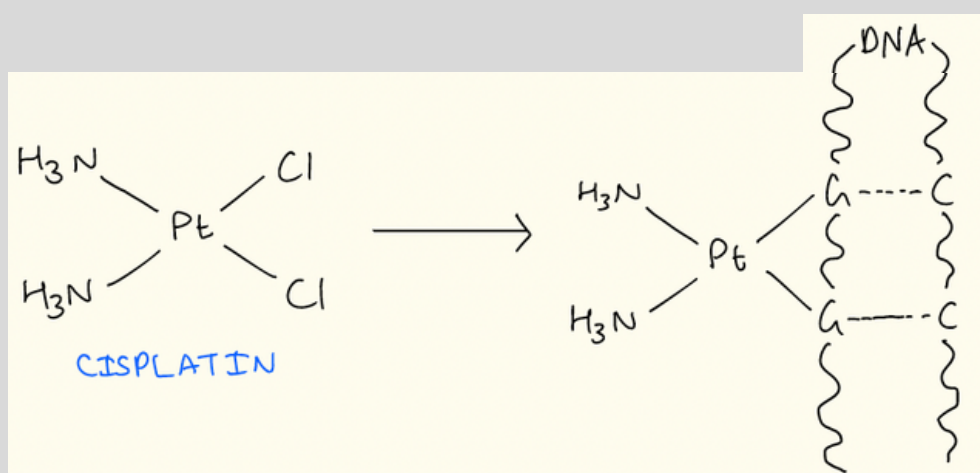
- Once cisplatin is bonded to the DNA, it distorts the DNA's shape, preventing it from replicating properly. This halts the replication process in cancer cells, leading to cell death.

Side Effects:

- Healthy cells are also affected by cisplatin because the drug will bind to DNA in normal cells as well. However, cancer cells are more rapidly dividing, so the drug has a greater effect on them.
- Cells that divide quickly in the body, such as those in hair follicles, are also impacted. This is why chemotherapy (treatment with cisplatin or other drugs) often causes patients to lose their hair.

Current Research:

- Scientists are working on developing new drugs and delivery systems that can better target cancer cells while reducing the impact on healthy cells.



06-CHEM-7

ORGANIC SYNTHETIC ROUTES



ORGANIC SYNTHESIS OF TARGET MOLECULES

In organic chemistry, synthesis refers to the process of creating a target molecule by linking a series of chemical reactions. This is a common practice in various industries, such as **drug and pesticide manufacture**, where the goal is to produce a specific compound efficiently and safely.

Steps in Organic Synthesis:

1. Identify the Starting Material and Target Molecule:

- Begin by determining the starting material (compound A) and the target molecule (compound X).
- These will form the basis for constructing the reaction pathway.

2. Devising the Reaction Pathway:

- Write down all possible reactions that could be performed on the starting material (A).
- Similarly, list all reactions that could lead to the target molecule (X).
- Then, determine the intermediate compounds B, C, D, or E that can be converted into T, U, V, or W, which eventually lead to X (Figure 1).
- Aim to keep the number of reaction steps as small as possible, as this will maximize the yield of the target compound.

3. Recognizing Key Reactions:

- Certain reactions may immediately stand out. For instance, if the target molecule has one more carbon atom than the starting material, the reaction involving cyanide ions with a halogenoalkane is likely needed to lengthen the carbon chain by one atom:
 - Example:
 - $\text{CH}_3\text{Br} + \text{CN}^- \rightarrow \text{CH}_3\text{C}\equiv\text{N} + \text{Br}^-$
 - (Bromomethane to Ethanitrile)

Functional Group Conversions:

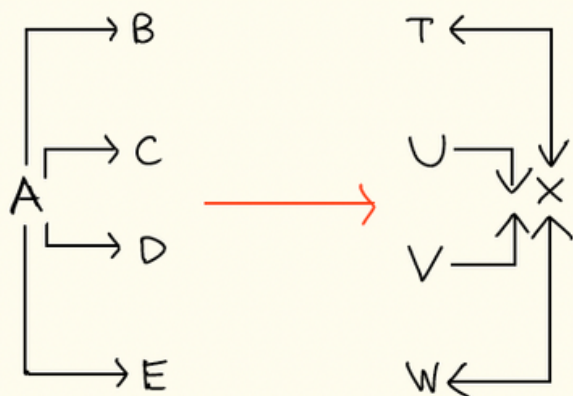
Organic synthesis relies heavily on the ability to interconvert different functional groups. The main functional groups and their inter-relationships are shown in Figure 2, and it is crucial to understand how to convert one functional group into another. **For example:**

- Alkene to Alcohol (Hydration)
- Alcohol to Aldehyde (Oxidation)
- Aldehyde to Carboxylic Acid (Further Oxidation)
- Carboxylic Acid to Ester (Esterification)

Practical Considerations:

- The number of steps in a synthetic route should be minimized to reduce by-products and maximize efficiency.
- The type of functional groups present in the starting and target molecules often dictates the reaction sequence.

STARTING
MATERIAL





REAGENTS USED IN ORGANIC CHEMISTRY

Oxidising Agents:

- Potassium dichromate(VI) ($K_2Cr_2O_7$) acidified with dilute sulfuric acid:
 - Oxidizes primary alcohols to aldehydes, and aldehydes to carboxylic acids.
 - Oxidizes secondary alcohols to ketones.

Reducing Agents:

Different reducing agents are used based on the type of bond that needs to be reduced:

- Sodium tetrahydridoborate(III) ($NaBH_4$):
 - Reduces polar $C=O$ groups but does not reduce non-polar $C=C$ bonds.
 - Works in aqueous solutions by generating the nucleophile H^- , which attacks the $C=O$ bond but is repelled by the electron-rich $C=C$ bond.
- Hydrogen with a nickel catalyst (H_2/Ni):
 - Used to reduce $C=C$ double bonds but not $C=O$ bonds.
- Tin and hydrochloric acid (Sn/HCl):
 - Reduces $R-NO_2$ (nitro group) to $R-NH_2$ (amine group).

Dehydrating Agents:

- Alcohols can be converted into alkenes by:
 - Passing their vapors over heated aluminium oxide.
 - Using acid-catalyzed elimination reactions.

Examples of Reaction Schemes

1. Synthesis of Propanoic Acid from 1-Bromopropane:

- Both the starting material and the target have the same number of carbon atoms, so no modification of the carbon skeleton is needed. The synthesis involves two steps:
- Step 1: Conversion of 1-bromopropane to propan-1-ol:
 - Reagent: $NaOH(aq)$ under reflux conditions.
 - Reaction:
 - $CH_3CH_2CH_2Br \rightarrow CH_3CH_2CH_2OH$ (propan-1-ol)
- Step 2: Conversion of propan-1-ol to propanoic acid:
 - Reagent: Acidified potassium dichromate(VI) ($K_2Cr_2O_7$).
 - Reaction:
 - $CH_3CH_2CH_2OH \rightarrow CH_3CH_2COOH$ (propanoic acid)

2. Synthesis of Propylamine from Ethene:

- Propylamine has one more carbon atom than ethene, suggesting the involvement of a nitrile intermediate. This reaction can be completed in three steps:
- Step 1: Conversion of ethene to bromoethane:
 - Reagent: Br_2 (bromination).
 - Reaction:
 - $CH_2=CH_2 \rightarrow CH_3CH_2Br$ (bromoethane)
- Step 2: Conversion of bromoethane to propanenitrile:
 - Reagent: KCN (cyanide ion).
 - Reaction:
 - $CH_3CH_2Br \rightarrow CH_3CH_2C\equiv N$ (propanenitrile)
- Step 3: Conversion of propanenitrile to propylamine:
 - Reagent: H_2/Ni (hydrogenation).
 - Reaction:
 - $CH_3CH_2C\equiv N \rightarrow CH_3CH_2CH_2NH_2$ (propylamine)

Aromatic Reactions

Some important aromatic reactions using benzene as a starting material include:

- Nitration of benzene to form nitrobenzene.
- Reduction of nitrobenzene to form phenylamine.
- Acylation to form acyl-substituted benzenes.

06-CHEM-8

STRUCTURE DETERMINATION



NUCLEAR MAGNETIC RESONANCE (NMR) IMAGING

NMR is particularly used in organic chemistry as a powerful technique for determining the structures of even complex molecules. The process involves:

- Applying a magnetic field to a sample.
- Surrounding the sample with a source of radio waves and a radio receiver.

This generates an energy change in the nuclei of atoms in the sample that can be detected. The sample emits electromagnetic energy, which is interpreted by a computer to generate a spectrum.

CARBON-13 (^{13}C) NMR

- Carbon-12 (^{12}C) has no nuclear spin, but carbon-13 (^{13}C) does.
- Although only 1% of carbon atoms are carbon-13, modern instruments are sensitive enough to obtain a ^{13}C NMR spectrum.

Not all carbon-13 atoms in a molecule resonate at the same magnetic field strength. This is because carbon atoms in different functional groups feel the magnetic field differently due to electron shielding:

- Nuclei with more electrons around them are better shielded.
- The greater the electron density around a carbon-13 atom, the smaller the magnetic field felt by the nucleus.
- This results in a lower frequency at which it resonates.

The NMR instrument produces a graph with:

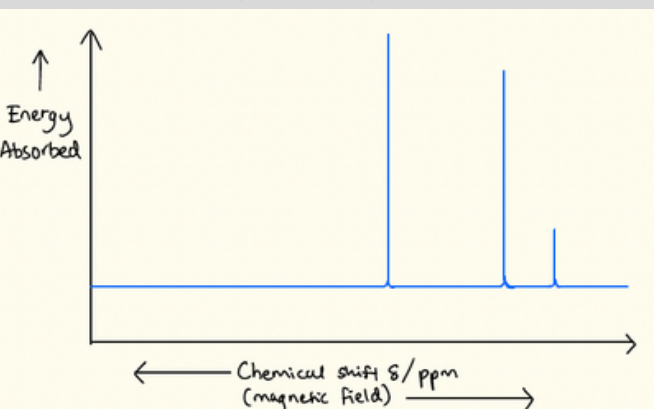
- Energy absorbed (from the radio signal) on the vertical axis.
- Chemical shift (related to the resonant frequency) on the horizontal axis.

CHEMICAL SHIFT

- **Chemical shift (δ)** is measured in parts per million (ppm), relative to a reference compound, tetramethylsilane (TMS).
- Chemical shift values in ^{13}C NMR range from **0 to around 200 ppm**.

The key point about ^{13}C NMR is that carbon atoms in different environments produce different chemical shift values. For example, in the ^{13}C NMR spectrum of ethanol, there are two peaks, **one for each carbon**:

- One carbon atom is further from the oxygen atom than the other.
- The electronegative oxygen draws electrons away from the carbon to which it is bonded, affecting the chemical shift.



Explanation:

- The electronegative oxygen atom draws electrons away from the carbon atom it is directly bonded to ($\text{CH}_3\text{CH}_2\text{OH}$).
 - This deshields the carbon, making it feel a greater magnetic field, causing it to resonate at a higher frequency. As a result, this carbon has a larger δ value (60 ppm).
- The other carbon atom (CH_3 group) is surrounded by more electrons, which means it is shielded from the magnetic field.
 - As a result, it resonates at a lower frequency, giving it a smaller δ value (15 ppm).

In general, carbon atoms closer to electronegative atoms (like oxygen) will have higher chemical shift (δ) values due to deshielding.

In ^{13}C NMR spectroscopy, the chemical shift (δ) values provide insight into the environment of carbon atoms in a molecule. Here's an explanation using the case of **ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)**:

- In **ethanol's spectrum**, the carbon atom at **$\delta = 60 \text{ ppm}$** is the one bonded to oxygen, **$\text{CH}_3\text{CH}_2\text{OH}$** .
- The carbon atom at **$\delta = 15 \text{ ppm}$** is the carbon in the methyl group (CH_3), which is not directly bonded to the oxygen.

06-CHEM-8

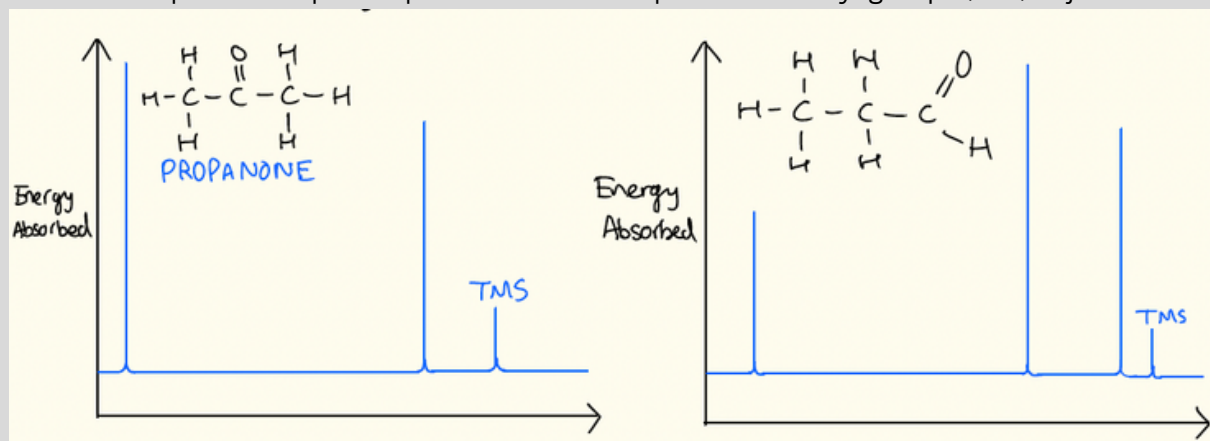
STRUCTURE DETERMINATION



MORE NMR EXAMPLES

Propanone (CH_3COCH_3)

- Number of Peaks: 2
- Carbon Environments:
 - C=O Carbon:
 - Chemical Shift (δ): 205 ppm
 - Description: This peak corresponds to the carbon atom in the carbonyl group, which is deshielded due to its double bond with oxygen.
 - CH_3 Groups:
 - Chemical Shift (δ): 30 ppm
 - Description: This peak represents the two equivalent methyl groups (CH_3) adjacent to the carbonyl group.



Propanal ($\text{CH}_3\text{CH}_2\text{CHO}$)

- Number of Peaks: 3
- Carbon Environments:
 - CH_3 Group:
 - Chemical Shift (δ): 5 ppm
 - Description: This peak corresponds to the carbon in the methyl group, which is relatively shielded.
 - CH_2 Group:
 - Chemical Shift (δ): 37 ppm
 - Description: This peak represents the methylene group (CH_2) adjacent to the carbonyl group, which experiences some deshielding due to its proximity to the carbonyl.
 - CHO Group:
 - Chemical Shift (δ): 205 ppm
 - Description: This peak corresponds to the carbon in the aldehyde group (CHO), which is deshielded similarly to the carbonyl carbon in propanone.

PRINCIPLES OF ^1H NMR SPECTROSCOPY

- **Nucleus Examined:** The ^1H nucleus (proton) is predominantly used, making it easier to obtain NMR spectra compared to ^{13}C .
- **Chemical Environment:** Hydrogen atoms attached to different functional groups experience different magnetic fields due to varying electron shielding.
- **Electron Shielding:**
 - Nuclei with more surrounding electrons are better shielded.
 - Greater electron density results in a smaller chemical shift (δ).
- **Chemical Shift Range:** The chemical shift values for ^1H NMR are typically between 0 and 10 ppm, which are smaller than those for ^{13}C NMR.

06-CHEM-8

STRUCTURE DETERMINATION

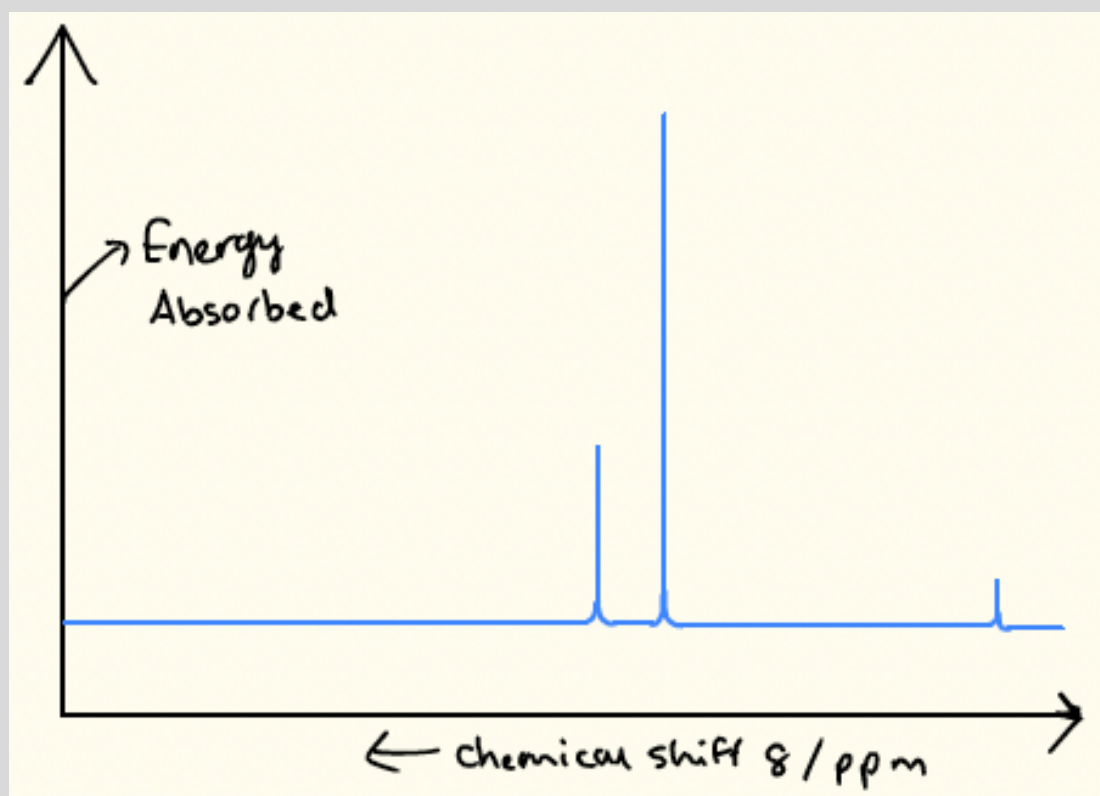


CHEMICAL SHIFT EXAMPLES

- **Identical Environments:** If all hydrogen nuclei are in identical environments, only one chemical shift value is observed.
 - Example: In methane (CH_4), all hydrogen atoms are equivalent and exhibit the same chemical shift.
- **Different Environments:** In compounds with hydrogen atoms in varying environments, multiple chemical shift values are present.
 - Example: In methanol (CH_3OH), there are two different hydrogen environments:
 - Three hydrogen atoms on the carbon (CH_3).
 - One hydrogen atom on the oxygen (OH).
 - The NMR spectrum will display two peaks corresponding to these environments.

EXAMPLE: ETHANOL

- **Chemical Shift Values:** Ethanol has three distinct hydrogen environments:
 - **CH_3 Group:**
 - Chemical shift: δ (approximately 1-2 ppm)
 - Represents three hydrogen atoms.
 - **CH_2 Group:**
 - Chemical shift: δ (approximately 3-4 ppm)
 - Represents two hydrogen atoms.
 - **OH Group:**
 - Chemical shift: δ (approximately 0.5-5 ppm)
 - Represents one hydrogen atom.
- **Peak Areas:** In the NMR spectrum, the areas under the peaks (denoted by numbers) correspond to the number of hydrogen atoms in each environment, indicating three for CH_3 and one for OH .



06-CHEM-8

STRUCTURE DETERMINATION



TETRAMETHYLSILANE- NMR

Chemical Formula: TMS is represented as $\text{Si}(\text{CH}_3)_4$.

Structure

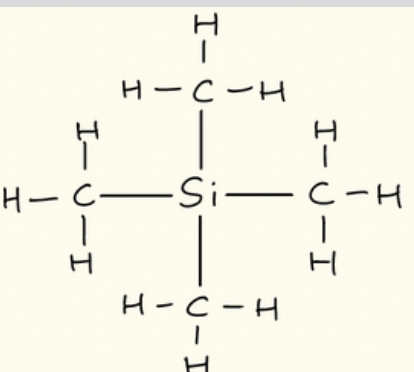
- TMS has a tetrahedral structure where:
 - Silicon Atom: Central silicon atom (Si) bonded to four methyl groups (CH_3).
 - Hydrogen Environment: All twelve hydrogen atoms are in identical environments, leading to a single signal in the ^1H NMR spectrum.

Role in NMR Spectroscopy

- Reference Standard:**
 - The chemical shift of the hydrogen atoms in TMS is defined as zero (0 ppm).
 - This serves as a reference point for measuring chemical shifts of other compounds.
- Calibration:
 - A small amount of TMS is often added to samples before running NMR spectra.
 - This provides a clear peak at 0 ppm, allowing for accurate calibration of the spectrum.

Advantages of TMS

- Inert: TMS does not react with most organic compounds.
- Non-toxic: Considered safe to use in laboratory settings.
- Easily Removable: Can be removed from samples after analysis without leaving residues.



ANALYSING PROTON NMR

Analyzing NMR Spectrum

1. Chemical Shift Values:

- Single Hydrogen at δ 9.7:
 - This value indicates the presence of an aldehyde group ($-\text{CHO}$). Aldehydes typically resonate downfield (higher δ values) due to the electronegative oxygen atom, which causes deshielding of the hydrogen nucleus.
- Three Hydrogens at δ 2.2:
 - This peak corresponds to a methyl group ($-\text{COCH}_3$). The three hydrogens suggest it is part of a carbonyl compound where the carbon is bonded to three hydrogens. While a methylene group ($-\text{COCH}_2\text{R}$) could also produce a peak in this region, the presence of three hydrogens confirms it must be a methyl group.

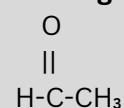
Conclusion:

- Based on the chemical shift analysis, the compound is identified as ethanal ($\text{C}_2\text{H}_4\text{O}$), which has the following structure:

Structural Formula of Ethanal:

- Chemical Structure: CH_3CHO

Diagram:



Summary

By analyzing the chemical shift values and the corresponding hydrogen environments, you can deduce that the compound in question is ethanal. This method of interpretation is fundamental in NMR spectroscopy, allowing chemists to determine molecular structures accurately.

06-CHEM-8

STRUCTURE DETERMINATION



SPIN-SPIN COUPLING

Definition:

- Spin-spin coupling (or spin-spin splitting) occurs when the magnetic field experienced by a hydrogen atom is influenced by the magnetic fields of nearby hydrogen atoms on adjacent carbon atoms. This results in the splitting of NMR peaks into distinct patterns.

$n + 1$ Rule

- The $n + 1$ rule is used to predict the number of peaks (or multiplet) that will appear in an NMR signal based on the number of hydrogen atoms on adjacent carbon atoms.

Key Points of the $n + 1$ Rule:

- n = Number of hydrogen atoms on an adjacent carbon atom.
- The peak of a hydrogen atom will be split into $n + 1$ smaller peaks.

Examples:

- One Adjacent Hydrogen ($n = 1$):
 - Splits into 2 peaks: 1:1 ratio
 - Example: A hydrogen atom next to a CH group.
- Two Adjacent Hydrogens ($n = 2$):
 - Splits into 3 peaks: 1:2:1 ratio
 - Example: A hydrogen atom next to a CH_2 group.
- Three Adjacent Hydrogens ($n = 3$):
 - Splits into 4 peaks: 1:3:3:1 ratio
 - Example: A hydrogen atom next to a CH_3 group.

Importance

- Understanding spin-spin coupling helps in determining the connectivity and arrangement of atoms within a molecule, providing valuable insight into its structure.

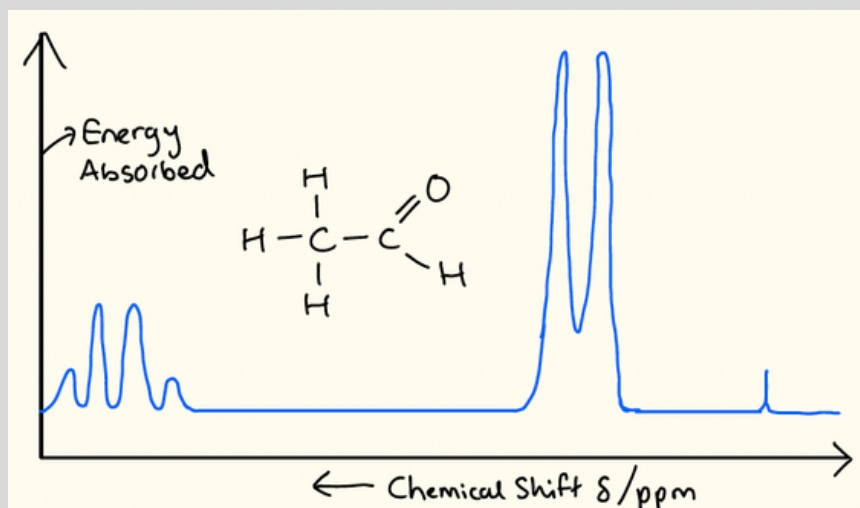
EXAMPLES OF INTERPRETING PROTON NMR SPECTRA: ETHANAL

1. Hydrogen Environments:

- Aldehyde Hydrogen ($-\text{CHO}$):
 - Peak at δ 9.7 ppm: This peak represents the single hydrogen of the $-\text{CHO}$ group.
 - Spin-Spin Splitting:
 - The peak is split into four peaks with a height ratio of 1:3:3:1.
 - This splitting occurs due to the influence of the three adjacent hydrogens from the $-\text{CH}_3$ group, following the $n + 1$ rule (where $n = 3$).

1. Methyl Hydrogen ($-\text{CH}_3$):

- Peak at δ 2.2 ppm: This peak corresponds to the three hydrogens of the $-\text{CH}_3$ group.
- Spin-Spin Splitting:
 - The peak is split into two peaks with a height ratio of 1:1.
 - This occurs due to the influence of the one adjacent hydrogen from the $-\text{CHO}$ group.



06-CHEM-8

STRUCTURE DETERMINATION



EXAMPLES OF INTERPRETING PROTON NMR SPECTRA: PROPANOIC ACID

Chemical Shift (ppm)	Corresponding Group	Analysis
11.7	-COOH (carboxylic acid)	This peak is not split because the adjacent carbon (-COOH) has no hydrogen atoms bonded to it.
2.4	-COCH ₂ R (methine group)	This peak is associated with two hydrogens. Although it could also suggest -COCH ₃ , the presence of two hydrogens indicates it corresponds to -COCH ₂ R. The peak is split into four, indicating three adjacent hydrogens bonded to the neighboring carbon.
1.1	-RCH ₂ (methyl group)	This peak is split into three, indicating that the adjacent carbon has two hydrogens bonded to it, confirming that R in RCH ₃ is -CH ₂ .

1. The ¹H NMR spectrum of propanoic acid shows:

1. Peak at 11.7 ppm: Non-split peak corresponding to the carboxylic acid group (-COOH).
2. Peak at 2.4 ppm: Split into four peaks, indicating the -COCH₂R group, with three hydrogens on the adjacent carbon.
3. Peak at 1.1 ppm: Split into three peaks, indicating the presence of the -RCH₂ group, with two hydrogens on the adjacent carbon.

Conclusion

Combining these functional groups leads to the structure of propanoic acid (C₂H₅COOH).

EXAMPLES OF INTERPRETING PROTON NMR SPECTRA: ETHANAL

• NMR Spectra in Solution:

- NMR spectra are typically obtained in a solution to ensure accurate results.
- The solvent used must not contain hydrogen atoms, as the signals from solvent hydrogen would overpower those from the sample.

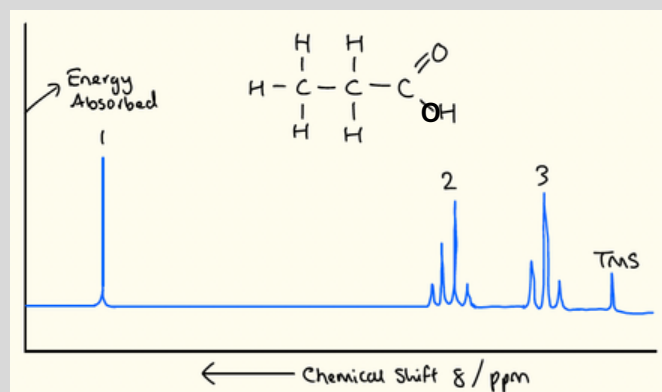
• Commonly Used Solvents:

a. Tetrachloromethane (CCl₄):

- Contains no hydrogen atoms, making it a suitable solvent for NMR.

b. Deuterated Solvents:

- These solvents contain deuterium (D), an isotope of hydrogen that does not produce an NMR signal in the same range as regular hydrogen.
- Deuterated solvents maintain similar chemical properties to regular solvents but allow for clearer spectra of the sample.
- Examples of deuterated solvents include:
 - Deuteriochloromethane (CDCl₃)
 - Deuterium Oxide (D₂O)
 - Perdeuterobenzene (C₆D₆)



06-CHEM-8

STRUCTURE DETERMINATION



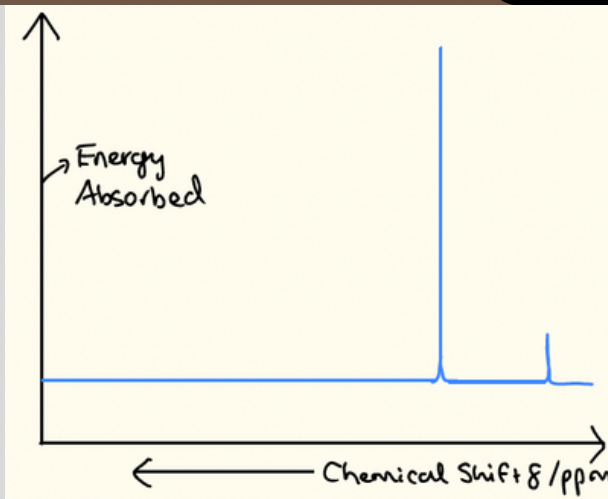
EXAMPLES OF INTERPRETING PROTON NMR SPECTRA: PROPANONE

- **NMR Spectrum Overview:**

- The NMR spectrum of propanone shows only one peak.
- This indicates that all hydrogen atoms in the molecule are in identical environments.

- **Chemical Shift Value:**

- The chemical shift value observed is 2.1 ppm.
- This value suggests that the hydrogens are likely part of a -COCH_3 or $\text{-COCH}_2\text{H}$ group.



PREDICTING NMR SPECTRA: ETHYL ETHANOATE

- Overview:

- Chemists often predict the NMR spectrum of a compound they are synthesizing to verify that the reaction has proceeded as intended.

- Molecular Structure:

- Ethyl ethanoate can be represented as:



Hydrogen Environments:

- In ethyl ethanoate, there are three sets of hydrogen atoms in different environments:
 - Methyl Group (CH_3):
 - Chemical Shift: Predicted around 1.2 ppm.
 - Methylene Group (CH_2):
 - Chemical Shift: Predicted around 4.1 ppm (next to the electronegative oxygen).
 - Aldehyde (if present) or another environment:
 - Chemical Shift: Depending on structure, potentially around 2.0-2.5 ppm.

Predicted Spectrum:

- By analyzing the molecular structure, the predicted NMR spectrum for ethyl ethanoate is expected to show three distinct peaks corresponding to the different hydrogen environments:
 - A peak for the methyl group.
 - A peak for the methylene group.
 - A peak for the hydrogens attached to the carbonyl group or another functional group.

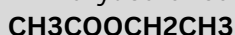
06-CHEM-8

STRUCTURE DETERMINATION



PREDICTING NMR SPECTRA: ETHYL ETHANOATE

- Overview:
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 - Chemical Shift: Predicted around 4.1 ppm (next to the electronegative oxygen).
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 - Chemical Shift: Depending on structure, potentially around 2.0-2.5 ppm.

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- By analyzing the molecular structure, the predicted NMR spectrum for ethyl ethanoate is expected to show three distinct peaks corresponding to the different hydrogen environments:
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OVERVIEW OF CHROMATOGRAPHY

Chromatography Overview

- **Definition:**

- Chromatography refers to a group of separation techniques that rely on the principle that a mixture can be separated by dissolving it in a solvent (mobile phase) and allowing the resulting solution to move over a solid (stationary phase).

- **Principles:**

- Mobile Phase:
 - Carries soluble components of the mixture.
 - Components more soluble in the mobile phase move faster.
 - In column chromatography, the solvent is often referred to as the eluent.
- Stationary Phase:
 - Retains components of the mixture that have a greater affinity for it.
 - Components with a higher affinity for the stationary phase move slower.

- **Separation Mechanism:**

- The balance between a component's affinity for the stationary phase and the mobile phase allows for the separation of similar substances. This is particularly useful for isolating components that are very similar in nature.

THIN LAYER CHROMATOGRAPHY (TLC)

Overview:

Thin-layer chromatography is an advanced form of paper chromatography where a glass, metal, or plastic sheet is coated with a thin layer of silica gel (SiO_2) or alumina (Al_2O_3) acting as the stationary phase.

Advantages of TLC:

- Speed: Runs faster than paper chromatography.
- Sample Size: Requires smaller amounts of the mixture for separation.
- Spot Resolution: Spots tend to spread out less, providing clearer separation.
- Durability: Plates are more robust than paper.

Detection of Components:

- Colorless Spots: Can be located by:
 - UV Light: Illuminating the plate with ultraviolet light.
 - Chemical Reagents: Spraying the plate with a locating agent that reacts with components to produce colored compounds.

CALCULATION OF R_f VALUES

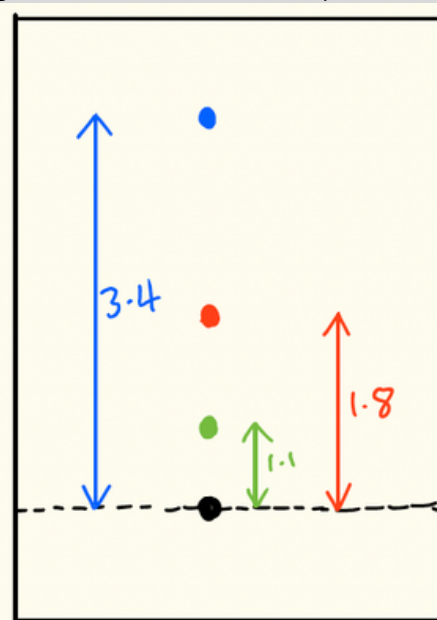
R_f Value (Retention Factor):

The R_f value is calculated to help identify components of the mixture using the formula:

$$R_f = (\text{distance moved by spot}) / (\text{distance moved by solvent})$$

- Interpretation of R_f Values:

- Each component's R_f value can aid in identification when compared to standard values.
- Consistency in R_f values suggests similar compounds or functional groups.



P-CHEM-3

CHROMATOGRAPHY



COLUMN CHROMATOGRAPHY

Definition: Column chromatography is a separation technique that utilizes a stationary phase (a solid) and a mobile phase (a solvent, known as the eluent) to separate components of a mixture.

Equipment:

- **Column:** A narrow tube packed with the stationary phase (e.g., silica, aluminium oxide, or resin).
- **Solvent (Eluent):** Added at the top of the column to initiate the separation process.

Process:

1. Packing the Column:

- The stationary phase is packed into the column to provide a surface for interaction with the components of the mixture.

2. Adding the Eluent:

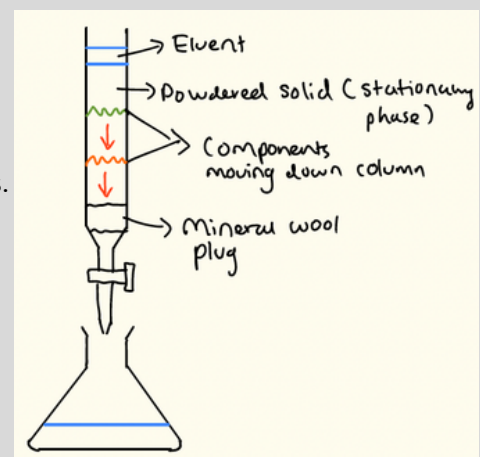
- The eluent is added to the top of the column. As it moves down, it carries the soluble components of the mixture with it.

3. Separation Mechanism:

- Components of the mixture move at different rates depending on their affinity for the stationary phase versus the mobile phase:
 - **More Affinity for Stationary Phase:** Slower movement through the column.
 - **More Affinity for Mobile Phase:** Faster movement through the column.

4. Collection of Fractions:

- As the eluent runs down the column, the separated components can be collected in flasks at the bottom. More than one eluent may be used to improve separation.



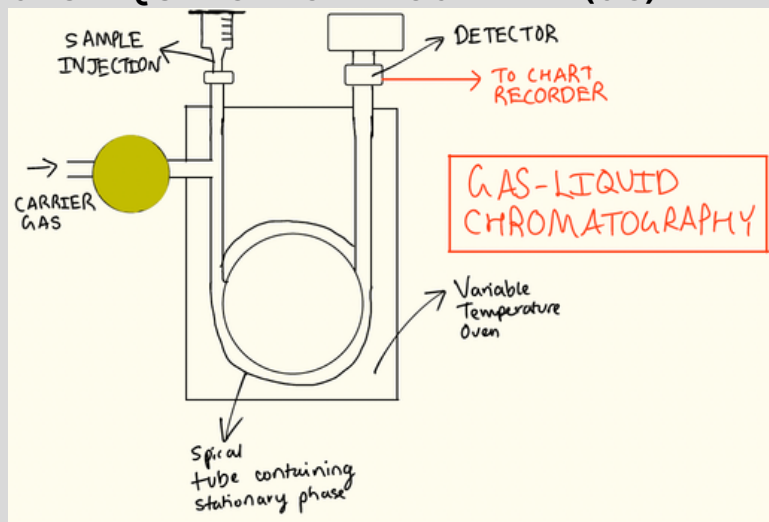
Advantages:

- Allows for the separation and collection of relatively large amounts of material.
- Effective for separating complex mixtures, such as amino acids, into their pure components.

Applications:

- Widely used in organic chemistry for purifying compounds and in biochemistry for isolating biomolecules.

GAS-LIQUID CHROMATOGRAPHY (GC)



P-CHEM-3

CHROMATOGRAPHY



GAS-LIQUID CHROMATOGRAPHY

Definition: Gas-liquid chromatography (GC) is a vital analytical technique used to separate and analyze compounds in a mixture based on their volatilities and interactions with a stationary phase.

Apparatus:

- **Capillary Column:**
 - Long, typically up to 100 meters in length and less than 0.5 mm in diameter.
 - Can be either packed with a powder coated with oil or have the oil coated on the inside surface.
- **Oven:**
 - Houses the capillary column, allowing for variable temperature control.
- **Mobile Phase:**
 - An inert gas such as nitrogen or helium, which carries the sample through the column.

Process:

1. Sample Injection:

- A small amount of the sample mixture is injected into the heated column.

2. Separation Mechanism:

- The sample is carried along by the mobile phase (inert gas).
- Components of the mixture separate based on their affinity for the stationary phase (the oil-coated surface) and their volatility:
 - Some components move quickly with the gas, while others are retained longer by the oil.

3. Retention Time:

- Each component exits the column at different times (retention times) after injection, depending on its properties.

4. Detection:

- Various detectors measure properties such as thermal conductivity of the emerging gas.
- The results are often presented as a chromatogram, where the area under each peak correlates with the amount of that component.

5. Identification:

- Components can be identified by matching their retention times with those of known substances under the same conditions.
- Confirmation can be achieved through mass spectrometry, infrared spectroscopy, or NMR spectroscopy.

Automation:

- The entire GC process is often automated and computer-controlled for efficiency and precision.

Applications:

- GC is highly sensitive and can detect trace amounts of substances, making it useful in various fields, including:
 - **Environmental Monitoring:** Linking crude oil pollution on beaches to its source by comparing oil samples.
 - **Food Safety:** Analyzing food products for contaminants.
 - **Sports Testing:** Screening athletes' blood or urine for banned substances.