KIPS
ENTRY TESTS
SERIES

PREP BOOK

CHEMISTRY

NATIONAL MDCAT

- Topic-wise Complete Syllabus
- Comprehensive Course Revision
- Detailed Explanation of Topics
- Key Points, Tables, Flow Sheets & Diagrams
- Easy to Remember; Points to Ponder

A Kitab Dost Publication

MDCAT SOCIETY FOR FUTURE DOCTORS

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CONTENT

TOPIC NO.		PAGE NO
1	Introduction to Fundamental Concepts of Chemistry	1
2	Atomic Structure	11
3	Gases	23
4	Liquids	31
5	Solids	39
6	Chemical Equilibrium	47
7	Reaction Kinetics	61
8	Thermochemistry and Energetics of Chemical reactions	75
9	Electrochemistry	84
10	Chemical Bonding	95
11	s and p Block Elements	107
12	Transition Elements	121
13	Fundamental Concepts of Organic Chemistry	129
14	Chemistry Hydrocarbons	142
15	Alkyl Halides	162
16	Alcohols and Phenols	174
17	Aldehydes and Ketones	182
18	Carboxylic Acids	193
19	Macromolecules	203
20	Environmental Chemistry	209

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INTRODUCTION

Atom

The smallest particle of an element which takes part in the chemical reaction is called an atom.

May exist independently

Monoatomic gases

Helium (He), Neon (Ne) and Argon (Ar)

May not exist independently

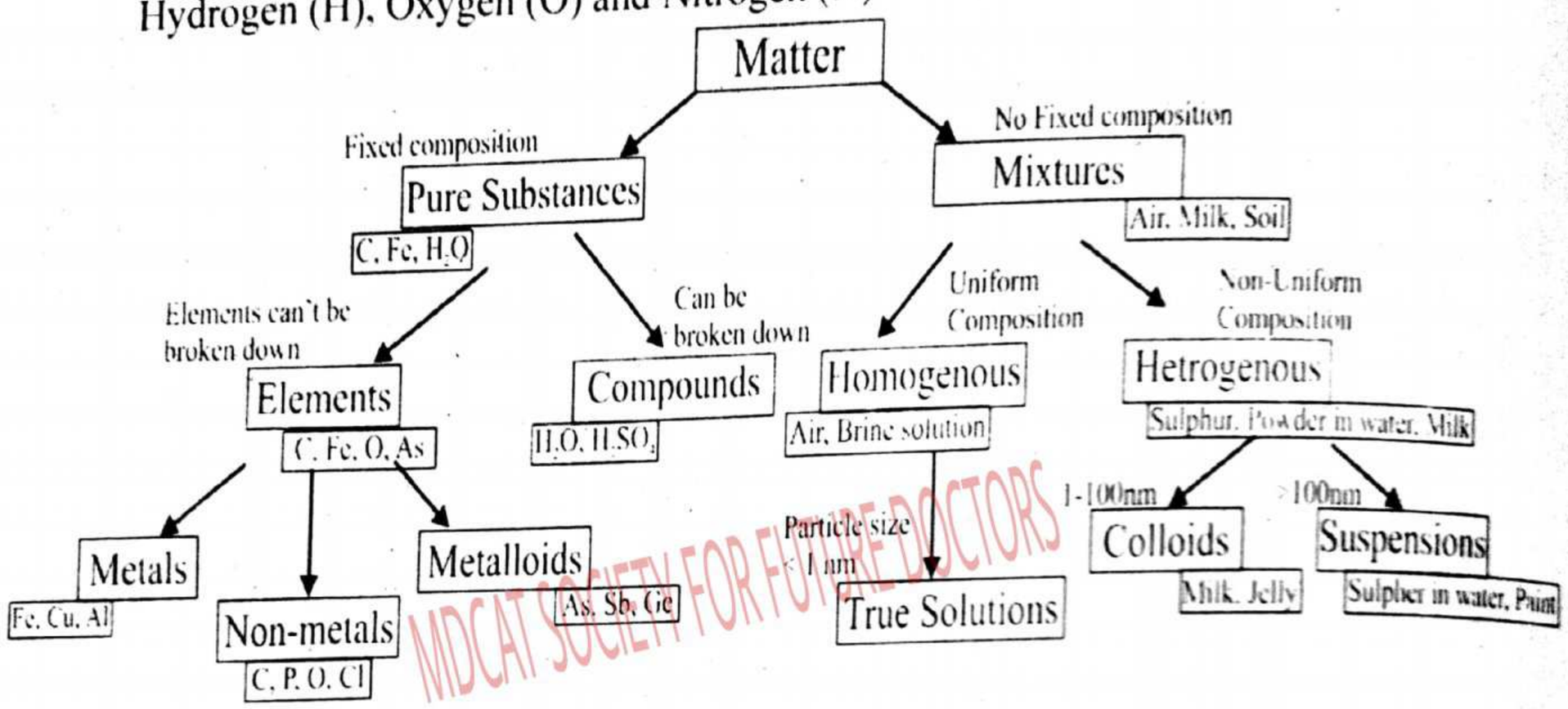
Hydrogen (H), Oxygen (O) and Nitrogen (N)

POINT TO PONDER

Atom is made up of more than 100 sub-atomic particles e.g

Electron
Proton
Neutron
Hypron
Neutrino

→ fundamental sub-atomic



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ION

The charged species which are formed by the loss or gain of one or more electrons are called ions.

Types of ions

	Cations		Anions
1	Cation is formed by the loss of one or more electrons as a result of oxidations. $A \xrightarrow{\text{oxidation}} A^+ + e^-$	1	Anions is formed by the gain of one or more electrons as a result of reduction. $B + e^- \xrightarrow{\text{reduction}} B^-$
2	Formation of cation is always an endothermic process.	2	Formation of uni-negative ion is exothermic but formation of all other negative ions is endothermic.
3	A cation may carry +1, +2, +3 etc.	3	An anion may carry –1, –2, –3 etc.
4	Size of cation is smaller than its parent atom.	4	Size of anion is greater than its parent atom.

Molecular Ion

The charged molecular species formed by the loss or gain of electron are called molecular ions.

Types of molecular ion

(a) Cationic molecular ion CH_4^+, CO^+, N_2^+

(b) Anionic molecular ion $(CH_3)_3C^-$, O_2^{2-}, O_2^-

POINT TO PONDER

Number of cationic molecular ions are greater than the number of anionic molecular ions.

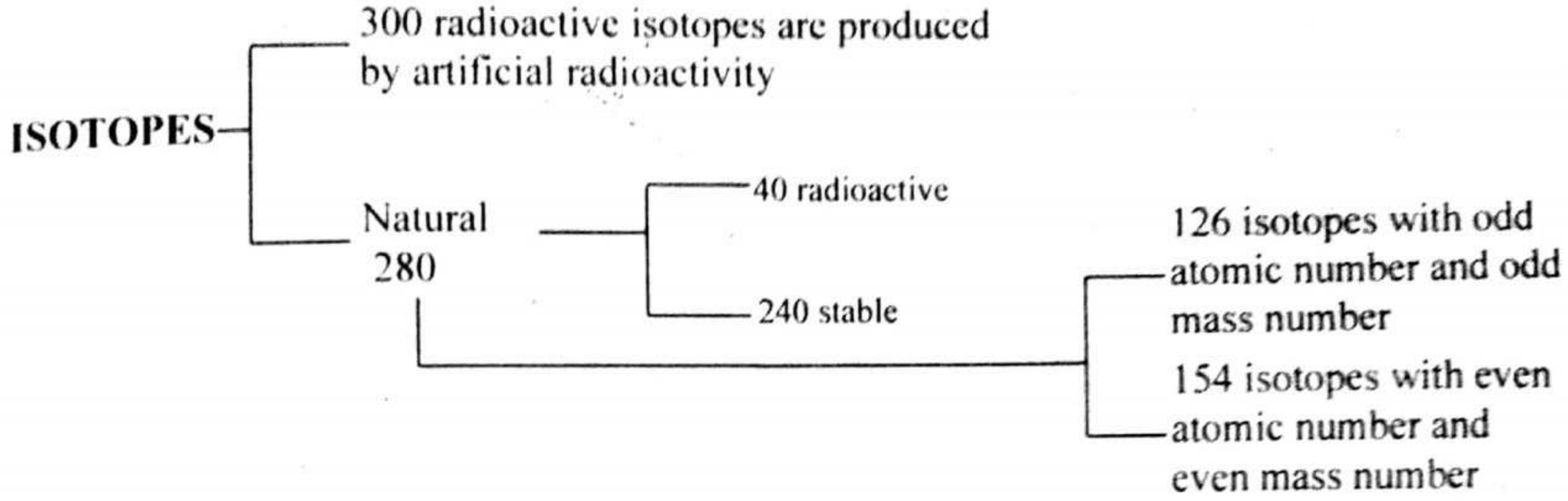
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ISOTOPES

Atoms of the same element having different mass number are called isotopes. The concept of isotopy was introduced by Soddy.

Occurrence

Elements occur in the nature in the form of isotopes. Occurrence of isotopes has been shown here.



- $^{16}_{8}O$, $^{24}_{12}Mg$, $^{28}_{14}Si$, $^{40}_{20}Ca$, $^{56}_{26}Fe$ form nearly 50% of the earth crust.

Similarities and dissimilarities in isotopes of elements

Similarities	Dissimilarities
• Atomic number • Number of Protons • Electronic configuration • Position in periodic table • Chemical properties	• Mass number • Number of Neutrons • Physical properties • Half life • Rate of reaction

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Classification of elements on the basis of isotopes

Basis	Examples
• Mono-isotopic (1) elements	F, I, As, Au, Na
• Di-isotopic (2) elements	Bi, Cl, Br
• Tri-isotopic (3) elements	Ne, C, H, O, N
• Tetra-isotopic (4) element	S
• Penta-isotopic (5) element	Ni
• Hexa-isotopic (6) elements	Ca, Pd
• Nano-isotopic (9) element	Cd
• Undeca-isotopic (11) element	Sn
• Hexdeca-isotopic (16) element	Ag

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RELATIVE MASSES

- Relative mass is the mass of a given substance scaled with carbon-12.
- C-12 is used as standard in this scale because
  1. It is highly stable isotope.
  2. Its mass is exactly in whole numbers i.e. 12.000
  3. It can be handled easily.

RELATIVE ATOMIC MASS

The mass of an atom of an element as compared to the mass of an atom of carbon-12

Atomic mass unit

The unit used to express the relative atomic mass is called atomic mass unit (amu) and it is $\frac{1}{12}$ of the mass of one atom of C-12

$$1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg} = 1.661 \times 10^{-24} \text{ g}$$

(i) Chlorine

Isotopes	$^{35}_{17}Cl$	$^{37}_{17}Cl$
Relative abundance	75%	25%
Relative isotopic mass	$^{35}_{17}Cl = 35$ amu	

RELATIVE MOLECULAR MASS

The mass of a molecule as compared to the mass of an atom of carbon-12

Relative molecular mass of water is 18 amu

Relative molecular mass of carbon dioxide is 44 amu

RELATIVE FORMULA MASS

The mass of a formula unit as compared to the mass of an atom of carbon-12

Relative formula mass of NaCl is 58.5 amu

Relative formula mass of Na_2SO_4 is 142 amu

MOLE AND AVOGADRO'S NUMBER

MOLE

The relative atomic mass of an element, relative molecular mass of covalent compound or relative formula mass of ionic compound or ionic specie expressed in grams is called **mole**. It is detonated by **'n'** and abbreviated as **'mol'**.

Examples:

1 mole of Na = 23.0g of sodium (One-gram atom of Na)

1 mole of H_2O = 18.0g of water (One-gram molecule of H_2O)

1 mole of NaCl = 58.5g of sodium chloride (One-gram formula of NaCl)

1 mole of SO_4^{-2} = 96g of sulphate ion (One-gram formula unit mass of SO_4^{-2})

Determination of Mole

There are three main methods to determine number of moles of a substance.

(i) When mass of substance is given in grams.

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$$\text{Number of moles of substance} = \frac{\text{Mass in grams of given substance}}{\text{Relative atomic mass/molecular mass/formula mass}}$$

(ii) For a certain number of particles (atoms, ions or molecules)

$$\text{Number of moles of a substance} = \frac{\text{Number of particles of the given substance}}{6.022 \times 10^{23}\ (\text{Avogadro's number of particles})}$$

(iii) For volume of a given gas in dm^3 at STP.

$$\text{Number of moles of gas} = \frac{\text{Volume of the gas in } dm^3 \text{ at STP}}{22.414\ dm^3}$$

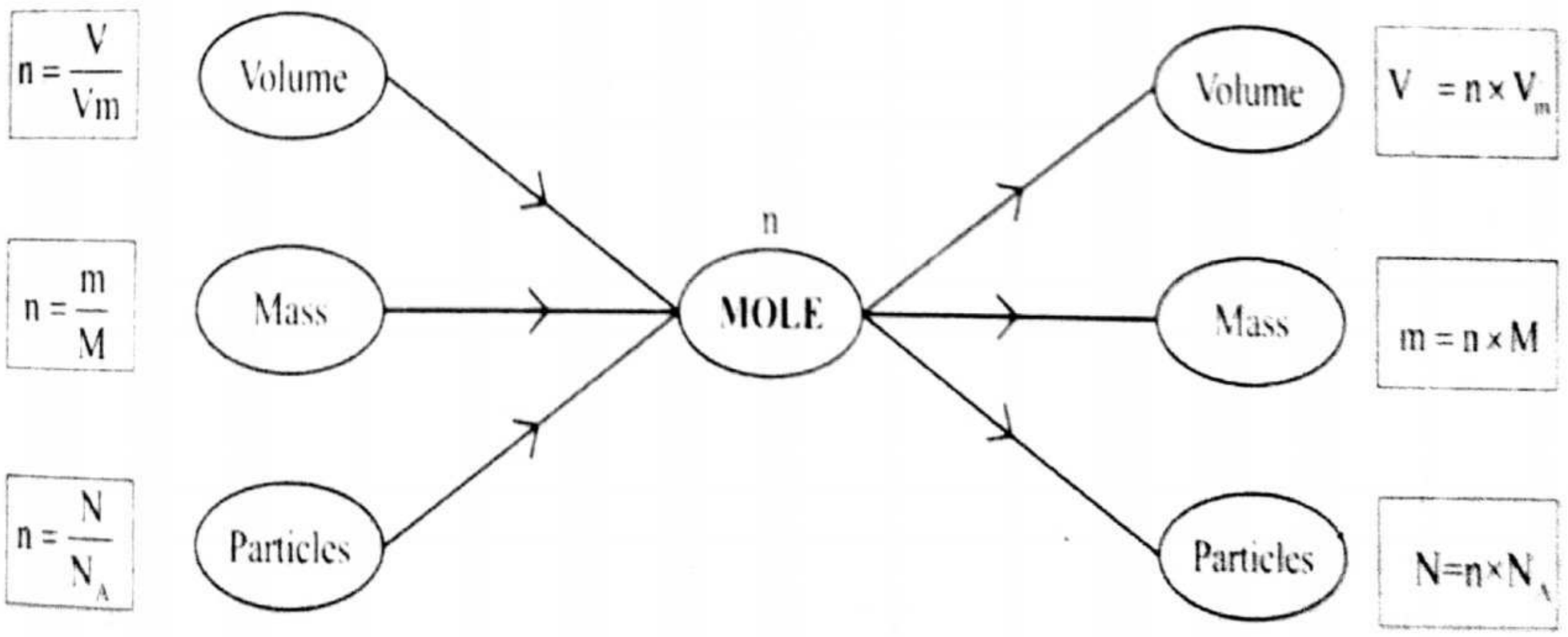
One mole	**Particles**	6.022×10^{23} Atoms	6.022×10^{23} Molecules	6.022×10^{23} Formula Units	6.022×10^{23} Ions
	Mass	Gram atomic mass of element	Gram molecular mass of the molecular substance	Gram formula mass of the ionic compound formula unit	Gram ionic mass of the ionic specie
	Volume	At STP (ideal gas) = 22.4 dm^3 and at RTP = 24.0 dm^3			

AVOGADRO'S NUMBER or CONSTANT (N_A)

It is the number of particles (atoms, ions or molecules) present in one mole of a substance. It is denoted by N_A. Its value is $\mathbf{6.022 \times 10^{23}}$.

Examples

23g Na	=	1 mole	=	6.022×10^{23} atoms
18.0g H_2O	=	1 mole	=	6.022×10^{23} molecules
58.5g NaCl	=	1 mole	=	6.022×10^{23} formula units
96g SO_4^{-2}	=	1mole	=	6.022×10^{23} ions

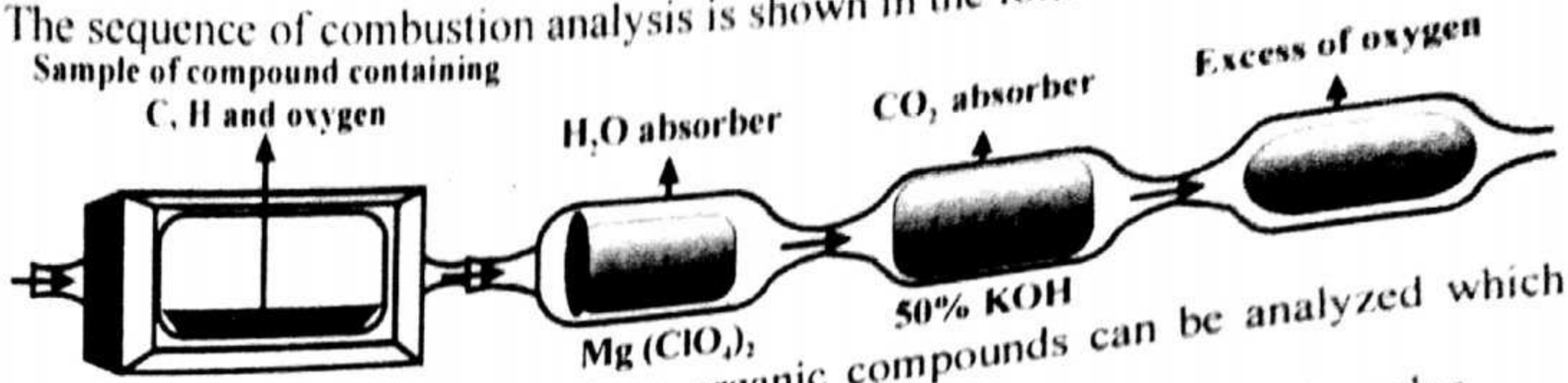


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EMPIRICAL AND MOLECULAR FORMULAE

COMBUSTION ANALYSIS

The sequence of combustion analysis is shown in the following diagram.



By combustion analysis only those organic compounds can be analyzed which simply contain carbon, hydrogen and oxygen.

From the masses, percentages are calculated by using the following formulae

(i) %age of Carbon $= \frac{\text{Mass of } CO_2 \text{ obtained in experiment}}{\text{Mass of organic compound}} \times \frac{12}{44} \times 100$

(ii) %age of Hydrogen $= \frac{\text{Mass of } H_2O \text{ obtained in experiment}}{\text{Mass of organic compound}} \times \frac{2.016}{18.0} \times 100$

(iii) %age of oxygen = 100 – (% of carbon + % of hydrogen)

Example

A sample of liquid consisting of carbon, hydrogen and oxygen was subjected to combustion analysis. 0.5439 g of the compound gave 1.039 g of CO_2, 0.6369 g of H_2O. Determine the empirical formula of the compound.

Solution

Element	%	No. of gram atoms	Atomic ratio	Empirical formula
C	$\frac{1.039g}{0.5439g} \times \frac{12.00}{44.00} \times 100 = 52.108$	$\frac{52.108}{12} = 4.34$	$\frac{4.34}{2.17} = 2$	C_2H_6O
H	$\frac{0.6369g}{0.5439g} \times \frac{2.016}{18} \times 100 = 13.115$	$\frac{13.115}{1.008} = 13.01$	$\frac{13.01}{2.17} = 6$	
O	100-(52.108+13.115) =34.77	$\frac{34.77}{16.00} = 2.17$	$\frac{2.17}{2.17} = 1$	

DIFFERENCE BETWEEN EMPIRICAL AND MOLECULAR FORMULA

	Empirical formula	Molecular formula
1	A formula which represents the simplest whole number ratio of atoms of elements in a compound is called empirical formula.	A formula which represents actual number of atoms of each element in a molecular compound is called molecular formula.
2	It is obtained from %age composition of elements i.e. chemical analysis	It is obtained by multiplying 'n' with empirical formula i.e. from empirical formula
3	This term is used for both molecular and ionic compounds	This term is used only for molecular compounds
4	Examples: NaCl, CH_2O, CH are empirical formula of sodium chloride, glucose and benzene respectively.	Examples: $C_6H_{12}O_6$ and C_6H_6 are molecular formulae of glucose and benzene respectively.

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Relationship between empirical and molecular formula

Molecular formula = n × Empirical formula

OR M.F. = n(E.F)

NOTE: The term empirical formula is used for ionic compounds and giant covalent structures (sand SiO_2, graphite and diamond C). It is also used for covalent compounds as CH_2O for glucose and acetic acid.

CONSTRUCTION OF MOLE RATIOS AS CONVERSION FACTORS IN STOICHIOMETRIC CALCULATIONS

MOLE RATIOS:

Mole ratios mean the ratios of number of moles of reactants taking part and the number of moles of product formed.

Example:

Combustion of propane

$$C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(g)}$$

The mole ratios between the reactants and products can be shown as. one mole of propane reacts with five moles of oxygen to produce three moles of carbon dioxide and four moles of water.

CONVERSION FACTOR:

A ratio of co-efficients found in a balanced chemical equation. which can be used to interconvert the amount of any two participants (reactants or product) in called conversation factor.

$$\text{Conversion Factor} = \frac{\text{Mole ratio of reactants in balanced chemical equation}}{\text{moles of the reactant to be calculated}} = \frac{\text{moles of the reactant to be calculated}}{\text{moles of the other reactant}}$$

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STOICHIOMETRIC CALCULATIONS

Stoichiometry is a branch of chemistry. which tells us the quantitative relationship between reactants and products in a balanced chemical equation.

CHEMICAL EQUATION

Chemical equation is the statement that describes a chemical reaction in term of symbols and chemical formulae.

Limitation of balanced chemical equations

They do not tell about the

(i) Conditions (temperature and pressure)

(ii) Rate of reaction

(iii) Physical state of reactants and products

(iv) Mechanism of reaction

(v) Feasibility of reaction

Conditions for stoichiometric calculations

Stoichiometric calculations are based on the following conditions: -

(i) All the reactants must be completely converted into the products.

(ii) The side reaction must not occur.

(iii) The law of conservation of mass and the law of definite proportions must be obeyed while doing the calculations.

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The following types of relationship can be studied with the help of a balanced chemical equation at S.T.P

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)} \qquad \Delta H = -482\ kJ$$

2 moles	1 mole	2 moles
4g	32g	36g
$44.828dm^3$	$22.414dm^3$	$44.828dm^3$

(i) Mass-mass relationship

If we are given the mass of one substance. we can calculate the mass of the other substance.

(ii) Mass-mole relationship or mole-mass relationship

If we are given the mass of one substance. we can calculate the moles of other substance and vice versa.

(iii) Mass-volume relationship

If we are given the mass of one substance. we can calculate the volume of the other substances and vice versa.

(iv) Mole-mole relationship

If we are given the mole of one substance. we can calculate the mole of the other substances and vice versa.

MOLAR VOLUME:

One mole of any gas at S.T.P (standard temperature and pressure) occupies a volume of $22.414dm^3$. This volume is called molar volume.

Mass of a gas can be converted into its volume at S.T.P (0°C, 1atm) and vice versa. Its mean molar volume of gases is also related with their density at S.T.P

i.e $22.414\ dm^3$ of any gas at S.T.P = 1 mole = 6.02×10^{23} molecules.

Example:

$22.414\ dm^3$ of H_2 gas at S.T.P = 2g = 1mole = 6.02×10^{23} molecules

$22.414\ dm^3$ of NH_3 gas at S.T.P = 17g = 1mole = 6.02×10^{23} molecules

Formula:

$$\text{Volume of a gas} = \text{moles} \times 22.414\ dm^3$$

$$\text{Volume of oxygen} = \frac{\text{mass in grams}}{\text{molecular mass}} \times 22.4\ dm^3$$

LIMITING REACTANT

Limiting reactant is a reactant that controls the amount of the products formed in a chemical reaction due to being less than the required amount. It can also be defined as follows:

(i) *It is a reactant that produces least number of moles of product.*

(ii) *It is consumed earlier in the reaction.*

Identification of limiting reactant

To identify a limiting reactant, the following three steps are performed.

(i) *Calculate the number of moles from the given amount of reactants.*

(ii) *Calculate the number of moles of product formed from the given moles of each reactant.*

(iii) *Identify the reactant as limiting reactant which produces least moles of the product.*

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YIELD:

The amount of the product obtained as a result of the chemical reaction is called yield.

Types of yield

(a) Theoretical yield

The amount of the product calculated from the balanced chemical equation is called the theoretical yield.

(b) Actual yield / Experimental yield

The amount of the product obtained in a chemical reaction experimentally is called actual yield.

(c) Percentage yield

$$\% \text{ Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

NOTE: Actual yield is always less than theoretical yield.

Reasons

(i) A practically inexperienced worker has many shortcomings and cannot get the expected yield.

(ii) The processes like filtration, crystallization etc if not properly carried out, decrease the actual yield.

(iii) Some of the reactants might take part in a competing side reaction and reduce the amount of the desired product.

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CONCENTRATION UNITS OF SOLUTIONS

PERCENTAGE COMPOSITION

Particular	Percentage composition
Definition	Number of parts of solute dissolved in hundred parts of solution. Four ways of expression of percentage composition 1- $\frac{w}{w}$% It is weight of solute dissolved per 100g of solution 2- $\frac{v}{w}$% It is volume of solute (cm^3) dissolved per 100g of solution. 3- $\frac{w}{v}$% It is a weight of solute (g) dissolved per100cm^3 of solution 4- $\frac{v}{v}$% It is volume of solute (cm^3) dissolved per 100 cm^3 of solution
Expression	Expressed by percentage (%)
Formula	$\%age\left(\frac{w}{w}\right) = \frac{\text{Amount of solute } (g)}{\text{Amount of solution } (g)} \times 100$

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MOLARITY

The number of moles of a solute dissolved per dm^3 of a solution is called molarity.

Symbol

It is denoted by 'M'.

Examples

0.1M NaOH solution and 0.02M $KMnO_4$ solution

Formulae

$$\text{Molarity(M)} = \frac{\text{Moles of solute}}{\text{Volume of solution in dm}^3} = \frac{n}{v}$$

$$\text{Molarity(M)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution in dm}^3} = \frac{w_2}{M_2} \times \frac{1000}{v(\text{cm}^3)}$$

NOTE: w/v% can be converted into molarity by using the following formula:

$$\boxed{M = \frac{(\%\ w/v) \times 10}{\text{Molar mass of solute}}}$$

Example: Molarity of 2% w/v solution of NaOH is

$$M = \frac{(2) \times 10}{40} = 0.5M$$

MOLE FRACTION

The ratio of the number of moles of a component to the total number of moles of all the components of solution is called mole fraction.

- *Especially suitable for solution having more than two components.*

Symbol

It is denoted by 'X'.

Explanation

Let us have components A, B and C making a solution and their number of moles are n_A, n_B and n_C respectively. X_A, X_B and X_C are their mole fractions and are given below: -

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

$$X_B = \frac{n_B}{n_A + n_B + n_C}$$

$$X_C = \frac{n_C}{n_A + n_B + n_C}$$

- The sum of the mole fractions of all the components of solution is unity (one).

$$\boxed{X_A + X_B + X_C = 1}$$

- To get mole percent, mole fraction is multiplied by 100.
- There are no formal units of mole fraction because it is a ratio of same quantity.
- Mole fraction of a component in a solution is always less than one.

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TOPIC-2 ATOMIC STRUCTURE

COURSE CONTENTS

- Properties of cathode ryas
- Properties of positive rays
- Properties of neutrons
- Discovery of electron
- Discovery of proton (positive rays)
- Charge on an electron
- e/m ratio of electron
- Discovery of neutron
- Bohr's atomic model
- Planck's quantum theory
- Spectrum
- Hydrogen spectrum
- Quantum numbers
- Shapes of orbitals
- Electronic configuration of elements
- Rutherford's model of atom (Discovery of nucleus)
- X-rays and atomic number

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DISCOVERY OF CATHODE RAYS

An English scientist. William Crooks performed discharge tube experiment for the discovery of electron.

Principle

Gases are non-conductor at ordinary pressure. They can be made conductor by decreasing pressure.

Experiment

- A gas is filled in discharge tube
- Strength of voltage depends upon the length of tube and pressure of gas filled.
- At pressure 0.01 torr. rays are produced in discharge tube on applying a potential difference of 5000-10,000 volts.
- Cathode rays are nothing but electrons.

PROPERTIES OF CATHODE RAYS

(a)	**Charge**	1895. J.Perrin observed the behavior of cathode rays under the influence of magnetic field. In 1897. J.J Thomson noted the negative charge on these rays when passed through electric field.
(b)	**Mode of movement**	These rays cast a sharp shadow of an opaque object placed in their path. They travel perpendicular to the surface of cathode.
(c)	**Material particles**	These rays consist of material particles because they possess momentum.
(d)	**e/m ratio**	Their e/m ratio is just equal to electrons.
(e)	**Penetration power**	Very low penetration power. However these rays can ionize gases.
(f)	**Naming**	Stoney named these particles as electrons.

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POINT TO PONDER

A television tube works through the deflection of a cathode rays beam by electromagnetic coil.

KEEP IN MIND

Particle	Symbol	Charges
Alpha	$^{4}_{2}He$	Positive
Beta	$^{0}_{-1}e$	Negative
Neutron	$^{1}_{0}n$	No charge
Proton	$^{1}_{1}H$	Positive
Neutrino	$^{0}_{0}n$	No charge

(g) They produce greenish fluoresence, on striking walls of glass tube (alumina glows red) (tin stone → yellow) (i) Produce x-ray, when strike anode of larger mass. (h) Have reducing effect.

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PROPERTIES OF POSITIVE RAYS AND NEUTRONS

Properties of positive rays

Positive Rays
Production They are produced when electric current is passed through gas at low pressure
Charge Have positive charge as deflected towards negative pole of electric field.
Move in straight line.
e/m ratio Smaller than electron Depends upon the gas filled in tube. Highest value was obtained when H_2 gas was filled.
Penetration power is very low. They can ionize gases.
They produce shadow of an opaque object. They were named canal rays because they travel through perforated cathode electrodes.

Properties of neutrons

Neutrons
Production They are produced when stream of α-particles are directed at beryllium ($^{9}_{4}Be$).
Charge They are passed undeflected through electric field and magnetic field, as have no charge
Move in straight line.
Penetration power is very high. They cannot ionize gases.

NOTE:

- German physicist, E. Goldstein performed positive rays experiment.
- Positive rays are also called canal rays or anode rays.
- Rutherford suggested a name proton for positive rays particle.
- Chadwick discovered neutron in 1932.
- Fast neutrons travel with an energy 1.2Mev.
- Slow neutrons travel with energy below 1ev.

Sr. No.	Quantity		Electron	Proton	Neutron
1.	Charge		-1.6022×10^{-19}C	$+1.6022\times10^{19}$C	Neutral
2.	Mass	kg	9.1095×10^{-31}	1.6726×10^{-27}	1.6750×10^{-27}
		a.m.u.	5.4858×10^{-4}	1.0073	1.0087
3.	Relative mass		1	1836 times	1840 times
4.	Relative charge		−1	+1	Neutral

MEASUREMENT OF e/m VALUE OF ELECTRON

- Joseph John Thomson calculated the e/m value of electron in 1897.
- Cathode rays are allowed to pass

(i) When both fields (electric and magnetic fields) are off.

(ii) When only magnetic field is applied.

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(iii) When only electric field is applied.

(iv) When both fields are applied simultaneously so that canceling the effect of each other and electrons are passed undeflected.

(v) Strengths of the two fields are compared.

- The e/m value of electron is -1.7588×10^{11} C/kg.
- One Kg of electrons have 1.7588×10^{11} Coulomb of charges.

MILLIKAN'S OIL DROP METHOD

An American physicist Robert Millikan determined the charge on an electron.

Mass of Electron	
Method I	**Method II**
$e/m = 1.7588\times10^{11}$ C/kg	$m/e = 5.686\times10^{-12}$ kg/C
Mass of electron $= \dfrac{1.6022\times10^{-19}C}{1.7588\times10^{11}C/kg}$	Mass of e $= 5.686\times10^{-12}$ kg/C x 1.6022×10^{-19}C
Mass of electron = 9.1095×10^{-31} kg	Mass of electron = 9.1095×10^{-31} kg

BOHR'S ATOMIC MODEL

Postulates

(i) Electron revolves in one of the circular orbits outside the nucleus.
Electron can revolve only in those orbits in which its angular momentum is integral multiple of unit $h/2\pi$.

$$mvr = \frac{nh}{2\pi}$$

Such orbits are called allowed orbits or stationary state or Bohr's orbits.

(ii) As long as an electron remains revolving in its allowed orbit, the energy of electron remains constant.

(iii) When an electron jumps from higher to lower orbit, it radiates energy in the form of photon of energy as given below.

$$\Delta E = E_2 - E_1 = h\nu$$

Objections

Bohr's Atomic model cannot explain

- The spectrum of poly electron system.
- The fine lines in the atomic spectrum.
- The three-dimensional movement of electrons.
- Zeeman effect and Stark effect.

Sommerfeld's modification of Bohr's atomic model

In 1915, Sommerfeld suggested the moving electrons might describe in addition to the circular orbits elliptic orbits as well wherein the nucleus lies at one of the focii of the eclipse.

DERIVATION OF RADIUS OF n^{th} ORBIT

(i) The electrostatic force of attraction between the electron and nucleus is

$$F = \frac{Ze^2}{4\pi\varepsilon_o r^2}$$

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(ii) Centrifugal force balance coulomb's force.

$$F = \frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

$$r = \frac{Ze^2}{4\pi\varepsilon_0 mv^2}$$ on further proceeding, we get;

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m e^2}$$

$$r = a_0 n^2$$

$$a_0 = \frac{\varepsilon_0 h^2}{\pi m e^2} = 0.529 A^o$$

By putting the value of n as 1,2,3,4..... we get

$n_1 = 1$	$r_1 = 0.529\ A^\circ$	$n_4 = 4$	$r_4 = 8.4\ A^\circ$
$n_2 = 2$	$r_2 = 2.11\ A^\circ$	$n_5 = 5$	$r_5 = 13.22\ A^\circ$
$n_3 = 3$	$r_3 = 4.75\ A^\circ$		

Conclusion

(i) The orbits are not equally spaced

$$r_2\text{-}r_1 < r_3\text{-}r_2 < r_4\text{-}r_3 <.....$$

(ii) The second orbit is four times away from the nucleus than first orbit, third orbit is nine times away and similarly fourth orbit is sixteen times away.

ENERGY OF REVOLVING ELECTRON

$$E = E_{kinetic} + E_{potential}$$

$$E = \frac{Ze^2}{8\pi\varepsilon_0 r} - \frac{Ze^2}{4\pi\varepsilon_0 r}, \quad KE = \frac{1}{2}mv^2 = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

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Energy of nth orbit

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2}\left[\frac{1}{n^2}\right]$$

$$E_n = -2.178\times10^{-18}\left[\frac{1}{n^2}\right] J \text{ per atom}$$

$$E_n = -\frac{1313.315}{n^2}\ kJmol^{-1}$$

$E_1 = -1313.315 kJmol^{-1}$

$E_2 = -328.32 kJmol^{-1}$

$E_3 = -145.92 kJmol^{-1}$

$E_4 = -82.08 kJmol^{-1}$

$E_\infty = 0\ kJmol^{-1}$

Conclusion

The difference in the values of energy go on decreasing from lower to higher orbits.

$$E_2\text{-}E_1 > E_3\text{-}E_2 > E_4\text{-}E_3 >.....$$

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PLANCK'S QUANTUM THEORY

In 1900 **Plank** put forward his theory to explain the emission and absorption of radiations. This theory gives the relationship of energy, frequency, wavelength and wave number of photon of light.

- Energy is emitted or absorbed only in terms of wave packets in a discontinuous manner. These wave packets are called quanta or photon.
- Energy of photon or quanta $E \propto \nu$.

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

Where,

h = planks constant = 6.625×10^{-34} Js.

ν = frequency

c = velocity of light = 3×10^{8} m/s

λ = wavelength in Å, nm, pm

$\bar{\nu}$ = wave number

POINT TO PONDER

Frequency: (ν)
Number of waves passing through a point in one second.

Wave length: (λ)
The distance between two adjacent crests or troughs.

Wave number: ($\bar{\nu}$)
The number of waves per unit length.

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SPECTRUM

A visual display or dispersion of the components of white light, when it is passed through a prism is called a spectrum.

Difference between continuous spectrum and line spectrum

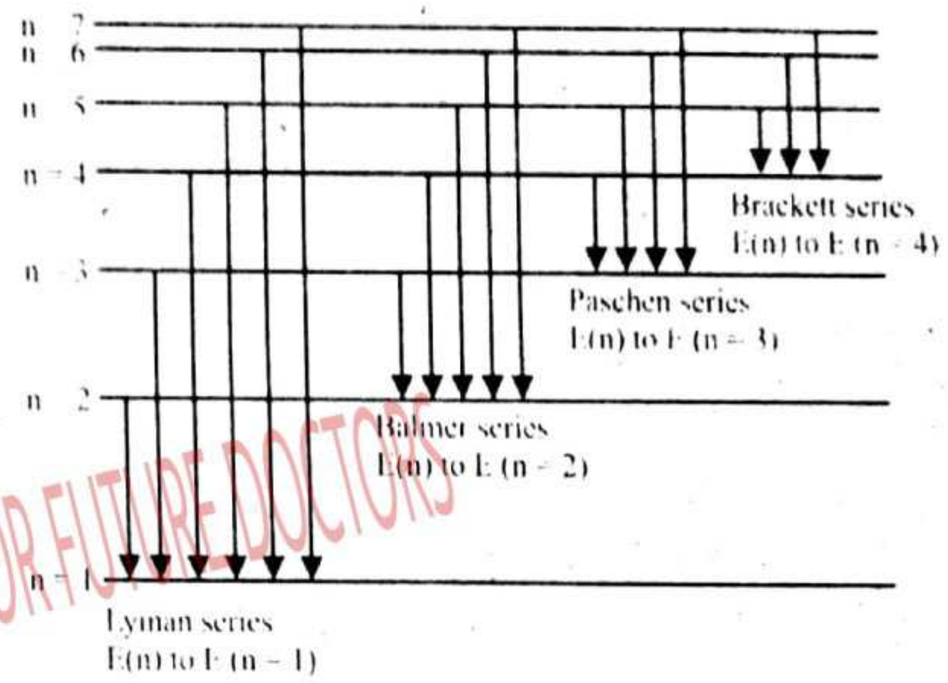
Continuous spectrum	Line spectrum
In this spectrum line or waves are diffused into one another.	In this spectrum lines are separated from each other by some dark spaces.
There is no sharp boundary between the colours.	There is gap between the lines.
It can be formed by dispersing some typical lights like sun light incandescent bulbs light etc.	It is produced by heating the element or its compound on flame or some other source of heat.
It is an effect of polychromatic light	It is an effect of monochromatic light.
Examples: rainbow, sunlight, electric bulb light.	Heating of sodium or potassium or their salts on flame.

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Atomic Emission spectra	Atomic Absorption spectra.
It is formed when the substance is in excited state.	It is formed when the substance is in its ground state.
It is produced when the substance reaches the gaseous or vapour state after absorbing energy	It is produced by gases and transparent liquids and solids.
It consists of bright lines present in a dark background.	It consists of black lines present in a bright background.
Emission spectrum of sodium gives two yellow lines of 589.0nm 589.6nm.	Absorption spectrum of sodium gives two dark lines at 589.0nm and 589.6nm.
Origin: When an excited electron jumps from higher to a lower energy level, it emits energy that form colored lines in emission spectra.	**Origin:** When an electron absorbs energy and moves to higher energy level, dark lines in absorption spectrum indicate the absorbed radiations.

EMISSION SPECTRUM OF HYDROGEN

- n_1=1;
  n_2=2,3,4.....
  (Lyman series)(U.V region)
- n_1=2;
  n_2=3,4,5.....
  (Balmer series)(Visible region)
- n_1=3;
  n_2=4,5,6.....
  (Paschen series)(I.R region)
- n_1=4;
  n_2=5,6,7.....
  (Brackett series)(I.R region)
- n_1=5;
  n_2=6,7.....
  (Pfund series)(I.R region)



$$\Delta E = 2.18\times10^{-18}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] J \quad , \quad \bar{v} = 1.0967\times10^{7}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] m^{-1}.$$

Dual Nature of Matter

According to de-Broglie "All matter particles (electrons, protons, neutrons, atoms and molecules) possess the characteristics of both the material particle as well as a wave".

de-Broglie's relationship $\lambda = \frac{h}{mv}$

Heisenberg's Uncertainty Principle

"It is impossible to determine simultaneously both the position and momentum of an electron with accuracy"

Mathematically $\Delta x.\Delta p \geq \frac{h}{4\pi}$

Reason

- The wavelength of visible light is million times larger as compared to diameter of electron. So the position becomes uncertain.
- The x-rays of short wavelength have high energy. So, the collision of X-rays with electron will bring about the great uncertainty in momentum.

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QUANTUM NUMBERS

The sets of numerical values, which give the acceptable solution to Schrodinger wave equation, are called quantum numbers.

The quantum numbers are;

1- Principal quantum number (n)
2- Azimuthal quantum number (ℓ)
3- Magnetic quantum number (m)
4- Spin quantum number (s)

Principal Quantum Number	Azimuthal Quantum Number	Magnetic Quantum Number	Spin Quantum Number	Number of Electrons in Shell	
1 (K)	0 (s)	0	+1/2, -1/2	2	2
2 (L)	0 (s)	0	+1/2, -1/2	2	8
	1 (p)	+1, 0, -1	+1/2, -1/2	6	
3 (M)	0 (s)	0	+1/2, -1/2	2	18
	1 (p)	+1, 0, -1	+1/2, -1/2	6	
	2 (d)	+2, +1, 0, -1, -2	+1/2, -1/2	10	
4 (N)	0 (s)	0	+1/2, -1/2	2	32
	1 (p)	+1, 0, -1	+1/2, -1/2	6	
	2 (d)	+2, +1, 0, -1, -2	+1/2, -1/2	10	
	3 (f)	+3, +2, +1, 0, -1, -2, -3	+1/2, -1/2	14	

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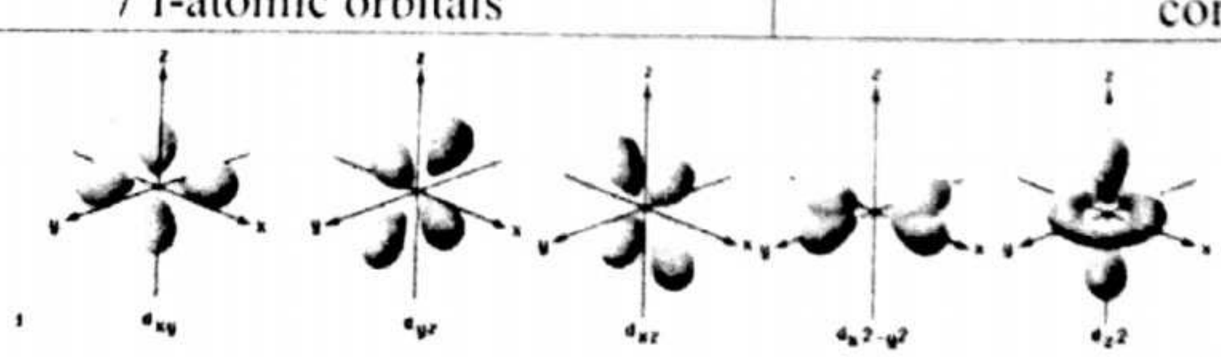
POINT PONDER

If we were to use a golf ball to represent the nucleus, the atom would be about three miles in diameter.

Orbital

The area around the nucleus, where the probability of finding an electron is maximum is called an orbital.

Sub-shell	Orbitals	shape
s	1 s-atomic orbital	spherical
p	3 p-atomic orbitals p_x, p_y, p_z	dumb-bell
d	5 d-atomic orbitals d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2}	satsage
f	7 f-atomic orbitals	complex



Arrangement of sub-shells

- The sub-shells are arranged in the increasing order of $(n+l)$ value and if any two sub-shells have same $(n+l)$ value, then that sub-shell is placed first whose n value is smaller.

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SHAPES OF ORBITALS

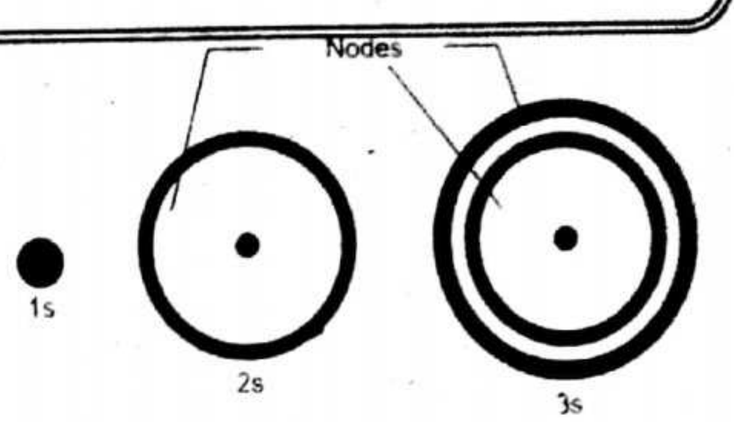
Shapes of s-orbitals:

s-orbital is spherical in shape and is represented by a circle (cut of sphere). Higher the value of 'n' for s-subshell, greater will be its size.

Example: 2s is larger in size than 1s.

POINT TO PONDER

The volume of space in which there is a 95% chance of finding the electron is called orbital.



Nodal Surface or Nodal Plane

The probability of finding the electron is zero between two orbitals. This plane is called Nodal plane or Nodal surface.

Shapes of p-orbitals

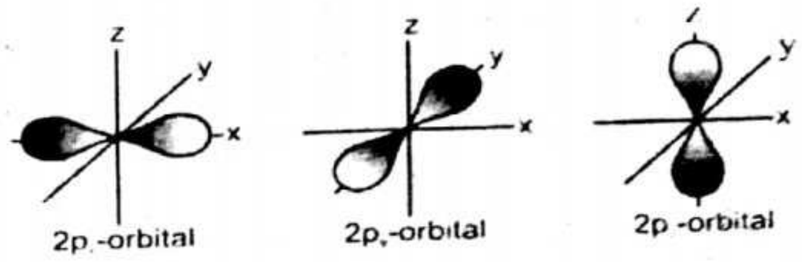
Each p-orbital has two lobes in dumb-bell shape.

These lobes are either oriented along

$p_x \longrightarrow$ X-axis

$p_y \longrightarrow$ Y-axis

$p_z \longrightarrow$ Z-axis



The size of p-orbital increases with increase in its 'n' value.

Example:

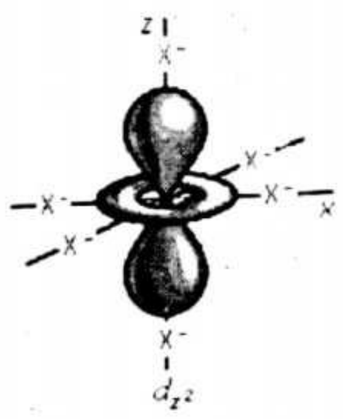
$3p_x$ orbital is larger in size than $2p_x$ but both have same shape (i.e. dumb-bell).

Shapes of d-orbitals

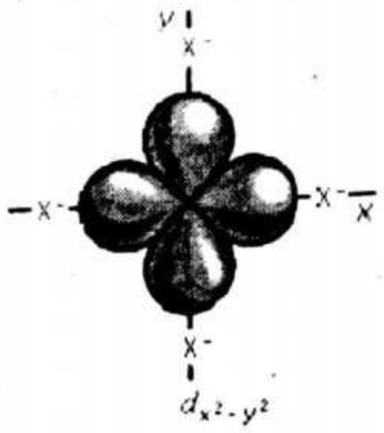
Each d-orbital has four lobes or two dumb-bell in sausage shape.

These lobes are either oriented along X-axis, Y-axis and Z-axis.

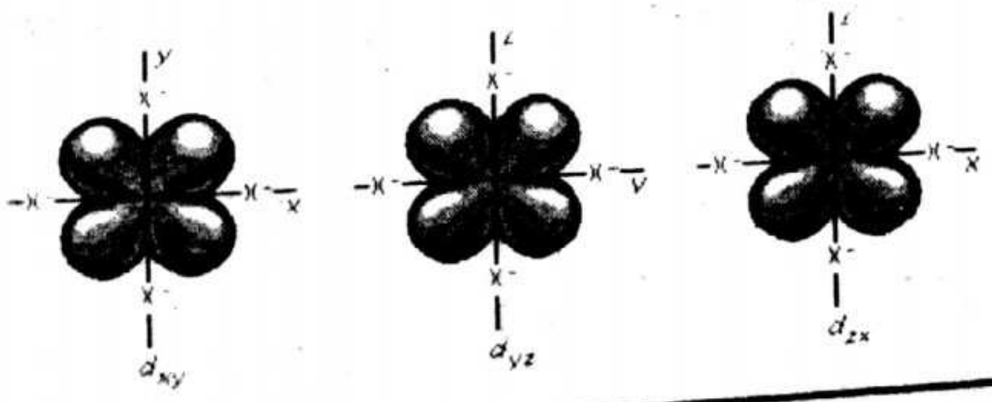
The size of d-orbital increases with increase in its 'n' value.



⟶ On axes (Dumb-bell with collar)



⟶ On axes (Double Dumb-bell / Clover-leave shape)



⟶ Between axis (Double Dumb-bell)

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ELECTRONIC CONFIGURATION OF ATOMS AND IONS (H → Kr)

It is distribution of electrons in shells, sub-shells and orbitals of an atom according to definite rules.

The following rules are adopted in order to distribute the electrons in the orbitals of sub-shells of shells in an atom.

Auf-bau principle

The electrons should be filled in energy sub shells in order of increasing energy values.

The electrons are first placed in

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s and so on.

(n + *l*) rule:

⟶ Filling of electrons in subshells

This gives us the arrangement of electrons in subshells.

Subshells are arranged in the increasing order of $n+l$ values and if any two subshells have the same $n+l$ values then the subshell is filled with electrons first whose 'n' value is smaller

It has two parts:

(a) The electrons are filled in subshells in increasing order of their (n+ *l*) values.

(b) If two subshells have same (n+ *l*) values, then the subshell with low 'n' value will be filled first.

This rule gives us the arrangement of subshells in increasing order of their energy.

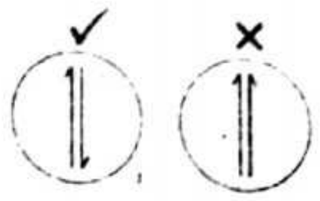
Ascending order of energy of sub-shells on the basis of (n + *l*) rule

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s

Pauli's exclusion principle

⟶ Filling of electrons in orbitals

Two electrons in the same orbital must have opposite spins.

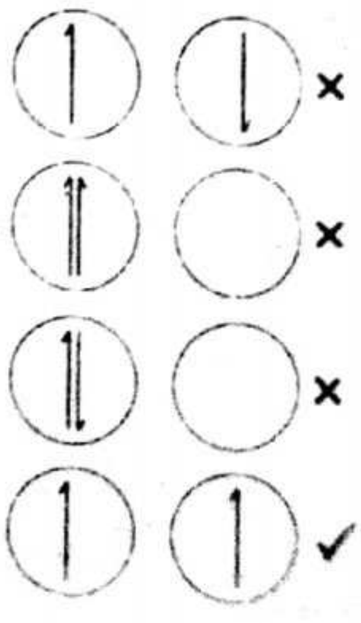


OR

It is impossible for two electrons residing in the same orbital of a poly electron atom to have the same values of four quantum numbers.

Hund's rule

⟶ Filling of electrons in degenerate orbitals



If degenerate orbitals are available and more than one electron are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins.

Half-filled and completely filled sub-shells, are more stable e.g. Cr and Cu.

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Element	Atomic Number	Electron configuration Notation
Hydrogen	1	$1s^1$
Helium	2	$1s^2$
Lithium	3	$1s^2 2s^1$
Beryllium	4	$1s^2 2s^2$
Boron	5	$1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$
Carbon	6	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$
Nitrogen	7	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
Oxygen	8	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
Fluorine	9	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$
Neon	10	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$
Sodium	11	$[Ne]3s^1$
Magnesium	12	$[Ne]3s^2$
Aluminium	13	$[Ne]3s^2 3p_x^1 3p_y^0 3p_z^0$
Silicon	14	$[Ne]3s^2 3p_x^1 3p_y^1 3p_z^0$
Phosphorus	15	$[Ne]3s^2 3p_x^1 3p_y^1 3p_z^1$
Sulphur	16	$[Ne]3s^2 3p_x^2 3p_y^1 3p_z^1$
Chlorine	17	$[Ne]3s^2 3p_x^2 3p_y^2 3p_z^1$
Argon	18	$[Ne]3s^2 3p_x^2 3p_y^2 3p_z^2$
Potassium	19	$[Ar]4s^1$
Calcium	20	$[Ar]4s^2$
Scandium	21	$[Ar]4s^2 3d_{xy}^1 3d_{xz}^0 3d_{yz}^0 3d_{x^2-y^2}^0 3d_{z^2}^0$
Titanium	22	$[Ar]4s^2 3d_{xy}^1 3d_{xz}^1 3d_{yz}^0 3d_{x^2-y^2}^0 3d_{z^2}^0$
Vanadium	23	$[Ar]4s^2 3d_{xy}^1 3d_{xz}^1 3d_{yz}^1 3d_{x^2-y^2}^0 3d_{z^2}^0$
Chromium	24	$[Ar]4s^1 3d_{xy}^1 3d_{xz}^1 3d_{yz}^1 3d_{x^2-y^2}^1 3d_{z^2}^1$
Manganese	25	$[Ar]4s^2 3d_{xy}^1 3d_{xz}^1 3d_{yz}^1 3d_{x^2-y^2}^1 3d_{z^2}^1$
Iron	26	$[Ar]4s^2 3d_{xy}^2 3d_{xz}^1 3d_{yz}^1 3d_{x^2-y^2}^1 3d_{z^2}^1$
Cobalt	27	$[Ar]4s^2 3d_{xy}^2 3d_{xz}^2 3d_{yz}^1 3d_{x^2-y^2}^1 3d_{z^2}^1$
Nickel	28	$[Ar]4s^2 3d_{xy}^2 3d_{xz}^2 3d_{yz}^2 3d_{x^2-y^2}^1 3d_{z^2}^1$
Copper	29	$[Ar]4s^1 3d_{xy}^2 3d_{xz}^2 3d_{yz}^2 3d_{x^2-y^2}^2 3d_{z^2}^2$
Zinc	30	$[Ar]4s^2 3d_{xy}^2 3d_{xz}^2 3d_{yz}^2 3d_{x^2-y^2}^2 3d_{z^2}^2$
Gallium	31	$[Ar]4s^2 3d^{10} 4p_x^1 4p_y^0 4p_z^0$
Germanium	32	$[Ar]4s^2 3d^{10} 4p_x^1 4p_y^1 4p_z^0$
Arsenic	33	$[Ar]4s^2 3d^{10} 4p_x^1 4p_y^1 4p_z^1$
Selenium	34	$[Ar]4s^2 3d^{10} 4p_x^2 4p_y^1 4p_z^1$
Bromine	35	$[Ar]4s^2 3d^{10} 4p_x^2 4p_y^2 4p_z^1$
Krypton	36	$[Ar]4s^2 3d^{10} 4p_x^2 4p_y^2 4p_z^2$

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RUTHERFORD'S ATOMIC MODEL

- Rutherford discovered nucleus in 1911.

Experiment

- Bombardment of alpha particles on 0.00004 cm thick gold foil.

Observations

- Rutherford observed the various angle of deflections of alpha particles.
- Most of the alpha particles were passed un-deflected.
- Some alpha particles were deflected at various angles

Conclusion

- Most of the part of atom is empty.
- Central part is tiny and positively charged. It is called nucleus.
- Almost the whole mass of an atom is concentrated in the nucleus (i.e. atom has non-uniform density).

Objections

If electron is revolving continuously then it will radiate energy continuously then

- Atomic assembly must collapse that doesn't happen.
- Atomic spectrum must be continuous rather than the line spectrum.

POINT TO PONDER

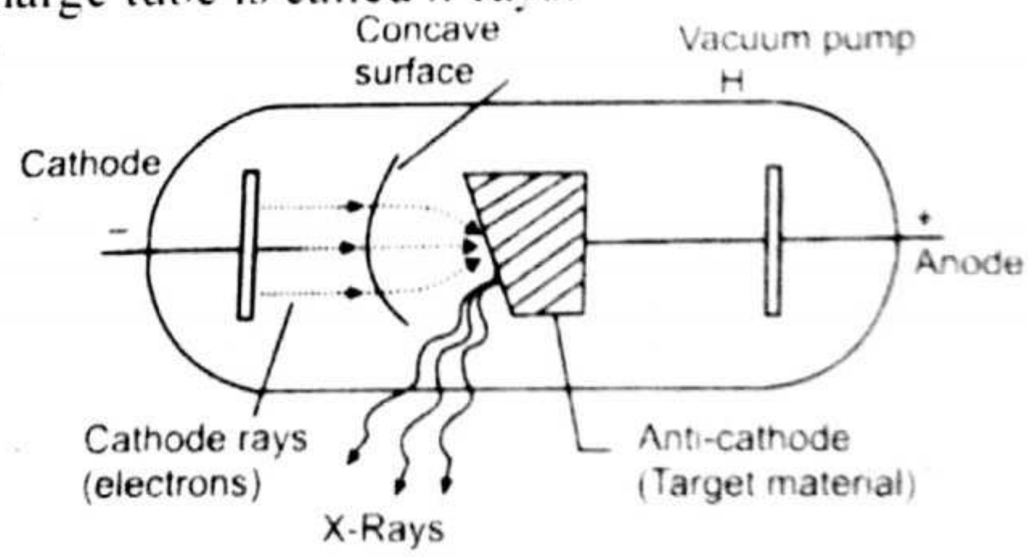
If we were to use a golf ball to represent the nucleus, the atom would be about three miles in diameter.

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X-RAYS AND ATOMIC NUMBER

Definition

The rays which are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube is called x-rays.



- Wavelength of X-rays depends upon nature of metal.
- Mosley's research work covers the range of wavelength 0.04-8A°.
- Spectral line of shorter wavelength is K-series and of longer wavelength is called L-series.
- X-rays become very short wavelength in case of heavy metals.

Moseley's equation

$\sqrt{\nu} = a(z - b)$

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TOPIC-3 GASES

COURSE CONTENTS

- Properties of gases
- Gas laws
  - (i) Boyle's law
  - (ii) Charles's law
  - (iii) Avogadro's law
- General gas equation (Ideal gases equation)
- Kinetic molecular theory of gases
- Kinetic interpretation of temperature
- Distinguish between Real and ideal gases (Van der Waals equation)

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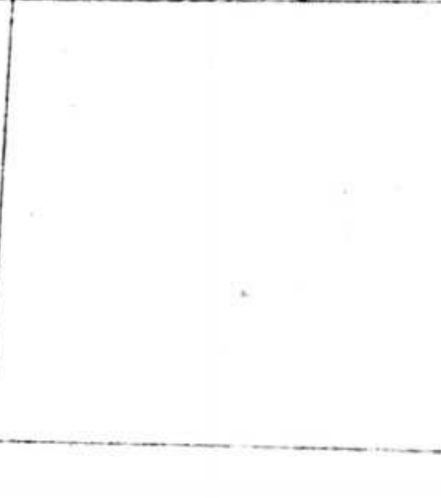
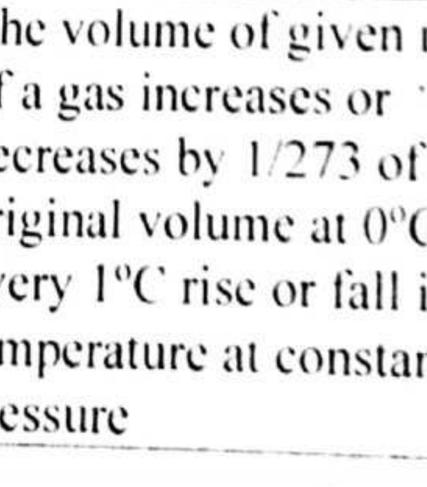
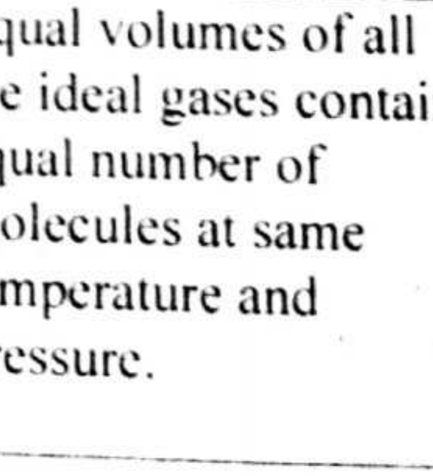
INTRODUCTION

- There are four states of matter namely, gas, liquid, solid and plasma.
- The simplest state is gas and complex one is plasma.
- Gas, liquid and solid states are considered to be phase transition states because they are interconvertible into each other at constant temperature.
- Whereas, plasma state is not a phase transition state because it is formed from gaseous state with continuously increasing temperature.

PROPERTIES OF GASES

1.	**General**	It has definite mass but no definite shape and volume
2.	**Forces**	Almost negligible
3.	**Density**	Low
4.	**Motion**	Molecules have large rotatory, vibratory and translatory motion
5.	**Packing**	No proper packing
6.	**Energy**	Least
7.	**Thermal expansion**	High
8.	**Compression**	High
9.	**Intermixing**	Spontaneous
10.	**Pressure**	Exert pressure on the walls of container

GAS LAWS

Particulars	Boyle's law	Charles's law	Avogadro's law
Statement	The volume of a given mass of an ideal gas is inversely proportional to the applied pressure at constant temperature.	The volume of the given mass of an ideal gas is directly proportional to the absolute temperature at constant pressure	The volume of a given ideal gas is directly proportional to the number of moles at STP.
		The volume of given mass of a gas increases or decreases by 1/273 of its original volume at 0°C for every 1°C rise or fall in temperature at constant pressure	Equal volumes of all the ideal gases contain equal number of molecules at same temperature and pressure.
Mathematical representation	$PV=K$ or $P_1V_1=P_2V_2$	$V/T=K$ or $V_1/T_1=V_2/T_2$	$V/n=K$ or $V_1/n_1=V_2/n_2$
Graphical verification			

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Experimental observation	By putting a weight on moveable piston of cylinder filled with gas. The volume of gas decreases.	On heating a cylinder filled with gases having a moveable piston. The volume of gases increases.	On increasing the number of moles of a gas in a closed cylinder. The volume increases.

GENERAL GAS EQUATION

General gas equation

On combining the Boyle's law, Charles's law and Avogadro's law,

$PV = K$

$V/T = K$

$V/n = K$

we get

$PV = nRT$ (R is called general gas constant)

This is called an ideal gas equation or general gas equation. This equation is completely obeyed by the ideal gases.

POINT TO PONDER

The pressure of air which can support 760 mm of Hg column at sea level is called one atmospheric pressure.

1-atm = 76 cm of Hg = 760 mm of Hg
= 760 torr = 14.7 psi
= 101325 Pa (Nm^{-2}) = 1.01325 Bar

Rearrangement of general gas equation

Boyle's law $PV = nRT = K$
(when "n" and "T" are constant)

Charles's law $\frac{V}{T} = \frac{nR}{P} = K$
(when "n" and "P" are constant)

Avogadro's law $\frac{V}{n} = \frac{RT}{P} = K$
(when "T" and "P" are constant)

Ideal gas constant (R)

The value of R depends upon the units chosen for pressure, volume and temperature. It is independent of the nature of gas.

The value of "R" can be derived by using general gas equation.

$PV = nRT$

$R = PV/nT$

Units of R

When P is in atm and V in dm^3

$R = 0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1}$

When P is in mm Hg or torr and V in dm^3 or cm^3.

$R = 62.4\ dm^3\ mm\ Hg\ K^{-1}\ mol^{-1}$

$R = 62400\ cm^3\ torr\ K^{-1}\ mol^{-1}$

When P is in Nm^{-2} and V in m^3 (SI units)

$R = 8.314 NmK^{-1}\ mol^{-1}$

$R = 8.314\ JK^{-1}\ mol^{-1}$

$R = 1.987\ calK^{-1}\ mol^{-1}$

POINT TO PONDER

$1\ m^3 = 1000\ dm^3$
$1dm^3 = 1000\ cm^3$
$1dm^3 = 0.001\ m^3$
$1cm^3 = 0.001dm^3$
$1cm^3 = 10^{-5}\ m^3$

1Nm = 1J
1cal. = 4.18J
1J = 0.239 cal
$1J = 10^7$ ergs

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Formula for density of gas

$$d = \frac{PM}{RT}$$

Where,

d = Density of ideal gas P = Pressure of gas

R = Ideal gas constant T = Absolute temperature

Hence, density of an ideal gas is directly proportional to pressure and molar mass and inversely proportional to the absolute temperature.

(i) $d \propto P$ (ii) $d \propto M$ (iii) $d \propto \frac{1}{T}$ (iv) $d \propto \frac{1}{V}$

NOTE: Kinetic equation of gases can be employed to justify all the gas laws. In other words, it proves the gas laws to get their explanation from kinetic theory of gases.

Name of Scientist	Contribution
Bernoulli	Founder of KMT
Clausius	Derived Kinetic equation and deduced all the gas laws from KMT
Maxwell	Presented the law of distribution of velocities
Boltzman	Studied the distribution of energies among the molecules
Van der Waal	Corrected the pressure and volume factors in ideal gas equation to make it applicable to the real gases.

POSTULATES OF KINETIC MOLECULAR THEORY

(i) Every gas consists of large number of very small particles called molecules. Gases like He, Ne, Ar have mono-atomic molecules.

(ii) The molecules of gas move haphazardly, colliding among themselves and with the walls of container changing their directions.

(iii) The pressure exerted by the gas molecules is due to the collision of its molecules with the walls of container. The collisions among the molecules are perfectly elastic.

(iv) The molecules of the gases are widely separated from one another and there are sufficient empty spaces among them.

(v) The molecules of the gases have no forces of attraction for each other

(vi) The actual volume of molecules of a gas is negligible as compared to the volume occupied by the gas

(vii) The motion imparted to the molecules by gravity is negligible as compared to the effect of the continued collisions between them

(viii) The average kinetic energy of the gas molecules varies directly as the absolute temperature of the gas

Clausius kinetic energy equation

$PV = \frac{1}{3}mN\overline{c^2}$ ($\overline{c^2}$ is called mean square velocity)

Relationship between the absolute temperature and velocities of gas molecules

According to Maxwell distribution law of velocities

- Root mean square velocity (C_{rms}) = $\sqrt{\frac{3RT}{M}}$

Conclusions

- In gases and liquids, temperature is the measure of average translational kinetic energy of the molecules

POINT TO PONDER

Determine the average speed of a helium atom at room temperature

$$C_{rms} = \sqrt{\frac{3RT}{M}}$$

$M = 4 \times 10^{-3}$ kg/mol

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- In solids, temperature is the measure of average vibrational kinetic energies of molecules.
- The average translational kinetic energy of gas molecules is directly proportional to the Kelvin temperature of a gas i.e.

$$E_k \propto T$$

- When heat flows from one body to another, the molecules in the hotter body give up some of their kinetic energy through collisions to the molecules in the colder body.

KINETIC INTERPRETATION OF TEMPERATURE

(i) Derivation

$$E_K = \frac{3RT}{2N_A}$$

$$E_k \propto T \text{ (since } \frac{3}{2}\frac{R}{N_A} \text{ is constant)}$$

(ii) Idea of heat flow:

When heat flows from a body at high temperature to a body at low temperature, molecules in the hotter body give up some of their kinetic energy to molecules of colder body through collisions.

(iii) Temperature of gases and liquids:

Temperature is measure of average translational kinetic energies of molecules.

(iv) Temperature of solids:

Temperature is measure of average vibrational kinetic energy of molecules because solid molecules show only vibrational motion.

(v) Absolute zero:

Temperature at which molecular *motion ceases.*

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POINT TO PONDER

Absolute zero

The temperature at which motion of molecules ceases.

$0K = -273.16^oC = -459^oF$

The absolute temperature is unattainable and the current attempts resulted in temperature as low as $10^{-5}K$

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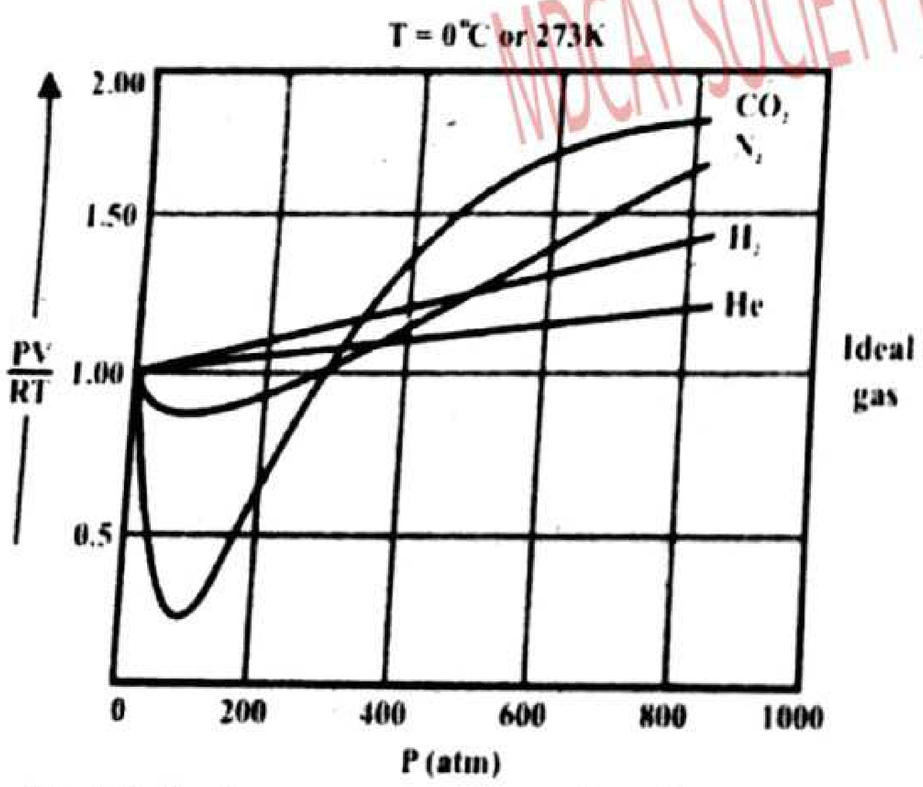
DISTINGUISH BETWEEN REAL AND IDEAL GASES

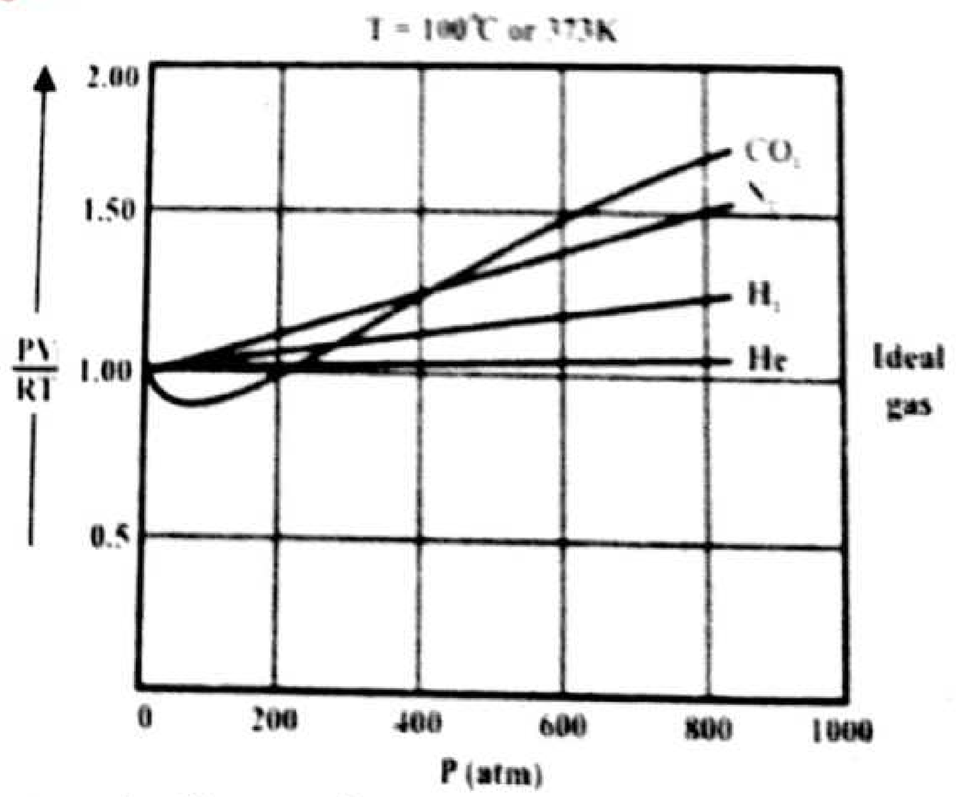
Comparative study of real and ideal gases

Ideal Gases	Real Gases
Ideal gas obeys the gas laws strictly under all T and P.	They do not obey the gas laws under all condition of T and P.
Their actual volume is negligible as compared to the volume of container.	They do possess some volume that is not negligible under highly compressed state.
There are no intermolecular attractions or repulsions.	There exist negligible forces of attraction or repulsion under ordinary conditions.
The molecules of an ideal gas undergo elastic collisions.	The molecules of a real gas undergo inelastic collisions.
They can not be liquefied.	They can be liquefied at critical temperature by applying critical pressure.

Non- Ideal Behavior of Gases

- If a graph is plotted between pressure on x-axis and the $\frac{PV}{nRT}$ (compressibility factor or Z) on y-axis for an ideal gas, a straight line parallel to the pressure axis is obtained.
- For real gases (non-ideal gases), the graph is no more parallel to the pressure axis.





At high temperature under low pressure, the graph for real gases come closer to the expected straight line.

- If $Z = 1$ then line would be parallel to x-axis.
- If $Z < 1$ then the line obtained will below the line of ideal gas which means that there is larger decrease in volume of the gas than predicted by general gas equation due to the appearance of attractive forces present among the molecules.
- If $Z > 1$ then the line obtained will be above the line of an ideal gas which means that there is less decrease in the volume of the gas than predicted by the general gas equation due to appearance of repulsive forces present among the molecules

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Conclusion

(i) Gases are ideal at low pressure and non-ideal at high pressure.

(ii) Gases are ideal at high temperature and non-ideal at low temperature.

Causes of deviation of real gases from ideal behavior

The real gases deviate from ideal behavior due to two faulty assumptions of KMT of gases.

These are;

(i) The volume of the gas molecules themselves is negligible as compared to the total gas volume.

(ii) There are no attractive forces among the molecules of a gas.

CONDITIONS NECESSARY FOR GASES TO APPROACH IDEAL BEHAVIOUR

(i) Gases behave ideally at high temperature. Because under these conditions, gases have high kinetic energy. That is the reason why the forces between them are weaker and each gas molecules behave almost independently and hence become ideally.

(ii) Gases behave ideally at low pressure. Because under these conditions, gases have great distances between them. That is the reason why the forces between them are weaker and each gas molecules behave almost independently and hence become ideally.

VAN DER WAALS EQUATION FOR REAL GASES

The real gases deviate from ideal behavior due to two faulty assumptions of KMT of gases.

These are;

(i) The volume of the gas molecules themselves is negligible as compared to the total gas volume.

(ii) There are no attractive forces among the molecules of a gas.

Experimental observation and volume correction

When a gas is highly compressed then the whole volume of the container is not available to molecules because of their actual volume together with their effective volume which is not negligible under this condition. So we have to exclude this volume.

Actual volume of one mole of gas molecule $= V_m$

Effective volume of one mole of gas molecules $= b$

$$b = 4V_m$$

so,

$$V_{free} = V_{vessel} - b$$

Microscopic study of gas and pressure correction

When pressure on the gas is increased and its temperature is decreased the molecules come close to each other which results in the appearance of attractive forces among gas molecules.

A molecule in the interior of a gas is attracted by the other molecules on all sides so these attractive forces are cancelled out. However, when a molecule strikes the wall of the container, it experiences a force of attraction towards the other molecules in the gas. This decreases the force of its impact on the wall. This results a decrease in pressure denoted by P′. so the observed pressure is less than the ideal pressure P_i by an amount P′.

$$P = P_i - P'$$

$$P_i = P + P'$$

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POINT TO PONDER

For real gases, it is observed that molecules occupy only 0.05% of the total volume at STP, but at 500 atm and 0°C, the volume occupied by gas molecules is 20% of the total volume. Molecules attract one another at distances up to about 10 molecular diameters.

Mathematical Representation

Both these corrections can be represented mathematically by the modification of the general gas equation called the van der Waals equation.

- The increase in V caused by the effect of molecular volume is corrected by subtracting an amount nb from the observed volume. i.e.

$$V - nb$$

- The change in pressure caused by the effect of intermolecular attractions is best corrected by adding an amount an^2/v^2 to the pressure.

Correction for intermolecular attraction — Correction for molecular volume

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Van der Waal's equation $\left(P+\frac{an^2}{V^2}\right)(V-nb) = nRT$

For n moles of gas $P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$

For one mole of gs $P = (RT/V-b) - a/V^2$

Here "a" and "b" are called Van der Waals constant.

Units of (a)

(i) $Nm^{+4}\ mol^{-2}$ (S.I Units)

(ii) $atm\ dm^6\ mol^{-2}$ (other common units)

Units of (b)

(i) $m^3\ mol^{-1}$ (S.I Units)

(ii) $dm^3\ mol^{-1}$ (other common units)

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TOPIC-4 LIQUID

COURSE CONTENTS

- Properties of liquids
- Intermolecular forces
  - (i) Dipole-Dipole forces
  - (ii) Dipole-Induced dipole forces
  - (iii) London dispersion forces
- Evaporation
- Vapour pressure
- Boiling point and external pressure
- Hydrogen bonding and physical properties, Anomalous behavior of water

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INTRODUCTION

- Liquids states of matter is the intermediate state between the gaseous and the solid state
- In liquids the molecules of the matter are held together by strong intermolecular forces in comparison to those in gases.
- On the bases of kinetic molecular model, the liquids state is described as follow:
  - **(i)** A liquid is composed of small molecules
  - **(ii)** The molecules of the liquids or held closer by some kind of intermolecular forces.
  - **(iii)** The intermolecular forces are not very strong and thus the molecule is always in constant random motion.
  - **(iv)** The average kinetic energy of molecules of a liquid is directly proportional to their absolute temperature.

PROPERTIES OF LIQUIDS

	Property	Liquid state
1.	**General**	It has definite mass and volume but no definite shape
2.	**Forces**	Weaker than those in solids
3.	**Density**	Lower than solids
4.	**Motion**	Low values of motions
5.	**Packing**	Less closely packed
6.	**Energy**	Higher than solids
7.	**Thermal expansion**	Higher than solids
8.	**Compression**	Slightly higher than solids
9.	**Intermixing**	Spontaneous but slow
10.	**Pressure**	Negligible

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FORCE OF ATTRACITONS

Intramolecular Forces

The forces, which are present within the molecules, are called intramolecular forces

Examples

- Covalent bond
- Ionic bond
- Co-ordinate covalent bond etc.

These forces are stronger as compared to intermolecular forces related to the chemical properties only.

Intermolecular Forces

The forces present among the molecules are called intermolecular forces.

1. Dipole-dipole forces
2. Ion-dipole forces
3. Dipole-induced dipole forces
4. Instantaneous dipole-induced dipole forces (London dispersion forces)
5. Hydrogen bonding

POINT TO PONDER

Intra: Attractive forces within molecules are called intramolecular forces.
Inter: Attractive forces between the molecules are called intermolecular forces.

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Significance

- All the intermolecular forces are electrostatic in nature and are resulted from the mutual attraction of unlike charges or the mutual repulsion of like charges.
- Many of the physical properties of liquids can be explained on the basis of intermolecular forces.

Dipole-Dipole Forces

The electrostatic forces of attraction produced when the positive end of one molecule attracts the negative end of neighbouring molecule are called dipole-dipole forces.

Factors affecting the strength of dipole-dipole forces

- Electronegativity difference between the bonded atoms
- Intermolecular distance

Examples

- These are present in polar molecules. e.g. HCl and $CHCl_3$
- These forces are approximately one percent as effective as a covalent bond.
- In gaseous phase, the dipole-dipole forces are least.
- Greater the strength of dipole-dipole forces, greater the values of melting point, boiling point, heat of vapourization and heat of sublimation.

Factors affecting the strength of intermolecular forces

Ion-dipole force	Dipole-induced dipole force	London dispersion forces	Dipole-dipole forces	Hydrogen bond
▸ Charge density of the ion ▸ polarity of the molecule ▸ size of the molecule	▸ Polarity of polar molecule ▸ Size of the molecules ▸ Collision frequency	▸ Size of the molecules ▸ Collision frequency	▸ Polarity of molecules ▸ Size of the molecules ▸ Collision frequency	▸ Polarity of molecules ▸ Number of utilizable lone pairs

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LONDON DISPERSION FORCES (LDF)

The short-range forces of attraction created between one end of instantaneous dipole and the opposite end of the induced dipole are called instantaneous dipole induced dipole interaction or London Dispersion forces.

POINT TO PONDER

Polar Molecules

- The heteroatomic molecules are usually polar.
  Examples: CH_3Cl, HOCl, H_2SO_4 etc.
- Binary compounds whose central atom is from group VA, VIA or VIIA are dipolar
  Examples: H_2S, HCl, HF etc.

Non-polar Molecule

- Mono-atomic or homoatomic molecules are always non-polar
  Examples: H_2, O_2, F_2, Cl_2, N_2
- Binary compounds whose central atom is from group IIA, IIIA or IVA are non-polar. They have symmetrical shape.
  Examples: $BeCl_2$, BH_3, CCl_4 etc. are also non-polar.

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- A German physicist **Fritz London** explained these forces in 1930.
- These forces are present in all types of molecules whether polar or non-polar.

Variations

- London dispersion forces increase down the group due to increase in size hence the polarizibility e.g. boiling point of fluorine (gas) is −188.1°C while that of iodine (solid) is +184.4°C.
- In hydrocarbon with the increase of chain length the intermolecular forces increase e.g. the boiling point of ethane (C_2H_6) is -88.6°C and of hexane (C_6H_{14}) is 68.7°C.

EVAPORATION

Evaporation

The spontaneous change of a liquid into its vapours is called evaporation and it continues at all temperatures.

Example: $H_2O_{(l)} \longrightarrow H_2O_{(g)}$ $\Delta H_v = 40.7\,kJ\,mol^{-1}$

Characteristics	Factors affecting
• Natural phenomenon • Cooling process • Continued at all temperature • Endothermic process • Surface phenomenon	• Surface area of the liquid • Nature of the liquid ▸ Size of the molecules ▸ Shape of the molecules ▸ Intermolecular forces • Temperature • External pressure

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POINT TO PONDER

- At equilibrium, the rate of evaporation equals the rate of condensation.
- Evaporation is surface phenomenon while boiling is the property of the bulk of liquid.
- The maximum vapour pressure developed by a liquid is its saturated vapour pressure at that temperature.

VAPOUR PRESSURE

Vapour Pressure

The pressure exerted by the vapours of a liquid in equilibrium with its liquid at a given temperature is called vapour pressure.

Factors affecting vapour pressure

- Nature of the liquid
  - ▸ Size of the molecules
  - ▸ Shape of the molecules
- Intermolecular forces

POINT TO PONDER

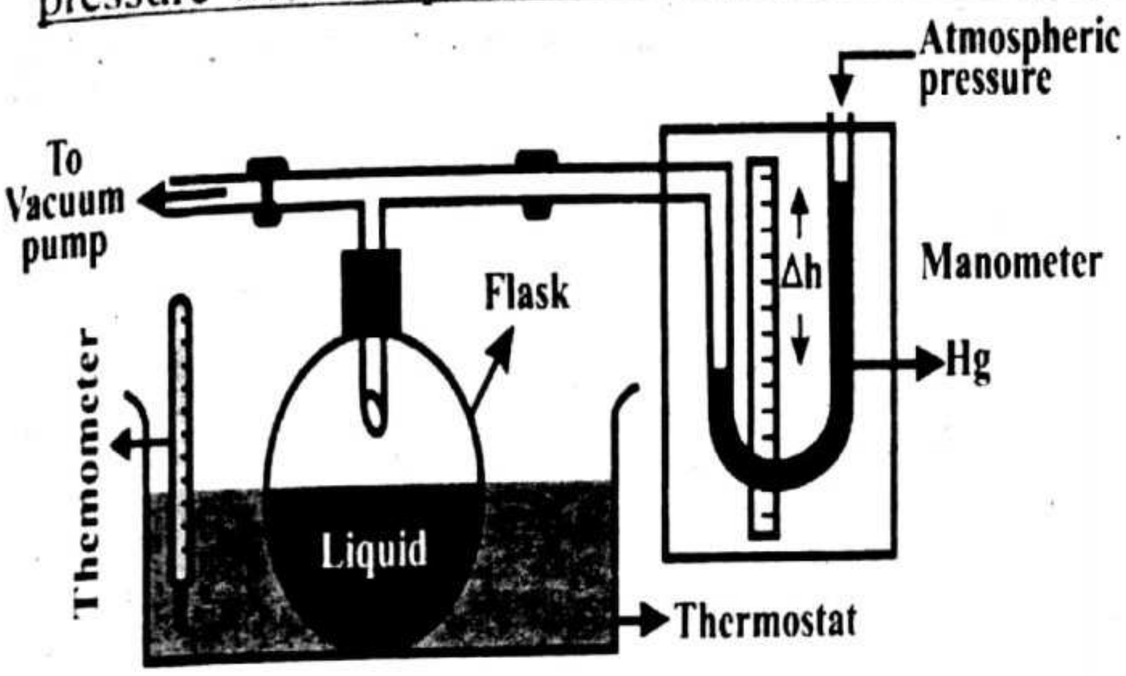
Barometer
A device for measuring the pressure of the atmosphere.

Manometer
A device for measuring pressure of a gas or a liquid in vessel.

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- Due to weaker intermolecular forces, at 20°C vapour pressure of isopentane is more (580 torr) than glycerol (0.00016 torr)
- External pressure

NOTE: Vapour pressure of water is 4.579 torr at 0°C. The rate of change of a vapour pressure with temperature can be calculated by Clausius Clapeyron equation.



Name of compound	Vapour pressure at 20°C (torr)
Isopentane	580
Ethyl ether	442.2
Chloroform	170
Carbon Tetrachloride	87
Water	17.54
Mercury	0.012
Glycerol	0.00016

Measurement of vapour pressure

- Mano-meter is used to measure vapour pressure
- Thermostat is a system whose temperature can be control by means of knob.
- Vacuum is created by vacuum pump
- Liquid is frozen and then melted, so that air can be removed

$$P = P_a + \Delta h$$

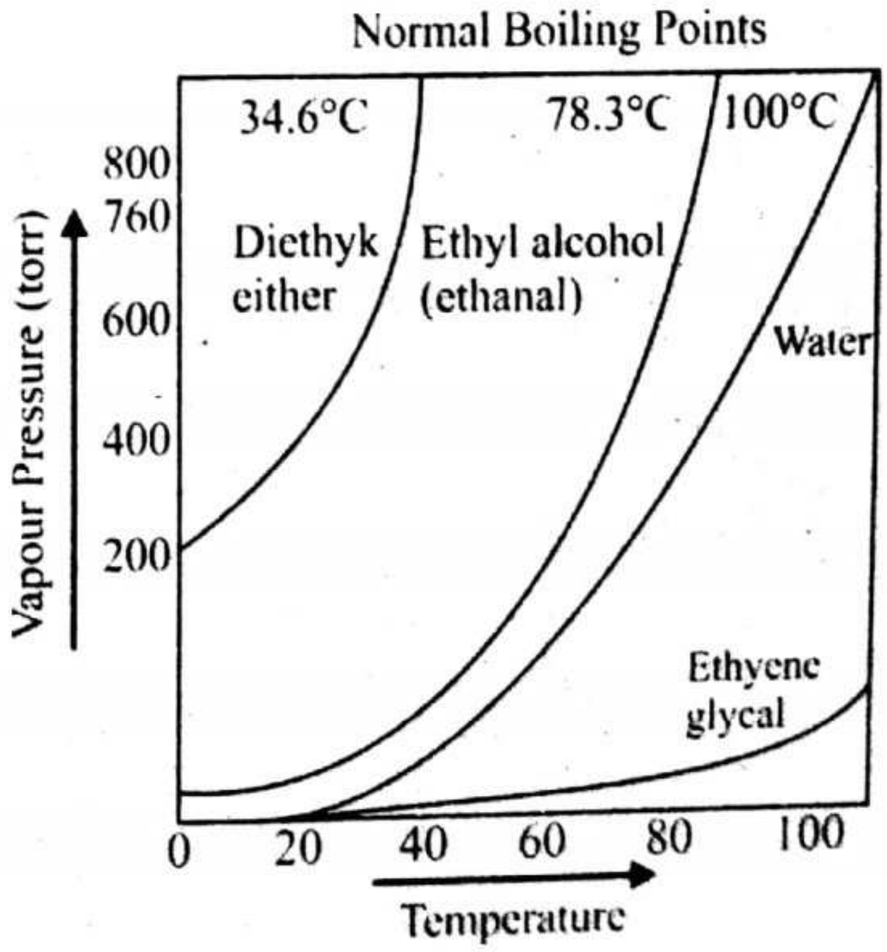
BOILING POINT

Boiling Point

The temperature at which the vapour pressure of the liquid becomes equal to external pressure is called boiling point.

Boiling point depends upon external pressure.

No.	External Pressure	Boiling Point of H_2O
(1)	1489 torr	120°C
(2)	700 torr	98°C (Murree Hills)
(3)	323 torr	69°C (Mount Everest)
(4)	23.7 torr	25°C



- Vapour pressure temperature curve shows that vapour pressure increases rapidly when the liquids are closer to their boiling points.

Factor affecting the boiling points:

Boiling points of liquids depend upon the following factors.

- Intermolecular forces
- External pressure

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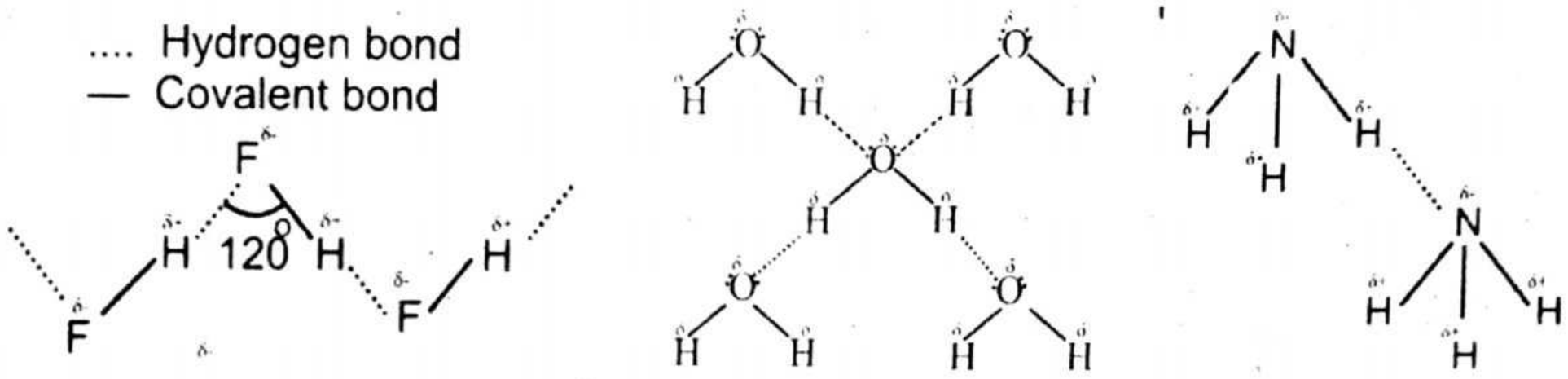
(i) Intermolecular forces:

Stronger the intermolecular forces. greater will be the boiling point and vice versa. Greater amount of heat will be required to

- Over-come strong intermolecular attractions
- Equalize vapour pressure with external pressure. Hence, boiling point will be high.

HYDROGEN BONDING

Hydrogen bonding is the electrostatic force of attraction between a highly electronegative atom and partial positively charged hydrogen atom.



HF **H_2O** **NH_3**

POINT TO PONDER

- Exceptionally low acidic strength of HF molecule as compared to HCl, HBr and HI is due to strong hydrogen bonding.
- Ammonia and hydrogen fluoride can form only one hydrogen bond due to presence of only one utilizable lone pair of electrons and one utilizable H-atom respectively.
- Water can form two hydrogen bonds as it has two utilizable hydrogen atoms and two utilizable lone pairs on oxygen atom.
- The strength of hydrogen bond is generally twenty times less than that of a covalent bond.

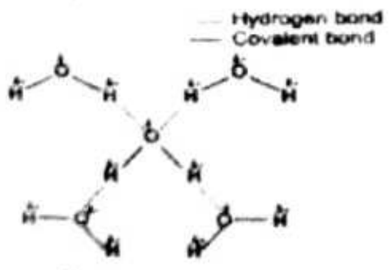
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A comparison of inter-molecular forces

Forces	Strength	Characteristics
Ion –dipole	Moderate (10-50kJ/mol)	Occurs between ions and polar solvents
Dipole-dipole	Weak (3-4kJ/mol)	Occurs between polar molecules
London dispersion	Weak (1-10kJ/mol)	Occurs between all molecules
Hydrogen bond	Moderate (10-40kJ/mol)	H and N or O or F usually

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Properties of compounds containing hydrogen bond

Property	Description
Thermodynamic properties of covalent hydrides	▸ Greater the E.N difference, stronger will be hydrogen bond. Compounds with such condition have higher B.P than those molecules, which does not have such property. ▸ In HF and H_2O, more E.N difference is between H and F than H and O, but water has high B.P than HF, it is due to greater number of H-bonds between water than in HF.
Application in biological compounds	**Fiber proteins** Fiber proteins consist of large chains of amino acids and these chains are coiled about one another into a spiral. This spiral is called **Helix**. Such a helix may either be right handed or left handed (α-helix and β-helix). In both cases >NH and >CO adjacent to one another are linked together by H-bond. **DNA** Deoxyribonucleic acid (DNA) has two spiral chains. These are coiled about each other and are linked together by H-bond between the nitrogenous bases i.e. A=T and G≡C and give rise to double helical structure. **Food Material** The food materials like carbohydrates e.g. glucose, fructose and sucrose have –OH groups which are responsible for the H-bond in them.
Clothing	Hydrogen bonding is involved in thread.
Solubility	▸ Compound with hydrogen bond is soluble in compound having hydrogen bond e.g. H_2O and C_2H_5OH are soluble with each other.
Cleansing action	▸ Soaps and detergents perform the cleansing action because the polar part of their molecules are water soluble due to hydrogen-bonding and the non-polar parts remain outside water, because they are alkyl or benzyl portions and are insoluble in water.
Hydrogen bonds in paints and dyes	▸ The adhesive property of paints and other dyes like glue etc. is due to hydrogen bond.
Structure of ice  Hydrogen bonding in water	▸ In ice, the oxygen atom of water molecule is surrounded by four H-atoms. The two H atoms are linked through covalent bond while the other two H-atoms are linked through H-bond. This is extended throughout creating the empty spaces in the structure. That is why when water freezes it occupies 9% more space and its density decreases. That's why ice floats on the surface of water.

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Factors affecting molar heats

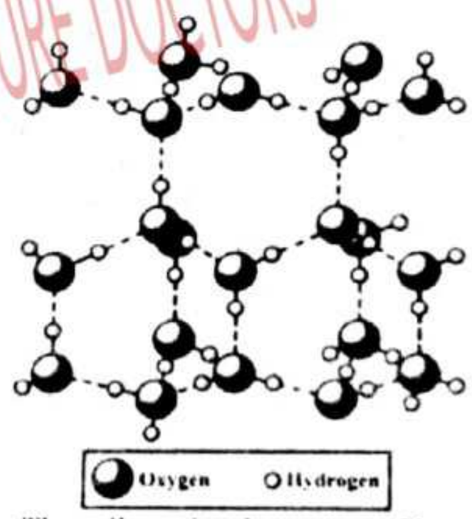
Nature of material	Polar liquids have high ΔH_v molar heat of vaporization than non-polar. Polar solids have high ΔH_f molar heat of fusion than non-polar.
Size of molecule	Larger the size of molecules, greater will be ΔH_v

Anomalous Behavior of Water (Structure of Ice)

- In ice, the oxygen atom of water molecule is surrounded by four H-atoms.
- The two H atoms are linked through covalent bond while the other two H-atoms are linked through H-bond.
- This is extended throughout creating the empty spaces in the structure.
- That is why when water freezes it occupies 9% more space and its density decreases.
- That's why ice floats on the surface of water.
- The lower density of ice than liquid water at 0°C causes water in ponds and lakes to freeze form surface to bottom.
- Water has maximum density 4°C.



A hexagon in the structure of ice



Three dimensional structure of ice

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TOPIC-5 SOLIDS

COURSE CONTENTS

- Introduction
- Types of solids
- Crystalline solids
- Properties of crystalline solids
- Crystal lattice
- Unit cell
- Crystal and their classification
- Classification of solids

  (i) Ionic solids

  (ii) Molecular solids

  (iii) Covalent solids

  (iv) Metallic solids

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TYPES OF SOLID

Name	Details
Crystalline solids	▪ Molecules, ions or atoms arranged in specific three-dimensional pattern e.g. NaCl, KCl, sucrose, I_2 and ice etc.
Amorphous solids (Pseudo solids)	▪ Molecules, ions or atoms do not have regular order of arrangement e.g. rubber, glue, glass etc.

PROPERTIES OF CRYSTALLINE SOLIDS

Property	Description
Geometric shape	Have definite geometry and shape.
Melting Point	Sharp melting points.
Cleavage planes	Whenever the crystalline solids are broken they do so along definite planes. These planes are called the **cleavage planes**.
Anisotropy	▪ The property which depends upon the direction of crystal. ▪ Anisotropic properties: **(i)** Refractive index **(ii)** Co-efficient of thermal expansion **(iii)** Electrical conductivities **(iv)** Thermal conductivities **(v)** Cleavage of crystalline solids
Symmetry	▪ The repetition of faces, angles and edges when a solid is rotated by 360° along its axis is called **symmetry**. ▪ There are many types of symmetry elements: - ➢ Centre of symmetry ➢ Plane of symmetry ➢ Axis of symmetry
Habit of a crystal	▪ The shape of crystal in which it usually grows is called **habit of a crystal**.
Isomorphism	▪ The phenomenon in which two different compounds exist in the same crystalline form is called **isomorphism**. ▪ Many solids show isomorphism e.g. $NaNO_3$ and KNO_3 exhibit rhombohedral crystalline form.
Polymorphism	▪ The phenomenon in which one compound contains more than one crystalline forms is called **polymorphism**. ▪ e.g. $AgNO_3$ exists in Rhombohedral and orthorhombic from. ▪ Compounds exhibit this phenomenon.
Allotropy	▪ The phenomenon in which an element exists in more than one crystalline form is called **allotropy**. ▪ Carbon exists as graphite, diamond and Bucky balls. ▪ Elements exhibit this phenomenon.
Transition temperature	It is that temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other. ▪ Above and below this temperature only one form exists. Grey tin (cubic) $\underset{}{\overset{13.2^{\circ}C}{\rightleftharpoons}}$ White tin (tetragonal)

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LATTICE STRUCTURE OF CRYSTALLINE SOLIDS

Definition:

"An array of points representing the arrangement of particles (atoms, ions or molecules) in three dimensional spaces is called crystal lattice".

The regular arrangement of the particles of a crystalline solid at the microscopic level produces characteristic shapes of crystals.

Lattice:

"The position of the particles in a crystalline solid is represented by a Lattice"

It represents the structure of any substance. A lattice is of three types:

(i) Three-dimensional lattice
(ii) Two-dimensional lattice
(iii) One dimensional lattice

Structure of a crystal:

External structure of crystal:

The external shape of a crystal depends upon the conditions of crystallization. It may be different in one form or the other e.g., NaCl is cubic at ordinary conditions but octahedral in the presence of urea as impurity.

Internal structure of crystal:

The internal structure is the same with basic structural unit, although the conditions for crystallization are different. This unit describes the pattern by which the particles are arranged in a crystal.

Factors:

Primarily a crystal depends upon,

(i) Shape of the unit cell
(ii) Contents of the unit cell

The atoms, molecules or ions in a crystal are repeated in a systematic manner.

Unit cell:

"The smallest unit of volume of a crystal, which shows all the properties of its pattern, is called a unit cell".

This is a basic structural unit of a crystal. It represents the structure of any substance. It has six parameters called cell dimensions or crystallographic elements i.e. three unit cell lengths a, b, c and three angles α, β, γ.

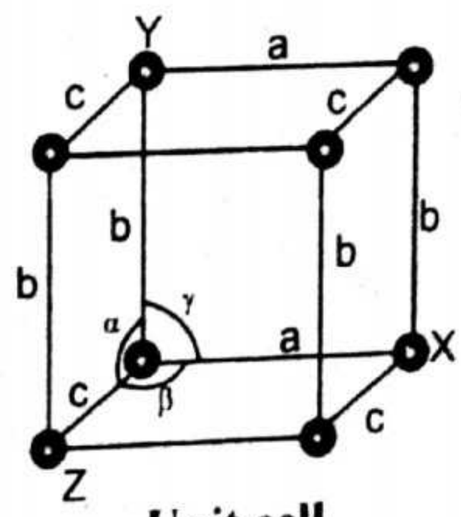
Contribution of cation or anion present at different positioning of cube in a unit cell.

Mid of cube = 1

Face of cube = $\frac{1}{2}$

Edge of cube = $\frac{1}{4}$

Corner of cube = $\frac{1}{8}$



Unit cell

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CLASSIFICATION OF SOLIDS

Ionic Solid

Definition:

Those solids in which ions are held together by electrostatic forces / ionic bonds are called the ionic solids.

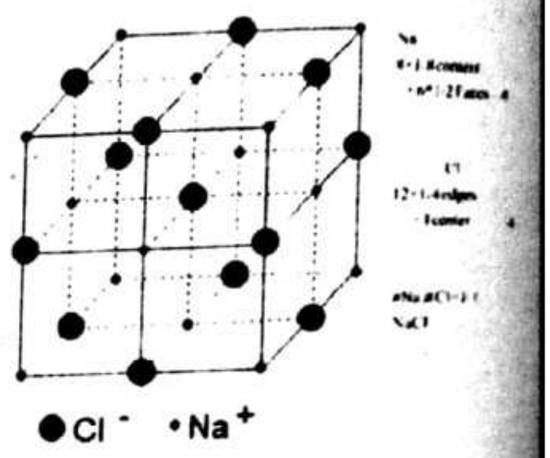
Properties of ionic solid

- The arrangement of ions in ionic solids is three-dimensional.
- They have high melting and boiling points and are non-volatile.
- The structure of an ionic crystal depends upon the radius ratio of cations and anions.
- They are non-conductors in solid state but they are conductors in molten state or solution form because in these forms, ions are free to move to conduct electricity.
- They are soluble in polar solvents and insoluble in non-polar solvents.

Structure of Sodium Chloride

Independent molecules of NaCl do not exist **in vapour phase** as well as in solid state. That is why NaCl is said formula unit of sodium chloride.

Sodium chloride has giant ionic structure



Co-ordination Number

The number of ions of same kind that surround an oppositely charged ion is called co-ordination number.

In NaCl, each Na^+ ion surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions.

So, **co-ordination number of NaCl is 6.**

Co-ordination No. of Na^+ is 6

Co-ordination No. of Cl^- is 6

POINT TO PONDER

The number of anions that can surround one cation is called coordination number

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Number of formula units per unit cell

The unit cells that share one Cl^- ion at one corner = 8

A unit cell gets a share of one Cl^- ion at one corner = $\frac{1}{8}$

A unit cell gets a total share of Cl^- ion at eight corners = $8 \times \frac{1}{8} = 1$

A unit cell gets a share of one Cl^- ion at one face = $\frac{1}{2}$

A unit cell gets a total share of Cl^- ions at six faces = $6 \times \frac{1}{2} = 3$

So, a unit cell gets a total number of Cl^- ions = $4Cl^-$

Similarly, there are four Na^+ ions in a unit cell. Hence, there are four formula units (4NaCl) of NaCl in a unit cell.

The Factors that affect the shape of an ionic solid

There are three factors which affect the shape of an ionic crystal.

- Electrostatic Forces of Attractions:
- Radius ratio
- Poor conductivity

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Electrostatic force of attractions

The ionic solids are composed of cations and anions. They are held together through strong electrostatic forces of attraction forming a well-defined geometric shape e.g. formation of NaCl. Sodium loses one electron and converted into Na^{+1} ions.

$$\underset{(2,8,1)}{Na} - 1e^{-1} \longrightarrow \underset{(2,8)}{Na^{+1}} \qquad \text{(A cation is formed)}$$

$$\underset{(2,8,7)}{Cl} + 1e^{-} \longrightarrow \underset{(2,8,8)}{Cl^{-1}} \qquad \text{(An anion is formed)}$$

These ions combine together due to strong electrostatic force.

$$Na^{+1} + Cl^{-1} \longrightarrow NaCl \qquad \Delta H = -787\ kJmol^{-1}$$

It is an exothermic reaction. To form a crystal lattice of NaCl, each Na^{+1} ion is surrounded by 6 Cl^{-1} ions and each Cl^{-1} ion is surrounded by 6 Na^{+1} ions. As a result a cubic structure of ionic solid of NaCl is formed.

(i) Radius Ratio:

The structure and shape of an ionic solid depends upon the radius ratio of cations and anions e.g. NaCl and CsF have the different geometry because the radius ratio is different in both the cases.

$$\text{Radius Ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}}$$

Thus knowledge of radius ratio consisting of cations and anions can give a good idea of the shape of crystal. And ionic compound with radius ratio greater than 0.732 will have cubic structure e.g. NaCl.

The radius ratio of an ionic compound with octahedral structure should be in between 0.414 and 0.732. Similarly, a tetrahedral structure is formed if the radius ratio is in between 0.22 to 0.414.

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The Radius Ratio of the following ionic crystals are:

1. NaCl = 0.522 — Octahedral arrangement or cubic structure.
2. CsCl = 0.93 — Body centred cubic arrangement.
3. ZnS = 0.40 — Tetrahedral arrangement.

The structure and Limiting radius ratio of certain crystalline substances are given below:

No.	Shape of ionic solid	Limiting Radius Radio r^+ / r^-
1.	Body centered cubic	0.732 and above
2.	Octahedral	0.414 to 0.732
3.	Tetrahedral	0.22 to 0.414
4.	Triangular	0.15 to 0.22

(ii) Poor Conductivity:

Ionic compounds do not have free ions to conduct electricity in solid state because ions are fixed at their positions. They conduct electricity in molten state or in aqueous solution when the ions are free to move.

In aqueous solution, the crystal lattice is broken into cation and anion because of high dielectric constant of water. Thus the ions are solvated.

$$NaCl_{(s)} \xrightarrow{\text{Water}} Na^{+1}_{(aq)} + Cl^{-1}_{(aq)}$$

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Lattice Energy

The lattice energy can be defined in two ways.

"The amount of energy released when gaseous ions of opposite charges combine to give one mole of a crystalline ionic compound is called lattice energy".

$$Na^{+1}_{(g)} + Cl^{-1}_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H = -787\ kJmol^{-1}$$

"The amount of energy required to break one mole crystal lattice into its gaseous ions is called lattice energy".

$$NaCl_{(s)} \longrightarrow Na^{+1}_{(g)} + Cl^{-1}_{(g)} \qquad \Delta H = +787\ kJmol^{-1}$$

Factors:

There are two factors which affect the lattice energy.

Size of ion (cation or anion):

Lattice energy decreases with the increase in the size of the ions (whether cations or anions), the packing of oppositely charged ions become less and less tight.

Charge of ion (cation or anion):

Lattice energy increases with increasing ionic charge. Increase in charge also increases the electrostatic force of attraction therefore lattice energy also increases.

Ionic compound	Lattice energy (kJ mol)
LiCl	–833
NaF	–895
NaCl	–787
KCl	–690
NaBr	–728
KBr	–665
NaI	–690

Molecular Solids

The solids in which polar or non-polar molecules are held together by Van der Waal's forces (London forces) or Dipole-dipole forces (Hydrogen bonding) are called **molecular solids.**

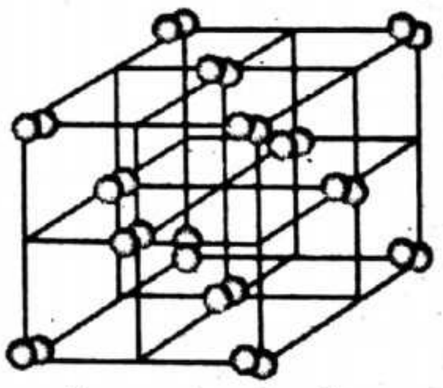
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Properties of molecular solids

- They are soft and easily compressible.
- They are mostly volatile and have low melting and boiling points
- They are bad conductors of electricity.

Structure of Iodine

- Iodine is a molecular solid.
- In the solid state, the molecules of iodine align in the form of layer lattice.
- I-I bond distance is 271.5 pm and it is appreciably longer than in gaseous iodine (266.6pm).
- Iodine is a poor conductor of electricity. Lattice points are occupied by I_2 molecules.
- It has face centered cubic structure.



Face centered cubic structure of iodine

COVALENT SOLIDS

Those solids in which neutral atoms (similar or different) are held together by covalent bonds to form covalent lattice or atomic solids.

Example:

Diamond, graphite, Silicon carbide (SiC), Aluminium nitride (AlN) etc.

Types:

(i) Giant covalent solids

Example: Diamond, SiC, AlN

(ii) Layered covalent solids

Example: Graphite, BN, CdI_2

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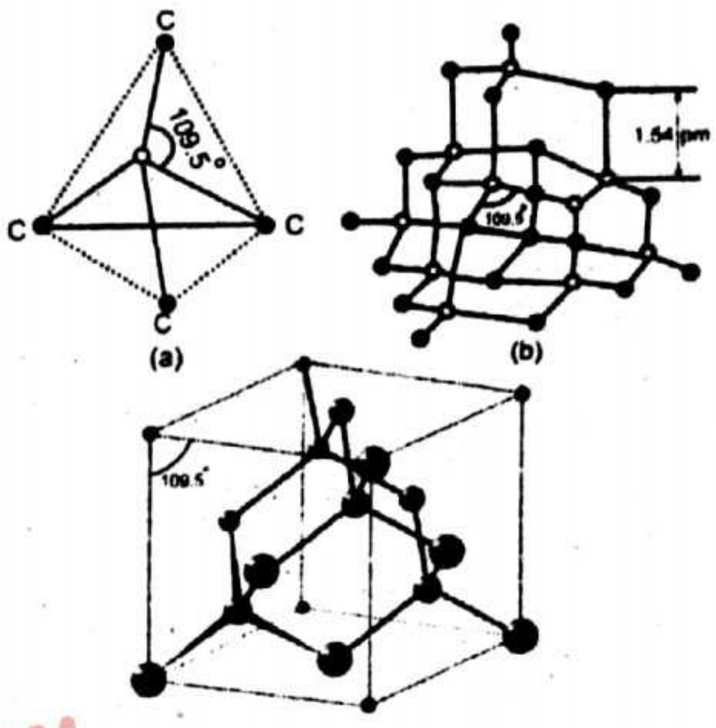
Properties of covalent solids

- Covalent crystals are extended in three dimensions. They contain a network of atoms.
- They have high melting and their volatility is very low.
- They are mostly **insoluble in polar solvents** like water but are readily **soluble in non-polar solvents** like benzene, carbon tetrachloride.

Structure of Giant Covalent Solids

Structure of diamond:

- In the structure of diamond, each carbon atom is linked with four other carbon atoms through covalent bonds which run through the crystals in three-dimensions. carbon has 4 valence electrons.
- The four atomic orbitals (one 2s and three 2p) undergo sp^3 hybridization to give four sp^3 hybridized orbitals.
- All the bond angles are 109.5° and the bond lengths are 154 pm. The whole lattice is the continuous because of C — C covalent bonding.
- The entire diamond crystal behaves as a huge giant three-dimensional carbon molecule. It is also called a macromolecule.
- It has no free electrons, so it does not conduct electricity. Each carbon atom in diamond has all the four valence electrons tightly bound in covalent bonds. Hence, are not available to conduct electricity.



METALLIC SOLIDS

Theories of metallic bonding

(a) Electron pool or electron gas theory.

This theory was proposed by Drude and extended by Loren in 1923.

According to this theory, each atom in a metal crystal loses all of its valence electrons. These valence electrons form a pool or a gas. The positively charged metal ions are believed to be held together by electron pool or gas.

(b) Valence bond theory

This theory was presented by L. Pauling.

According to his theory, the metallic bond is treated essentially as covalent in character.

(c) Molecular orbital theory Or band theory

According to this theory, it is assumed that the electrons in the completely filled orbitals are essentially localized, while atomic orbitals containing the valence electrons interact or overlap to form a set of delocalized orbitals. These delocalized orbitals are the molecular orbitals which extend over the entire crystal lattice. Such a combination of atomic orbitals produces a large number of closely spaced states. These states of energy are also known as bands of energy.

Structure of Metals

In the metals the atoms are packed together in the form of layers to fill the spaces completely as much as possible. This packing is of two types based on the arrangement of the third layer of atoms.

- Hexagonal Close Packing
- Cubic Close Packing

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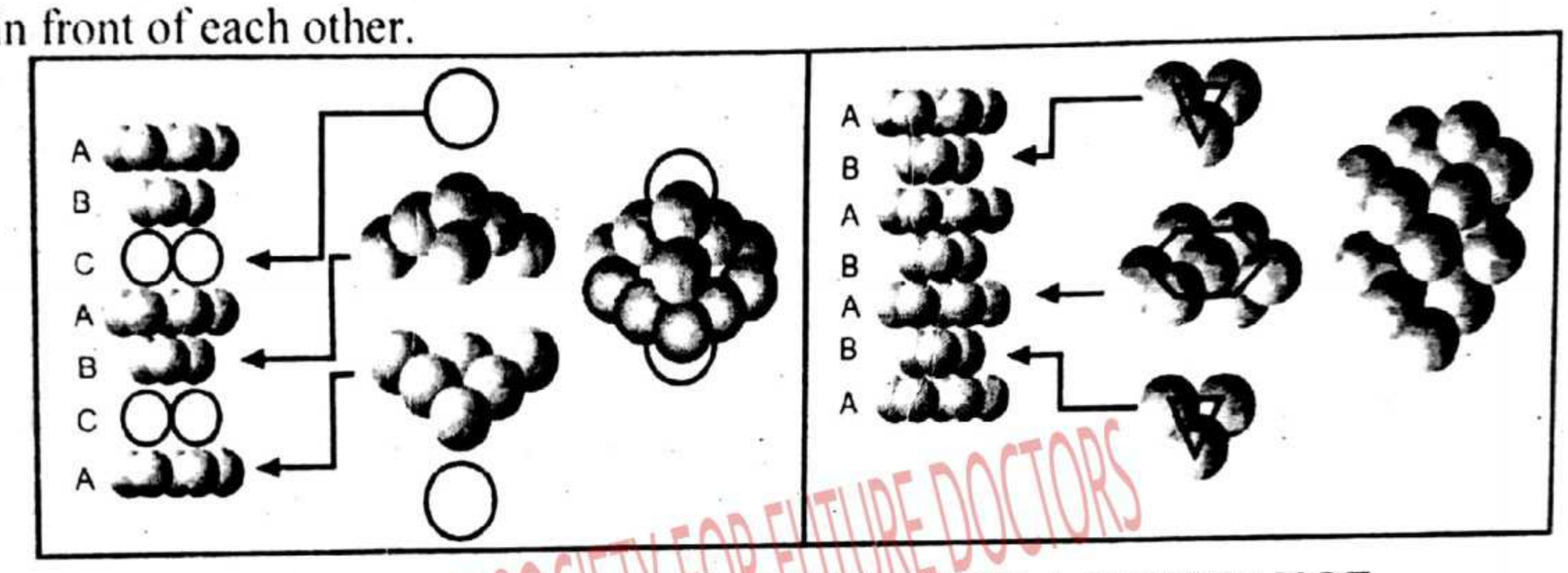
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Cubic close packing (ABC, ABC or123,123)

When the atoms of the third layer fit into the interstices marked **b,** then the atoms of the third layer will not lie directly above
those of the atoms of first layer. This pattern of arrangement is called ABC ABC ..... Or 123 123..... It is named as face centered cubic arrangement. The balls of fourth, seventh and tenth layers will be in front of each other.

Hexagonal close packing (AB, AB or 12,12)

When the atoms of the third layer are arranged in such a way that they occupy the depressions created by the second layer. Then these atoms will directly lie above the atoms of first layer.
It is written as ABAB..... or 1212. The balls of third, fifth and seventh layers will be in front of each other.



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TYPE OF STRUCTURE AND BONDING PRESENT IN A SUBSTANCE

Type of Solid	Structural	Intermolecular Forces	Typical Properties	Examples
Metallic	cations plus delocalized electrons	metallic bonds	hardness varies from soft to very hard; melting points varied from low to very high; lustrous; ductile; malleable; very good conductors of heat and electricity	Na, Mg, Al Fe, Zn, Cu, Ag, W
Ionic	cations and anions	electrostatic attractions	hard; moderate to very high melting points; nonconductors of electricity (but good electrical conductors in the molten state)	NaCl, $NaNO_3$, MgO
Molecular	molecules (atoms of noble gases)	London or dipole-dipole or hydrogen bonds	soft; low melting points; nonconductors of heat and electricity; sublime easily in many cases	Noble gas elements, CH_4,CO_2,P_4 S_8,I_2,H_2O
Covalent network	atoms	covalent bonds	very hard; very high melting points; nonconductors of electricity	C(diamond), SiC,SiO_2

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TOPIC-6 CHEMICAL EQUILIBRIUM

COURSE CONTENTS

- Reversible and irreversible reactions
- State of chemical equilibrium
- Equilibrium constant expression for important reactions
- Applications of equilibrium constant
- The Le-Chatelier's principle
- Applications of chemical equilibrium in industry
- Synthesis of ammonia by Haber's process
- Qualitatively the differences in behavior of strong / weak acids and bases Ka, pKa, Kb, pKb, Kw
- $[H^+_{(aq)}]$, $[OH^-_{(aq)}]$, pH and pOH values for strong and weak acids and bases
- Common ion effect
- Buffer solution
- Equilibria of slightly soluble ionic compounds (Solubility product)

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INTRODUCTION

Rate of chemical reaction

The change in the molar concentration of the reactants or products per unit time is called rate of chemical reaction.

Its units are $mol.dm^{-3}s^{-1}$.

Chemical equilibrium

An apparent state of rest in a reversible chemical reaction where the rate of forward chemical reaction becomes equal to the rate of reverse reaction is called chemical equilibrium.

Characteristics of Chemical Equilibrium:

- It is established only in close system
- It can be established from either side
- It is a macroscopic property.
- It is a dynamic state because reaction is not stationary rather moving in both directions.

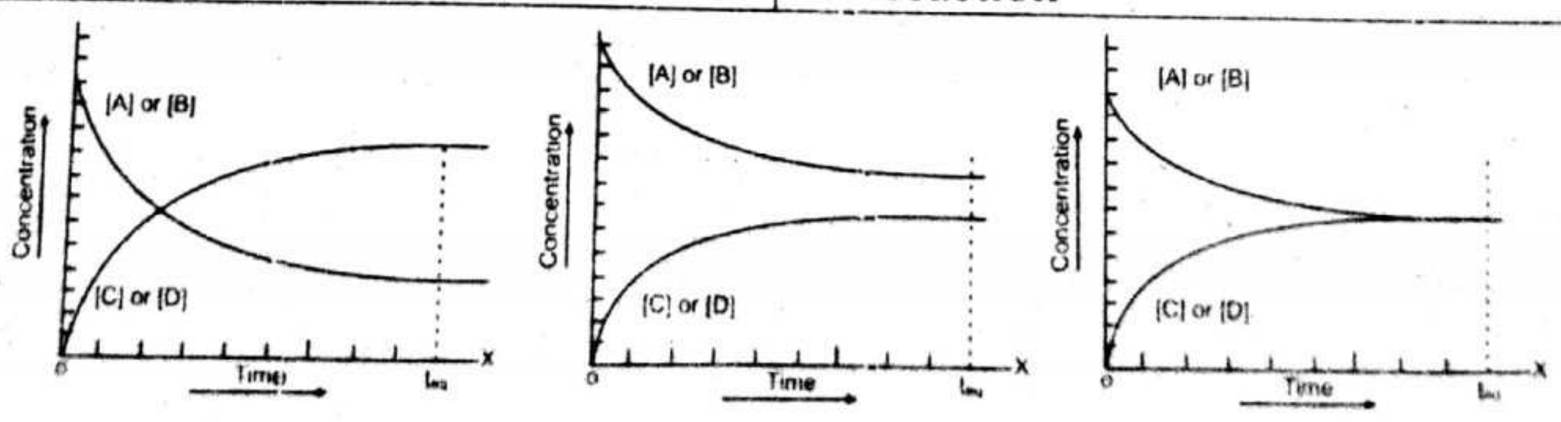
RATES OF FORWARD AND REVERSE REACTIONS AND DYNAMIC EQUILIBRIUM

Reversible Reactions	Irreversible Reactions
Proceed in both directions i.e., forward and reverse	Proceed in one direction i.e., forward.
Reaction does not go to completion.	Reaction goes to completion usually.
represented by $(\rightleftharpoons)$	represented by $(\rightarrow)$
Dynamic equilibrium state is present	Dynamic equilibrium state is absent.
Examples $N_2 + 3H_2 \overset{Fe/450^{\circ}C}{\rightleftharpoons} 2NH_3$ $PCl_5 \overset{High\ Presssure}{\rightleftharpoons} PCl_3 + Cl_2$	**Examples** $2Na + 2H_2O \longrightarrow 2NaOH + H_2$ $2H_2 + O_2 \longrightarrow 2H_2O$

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Types of Equilibria

Homogeneous Equilibrium	Heterogeneous equilibrium
A chemical equilibrium in which the reactants and products are in the same phase is called a homogeneous equilibrium e.g. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$	A chemical equilibrium in which the reactants and products are present in different phases is called a heterogeneous equilibrium e.g. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
Static Equilibria	**Dynamic Equilibria**
○ Conc. of reactant and products are constant ○ Rate of reaction is zero	○ Conc. of reactant and products are constant ○ Rate of reaction is not zero ○ Rate of forward reaction = rate of reverse reaction



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Law of Mass Action

C.M Guldberg and P.Waage introduced this law in 1864.

Statement

It states that the rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants or their molar concentration.

POINT TO PONDER

Active mass means the concentration in mole dm^{-3} of the reactants which alter as a result of chemical reaction.

Explanation

Consider a general reaction in which A and B are the reactants and C and D are the products.

$$A + B \underset{K_r}{\overset{K_f}{\rightleftharpoons}} C + D$$

$$R_f \propto [A][B]$$

$$R_f = k_f [A][B]$$

$$R_r \propto [C][D]$$

$$R_r = k_r [C][D]$$

At equilibrium state

$$R_f = R_r$$

$$k_f [A][B] = k_r [C][D]$$

On rearranging, we get

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

$$\frac{k_f}{k_r} = K_c$$

$$K_c = \frac{[C][D]}{[A][B]}$$

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The constant K_c is called the equilibrium constant of the reaction.

For a more general reaction

$$aA + bB \underset{K_r}{\overset{K_f}{\rightleftharpoons}} cC + dD, \quad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

What is K_c

The ratio of the product of the concentrations of the products to the product of the concentrations of the reactants is called equilibrium constant (K_c)

EQUILIBRIUM CONSTANT EXPRESSION FOR IMPORTANT REACITON

Reactions	Rate expression		
$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$	$K_c = \frac{x^2}{V(a-x)}$	$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$
$N_2O_4 \rightleftharpoons 2NO_2$	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$	$K_c = \frac{4x^2}{v(a-x)}$	$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}}$
$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$	$K_c = \frac{4x^2V^2}{(a-x)(b-3x)^3}$	$K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}}$
$2SO_2 + O_2 \rightleftharpoons 2SO_3$	$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$	$K_c = \frac{4x^2.V}{(a-2x)^2(b-x)}$	$K_p = \frac{p^2_{SO_3}}{p_{O_2} \times p^2_{SO_2}}$

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Relation between different equilibrium constants

When concentrations are expressed in mole dm^{-3}, then

$$aA + bB \rightleftharpoons cC + dD$$

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

$$K_c = \frac{C_C^c \, C_D^d}{C_A^a \, C_B^b}$$

In case of gases, we use partial pressure and K_c changes to K_p.

$$K_p = \frac{p_C^c \, p_D^d}{p_A^a \, p_B^b}$$

$$K_p = K_c(RT)^{\Delta n}$$

POINT PONDER

$K_p = K_c(RT)^{\Delta n}$

Δn = number of moles of products - number of moles of reactants

R = General gas constant

T = Absolute temperature

When $\Delta n = 0$ then, $K_p = K_c$

Calculation of Value of Equilibrium Constant:

Calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data.

Consider the following gaseous reaction system having partial pressure at equilibrium

$$\underset{100 \text{ torr}}{2HI} \rightleftharpoons \underset{50 \text{ torr}}{H_2} + \underset{50 \text{ torr}}{I_2}$$

Its Kp can be calculated as

$$Kp = P_{H_2} \cdot P_{I_2} / (P_{HI})^2$$
$$= 50 \times 50 / (100)^2$$
$$= 2500 / 10000$$
$$= 0.25$$

Calculating the Quantities Present at Equilibrium:

Calculate the quantities present at equilibrium, given appropriate data

Consider the following reaction

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

When two moles of acetic acid and two moles of ethanol are present at equilibrium, the number of moles of ester formed if Kc is 0.25.

$$Kc = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$0.25 = \frac{(x)(x)}{(2)(2)}$$

$$0.25 \times 4 = x^2$$

$$x = 1$$

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APPLICATIONS OF EQUILIBRIUM CONSTANT (K_c)

(i) Direction of Reaction:

$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

a) If [Products]/[Reactants] $< K_c$ then reaction will proceed (forward)
b) If [Products]/[Reactants] $> K_c$ then reaction will move backward (reverse)
c) If [Products]/[Reactants] $= K_c$ then it means reaction is already at equilibrium.

(ii) Extent of Reaction:

(a) If the value K_c is very large: reaction is almost complete

$$2O_3 \rightleftharpoons 3O_2 \ (K_c = 10^{55} \text{ at } 25°C)$$

(b) If K_c value is small : reaction does not proceed(moves forward) appreciably

$$2HF \rightleftharpoons H_2 + F_2 \ (K_c = 10^{-13} \text{ at } 2000°C)$$

(c) If value of K_c is very small this shows a very little forward reaction.

(iii) The Effect of Conditions on The Position Of Equilibrium:

- K_c is equilibrium constant, it remains constant for a particular reaction at constant temperature
- It can be varied if external conditions like temperature, pressure and concentrations are altered.

NOTE:

If K_c is very small then products will be very much unstable.
If K_c is very large then the products will be very much stable.

THE LE-CHATELIER'S PRINCIPLE

Statement

This principle states that if a stress is applied to a system at equilibrium, the system acts in such a way so as to nullify it, as far as possible.

Applications of Le-Chatelier's principle

Le-Chatelier's principle helps in studying effect of followings on equilibrium position and equilibrium constant

(i) Effect of change of concentration.
(ii) Effect of change of pressure or volume.
(iii) Effect of change of temperature.
(iv) Effect of catalyst on equilibrium.

Effect of change of concentration

- The addition of substance among the reactants, or the removal of a substance among the products at equilibrium stage disturbs the equilibrium position and reaction is shifted to forward direction.
- The addition of a substance among the products or the removal of a substance among the reactants will drive the equilibrium towards the backward direction.

NOTE: The reaction shifts in any direction on the addition of any substance just to keep the value of K_c constant.

Effect of change in pressure or volume

- The change in pressure or volume is important only for the reversible gaseous reactions where the number of moles of reactants and products are not equal.

(i) Theoretical study of effect of change of pressure or volume

The increase of pressure or decrease in volume shifts the reaction in direction of less number of moles and vice versa.

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Examples:

(a) $$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

The increase in pressure shifts the above reaction in forward direction and vice versa.

(b) $$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

The increase in pressure shifts the above reaction in backward direction and vice versa.

(ii) Quantitative study of effect of pressure or volume

(a) If volume term is present in the numerator of K_c expression, then increase in pressure decreases the volume and reaction will shift in forward direction to increase the value of x^2 and to keep the value of K_c constant.

$$K_c = \frac{4x^2V}{(a-2x)^2(b-x)}$$

(b) If volume term is present in the denominator of K_c expression, then increase in pressure decreases the volume and reaction will shift in backward direction to decrease the value of x^2 and to keep the value of K_c constant.

$$K_c = \frac{x^2}{V(a-x)}$$

Effect of change in Temperature

(i) On Endothermic reactions.

- By increasing the temperature, reaction is favoured in forward direction.
- By decreasing the temperature, reaction is favoured in backward direction.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad \Delta H = +ve$$

(ii) On Exothermic reactions.

- *By decreasing the temperature, reaction is favoured in forward direction.*
- *By increasing the temperature, reaction is favoured in backward direction.*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -ve$$

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Effect of catalyst on Equilibrium Constant

A catalyst does not affect the equilibrium position and equilibrium constant of the reaction. It increases the rates of both forward and backward reactions, as it reduces the time to attain the equilibrium.

EFFECT OF CONDITIONS ON EQUILIBRIUM CONSTANT

Conditions	Position of equilibria	Equilibrium constant
Conc.	○ $[R] > [P]$ on reactant side ○ $[R] < [P]$ on product side	No effect
P or V	○ $n_R > n_P$ Pressure is increased → on product side Pressure is decreased → on reactant side	No effect
	○ $n_R < n_P$ Pressure is increased → on reactants side Pressure is decreased → on products side	
Temperature	○ Temperature increase favours endothermic reaction ○ Temperature decrease favours exothermic reaction	○ $T \propto K_c$ for endothermic reaction ○ $T \propto 1/K_c$ for exothermic reaction

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Characteristics of K_c

Factors	Expression
Depends upon	**Temperature.** i) Greater the temperature, greater will be the K_c value for endothermic reactions and vice versa. ii) Greater the temperature, lesser will be the K_c value for exothermic reactions and vice versa.
Independent of	○ Initial concentration of reactants ○ Pressure or volume ○ Direction of reaction ○ Catalyst
Units	○ When number of moles of reactants = number of moles of products, then Kc has no units. ○ When number of moles of reactants ≠ number of moles of products, then K_c has some units and can be calculated by using formula **$K_c = (moles.dm^{-3})^{\Delta n}$ where $\Delta n = n_P - n_R$**

APPLICATIONS OF CHEMICAL EQUILIBRIUM IN INDUSTRY

Particulars	Synthesis of NH_3 by Haber's process	Synthesis of SO_3
Introduction	F. Haber prepared in 1933.	In contact process H_2SO_4 is prepared.
Reaction	$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.46kJ$	$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \Delta H = -194$ kJ
Conditions for maximum production	○ Removal of ammonia after regular intervals. ○ Increase in pressure. ○ Decrease in temperature.	○ Continuous supply of O_2. ○ Increase in pressure. ○ Decrease in temperature.
Catalyst	Pieces of iron crystals are embedded in fused mixture of MgO, Al_2O_3 and SiO_2.	V_2O_5, NO or Pt are used as catalyst.
Favorable conditions	P= 200-300atm T= 673K(400°C)	P= 1atm T= 400-500°C / 650°C.
Others	○ Equilibrium mixture contain 35% NH_3 by volume. ○ Ammonia is separated by refrigeration. ○ 110 million tons ammonia is produced per annum. ○ 80% is used in fertilizer. ○ 13% Nitrogen fixation is done by Haber's process.	

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NOTE:

- Equilibrium mixture contains 35% NH_3 by volume.
- Ammonia is separated by refrigeration of reaction mixture.
- 110 million tons ammonia is produced per anum.
- 80% is used in fertilizer.
- 13% Nitrogen fixation is done by Haber's process.

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QUALITATIVE BEHAVIOUR OF STRONG / WEAK ACIDS AND BASES

Acid:

Those species which donate the proton or have a tendency to donate protons are called acids.

Base:

Those species which accept the proton or have tendency to accept the proton are called bases.

> Conjugate base of a very weak acid is relatively very strong.
> Conjugate acid of a very strong base is relatively very weak.

Example:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

(Acid) (Base) — Conjugate Acid — Conjugate Base

$$K_a \times K_b = [H^+][OH^-]$$

$$K_a \times K_b = K_w = 10^{-14} \text{ at } 25^\circ C$$

$$K_a = K_w \times \frac{1}{K_b}$$

$$K_a \propto \frac{1}{K_b}$$

$$pK_a + pK_b = pK_w \qquad (pK_w = 14, \text{ at } 25^\circ C)$$

$$pK_a + pK_b = 14 \text{ at } 25^\circ C$$

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TERMS: pH, K_a, pK_a K_b, pK_b K_w and K_{sp}

IONIC PRODUCT OF WATER (Kw)

Water undergoes self-ionization as follows and the reaction is reversible.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_c[H_2O] = [H^+][OH^-]$$

$$K_w = [H^+] = [OH^-] = 10^{-14} \text{ at } 25^\circ C$$

K_w is called ionic product of water or dissociation constant of water.

Kw varies with temperature

Temperature (°C)	K_w	ΔT (°C)	Change in K_w
0	0.11×10^{-14}		
10	0.30×10^{-14}	0-10	Increases by 3 times
25	1.0×10^{-14}	0-25	Increases by 10 times
40	3.00×10^{-14}	0-40	Increases by 30 times
100	7.5×10^{-14}	0-100	Increases by 75 times

pK_w:

Negative log of K_w is called pK_w.

$$pK_w = -\log K_w$$

pH

The negative log of hydrogen ion concentration $[H^+]$ is called pH.

$$pH = -\log[H^+]$$

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POINT TO PONDER

K_w is directly related to temperature.
pK_w is inversely related to temperature.
K_w and pK_w are inversely related to each other.

POINT TO PONDER

pH and hydrogen ion concentration $[H^+]$ are inversely related to each other.
pOH and hydroxyl ion concentration $[OH^-]$ are inversely related to each other.

pOH

The negative log of hydroxyl ion Concentration $[OH^-]$ is called pOH.

$$pOH = -\log[OH^-]$$

Conclusion:

For neutral water

$$pH = -\log 10^{-7} = 7$$
$$pOH = -\log 10^{-7} = 7$$
$pH = 7 \rightarrow$ solution is neutral
$pH < 7 \rightarrow$ solution is acidic
$pH > 7 \rightarrow$ solution is basic

NOTE: $pH + pOH = pK_w = 14$ at 25^oC

Ionization Constant of Acids (K_a)

The dissociation constant of an acid is the ratio of the product of molar concentration of the ionized species to the molar concentration of unionized species.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

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- Acid strength $\propto K_a$ value
- Dissociation constant of an acid shows the strength of an acid.
- When $K_a < 10^{-3}$, acid is weak.
- When K_a = 1to 10^{-3}, acid is moderately strong.
- When $K_a > 1$, acid is strong.

$$\text{Percentage of ionization} = \frac{\text{Amount of an acid ionized}}{\text{Acid initially available}} \times 100$$

Dissociation constants of some acids at 25°C

Acid	K_a	Relative strength
HCl	Very large	Very strong
HNO_3	Very large	Very strong
H_2SO_4	Large	Very strong
HSO^-_4	1.3×10^{-4}	Strong
HF	6.7×10^{-5}	Weak
CH_3COOH	1.85×10^{-5}	Weak
$H_2CO_3(H_2O+CO_2)$	4.4×10^{-7}	Weak
H_2S	1.0×10^{-7}	Weak
NH_4^+	5.7×10^{-10}	Weak
HCO^-_3	4.7×10^{-11}	Weak
H_2O	1.8×10^{-16}	Very weak

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Ionization Constant of Bases (K_b)

The substances which have ability to accept proton are called Lowry – Bronsted base. When such substances are dissolved into water then they take hydrogen ions and release hydroxyl ions from water.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

- Base strength $\propto$ K_b value
- Strength of base is expressed by K_b.
- Any substance that accepts H^+ or generates OH^- is a base.
- Dissociation **constants of some bases at 25°c**

Base	K_b	Relative strength
NaOH	Very high	Very strong
KOH	Very high	Very strong
$Ca(OH)_2$	High	Strong
NH_4OH	1.81×10^{-5}	Weak
CH_3NH_2(Methylamine)	4.38×10^{-4}	Weak
$C_6H_5NH_2$ (Aniline)	4.7×10^{-10}	Very weak

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pK_a and pK_b

The value of pK_a and pK_b can be defined and related as follow

$$pK_a = -\log K_a$$

$$pk_b = -\log K_b$$

NOTE: K_a is inversely related to pK_a.

K_b is inversely related to pK_b.

Conclusion

- Greater the value of K_a, stronger will be acid and vice versa.
- Greater the value of pK_a, weaker will be the acid and vice versa.
- Greater the value of K_b, stronger will be base and vice versa.
- Greater the value of pK_b, weaker will be the base and vice versa.

POINT TO PONDER

- If the difference of pK_a values of the two acids is one, then acid with smaller pK_a is ten times stronger than the other.
  $pK_a(I) - pK_a(II) = 1$, acid II is ten times stronger than acid I.
- If the difference of pK_a values of the two acids is two, then acid with smaller pK_a is hundred times stronger than the other.
  $pK_a(I) - pK_a(II) = 2$, acid II is hundred times stronger than acid I.

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[H+], [OH-], pH AND pOH VALUES FOR STRONG AND WEAK ACIDS AND BASES

Calculation $[H^+_{(aq)}]$ and pH values for strong and weak acids and strong bases.

(i) 10^{-4} mol.dm^{-3} of HCl

$$[H^+] = 10^{-4}\ \text{mol.dm}^{-3}$$

$$pH = -\log[H^+]$$

$$= -\log[10^{-4}] = 4$$

(ii) 10^{-4} mol.dm^{-3} of $Ba(OH)_2$

10^{-4}mol.dm^{-3} of $Ba(OH)_2$

0.0001 M $Ba(OH)_2$ solution contains 0.0002 M $OH^- = 2\times10^{-4}$ mol/dm^3

$$pOH = -\log [OH^-]$$

$$pOH = -\log 2 \times 10^{-4}$$

$$pOH = 3.7$$

$$pH = 14-3.7$$

$$pH = 10.3$$

(iii) 1.0 mol.dm^{-3} of H_2X, which is only 50% dissociated.

1 mol.dm^{-3} of H_2X.50% Dissociated means 0.5 mol/dm^3 of H_2X completely dissociated.

$$[H^+] = 1\ \text{mol.dm}^{-3}$$

$$pH = -\log[H^+] = -\log 1$$

$$pH = 0$$

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Calculating the pH of Buffer

Henderson's Equation for Acidic Buffer

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

Other formations of this equation are

$$pH = pKa - \log\frac{[Acid]}{[Salt]}$$

$$pH = pKa - \log\left[\frac{Acid}{Base}\right]$$

$$pH = pKa + \log\frac{[Base]}{[Acid]}$$

Cases:

(i) If [salt] = [acid] then pH = pKa

(ii) If [salt] > [acid] then pH > pKa

(iii) If [salt] < [acid] then pH < pKa

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Henderson's Equation for Basic Buffer

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Cases:

(i) If [salt] = [base] then $pOH = pK_b$

(ii) If [salt] > [base] then $pOH > pK_b$

(iii) If [salt] < [base] then $pOH < pK_b$

COMMON ION EFFECT

The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as precipitates.

Common ion effect increases

(i) Crystallization

(ii) Association of ions

Common ion effect decreases

(i) Ionization / dissociation

(ii) solubility

Applications

(i) Purification of NaCl

$$NaCl \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$HCl \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

(ii) The solubility of a less soluble salt $KClO_3$ in water is suppressed by the addition of a more soluble salt KCl by common ion effect.

$$KClO_{3(S)} \rightleftharpoons K^+_{(aq)} + ClO^-_{3(aq)}$$

$$KCl_{(S)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

(iii) Decrease in dissociation of H_2S

$$H_2S \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$

$$HCl \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

(iv) An addition of NH_4Cl in NH_4OH solution suppresses the concentration of $OH^-_{(aq)}$ due to the presence of a large excess of NH_4^+ from NH_4Cl.

$$NH_4OH_{(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

$$NH_4Cl_{(aq)} \rightleftharpoons NH^+_{4(aq)} + Cl^-_{(aq)}$$

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BUFFER SOLUTIONS

The solutions, which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions.

How Buffer controls the pH?

Buffer action can be explained by keeping in view the concepts of common ion effect and Le-Chatelier's principle.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$CH_3COONa_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

If we go on adding CH_3COONa in CH_3COOH solution, then common ions i.e. CH_3COO^- decreases the ionization of CH_3COOH.

The solution will have less hydrogen ion concentration and high pH value.

If CH_3COOH is in high concentration as compared to CH_3COONa then pH value of solution will be less.

Greater the concentration of acetic acid as compared to CH_3COONa, lesser will be the pH of the solution and vice versa. This is shown in table.

$[CH_3COOH]$(mole dm^{-3})	$[CH_3COO^-]$(mole dm^{-3})	% Dissociation	pH
0.10	0.00	1.3	2.89
0.10	0.05	0.036	4.44
0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

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The buffer mentioned above is the large reservoir of CH_3COOH and CH_3COO^- components.

- Whenever an acid is added to this buffer and 'H^+' concentration increases, at this stage CH_3COO^- reacts to form undissociated CH_3COOH. So, pH of the buffer will remain almost same because 'H^+' ions which are added are captured by CH_3COO^- ion and pH will not vary too much.
- If base is added in this buffer, base will produce OH^- ions which combine with H_3O^+ to form neutral compound i.e H_2O. So, pH will remain almost unchanged.

NOTE: The buffer solution consisting of NH_4Cl and NH_4OH can resist the change in pH and pOH when acid or base is added from outside.

EQUILIBRIA OF SLIGHTLY SOLUBLE IONIC (Solubility Product)

The product of the concentration of ions raised to an exponent equal to the co-efficient of the balanced equation.

General Expression

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

$$K_{sp} = \left[A^{+y}\right]^x \left[B^{-x}\right]^y$$

Applications

- Determination of Ksp from solubility of salts
- Determination of solubility from Ksp
- Prediction of precipitation
- Effect of common ion effect on solubility

POINT TO PONDER

It is only applicable for those substances whose molar concentrations are less than 0.01M

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General Ksp expressions for some salts

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \quad K_{sp} = 1.8\times10^{-10}$$

$$Ksp = [Ag^{+}][Cl^{-}]$$

$$Ksp = s^2$$

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \quad K_{sp} = 1.6\times10^{-5}$$

$$Ksp = [Pb^{2+}][Cl^{-}]^2$$

$$Ksp = 4s^3$$

$$AlCl_{3(s)} \rightleftharpoons Al^{+3}_{(aq)} + 3Cl^{-}_{(aq)}$$

$$Ksp = [Al^{+3}][Cl^{-}]^3$$

$$Ksp = 27s^4$$

Calculate K_{SP} From Concentrations And Vice Versa

(i) The solubility of PbF_2 is 2×10^{-3} moles / dm^3. Its solubility product will be

$$PbF_{2(s)} \longrightarrow Pb^{+2}_{(aq)} + 2F^{-}_{(aq)}$$

$$2\times10^{-3} \qquad 2\times10^{-3} \qquad 2\times2\times10^{-3}$$

$$Ksp = [Pb^{+2}][F^{-}]^2 = [2\times10^{-3}][2\times2\times10^{-3}]^2$$

$$= 32\times10^{-3} = 3.2\times10^{-2}$$

(ii) The solubility product of $Ca(OH)_2$ is 3.6×10^{-8}. Its solubility is

$$Ca(OH)_{2(s)} \longrightarrow Ca^{+2}_{(aq)} + 2OH^{-}_{(aq)}$$

$$s \qquad s \qquad 2s$$

$$Ksp = [Ca^{+2}][F^{-}]^2 = [s][2s]^2$$

$$3.6\times10^{-8} = 4s^3$$

$$s^3 = \frac{3.6\times10^{-8}}{4}$$

$$s = (9\times10^{-9})^{1/3} = 3\times10^{-3}$$

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TOPIC-7 ⟫ REACTION KINETICS

COURSE CONTENTS

- Rate of reaction
- Determination of the rate of a chemical reaction
- Factors affecting rate of reaction
- Specific rate constant or velocity constant
- Units of rate constant
- Order of reaction and its determination
- Explain what is meant by the terms activation energy and activated complex
- Relate the ideas of activation energy and the activated complex to the rate of a reaction

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INTRODUCTION

Reaction kinetics

The studies concerned with rates of chemical reactions and factors that affect the rates of chemical reactions and the mechanism of reactions constitute the subject matter of reaction kinetics

Chemical reactions

The breaking of pre-existing bonds and the formation of new bonds is called chemical change or chemical reaction.

On the basis of rate of reaction, chemical reactions can be broadly classified into three types

(i) Very fast reaction $(AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3)$

(ii) Very slow reaction $(2Fe + 3H_2O + O_2 \longrightarrow Fe_2O_3.\ 3H_2O)$

(iii) Moderately slow reactions $(C_2H_5OH + CH_3COOH \longrightarrow H_3COOC_2H_5 + H_2O)$

RATE OF REACTION

The change in concentration of a reactant or a product divided by the time taken for the change is called rate of reaction.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of the substance}}{\text{Time taken for the change}}$$

$$\text{Rate of reaction} = dx/dt$$

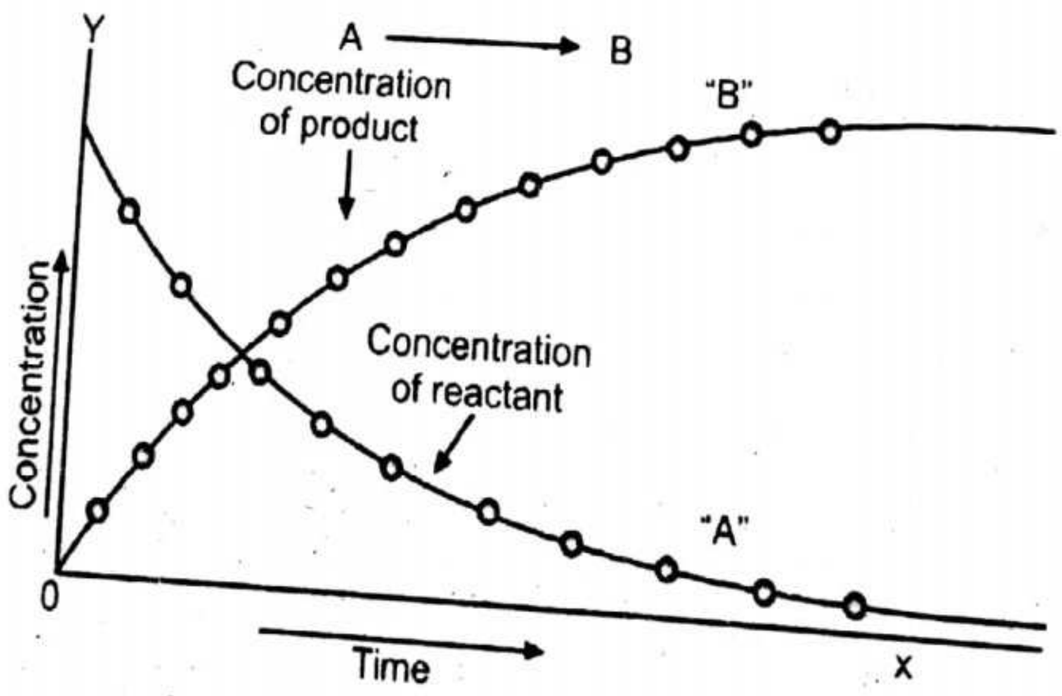
The rate of a general reaction.

$A \longrightarrow B$ can be expressed as

$$\text{Rate of reaction} = \frac{-d[A]}{dt} = \frac{+d[B]}{dt}$$

Units of rate of reaction:

The units for rate of reaction are moles $dm^{-3}s^{-1}$



Example:

For a certain reaction, the concentration of reactant changes from 0.75 mol dm^{-3} to 0.50 mole dm^{-3} in 25 sec then rate of reaction is

$$\text{Rate of reaction} = \frac{\Delta C}{dt} = \frac{0.25}{25} = \frac{1}{100}$$

$$\text{Rate of reaction} = 10^{-2}\ \text{mol}\ dm^{-3}s^{-1}$$

NOTE: For a gas phase reaction, units of pressure are used in place of molar concentration.

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Types of reaction rate

Average rate

The rate of reaction between two specific time intervals is called average rate.

Instantaneous rate

The rate at any one instant during a specific interval of time is called instantaneous rate.

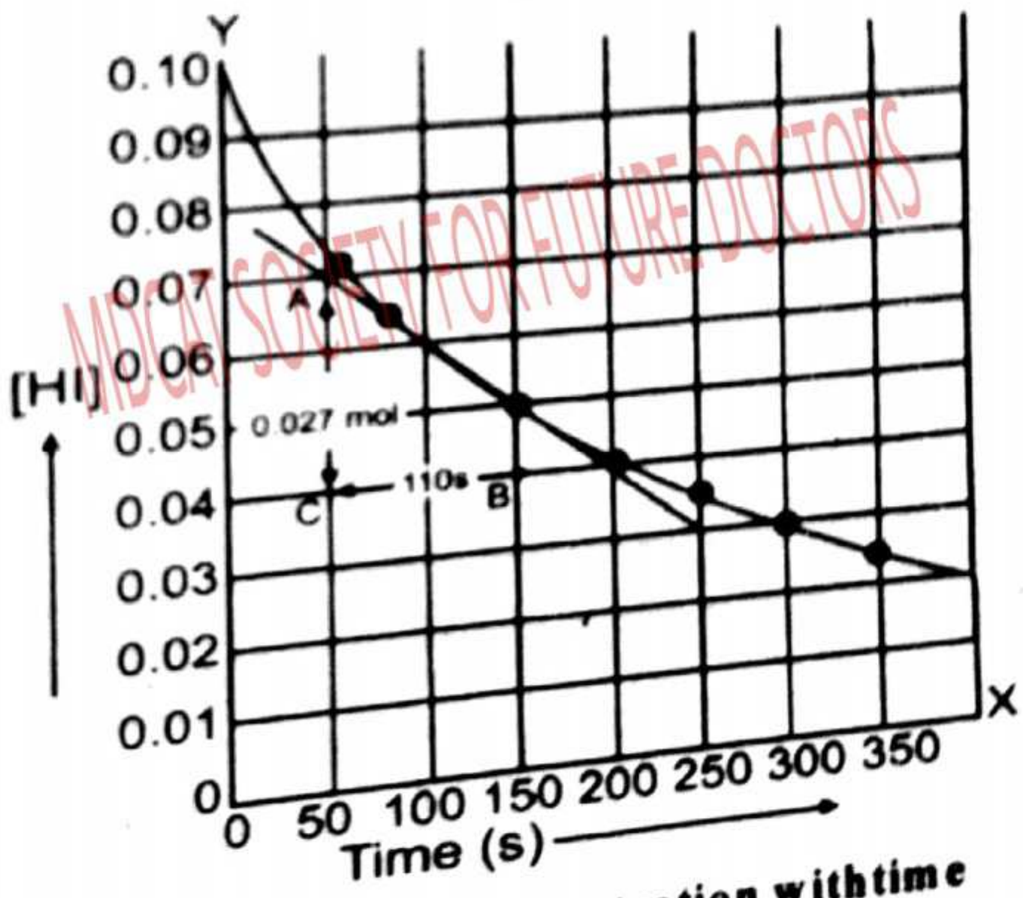
Comparison of instantaneous and average rate:

- The average rate and instantaneous rate are equal for only one instant in any time interval.
- At the beginning of reaction, the instantaneous rate is higher than the average rate.
- At the end of reaction, the instantaneous rate is less than the average rate
- The average rate will be equal to instantaneous rate, when the time interval approaches zero.

DETERMINATION OF RATE OF REACTION

- Determination of rate of reaction involves the measurement of concentration of reactants.
- Graph is plotted between concentration of reactant and time and we get a curve.
- Select any two points in a curve.
- Make a right angle triangle of these points.
- Getting the tanθ of right angle triangle, we shall get

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactant}}{\text{Change in time}}$$



The change in the HI concentration withtime for the reaction $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ at 508° C

$$\text{Rate of reaction} = \frac{\Delta c}{\Delta t} = \frac{0.027}{110} = 2.5 \times 10^{-4}\ mol/dm^3/Sec$$

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Methods for the determination of rate of a chemical reaction

Physical Methods

Techniques	Details
Spectrometry	▸ Spectrophotometer is used. ▸ Reactants and products absorb U.V, I.R radiations ▸ Amount of radiation absorbed give rate of reaction
Electrical conductivity method	▸ Conductometer is used ▸ Conductivity depends on the concentration of ions in the solution. ▸ Conductivity of ions of reactants give rate of reaction
Dilatometric method	▸ It is applied to the reaction in which volume of solution is changed. ▸ Volume change of a reaction is proportional to extent of reaction.
Optical rotation method	▸ Polarimeter is used ▸ Reacting molecules rotates angle of rotation of plane polarized light ▸ Value of angle of rotation gives information about rate of reaction
Refractometric method	▸ Refractometer is used ▸ It is applied to the reaction in which change in refractive indices occurs ▸ Transformation of glucose into alcohol can be analyzed regarding rate of reaction through this method

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Chemical Method

- In chemical method acid based is titration is used to determine the rate of reaction

FACTORS AFFECTING THE RATE OF REACTION	
Name	Details
Nature of reactant	○ More active reactants give fast rate of reaction ○ Number of electrons present in innermost shell affects the reactivity of reactant. ○ Elements of **IA** are more reactive than **IIA.** ○ Neutralization reactions and decomposition reactions are very fast. ○ Oxidation reduction reactions are slower. ○ Ionic reactions are very fast.
Concentration of reactant	○ Reaction is due to effective collision of reactant molecules. ○ Greater concentration of reactants, more effective collisions, thus, rate of reaction will be high. ○ In case of reactants in gases, their concentration is increased by increasing their partial pressures ○ Rate of reaction is directly proportional to concentration of reactants ○ Sometime concentration of reactant become double and rate of reaction increases four times.
Surface area	○ Greater the surface area, greater will be chance of contact of molecules ○ Greater surface area of molecules, greater will be rate of reaction.

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Light	○ Light travel in the form of photons. ○ Photons have energy depending on frequency of light. ○ Light gives the energy to reactants to form activated complex in minimum time. ○ Light increases the rate of reaction.
Temperature	○ By increasing temperature, the number of collisions of molecule increases. ○ Rate of reaction increases by increase in temperature of reaction ○ On increasing temperature by 10K, the rate of reaction becomes doubled. ○ Arrhenius equation: $k=Ae^{-Ea/RT}$ (it gives us the quantitative effect of temperature on rate of reaction.

Arrhenius equation

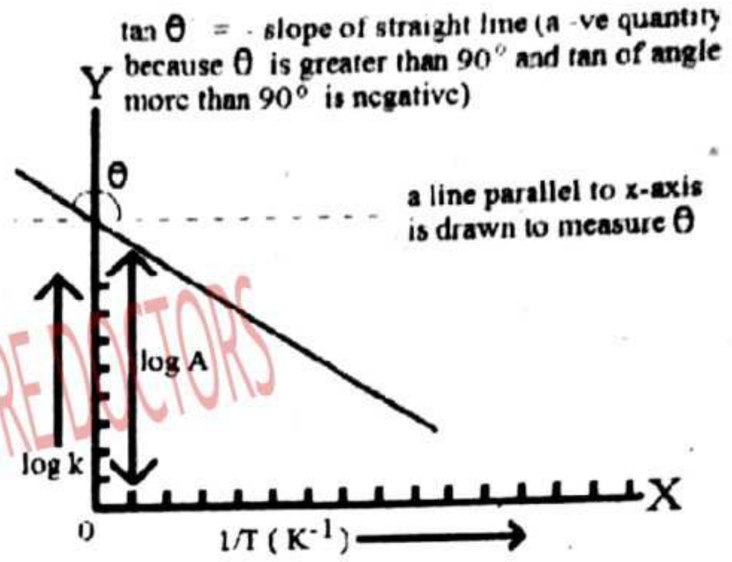
According to Arrhenius Equation

$$k = Ae^{-Ea/RT}$$

In this equation

k = specific rate constant

A = Arrhenius constant



It tells us about collision frequency.

- This equation explains the effect of temperature on the rate constant of reaction.
- k is exponentially related to activation energy and temperature.
- When a graph is plotted between $\frac{1}{T}$ on x-axis and log k on y-axis, a straight line is obtained with a negative slope. Actually, $\frac{E_a}{RT}$ has negative sign so the straight line has two ends in second and fourth quadrants.
- Slope = $\frac{-E_a}{2.303R}$ unit of slope is Kelvin
- This equation helps us to determine activation energy of the reaction.
- E_a = -Slope x 2.303R

Unit of activation energy is Joule mole^{-1}, greater is value of activation energy smaller is k value hence smaller will be the rate

Rate determining step

When the reaction completes in more than one step, then the slowest step will give the overall rate of reaction, thus slowest step of such a reaction is called rate determining step.

Consider the following reaction.

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$

The rate equation of this reaction is found to be:

$$Rate = k[NO_2]^2$$

This equation shows that rate of reaction is independent of the concentration of CO. In other words, the equation gives us information that

(i) Reaction takes place in more than one step i.e the mechanism of this reaction is different than as shown in balanced chemical equation.

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(ii) Two molecules of NO_2 are involved in the rate determining step.
The proposed mechanism for this reaction is as follows.

$$NO_{2(g)} + NO_{2(g)} \xrightarrow{\text{slow}} NO_{3(g)} + NO_{(g)}$$

$$NO_{3(g)} + CO_{(g)} \xrightarrow{\text{fast}} NO_{2(g)} + CO_{2(g)}$$

- The first step is the slowest step and the rate determining step.
- Order of reaction is two with respect to NO_2 but it is independent of CO concentration.
- NO_3 which does not appear in balanced chemical equation is reaction intermediate.

Reaction Intermediate:

A species which has temporary existence and it is unstable relative to the reactants and products and does not appear in the balanced chemical equation is called reaction intermediate.

This is a specie with normal bonds and may be stable enough to be isolated under special conditions.

Example:

In above reaction, NO_3 is reaction intermediate.

SPECIFIC RATE CONSTANT OR VELOCITY CONSTANT

Definition:

The rate of reaction when the concentrations of the reactants are unity is called specific rate constant of a chemical reaction.

Explanation

According to law of mass action for a general chemical reaction

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate of reaction} = k[A]^a[B]^b$$

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Here 'k' is called specific rate constant or velocity constant for the reaction.

- Let $[A]=1 mol\ dm^{-3}$ and $[B] = 1\ mol\ dm^{-3}$

$$\text{Rate of reaction} = k \times 1^a \times 1^b = k$$

- Under the given conditions, k remains constant, but it changes with temperature.

NOTE: There is only one factor i.e. temperature which affects the specific rate constant

Difference between rate of reaction and rate constant of reaction

Rate of reaction	Rate constant of reaction
▸ The change in concentration of a reactant or a product divided by the time taken for the change is called rate of reaction. ▸ Its unit is mol $dm^{-3}s^{-1}$. ▸ It depends upon concentrations of reactants. ▸ It varies with the passage of time under given conditions. **Example** $aA + bB \longrightarrow cC + dD$ Rate of reaction = $k[A]^a[B]^b$	▸ It is the proportionality constant, which is represented by k, in rate equation. ▸ Its units depend on the order of reaction. ▸ It is independent of the concentration of reactant or products. ▸ It always remains constant under the given conditions. **Example:** $aA + bB \longrightarrow$ Product $k = \frac{\text{Rate}}{[A]^a[B]^b}$

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CALCULATION OF RATE CONSTANT

(i) When rate equation, rate of reaction and concentrations are given

For a reaction $A + B \longrightarrow$ Products

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

If rate $= 1.0\ \text{mol dm}^{-3}\text{s}^{-1}$ and $[A] = [B] = 0.05\text{moldm}^{-3}$

Then

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

$$1.0 = k[0.05][0.05]$$

$$k = \frac{1.0}{[0.05][0.05]}$$

$$k = \frac{10000}{25} = 400\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$$

(ii) When half-life period in order of reaction are known

Following formulae are used

Order	Zero	First	Second	Third
Relation	$\left(t_{\frac{1}{2}}\right)_0 = \frac{a}{2k}$	$\left(t_{\frac{1}{2}}\right)_1 = \frac{0.693}{k}$	$\left(t_{\frac{1}{2}}\right)_2 = \frac{1}{ka}$	$\left(t_{\frac{1}{2}}\right)_3 = \frac{1.5}{ka^2}$

Example:

For 1st order reaction $t_{\frac{1}{2}}$ is 69. 3 seconds, its specific rate constant is

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$$\left(t_{\frac{1}{2}}\right)_1 = \frac{0.693}{k}$$

$$69.3 = \frac{0.693}{k}$$

$$k = 10^{-2}$$

(iii) When Ea and T are given

The formulae used are $k = Ae^{-\frac{Ea}{RT}}$

$$\log k = \frac{-Ea}{2.303R} \times \frac{1}{T} + \log A$$

If value of $e^{-\frac{Ea}{RT}}$ factor is 1.71×10^{-9} and A is 10^3 Then

$$k = Ae^{-\frac{Ea}{RT}}$$

$$k = 10^3 \times 1.71 \times 10^{-9}$$

$$k = 1.71 \times 10^{-6}$$

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UNITS OF RATE CONSTANT

By using the expression,

$k = (\text{Concentration})^{1-n}\,(\text{time})^{-1}$, the unit of rate constant for nth order reaction can be determined.

Examples:

(i) For **zero order** reaction, the units of rate constant k are given by:

Units of $k = (\text{concentration})^{1-n}\,(\text{time})^{-1}$

For zero Order $n = 0$

Units of $k = (\text{mole/dm}^3)^{1-0}\,(\text{s})^{-1}$

Unit of $k = (\text{mole/dm}^3)^1\ \text{s}^{-1}$

$k = \text{moles.dm}^{-3}.\text{s}^{-1}$

(ii) For **first order** reaction, the units of rate constant are given by:

Units of $k = (\text{concentration})^{1-n}\,(\text{time})^{-1}$

For first order $n = 1$

Units of $k = (\text{moles/dm}^3)^{1-1}\ \text{s}^{-1}$

Units of $k = (\text{moles/dm}^3)^0\ \text{s}^{-1}$

Units of $k = \text{s}^{-1}$

(iii) For **second order** reaction, the units of rate constants k are given by:

Units of $k = (\text{concentration})^{1-n}\,(\text{time})^{-1}$

For second order $n = 2$

Units of $k = (\text{mole/dm}^3)^{1-2}\,(\text{s})^{-1}$

Units of $k = (\text{mole/dm}^3)^{-1}\ \text{s}^{-1}$

Units of $k = \text{moles}^{-1}\ \text{dm}^3\ \text{s}^{-1}$

Units of $k = \text{dm}^3\ \text{moles}^{-1}\ \text{s}^{-1}$

(iv) For **third order** reaction, the units of rate constant are given by

Units of $k = (\text{concentration})^{1-n}\,(\text{time})^{-1}$

For third order $n = 3$

Units of $k = (\text{moles / dm}^3)^{1-3}\,(\text{s})^{-1}$

Units of $k = (\text{mole/dm}^3)^{-2}\ \text{s}^{-1}$

Units of $k = \text{mole}^{-2}.\text{dm}^{-6}\ \text{s}^{-1}$

Units of $k = \text{dm}^6\ \text{moles}^{-2}\ \text{s}^{-1}$

ORDER OF REACTION AND ITS DETERMINATION

The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction.

OR

The number of reacting molecules, whose concentration alter as a result of the chemical change, is called order of reaction.

$$aA + bB \longrightarrow P$$

$$\frac{dx}{dt} = k[A]^a[B]^b$$

Order of reaction $= a + b$

Important points

- The order of a reaction is an experimentally determined quantity and cannot be inferred simply by looking at the reaction equation.
- The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation.
- The order of reaction provides valuable information about the mechanism of a reaction.

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- Maximum order of reaction is three
- Order of reaction can be zero or can be in fraction
- Order of reaction is related with rate equation and is controlled by rate law.
- Order of reaction help us to determine mechanism of reaction
- If the molecularity and order of reaction is same then it is said to be a simple reaction, otherwise it is multistep reaction.

The chemical reactions are classified as

- Zero order reaction
- First order reaction
- Second order reaction
- Third order reaction
- Pseudo first order reaction
- Fractional order reaction

POINT TO PONDER

- The order of a reaction can be found by comparing the initial rates of two reactants of known concentration
- Once the order has been found, the rate constant can be calculated.

Examples of order of reactions

Zero order reactions

Photochemical reactions are usually zero order

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

First order reaction

$$2\,N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

Second order reactions

$$2CH_3CHO \longrightarrow 2CH_4 + 2CO$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

Third order reactions

$$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$$

$$2NO + Cl_2 \longrightarrow 2NOCl$$

DETERMINATION OF ORDER OF REACTION

Finding the Order of Reaction

Methods to determine the order of reaction

Five methods are available.

(i) Method of hit and trial
(ii) Graphical method
(iii) Differential method
(iv) Half-life method
(v) Method of large excess

From Half-life:

It is mentioned earlier, half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction.

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Therefore, $$(t_{1/2})_n \propto \frac{1}{a^{n-1}}$$

Let us perform a reaction twice by taking two different initial concentrations 'a_1' and a_2 their half-life periods are found to be t_1 and t_2 respectively.

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

Dividing the two relations:

$$\frac{t_1}{t_2} = \frac{a_2^{n-1}}{a_1^{n-1}}$$

$$\frac{t_1}{t_2} = \left[\frac{a_2}{a_1}\right]^{n-1}$$

Taking 'log' on both sides

$$\log\frac{t_1}{t_2} = (n-1)\log\left[\frac{a_2}{a_1}\right]$$

On rearranging the above equation:

$$n = 1 + \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

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So, if we know the two initial concentrations and two half-life values we can calculate the order of reaction (n).

From concentration:

The effect of change in concentration on the rate of a chemical reaction can be understood from the following gaseous reaction.

$$2NO_{(g)} + 2H_2 \longrightarrow 2H_2O_{(g)} + N_{2(g)}$$

$[NO]$ (moldm^{-3})	$[H_2]$ (moldm^{-3})	Rate (atm min^{-1})
0.006	0.001	0.025
0.006	0.002	0.050
0.006	0.003	0.075
0.001	0.009	0.0063
0.002	0.009	0.025
0.003	0.009	0.056

$$\text{Rate} \propto [H_2]$$

$$\text{Rate} \propto [NO]^2$$

$$\text{Rate} = K[H_2][NO]^2$$

It is third order reaction.

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HALF-LIFE AND 1ST ORDER OF REACTION

Half-life and order of reaction are related to each other as follows

$$[t_{1/2}]_n \ \alpha \ \frac{1}{a^{n-1}}$$

The relationship between the half-life and initial concentration of the reactants of different order reactions are given below

Order	Zero	First	Second	Third
Relation	$\left(t_{\frac{1}{2}}\right)_0 = \frac{a}{2k}$	$\left(t_{\frac{1}{2}}\right)_1 = \frac{0.693}{k}$	$\left(t_{\frac{1}{2}}\right)_2 = \frac{1}{ka}$	$\left(t_{\frac{1}{2}}\right)_3 = \frac{1.5}{ka^2}$

HALF-LIFE PERIOD OF FIRST ORDER REACITON

The time required to convert 50% of the reactants into products is called half-life period.

Example

(i) Half-life period of N_2O_4 at 45°C is 24 minutes.

(ii) Half-life period of $^{235}_{92}U$ is 7.1×10^8 or 710 million years.

Important points

- Half-life period of zero order reaction is directly proportional to the initial concentration of the reactants.
- Half-life period of first order reaction is independent to the initial concentration of the reactants.
- Half-life period of second order reaction is inversely proportional to the initial concentration of the reactants.
- Half-life period of third order reaction is inversely proportional to the square of initial concentration of reactants.

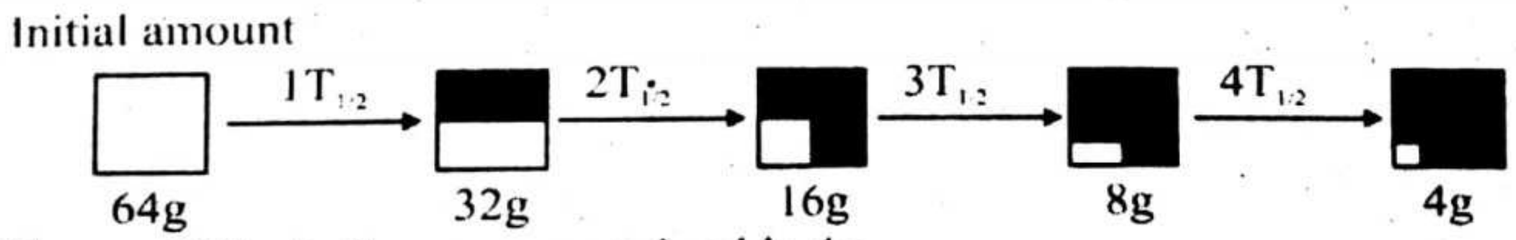
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Example:

Half-life of radioactive decay is 1.5 hours. Mass of it remained after 6 hours is (initial mass of isotope is 64 g)

$$\text{Number of half-lives} = \frac{\text{Total time taken}}{\text{Half-life period}}$$

$$\text{Number of half-lives} = \frac{6\,\text{hours}}{1.5\,\text{hours}} = 4$$



After 6 hours ($4T_{1/2}$), the mass remained is 4g

Example:

75% of A 1st order reaction was completed in 32Min, when was 50% of the reaction was completed:

75% of reaction is completed in 2 half-lives.

Therefore,

$$2[t_{1/2}] = 32\,\text{min}$$

$$[t_{1/2}] = \frac{32}{2}\,\text{min} = 16\,\text{min}$$

Hence, 50% of the reaction is completed in 16 min.

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NOTE: This example shows that half-life of first order reaction always remains same with different initial concentration.
The half-life period for the decomposition of N_2O_5 at 45°C is 24minutes. It means that if we decompose 1 mol/dm^3 of N_2O_5 then
After 24 minutes half amount will be decomposed and 0.5 mol/dm^3 will be left behind.

POINT TO PONDER

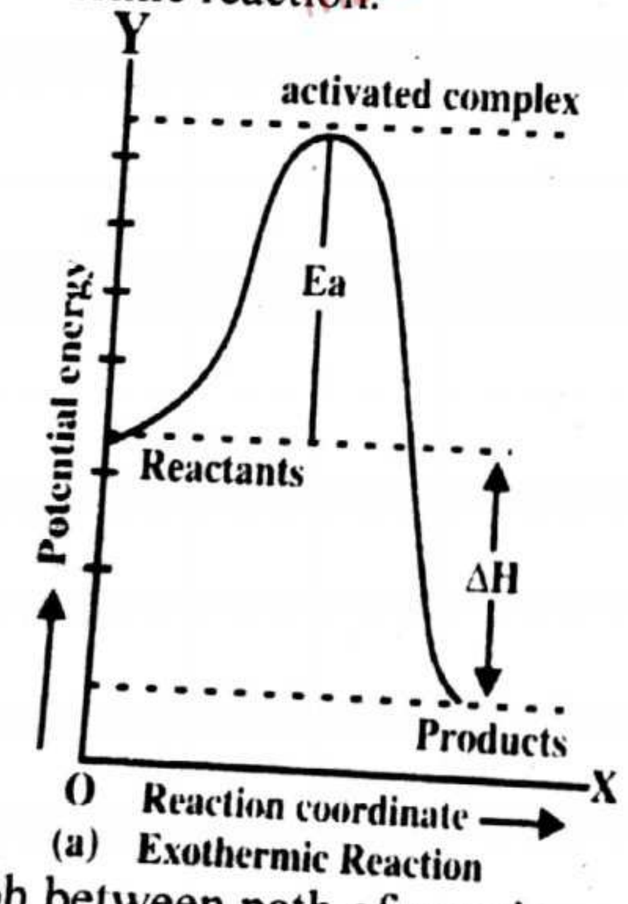
There is only one factor i.e. temperature which affects the specific rate constant.

ACTIVATION ENERGY AND ACTIVATED COMPLEX

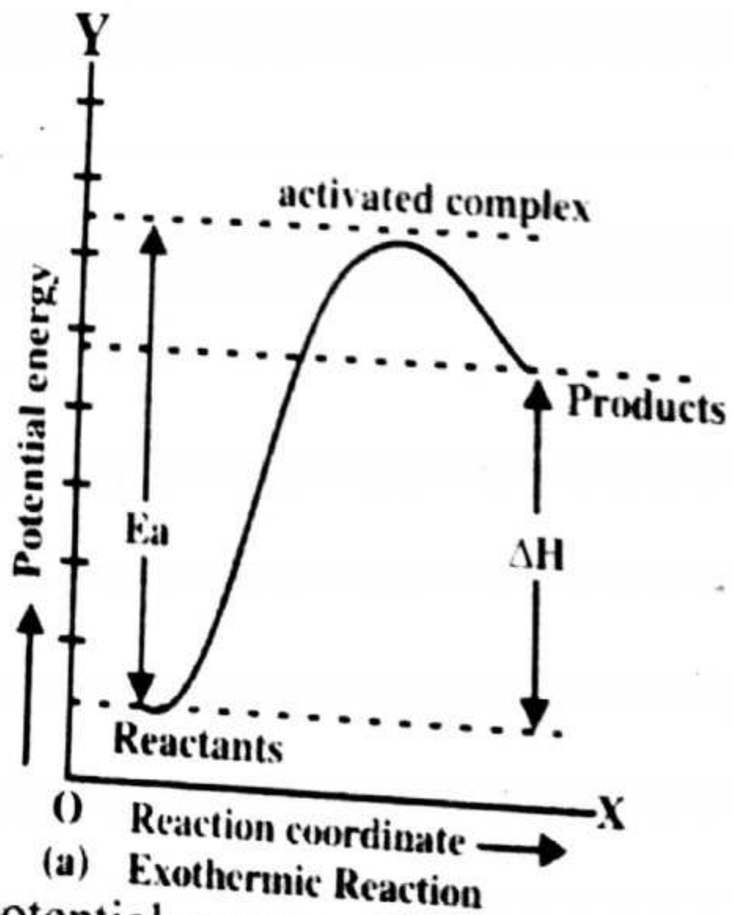
The minimum amount of energy, in addition to the average kinetic energy, which the particles must have for effective collisions, is called activation energy.

Important points

- Reactants go into transition state before going into product called activated complex.
- Energy of activated complex is higher than reactants and products.
- In effective collision, molecules have certain amount of energy and collide in certain orientation.
- When the energy of products is lesser than reactants, the reaction is exothermic.
- When the energy of products is higher than reactants, the reaction is endothermic.
- Energy of activation of forward reaction is less than backward reaction for an exothermic reaction.
- Energy of activation for backward reaction is less than forward reaction for an endothermic reaction.



(a) Exothermic Reaction



(a) Exothermic Reaction

A graph between path of reaction and the potential energy of the reaction
The reactants reach the peak of curve to form activated complex. E_a is the energy of activation and it as potential energy hill between reactants and products.

(i) Colliding molecules which have proper energy will be able to climb up the hill and will give product.

(ii) Colliding molecules whose initial kinetic energy is less than E_a will fail to climb up the hill fall back chemically unchanged.

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Exothermic Reaction:

In exothermic reaction, the potential energy of the products is lower than the potential energy of the reactants. The difference is denoted by ΔH. The value of ΔH depends upon the initial state (the potential energy of reactants) and final state (the potential energy of products). It does not depend upon route of reaction, rate of reaction and activation energy of reaction. The reactants require energy E_{a_1} which is equal to the activation energy to get the top of barriers. Anyhow, products require energy E_{a_2} which their activation energy to get to top of higher hill to form activated state. This energy is more than E_{a_1}.

E_{a_1} = Energy of activation for forward step

E_{a_2} = Energy of activation for backward step.

The magnitude of ΔH is also the difference of these two energies of activation.

$$E_{a_1} - E_{a_2} = \Delta E \text{ or } \Delta H$$

From this it is clear that for exothermic reactions the activation energy for forward reaction is less than the activation energy for backward reaction.

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NOTE:

(i) ΔH is the difference of potential energies of products and reactants.

(ii) ΔH is also the difference of activation energy of reactants and products.

Endothermic Reaction:

In endothermic reactions the potential energy of the products is higher than the potential energy of the reactants and for such reactions a continuous source of energy is needed to complete the reaction. In such reactions, the enthalpy change ΔH is positive since energy is absorbed in the reaction. For endothermic reversible reaction, the energy of activation for forward reaction is greater than the energy of activation for backward reaction.

Conclusions

Energy of activation for forward and backward reactions are different for all reactions.

For exothermic reaction, energy of activation for forward reaction is less than the energy of activation for backward reaction.

For endothermic reaction, energy of activation for forward reaction is greater than the energy of activation for backward reaction.

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ENZYMES CATALYSIS

Enzyme catalysis

Enzymes are bio-catalytical proteins, which increase the rate of biochemical reactions.

- The substance on which an enzyme can attack is called substrate.
- The point through which an enzyme attacks on substrate called active site.
- Each enzyme has its own active site.
- Enzymes are highly specific for substrate.
- Enzyme and substrate form enzyme-substrate complex, which then breaks into product and enzyme.
- The name of enzyme usually ends on "ase".

Examples

(i) Urea undergoes hydrolysis into NH_3 and CO_2 in the presence of enzyme urease, which is present in soyabean.

$$H_2N-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O \xrightarrow{\text{urease}} 2NH_3 + CO_2$$

(ii) Concentrated sugar solution undergoes hydrolysis into glucose and fructose by an enzyme called **invertase** present in yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{fructose}}{C_6H_{12}O_6} + \underset{\text{glucose}}{C_6H_{12}O_6}$$

(iii) Glucose can be converted into alcohol by the enzyme zymase present in the yeast.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{yeast}]{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

(iv) Starch can be converted into maltose by the enzyme diastase.

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\text{Yeast}]{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

Starch

(v) Maltose can be converted into glucose by the enzyme maltase.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Yeast}]{\text{Maltase}} 2C_6H_{12}O_6$$

Maltose Glucose

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TOPIC-8 ⟫ THERMOCHEMISTRY AND ENERGETICS OF CHEMICAL REACTIONS

COURSE CONTENTS

- System, Surrounding and State function
- Definitions of terms used in thermodynamics
- Standard states and standard enthalpy changes
- Energy in chemical reactions
- First law of thermodynamics
- Sign of ΔH
- Enthalpy of a reaction and its Types
- Born-Haber cycle
- Hess's law of constant heat summation

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INTRODUCTION

Thermochemistry

The study of heat changes during a chemical reaction is called thermochemistry.

Energy

"Ability of a body to do work is called energy."

Types of energies

(i) Kinetic energy (K.E) →Energy due to motion

(ii) Potential energy (P.E) →Energy due to position, shape and orientation

Units of Energy

Units	Relation
Joule (SI Unit)	$J=kgm^2s^{-2}$
Calorie	1 cal = 4.184J

POINT TO PONDER

Other forms of energies are

Sound energy, Heat energy, Magnetic energy, Mechanical energy and Solar energy

CONCEPT OF ENERGY CHANGES DURING CHEMICAL REACTIONS

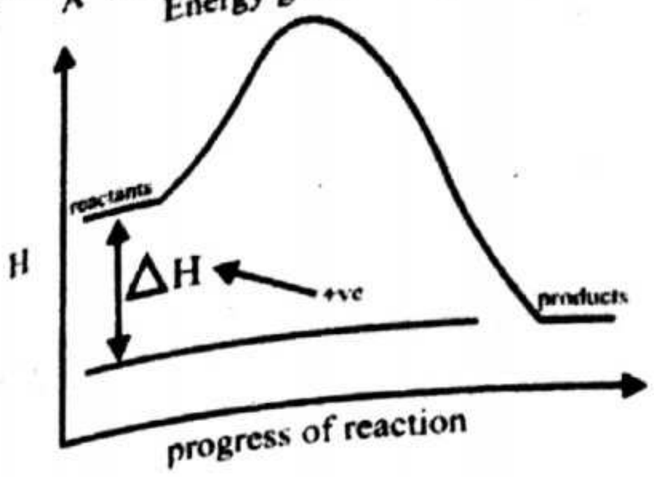
Sr.	Properties	Exothermic	Endothermic
1	Flow of heat energy	System to surrounding	Surrounding to system
2	Temperature of surrounding	Increases	Decreases
3	Temperature of the system	Decreases	Increases
4	Energy of products	Low	High
5	Energy of reactants	High	Low
6	Strength of bonds in products	Strong	Weak
7	Strength of bonds in reactants	Weak	Strong
8	Enthalpy change (ΔH)	Negative	Positive
9	Examples	**Combustion** $C + O_2 \rightarrow CO_2\ \Delta H = -393.7kJ/mol$ **Respiration** $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ **Neutralization** $NaOH + HCl \rightarrow NaCl + H_2O$	**Oxidation** $N_2 + O_2 \rightarrow 2NO$ $\Delta H = +180.51kJ/mol$ **Thermal decomposition** $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ **Dissolving** $NH_4NO_{3(s)} \rightarrow NH_4NO_{3(aq)}$

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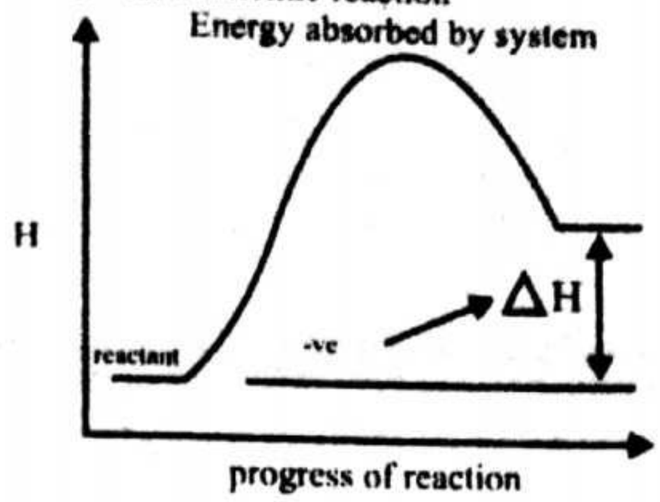
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Graphical representation of exothermic and endothermic reactions

A Exothermic reaction
Energy given off by system



B Endothermic reaction
Energy absorbed by system



POINT 70 PONDER

By definition standard enthalpy of an element is zero.

SYSTEM, SURROUNDING AND STATE FUNCTION

System

"The portion of universe which is set aside for consideration, observation, discussion, argumentation or experimentation is called system"

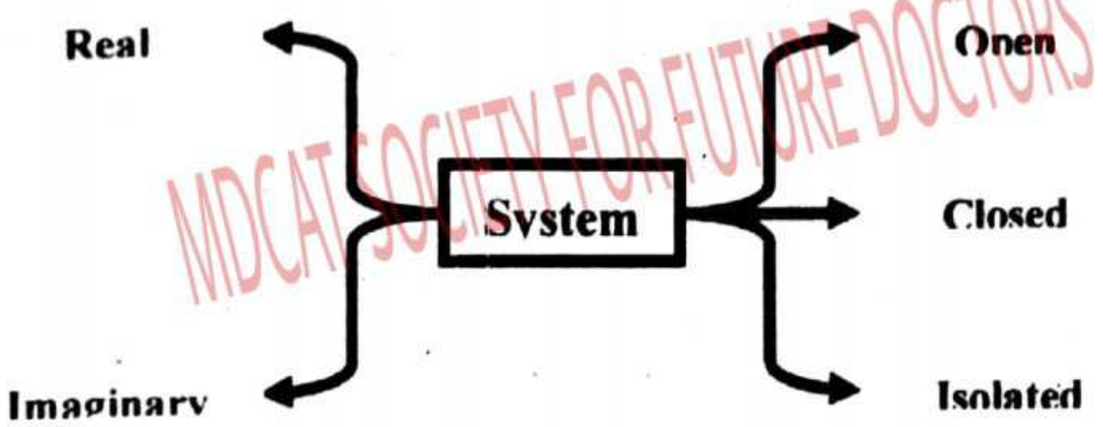
OR

"The substance under consideration is called chemical system"

Examples:

(i) $Pb(NO_3)_2$ under consideration is a system.

(ii) The liquid whose boiling point is to be measured is a system.



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Isolated System

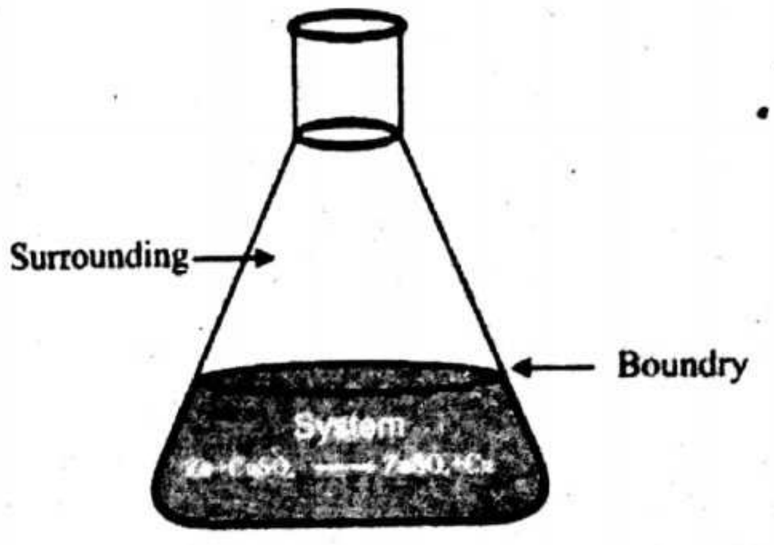
If a system is isolated, then nothing can enter or leave. Its energy and matter remain the same. Any change goes on inside the system, and it remains isolated, we cannot know anything about an isolated system from the outside.

Open System

When both matter and energy can be exchanged, is called open system, when matter is added. In this case the system is open system. For example, when we perform titration.

Closed System

In closed system energy can be exchanged but matter cannot exchanged between system and surrounding, the system is called closed. A bomb calorimeter only allows heat to be exchanged. Such a system is called closed.



Surrounding

The portion of universe except system is called surrounding.

Example:

A chemical reaction happening in a conical flask is a system, while the walls of the conical flask and the atmosphere are its surrounding.

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Boundary

The real or imaginary surface, separating the system from surrounding is called boundary of a system.

State

The condition of a system is called state of the system.

Examples:

Volume, Temperature, Pressure, Energy etc

	State	Examples
1	Conditions describing the system before it undergoes a change are called initial states of system.	V_1, T_1, P_1, E_1
2	Conditions describing the system after it undergoes a change are called final states of system.	V_2, T_2, P_2, E_2

Change in the state of system

$\Delta V = V_2 - V_1$ (Change in volume)

$\Delta P = P_2 - P_1$ (Change in pressure)

$\Delta G = G_2 - G_1$ (Change in free energy)

$\Delta H = H_2 - H_1$ (Change in enthalpy)

$\Delta T = T_2 - T_1$ (Change in temperature)

$\Delta E = E_2 - E_1$ (Change in internal energy)

$\Delta S = S_2 - S_1$ (Change in entropy)

State function

A macroscopic property of a system which has some definite values for initial and final states, and is independent of the path adopted to bring about a change.

Examples:

Pressure (P), Temperature (T), Volume (V), Internal energy (E) and enthalpy (H) are all state functions.

- Capital symbols are used for state function.
- Heat and work are not state functions.
- Entropy and Gibb's free energy is also a state function.

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BOND ENERGY

The average amount of energy required to break all bonds of a particular type in one mole of the substance is called bond energy.

- Unit of bond energy is kJ/mole.

Factors affecting bond energy

The bond energy is the measure of the strength of bond. The strength of a bond depends upon the following factors.

(i) Electronegativity difference of bonded atoms

(ii) Sizes of the atoms

(iii) Bond length

POINT TO PONDER

The amount of heat evolved or absorbed when one mole of gaseous ions are dissolved in water is called enthalpy of hydration (ΔH_h°). It May be negative or positive

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Applications of bond energy

- Relative strength of bonds
- % of ionic character in bond
- Estimation of ΔH

$$\Delta H_{\text{Bond formation}} = \Delta H_{\text{Reactant}} - \Delta H_{\text{Product}}$$

Average bond energies

- During a chemical reaction, the bonds in the reactants are broken. This is an endothermic process; energy is required to do this.
- After the bonds have been broken, however, the bonds in the products are formed.
- This is an exothermic process; energy is released when this happens.
- The enthalpy change for a chemical reaction can be deduced from consideration of the energy required to break bonds in the reactants and the energy released when the bonds in the products are formed. It can be calculated from the following equation:
  ΔH = Energy required to break bonds in reactants - Energy released to make bonds in products
- This method can be used to calculate the enthalpy changes for any reaction which does not involve ionic bonds.
- The breaking and making of ionic bonds involve a more complicated sequence of energetic processes and thus cannot be considered in this way.

INTERNAL ENERGY AND FIRST LAW OF THERMODYNAMICS

INTERNAL ENERGY

"The sum of potential energy and kinetic energy of a substance is called its internal energy."

OR

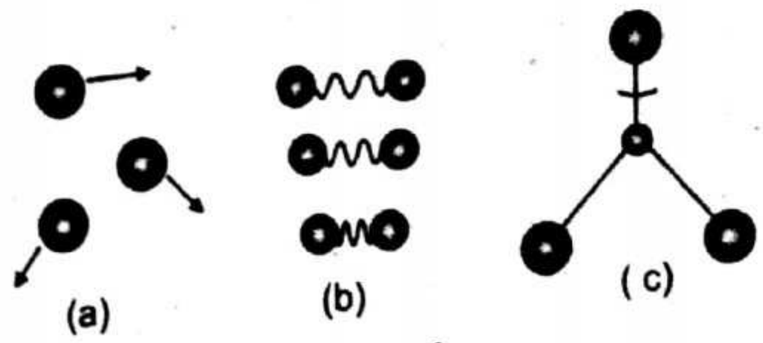
"The sum of all the possible kinds of energies of a system is called its internal energy (E)."

$$E_T = K.E + P.E + \ldots\ldots$$

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Internal energy is comprised of

- **Kinetic energy**
  - Translational kinetic energy (a) (mono-atomic)
  - Vibrational kinetic energy (b) (di-atomic)
  - Rotational kinetic energy (c) (tetra-atomic)
- **Potential energy**
  - Intra-molecular forces
  - Inter-molecular forces
- **Effect of increase in Internal Energy:**
  - (i) The temperature of the system may increase
  - (ii) A phase change may occur.
  - (iii) A chemical reaction may take place.



FIRST LAW OF THERMODYNAMICS (Law of conservation of energy)

"Energy can neither be created nor be destroyed, but can be changed from one form to another."

$$\Delta E = q + P\Delta V$$

$$\Delta E = q_v$$

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ENTHALPY CHANGE OF REACTION

Enthalpy	Definition	Symbol	Positive or negative
Enthalpy of reaction	The enthalpy change which occurs when the certain number of moles of reactants as indicated by the balanced chemical equation, react together completely to give the products under standard condition. $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}\ \Delta H^\circ = -285.8 kJmol^{-1}$	ΔH°	May be positive or negative
Enthalpy of formation	The change of enthalpy when one mole of the compound is formed from atoms of its elements. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}\ \ \Delta H^\circ_f = -393.7 kJmol^{-1}$	ΔH°_f	May be positive or negative
Enthalpy of atomization	The enthalpy change when one mole of gaseous atoms are formed from a molecule or an element under standard conditions. $1/2H_{2(g)} \rightarrow H_{(g)} \qquad \Delta H^\circ_{at} = -218 kJmol^{-1}$	ΔH°_{at}	Always positive
Enthalpy of neutralization	The amount of heat evolved when one mole of hydrogen ions H^+ from an acid, react with one mole of hydroxide ions (OH^-) from a base to form one mole of water. Example: The enthalpy of neutralization of sodium hydroxide by hydrochloric acid is $-57.4 kJmol^{-1}$ $NaOH + HCl \rightarrow NaCl + H_2O\ \Delta H_n = -57.4 kJmol^{-1}$	ΔH°_n	Always negative
Enthalpy of combustion	The enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions. $C_2H_5OH_{(l)} + 3O_2 \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H^\circ_c = -1368 kJmol^{-1}$	ΔH°_c	Always negative
Enthalpy of solution	The amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change. $NH_4Cl_{(s)} + (aq) \rightleftharpoons NH_4Cl_{(aq)}$ $\Delta H^\circ_{(sol)} = +16.2 kJmol^{-1}$	ΔH°_{sol}	May be negative or positive

NOTE: (i) ΔH_n = -57.4 KJ / mole (maximum for strong acids and bases)

(ii) $\Delta H_n > -57.4$ (not possible)

(iii) $\Delta H_n < -57.4$ (when one of the acid or base is stronger and other is weaker)

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HEAT OF REACTIONS / NEUTRALIZATION FROM EXPERIMENTAL RESULTS

There are two basic methods to measure the enthalpy of reactions

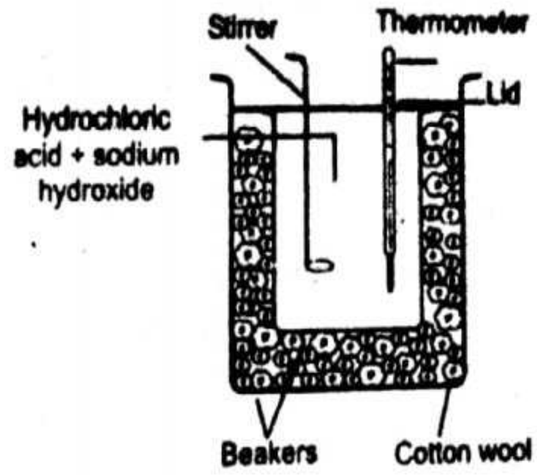
(i) Glass Calorimeter (ΔH_n and ΔH_s)

(ii) Bomb Calorimeter (ΔH_c of food and fuel)

- Theoretical methods for calculation of enthalpy of reaction indirectly

(i) Hess's Law for constant heat summation

(ii) Born-Haber's cycle



By glass calorimeter

- Glass calorimeter is used to measure the enthalpy of solution and enthalpy of neutralization.
- By using following relationship, heat of reaction is calculated.

$$q = m \times s \times \Delta T$$

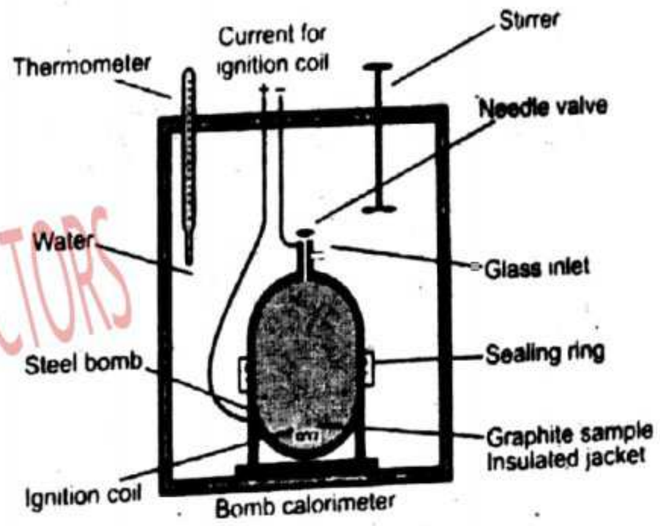
Where,

m = mass of reactant, Units = 'g' or 'Kg'

s = specific heat of reacting mixture, Units = $JK^{-1}g^{-1}$

ΔT = change in temperature, Units = K

NOTE: In glass chlorimeter, pressure remains constant. At constant pressure $q = \Delta H$ Hence ΔH can be determined by using the formula $\Delta H = mc\Delta T$, where "c" is specific heat of reacting mixture



By bomb calorimeter

- Bomb calorimeter is used to measure enthalpy of combustion and enthalpy of reaction.
- By using following relationship, heat of reaction is calculated.

$$q = C \times \Delta T$$

Where,

C = Heat capacity, Units = kJK^{-1}

ΔT = change in temperature, Units = K

$$\Delta E = \Delta H = \frac{C\Delta T}{n}$$

NOTE: Volume remains constant in bomb calorimeter.

BORN-HABER CYCLE OF NaCl

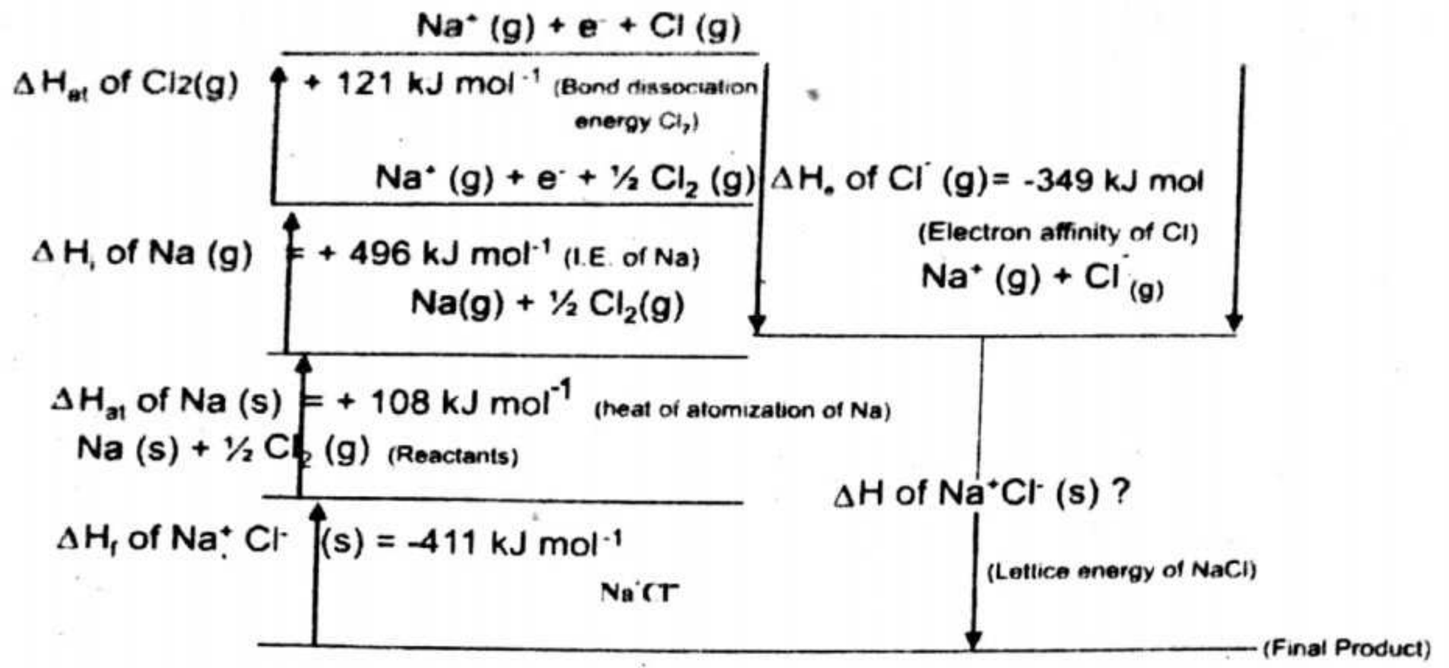
(Including ionization energy and electron affinity)

Born-Haber cycle

Energy change in cyclic process is always zero. It enables us to calculate the lattice energy of binary compounds (ionic); this is called Born-Haber cycle.

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$$\Delta H_{latt.} = \Delta H_f - \Delta H_x$$

$$\Delta H_x = \Delta H_{at(Na)} + \Delta H_{I.E(Na)} + \Delta H_{at(Cl_2)} + \Delta H_{E.A(Cl)}$$

$$\Delta H_x = 108 + 496 + 121 - 349$$

$$\Delta H_x = 376\,kJmol^{-1}$$

$$\Delta H^o_{latt} = \Delta H^o_f - \Delta H_x = -411 - 376 \Rightarrow \Delta H^o_l = -787\ kJ\ mol^{-1}$$

HESS'S LAW TO CONSTRUCT SIMPLE ENERGY CYCLES

(i) Determining enthalpy changes that cannot be found by direct experiment

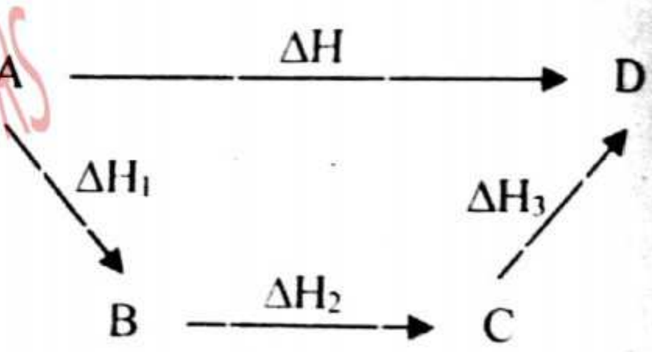
Hess's law of constant heat summation

Energy contents of a reaction remain constant whether reaction takes place in single step or many steps.

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

The sum of enthalpy changes in a cyclic process is zero.

$\sum(\Delta H)cycle = 0$

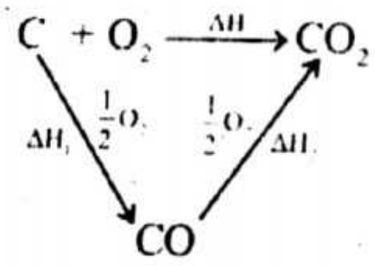


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Example:

If the enthalpy of combustion for graphite to form CO_2 and enthalpy of combustion of CO to form CO_2 are known, then by using Hess's law we can determine the enthalpy of formation of CO.

Consider the following cycle.



$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_{(for\ CO_2\ from\ graphite)} = -393.7\,kJmol^{-1}$$

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_2\ (for\ CO_2\ from\ CO) = -283\ kJ\ mol^{-1}$$

$$C_{(graphite)} + \frac{1}{2}O_2 \longrightarrow CO_{(g)} \qquad \Delta H_1(CO) = ?$$

From cycle, it is clear that

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$\Delta H_1 = \Delta H - \Delta H_2$$

$$= -393.7 - (-283)$$

$$\Delta H_1 = -110.7\ kJ\ mol^{-1}$$

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So, the enthalpy change for the formation of $CO_{(g)}$ is -110 kJmol^{-1}.

Using Hess's law for numerical problems

Sample problem: If the heats of combustion of CH_4, H_2 and C_2H_6 are –337.2, –68.3 and –372.8 k calories respectively, then calculate the heat of the following reaction.

$$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$$

Given information:

i) $C_2H_{2(g)} + \frac{5}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(g)}$ $\Delta H = -337.2$ kcal.

ii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H = -68.3$ kcal

iii) $C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$ $\Delta H = -372.8$ kcal

Required:

Heat of the following reaction?

$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$ $\Delta H = ?$

Solution:

Multiply equation ii) by '2' and add (i) and (ii)

$C_2H_{2(g)} + \frac{5}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(g)}$ $\Delta H = -337.2$ kcal

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$ $\Delta H = 68.3 \times 2 = -136.6$ kcal

$C_2H_{2(g)} + \frac{7}{2}O_{2(g)} + 2H_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$ $\Delta H = -473.8$ kcal

Subtract eq (iii) from above

$C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$ $\Delta H = -372.8$ kcal

$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$ $\Delta H = 101$ kcal mol^{-1}

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TOPIC-9 ELECTROCHEMISTRY

COURSE CONTENTS

- Oxidation number or state
- Oxidation state and balancing of redox equations
- Balancing of redox equations by ion-electron method
- Balancing of redox equations by oxidation number change method
- Explanation of electrolysis (Predict the product)
- Standard electrode (redox) potential
- Standard hydrogen electrode (SHE)
- Standard cell potential
- Electrode potential
- Electrochemical series (ECS)
- Applications of ECS

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INTRODUCTION

Electrochemistry

It is the branch of chemistry which is concerned with the inter-conversion of chemical energy and electrical energy.

- Electrical energy is converted into chemical energy through electrolytic cells.
- Chemical energy is converted into electrical energy through galvanic or voltaic cells.

Oxidation	Reduction
Gain of oxygen	Loss of oxygen
Loss of hydrogen	Gain of hydrogen
Loss of electrons including anode reactions	Gain of electrons including cathode reactions
Increase in oxidation state	Decrease in oxidation state
$Zn \rightarrow Zn^{2+} + 2e^-$	$Cu^{2+} + 2e^- \rightarrow Cu$

OXIDATION NUMBERS OF ELEMENTS

Apparent charge on an atom of an element in a molecule or an ion is called oxidation number. It may be positive or negative or zero.

Element	○ Molecular form ○ Bulk / chunk	H_2, S_8 0 Diamond (C) 0
Compound	**Covalent compound** ▸ Molecular / Bulk / chunk Non-Metal – Non-Metal ○ Less electronegative non-metal = +ve ○ More electronegative non-metal = –ve ○ Algebraic sum of oxidation numbers = 0 **Ionic compound** ▸ Metal – Non-Metal Metal = +ve Non-metal = –ve Algebraic sum of oxidation numbers = 0	**Molecular** HCl $(+1)+(-1) = 0$ **Bulk / chunk** SiO_2 $[+4+2(-2)] = 0$ **Ionic compound** NaCl $(+1)+(-1) = 0$
Ion	**Mono-atomic ion** ▸ Oxidation number will be equal to the charge on the ion. **Poly-atomic ion** ▸ The algebraic sum of oxidation number is equal to charge on that ion.	**Mono-atomic ion** Cl^{-1} = -1 **Poly-atomic ion** SO_4^{-2} = $+6+[-2(4)]$ = -2
Hydrogen	**Ionic compound** ▸ Always –ve oxidation number **Covalent compound** ▸ Always +ve oxidation number	**Ionic compound** NaH $(+1)+(-1) = 0$ **Covalent compound** H_2O $[+1(2)]+(-2) = 0$
Oxygen	**With all elements** ▸ –2 oxidation number(normal oxides) ▸ –1 oxidation number(per oxides) ▸ –1/2 oxidation state (super oxides) **With Fluorine** ▸ + 2 oxidation state	H_2O $-1(2) -2 = 0$ H_2O_2 $=(+1)2+(-1)2 = 0$ KO_2 $[+1+2(-1/2)] = 0$ OF_2 $[+2+2(-1)] = 0$

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POINT TO PONDER

Oxidation number of IA group = (+1)

Oxidation number of II-A group = (+2)

Oxidation number of III-A group = (+3)

Examples

$K_2Cr_2O_7$

$(+1)2 + 2Cr - 2(7) = 0$

$+ 2 + 2Cr - 14 = 0$

$2Cr = + 14 - 2 = + 12$

$Cr = + 6$

$NaBrO_3$

$1 + Br + (-2)(3) = 0$

$1 + Br - 6 = 0$

$Br - 5 = 0$

$Br = + 5$

REDOX REACTION

Oxidation and reduction always takes place together. There can be no oxidation without reduction and vice versa. This combined process is called Redox Reaction.

Redox process in terms of electron transfer or change in oxidation number explained in following example. $Zn_{(s)} + CuSO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$

Its ionic equation is $Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$

Oxidation	Reduction
o $Zn \rightarrow Zn^{2+} + 2e^-$	o $Cu^{2+} + 2e^- \rightarrow Cu$
o Zinc atom has lost two electrons	o Copper ion has accepted two electrons
o Oxidation state of Zinc has increased from 0 to +2	o Oxidation state of Copper has decreased from +2 to 0.
o Zinc atom has been oxidized to Zinc ion	o Copper ion has been reduced to copper atom
o Zn atom given up its electrons to copper ion to reduce copper ion so Zn atom act as reducing agent (Reductant).	o Cu ion removes electrons from Zn atom to oxidize Zn atom so Cu ion act as oxidizing agent (Oxidant).

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BALANCING OF REDOX EQUATIONS BY ION-ELECTRON METHOD

o **Example: (Acidic medium)**

Given equation $Cl^- + MnO_4^- \longrightarrow Cl_2 + Mn^{2+}$

Balanced equation $10Cl^- + 16H^+ + 2MnO_4^- \rightarrow 5Cl_2 + 2Mn^{2+} + 8H_2O$

o **Example: (Basic medium)**

Given equation $MnO_4^-{}_{(aq)} + C_2O_4^{2-}{}_{(aq)} + H_2O \longrightarrow MnO_{2(s)} + CO_{2(g)} + OH^-_{(aq)}$

Balanced equation $3C_2O_4^{-2} + 4H_2O + 2MnO_4^- \longrightarrow 6CO_2 + 2MnO_2 + 8OH^-$

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Topic-9

BALANCING OF REDOX EQUATION BY OXIDATION NUMBER METHOD

The steps involved can be memorized by following sequence

- Skeleton equation
- Identification of elements whose O.N changed
- Indication of number of electrons gained or lost
- Equating the increase or decrease in oxidation number → use suitable multiplier
- Balancing the rest of equation → by inspection method

Balance the following equation by oxidation number method.

$$K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + Cl_2 + H_2O$$

$$\boxed{K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O}$$

Balance the following equation by oxidation number method.

$$P + HNO_3 + H_2O \rightarrow H_3PO_4 + NO$$

$$3P + 5HNO_3 + H_2O \rightarrow 3H_3PO_4 + 5NO$$

$$3P + 5HNO_3 + 2H_2O \rightarrow 3H_3PO_4 + 5NO$$

Electrolytic Conduction:

Conduction is of two types.

(i) Electrolytic conduction

(ii) Electronic or metallic conduction

Electrolytic Conduction:

- The conduction in which current is carried by positively and negatively charged ions is solution or in fused state is called **electrolytic conduction.**
- Chemical change takes place in it.
- It increases with increase in temperature.

Electronic Conduction or Metallic Conduction:

- The conduction of electricity due to **free movement of electrons in the metallic lattice** is called **electronic** conduction or **metallic** conduction.
- No chemical change takes place in it.
- It decreases with increase in temperature.

Ionization:

The process of splitting of ionic compounds into charged particles when fused or dissolved in water is called ionization.

Electrolysis:

The process in which non – spontaneous reaction takes place at the expense of electricity is called electrolysis.

EXPLANATION OF ELECTROLYSIS

The process of electrolysis is carried out by using aqueous solution of salts or molten salts.

(a) Electrolysis of Fused Salts

i) Reaction at cathode:

When fused salts are electrolyzed, the metal ions called cations carrying positive charge move towards cathode. Cathode provides electrons to them and they get reduced.

Example:

In the case of fused $PbCl_2$, Pb^{+2} ions being positively charged move towards cathode and gain electrons.

$$Pb^{+2}_{(l)} + 2e^- \longrightarrow Pb_{(s)} \text{ (reduction)}$$

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i) Reaction at Anode:

The anions move towards anode and they lose their electrons at anode and get oxidized.

Example:

In case of $PbCl_2$, Cl^- ions being negatively charged move towards anode and lose electrons.

$$2Cl^-_{(l)} \longrightarrow Cl_{2(g)} + 2e^- \qquad \text{(oxidation)}$$

Similarly, for fused NaCl and fused $PbBr_2$, electrolytes are decomposed during electrolysis. 'Pb' and Na are produced at cathode while Br_2 and Cl_2 gases are formed at anode.

ii) Flow of Electrons and Ions

In the fused salt there is electrolytic conduction in the cell while there is electronic conduction in the external circuit. In, the cell ions move towards anode and cathode to get oxidized or reduced respectively. The flow of electrons takes place through external circuit from anode to cathode.

Current is conducted by electrons outside the cell in the external circuit from anode to cathode. Current is conducted by ions inside the cell from cathode to anode.

(b) Electrolysis of Aqueous Solutions of Salts

The electrolysis of aqueous solutions of salt is not so simple and is somewhat complicated. The reason is that water molecules are oxidized as well as reduced that is why products of electrolysis of aqueous solutions of salts are not precisely predictable.

Example:

Let us take the example of aqueous solutions of $NaNO_3$. It dissociates in water as follows:

$$NaNO_3 \rightleftharpoons Na^{+1} + NO_3^{-1}$$

Water molecules also get ionized

$$H_2O + H_2O \longrightarrow H_3O^+_{(aq)} + OH^{-1}_{(aq)}$$

i) Reaction at Cathode:

H_3O^+ ions being positively charged move towards cathode and get reduced in competition of Na^{+1} ions.

$$H_3O^{+1} + 1e^- \longrightarrow H_2O_{(l)} + H_{(g)} \qquad \text{(reduction)}$$

Similarly, one more hydrogen atom is formed. Then both hydrogen atoms react to form hydrogen gas.

$$H_{(g)} + H_{(g)} \longrightarrow H_{2(g)}$$

H_2 gas is evolved at cathode. Na^{+1} ion will remain as such at cathode and does not get reduced because H^{+1} ion has greater tendency to gain electrons.

Electrolyte	Cathode	Anode
$PbBr_{2(molten)}$	$Pb_{(s)}$	$Br_{2(g)}$
$NaCl_{(molten)}$	$Na_{(s)}$	$Cl_{2(g)}$
$NaCl_{(aq)}$	$H_{2(g)}$	$Cl_{2(g)}$
$CuCl_{2(aq)}$	$Cu_{(s)}$	$Cl_{2(g)}$
$CuSO_{4(aq)}$	$Cu_{(s)}$	$O_{2(g)}$
$KNO_{3(aq)}$	$H_{2(g)}$	$O_{2(g)}$
$NaOH_{(aq)}$	$H_{2(g)}$	$O_{2(g)}$
$H_2SO_{4(aq)}$	$H_{2(g)}$	$O_{2(g)}$

The concentration of H_3O^+ is 10^{-7} moles/dm^3 in water. When these are discharged, more are formed by dissociation of water molecules to give continuous supply of H_3O^+.

ii) Reaction at anode:

At anode, both nitrate and hydroxide ions are present. Hydroxide ions are easier to discharge than nitrate ions. Nitrate ions will remain in the solution while the electrode reaction is as follow.

$$(OH^- \longrightarrow OH + e^-) \times 4 \qquad \text{(oxidation)}$$

The OH groups decompose to give oxygen and water molecules.

$$4OH \longrightarrow O_2 + 2H_2O$$

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So, oxygen gas is obtained at anode. Na^{+1} ions and NO_3^{-1} ions will remain in the solution.

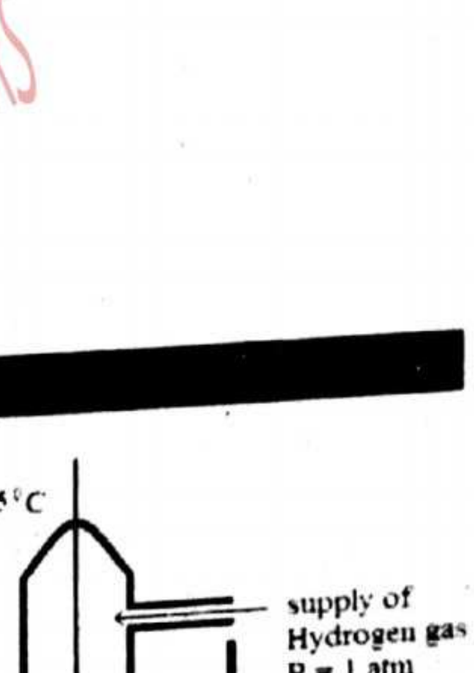
Expected order of discharge of ions may also depend upon their **concentration**. If an ion with greater tendency to discharge has low concentration in comparison to ion which has less tendency to discharge itself then ion with greater concentration may get discharged.

STANDARD ELECTRODE (REDOX) POTENTIAL

STANDARD ELECTRODE POTENTIAL

The potential setup when an electrode is in contact with one molar solution of its own ions at 298K is known as **standard electrode potential**. It is represented as E^o.

When Zn rod is dipped in the solution of its own ions, then Zn rod will bear an accumulation of negative charge. This is due to greater tendency of Zn atom to lose electrons. The negative charge on the Zn rod will attract an atmosphere of positively charged zinc ions around the rod to form an electrical double layer as shown in figure.



Equilibrium between zinc and its ions in solution

Equilibrium can be represented as $Zn_{(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2e^-$

- Electrode potential, of any element, can be calculated by comparing it with standard hydrogen electrode (SHE).

Types of standard electrode potentials

There are two type of standard electrode potentials

(i) Standard oxidation potential

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad E^\circ_{ox} = +0.76V$$

(ii) Standard reduction potential

$$Cu^{2+} + 2e^- \longrightarrow Cu \quad E^\circ_{red} = +0.34V$$

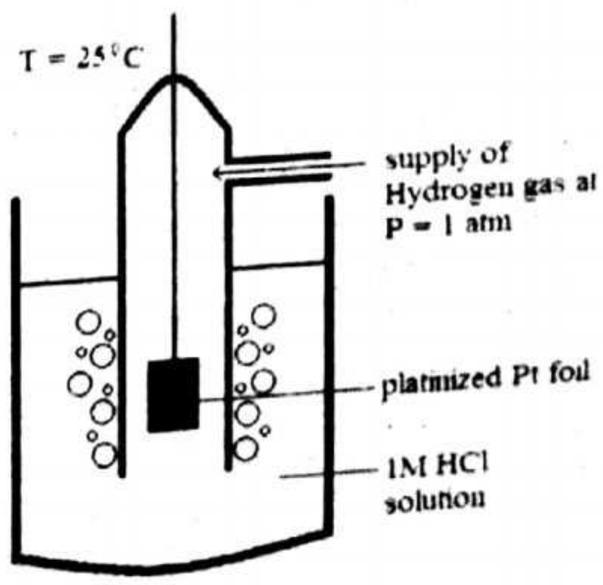
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STANDARD HYDROGEN ELECTRODE

Standard hydrogen electrode (SHE)

SHE consists of

- Glass Tube filled with H_2 gas at 1 atm pressure Pt–foil, coated with finally divided platinum black is suspended in it.
- The whole system mentioned above is dipped in 1M solution of HCl
- Electrode Potential of SHE is arbitrarily considered as zero Electrode potential, of any element, can be calculated by comparing it with standard hydrogen electrode (SHE).



SHE

Reactions that take place in the S.H.E are

$H_{2(gas)} \longrightarrow 2H^+_{(aq)} + 2e^-$ Oxidation $E^\circ_{ox} = 0.0V$

$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(gas)}$ Reduction $E^\circ_{red} = 0.0V$

Under standard conditions the e.m.f of S.H.E is defined to be arbitrarily zero volts as its oxidation potential is equal to reduction potential.

So $E^\circ_{SHE} = 0.000\,V$

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So. oxygen gas is obtained at anode. Na^{+1} ions and NO_3^{-1} ions will remain in the solution.

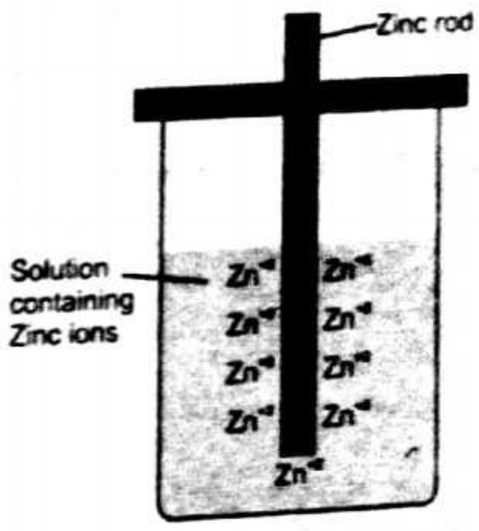
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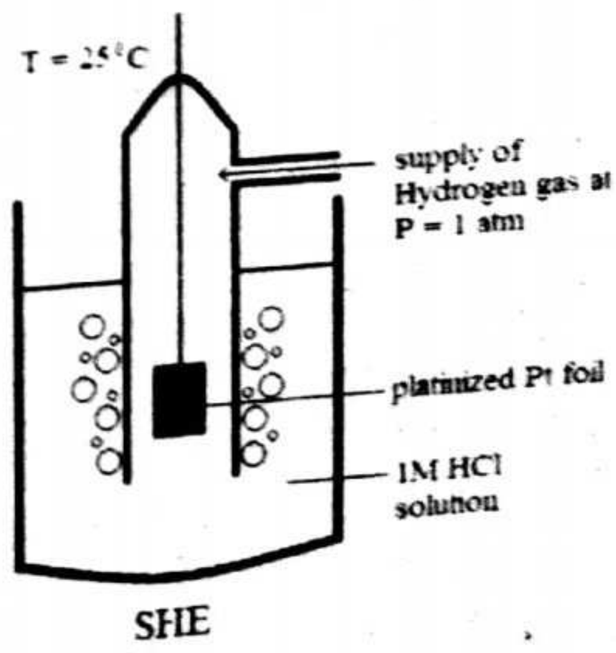
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Under standard conditions the e.m.f of S.H.E is defined to be arbitrarily zero volts as its oxidation potential is equal to reduction potential.

So $E^\circ_{SHE} = 0.000\,V$

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STANDARD CELL POTENTIAL

Electrochemical cells

The cells consisting of electrodes dipped into an electrolyte which make the inter-conversion of electrical energy and chemical energy possible are called electrochemical cells.

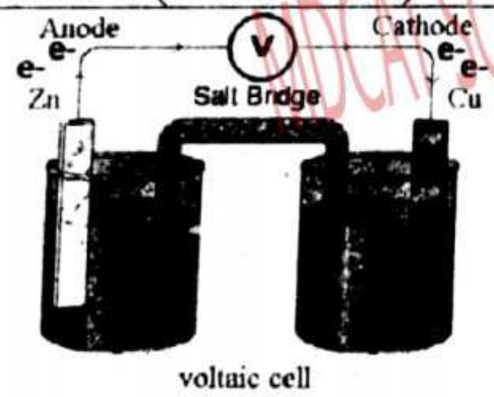
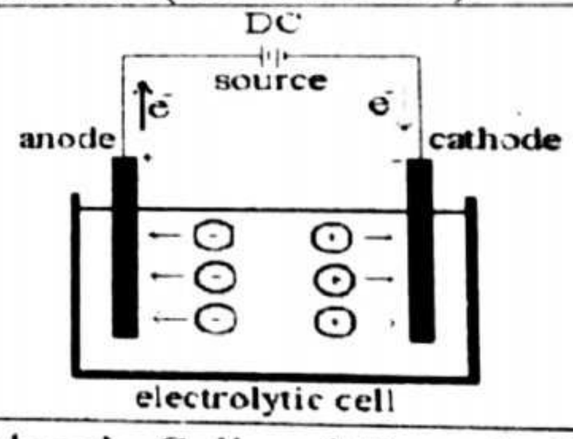
POINT PONDER

In disproportionation one part of a substance is oxidized and other part is reduced.

Types of electrochemical cells

(i) Electrolytic cell

(ii) Voltaic or galvanic cell

Voltaic/Galvanic Cell	Electrolytic Cell
A cell in which redox reaction generates electric current through chemical reaction is called voltaic or galvanic cell.	A cell in which a redox reaction occurs at the expense of electrical energy is called electrolytic cell.
Anode is –vely charged.	Anode is +vely charged
Cathode is +vely charged.	Cathode is –vely charged
Chemical energy ⟶ electrical energy	Electrical energy ⟶ chemical energy
Reduction reaction and oxidation reaction occur in the separate compartment.	Both reduction reaction and oxidation reaction occur in the same compartment.
Spontaneous redox reaction occurs.	Non-spontaneous redox reaction occurs.
Salt bridge is used.	Salt bridge is not used.
Used for the measurement of electrode potential.	Used for the extraction of metals, purification, electroplating and anodizing.
It generates heat (exothermic)	It consumes heat (endothermic)
 voltaic cell	 electrolytic cell
Daniel's cell, Ni-Cd cell, fuel cell	Nelson's Cell and Down's Cell

Voltaic or galvanic cell

Two half cells are present in voltaic cell

Left half cell (Oxidation half-cell)

Zn – electrode is dipped in 1M solution of $ZnSO_4$

Right half cell (Reduction half-cell)

Cu – electrode is dipped in 1M solution of $CuSO_4$

Salt bridge

It is aqueous solution of KCl in a gel

Working

- Connect both the half cells electrolytically through the salt bridge
- Close the external circuit by connecting the Zn and Cu electrodes.
- The electrons will flow from Zn to Cu through external circuit. The following reactions will occur at respective electrodes.

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At anode

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^- \text{ Oxidation}$$

At cathode

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \text{ Reduction}$$

- The voltaic cell reaction is represented by

$$Zn_{(s)} / Zn^{2+}_{(aq)}\ 1M \parallel Cu^{2+}_{(aq)}\ 1M / Cu_{(s)}$$

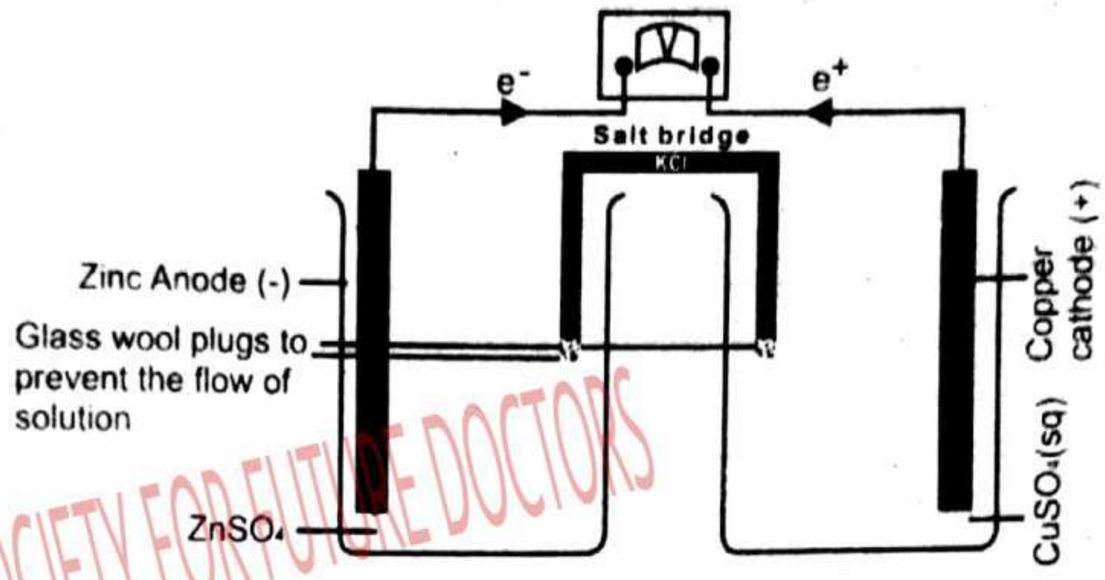
- emf of the cell

$$E^0 = 1.10\ V$$

Function of salt bridge

- Salt bridge acts as a passage for the transfer of negative ions (SO_4^{2-}) from right half-cell to left half-cell.
- If the exchange of SO_4^{2-} ions is stopped, then the oxidation-reduction reaction will stop due to charge accumulation in both half cells.

Replacing the external circuit by a source of high voltage can reverse the voltaic cell reactions. Such cell is called reversible cell.



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CALCULATION OF STANDARD CELL POTENETIAL

- Electrode having higher position in series will act as an anode, oxidation will take place on it
- Electrode having lower position in series, will act as cathode, reduction will take place on it.

For example in $Cu^{+2}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq)}$

Zn is at higher position in series so act as anode and oxidation will take place on it and Cu is at lower position in series so act as cathode and reduction will take place on it.

Standard Reduction potential of Cu

$$Cu^{2+} + 2e^- \rightarrow Cu \quad E^o_{red} = +0.34 \text{ Volts}$$

Standard Reduction potential of Zn

$$Zn^{+2} + 2e^- \longrightarrow Zn \quad E^o_{red} = -0.76 \text{ Volts}$$

Standard Oxidation potential of Zn

$$Zn \rightarrow Zn^{2+} + 2e^- \quad E^o_{oxi} = +0.76 \text{ Volts}$$

$$E^o_{cell} = E^o_{Oxi} + E^o_{red}$$

$$E^o_{cell} = +0.76 + (+0.34)$$

$$E^o_{cell} = 1.10 \text{ Volts}$$

$$Cu^{+2}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq)} \quad E^o_{(cell)} = 1.10 \text{ Volts}$$

Standard cell potential of Zn-Cu cell is 1.10 volts.

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USES OF STANDARD CELL POTENTIAL

(i) Explain/deduce the direction of electron flow in the external circuit

In voltaic cell electrons travel from oxidation half-cell to reduction half-cell externally through voltmeter. So direction of electrons is from anode to cathode.

- The electrons will flow from Zn to Cu through external circuit. The following reactions will occur at respective electrodes.

At anode

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^- \text{ oxidation}$$

At cathode

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \text{ Reduction}$$

(ii) Prediction of the feasibility of a chemical reaction

If the sum of E° values of the two half-cell reaction is positive, the reaction is feasible (spontaneous) and if it is negative then the reaction will not be feasible (non-spontaneous).

$$Cu^{+2}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq)} \quad E^o_{(cell)} = 1.10 \text{ Volts}$$

Voltaic cell consist of two half cells.

Methods used to measure the standard electrode potentials of metals

- Concerned electrode is joined with SHE and form a voltaic cell
- Salt bridge is used to connect both cells, filled with solution of KCl
- Voltmeter is attached to measure electrode potential
- Oxidation or reduction reaction occurs at SHE depending on the nature of the concerned electrode.
- When reduction occurs on SHE then volt meter reading will be +ve.

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(gas)}$$

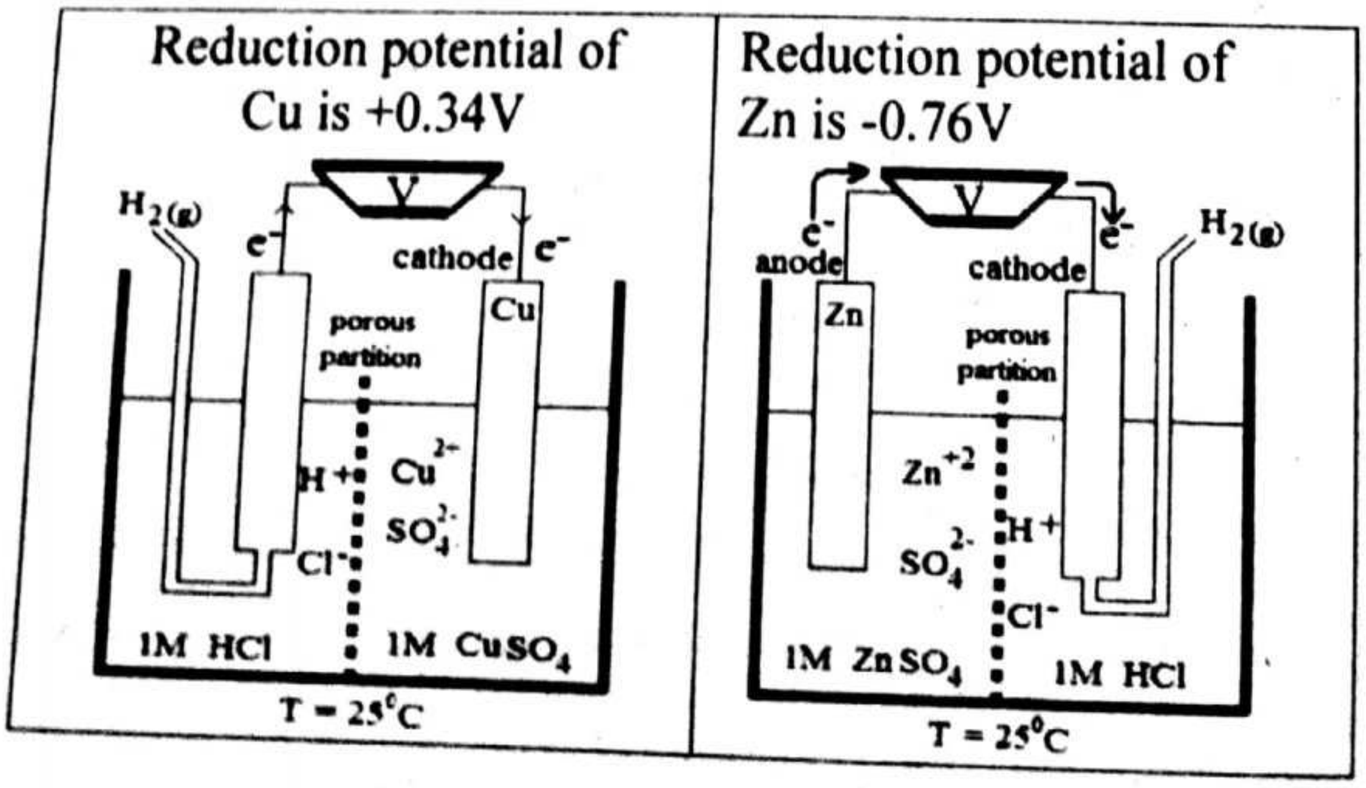
- When oxidation occurs on SHE then voltmeter reading will be in –ve

$$H_{2(gas)} \longrightarrow 2H^+_{(aq)} + 2e^-$$

- SHE act as cathode when connected with Zn
- Potential of Zn is called oxidation potential that is +0.76V so its reduction potential is –0.76
- SHE acts as anode when connected with Cu
- Potential of Cu is called reduction potential that is +0.346V so its oxidation potential is -0.34

POINT TO PONDER

An electrode potential is measured by finding the emf of a cell composed of the electrode and a standard electrode, e.g. the SHE which has E = 0, or the calomel electrode.



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THE ELECTROCHEMICAL SERIES

When elements are arranged in the order of their increasing standard reduction potentials on the hydrogen scale, the resulting list is known as electrochemical series.

Element	Electrode	Standard Reduction Potential (E°)
Li	$Li^+ + e^- \rightarrow Li$	
K	$K^+ + e^- \rightarrow K$	-3.045
Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.925
Na	$Na^+ + e^- \rightarrow Na$	-2.87
Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.714
Al	$Al^{3+} + 3e^- \rightarrow Al$	-2.37
Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	-1.66
Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.76
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.74
Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.44
Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.403
Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.25
Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.14
H_2	$2H^+ + 2e^- \rightarrow H_2$	-0.126
Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	0.000
Cu	$Cu^+ + e^- \rightarrow Cu$	+0.34
I_2	$I_2 + 2e^- \rightarrow 2I^-$	+0.521
Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	+0.535
Ag	$Ag^+ + e^- \rightarrow Ag$	+0.771
Hg	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.794
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	0.885
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.08
Au	$Au^{3+} + 3e^- \rightarrow Au$	+1.360
F_2	$F_2 + 2e^- \rightarrow 2F^-$	+1.50
		+2.87

Increasing strength as an oxidizing agent / Increasing reduction potentials

Increasing strength as a reducing agent / decreasing reduction potentials

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APPLICATIONS OF ELECTROCHEMICAL SERIES

Prediction of the feasibility of a chemical reaction

If the sum of E° values of the two-half-cell reaction is positive, the reaction is feasible and if it is negative then the reaction will not be feasible.

$$Cu^{+2}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq)} \qquad E^\circ_{(cell)} = +1.10 \text{ Volts}$$

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Calculation of the voltage or emf of the cell

- Electrode having higher position in series will act as an anode, oxidation will take place on it
- Electrode having lower position in series, will act as cathode, reduction will take place on it

$$E^{o}_{cell} = E^{o}_{Oxi} + E^{o}_{red}$$

Comparison of relative tendency of metals and non-metals to get oxidized or reduced

Greater value of standard reduction electrode potential greater will be the tendency to accept electron and undergo reduction and vice versa.

Relative chemical reactivity of metals

Greater value of the standard reduction potential of a specie lesser will be its tendency to lose electron to form +ve ion hence lesser will be its reactivity.

POINT TO PONDER

A redox reaction will go almost to completion between two redox systems which differ in their reduction potential.

Reaction of metals with dilute acids

Greater the value of standard reduction potential of a metal, lesser its tendency to lose electrons to form metal ions and so weaker its tendency to displaced H_2 from acids. For example, Au, Pt, Ag and Cu do not liberate hydrogen from acids.

Displacement of one metal by another from its solution

Metal will displace another metal from the aqueous solution of its salt if it lies above the electrochemical series. For example, Fe can displace Cu from $CuSO_4$. Zn does not displace Mg from solution of $MgSO_4$.

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TOPIC-10 CHEMICAL BONDING

COURSE CONETENTS

- Atomic size, Ionic radii and covalent radii
- Ionization energy
- Electron affinity and electronegativity
- Types of bonds
- Electrovalent or ionic bond
- Covalent bond
- Co-ordinate covalent or dative bond
- The valence shell electron pair repulsion theory
- Postulates of VSEPR theory
- Sigma bond pi bond
- Hybridization (sp^3, sp^2, sp)
- Bond energy and bond length
- Energetic of bond formation
- Ionic character of covalent bond (Dipole moment)

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INTRODUCTION

Chemical bond

- The force which holds two or more atoms or ions to form a large variety of compounds is called chemical bond.

Causes of chemical combination

Atoms of elements combine with each other to stabilize themselves. Two factors are necessary for their satisfaction;

- Every atom tries to attain electronic configuration near to a noble gas. (Wants to follow octet rule). The tendency of atoms to attain a maximum of eight electrons in the valence shell is called octet rule.
- Each atom tries to attain lowest energy state because it is a stable state.

ATOMIC SIZES

Particulars	Atomic radii	Ionic radii	Covalent radii
Definition	It is the average distance between the nuclei of an atom and its outermost electronic shell	It is the average distance between the nuclei of an ion and its outermost electronic shell	It is the half of the single bond length between two similar atoms covalently bonded in a molecule
Trend along the period	From left to right, it decreases	From left to right, it decreases	From left to right, it decreases
Trend down the group	Increases from top to bottom	Increases from top to bottom	Increases from top to bottom
Effect of the shielding effect	Greater shielding effect results in larger radii	Greater shielding effect results in larger radii	Greater shielding effect results in larger radii

NOTE: Cationic radius is smaller than parent atom while the anionic radius is larger than the parent atom.

IONIZATION POTENTIAL, ELECTRON AFFINITY AND ELECTRONEGATIVITY

Particular	I.P/I.E	E.A	E.N
Definition	Energy required to remove an electron from the outer most shell of gaseous atom	Energy released when an electron is added to the outer most shell of gaseous atom	Tendency of an atom to attract a shared pair of electron
First, second and third energies	1^{st} I.P is lesser, 2^{nd} is higher and 3^{rd} is much higher	1^{st} E.A is exothermic while 2^{nd} and 3^{rd} E.A is endothermic.	Not applicable
Trend down the group	Top to bottom decreases	Top to bottom decreases; sometimes energy is absorbed	Top to bottom decreases
Trend along the period	Left to right increases	Left to right increases	Left to right increases
Effect of atomic size	I.P decreases as atomic size increases	E.A decreases as atomic size increases	E.N decreases as atomic size increases
Effect of nuclear charge	High nuclear charge, high value of I.P	High nuclear charge, high value of E.A	High nuclear charge, high value of E.N
Effect of the shielding effect	Greater shielding effect results in lesser I.P value	Greater shielding effect results in lesser E.A value	Greater shielding effect results in lesser E.N value

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POINT TO PONDER

Ionization energy is the index of Metallic Character

Low I.E → metals. Intermediate I.E → metalloids and high I.E → nonmetals

Exceptional Cases of Ionization energy:

- Among **Li, Be, B → Be** has maximum I.E
- Among **N, O, F, Ne, → Ne** has maximum I.E because Ne has stable electronic configuration
- Among **B,C,N,O, → N** has maximum I.E because N has half filled p-sub-shell
- Among **Ga, In, Tl, → Tl** has highest I.E because of poor shielding effect
- Among **Ca, Sr, Ba, → Sr** has maximum I.E because of poor shielding effect
- Among **F, Cl, → Cl** has more electron affinity
- The element of group IIA, VA, and VIIIA shows abnormal trend. This can be understood from the distribution of the electrons.

TYPES OF BOND

(i) Electrovalent or ionic bond
(ii) Covalent bond
(iii) Co-ordinate covalent or dative bond

ELECTROVALENT OR IONIC BOND

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Ionic Bond

The electrostatic force of attraction between oppositely charged ions is called ionic bond or electrovalent bond.

OR

Ionic bond is formed by the complete transfer of electrons from more electropositive elements to more electronegative elements.

POINT TO PONDER

In some ionic compounds there is a degree of sharing of electron clouds between cations and anions.

Conditions necessary for ionic bond formation

- Electropositive elements with low ionization energy like I-A and II-A that lose electron and form cation.
- Electronegative elements with high electron affinity like VI-A and VII-A that gain electron and form anion.

Ionic bond is non-rigid and non-directional.

(I) Formation of NaCl

(i) $Na_{(g)} \longrightarrow Na^{+}_{(g)} + 1e^{-}$ $\quad \Delta H = 496$ kJ/mole

2, 8, 1 $\quad$ 2, 8

(ii) $Cl_{(g)} + 1e^{-} \longrightarrow Cl^{-}_{(g)}$ $\quad \Delta H = -349$ kJ/mole

2, 8, 7 $\quad$ 2, 8, 8

Then sodium and chloride ions combine to form NaCl.

$Na^{+}_{(g)} + Cl^{-}_{(g)} \longrightarrow NaCl_{(s)}$ $\quad \Delta H_f = -787 kJmole^{-1}$

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(2) Formation of CaO

(i) $Ca_{(g)} \longrightarrow Ca^{+2}_{(g)} + 2e^-$ $\Delta H = 1735 kJmole^{-1}$ $(I_1 = 590 + I_2 = 1145)$

2,8,8,2 2, 8, 8

(ii) $O_{(g)} + 2e^- \longrightarrow O^{-2}_{(g)}$ $\Delta H = 639 kJmole^{-1}$ $(E.A_1 = -141 + E.A_2 = +780)$

2, 6 2, 8

Then Ca^{+2} and O^{-2} combine to form CaO.

$Ca^{+2}_{(g)} + O^{-2}_{(g)} \longrightarrow CaO_{(s)}$ $\Delta H_f = -3414 kJmole^{-1}$

COVALENT BOND

(i) Covalent Bond

A bond formed by mutual sharing of electron between the two atoms is called covalent bond.

Hydrogen molecule

When two hydrogen atoms share their valence electrons, a covalent bond is formed.

$$H\times + \bullet H \rightarrow H\times\bullet H \text{ or } H—H$$

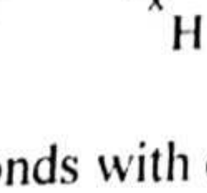
Chlorine molecules

When two chlorine atoms share their valence electrons, a covalent bond is formed.

$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \rightarrow :\ddot{\underset{\cdot\cdot}{Cl}}\cdot\cdot\ddot{\underset{\cdot\cdot}{Cl}}: \text{ or } Cl — Cl$$

Hydrogen chloride molecule $H\cdot\cdot\ddot{\underset{\cdot\cdot}{Cl}}:$ or H – Cl

Methane molecule



Oxygen molecules

When two oxygen atoms share their valence electrons, a double covalent bond is formed.

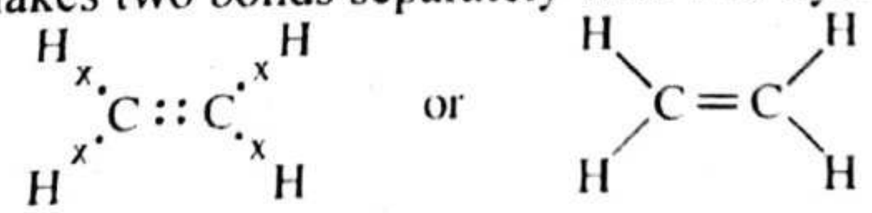
$$\ddot{\underset{\times\times}{O}} :: \ddot{\underset{\cdot\cdot}{O}} \quad \text{or} \quad \ddot{\underset{\times\times}{O}} = \ddot{\underset{\cdot\cdot}{O}}$$

POINT TO PONDER

There is no sharp distinction between an ionic bond and a covalent bond.

Ethene

When two carbon atoms share their valence electrons, a double covalent bond is formed. Each carbon atom makes two bonds separately with two hydrogen atoms.



Carbon dioxide:

Two carbon atoms two bonds with each of the oxygen atoms separately.

$$\ddot{\underset{\times\times}{O}} :: C :: \ddot{\underset{\times\times}{O}} \quad \text{or} \quad \ddot{\underset{\times\times}{O}} = C = \ddot{\underset{\times\times}{O}}$$

NOTE: *A bond formed by the sharing of one electron from each of the bonding atoms is called* ***single covalent bond****. It is represented by (—)*

A bond formed by sharing of two electrons from each of the bonding atoms is called ***double covalent bond****. It is represented by two dashes (=)*

A bond formed by the sharing of three electrons from each of the two bonding atoms is called as ***triple covalent bond****. It is represented by three dashes (≡).*

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TYPES OF COVALENT BONDS

Non-polar Covalent Bond	Polar Covalent Bond
A covalent bond between two similar atoms or those having negligible electronegativity difference. 0 – 0.4	A covalent bond between two dissimilar atoms having appreciable electronegativity difference but less than 1.7 and greater than 0.4
The shared pair of electrons is equally attracted by the two bonded nuclei	The shared pair of electron is un- equally attracted by the two bonded nuclei.
Electron cloud is symmetrical around the two nuclei.	Electron cloud is unsymmetrical around the two nuclei.
No partial charges appear on the molecule because of symmetrical electrons cloud.	Partial positive and partial negative charges appear because of unsymmetrical electrons cloud.
No polarity is developed on the molecule.	There is polarity in the molecule.
Compounds having non-pólar bonds have weak intermolecular attraction.	Compounds having polar bonds have strong intermolecular attraction usually
Compounds having non-polar bond have low boiling point and melting point with less solubility in water.	Compounds having polar bonds have high melting point and boiling point with high solubility in water.
It is a weak bond	It is a strong bond.
Example: H — H	Example: $H^{\delta+} — Cl^{\delta-}$

PROPERTIES OF IONIC COMPOUNDS AND COVALENT COMPOUNDS

No.	Properties	Ionic Compounds	Covalent Compounds
1	Conductivity	Conduction of electricity Non-conductor in solid state. Conductor in fused or aqueous state.	Non-conductor but electrolytic solutions are conductor
2	Thermodynamic properties	High melting point	Low melting point and boiling point
3	Alignment	The bond is non-directional and non-rigid.	The bond is directional and rigid
4	Crystalline properties	Show polymorphism and isomorphism.	Show isomerism
5	Reaction rate	Rate of reaction is very high	Rate of reaction is low
6	Solubility	Soluble in polar solvents.	Like dissolve like

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CO-ORDINATE COVALENT BOND (DATIVE BOND)

- A covalent bond formed by the donation of an electron-pair by one of the bonded atoms to other is called Co-ordinate covalent bond or dative or Donor-acceptor bond.
- Co-ordinate covalent bond is formed by overlapping of one completely filled orbital with one empty orbital.
- An atom that donates a pair is called donor atom (Lewis base) and one that accepts a pair is called acceptor (Lewis acid).
- This bond is represented by an arrow pointing from donor to acceptor.

Ammonium ion formation

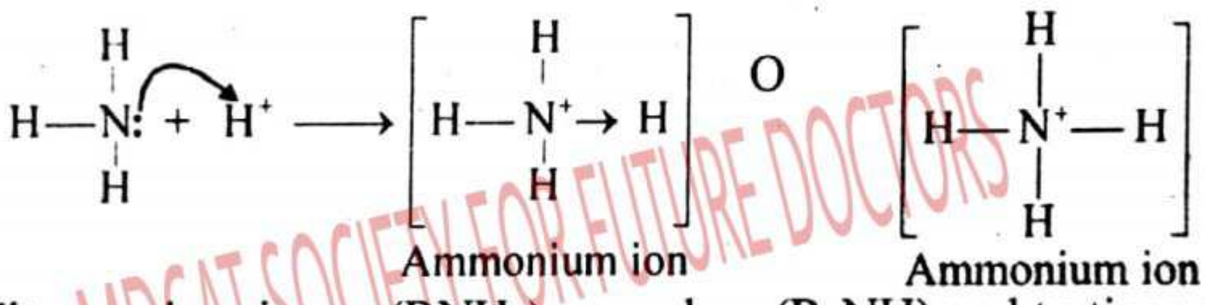
- Nitrogen in NH_3 donates its lone pair to H^+ to form Co-ordinate covalent bond and to give $^+NH_4$ (Ammonium ion). In ammonium ion all the bonds behave alike with 25% coordinate covalent and 75% covalent character.

POINT TO PONDER

In Co-ordinate covalent formation

(i) If both donor and acceptor are neutral, before the bond formation, then donor will get positive charge and acceptor will get negative charge after the bond formation.

(ii) If donor is negatively charged and acceptor is positively charge before bond formation, then both will become neutral after bond formation.

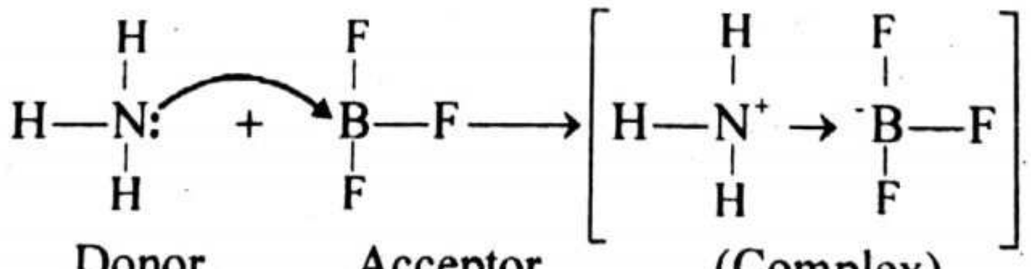


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Similarly, Nitrogen in primary (RNH_2) secondary (R_2NH) and tertiary amines (R_3N) form this bond with H^+.

Dative bonding between NH_3 and BF_3

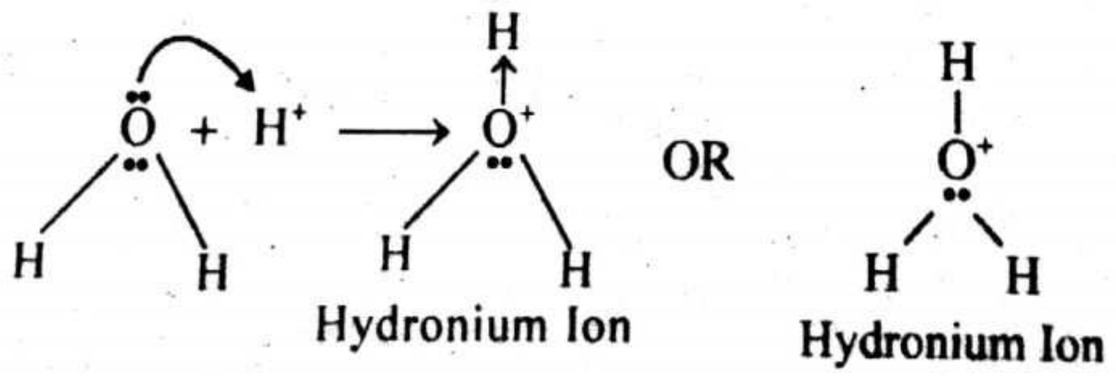
Nitrogen atom in $\ddot{N}H_3$ have lone pair and it donates it to Boron in BF_3 (which is electron deficient of octet) to form a co-ordinate covalent bond.



In this case donor develops a positive charge and acceptor gets negative charge.

Hydronium ion formation

Oxygen in water donates a lone pair to form co-ordinate covalent bond to give H_3O^+. After this bond formation, distinction between covalent and Co-ordinate covalent bond vanishes i.e. all the bonds behave alike with 33% co-ordinate covalent and 66% covalent character.



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VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR THEORY)

"The valence electron pairs (lone pairs and the bond pairs) are arranged around the central atom to remain at a maximum distance apart to keep repulsion at a minimum."

Lone Pair is not involved in determining the shape of the molecules. The acronym "VSEPR" is pronounced "vesper"

Introduced by

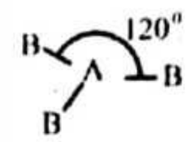
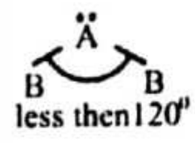
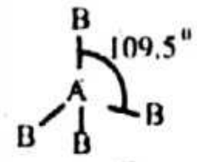
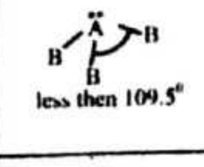
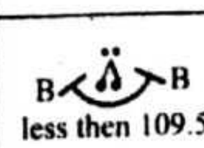
Sidgwick and Powell and Nylholm and Gillespie

Postulates

- Both lone pair and bond pair determine the geometry of the molecules
- Lone pair occupies more space than a bond pair
- The magnitude of repulsion is in the following order
- Lone pair – Lone pair > Lone pair – Bond pair > Bond pair – Bond pair
- Double bond and triple bond behaves like a single bond in determining the geometry of the molecule.

POINT PONDER

Lone pairs are closer to the nucleus than bonding pairs and exert a greater repulsive force.

Type	Electron Pairs: Total	Electron Pairs: Bonding	Electron Pairs: Lone	Arrangement of pairs	Molecular geometry	Shape	Examples
AB_2	2	2	0	Linear	Linear	B–A–B	$BeCl_2$, $HgCl_2$, CO_2
AB_3	3	3	0	Trigonal planar	Trigonal planar		BH_3, BF_3 $AlCl_3$, SO_3
		2	1		Bent (or angular)		$SnCl_2$, SO_2
AB_4	4	4	0	Tetrahedral	Tetrahedral		CH_4, $SiCl_4$, CCl_4, BF_4^- NH_4^+, SO_4^{-2}
		3	1		Trigonal pyramidal		NH_3, NF_3 PH_3
		2	2		Bent (or angular)		H_2O, H_2S

Limitations

VSEPR theory predicts and explains the shapes of molecules but does not give reasons for the formation of bonds.

It is not applicable for single bond pair system means di-atomic molecules.

Complexes do not follow this theory.

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SIGMA AND Pi BOND (VALANCE BOND THEORY)

Postulates of VBT:

Over-lapping is a necessary condition for bond formation.
Only half filled orbitals participate in overlapping during covalent bond formation.
Greater the overlapping, stronger is the bond formed.
Electrons with opposite spin pair up to stabilize themselves during bond formation (overlapping).

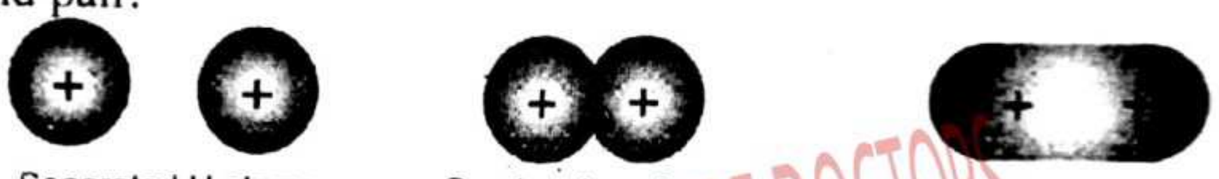
Sigma(σ) bond: A bond formed by head to head (end to end) overlapping where the probability of finding the **shared pair around the line joining the two nuclei is maximum** is called as sigma bond.

Pi(π) bond: A bond formed by the parallel overlapping where the **probability of finding shared pair above and below the line joining the two nuclei is maximum** is called pi bond.

π-bond is a weaker bond than sigma bond.

H_2-molecule

When two hydrogen atoms approach each other, their half-filled 1s orbital undergo overlapping to form a sigma bond. One electron from each of 1s form a pair called shared/bond pair.



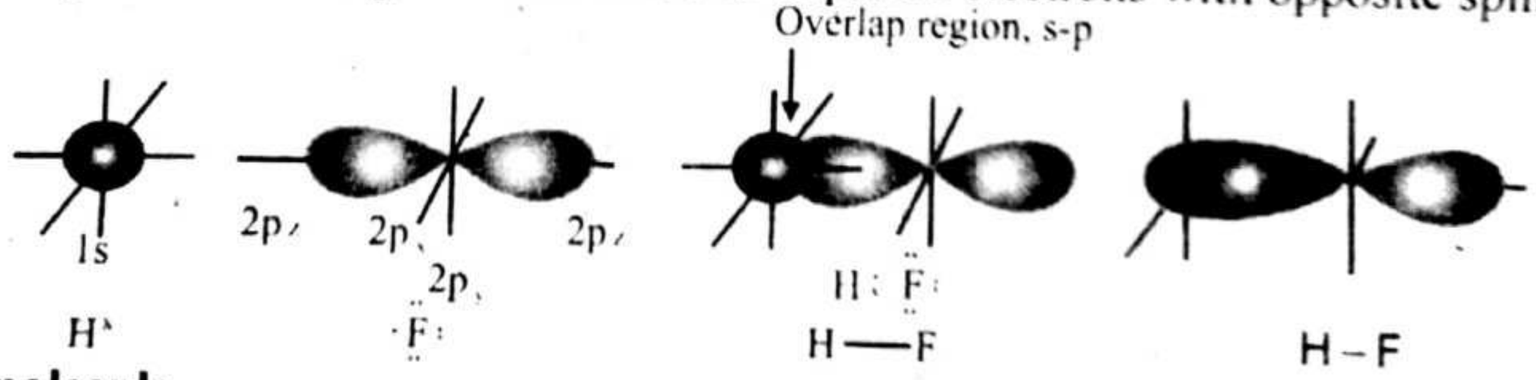
HF molecule

The electronic configuration of both atoms are

$H_1 = 1s^1$

$F_9 = 1s^2, 2s^2, 2p^2_x, 2p^2_y, 2p^1_z$,

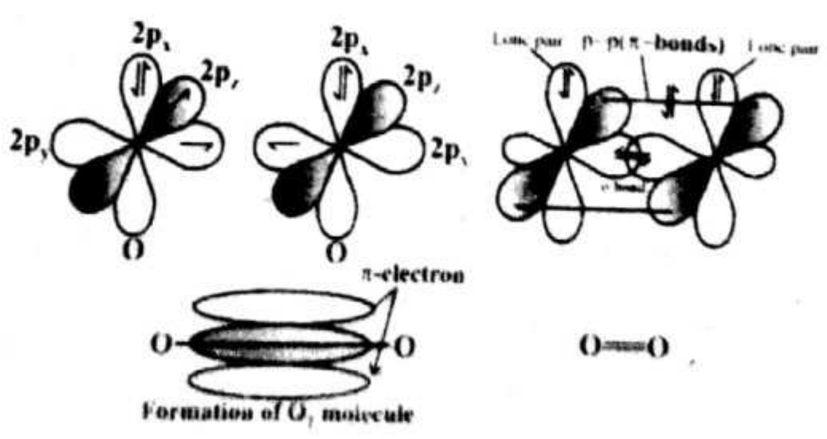
The two half-filled orbitals (1s from H-atom and $2p_z$ from F-atom) undergo linear overlap and form a sigma bond. The two unpaired electrons with opposite spin paired up.



O_2 molecule

The electronic configuration of oxygen atoms is $O_8 = 1s^2, 2s^2, 2p^2_x, 2p^1_y, 2p^1_z$.

Each oxygen atom has two partially filled p-orbitals i.e. p_y and p_z. One p_x orbital from each of the two oxygen atoms undergo linear overlapping to form a sigma bond. Whereas, two p_z orbitals from each oxygen atom undergo parallel overlapping to form a pi-bond.



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COMPARISON BETWEEN σ-BOND AND π-BOND

Sigma bond	Pi bond
A bond formed by linear overlapping of two half filled atomic orbitals of adjacent atoms is called a sigma bond.	A bond formed by the sidewise overlapping of two half filled parallel atomic orbitals of adjacent atoms is called a pi bond.
Electron density is concentrated around the bond axis.	Electron density lies above and below the bond axis.
It has only one lobe of electron density between the nuclei.	It has two lobes of electron density on opposite sides of bond axis.
Only one sigma bond can exist between two atoms.	One or more pi bonds can exist between two atoms.
It offers free rotation about the bond axis	It offers no free rotation about the bond axis.
It has no nodal plane.	It has a nodal plane along the bond axis.
The sigma bonds present in the molecule determine its shape.	Pi bond has no effect on the shape of the molecule.

ATOMIC ORBITAL HYBRIDIZATION

Hybridization

A process in which atomic orbitals of different energies and shapes are mixed together to form a new set of equivalent orbitals of the same energy and same shape is called hybridization

- Hybridization is a process of mixing of orbitals in a single atom (or ion).
- Only orbitals of comparable (relatively close) energies can be mixed to form hybrid orbitals.
- The number of hybrid orbitals is always equal to the number of orbitals which are mixed.
- Once an orbital has been used to form hybrid orbitals, it is no longer available for the electrons.

Hybrid atomic orbitals

The atomic orbitals of same energy, which have been formed due to mixing of different orbitals of different energies, are called the hybrid atomic orbitals.

TYPES OF HYBRIDIZATION

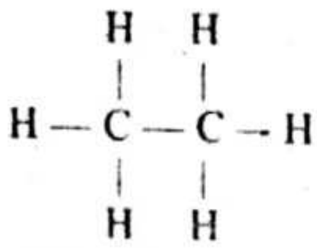
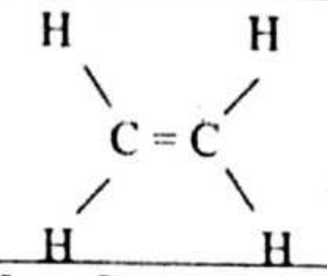
In Hydrocarbons

Particular	sp^3	sp^2	sp
Definition	Mixing of one-s and three p-atomic orbitals	Mixing of one-s and two p-atomic orbitals	Mixing of one-s and one p-atomic orbitals
Geometry	Tetrahedral	Trigonal planar	Linear
Nature of bonds	4 σ-bonds	3 σ-bonds, 1π-bond	2 σ-bonds and 2 π-bonds

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Structure of hydrocarbons on basis of hybridization

Structure	Number of bonds	Hybridization	Bond angle	Sigma bonds	Pi bonds
	7	sp^3	109.5^0	7	0
	6	sp^2	120^0	5	1
H – C ≡ C – H	5	sp	180^0	3	2

BOND ENERGY, BOND LENGTH

Bond energy

The average amount of energy required to break all bonds of a particular type in one mole of the substance is called bond energy.

- Unit of bond energy is kJ/mole.

Factors Effecting Bond Energy

The bond energy is the measure of the strength of bond. The strength of a bond depends upon the following factors.

(i) Electronegativity difference of bonded atoms
(ii) Sizes of the atoms
(iii) Bond length
(iv) Nature of orbital

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Applications of bond energy

- Relative strength of bonds
- % of ionic character in bond
- Estimation of ΔH (Difference of bond breaking and bond forming energies)

Bond	Bond energy ($kJmol^{-1}$)	Bond	Bond energy ($kJmol^{-1}$)	Bond	Bond energy ($kJmol^{-1}$)
C — C	348	H — F	567	F — F	155
C = C	614	H — Cl	431	Cl — Cl	242
C ≡ C	839	H — Br	366	N ≡ N	941
C — H	413	H — I	299	Br — Br	193
H — H	436	O = O	495	I — I	151

Bond Length

The distance between the nuclei of two atoms forming a covalent bond is called bond length.

- Techniques used to determine bond length are electron diffraction, X-ray diffraction or spectral studies.
- Greater the E.N difference between bonded atoms, shorter will be bond length.
- Ionic character shortens bond length.
- Greater the atomic radii of the bonded atoms larger will be the bond length.

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- Involvement of π-bond reduces bond length.
- Greater s-character in the hybrid orbital lower will be the bond length
- Along the period, bond length decreases.
- Down the group, bond length increases.

Compound	Bond	Bond length (pm)	Compound	Bond	Bond length (pm)
BF_3 (sp^2 hybridized)	B-F	130	C_2H_6 (sp^3 hybridized)	C-C	154
BCl_3 (sp^2 hybridized)	B-Cl	175	C_2H_4 (sp^2 hybridized)	C=C	133
SiH_4 (sp^3 hybridized)	Si-H	148	C_2H_2 (sp hybridized)	C≡C	120
SiF_4 (sp^3 hybridized)	SI-F	155	$(CH_3)_2C=O$ (sp^2 hybridized)	C=O	122

DIPOLE MOMENT

"The product of electric charge and the distance between two opposite charged centres is called the dipole moment". It is a vector quantity.

Formula:

The mathematical form is, $\mu = q \times r$

Where μ = dipole moment,

q = charge,

r = distance between the center of charges

Unit:

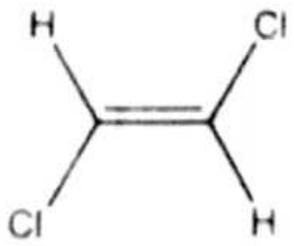
Its unit is mC (SI unit) or Debye (D). $1D = 3.336 \times 10^{-30}$ mC

Applications:

Determination of polarity of molecule:

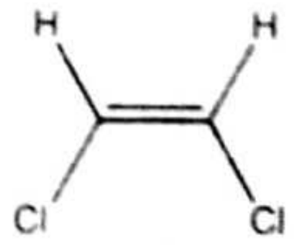
Molecules which have zero dipole moment are non-polar whereas molecules which have some dipole moment are polar. For example benzene has zero dipole moment, so it is non polar. But chlorobenzene has dipole moment of 1.54D, so it is polar.

The study of dipole moment also finds applications in stereochemistry. For example, dipole moments of isomer 1,2-dichloroethene have been calculated are given below:



Trans

$\mu = 0$ D



Cis

μ = 1.89D

Thus knowing the dipole moment of the given sample of 1,2-dichloroethene, one can predict whether it is Cis or the Trans isomer.

Calculation of %age ionic character in a bond:

It is used to find the %age ionic character in a compound by the following formula.

$$\%\text{age ionic character} = \frac{\mu_{(obs)}}{\mu_{(ionic)}} \times 100$$

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Relation between molecular geometry and dipole moment

Formula	Dipole Moment	Molecular Geometry
AX	Can be non-zero	Linear
AX_2	Zero	Linear
	Can be non-zero	Bent
AX_3	Zero	Trigonal planar
	Can be non-zero	Trigonal pyramidal
	Can be non-zero	T-shaped
AX_4	Zero	Tetrahedral
	Zero	Square planar
	Can be non-zero	See saw
AX_5	Zero	Trigonal bipyramidal
	Can be non-zero	Square pyramidal
AX_6	Zero	Octahedral

Electronegativity difference and nature of bond

(i) If electronegativity difference between two atoms is zero or ≤ 0.4 then bond will be non-polar covalent bond

(ii) If electronegativity difference between two atoms is greater than 0.4 and less than 1.7 then bond will be polar covalent bond

(iii) If electronegativity difference is equal to 1.7 then 50% ionic and 50% covalent character

(iv) If electronegativity difference is greater than 1.7 then bond will be ionic

NOTE: Electronegativity difference in H – F is 1.9 but it is polar covalent bond

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TOPIC-11 ⟫ s AND p BLOCK ELEMENTS

COURSE CONTENTS

- Atomic Radius, Ionic Radius
- Ionization Energy, Electronegativity, Electron Affinity
- Metallic Character
- Melting and Boiling Point
- Electrical Conductivity
- Group-1 Element (Alkali Metals), Trends in Reactivity
- Reactions of Group-IA with Water, Oxygen and Chlorine
- Group-2 Elements (Alkaline earth metals), Trends in reactivity
- Reaction of Group-IIA with Water, Oxygen and Nitrogen
- Reaction of Period III-A Elements with Water, Oxygen and Chlorine
- Reaction of Group III-A Elements (Only Aluminium)

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INTRODUCTION

Modern periodic law (Moseley)

The physical and chemical properties of elements are the periodic function of their atomic numbers.

Periodicity

The repetition of properties after regular intervals is called periodicity

POINT TO PONDER

Periodic Table	Elements arranged in order of increasing proton number
Group Number	Number of electrons in outermost shell (valence electrons)
Period Number	Number of shells of electrons
Valence Electron	Electron in outermost shell
Metals	Elements with 1-3 valence electrons except boron
Non-metals	Elements with 4-7 valence electrons
Inert gases	Elements with full outermost-shell

Periods

- The horizontal rows of elements in the periodic table are called periods.
- All elements in a period have same number of shells.
- There are seven periods in the periodic table that are known by Arabic numerals 1 to 7.

Sr. No.	Peculiarity	Sub-groups present	No. of elements	s-block elements	p-block elements	d-block elements	f-block elements
1	Shortest	A	2	2	0	0	0
2	Short	A	8	2	6	0	0
3	Short	A	8	2	6	0	0
4	Long	A and B	18	2	6	10	0
5	Long	A and B	18	2	6	10	0
6	Longest	A and B	32	2	6	10	14
7	Incomplete	A and B	26	2	-	10	14

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POINT TO PONDER

The period 2 and 3 contain eight elements each and are called short periods. All the elements in these periods are representative and belong to A subgroups. In these periods, every eighth element resembles in properties with the first one.

- Lithium and Beryllium in the second period resemble in most of their properties with Sodium and Magnesium in the third period respectively.
- Boron in the second period and Aluminium in the third period have same oxidation state of +3.
- Fluorine in the second period has close resemblance with Chlorine in the third period.

s-Block Elements:

The elements in which s-orbital is under the process of filling or has filled are called s-block elements. OR The valence electrons in these elements occupy the "s" orbital.

Example:

For example, the elements of IA (alkali metals) and IIA (alkaline earth metals) groups constitute the "s" block of the periodic table. s-Block elements consist of only metals.

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p-Block Elements:

The elements in which p-orbital is under the process of filling or has filled are called p-block elements. OR These elements have outer electronic configuration of ns^2np^{1-6}.

Example:

For example, elements of Group IIIA, IVA, VA, VIA, VIIA (halogens) and VIIIA (noble gases or zero group) are known as p-block elements. p-Block elements include both metals and non-metals.

VARIATION IN THE PHYSICAL PROPERTIES OF ELEMENTS BELONGING TO PERIOD 2 AND 3

Property	Definition	Trend in a group (down the group)	Responsible Factors.	Trend along a period (from left to right)
Atomic radius	Half of the distance between the centers of two adjacent atoms of any element.	Increases	Nuclear charge and number of shells	Decreases
Ionic radius	Distance between the center of an ion and the outer boundary of its electron cloud.	(for similar charged ions)increases	Nuclear charge and number of shells.	Decreases for iso-electronic +ve and –ve ions.
Melting and boiling points	Specific temperature at which an element changes to liquid or gaseous state.	In case of IA and IIA decreases and for VIIA increases	Number of valence electrons	I-A to IV-A increases V to VIII decreases
Ionization energy	Minimum quantity of energy, which is required to remove an electron from the outer most shell of its isolated, gaseous atom in its ground state.	Decreases	Nuclear charge, atomic size and shielding effect.	Increases
Electronegativity	The tendency of an atom to attract a shared electron pair to words it self	Decreases	I.E and E.A of bonded atoms The structure of the atom and the number and kind of atoms with which it may combine.	Increases
Electron affinity	Energy released or absorbed, when an electron is added to a gaseous atom to form a negative ion.	Decreases	Size of atom, nuclear charge and vacancies in valence shell.	Increases
Metallic character	Tendency to lose electron and form cations and basic oxides.	Increases	Atomic size and nuclear charge.	Decreases
Electrical conductance	Ability to conduct electricity.	(increases for IA and IIA) no regular trend for transition metals	Lose electrons in outer shell	Decreases

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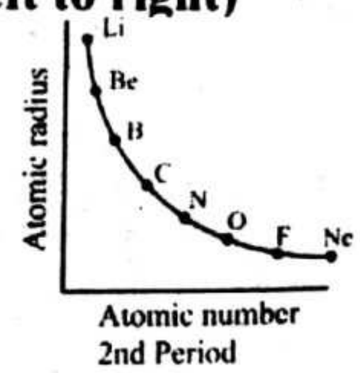
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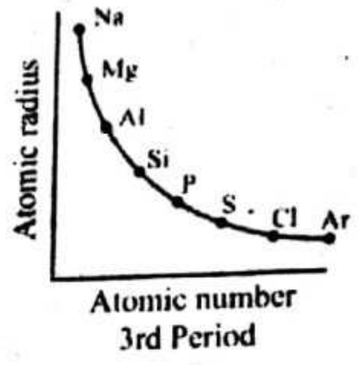
The most E.N element in the periodic table is fluorine. On Pauling scale its value is 4.00 with no unit

GRAPHS FOR VARIOUS TRENDS IN PERIODIC TABLE

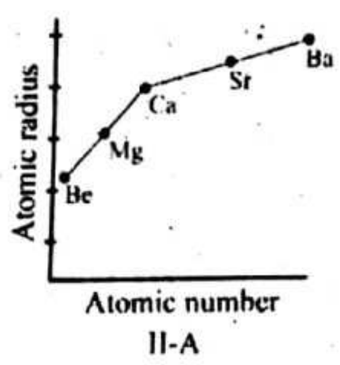
(i) Atomic radius

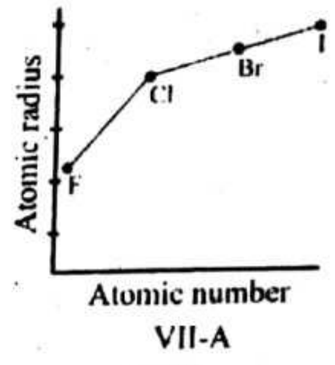
Along the period (left to right)





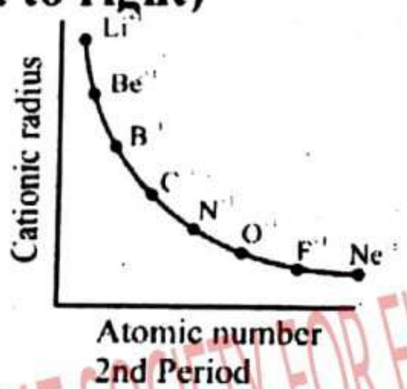
Down the group

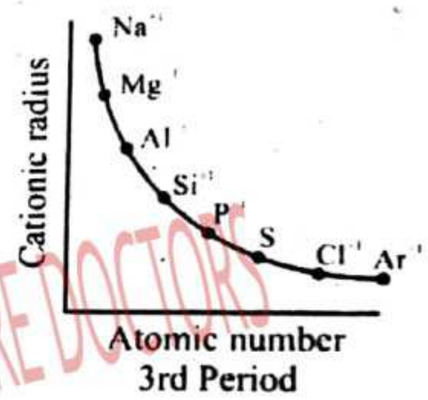




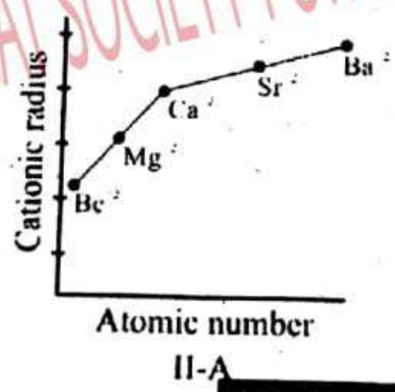
(ii) Ionic radius

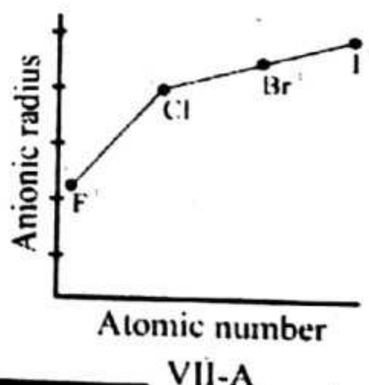
Along the period (left to right)





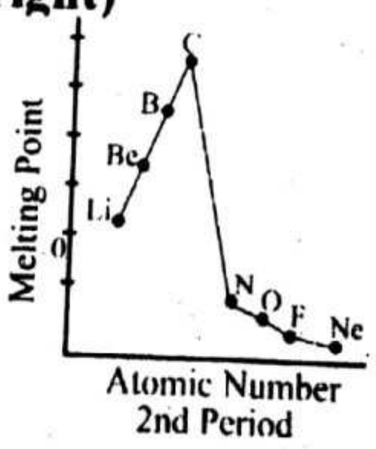
Down the group

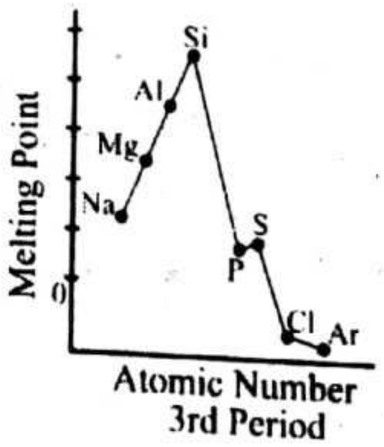




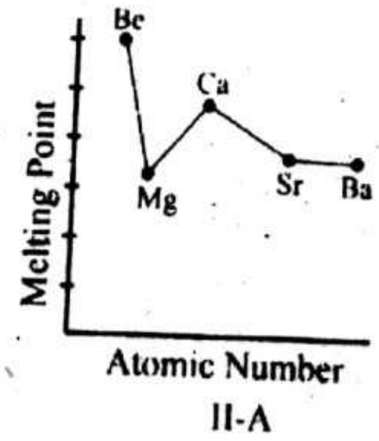
(iii) Melting point

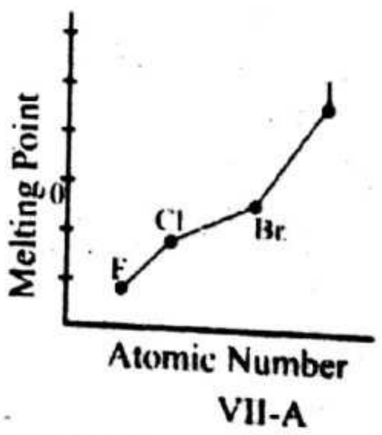
Along the period (left to right)





Down the group



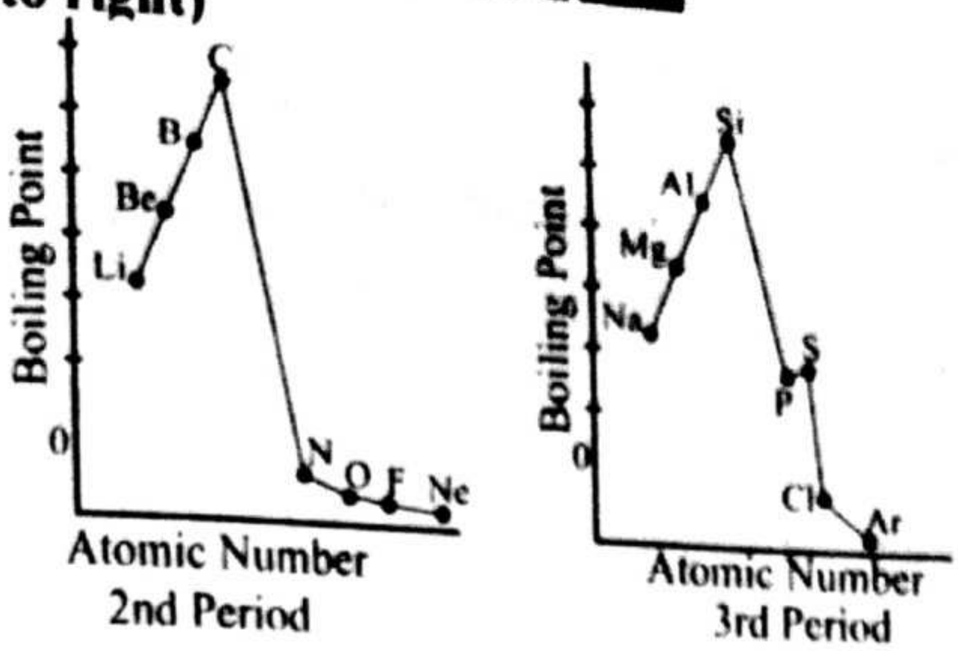


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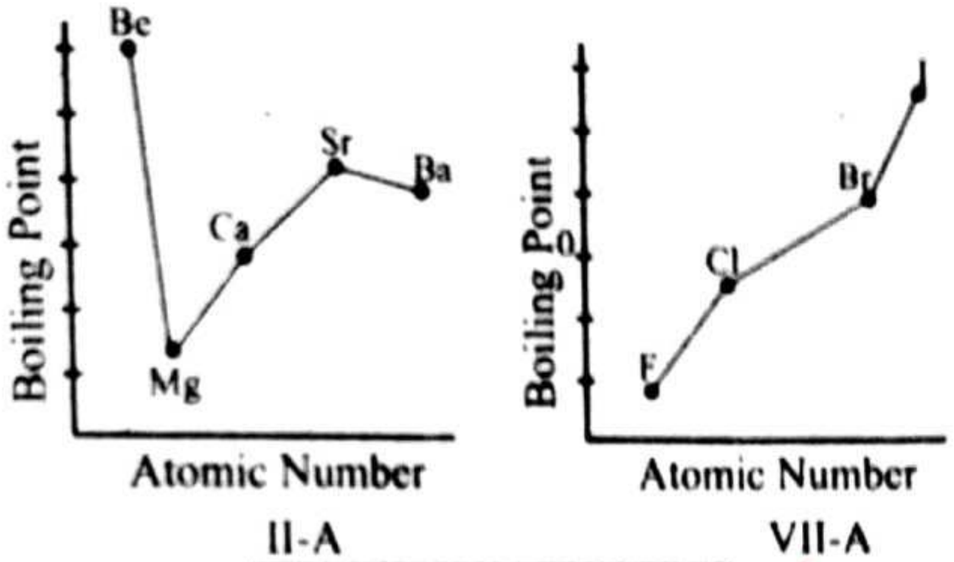
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(iv) Boiling point

Along the period (left to right)

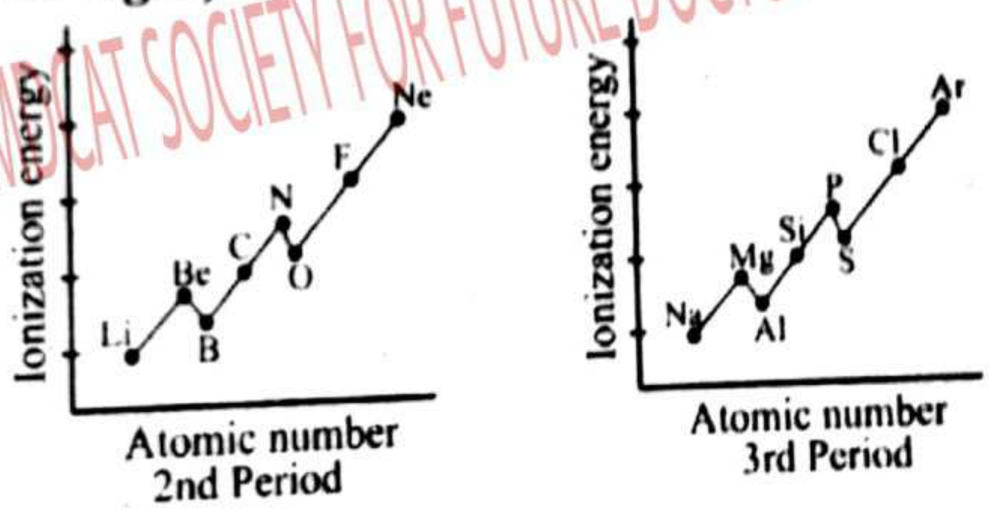


Down the group

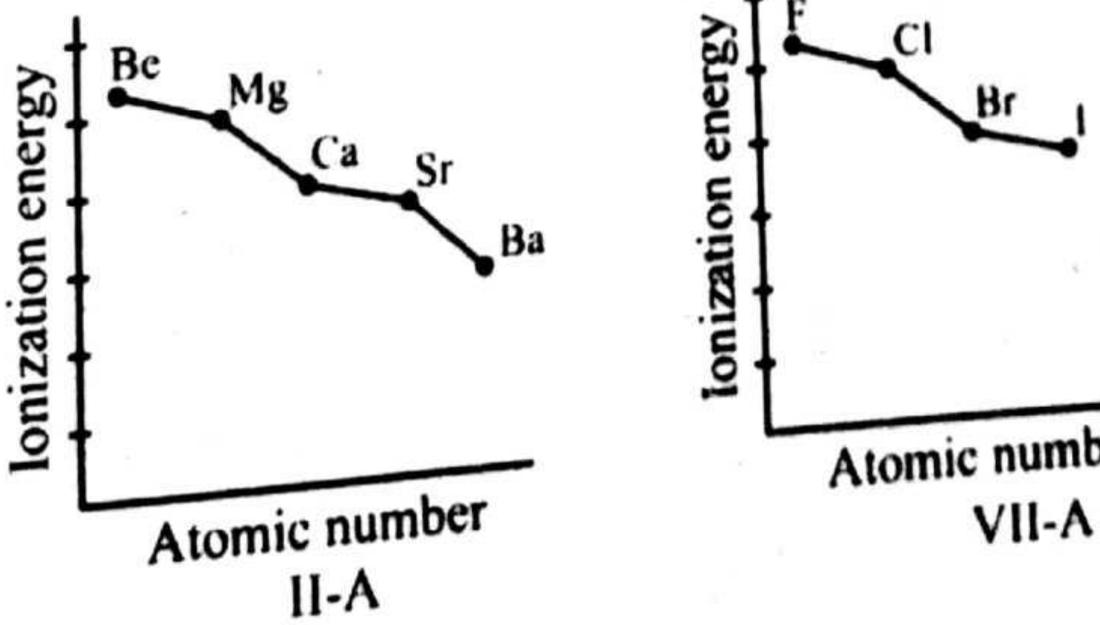


(v) Ionization energy

Along the period (left to right)



Down the group



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MODERN PERIODIC TABLE OF THE ELEMENTS

Atomic Number: 1 — Atomic Mass: H 1.00794

← New proposal of IUPAC

← Old proposal of IUPAC

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 0 or VIIIA
1	1 H 1.00794																	2 He 4.002602
2	3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0063	8 O 15.9994	9 F 18.9984	10 Ne 20.180
3	11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 65.4522	18 Ar 39.948
4	19 K 39.0938	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.59	33 As 74.9216	34 Se 7896	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Te (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.905	54 Xe 131.29
6	55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.59	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226.02	89 +Ac 227.02	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (268)	110 Ds (269)	111 Rg (272)	112 Cn (277)						

s-block — d-block — p-block

Noble Gases

2 He 4

Metals

11 Na 23

Non-metals

7 N 14

Metalloids

32 Ge 73

*Lanthanide series:

58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967

+Actinide series:

90 Th 323.038	91 Pa 231.036	92 U 28.029	93 Np 237.048	94 Pu (244)	95 Am (245)	96 Cm (246)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

f-block

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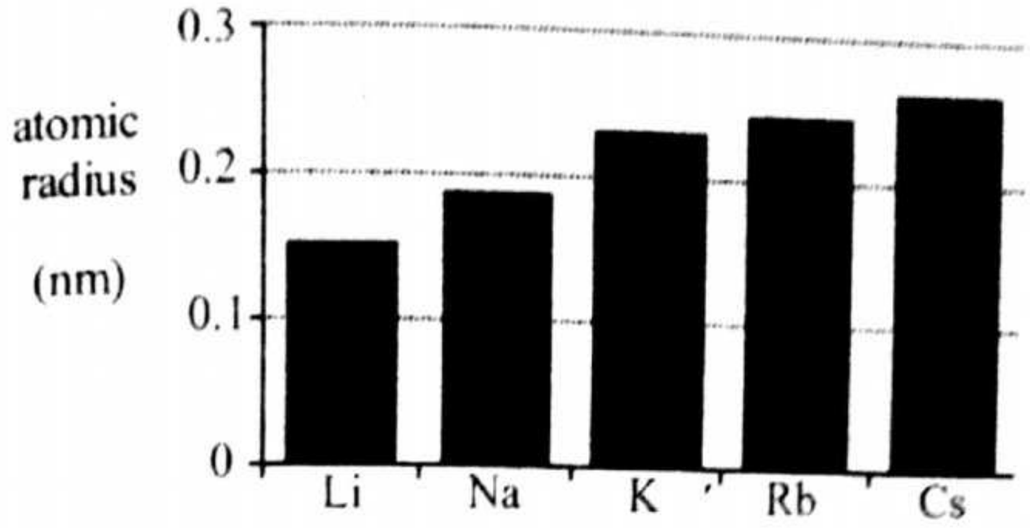
GROUP-IA ELEMENTS (ALKALI METALS)

Atomic and Physical Properties of the Group 1 Elements (Alkali Metals):

This section explores the trends in some atomic and physical properties of the Group 1 elements - lithium, sodium, potassium, rubidium and caesium.

Trends in Atomic Radius:

As we move from lithium to caesium, an extra shell of electrons is added to each element. The addition of an extra shell increases the atomic volume and hence atomic and ionic radii (of M^+ ions).



Some physical properties of alkali metals

Property	Li	Na	K	Rb	Cs
Atomic weight	6.94	22.99	39.1	25.47	132.91
Atomic volume	12.97	23.63	45.36	55.8	69.95
Atomic (i.e metallic radius for coordination number 12	1.55	1.9	2.35	2.46	2.6
Covalent radius	1.23	1.54	2.03	2.16	2.36
Ionic radius of M+ ions	0.6	0.95	1.33	1.48	1.69
Melting point	180.5	97.8	63.7	38.9	28.7
Boiling point	1330	892	760	688	670
Ionization energies (kJ/mol) (I_1)	520.3	495.8	416.9	403.0	375.7
I_2	7298.1	4562.4	3051.4	2633.0	2230.0
Standard oxidation potential	3.04	2.71	2.99	2.99	2.99
Sublimation energy (eV/ion)	1.7472	1.2432	1.032	0.984	0.9024
Hydration energy (eV/ion)	5.904	3.792	3.6955	3.36	0.624
Electronegativity	1	0.9	0.8	0.8	0.7
Color of the flame	Crimson red	Golden yellow	Violet	Violet	Violet
Heat of atomization at 25°C (eV/atm)	1.7472	1.2432	1.032	0.984	0.9024
Ionic conduction of M+ ion	33.5	43.5	64.6	67.5	63

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REACTIONS OF GROUP-IA ELEMENTS WITH WATER

- The reaction of alkali metals with water is highly exothermic.
- A small piece of Li, Na and K floats on water.
- They react vigorously and liberate metal hydroxide and hydrogen gas. These reactions are highly exothermic.
- The energy which is produced can burn the hydrogen gas. It is for this reason that alkali metals are stored in kerosene or paraffin oil.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2 \qquad \Delta H = -ve$$

- The reactivity of alkali metals with water becomes more and more vigorous as we move down the group.
- K, Rb and Cs are so reactive with water that they react with ice at –100°C.

REACTIONS OF GROUP-IA WITH OXYGEN

Reactions with Oxygen:

This topic mainly looks at the reactions of the Group-1A elements (lithium, sodium, potassium, rubidium and cesium) with oxygen-including the simple reactions of the various kinds of oxides formed.

Reaction with Air or Oxygen:

Alkali metals react with O_2 or air rapidly and thus get tarnished due to the formation of their oxide on the surface of the metals. It is for this reason that alkali metals are stored in kerosene or paraffin oil.

- Li when burnt in O_2 gives mainly lithium monoxide, (normal oxide) Li_2O.

$$4Li + O_2 \longrightarrow 2Li_2O$$

- Na when burnt in O_2 forms sodium peroxide, Na_2O_2.

$$2Na + O_2 \longrightarrow Na_2O_2$$

- Other alkali metals react with O_2 to form super oxide of MO_2 type.

$$M + O_2 \longrightarrow MO_2$$

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Normal oxides of alkali metals other than that of Li (Li_2O) are not formed by the direct reaction between the metals and O_2 they are formed by indirect methods, e.g. by reducing peroxides, nitrite and nitrates with the metals itself.

$$2Na_2O_2 + 4Na \longrightarrow 4Na_2O$$

$$2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$$

$$2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$$

REACTIONS OF THE ALKALI METALS WITH CHLORINE

- Alkali metals react with halogens (chlorine) to give halides (chlorides).
- Li and Na react slowly with chlorine at room temperature to give LiCl and NaCl.
- Molten Na burns with a brilliant yellow flame in the atmosphere of chlorine to form NaCl.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

K, Rb and Cs react vigorously with all the halogens to form metal halides,

Flame Tests

Flame test is an analytical procedure used to detect the presence of certain metal ions, based on each element's characteristic emission spectrum.

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Procedure:

- Clean a platinum or nichrome (a nickel-chromium alloy) wire by dipping it into concentrated hydrochloric acid and then holding it in a hot Bunsen flame.
- Repeat this until the wire doesn't produce any colour in the flame.
- When the wire is clean, moisten it again with some of the acid and then dip it into a small amount of the solid you are testing so that some sticks to the wire.
- Place the wire back in the flame again.
- If the flame colour is weak, it is often worthwhile to dip the wire back in the acid again and put it back into the flame as if you were cleaning it. You often get a very short but intense flash of colour by doing that.

Different colours shown by different elements are given below:

Elements	Flame colour	Elements	Flame colour
Li	Crimson red	Ca	Brick-red
Na	Golden yellow	Sr	Crimson Red
K	Violet	Ba	Pale green / grassy green
Rb	Red (reddish-violet)	Cu	blue-green (often with white flashes)
Cs	Blue	Pb	Greyish-white

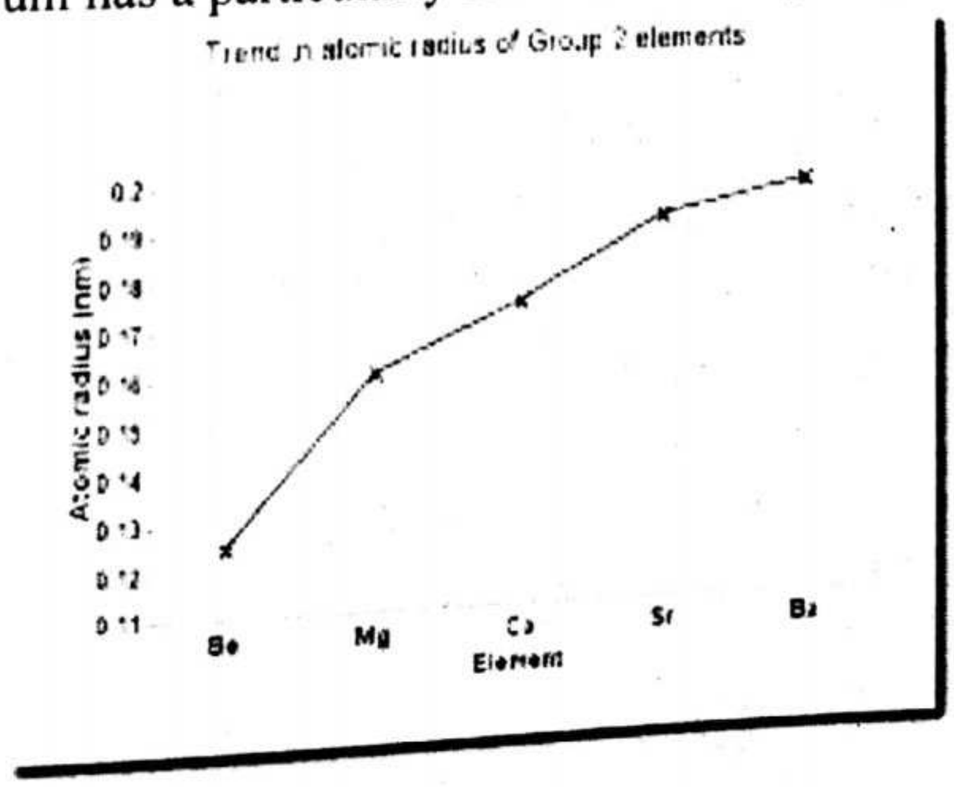
The Origin of Flame Colours:

The loosely held outer electron (i.e. ns^1 electron) of atoms of alkali metals can be easily excited to the higher energy levels even by a small amount of heat energy (e.g. by heating the metals or their salts into Bunsen burner). During the excitation process the electron absorbs some energy and when this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region of the electromagnetic spectrum and hence the colour is imparted by the atoms to the flame. Since the amount of energy absorbed during the excitation process is different in different atoms, different colours are imparted by the atoms to the flame.

GROUP -IIA ELEMENTS (ALKALINE EARTH METALS)

Trends in Atomic Radius:

The atomic radius increases as you go down the Group due to the addition of extra shells. Notice that beryllium has a particularly small atom compared with the rest of the Group.



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Reason:
Because of the addition of an extra shell of electrons to each element from Be to Ra, the atomic volume increases from Be to Ra.

- With the increases of atomic volume, the atomic and ionic radii (of M^{2+} ions) also increase from Be to Ra.
- The atomic radii of these elements are however, smaller than those of alkali metals in the same period. This is due to the fact that the alkaline earth metals have higher nuclear charge which tends to draw the orbit electrons towards the nucleus.
- The smaller values of atomic radii result in that the alkaline earth metals are harder, have higher densities and higher melting points than alkali metals.

Some physical properties of alkaline earth metals

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic weight	9.01	24.31	40.08	87.62	137.34	226
Abundance (%	6.4x10.4	2.0	3.45	0.915	0.040	1.3x10.10
Density (gm/c.c)	1.84	1.74	1.55	2.54	3.75	6.00
Melting point (°C)	1277	650	838	763	714	700
Boiling point (°C)	2770	1107	1440	1380	1610	-
Atomic volume (c.c)	4.90	13.97	25.9	34.54	63.7	38.0
Atomic (i.e metallic radius for coordination number 12 (A°)	1.12	1.60	1.97	2.15	2.22	-
Covalent radium (A°)	0.90	1.36	1.74	1.91	1.98	-
Ionic (crystal radius of M^{2+}ion for Coordination number 6 ((A°))	0.31	065	0.99	1.13	1.35	140
Ionizations energies (KJ/mole I_1)	899.5	737.7	829.8	547.5	502.9	509.4
2nd ionization energy I_2	1757.1	1450.7	1145.4	1064.3	965.2	979.06
1st + 2nd ionization energy	2656.6	2188.4	1735.2	1613.8	1468.1	1488.46
Oxidation state	+2	+2	+2	+2	+2	+2
Electronegativity	1.5	1.2	1.0	1.0	0.9	0.9
Flame colouration	None	None	Brick red	Crimson	Apple green	Red
Oxidation potentials (volts) for M (s) $M_{(s)} \longrightarrow M^{2+}_{(aq)} + 2e$	1.70	1.37	2.87	2.89	2.90	2.92
Heat of atomization at 25 °C and I atm pressure (kJ/mole)	327.26	146.89	181.21	-	-	--
	2385.45	1925.1	1653.07	1458.67	1276.42	

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REACTION OF GROUP -IIA ELEMENTS WITH WATER

Group 2 elements: beryllium, magnesium, calcium, strontium and barium react with water (or steam). It uses these reactions to explore the trend in reactivity in Group 2.

Beryllium

Beryllium has no reaction with water or steam even at red heat.

Magnesium

Magnesium burns in steam to produce white magnesium oxide and hydrogen gas.

$$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$$

Very clean magnesium ribbon has a very slight reaction with cold water. After several minutes, some bubbles of hydrogen form on its surface, and the coil of magnesium ribbon usually floats to the surface. However, the reaction soon stops because the magnesium hydroxide formed is almost insoluble in water and forms a barrier on the magnesium preventing further reaction.

$$Mg_{(s)} + 2H_2O_{(l)} \longrightarrow Mg(OH)_{2(s)} + H_{2(g)}$$

Calcium, Strontium and Barium

These all react with cold water with increasing vigour to give the metal hydroxide and hydrogen.

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- Strontium and barium have reactivities similar to lithium in Group 1 of the Periodic Table.
- Calcium, for example, reacts fairly vigorously with cold water in an exothermic reaction. Bubbles of hydrogen gas are given off, and a white precipitate (of calcium hydroxide) is formed, together with an alkaline solution (also of calcium hydroxide - calcium hydroxide is slightly soluble).

The equation for the reactions of any of these metals would be:

$$M_{(s)} + 2H_2O_{(l)} \longrightarrow M(OH)_{2(aq\,or\,s)} + H_{2(g)}$$

REACTION OF GROUP -IIA ELEMENTS WITH OXYGEN

Reactions of the Group 2 Elements With Air Or Oxygen:

Formation of Simple Oxides:

Preparation:

The alkaline earth metals form the normal oxides of MO type which are obtained by heating the metal in O_2 or by heating their carbonates at high temperature e.g.

$$2Ca + O_2 \longrightarrow 2CaO$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

Properties:

- **Physical state:**

These oxides are extremely stable white crystalline solids due to their high crystal lattice energy.

Solubility:

BeO and MgO are quite insoluble in H_2O while CaO, SrO and BaO react with H_2O to give soluble hydroxides, $M(OH)_2$ which are strong bases.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

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- **Basicity:**

BeO is not at all basic in nature; in fact it is amphoteric since it reacts with acids to form salts and with alkalis to give beryllates.

$$BeO + 2\,HCl \longrightarrow BeCl_2 + H_2O$$

$$BeO + 2\,NaOH \longrightarrow Na_2BeO_2 + H_2O$$

The oxides of other metals are basic in character. Their basic character increases on moving down the group.

- **Chemical nature:**

Due to small size Be^{2+} ion, BeO is covalent while other oxide are ionic.

- **High Melting point and Boiling point of BeO:**

Although BeO is covalent yet it has a higher melting point and is harder than the oxides of other metals as it is polymeric. Each Be atom is tetrahedrally coordinated by four oxygen atoms.

Peroxides:

Preparation:

The peroxides of heavier metals (Ca, Sr, Ba etc.) can be obtained on heating the normal oxides with O_2 at high temperature.

$$2BaO + O_2 \longrightarrow 2BaO_2$$

Properties:

The peroxides are white, ionic solids having peroxide anion, $[O\text{-}O]^{2-}$. They react with acids to produce H_2O_2.

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

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REACTION OF GROUP -IIA ELEMENTS WITH NITROGEN

All the elements burn in nitrogen to form nitrides, M_3N_2 e.g.

$$3Ca + N_2 \longrightarrow Ca_3N_2$$

These react with H_2O to liberate NH_3 e.g.

$$Ca_3N_2 + 6\,H_2O \longrightarrow 2\,NH_3 + 3\,Ca(OH)_2$$

Be_3N_2 is volatile while other nitrides are not so.

REACTION OF PERIOD 3 ELEMENTS WITH WATER

ELEMENTS	CHEMICAL REACTIONS
Sodium: (Na)	Sodium has a very exothermic reaction with cold water producing hydrogen and a colourless solution of sodium hydroxide. $2Na + 2H_2O \longrightarrow 2NaOH + H_2$
Magnesium: (Mg)	Magnesium has a very slight reaction with cold water, but burns in steam. A very clean coil of magnesium dropped into cold water eventually gets covered in small bubbles of hydrogen which float it to the surface. Magnesium hydroxide is formed as a very thin layer on the magnesium and this tends to stop the reaction. $Mg + 2H_2O \xrightarrow[Cold]{} Mg(OH)_2 + H_2$ Magnesium burns in steam with its typical white flame and produces white magnesium oxide and hydrogen. $Mg + H_2O \xrightarrow[Steam]{} MgO + H_2$
Aluminium: (Al)	*Aluminium powder heated in steam produces hydrogen and aluminium oxide. The reaction is relatively slow because of the strong aluminium oxide layer on the metal, and the build-up of even more oxide during the reaction.* $2Al + 3H_2O \xrightarrow[Steam]{} Al_2O_3 + 3H_2$
Silicon, Phosphorus and Sulphur:	*These have no reaction with water.*
Chlorine: (Cl_2)	*Chlorine dissolves in water to some extent to give a green solution. A reversible reaction takes place to produce a mixture of hydrochloric acid and chlorous (I) acid (hypochlorous acid).* $Cl_2 + H_2O \rightleftharpoons HCl + HOCl$ *In the presence of sunlight, the chlorous (I) acid slowly decomposes to produce more hydrochloric acid, releasing oxygen gas. Overall reaction is given as:* $2Cl_2 + 2H_2O \xrightarrow{Sunlight} 4HCl + O_2$
Argon: (Ar)	There is no reaction between argon and water.

REACTION OF PERIOD 3 ELEMENTS WITH OXYGEN

ELEMENTS	CHEMICAL REACTIONS
Sodium:	*Sodium burns in oxygen with an orange flame to produce a white solid mixture of sodium oxide and sodium peroxide.* *For the simple oxide:* $4Na + O_2 \longrightarrow 2Na_2O$ *For the peroxide:* $4Na + 2O_2 \longrightarrow 2Na_2O_2$
agnesium:	*Magnesium burns in oxygen with an intense white flame to give white solid magnesium oxide.* $2Mg + O_2 \longrightarrow 2MgO$

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Aluminium:	Aluminium combines with oxygen on heating to produce a thin protective layer of aluminium oxide which protects the metal from further corrosion. $4Al+3O_2 \longrightarrow 2Al_2O_3$
Silicon:	Silicon will burn in oxygen if heated strongly. Silicon dioxide is produced. $Si+O_2 \longrightarrow SiO_2$
Phosphorus:	White phosphorus catches fire spontaneously in air, burning with a white flame and producing clouds of white smoke - a mixture of phosphorus (III) oxide and phosphorus (V) oxide. The proportions of these depend on the amount of oxygen available. In an excess of oxygen, the product will be almost entirely phosphorus (V) oxide. For the phosphorus (III) oxide: $P_4+3O_2 \longrightarrow P_4O_6$ For the phosphorus (V) oxide: $P_4+5O_2 \longrightarrow P_4O_{10}$
Sulphur:	Sulphur burns in air or oxygen on gentle heating with a pale blue flame. It produces colourless sulphur dioxide gas. $S+O_2 \longrightarrow SO_2$
Chlorine and Argon:	Despite having several oxides, chlorine would not react directly with oxygen. Argon does not react either

REACTION OF PERIOD 3 ELEMENTS WITH CHLORINE

ELEMENTS	CHEMICAL REACTIONS
Sodium:	Sodium burns in chlorine with a bright orange flame. White solid sodium chloride is produced. $2Na+Cl_2 \longrightarrow 2NaCl$
Magnesium:	Magnesium burns with its usual intense white flame to give white magnesium chloride. $Mg+Cl_2 \longrightarrow MgCl_2$
Aluminium:	Aluminium is often reacted with chlorine by passing dry chlorine over aluminium foil heated in a long tube to produce very pale yellow aluminium chloride. $2AI+3Cl_2 \longrightarrow 2AlCl_3$
Silicon:	When chlorine is passed over silicon powder heated in a tube, it reacts to produce silicon tetrachloride. $Si+2Cl_2 \longrightarrow SiCl_4$
Phosphorus:	White phosphorus burns in chlorine to produce a mixture of two chlorides, phosphorus (III) chloride and phosphorus (V) chloride (phosphorus trichloride and phosphorus pentacl.loride). Phosphorus (III) chloride is a colourless fuming liquid. $P_4+6Cl_2 \longrightarrow 4PCl_3$ Phosphorus (V) chloride is an off-white (going towards yellow) solid. $P_4+10Cl_2 \longrightarrow 4PCl_5$
Sulphur:	When a stream of chlorine is passed over some heated sulphur, it reacts to form an orange, evil-smelling liquid, disulphur dichloride, S_2Cl_2. $2S+Cl_2 \longrightarrow S_2Cl_2$
Chlorine and Argon	It obviously doesn't make sense to talk about chlorine reacting with itself, and argon doesn't react with chlorine.

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REACTIONS OF ALUMINUM

Reaction with Air

- When a piece of aluminum sheet is exposed to moist air, it acquires a thin, continuous coating of aluminum oxide, which prevents further attack on the metal by atmospheric oxygen and water under normal conditions. Because of this, aluminum sheets are said to be **corrosion free**.
- However, if the aluminum powder is heated to 800°C and above, the metal will react with air to form aluminum oxide, Al_2O_3, and aluminum nitride, AlN. The reaction is accompanied by the evolution of heat and intense white light. This property of aluminum is made use of in flash light photography.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

$$2Al + N_2 \longrightarrow 2AlN$$

Because of its ability to combine with both oxygen and nitrogen, the metal is often used to remove air bubbles from molten metals. Salt solutions corrode aluminum badly, so aluminium and aluminium alloys are not suitable for marine use.

Reaction with Non-Metals

Heated aluminium combines with the halogens, sulphur, nitrogen, phosphorus and carbon, accompanied by the evolution of heat.

$$2Al_{(s)} + 3Cl_{2(g)} \longrightarrow 2AlCl_{3(s)}$$

$$2Al_{(s)} + 3S_{(s)} \longrightarrow Al_2S_{3(s)}$$

$$2Al_{(s)} + N_{2(g)} \longrightarrow 2AlN_{(s)}$$

$$Al_{(s)} + P_{(s)} \longrightarrow AlP_{(s)}$$

$$4Al_{(s)} + 3C_{(s)} \longrightarrow Al_4C_{3(s)}$$

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Aluminum on heating with hydrogen forms aluminium hydride.

$$2Al + 3H_2 \longrightarrow 2AlH_3$$

Reaction with Acids and Alkalies

- Aluminium is **amphoteric**. It dissolves in both acids and bases with the liberation of hydrogen gas.
- **Reaction with alkali:**

Aluminium dissolves in both sodium and potassium hydroxides to form a soluble aluminates, with the evolution of hydrogen.

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \longrightarrow 2NaAl(OH)_{4(aq)} + 3H_{2(g)}$$

Sodium aluminate

- **Reaction with acids:**

Aluminium reacts slowly with dilute acid and more rapidly with concentrated hydrochloric acid to displace hydrogen.

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_{2(g)}$$

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TOPIC-12 TRANSITION ELEMENTS

COURSE CONTENTS

- General characteristics
- Describe electronic structure of elements and ions of d-block elements
- Chemistry of transition elements of 3d series
- (a) Electronic configuration
  (b) Variable oxidation states
  (c) Uses as a catalyst
  (d) Formation of complexes
  (e) Colour of transition metal complexes
- Magnetic behaviour , Alloy formation , Binding Energy
- Complexes important terminologies
- Nomenclature

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INTRODUCTION

Transition Elements:

"The elements which have partially filled d or f-orbital either in their atomic states or in other common oxidation states are called transition elements." They are called d-block or f-block elements.

Typical and non-typical transition elements

- Elements of group II-B (Zn, Cd and Hg), III-B (Sc, Y and La) are non-typical transition elements.
- Coinage metals (Cu, Ag and Au) are considered as transition elements as their d-orbitals are in process of completion in their ionic states.

Cu^{+2} ----------$3d^9$
Ag^{+2} ---------- $4d^9$
Au^{+3}---------- $5d^8$

- d-Block elements are called outer transition elements while f-block elements are called inner transition elements.

Series of transition elements

The d-block elements consist of following three series of ten elements each:

- **3d-series:** from Scandium (Sc =21) to Zinc (Zn =30)
- **4d-series:** from Yttrium (Y =39) to Cadmium (Cd = 48)
- **5d-series:** from Lanthanum (La = 57) to Mercury (Hg = 80)

The f-block elements constitute two series which are:

- **4f-series** from Cerium (Ce = 58) to Lutetium (Lu = 71)
- **5f-series** from Actinium (Ac = 89) to Lawrencium (Lr = 103) which are called actinides.

General outermost configurations:

- First series (d-block elements) = $(n-1)d^{1-10}ns^2$
- Second series (f-block elements) = $(n-1)d^1(n-2)f^{1-14}ns^2$

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GENERAL CHARACTERISTICS

- **Metals:**
  They are all metallic in nature.
- **Catalyst:**
  Some of the transition elements play an important role in the industry. These metals are Ti, Cr, Fe, Ni, Cu, Mo, W, Zr, Nb, Ta and Th etc.
- **Hard and conductor:**
  They are all hard and strong metal with high melting and boiling points. They are good conductors of heat and electricity.
- **Alloys:**
  They form alloys with one another and other elements of periodic table as well.
- **Variable oxidation state:**
  With a few exceptions, they show variable oxidation states.
- **Coloured compounds:**
  Their ions and compounds are colored in the solid state and the solution state.

ELECTRONIC CONFIGURATION

- Transition elements may be defined as those elements which have partially filled 'd' or 'f' sub shells in atomic state or in any of their commonly occurring oxidation states.
- d-Block elements are known as outer transition elements while f-Block elements are also known as inner transition elements.
- Transition elements usually show variable oxidation states, coloured compounds and form complex compounds

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3d-block elements		4d-block elements		5d-block elements	
Elements	Electronic Configuration	Elements	Electronic Configuration	Elements	Electronic Configuration
Sc (21)	$[Ar]3d^14s^2$	Y (39)	$[Kr]4d^15s^2$	La (57)	$[Xe]5d^16s^2$
Ti (22)	$[Ar]3d^24s^2$	Zr (40)	$[Kr]4d^25s^2$	Hf (72)	$[Xe]4f^{14}5d^26s^2$
V (23)	$[Ar]3d^34s^2$	Nb (41)	$[Kr]4d^45s^1$	Ta (73)	$[Xe]4f^{14}5d^36s^2$
Cr (24)	$[Ar]3d^54s^1$	Mo (42)	$[Kr]4d^55s^1$	W (74)	$[Xe]4f^{14}5d^46s^2$
Mn (25)	$[Ar]3d^54s^2$	Te (43)	$[Kr]4d^55s^2$	Re (75)	$[Xe]4f^{14}5d^56s^2$
Fe (26)	$[Ar]3d^64s^2$	Ru (44)	$[Kr]4d^75s^1$	Os (76)	$[Xe]4f^{14}5d^66s^2$
Co (27)	$[Ar]3d^74s^2$	Rh (45)	$[Kr]4d^85s^1$	Ir (77)	$[Xe]4f^{14}5d^76s^2$
Ni (28)	$[Ar]3d^84s^2$	Pd (46)	$[Kr]4d^{10}5s^0$	Pt (78)	$[Xe]4f^{14}5d^96s^1$
Cu (29)	$[Ar]3d^{10}4s^1$	Ag (47)	$[Kr]4d^{10}5s^1$	Au (79)	$[Xe]4f^{14}5d^{10}6s^1$
Zn (30)	$[Ar]3d^{10}4s^2$	Cd (48)	$[Kr]4d^{10}5s^2$	Hg (80)	$[Xe]4f^{14}5d^{10}6s^2$

Electronic configuration of 3d-series elements:

3d – series elements	
Elements	Electronic Configuration
Sc (21)	$[Ar]\ 3d^14s^2$
Ti (22)	$[Ar]\ 3d^24s^2$
V (23)	$[Ar]\ 3d^34s^2$
Cr (24)	$[Ar]\ 3d^54s^1$
Mn (25)	$[Ar]\ 3d^54s^2$
Fe (26)	$[Ar]\ 3d^64s^2$
Co (27)	$[Ar]\ 3d^74s^2$
Ni (28)	$[Ar]\ 3d^84s^2$
Cu (29)	$[Ar]\ 3d^{10}4s^1$
Zn (30)	$[Ar]\ 3d^{10}4s^2$



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VARIABLE OXIDATION STATES

- Transition elements are electropositive, so they have positive oxidation states.
- All 3d series elements show an oxidation state of +2 in addition to higher oxidation states when the electrons of 4s-orbital take part in bonding.

Transition elements show variable oxidation states.

The reason is that they have d-electrons in addition to s-electron for bond formation. These elements have several (n–1) d and ns electrons. The energies of (n-1) d and ns orbitals are very close to each other. The d-electrons are as easily lost as ns electrons lost as ns electrons.

- In the highest oxidation states of first five elements, all s and d-electrons are used for bonding.
- Among the 3d series, Mn has maximum oxidation states, and goes up to +7
- The oxidation numbers +2 and +3 are more common.
- Positive oxidation states increase up to the middle of series and after that they decrease. It

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is because the number of unpaired electrons increases up to the middle and then decreases.

Element	Electronic Configuration	Oxidation State
Sc - 21	[Ar] $3d^1\ 4s^2$	+3
Ti - 22	[Ar] $3d^2\ 4s^2$	+2, +3, +4
V - 23	[Ar] $3d^3\ 4s^2$	+2, +3, +4, +5
Cr - 24	[Ar] $3d^5\ 4s^1$	+2, +3, +4, +5, +6
Mn - 25	[Ar] $3d^5\ 4s^2$	+1,+2, +3, +4, +5, +6, +7
Fe - 26	[Ar] $3d^6\ 4s^2$	+1,+2, +3, +4, +6
Co - 27	[Ar] $3d^7\ 4s^2$	+2, +3, +4
Ni - 28	[Ar] $3d^8\ 4s^2$	+2, +3, +4
Cu - 29	[Ar] $3d^{10}\ 4s^1$	+1, +2 , +3
Zn - 30	[Ar] $3d^{10}\ 4s^2$	+2

CATALYTIC ACTIVITY

Most of the transition elements are used as catalysts. The compounds of transition metals are also catalysts.

Reason:

- The reason is that the transition metals show variety of oxidation states. In this way, they can form intermediate products with various reactants.
- They also form interstitial compounds which can absorb an activator to the reacting species.

Examples:

Some of the important examples of catalysts are as follows:

- A mixture of ZnO and Cr_2O_3 is used for the manufacture of methyl alcohol.
- Ni, Pt and Pd are catalysts for the hydrogenation of vegetable oil and saturation of alkenes and alkynes to alkanes.
- MnO_2 can be used as a catalyst for the decomposition of H_2O_2.
- $TiCl_4$ is used as catalyst for the manufacture of plastics.
- V_2O_5 is used to oxidize SO_2 to SO_3 in the manufacture of H_2SO_4.
- Fe is used as a catalyst for synthesis of NH_3 in Haber's process. About 1% of Na_2O or K_2O and about 1% SiO_2 or Al_2O_3 are added as promoter. Mo is also sometimes used as a promoter.

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COLOUR OF TRANSITION METAL COMPLEXES

When white light is allowed to fall on a complex. The following things may occur

(i) The complex may absorb the whole of white light. In this case complex appears black.

(ii) The complex may reflect or transmit the whole light. In this case it appears white.

(iii) The complex may absorb some of it and may reflect or transmit the remaining light.

POINT TO PONDER

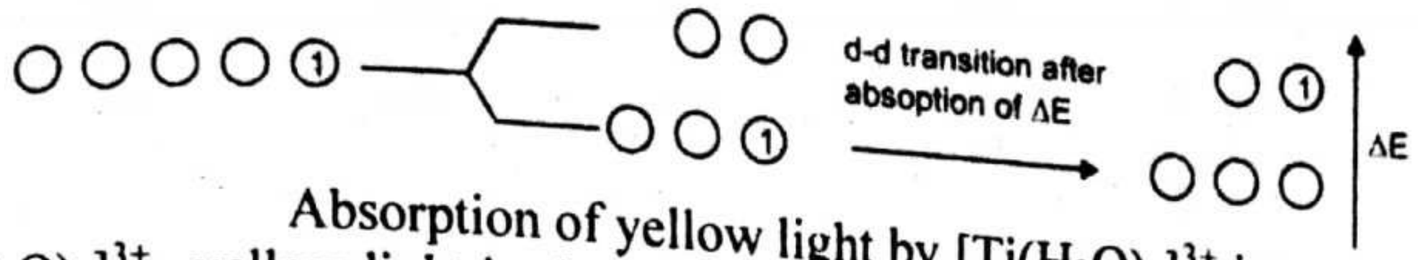
The colour of the transition metal ions is due the presence of unpaired electrons or incomplete d-orbitals. Due to d-d transition.

Mechanism:

- When light is allowed to fall on a substance, it absorbs from it the light of a particular colour whose wavelength is in the visible region (4000-7000Å) and reflects the remaining light which has the colour complementary to that of the absorbed light.

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- Complementary colour which is actually the colour of reflected light becomes the colour of the substance.
- Every ion absorbs a different wavelength and transmits the remaining set of wavelengths that gives different colours to the ions.



Absorption of yellow light by $[Ti(H_2O)_6]^{3+}$ ion.

In $[Ti(H_2O)_6]^{3+}$, yellow light is absorbed, while most of the blue and red lights are transmitted, therefore the solution of $[Ti(H_2O)_6]^{3+}$ ions look violet in colour..

MAGNETIC BEHAVIOUR

Many transition elements and their compounds are paramagnetic.

Paramegnetism:

The compounds attracted into the magnetic field are called paramagnetic. Paramegnetism is due to the unpaired electrons present in the metals and their compounds.

Examples: Mn^{+2}, Fe^{+2} etc.

Ferromegnetism:

The substances which can be magnetized are called ferromagnetic.

Examples: Fe, Co and Ni etc.

Diamegnetism:

Some substances in which even number of electrons are present, and have paired spins are diamagnetic. They are slightly repelled by magnetic field.

Examples: Zn^{+2}, Sc^{+3} etc.

Magnetic moment:

- The magnetic moment (μ) is related to the number of unpaired electrons (n) by the equation:

$$\mu = \sqrt{n(n+2)}$$

- It is measured in Bohr magneton, BM.
- By measuring magnetic moment, the nature of transition metal compound and oxidation state of transition metal can be calculated.

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ALLOY FORMATION

Alloy is mixture of two or more than two metals. Transition metals form alloys with each other.

Reason:

Transition elements have almost similar sizes and atoms of the one metal can easily take up positions in crystal lattice of the other. They form substitutional alloys among themselves.

Example

- Alloy steels are the materials in which the iron atoms are substituted by Cr, Mn and Ni. Steel has more useful properties than iron.
- Brass, bronze and coinage alloys are the best alloys.

Properties:

As alloys are prepared according to the requirements, their characteristics are different, yet few properties are common which are as follows:

- Alloys are comparatively cheap.
- They are strong and flexible but hard alloys can also be prepared.
- They have long life because they do not corrode.
- They are durable.
- They have high melting points.

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- They are better conductor but non-conductor alloys are also prepared.

Alloys of Metals	Composition	Properties and Uses
Brass	Cu = 60 – 80% Zn = 20 – 40%	• It is strong alloy of copper which is soft and flexible. • It does not corrode. • Due to low melting point, it is easy to use. • It is used to make locks, keys, water taps, pipes artificial jewelry, door handles and parts of machines.
Bronze	Cu 90 – 95% Sn 5 – 10%	• It is strong, brilliant and long lasting. • It does not corrode. • It is used to prepare medals, coins, badges and bullets etc. besides these; decorative articles are also made from this alloy.
Nichrome	Ni = 60% Cr = 15% Fe = 25%	It is used in electric heaters and filaments of furnaces.

BINDING ENERGY

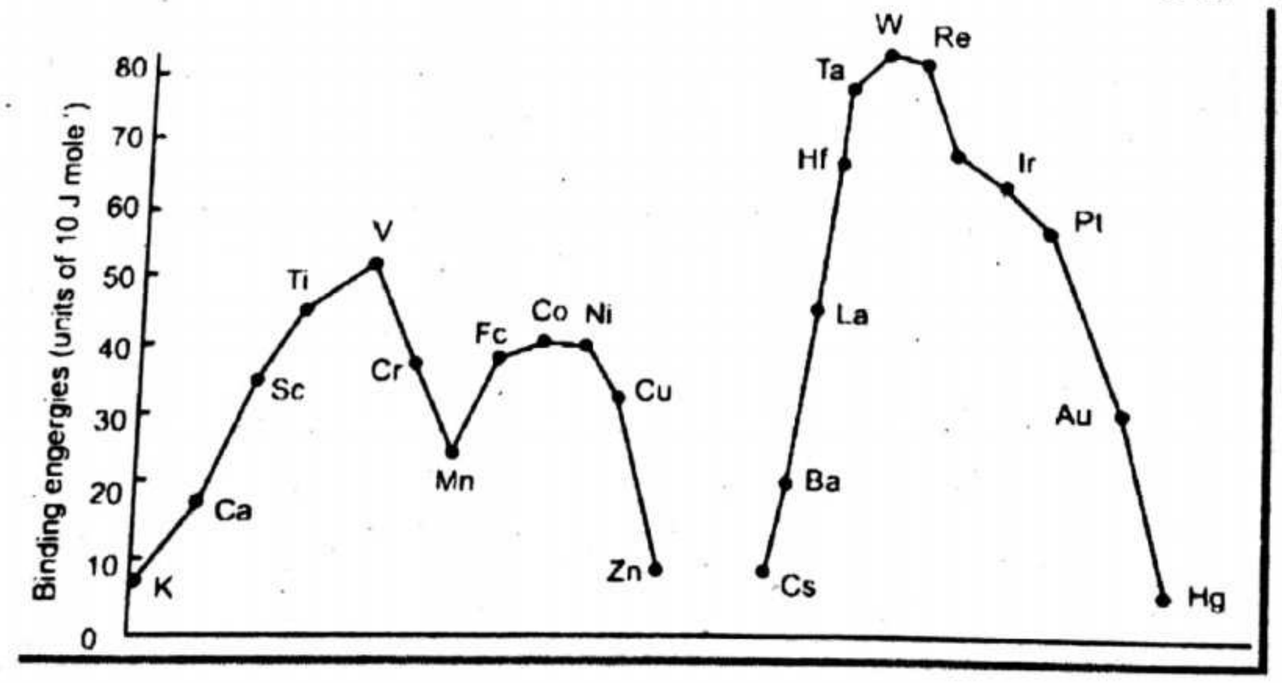
- Transition elements are tough, malleable and ductile.
- The toughness of the metals is due to greater binding energies.

Reason:

It is because the s-electron of outermost shell takes part in chemical bonding. However, the electrons of half-filled d-orbitals also participate in bonding. So, they have greater binding energies and toughness.

Variation in Binding Energies:

- When we move from left to the right in any d-block series, the number of electrons increase up to group V-B; that is vanadium family and VI-B i.e. Cr family.
- After that the pairing of electron starts.
- The unpaired electrons become zero at group II-B.
- It means that binding forces go on increasing up to Cr and then decrease after that. This is shown for the elements of 3d and 5d series in the following graph.



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FORMATION OF COMPLEXES AND THEIR NOMENCLATURE

The compounds containing the complex molecules or complex ions and capable of independent existence are called coordination compounds complexes.

A complex compound may contain

(i) A simple cation and a complex anion

(ii) A complex cation and a simple anion

POINT TO PONDER

- Many important reactions are catalyzed by transition metals.
- Transition metal ions are often coloured because d-d transition.

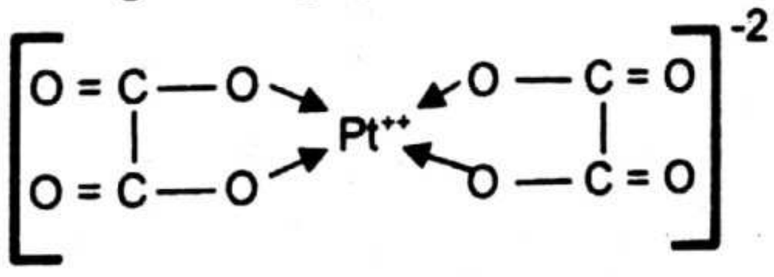
Component of complex compound

Component	Description	Examples
Central metal atom or ion	Metal atom or metal ion surrounded by number of ligands in the complex compound	$K_4[Fe(CN)_6]$ Fe^{2+} is the central metal ion
Ligand	Ion, atom or neutral molecule that donates electron pairs to central metal atom/ion. Ligand with two donor atoms is called bidentate	OH^-, CN^-, NH_3, H_2O, $C_2O_4^{-2}$
Co-ordination Number	The number of lone pair of electrons provided by ligands to central atom or ion.	$[Cu(NH_3)_4]SO_4$ The co-ordination number of Copper in this complex is 4.
Co-ordination sphere	The central metal atom or ion along with ligands is called co-ordination sphere	In $[Ni(CO)_4]$ $[Ni(CO)_4]^0$ is neutral co-ordination sphere.
Charge on co-ordination sphere	Algebraic sum of charges presents on central metal ion and the total charge on the ligands	$[Fe(CN)_6]^{4-}$ Charge on iron = + 2 Total charge on six CN ions = - 6 Charge on the coordination sphere = - 6 + 2 = - 4

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Chelates:

A complex compound, in which one or more than one ring is formed due to donation of electrons by poly dentate ligand. e.g. $[Pt(C_2O_4)_2]^{2-}$



$[Pt(C_2O_4)_2]^{-2}$

Dioxalato-platinate (II) ion

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Naming the complex compound

The IUPAC rules for naming the complex compounds are as follows.

- Cations are named before anions.
- In naming the coordination sphere, ligands are named in alphabetical order regardless of the nature and number of each followed by the name of central metal ion.
- The prefixes di, tri, tetra, penta, hexa, etc, are used to specify the number of coordinated same ligand.
- The names of anionic ligands end in suffix "O" e.g. hydroxo, OH^- carbonato CO_3^{-2}
- The names of neutral ligands are usually unchanged, e.g. for NH_3 ammine and for H_2O, aqua……etc.
- The suffix 'ate' comes at the end of the name of metal if the co-ordination sphere is negative otherwise it remains unchanged.
- The oxidation number of the metal ion is represented by a Roman numeral in parenthesis following the name of the metal.

Examples:

$K_4[Fe(CN)_6]$	Potassiumhexacaynoferrate(II)
$[PtCl(NO_2)(NH_3)_4]SO_4$	Tetraamminechloronitro-platinum (IV) sulphate.

Writing the formulae of complex compound

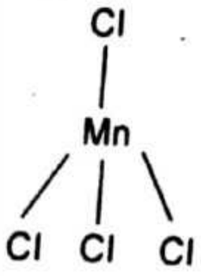
- In writing the formula of complex ion, the usual practice is the symbol of the central metal atom first, followed by the formulae of the ligands.
- The ligands are written anionic ligands first and then neutral ligands.
- Following this sequence, more than one anionic or neutral ligands are written in alphabetical order
- The formula of whole complex ion is enclosed in square brackets.

Examples:

Sodiumhexafluorocobaltate (III)	$Na_3[CoF_6]$
Potassiumtetracyanocupparate (II)	$K_2[Cu(CN)_4]$
Triaquatrihydroxochroonium (III)	$[Cr(OH)_3(H_2O)_3]$

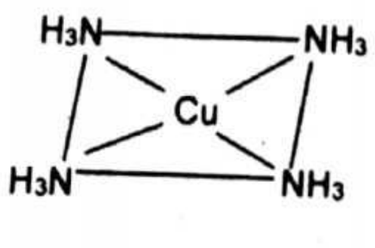
Geometry of complex compound

$[MnCl_4]^{-2}$



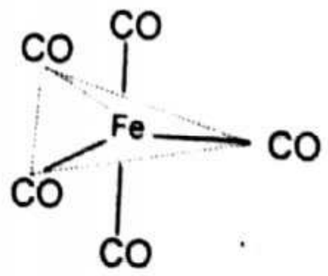
tetrahedral (sp^3)

$[Cu(NH_3)_4]^{+2}$



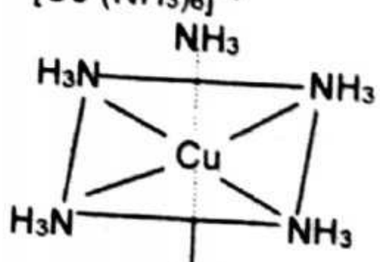
square planar (dsp^2)

$[Fe(CO)_5]$



trigonal bipyramidal (dsp^3)

$[Co(NH_3)_6]^{+3}$



octahedral (d^2sp^3)

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TOPIC-13 FUNDAMENTAL CONCEPTS OF ORGANIC CHEMISTRY

COURSE CONTENTS

- Classification of organic compound
- Isomerism
- Functional group
- Nomenclature of organic compounds (All families)

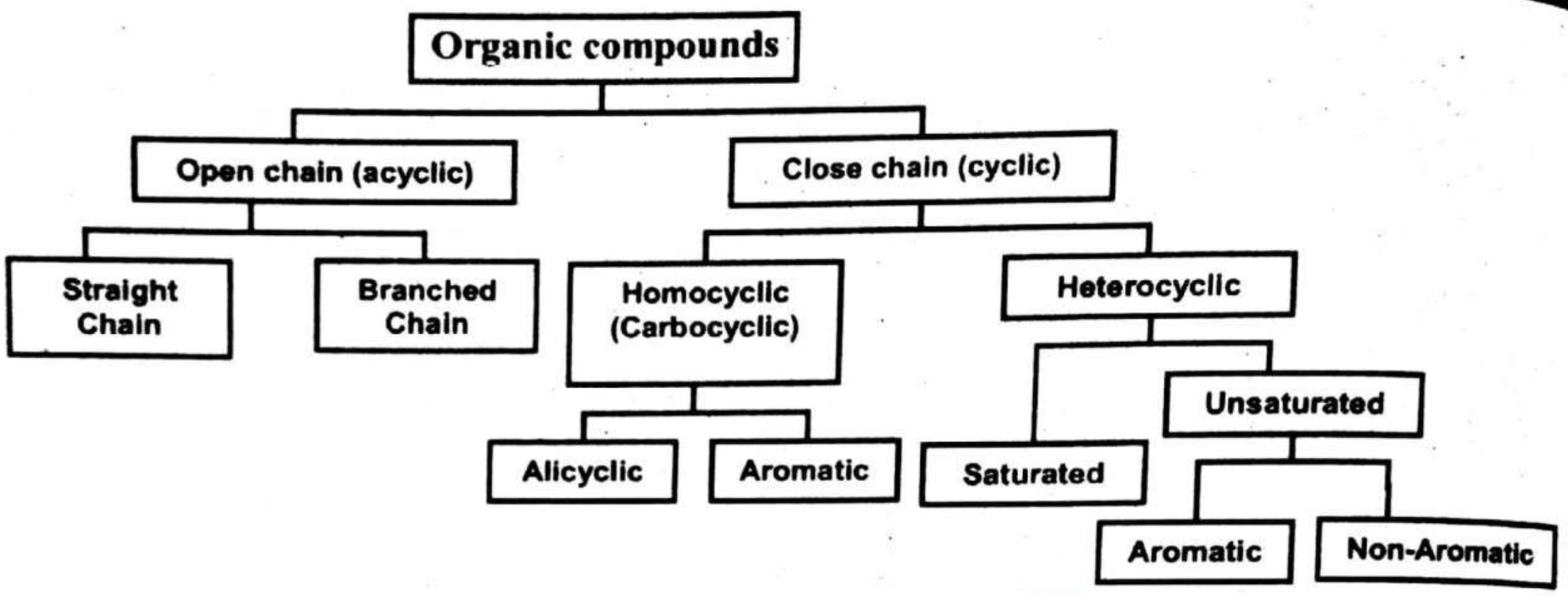
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Organic Compound

- Compounds of carbon and hydrogen (hydrocarbons) and their derivatives
- Fridrick Wohler broke vital force theory
- First laboratory prepared organic compound is urea
- $NH_4CNO \rightleftharpoons (NH_2)_2CO$
- Exceptions are CO, CO_2, Carbonates, Bicarbonates etc.

CLASSIFICATIONS OF ORGANIC COMPOUNDS



The carbon skeleton is the basis of classification.

(1) Open chain (Acyclic or Aliphatic) compounds:

The class of compounds containing open chain of carbon atoms.

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$ n-Butane

$CH_3\text{-}CH(CH_3)\text{-}CH_3$ Isobutane

They are further classified into two classes.

(i) Straight Chain or Unbranched Compounds

The compounds having carbon chains without branches.

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$ n-Butane

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ n-Pentane

(ii) Branched chain compounds

The compounds in which carbon chains have side branches.

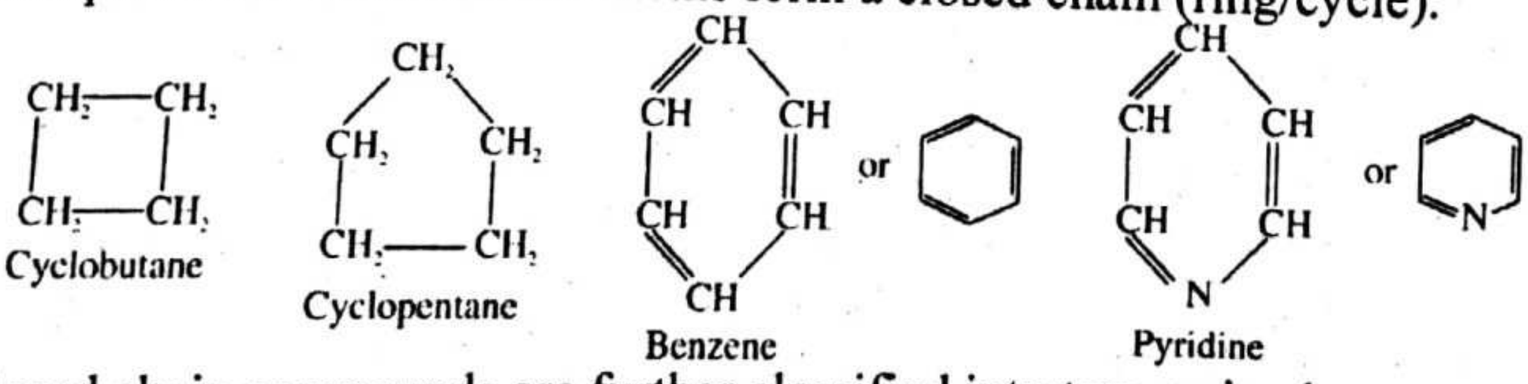
$CH_3\text{-}CH(CH_3)\text{-}CH_3$ Isobutane

$CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$ Isopentane

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$ Isohexane

(2) Closed chain compounds (cyclic compounds)

The compounds in which carbon atoms form a closed chain (ring/cycle).

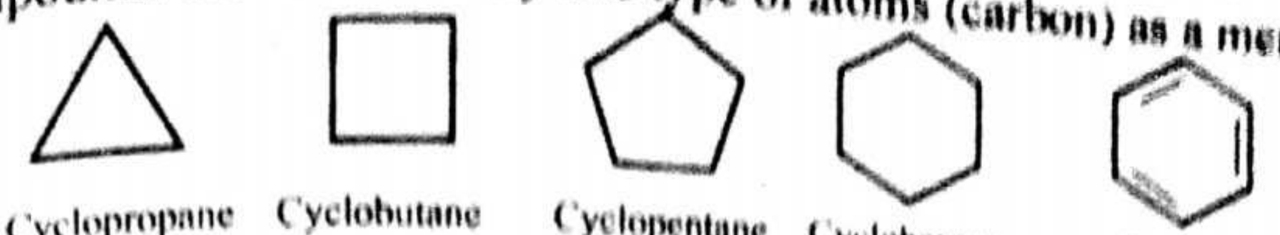


The closed chain compounds are further classified into two main classes.

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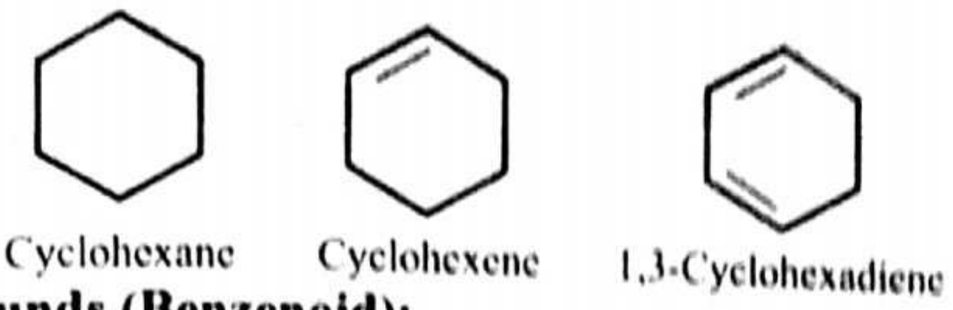
(i) Homocyclic or carbocyclic compounds:
The cyclic compounds that contain only one type of atoms (carbon) as a member of ring



Cyclopropane Cyclobutane Cyclopentane Cyclohexane Benzene

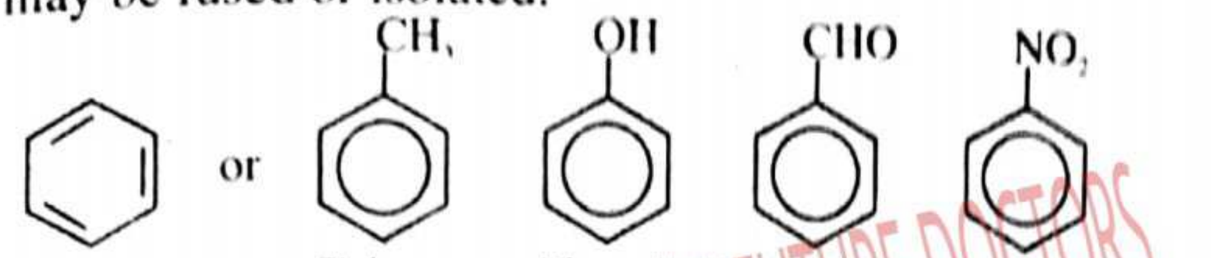
They are further classified into two classes.

(a) Alicyclic compounds (Non-benzenoid or non-aromatic)
The compounds that contain a ring of three or more carbon atoms and resemble with aliphatic compounds.



Cyclohexane Cyclohexene 1,3-Cyclohexadiene

(b) Aromatic compounds (Benzenoid):
The compounds that contain atleast one benzene ring (ring of six carbon atoms with three alternate double and single bonds). Aromatic Compounds may contain more benzene rings which may be fused or isolated.



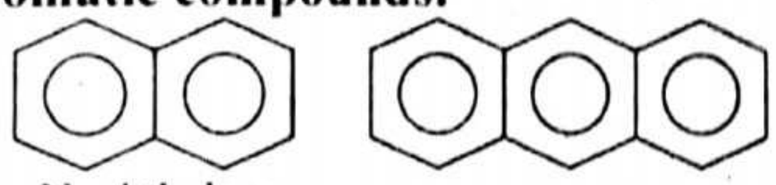
Benzene Toluene Phenol Benzaldehyde Nitrobenzene

(i) Isolated ring aromatic compounds:



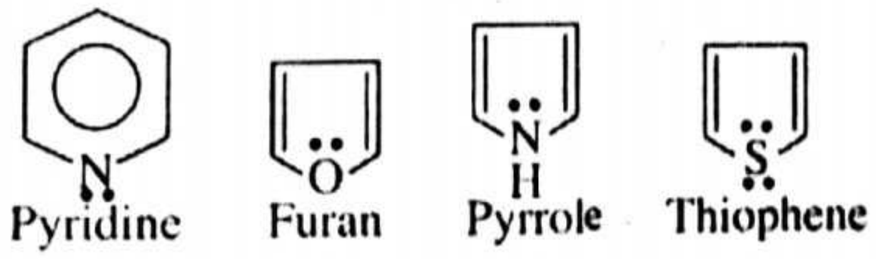
Biphenyl Biphenyl methane

(ii) Fused ring aromatic compounds:



Naphthalene Anthracite

(ii) Heterocylic compounds:
The compounds which contain atleast one atom other than carbon in the ring.



Pyridine Furan Pyrrole Thiophene

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ISOMERISM

Isomerism (Iso = same; Merose = units)

Two or more compounds having same molecular formula but different structures are called isomers and the phenomenon is known as isomerism.

- In saturated hydrocarbons methane, ethane and propane (amongst alkanes) have one structural form only i.e., no isomerism
- Isomerism is possible for compounds having at least four *carbon atoms*.
- Number of isomers in case of saturated hydrocarbons.
- Number of isomers increases with increase in number of carbon atoms in saturated hydrocarbon.

Number of carbons	Number of Isomers
4	2
5	3
6	5

Types of Isomerism

(i) Structural Isomerism **(ii)** Geometric isomerism

(i) Structural Isomerism

The compounds having same molecular formula but different structural formulas and properties.

$CH_3\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}CH_3$ and $CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}CH_3$

3-Pentanone 2-Pentanone

Structural isomers having same formula $C_5H_{10}O$.

Types of Structural Isomerism:

(i) Chain or skeletal isomerism
(ii) Position isomerism
(iii) Functional group isomerism
(iv) Metamerism
(v) Tautomerism

(1) Chain Isomerism or skeletal Isomerism:

The compounds which have same molecular formula but differ with respect to carbon chain (carbon skeleton)

Chain isomers of C_5H_{12}

(i) $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ $CH_3\text{-}\overset{\overset{CH_3}{|}}{CH}\text{-}CH_2\text{-}CH_3$ & $CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}CH_3$

n-Pentane Isopentane Neopentane

Chain isomers of C_4H_8

(ii) $CH_3\text{-}CH_2\text{-}CH=CH_2$ & $CH_3\text{-}\overset{\overset{CH_3}{|}}{C}=CH_2$

1-Butene 2-Methylpropene

The classes of compounds that can usually show chain isomerism are

(i) Alkanes (ii) Alkenes (iii) Alkynes

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(2) Position Isomerism:

The compounds that have same molecular formula but differ with respect to position of same functional group on carbon chain. The classes of compounds that can show position isomerism are:

(i) Alkenes **(ii)** Alkynes **(iii)** Alcohols **(iv)** Alkyl halides
(v) Amines **(vi)** Nitroalkanes **(vii)** Thio-alcohols **(viii)** Cyano alkanes

$CH \equiv C\text{-}CH_2\text{-}CH_3$ and $CH_3\text{-}C \equiv C\text{-}CH_3$
1- Butyne 2-Butyne

$CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl$ and $CH_3\text{-}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{-}CH_3$
1-Chloropropane 2- Chloropropane

(3) Functional Group Isomerism:

The compounds that have same molecular formula but differ with respect to functional group are called functional group isomers.

The pair classes of compounds that can show functional group isomerism are

1. Alcohols and ethers 2. Aldehydes and Ketones 3. Carboxylic acids and esters.

Functional group isomers of C_2H_6O

(i) $CH_3\text{-}CH_2\text{-}OH$ and $CH_3\text{-}O\text{-}CH_3$
Ethyl alcohol Dimethyl ether

(ii) $CH_3\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}H$ and $CH_3\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_3$
Propanal Propanone

(4) Metamerism:

The compounds having same molecular formula but different distribution of carbon atoms on either side of same functional group.

The classes of compounds that can show metamerism are:

(1) ethers (2) ketones (3) esters

Metamers of $C_4H_{10}O$

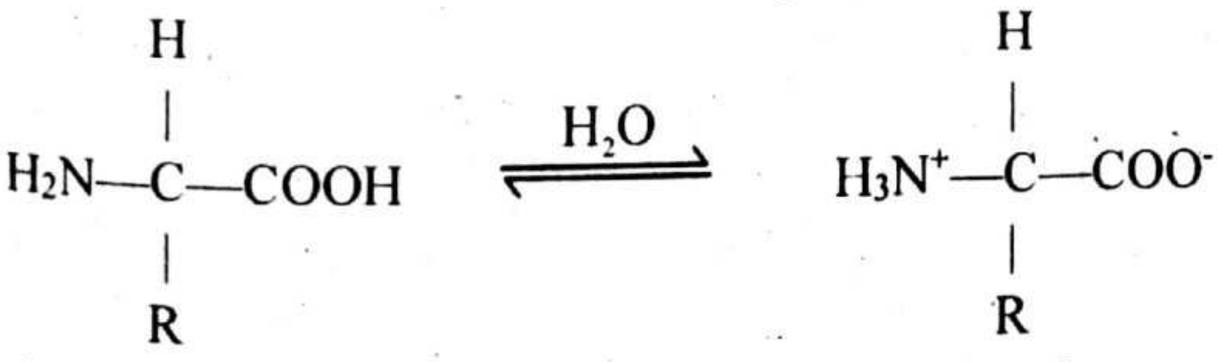
(i) $CH_3CH_2\text{-}O\text{-}CH_2\text{-}CH_3$ and $CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$
Diethyl ethers Methyl n-propyl ether

Metamers of $C_5H_{10}O$

(ii) $CH_3CH_2\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_3$ and $CH_3\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_2\text{-}CH_3$
Diethyl Ketone Methyl n-propyl ketone

(5) Tautomerism:

The compounds which differ with respect to position of H-atom within the same molecule. These isomers are usually rapidly interconvertable with each other.



Amino acid Zwitter ion

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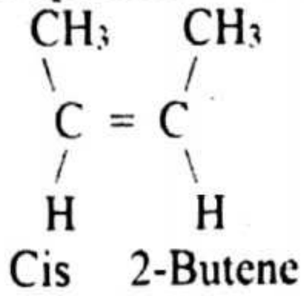
(2) GEOMETRIC (CIS-TRANS) ISOMERISM

The compound having same molecular formula and structural formula but differ with respect to the position of identical groups in space.

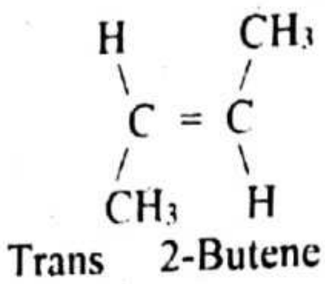
Conditions to show geometric isomerism:

(i) There should be a double bond between the two carbon atoms. As a result, position of groups become fixed due to restricted rotation.

(ii) Two groups attached to the same carbon atoms must be different



Cis 2-Butene



Trans 2-Butene

Cis isomer

An isomer in which identical groups across the double bond are on the same side is called cis isomer. eg. cis-2-Butene.

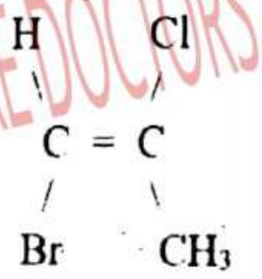
Trans isomer

An isomer in which identical groups across the double bond are on the opposite sides is called trans isomer. eg. trans-2-Butene.

Geometric isomer of 1-Bromo-2-Chloropropene:



Cis-1-Bromo-2-chloroprepene



Trans-1-Bromo-2-chloropropene

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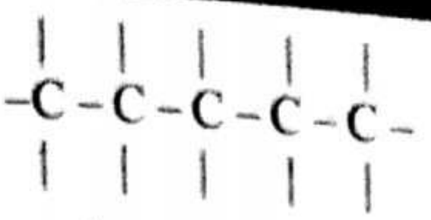
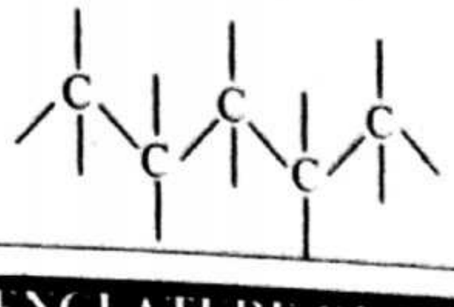
Difference between homologues and isomers

	Homologues	Isomers
General formula	Applicable	No
Functional group	Same	May or may not be same
Periodic difference of CH_2	Present	Absent
Structural formula	Similar	Different
Molecular formula	Different	Same
Molecular weight	Different	Same

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Formulae of organic compounds

The molecular formula of organic compound may be expressed as: e.g. pentane

Condensed Structural Formula	Displayed Formula	Skeletal Formula
(a) Simple molecular formula: C_5H_{12} (b) Simple structural formula: $CH_3(CH_2)_3CH_3$	(a)  (b) 	

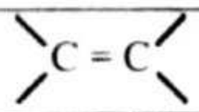
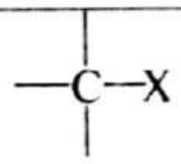
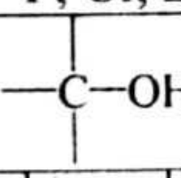
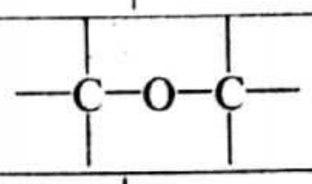
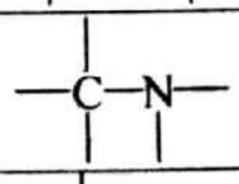
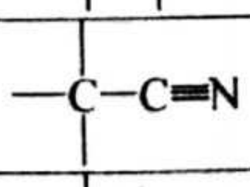
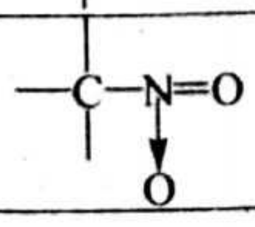
FUNCTIONAL GROUP AND NOMENCLATURE OF ORGANIC COMPOUNDS

FUNCTIONAL GROUP

An atom or a group of atoms or a double bond or a triple bond whose presence imparts specific properties to organic compounds is called a functional group.

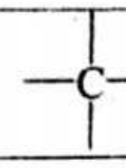
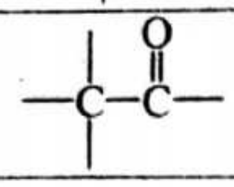
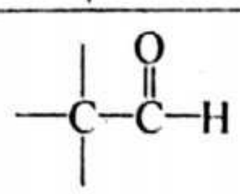
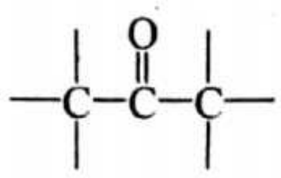
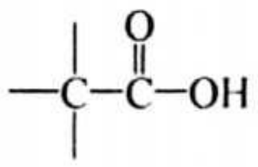
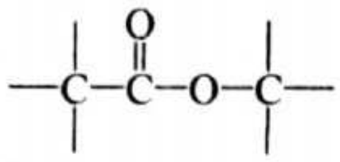
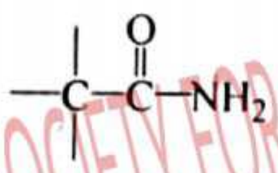
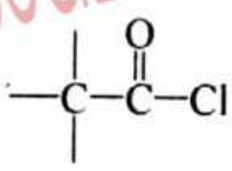
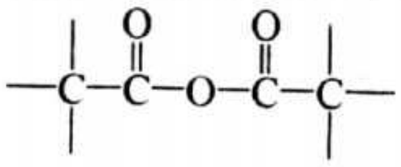
Characteristics

- Each functional group defines an organic family.
- They are the chemically functional parts of molecules.
- Although over seven million organic compounds are known, but there are only a hundred of functional groups.

Family	Structure of Functional Group	Simple Example
Alkane	Containing only C-H and C-C single bonds Contain no functional group	CH_4 (Methane), CH_3-CH_3 (Ethane)
Alkene		$CH_2 = CH_2$ (Ethene)
Alkyne	$-C \equiv C-$	$HC \equiv CH$ (Ethyne or acetylene)
Halide	 (X = F, Cl, Br, I)	CH_3-Cl Methyl chloride
Alcohol		Methyl alcohol (Methanol)
Ether		CH_3-O-CH_3 Dimethyl ether
Amine		CH_3-NH_2 Methyl amine
Nitrile		CH_3CN Methyl cyanide (or Ethanitrile)
Nitro		CH_3NO_2 Nitromethane

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Thiol		CH_3 - SH Methane thiol (Methylthiol)
Carbonyl		Aldehydes, ketones, acids and derivatives of acids
Aldehyde		$CH_3-\overset{O}{\overset{\|\|}{C}}-H$ (Acetaldehyde)
Ketone		$CH_3-\overset{O}{\overset{\|\|}{C}}-CH_3$ Dimethyl ketone (Acetone)
Carboxylic acid		$CH_3-\overset{O}{\overset{\|\|}{C}}-OH$ (Acetic acid)
Ester		$CH_3-\overset{O}{\overset{\|\|}{C}}-OCH_3$ (Methyl acetate)
Acid amide		$CH_3-\overset{O}{\overset{\|\|}{C}}-NH_2$ (Acetamide)
Carboxylic acid chloride		$CH_3-\overset{O}{\overset{\|\|}{C}}-C\ell$ (Acetyl chloride)
Carboxylic acid anhydride		$H_3C-\overset{O}{\overset{\|\|}{C}}-O-\overset{O}{\overset{\|\|}{C}}-CH_3$ (Acetic anhydride)

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NOMENCLATURE

Alkanes	Alkenes
Selection of longest continuous carbon chain	Selection of longest continuous carbon chain containing double bond
Start numbering from where any branch is nearest	Start numbering from where double bond is nearest
Write the position of substituent and write the name of substituent alphabetically. use prefix di, tri,tetra if required	Write the position and name of substituent alphabetically, use prefix di, tri,tetra if required
.	Write the position of double bond of lower carbon
Write the name of root chain	Write the name of alkene according to number of C-atoms
	If there are more than one double bond present then write position of each double bond and ene is replaced with suffix diene, triene and tetraene etc.

Formula	IUPAC Name
$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	2- Methylpentane
$CH_3-CH_2-\underset{\displaystyle H_3C}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	2,3 – Dimethylpentane
$CH_3-CH_2-CH_2-\underset{\displaystyle H_3C}{\underset{\vert}{CH}}-\underset{\displaystyle C_2H_5}{\underset{\vert}{CH}}-CH_3$	3,4-Dimethylheptane
$CH_3-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_2-\underset{\displaystyle Br}{\underset{\vert}{CH}}-CH_3$	2–Bromo–4–chloropentane
$CH_3-CH_2-CH_2-\underset{\displaystyle Br}{\underset{\vert}{CH}}-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_3$	3–Bromo–2–chlorohexane.

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Unsaturated hydrocarbons

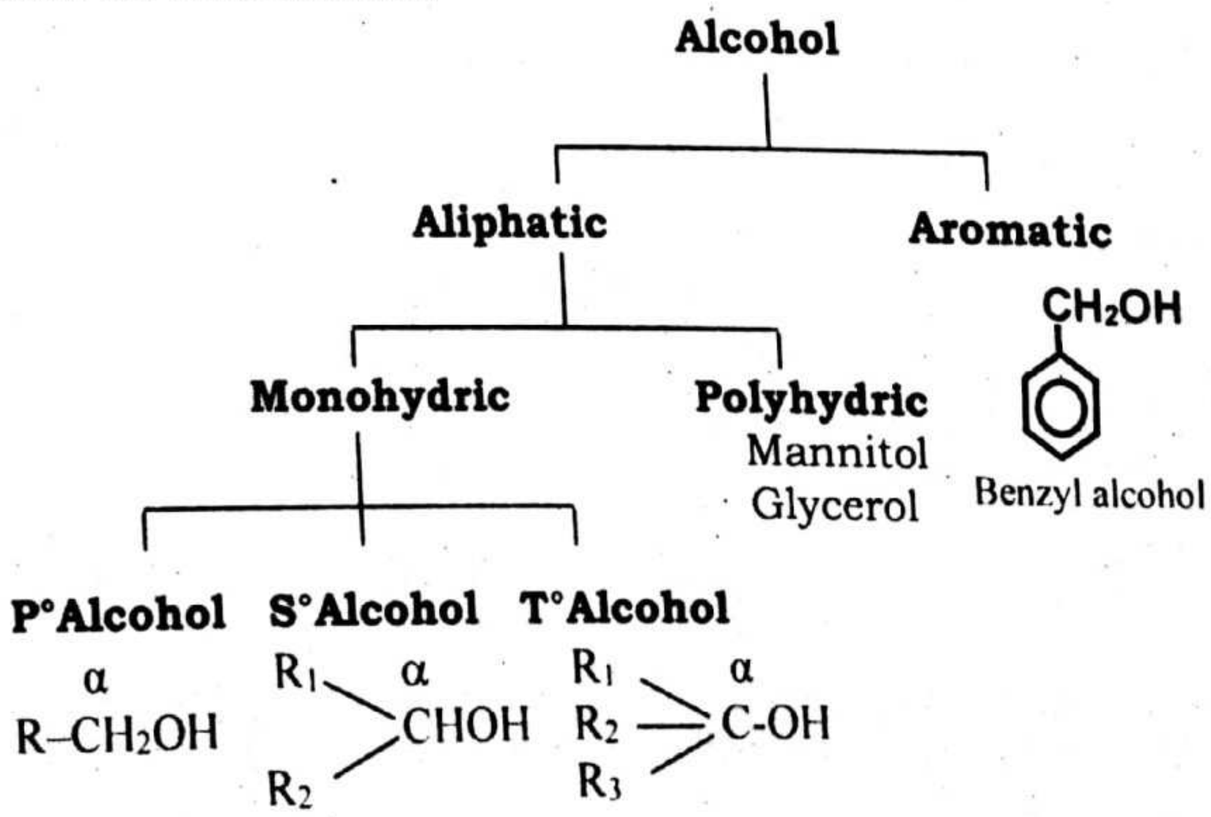
- Alkanes are said to be saturated hydrocarbons as they contain only single bonds between carbon atoms.
- Alkenes and alkynes are unsaturated hydrocarbons: they contain multiple bonds between carbon atoms.
- The simplest alkene is ethene $H_2C = CH_2$
- It is the first member of the homologous series of alkenes, which have general formula C_nH_{2n}.
- Alkynes contain one or more carbon – carbon triple bonds. Ethyne $HC \equiv CH$ is the first member of the homologous series of alkynes, which have the general formula C_nH_{2n-2}

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No. of C atoms	Alkane		Alkene		Alkyl Group	
	Formula	Name	Formula	Name	Formula	Name
1	CH_4	Methane			CH_3	Methyl
2	C_2H_6	Ethane	C_2H_4	Ethene	C_2H_5	Ethyl
3	C_3H_8	Propane	C_3H_6	Propene	C_3H_2	Propyl
4	C_4H_{10}	Butane	C_4H_8	Butene	C_4H_9	Butyl
5	C_5H_{12}	Pentane	C_5H_{10}	Pentene	C_5H_{11}	Pentyl
n	C_nH_{2n+2}	Alkane	C_nH_{2n}	Alkene	C_nH_{2n+1}	Alkyl (R)

Formula	IUPAC Name
$CH_3 = CH - CH_2 - CH_3$	But–1–ene
$CH_2 = CH - CH = CH_2$	Buta–1, 3–diene
$CH_3-CH_3-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle \vert}{C}}-CH_3$	4–Methylpent–2–ene
$H_3\overset{3}{C}-\overset{2}{C}\equiv\overset{1}{C}H$	Propyne
$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle \vert}{CH}}-CH_2-CH_2-C\equiv CH$	5–Methyl–1–hexyne
$H\overset{1}{C}\equiv\overset{2}{C}-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_3$	3–Penten–1–yne
$H\overset{5}{C}\equiv\overset{4}{C}-\underset{\displaystyle 3}{\overset{\displaystyle CH_3}{\overset{\displaystyle \vert}{C}}}H-\overset{2}{C}H=\overset{1}{C}H_2$	3–Methyl–1–penten–4–yne

NOMENCLATURE OF ALCOHOLS

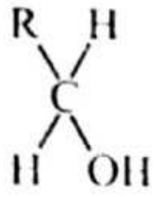
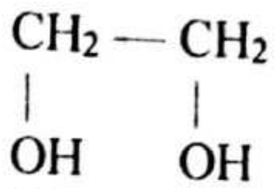
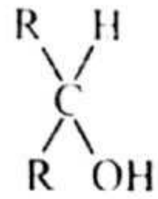
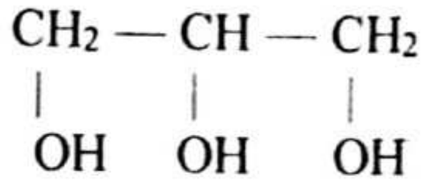
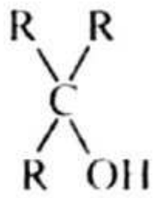
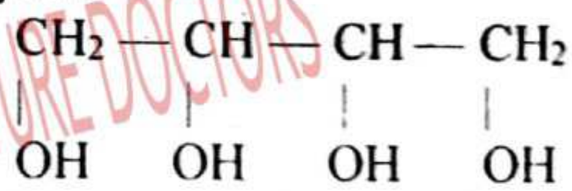


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- They can be regarded as alkanes in which one H atom is replaced by a –OH group and are often called the alkanols.
- The names are arrived at by adapting the name of the parent alkane by changing the terminal ane to – ol.

Formula	IUPAC Name	Formula	IUPAC Name
CH_3OH	Methanol	C_4H_9OH	Butanol
C_2H_5OH	Ethanol	$C_5H_{11}OH$	Pentanol
C_3H_7OH	Propanol	$C_6H_{13}OH$	Hexanol

Monohydric Alcohol	Polyhydric Alcohol
Primary 	Dihydric  Ethane-1,2-diol
Secondary 	Trihydric  Propane-1,2,3-triol (glycerol)
Tertiary 	Tetrahydric  Butane-1,2,3,4-tetraol

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NOMENCLATURE OF HALOALKANES

Monohaloalkanes are named as alkyl halides while polyhalo derivative of alkanes are known as haloalkanes.

Alkyl halides

a) Common Names:

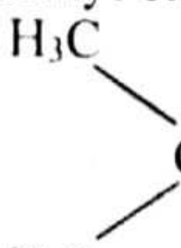
Alkyl halides (monohaloalkanes) are named according to the nature of the alkyl group to which halogen atom is attached.

Example:

$CH_3—Cl$
Methyl chloride

$CH_3—CH_2—Br$
Ethyl bromide

$CH_3—CH_2—CH_2—Br$
n-Propyl bromide


Isobutyl chloride

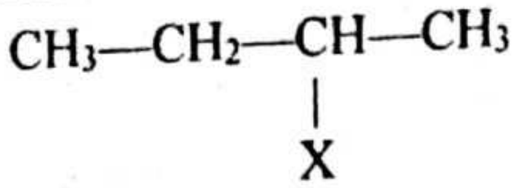
$CH_3—CH_2—CH_2—CH_2—Cl$
n-Butyl chloride

b) IUPAC Nomenclature:

The systematic names given to alkyl halide follow the underlying rules

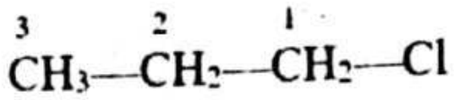
- Select the longest continuous carbon chain and consider the compound to have been derived from this structure.
- Number the carbon atoms in chain so that the carbon atom containing the functional group (F,Cl,Br,I) gets the lowest possible number.

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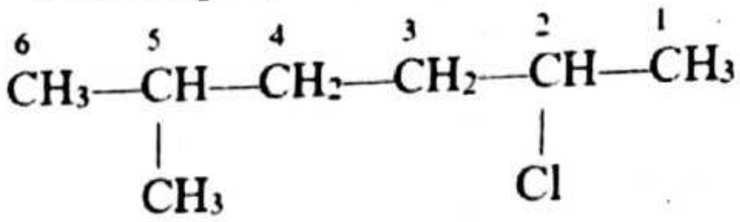


2-Halobutane

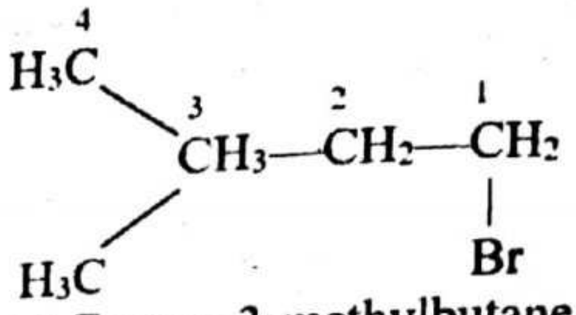
- If the same alkyl substituent occurs more than once in the chain, the prefix di, tri, and so on are used before the name of alkyl group.
- The position of the substituent is indicated by the appropriate numbers separated by commas. If the same substituent occurs twice on the same carbon atom, the number is repeated.



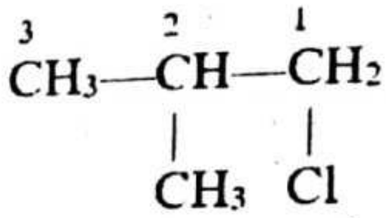
1-Chloropropane



2-Chloro-5-methylhexane



1-Bromo-3-methylbutane



1-Chloro-2-methylpropane

Ethers

Formula	Common Names	IUPAC
CH_3OCH_3	Dimethyl ether	Methoxy methane
$CH_3OC_2H_5$	Methyl ethyl ether	Methoxy ethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxy ethane
$CH_3OC_6H_5$	Methyl phenyl ether (Anisol)	Methoxy benzene

Aldehydes

Trivial name	IUPAC rule
The common names of aldehydes are obtained from the common names of carboxylic acids containing the same number of carbon atoms. The ending –ic acid in the common name of the acid is replaced by the word aldehyde.	• Select longest chain containing –CHO group • C of aldehyde will get number 1 which is usually not written • Write down the position of substituent and name alphabetically • Replace the "e" of alkane by "al"

Ketones

Trivial name	IUPAC rule
• Write alkyl group alphabetically followed by the name ketone. • If both groups are same then prefix di is used before the name of alkyl group • If both alkyl groups are different called unsymmetric or mixed ketones.	• Select longest chain containing carbonyl group • Start numbering with least number to C of carbonyl group. • Write down position and name of Substituent alphabetically • The position of carbonyl group is prefixed to the alkanone • Replace the "e" of alkane with "one"

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NOMENCLATURE OF CARBOXYLIC ACIDS

- Organic compounds containing –COOH as a functional group (carb from carbonyl and oxyl from hydroxyl).
- Their general formula is R-COOH

Sr. No.	Formula	IUPAC Name	Common Name
1	HCOOH	Methanoic acid	Formic acid
2	CH_3COOH	Ethanoic acid	Acetic acid
3	CH_3CH_2COOH	Propanoic acid	Propionic acid
4	$CH_3(CH_2)_2COOH$	Butanoic acid	Butyric acid
5	$CH_3(CH_2)_3COOH$	Pentanoic acid	Valeric acid
6	$CH_3(CH_2)_4COOH$	Hexanoic acid	Caproic acid
		Dicarboxylic acids	
7	HOOCCOOH	Ethanedioic acid	Oxalic acid
8	$HOOC(CH_2)COOH$	Propanedioic acid	Malonic acid
9	$HOOC(CH_2)_2COOH$	Butanedioic acid	Succinic acid
10	$HOOC(CH_2)_3COOH$	Pentanedioic acid	Glutaric acid
11	$HOOC(CH_2)_4COOH$	Hexanedioic acid	Adipic acid
		Aromatic acid	
12	C_6H_5COOH	Benzoic acid	Benzenecarboxylic acid
13	$C_6H_4(COOH)_2$	Phthalic acid	Benzenedicarboxylic acid

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TOPIC-14 CHEMISTRY OF HYDROCARBONDS

COURSE CONTENTS

- Describe free radical mechanism (Initiation, Propagation and Termination)
- Describe the mechanism of free radical substitution in alkanes examplified by methane and ethane
- Structure and reactivity of alkenes as examplified by ethene.
- Explain dehydration of alcohols and dehydrohalogenation of R – X for the preparation of ethene.
- Describe the preparation of alkynes using elimination reactions
- Discuss the shapes of alkynes in terms of sigma and pi C – C bond.
- Discuss the chemistry of alkynes by hydrogenation, hydrohalogenation, hydration.
- Describe acidity of alkynes.
- Compare the reactivity of alkynes with alkanes, alkenes and arenes
- Describe and differentiate between substitution and addition reactions
- Benzene: Properties, Structure, Modern representation, Resonance method, Electrophilic substitution
- The molecular orbital treatment of benzene
- Describe the mechanism of electrophilic substitution in benzene

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CHEMISTRY OF ALKANES

Radical Substitution Reactions

- Substitution of R-H by X provides the alkyl halide, R-X and HX.
- Alkane R-H relative reactivity order: $3^o > 2^o > 1^o >$ methyl.
- Halogen reactivity $F_2 > Cl_2 > Br_2 > I_2$.
- Only chlorination and bromination are useful in the laboratory.
- Reaction proceeds *via* free radical chain mechanism.

THE MECHANISM OF FREE RADICAL SUBSTITUTION REACTION

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{Methylene chloride}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloroform}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$$

Mechanism:

(i) Initiation step:

$$\underset{\substack{\text{Chlorine}\\\text{molocule}}}{Cl\text{-}Cl} \xrightarrow{\text{sunlight}} \underset{\text{Chlorine free radicals}}{Cl^{\bullet} + Cl^{\bullet}}$$

(ii) Propagation step:

(a) $CH_3\text{-}H + Cl^{\bullet} \longrightarrow \underset{\substack{\text{Methyl free}\\\text{radical}}}{CH_3^{\bullet}} + HCl$

(b) $CH_3^{\bullet} + Cl\text{-}Cl \longrightarrow \underset{\substack{\text{Methyl}\\\text{Chloride}}}{CH_3\text{—}Cl} + \underset{\substack{\text{Chlorine}\\\text{free radical}}}{Cl^{\bullet}}$

(iii)Termination step:

$$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow \underset{\text{Methyl chloride}}{CH_3\text{—}Cl}$$

Points to Remember:

The following facts must be accommodated by any reasonable mechanism for the halogenation reaction.

- The reactivity of the halogens decreases in the following order: $F_2 > Cl_2 > Br_2 > I_2$.
- We shall confine our attention to chlorine and bromine, since fluorine is so vigorously reactive and it is difficult to control, and iodine is generally unreactive.
- Chlorination and bromination are normally exothermic.
- Energy input in the form of heat or light is necessary to initiate these halogenations.
- If light is used to initiate halogenation, thousands of molecules react for each photon of light absorbed.
- **Inhibiters:** Halogenation reactions may be conducted in either the gaseous or liquid phase.
- **Facilitators:** In gas phase chlorination the presence of oxygen (a radical trap) inhibits the reaction.
  In liquid phase halogenation radical initiators such as peroxides facilitate the reaction.

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Mechanism of the chlorination of ethane

Step 1:

Homolysis of the Cl — Cl bond. The necessary energy comes from the light absorbed or the heat supplied. It is easier to split the Cl — Cl bond than the C — H bond. (Bond energy, Cl — Cl = 242 kJ mol^{-1}; C — H = 435 kJ mol^{-1}

$$Cl_2 \xrightarrow[\text{or heat}]{\text{light}} 2Cl^{\bullet}$$

Step 2:

The chlorine atoms formed are very reactive. Since they are surrounded by ethane molecules:

$$Cl^{\bullet} + CH_3—CH_3 \longrightarrow HCl + {}^{\bullet}CH_2—CH_3$$

The second possibility is more likely because the formation of an H — Cl bond is more exothermic than the formation of a C — Cl bond. (Bond energy, H – Cl = 431 kJ mol^{-1}; C – Cl = 350 kJ mol^{-1}.)

Step 3:

The methyl radicals formed collide with methane molecules and chlorine molecules. The reaction $^{\bullet}CH_2—CH_3 + CH_3—CH_3 \longrightarrow CH_3—CH_3 + {}^{\bullet}CH_2—CH_3$ results in no net change.

The reaction $^{\bullet}CH_2—CH_3 + Cl_2 \longrightarrow CH_3CH_2Cl + {}^{\bullet}Cl$ leads to a chain reaction.

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Step 4:

Thousands of molecules of chloroethane are formed for every photon of light absorbed. The high yield is due to the chain reaction – steps 2 and 3. The reason why yield is not higher is that radicals can combine with each other and bring the chain to an end. The reactions

$$2Cl^{\bullet} \longrightarrow Cl_2$$

$$2CH_3— {}^{\bullet}CH_2 \longrightarrow C_4H_{10}$$

$$Cl^{\bullet} + {}^{\bullet}CH_2— CH_3 \longrightarrow CH_3CH_2Cl$$

Bring the chain reaction to an end. Some ethane can be detected in the product.

Formation of other halogen substituted products of alkanes

Step 3 can give rise to the chain:

$$CH_3CH_2Cl + Cl^{\bullet} \longrightarrow HCl + {}^{\bullet}CH_2—CH_2Cl$$

$$^{\bullet}CH_2—CH_2Cl + Cl_2 \longrightarrow (CH_2)_2Cl_2 + Cl^{\bullet}$$

$(CH_2)_2Cl_2$ can undergo further chlorination to CH_3CCl_3, CH_2ClCCl_3, $CHCl_2CCl_3$ and C_2Cl_6

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CHEMISTRY OF ALKENES

PREPARATION OF ALKENES

Preparation of alkenes

Reactions	Remarks
Dehydrohalogenation	Removal of hydrogen and halogen from two adjacent carbon atoms is called dehydrohalogenation.
Dehydration of alcohol	▸ Removal of water molecule is called dehydration ▸ Tendency of dehydration is as given below. Tertiary alcohol > Secondary alcohol > Primary alcohol
Dehalogenation of Vic-dihalide	Removal of halogen is called dehalogenation
Kolbe's electrolysis of dicarboxylic acid salts	Salts of saturated dicarboxylic acid are subjected to electrolysis in an aqueous solution and alkenes are formed

General methods of preparation

(i) Dehydration of alcohols

Alcohols can be dehydrated in the presence of certain catalysts. The catalysts are called dehydrating reagents. The best dehydrating reagents are

(i) Conc. H_2SO_4 (ii) Al_2O_3 (iii) P_2O_5 or H_3PO_4

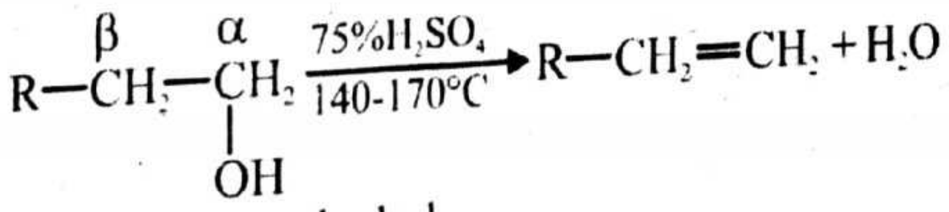
All these dehydrating reagents operate at elevated temperature.

$$\underset{\text{Alcohol}}{R-CH_2-CH_2-OH} \xrightarrow[340-350^\circ C]{Al_2O_3} \underset{\text{An Alkene}}{R-CH=CH_2} + H_2O$$

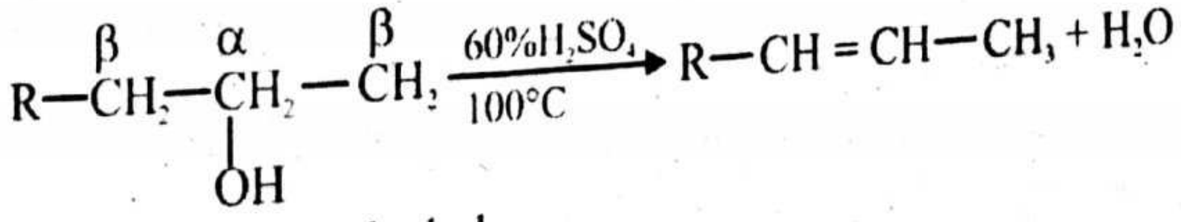
$$\underset{n-\text{Propanol}}{CH_3-CH_2-CH_2-OH} \xrightarrow[340-350^\circ C]{Al_2O_3} \underset{\text{Propene}}{CH_3-CH=CH_2} + H_2O$$

The order of reactivity of these alcohols is as follows

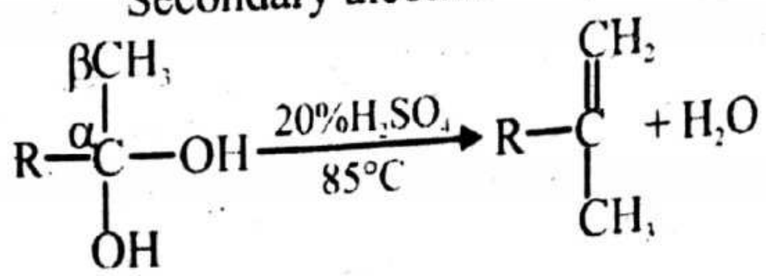
3° alcohol > 2° alcohol > 1°alcohol



Primary alcohol



Secondary alcohol



Tertiary alcohol

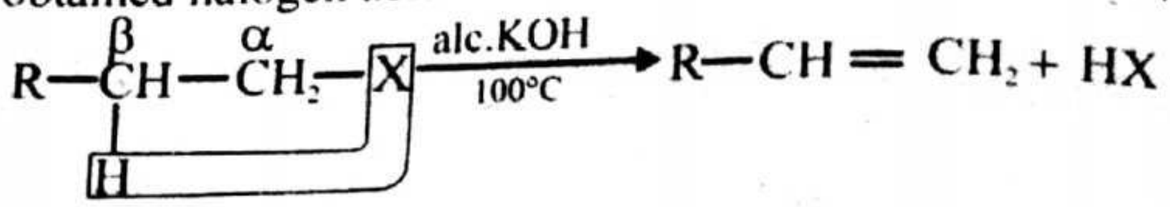
(ii) Dehydrohalogenation of alkyl halide

- Alkyl halides on heating with alcoholic potassium hydroxide undergo dehydrohalogenation.

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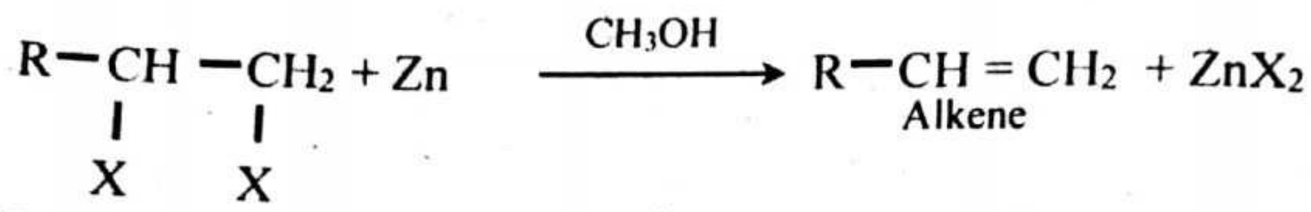
- Elimination of a halogen atom from the α-carbon together with a hydrogen atom from adjacent β-carbon atoms.
- The product obtained halogen acid reacts with KOH to give salt and water.



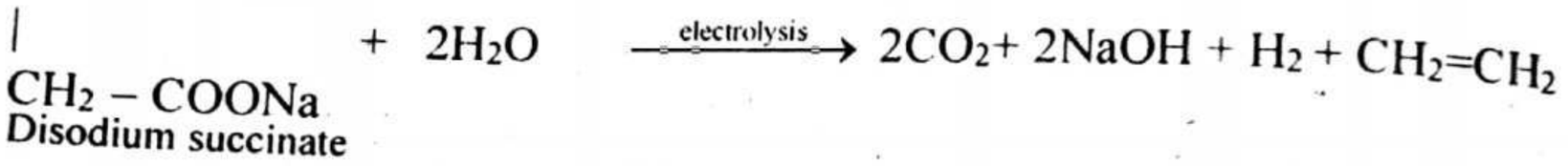
Alkyl halide

$$HX + KOH \longrightarrow KX + H_2O$$

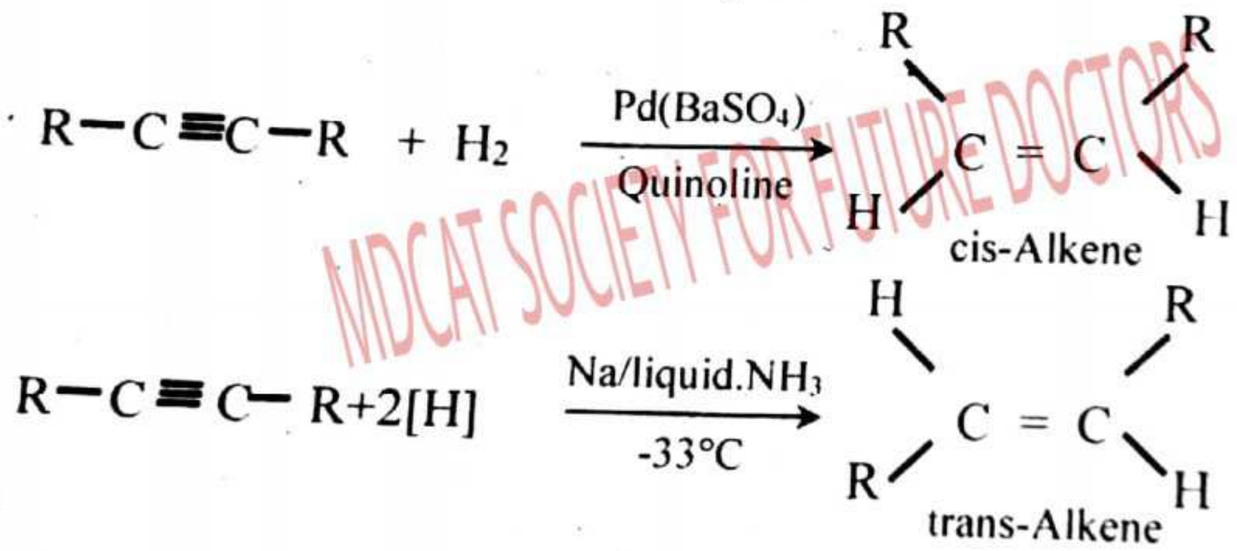
(iii)Dehalogenation of Vic-Dihalides



(iv)Kolbe's Electrolytic Method (Electrolysis of salts of dicarboxylic acids)



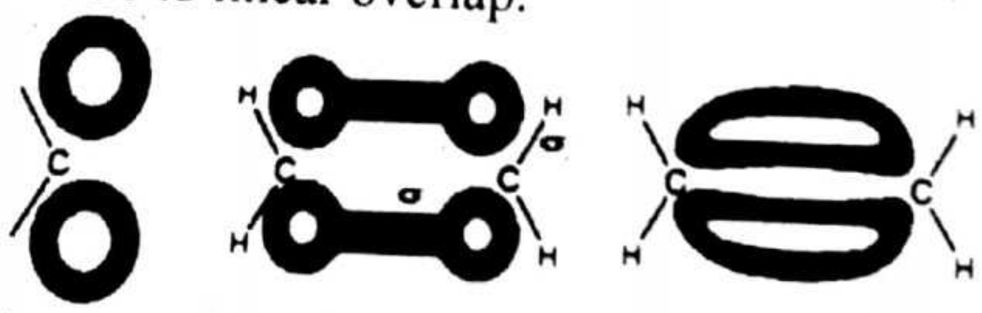
(v) Partial Hydrogenation of Alkynes



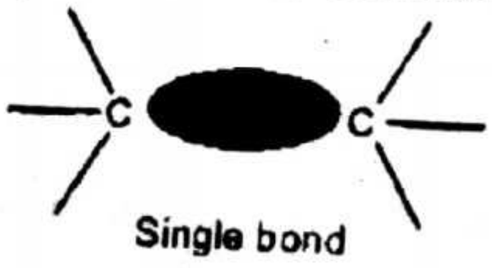
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Structure:

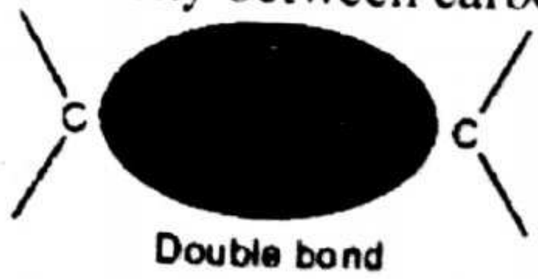
The carbon atoms linked through π-bond are sp^2 hybridized. Therefore, each atom carries three sp^2-hybrids and one p-orbital. The p-orbital overlap to form π-bond and hybrid orbitals form σ-bonds due to linear overlap.



The carbon-carbon distance in ethene is shorter (1.34Å) than the C-C bond distance of ethane (1.54Å). It is due to increased electron density between carbon atoms.



Single bond



Double bond

Carbon atoms are coplanar, and the rotation of one C-atom with respect to other is restricted which results in cis-trans isomerism in alkene.

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REACTIONS OF ETHENE

ADDITION REACITONS

Catalytic hydrogenation

- Addition of hydrogen molecule to an unsaturated compound in the presence of catalyst an moderate pressure to give a saturated compound.
- The catalysts which are mostly employed are platinum, palladium and Raney nickel
- Raney nickel is prepared by treating an alloy of Ni and Al with caustic soda. It functions better at about 100°C and 3atm pressure.

$$Ni - Al + NaOH + H_2O \longrightarrow Ni + NaAlO_2 + \frac{3}{2}H_2$$

- Hydrogenation is an exothermic process

$$CH_2 = CH_2 + H_2 \xrightarrow[100°C]{\text{Raney Ni pressure 3atm}} CH_3 - CH_3$$

Ethene → Ethane

Halogenation

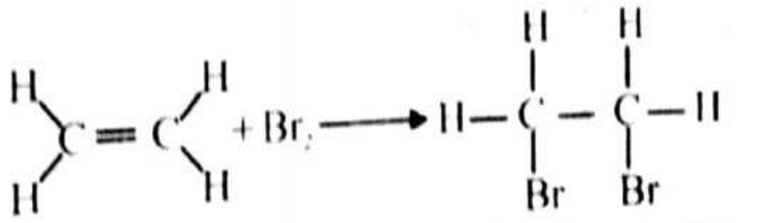
- Alkenes react with halogens to give dihaloalkanes (vicinal dihalides).
- The solvent used in the halogenation is inert, like CCl_4
- This reaction happens at room temperature.
- Halogen attack at the double bond in the form of electrophiles.
- The order of ease of addition of halogen in an alkene is

$$F_2 > Cl_2 > Br_2 > I_2$$

Iodine does not react with alkenes.

- The reddish brown colour of Br_2 in this reaction is discharged therefore it is used to verify the presence of carbon – carbon double bond in the compound.

Reaction

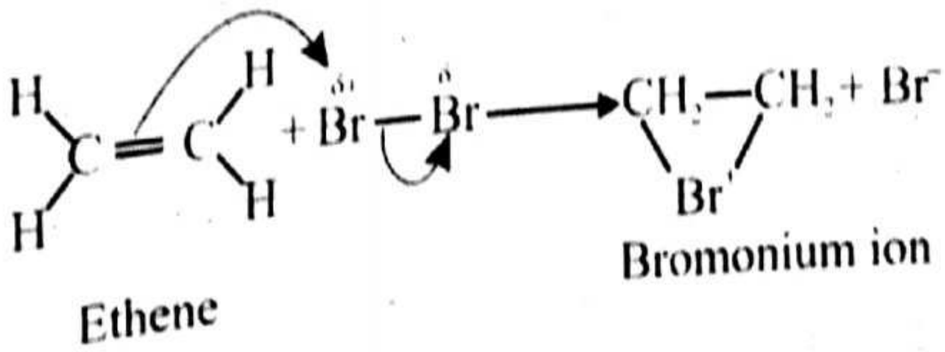


Ethene → 1,2-Dibromoethane

Mechanism

Addition of halogen in alkene is two step mechanism

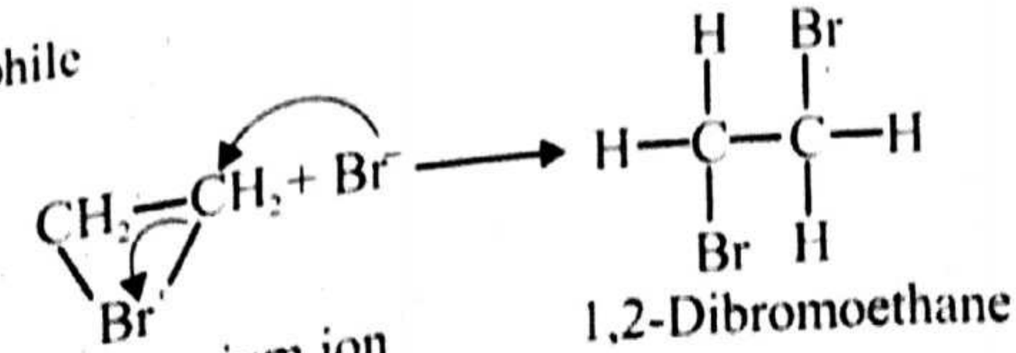
Step-1



Ethene → Bromonium ion

Step-2

Br^- acts as nucleophile



Bromonium ion → 1,2-Dibromoethane

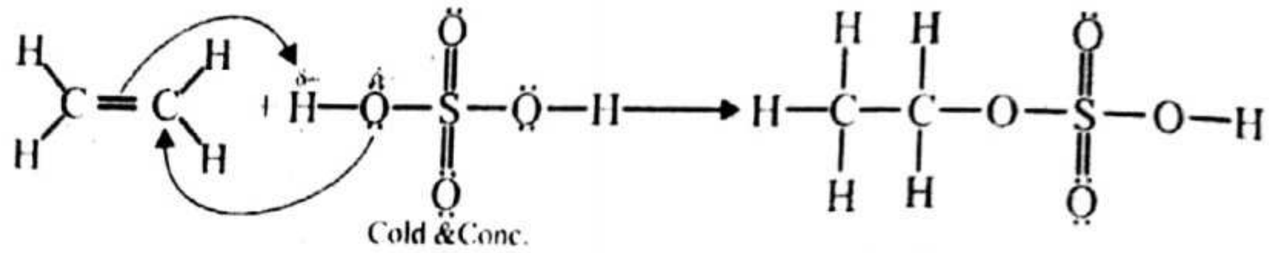
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Hydration of alkenes (Addition of sulphuric acid)

- When alkenes are treated with cold concentrated sulphuric acid, they are dissolved because they form alkyl hydrogen sulphate.
- Alkyl hydrogen sulphates on boiling with water decompose to give corresponding alcohols.
- This reaction can be used to convert alkenes into alcohols.
- If 10% H_2SO_4 is used, then alcohols are produced directly

Reactions



Ethyl hydrogen sulphate

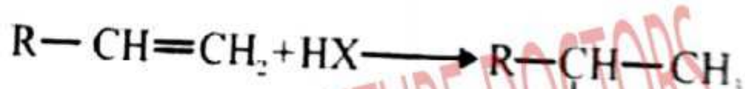
$$CH_3-CH_2-O-SO_3H \xrightarrow[HOH]{100°C} CH_3-CH_2-OH + H_2SO_4$$

Ethyl alcohol

Reaction with HBr with special reference to Markownikov's rule

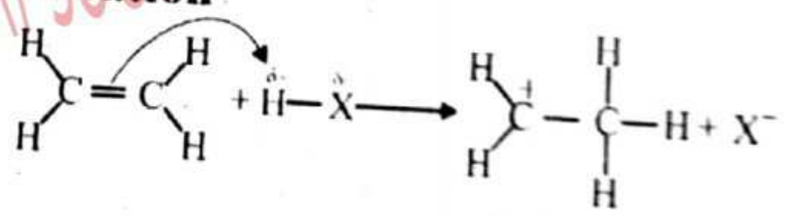
- Alkenes react with dry gaseous hydrogen halides to form alkyl halides.
- The order of reactivity of halogen acids is HI > HBr > HCl.
- Reaction mechanism involves carbocation formation.

Reaction



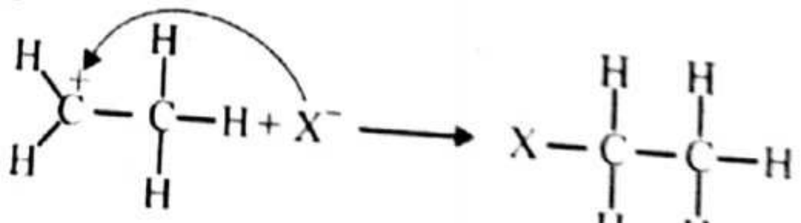
Mechanism

Step-1 Formation of carbocation



Carbocation

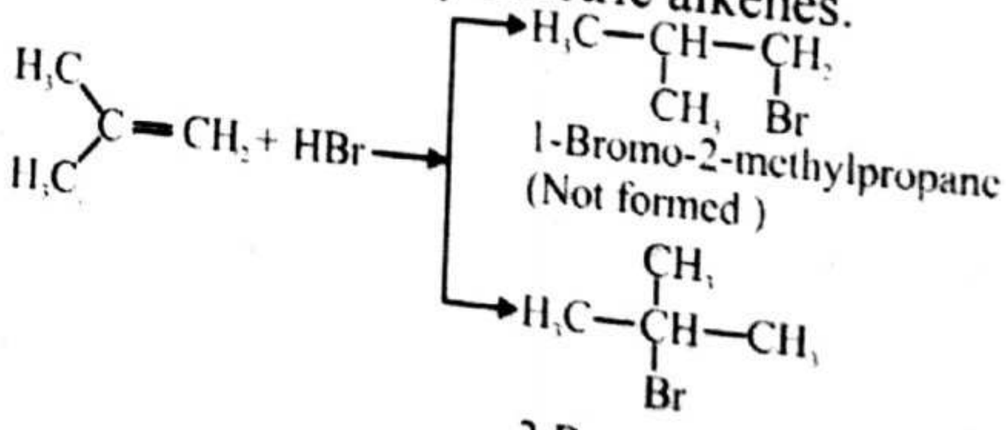
Step-2 Attack of nucleophile



Markownikov's rule

"In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, constituting the double bond, which has least number of hydrogen atoms."

Markownikov's rule is implemented on asymmetric alkenes.



1-Bromo-2-methylpropane
(Not formed)

2-Bromo-2-methylpropane
(Actual product)

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Topic-14

OXIDATION REACITONS

Addition of oxygen

$$CH_2=CH_2 + \tfrac{1}{2}O_2 \xrightarrow[300°C]{Ag_2O} \underset{\text{Ethylene epoxide}}{\overset{H_2C}{\underset{H_2C}{\diagdown\!\diagup O}}}$$

- Epoxides serve as the starting substances for the industrial production of **glycols**.

Hydroxylation

(i) Using cold alkaline or acidic $KMnO_4$ (Baeyer's reagent)

- This is also known as hydroxylation of alkene.
- Dilute 1% alkaline $KMnO_4$ solution is called Baeyer's reagent.
- The pink colour of $KMnO_4$ solution is discharged during the reaction.
- This reaction can be used to check the presence of carbon – carbon double bond in a molecule.

$$3H_2C=CH_2 + 2KMnO_4 + 4H_2O \xrightarrow[OH^-]{Cold} 3\underset{OH}{\overset{|}{CH_2}}-\underset{OH}{\overset{|}{CH_2}} + 2MnO_2 + 2KOH$$

Ethylene glycol

(ii) Using hot concentrated acidic or alkaline $KMnO_4$ (Oxidative Cleavage)

- Alkenes when heated with alkaline $KMnO_4$ are cleaved at the double bond to form carboxylic acids.
- Carboxylic acids are formed from oxidative cleavage of alkene.

$$R-CH=CH-R + 4[O] \xrightarrow[\Delta]{KMnO_4/OH^-} 2RCOOH$$

Symmetrical alkene — Carboxylic acid

$$H_3C-CH=CH-CH_3 + 4[O] \xrightarrow[\Delta]{KMnO_4/OH^-} 2CH_3COOH$$

2 – Butene — Ethanoic acid

(3) Combustions

$$CH_2=CH_2 + 3O_2 \xrightarrow{Flame} 2CO_2 + 2H_2O + Heat$$

(4) Ozonolysis

$$CH_2=CH_2 + O_3 \xrightarrow{Ether} \underset{\text{Ethylene ozonide}}{\overset{O-CH_2}{\underset{O-CH_2}{\diagdown\!\diagup O}}}$$

$$\underset{O-CH_2}{\overset{O-CH_2}{\diagdown\!\diagup O}} + 2H_2O \longrightarrow 2H-CHO + 2H_2O_2$$

$$H_2O_2 + Zn \longrightarrow ZnO + H_2O$$

Ozonolysis is used to locate the **position of double bond** in an alkene.

Polymerization:

In this process small organic molecules (monomers) combine together to form larger molecules known as polymers.

Ethene at 400°C and 100 atm pressure, polymerize to polythene or polyethylene.

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$$n\,CH_2 = CH_2 \xrightarrow[\text{100 atm pressure}]{\text{400°C}} \underset{\text{Polyethylene}}{-[-CH_2 - CH_2-]_n}$$

Traces of O_2(0.1%)

A good quality polythene is obtained, when ethene is polymerized in the presence of aluminium triethyl Al $(C_2H_5)_3$ and titanium tetrachloride catalysts ($TiCl_4$).

POINT PONDER

Alkanes	Alkenes
▸ Alkanes containing →C_1-C_4 colourless and odourless gases →C_5-C_{17} colourless and odourless liquids →C_{18} -onwards colourless and odourless waxy solids ▸ Being non-polar, they are insoluble in water but soluble in non-polar solvents ▸ Physical constants ↑ Number of carbon atoms ↑ ▸ Solubility ↓ Molecular mass ↑	▸ First three members i.e ethene, propene and butene are gases at room temperature while C_5 to C_{15} are liquids and the higher members are solids ▸ They are insoluble in water but soluble in alcohol ▸ They have characteristic smell and burn with luminous flame ▸ Unlike alkanes, they show weakly polar properties because of sp^2 hybridization

PREPARATION OF ALKYNES BY ELIMINATION REACTIONS

Alkynes can be prepared by the following methods:

(i) Elimination reaction

(ii) Alkylation of sodium acetylide

But we discuss here only elimination reactions.

(i) Elimination of Hydrogen Halide (Dehydrohalogenation):

Alkynes can be prepared by dehydrohalogenation of vicinal and geminal dihalides in the presence of some alkaline reagents.

Dehydration of Alcohols:

Removal of water molecule is called dehydration.

Example:

When vapours of alcohol are passed over heated alumina, dehydration takes place with the formation of alkene. P_4O_{10}, H_2SO_4, H_3PO_4 are also used for dehydration.

$$\underset{\text{Alcohol}}{R-\overset{OH}{\overset{|}{CH}}-CH_2} \xrightarrow[340-450°C]{Al_2O_3} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

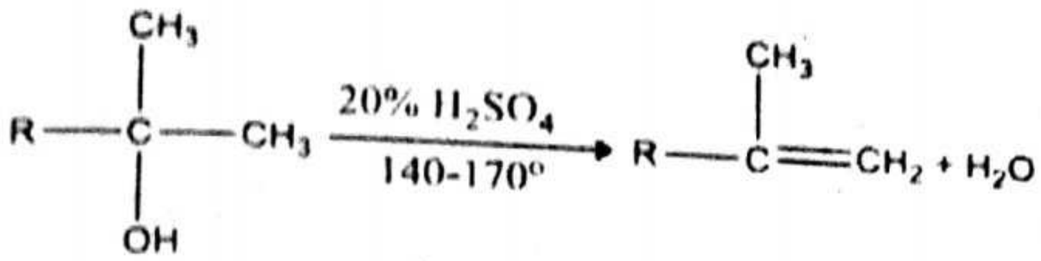
The ease of dehydration of various alcohols is in the order. ter. alcohol > sec. alcohol > pri. alcohol

For secondary alcohol,

$$R-\overset{OH}{\overset{|}{CH}}(CH_3)-CH_2 \xrightarrow[140-170°C]{75\%\ H_2SO_4} R-CH=CH_2 + H_2O$$

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For tertiary alcohol,

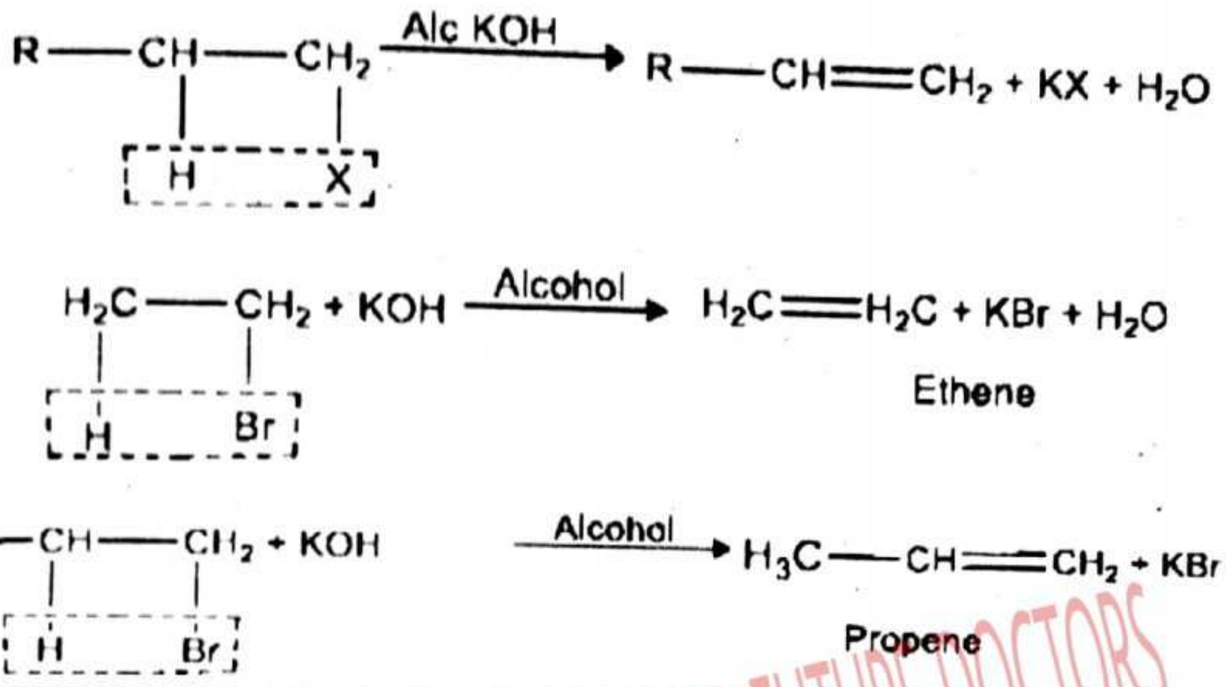


Dehydrohalogenation of Alkyl Halides

Removal of hydrogen halide (HX) from alky halides is called Dehydrohalogenation"

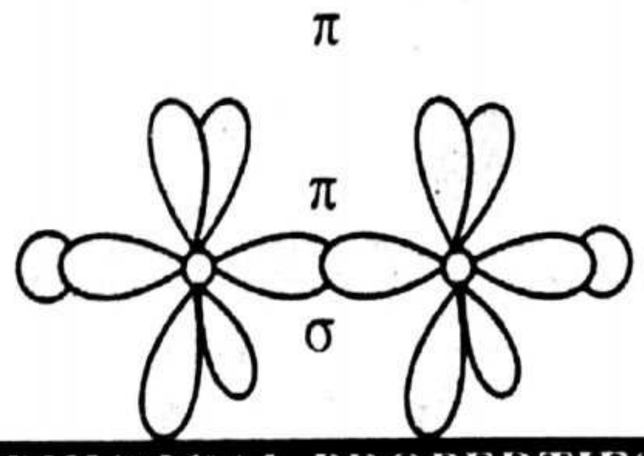
Example:

Alkyl halides on heating with alcoholic potassium hydroxide undergo Dehydrohalogenation to form alkenes.



STRUCTURE

The two carbons of acetylene (alkyne) are sp-hybridized. They are linked by a sigma bond due to sp-sp orbitals overlap. The unhybridized two p-orbitals on one carbon overlap with two p-orbitals on other carbon to form two pi-bonds. The cloud of pi-electrons is present cylindrically symmetrical about the carbon-carbon sigma-bond. Rotation about carbon-carbon sigma bond does not cause any change in energy and electron density. It is a linear molecule, and hence geometrical isomer is not observed in it.



PHYSICAL PROPERTIES

(i) Solubility:

In general, alkynes are non-polar and are insoluble in water but soluble in non-polar organic solvents.

(ii) Color and odour:

They are colourless, odourless except acetylene which has a garlic like odour.

(iii)Melting point, boiling point and densities:

The melting points, boiling points and densities increases gradually with the increase in molecular masses.

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(iv) Physical state:
The first three members carbon alkynes (C_2-C_4) are gases. The next eight members (C_5-C_{12}) are liquids and higher members are solids at room temperature.

Reactivity
Acetylene (alkyne) is an unsaturated hydrocarbon and shows addition reactions. It also undergoes substitute reactions due to easy cleavage of C-H bond. The pi-electrons are cylindrically symmetrical about carbon-carbon sigma bond and the removal of terminal hydrogen is possible without disturbing carbon–carbon bonding. Therefore, electrophile substitute reactions are possible in 1-alkynes.

ADDITION REACTIONS OF ALKYNES

(i) Alkynes undergo addition reactions in an analogous fashion to those of alkenes.
(ii) The high electron density of the pi bonds makes them nucleophile.
(iii) Two factors influence the relative reactivity of alkynes compared to alkenes:
(iv) Increased nucleophilicity of the starting pi system
(v) Stability of any intermediates (for example carbocations)

Hydrogenation:
Alkynes react with hydrogen gas in the presence of suitable catalysts like finely divided Ni, Pt or Pd. In the first step alkenes are formed which them take up another molecule of hydrogen to form an alkane.

$$HC\equiv CH + H_2 \xrightarrow[\text{Heat}]{\text{Ni}} H_2C=CH_2$$

Ethyne → Ethene

$$CH_2=CH_2 + H_2 \xrightarrow[\text{Heat}]{\text{Ni}} H_3C-CH_3$$

Ethene → Ethane

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Dissolving Metal reduction as Addition of hydrogen:
Alkynes can be reduced to *trans*-alkenes using Na in NH_3 (liq.). This reaction is stereospecific giving only the *trans*-alkene through an *anti* addition.
The stereochemistry of this reaction complements that of catalytic hydrogenation. The reaction proceeds through single electron transfer from the Na with H coming from the NH_3. These reaction conditions do not reduce alkenes, hence the product is the alkene.

$$-C\equiv C- + 2[H] \xrightarrow[Na/NH_3(l)]{-33^\circ C} \begin{matrix} & & H \\ & C=C & \\ H & & \end{matrix}$$

Hydrohalogenation:
Alkynes react with hydrogen chloride and hydrogen bromide to form dihaloalkenes. The reaction occurs in accordance with Markownikov's rule.

$$CH\equiv CH + H-Br \longrightarrow H_2C=CHBr$$

Vinyl bromide

$$H_2C=CH(Br) + H-Br \xrightarrow[\text{Addition}]{\text{Markownikov's}} H_3C-CH(Br)_2$$

1,1-Dibromoethane

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Hydration:

Water adds to acetylene in the presence of mercuric sulphate dissolved in sulphuric acid at 75°C.

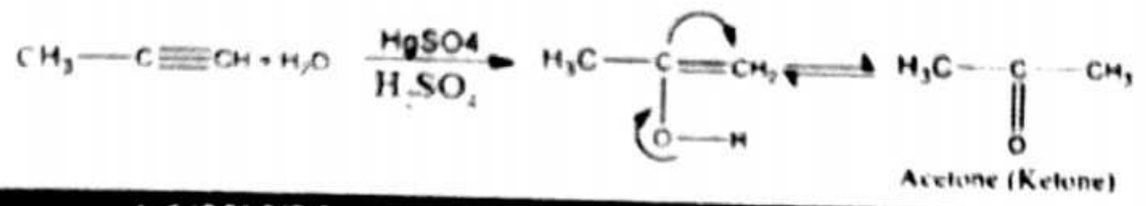
$$HC\equiv CH + H-OH \xrightarrow[H_2SO_4]{HgSO_4} H_2C=CHOH$$

Vinyl alcohol

Vinyl alcohol is unstable. It has the hydroxyl group attached to a doubly bonded carbon atom and isomerizes to acetaldehyde. Except acetylene all others alkynes give ketones. This reaction is industrially important because aldehydes can be prepared by this method.



Acetaldehyde



Acetone (Ketone)

ACIDITY OF TERMINAL ALKYNES

In ethyne and other terminal alkynes like propyne, the hydrogen atom is bonded to the carbon atoms with sp-s overlap. As sp hybrid orbital has 50% s-character in it and renders the carbon atoms more electronegative. As a result, the sp hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic. This can be substituted with metal. Thus substitution reaction occurs due to $H^{+\delta}$.



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Examples:

(i) When 1-alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained. Sodium acetylide is a very valuable reagent for chemical synthesis and is essentially ionic in nature.

$$R-C\equiv CH + 2NaNH_2 \xrightarrow{liq\ NH_3} R-C\equiv C^-Na^+ + NH_3$$

$$HC\equiv CH + 2Na \longrightarrow Na\,C\equiv C^-Na^+ + NH_3$$

Disodium acetylide

(ii) Acetylides of copper and silver are obtained by passing acetylene in the ammonical solution of cuprous chloride and silver nitrate respectively.

$$HC\equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow AgC\equiv CAg + 2NH_4NO_3 + 2H_2O$$

Disilver acetylide or silver ethynide, (white ppt.)

$$HC\equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow CuC\equiv CCu + 2NH_4Cl + 2H_2O$$

Dicopper acetylide or copper ethynide (Reddish brown)

Silver and copper acetylides react with acids to regenerate alkynes.

$$AgC\equiv CAg + dil.\ H_2SO_4 \longrightarrow CH\equiv CH + Ag_2SO_4$$

$$AgC\equiv CAg + dil.\ HNO_3 \longrightarrow HC\equiv CH + 2AgNO_3$$

These alkynides are used for the preparation, purification separation, and identification of alkynes. similar whether in the gas phase or solution phase.

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Reactions of organic compounds

Types of Reactions

The reactions of organic compounds fall into four classes. These are listed below.

Substitution

An atom or group of atoms replaces another, e.g. in hydrolysis.

$C_2H_5Cl + OH^- \rightarrow C_2H_5OH + Cl^-$

Chloroethane + Hydroxide ion → Ethanol + Chloride ion

Addition

Two molecules react to form one:

$Br_2 + CH_2 = CH_2 \rightarrow BrCH_2CH_2Br$

Bromine + Ethene → 1,2-Dibromoethane

Elimination

One molecule reacts to form more than one:

$C_2H_5OH \rightarrow C_2H_4 + H_2O$

Ethanol → Ethene + Water

Rearrangement

One molecule reacts to give different molecule

$CH_3 - CH - CH = CH \rightleftharpoons CH_3 - CH = CH - CH_2 - Cl$

$\quad\quad\quad

The resonance method

Resonance

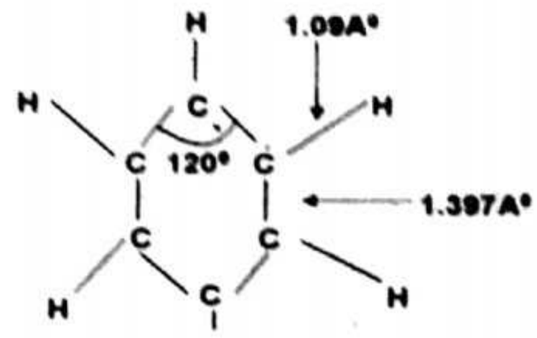
The possibility of different pairing schemes of valence electrons of atoms is called resonance and the different structures thus arranged are called resonance structures.

- Different Lewis structures are called resonance contributing structures or canonical forms.
- The resonance structures are represented by (↔) double headed arrow
- Dewar is the scientist, who gave the concepts of para bonds in structure of benzene. But his structure contributes very little in prediction of actual structure of benzene
- Kekule's structure of benzene (alternate double bonds in planar hexagonal ring) contributed more in prediction of actual structure of benzene.
- Bond lengths in hydrocarbon are as under:
- Bond length in C-C in benzene (1.397A°) shows that it is in between single and double bond
- Due to fact of bond length, it was proposed that actual structure of benzene will be hybrid of Kekule's and Dewar's structures.

POINT TO PONDER

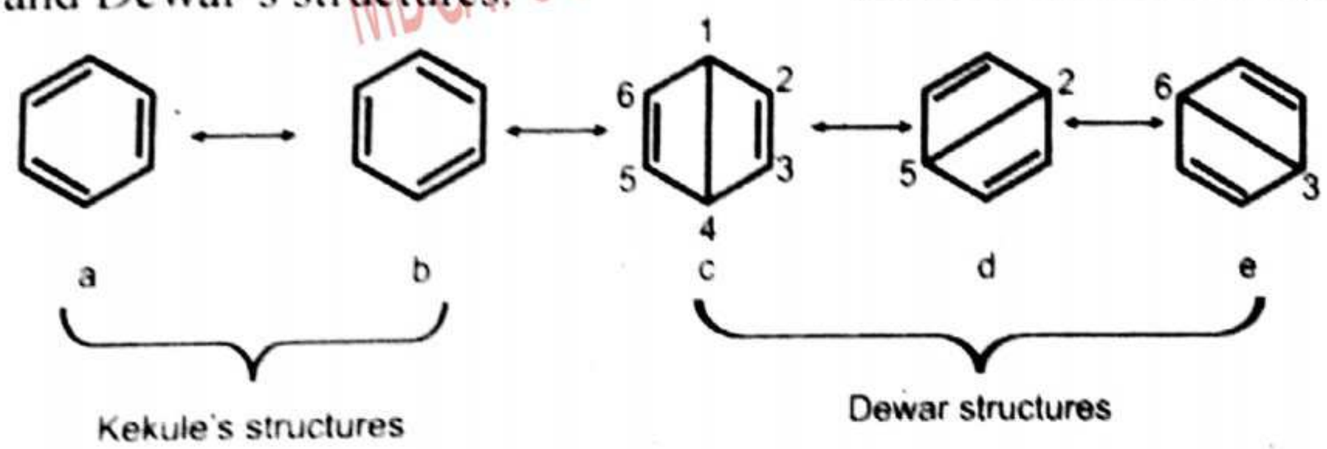
X-ray studies of benzene structure

- Benzene is hexagonal structural compound
- C - C-H and C–C–C bond angle is 120°
- Bond length of C-C bond is 1.397A°
- Bond length of C-H bond is 1.09A°



Nature of bond	Bond length
C – C	1.54 A°
C = C	1.34 A°
C ≡ C	120 A°
C–C in benzene	1.397A°

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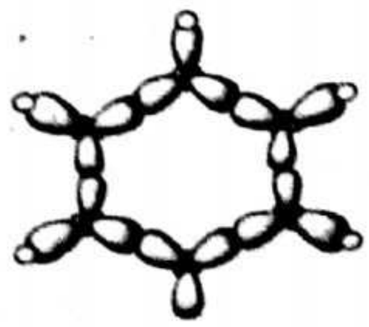


Molecular orbital treatment:

Thus each C-atom is in a state of sp^2-hybridization because each C-atom is attached to three atoms.

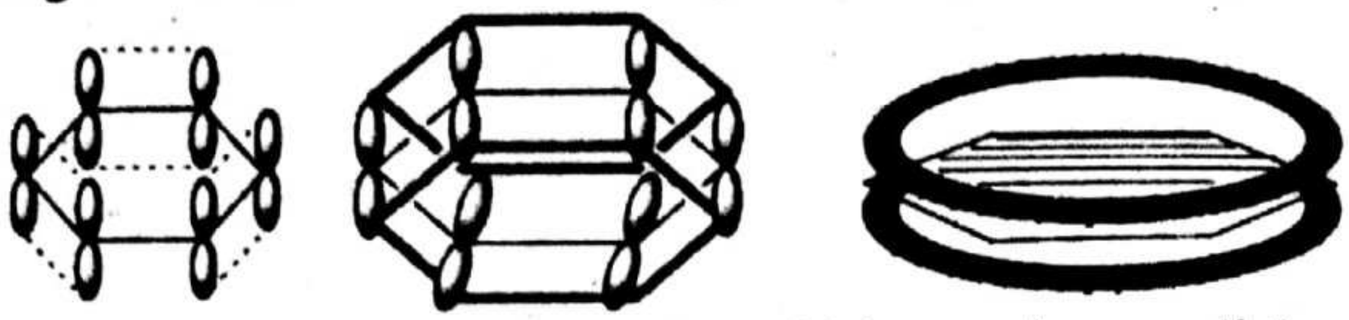


Combination of such six structures and overlap of six hydrogen atoms ($1s^1$) produces the sigma framework of benzene.



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Six atomic p-orbitals one on each C-atom, are present perpendicular to this sigma bonding. Each p-orbital is in a position to overlap in parallel manners with neighbouring p-orbitals to give a continuous sheath of negative charges.

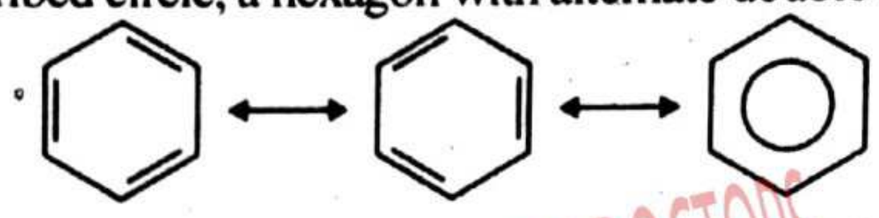


It results in extensive delocalized pi-bonding which spreads over all the carbon nuclei of benzene. Delocalization of p-orbitals over the entire ring produces sandwich like structure of benzene and decreases the energy of molecule. Consequently, the molecule becomes more stable and less reactive.

According to this molecular orbital picture each carbon-carbon bond in benzene consists of one full sigma-bond and half a pi-bond. Because of this reason, the carbon-carbon bond length is equal and benzene shows substitution as well as addition reactions.

Modern representation of benzene:

With the help of molecular orbital behaviour we conclude that benzene has a regular hexagonal structure with an inscribed circle, a hexagon with alternate double and single bonds.



ELECTROPHILIC SUBSTITUTION REACTIONS AND THE MECHANISM

The species which are electron deficient called **electrophiles**.

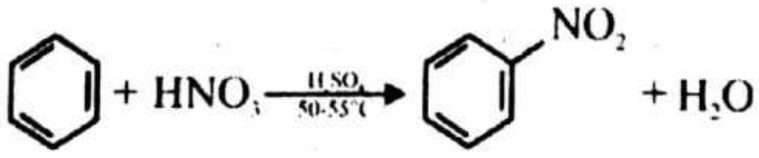
- Presence of delocalized electrons in benzene increases the stability of benzene, so **very strong electrophile is required** for attacking purpose.

(1) Nitration

The introduction of nitro group (NO_2) in benzene ring is called nitration of benzene.

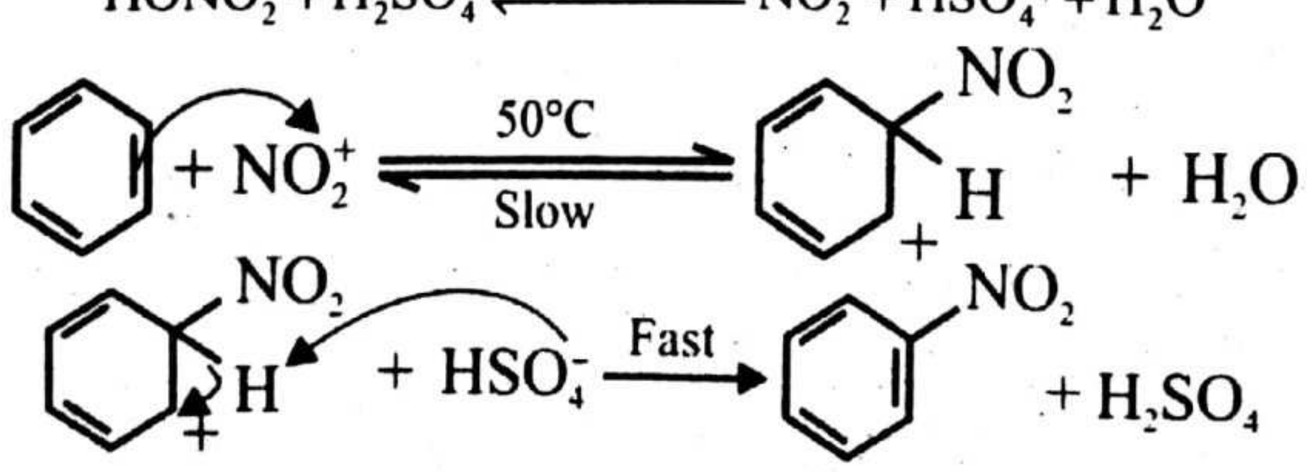
- The nitration takes place when it is heated with 1: 1 mixture of concentrated HNO_3 and concentrated H_2SO_4 at 50-55° C.
- Sulphuric acid reacts with nitric acid to generate nitronium ion NO_2^+

Reaction



Mechanism

$$HONO_2' + H_2SO_4 \rightleftharpoons[50°C-55°C] NO_2^+ + HSO_4^{-1} + H_2O$$



Nitrobenzene

(2) Halogenation (Chlorination and bromination)

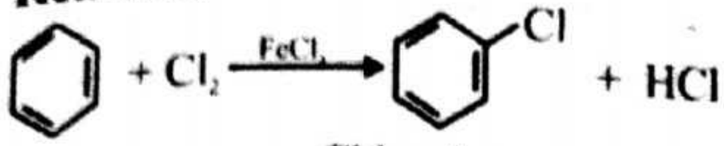
The introduction of halogen group in benzene ring is called halogenation of benzene.

- Benzene reacts with halogen in presence of catalyst Lewis acid like $FeBr_3$, $AlCl_3$ etc.

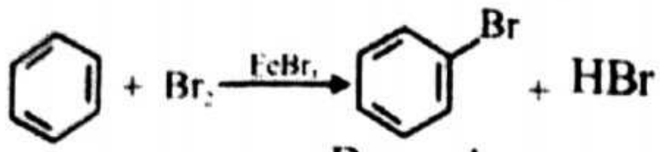
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- Chlorination and bromination are normal; reactions but fluorination is too vigorous to control.
- Iodination gives poor yield.

Reaction



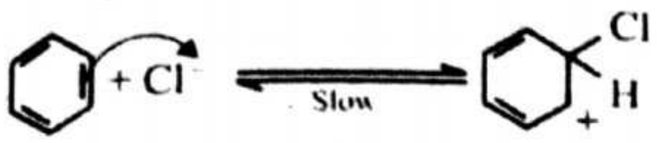
Chlorobenzene



Bromobenzene

Mechanism

$$Cl_2 + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$$

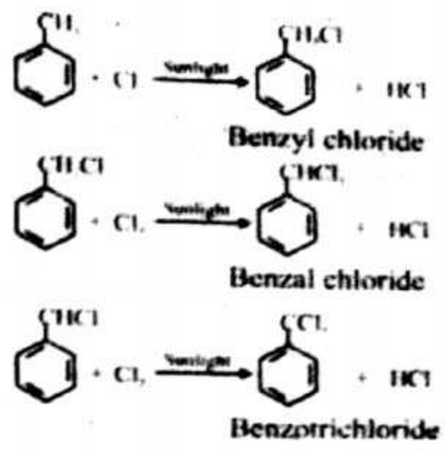




$$FeCl_4^- + H^+ \longrightarrow HCl + FeCl_3$$

POINT TO PONDER

When alkyl benzene is treated with chlorine or bromine in the presence of sunlight, only alkyl groups are substituted.



(3) FRIEDEL-CRAFT'S REACTIONS

The substitution of hydrogen of benzene ring by an alkyl, aryl or acyl group is called Friedel-Craft's reactions.

The catalyst used in Friedel-Craft's reactions are Lewis acids like $AlCl_3$, BF_3 etc.

(i) Friedel-Craft's Alkylation

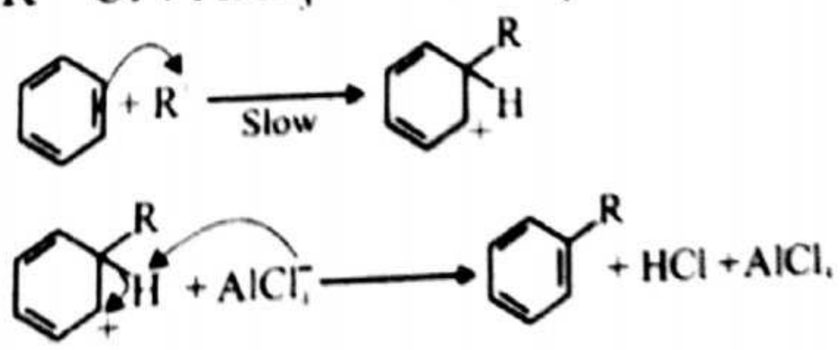
When alkyl chlorides are treated with benzene in the presence of $AlCl_3$ then alkylation takes place. The product obtained is alkyl benzene.

Reaction



Mechanism

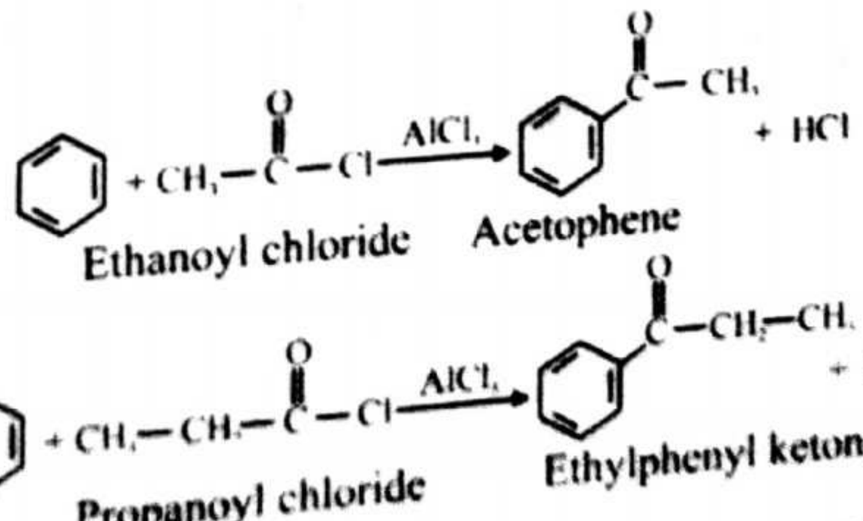
$$R - Cl + AlCl_3 \longrightarrow AlCl_4^- + R^+$$



(ii) Friedel-Craft's Acylation

When acyl chloride is treated with benzene in the presence of $AlCl_3$ then acylation takes place. The product obtained is aromatic ketone.

Reaction



Ethanoyl chloride — Acetophene

Propanoyl chloride — Ethylphenyl ketone

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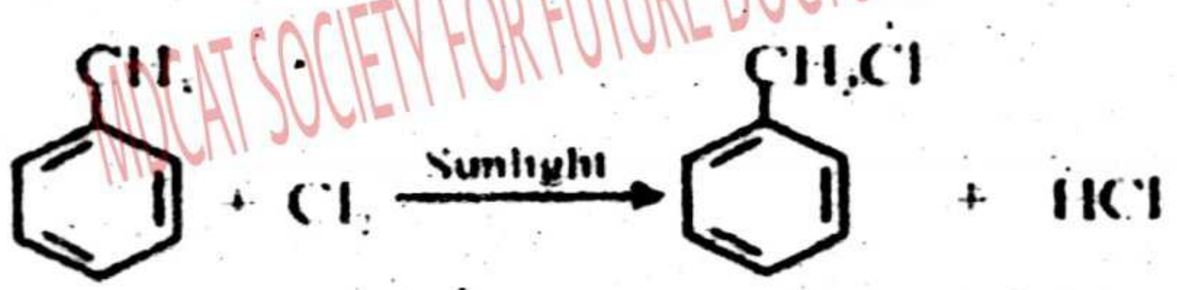
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; reactions but fluorination is too vigorous t

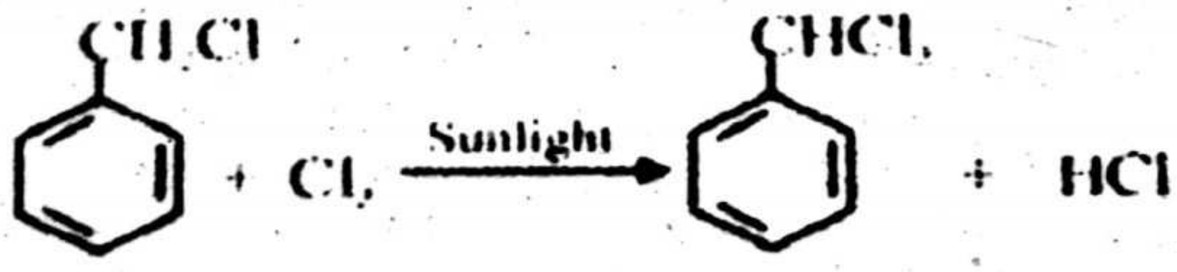
POINT TO PONDER

When alkyl benzene is treated with chlorine or bromine in the presence of sunlight, only alkyl groups are substituted.

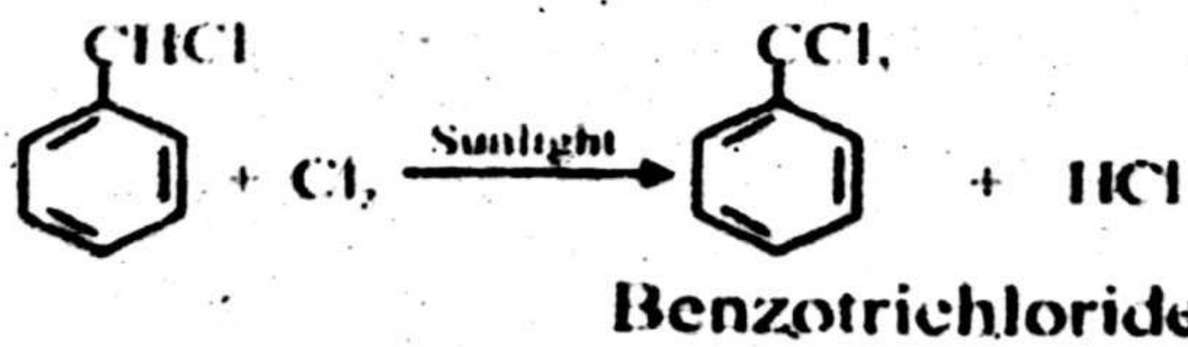
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Benzyl chloride



Benzal chloride

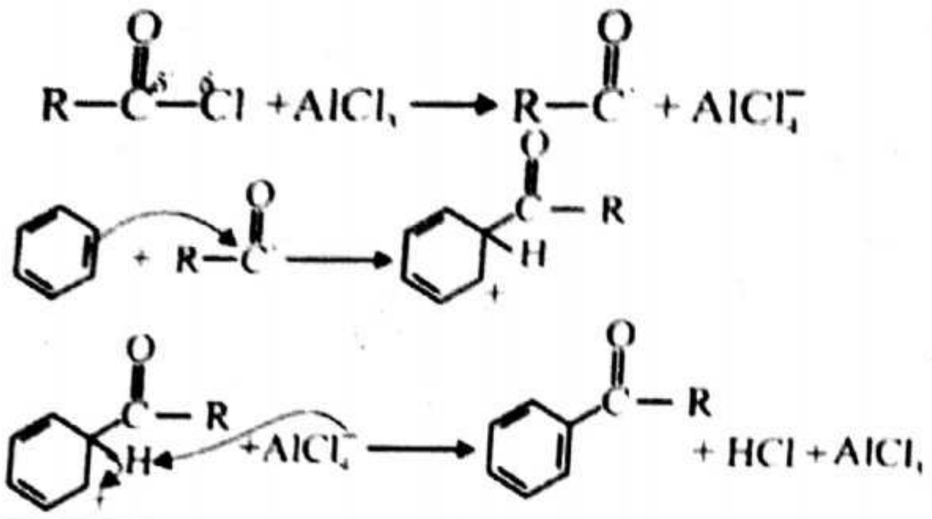


Benzotrichloride

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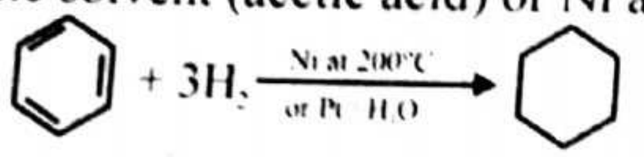
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Mechanism



HYDROGENATION OF BENZENE RING

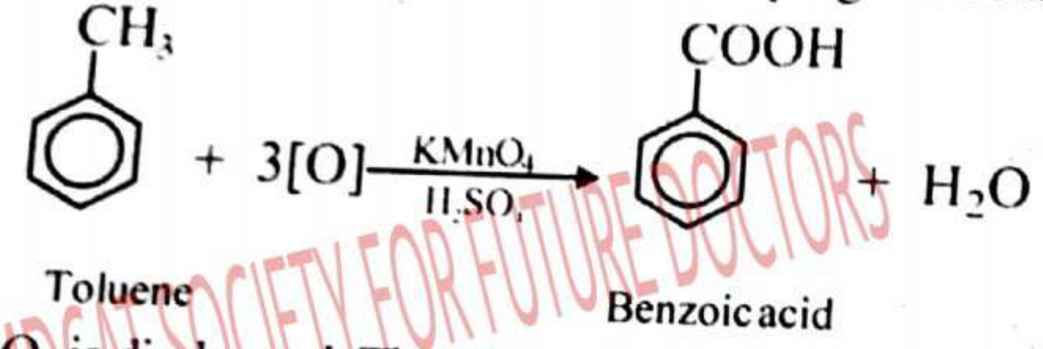
Benzene is reduced to cyclohexane on heating at high temperature with hydrogen in the presence of Pt in an acidic solvent (acetic acid) or Ni at 200°C as a catalyst.



Cyclohexane

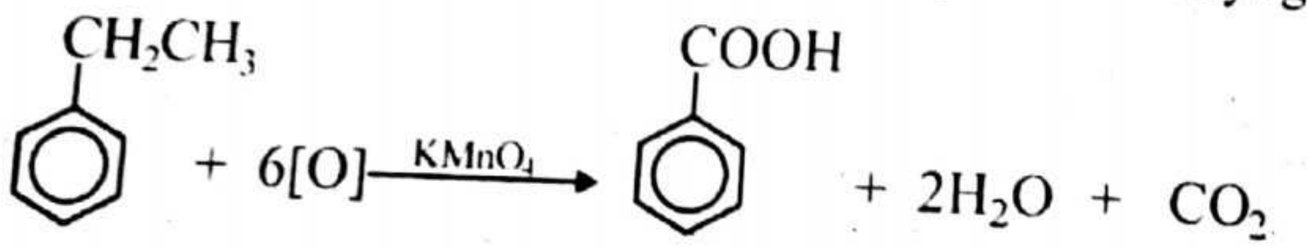
SIDE CHAIN OXIDATION OF ALKYL BENZENE

- Alkyl benzenes are readily oxidized by acidified $KMnO_4$ or $K_2Cr_2O_7$.
- In these reactions, the alkyl groups are oxidized keeping the benzene ring intact.



Toluene Benzoic acid

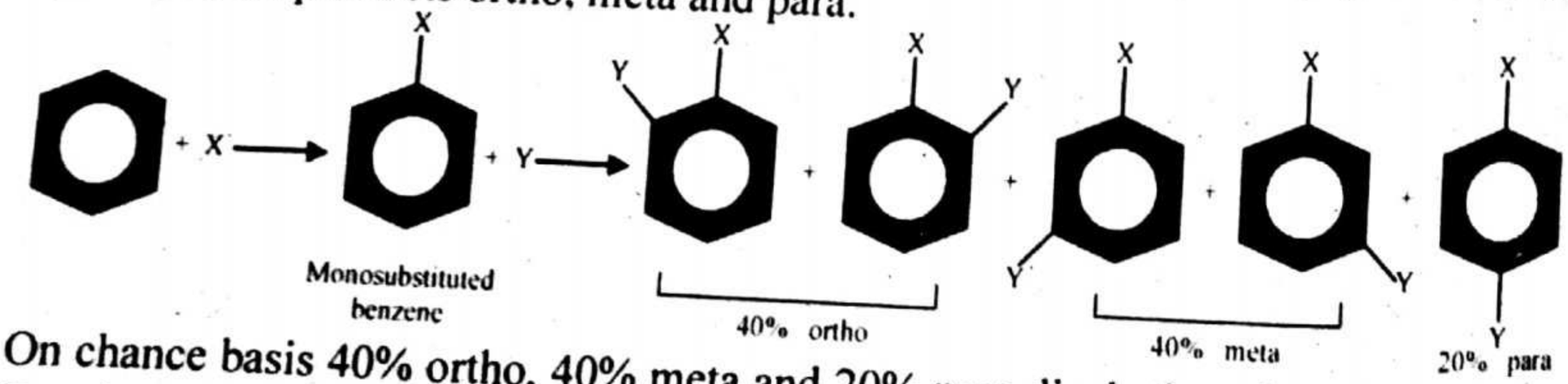
- The colour of $KMnO_4$ is discharged. Therefore, this reaction is used as a test for alkyl benzenes.
- Whatever the length of an alkyl group may be it gives only one carboxyl group.



Ethyl Benzene Benzoic acid

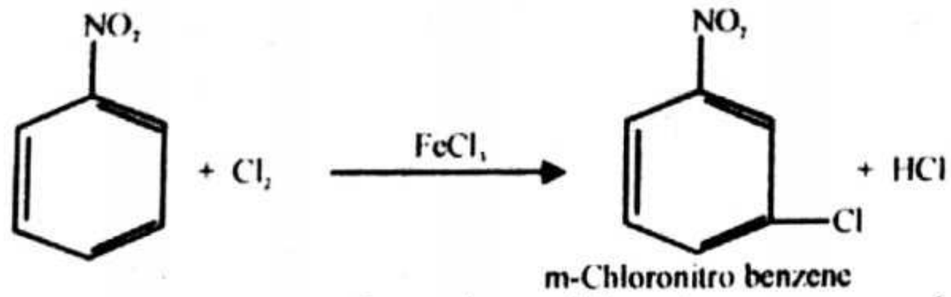
BENZENE RING BY 2, 4 DIRECTING AND 3, 5 DIRECTING GROUPS

When an electrophilic substitution reaction takes place on benzene ring we get only one mono substituted benzene because all the six positions in the ring are equivalent. However, the introduction of a second group into the ring may give three isomeric disubstituted products ortho, meta and para.



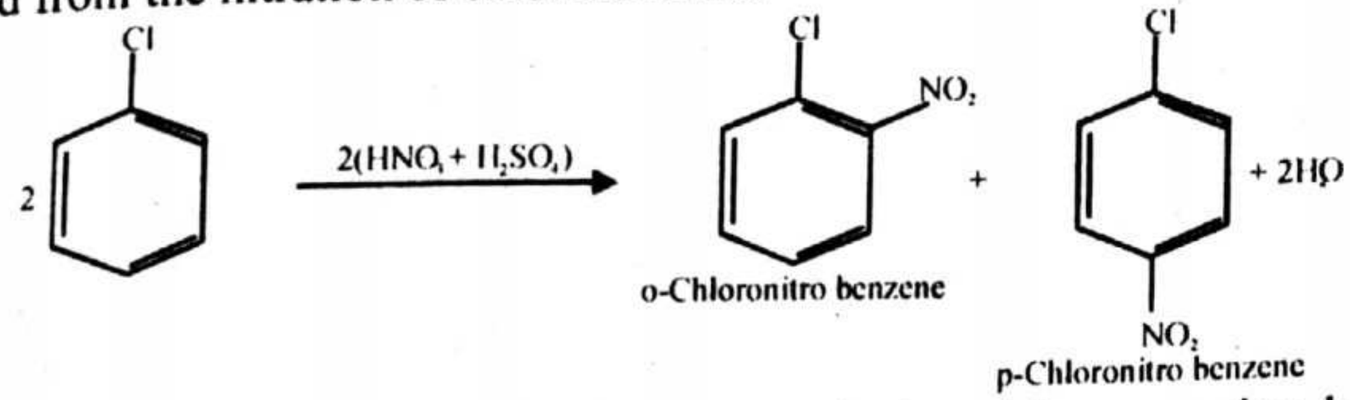
On chance basis 40% ortho, 40% meta and 20% para disubstituted products are expected. But the actual disubstitution of benzene does not follow this principle of chance. eg m-nitrochlorobenzene is the main product of the following halogenation reaction.

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m-Chloronitro benzene

On the other hand, a mixture of o-nitro-chlorobenzene and p-nitrochlorobenzene is obtained from the nitration of chlorobenzene.



o-Chloronitro benzene

p-Chloronitro benzene

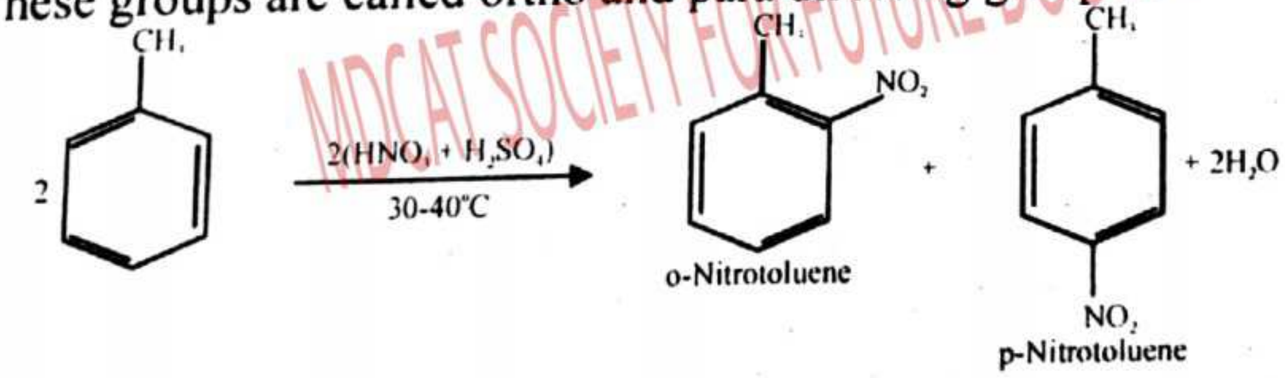
It means that the group present in the mono-substituted benzene ring has the directive effect and thus determines the position or orientation for the new incoming groups.

There are two types groups.

1- Ortho and para-directing groups 2-Meta-directing groups

1. Ortho and para directing groups (2,4-directing group):

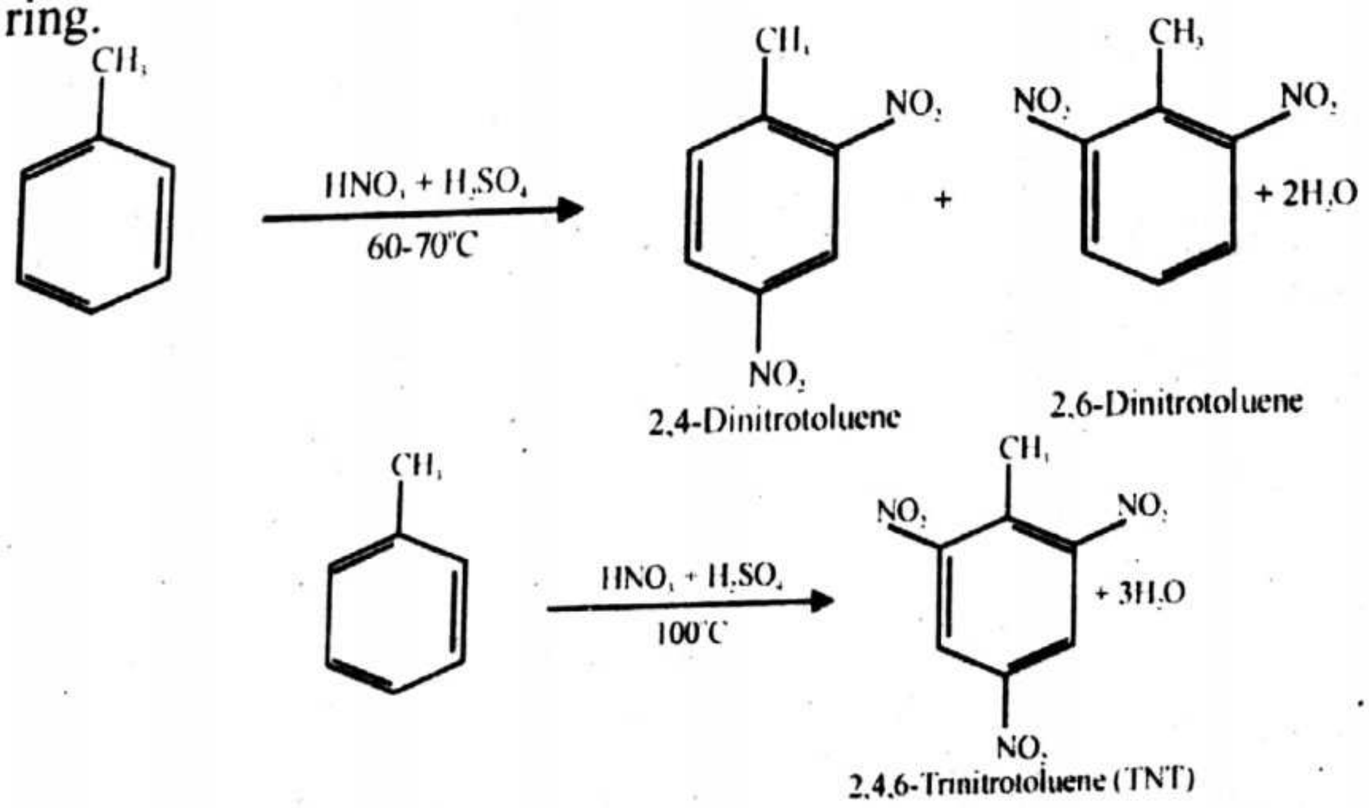
- These groups release electrons to the benzene ring thereby facilitating the availability of electrons to the electrophiles at ortho and para positions.
- This results in the increased chemical reactivity of benzene ring towards electrophiles.
- The benzene ring can offer more than one positions (ortho and para) to the new incoming groups. These groups are called ortho and para directing groups.



o-Nitrotoluene

p-Nitrotoluene

- The electron releasing effect of methyl group is significant and it makes the ring a good nucleophile. Due to this increased reactivity, more nitro groups can be substituted on benzene ring.



2,4-Dinitrotoluene

2,6-Dinitrotoluene

2,4,6-Trinitrotoluene (TNT)

These groups are $-\ddot{O}H, -\ddot{S}H, -\ddot{N}H_2, -\ddot{N}HR, -\ddot{N}R_2, -\ddot{O}CH_3, -\ddot{S}CH_3$, — Cl, - Br, - I

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2. Meta-Directing Groups (deactivators of benzene ring): 3, 5-directing groups

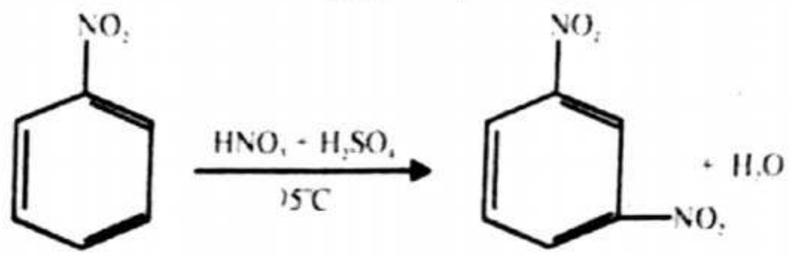
These groups withdraw electrons of the benzene ring towards themselves, thereby reducing the availability of electrons to the electrophiles at ortho and para positions.

This results in the decreased chemical activity of benzene.

Moreover, due to the electron withdrawing effect of such substituents, the ortho and para positions are rendered more electron deficient than the meta position.

Thus the incoming electrophile will prefer to attack on meta position rather than ortho and para positions.

These groups are called meta directing groups e.g.



These groups are $-NO_2$, –R, $-NR_3^+$, $-C \equiv N$, – COOH, – CHO, – COR, $-NH_3^+$, $-CCl_3$

COMPARISON OF REACTIVITIES OF ALKANE, ALKENE AND ALKYNE

Reactivity order of alkane, alkene and alkyne is as follows:

Alkene > Alkyne > Alkane

Alkenes: π-bond in alkene is not only weak but its electrons are more exposed to an electrophilic attack. Both these facts make alkene very reactive class of compounds.

Alkynes: Alkynes are les reactive than alkenes for electrophilic reagents although contain two π-bonds. This is because bond distance between two triply bonded carbon atoms is very short. As a result, its π-electrons are tightly bound and are not available for electrophilic attack. Hence, are less reactive than alkenes.

However, alkynes are more reactive than alkenes for nucleophilic reagents.

Alkane: Alkanes are least reactive due to the presence of σ-bonds. σ-bonds are stable because σ-electrons revolve around internuclear axis and are tightly bound between the nuclei. As a result, electrophiles cannot attack on them.

Carbon to carbon bond lengths:

(i) C-C = 154pm (ii) C=C = 134pm (iii) C≡C = 120pm

COMPARISON OF REACTIVITIES OF ALKANES, ALKENES AND BENZENE

Alkanes are unreactive class of compounds and their unreactivity is due to their non-polar nature and inertness of σ-bond. But they undergo substitution reaction relatively easily involving free radicals.

Alkenes, are very reactive class of compounds and their reactivity is due to the inherent weakness of the π-bond and availability of π-electrons for the electrophilic reagent.

- They undergo electrophilic addition reactions easily.
- Relatively unstable, alkenes undergo polymerization reactions.
- They also undergo oxidation readily.

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Benzene is unique is its behaviour.

- It is highly unsaturated compound but very stable molecule as well.
- Its stability is due to the extensive delocalization of π-electrons.
- It resembles alkenes when it gives addition reactions.
- Its substitution does not involve free radicals but follow electrophilic substitution reactions.
- It requires drastic conditions as compared to alkenes.
- It is also resistant to oxidation.

Some examples of comparison:

	Alkanes	Alkenes	Benzene
1. Structure	Open Chain	Open Chain	Closed Chain
2. Reactions			
(a) H_2	No reaction	Addition reaction	Addition reaction
(b) Cl_2	Photochemical Substitution	Addition	Photochemical Addition and electrophilic substitution
(c) $KMnO_4$	No reaction	Colour of $KMnO_4$ is discharged	No reaction

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TOPIC-15 ALKYL HALIDES

COURSE CONTENTS

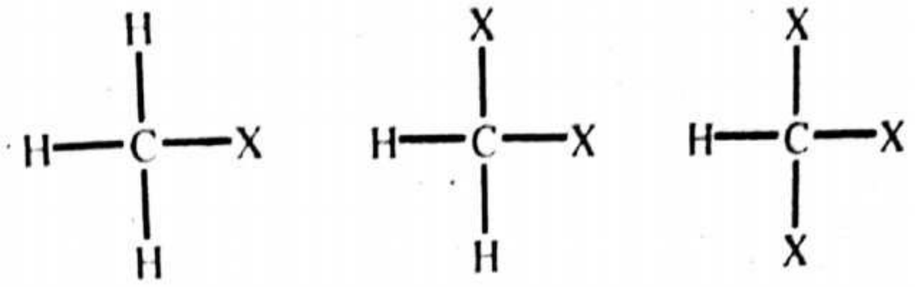
- Classification of alkyl halides
- Discuss structure and reactivity of alkyl halides
- Mechanism of nucleophilic substitution reaction (S_N1. S_N2 reaction)
- Elimination reactions (E_1 and E_2 reaction)

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Definition:
Alkyl halides are the compounds in which one hydrogen atom of alkanes has been replaced by one halogen atom. They are also known as halogen derivatives of alkanes.

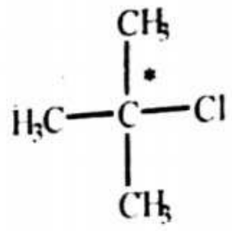
Types:
They may be mono, di, tri or poly haloalkanes depending upon the number of halogen atoms present in the molecule. Monohaloalkanes are called alkyl halides having general formula R-X.



Monohaloalkane Dihaloalkane Trihaloalkane

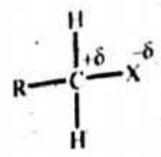
CLASSIFICATION OF ALKYL HALIDES

Alkyl halides are classified into primary, secondary and tertiary alkyl halides.

Primary alkyl halide	Secondary alkyl halide	Tertiary alkyl halide
○ Alkyl halides in which halogen atom is attached with primary carbon are called primary alkyl halides. ○ Carbon atom attached to one or no carbon atom is called primary C-atom.	○ Alkyl halide in which halogen atom is attached with a secondary carbon atom is called secondary alkyl halide. ○ C-atom, attached to two C-atoms simultaneously is called secondary C-atom.	○ Alkyl halides, in which halogen atom is attached to a tertiary carbon is called tertiary alkyl halide. ○ C-atom, attached to three C-atoms simultaneously is called tertiary C-atom.
Example: $*CH_3–Cl$, $CH_3–*CH_2–Cl$ *C is a primary carbon atom	$H_3C–{}^{*}C(H)(CH_3)–Cl$ Isopropyl chloride 2-cholopropane *C is a secondary carbon atom	 t-Butyl chloride 2-Methyl-2-chloropropane * = Tertiary carbon atom

STRUCTURE

- The alkyl halide functional group consists of a sp^3 hybridized C atom bonded to a halogen (X) via σ bond.
- The carbon halogen bonds are typically quite polar due to the electronegativity and polarizability of the halogen.



R = Alkyl group

REACTIVITY

There are two main factors which control the reactivity of alkyl halides:
(i) Bond polarity of C-X bond
(ii) Bond energy of C-X bond

(i) Bond Polarity
The molecule of alkyl halide is polarized due to the greater electronegativity of halogens as compared to carbon. Carbon acquires partial positive whereas halogens acquires partial

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negative charge. Halogen becomes nucleophilic and can be replaced by another nucleophiles. On the basis of bond polarity, reactivity of alkyl halides decreases in the following order,

R-F > R-Cl > R-Br > R-I

Atom	Electronegativity	Atom	Electronegativity
F	4.0	I	2.5
Cl	3.0	H	2.1
Br	2.8	C	2.5

(ii) Bond Energy

Experiments have shown that the bond energy of C-X bond is the main factor which decides the reactivity of alky halides, and not the polarity of the molecule.

A study of bond energies of C-X bond shows that C-F bond is the strongest. So, the overall order of reactivity of alkyl halides is:

R-I > R-Br > R-Cl > R-F

In fact the C-F bond is so strong that alkyl fluorides do not react under ordinary conditions.

Bond	Bond energy (kJ/mole)
C – F	467
C – H	413
C – Cl	346
C – Br	290
C – I	228

NUCLEOPHILIC SUBSTITUTION REACTIONS OF ALKYL HALIDES

Nucleophile:

A nucleophile is electron rich species.

- It will react with an electron poor species.
- It has an unshared pair of electrons available for bonding.
- In most cases it is basic.
- It may be negatively charged or neutral.

Examples:

HO^-, $C_2H_5O^-$, SCN^-, HS^-, H_2O, NH_2^-, Cl^-, Br^-, I^-, NH_3 etc.

Electrophile:

An electrophile is electron deficient species.

- It will react with an electron rich species.
- It has empty orbitals available for bonding.
- In most cases it is acidic.
- It may be positively charged or neutral.
- The electrophilic C can be recognized by looking for the polar sigma bond due to the presence of an electronegative substituent (esp. C-Cl, C-Br, C-I and C-O).

Examples:

BF_3, $AlCl_3$, $FeCl_3$, carbocation like CH_3^+ etc.

Substitution:

A substitution implies that one group replaces another in a molecule.

Substrate:

The alkyl halide molecule on which nucleophile attacks is called substrate.

Alkyl chlorides, bromides and iodides are good substrates for nucleophilic substitution reactions.

Leaving Group (LG):

Leaving group is also a nucleophile. It departs with an unshared pair of electrons.

- The incoming nucleophile must be stronger than the departing one, Cl^-, Br^-, I^-, HSO_4^- are good leaving groups. Poor leaving groups are OH^-, RO^- and NH_2^-.
- Iodide ion is a good nucleophile as well as a good leaving group.

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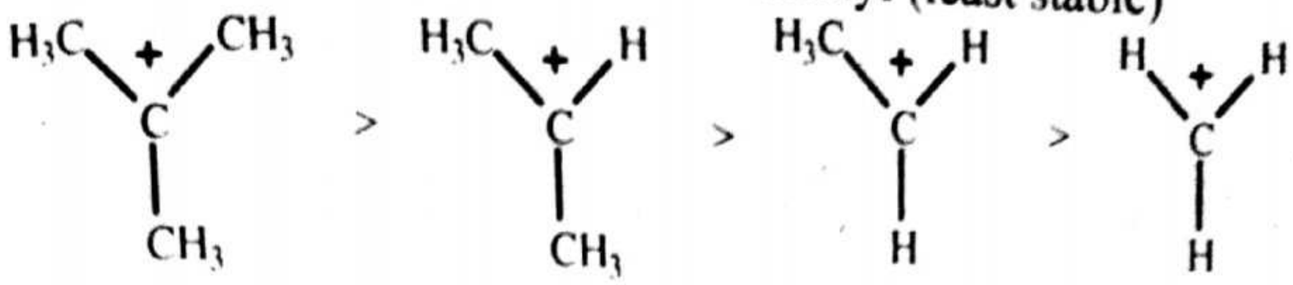
Carbocations:

The species in which one carbon atom is positively charged is called carbocation. It can be primary, secondary or tertiary.

Stability of carbocations:

The general stability order of simple alkyl carbocations is,

(most stable) $3^o > 2^o > 1^o >$ methyl (least stable)



3° 2° 1° methyl

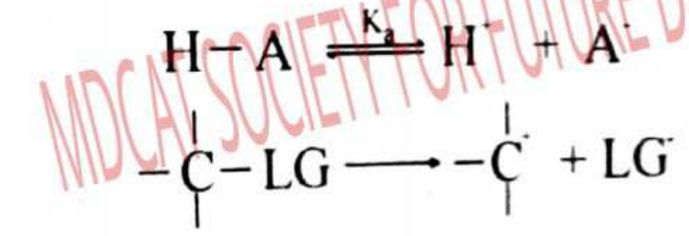
This is because alkyl groups are weakly electron donating due to hyperconjugation and inductive effects. Resonance effects can further stabilize carbocations when present.

Reactions involving carbocations:

- Substitutions via the SN_1
- Eliminations via the E_1
- Additions to alkenes and alkynes

Bronsted acid dissociation and SN_1 reaction:

These two equations represent Bronsted acid dissociation and loss of a leaving group in a SN_1 type reaction.



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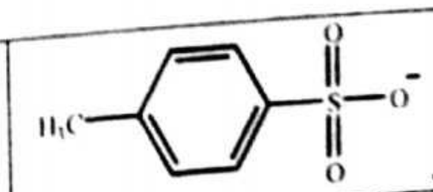
Similarities:

- Both show heterolytic cleavage of a sigma bond to create an anion and a cation.
- For acidity, the more stable A^- is, then the more the equilibrium will favour dissociation, and release of protons meaning that HA is more acidic.

For the leaving group, the more stable LG^- is, the more it favors "leaving".

- Hence factors that stabilize A^- also apply to the stabilization of a LG^-.

Common leaving groups:

Excellent	 , NH_3
Very good	I^-, H_2O
Good	Br^-
Fair	Cl^-
Poor	F^-
Very poor	OH^-, NH_2^-, RO^-

But water itself is a good leaving group, since it is the conjugate base of H_3O^+.

Importance of nucleophilic substitution reactions:

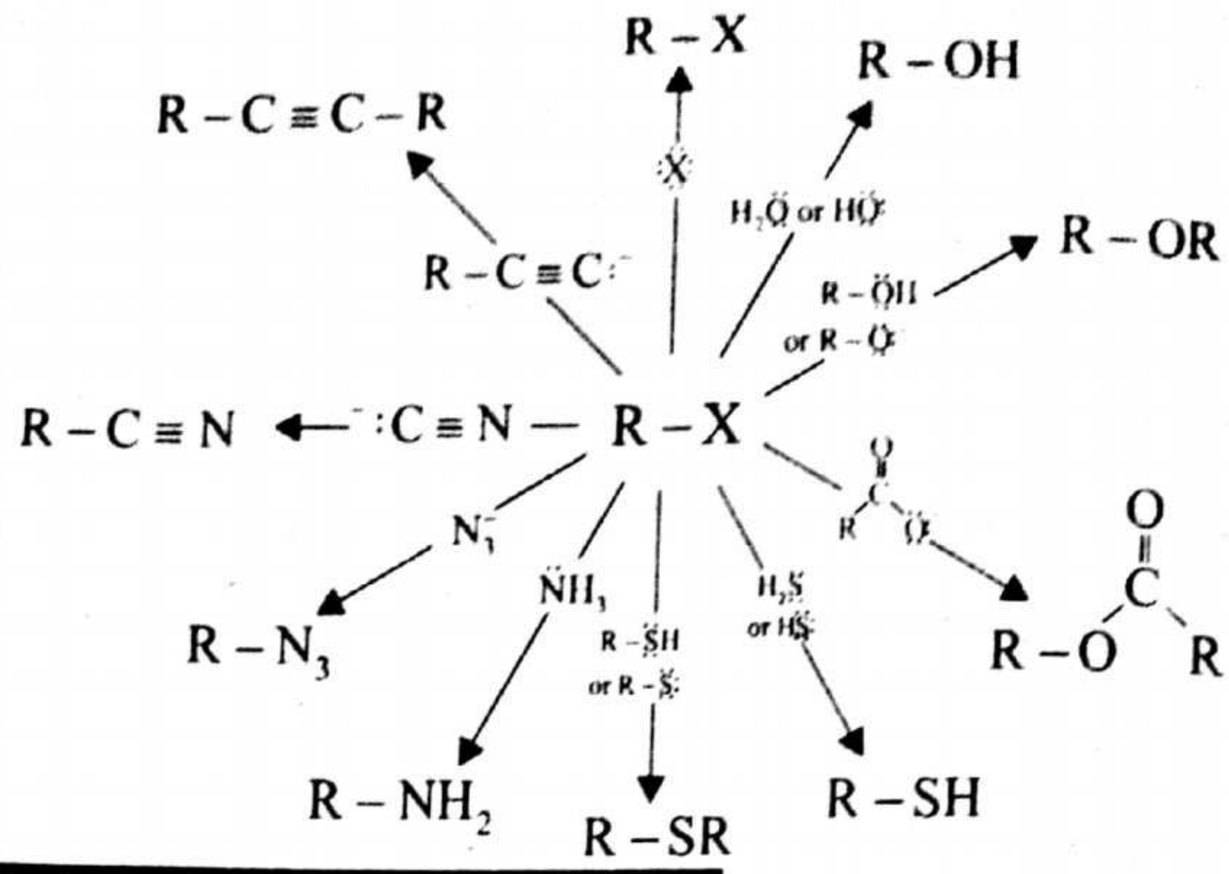
Nucleophilic substitution reactions are an important class of reactions that allow the interconversion of functional groups. A variety of nucleophiles can be used to generate a range of new functional groups.

Examples:

The following diagram reflects some of the more important reactions you may encounter.

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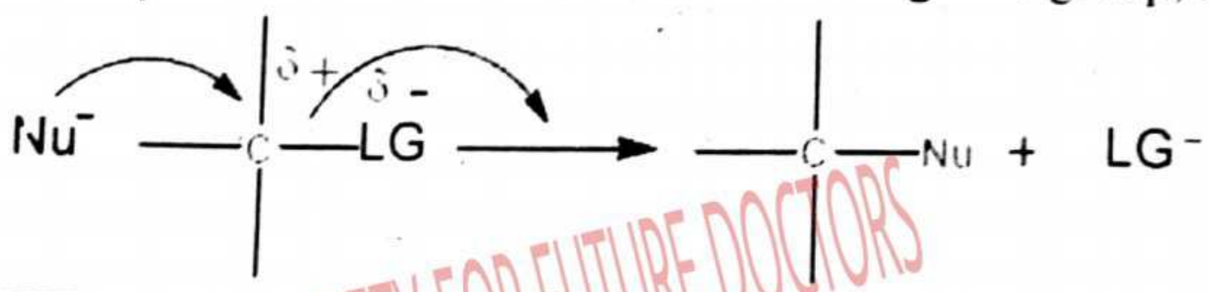
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NUCLEOPHILIC SUBSTITUTION REACTIONS

Nucleophilic substitution reactions:

Nucleophilic substitution reactions occur when an electron rich species, the nucleophile, reacts at an electrophilic C atom attached to an electronegative group, the leaving group.



MECHANISMS FOR NUCLEOPHILLIC SUBSTITUTION REACTIONS

There are two fundamental events in a nucleophilic substitution reaction:

- Formation of the new σ bond to the nucleophiles
- Breaking of the σ bond to the leaving group

Depending on the relative timing of these events, two different mechanisms are possible:

- Bond breaking to form a carbocation proceeds the formation of the new bond: SN_1 reaction
- Simultaneous bond formation and bond breaking: SN_2 reaction

SN_1 MECHANISM:

It is substitution nucleophilic unimolecular two step reaction.

Explanation:

The substrate R-X first ionizes reversibly into R+ and X- ions. Then the carbonium ion combines with the attacking nucleophiles to form product.

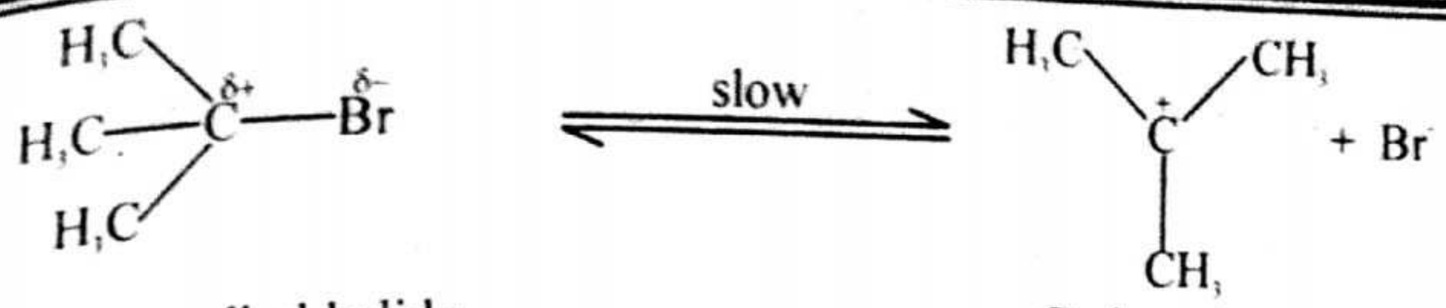
$$R—X \underset{}{\overset{\text{Slow}}{\rightleftharpoons}} R^+ + X^-$$

$$R^+ + Nu^- \xrightarrow{\text{Fast}} R—Nu$$

Step 1:

- This step involves the ionization of tertiary alkyl halide in the presence of polar solvent.
- This step is reversible in the presence of aqueous acetone or aqueous ethyl alcohol.
- This step results in the formation of carbocation as an intermediate.

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Tertiary alkyl halide
sp^3-hybridized
carbon
tetrahedral

Carbocation
sp^2-hybridized
carbon
planer triangular

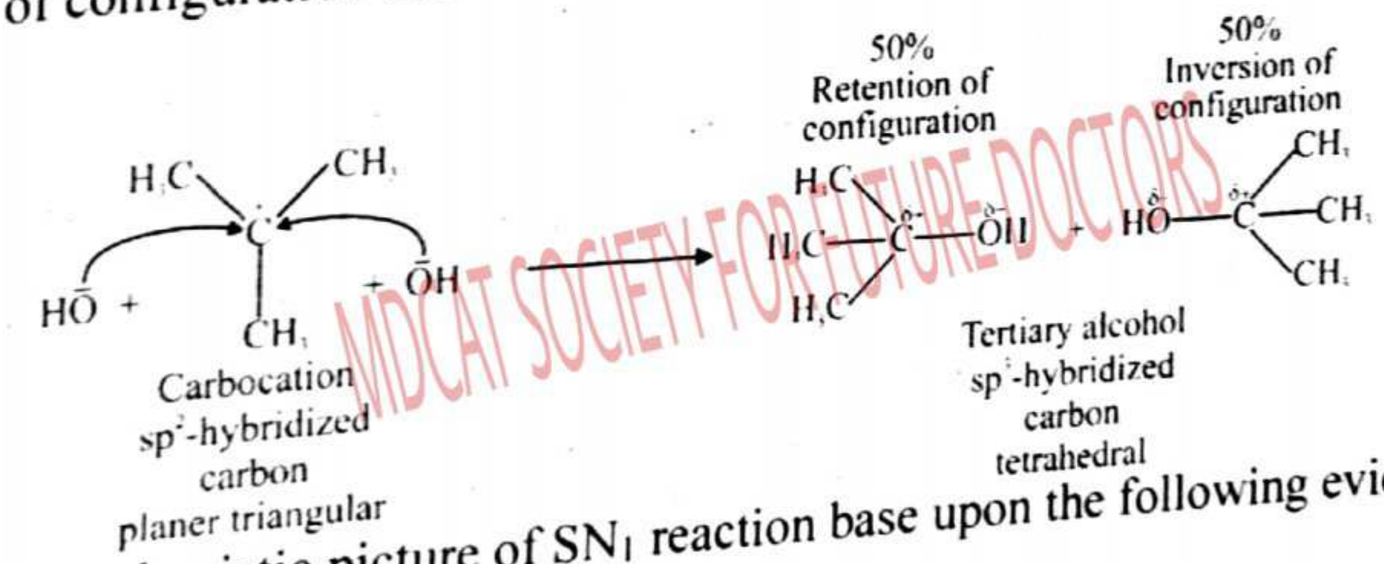
- This step involves the breakage of covalent bond, so it is a slow step. This step is rate determining step.
- During this step, there is variation in hybridization form tetrahedral sp^3 to planar triangular sp^2.

Step 2:

- This step involves the attack of nucleophile on carbocation

(i) The nucleophile attacks when the leaving group had already gone. So, the question of the direction of the attack does not arise.

(ii) The intermediate carbocation is a planar specie allowing the nucleophile to attack on it from both the directions with equal ease. Therefore, there is 50% inversion of configuration and 50% retention of configuration.



Carbocation
sp^2-hybridized
carbon
planer triangular

Tertiary alcohol
sp^3-hybridized
carbon
tetrahedral

The brief mechanistic picture of SN_1 reaction base upon the following evidences:

Kinetic Evidence:

The rate of an SN_1 reaction depends upon the concentration of alky halide only. The change in concentration of attacking nucleophile has no effect on the rate.

$$\text{Rate} = k\,[R\text{-}X]$$

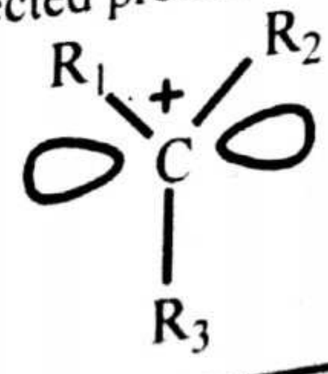
It is because the nucleophile combines with the carbonium ion in the second step. For the same reason, the rate of an SN_1 reaction does not depend on the nature of attacking nucleophile.

Stereo Chemical Evidence:

Experiments have shown that SN_1 reaction occur with partial racemization. The extent of partial racemization depends upon several factors including stability of carbonium ion.

Racemization:

The carbon atom of carbonium ion is sp^2 hybridized and carries one empty p-orbital. The nucleophile can attach itself to the p-orbital either on the right or on the left side of carbon with equal ease. The expected product is a racemic mixture and optically inactive.



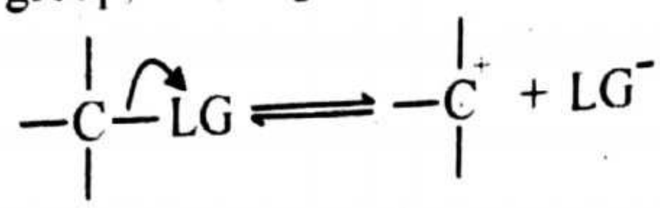
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Partial racemization:

In case of unstable carbonium ion, the side of leaving group is somewhat shielded. The attack of nucleophile occurs more often on the side opposite to the leaving group, leading to partial inversion of configuration. Therefore, the product has some optical activity.

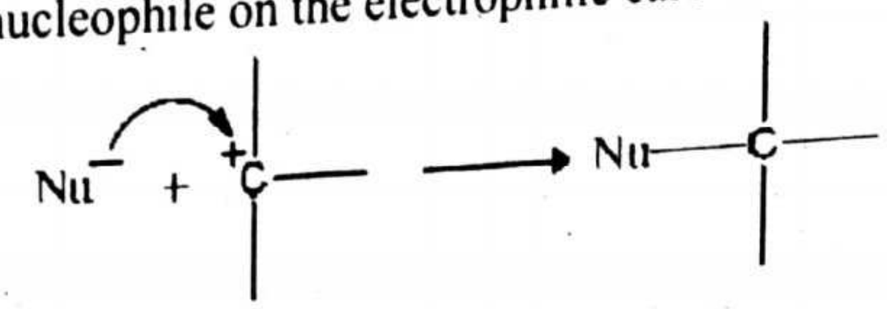
Step 1:

Slow loss of the leaving group, LG, to generate a carbocation intermediate, then



Step 2:

Rapid attack of a nucleophile on the electrophilic carbocation to form a new σ bond.



SN_2 MECHANISM:

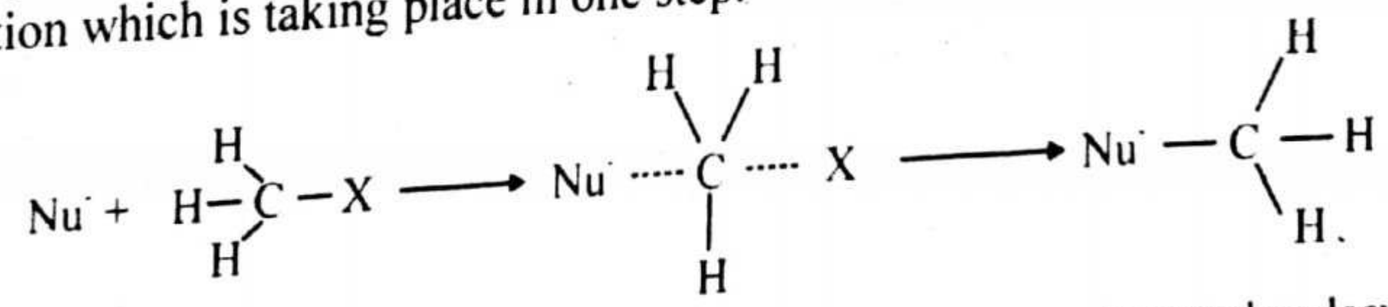
It is substitution nucleophilic bimolecular reaction. It occurs in one step.

$$R - X + Nu^- \longrightarrow R - Nu + X^-$$

$$CH_3 - Br + OH^- \longrightarrow CH_3 - OH + Br^-$$

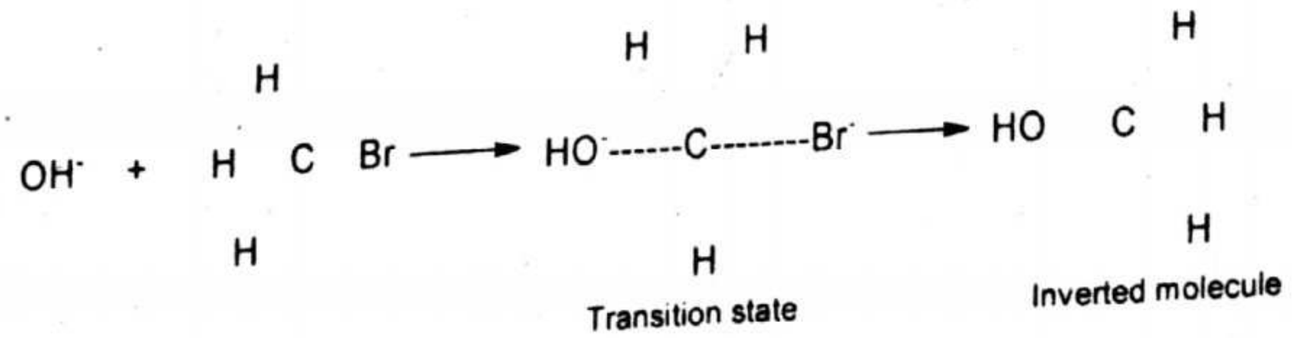
Mechanism:

The attack of nucleophile on carbon and the departure of the halide ion take place simultaneously in single step. This is rate-determining step because the bond breaking and bond making processes occur simultaneously. Since two molecules are undergoing change in covalency in rate determining step. It is a bimolecular nucleophilic substitution reaction which is taking place in one step.



Transition state

Inverted molecule



Transition state

Inverted molecule

This mechanistic picture is based upon the following evidences.

(1) Kinetic Evidence:

The rate of an SN_2 reaction depends upon the concentration of nucleophile as well as the concentration of alkyl halide. The rate expression for the reaction can be written as;

$$Rate = k\,[Nu]\,[R\text{-}X]$$

Where k is specific rate constant

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This means that the rate of reaction will be double if the concentration of any of the two is double e.g., the rate of following reaction increases when conc. of either OH^- or $CH_3 - Br$ is increased.

$$H_3C - Br + OH^- \longrightarrow CH_3 - OH + Br^-$$

(2) Stereo-chemical Evidence:

A bimolecular nucleophilic substitution always occurs with inversion of configuration. The carbon atom in transition state is sp^2-hybridized and is planar. The attacking nucleophile and the leaving group are present in the transition state on opposite sides of electrophilic carbon atom.

Comparison of S_N1 and S_N2 Mechanisms:

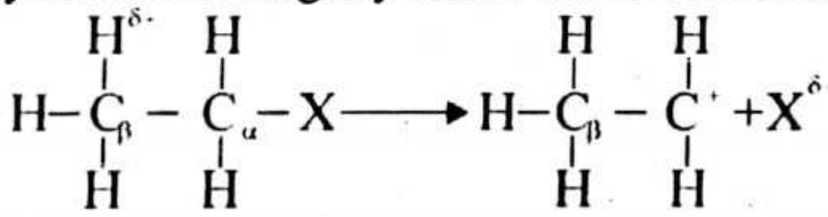
	S_N1 reaction		S_N2 reaction
1	It is a two steps mechanism.	1	It is a single step mechanism.
2	First step is slow one and second is fast.	2	It has only one step that is slow.
3	It is a unimolecular reaction.	3	It is a bimolecular reaction.
4	It is favoured in polar solvents.	4	It is favoured in non-polar solvents.
5	Mostly tertiary alkyl halides show this reaction.	5	Mostly primary alkyl halides show this reaction.
6	50% inversion and 50% retention of configuration takes place.	6	100% inversion of configuration takes place.
7	Rate = k [R-X]	7	Rate = k [Nu] [R-X]

ELIMINATION REACTIONS

The chemical reaction in which two groups are eliminated from two adjacent atoms is called elimination reaction. Since β-hydrogen is necessary for eliminations, it is also called β-elimination.

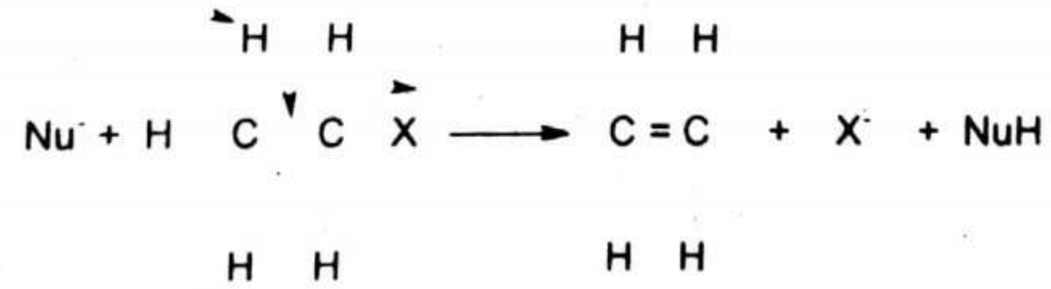
Explanation:

β-hydrogen atom in alkyl halides is slightly acidic due to electron withdrawing effect of halogen.

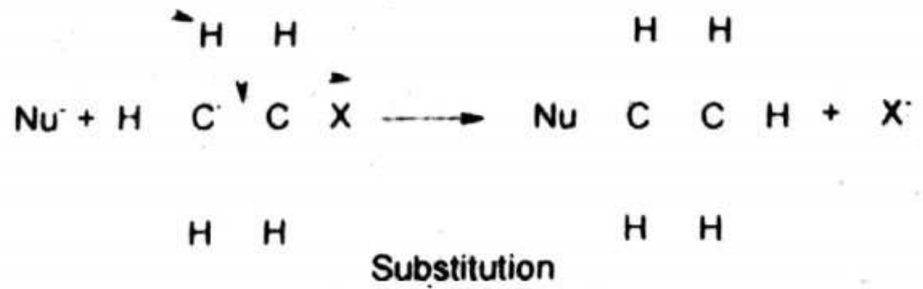


Substitution and elimination reactions:

The attacking nucleophile can either attack α-carbon to give substitution product or β-hydrogen to give elimination reaction.



Elimination

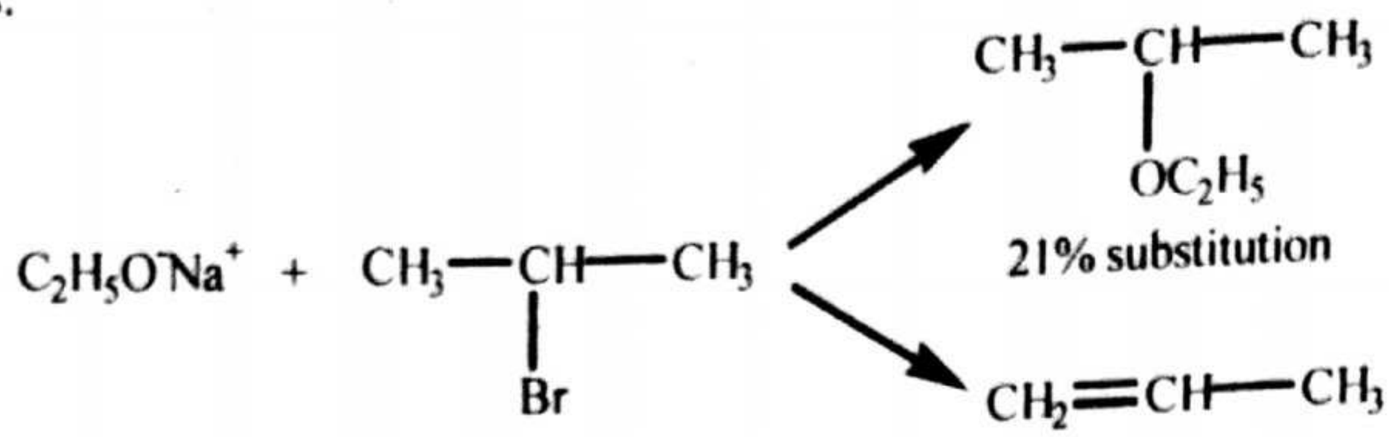


Substitution

Strong bases such as OH^-, RO^-, NH_2^- etc cause elimination in preferences to substitution.

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Highly polarizable nucleophile and weak bases such as I^-, RS^- etc give substitution reactions.

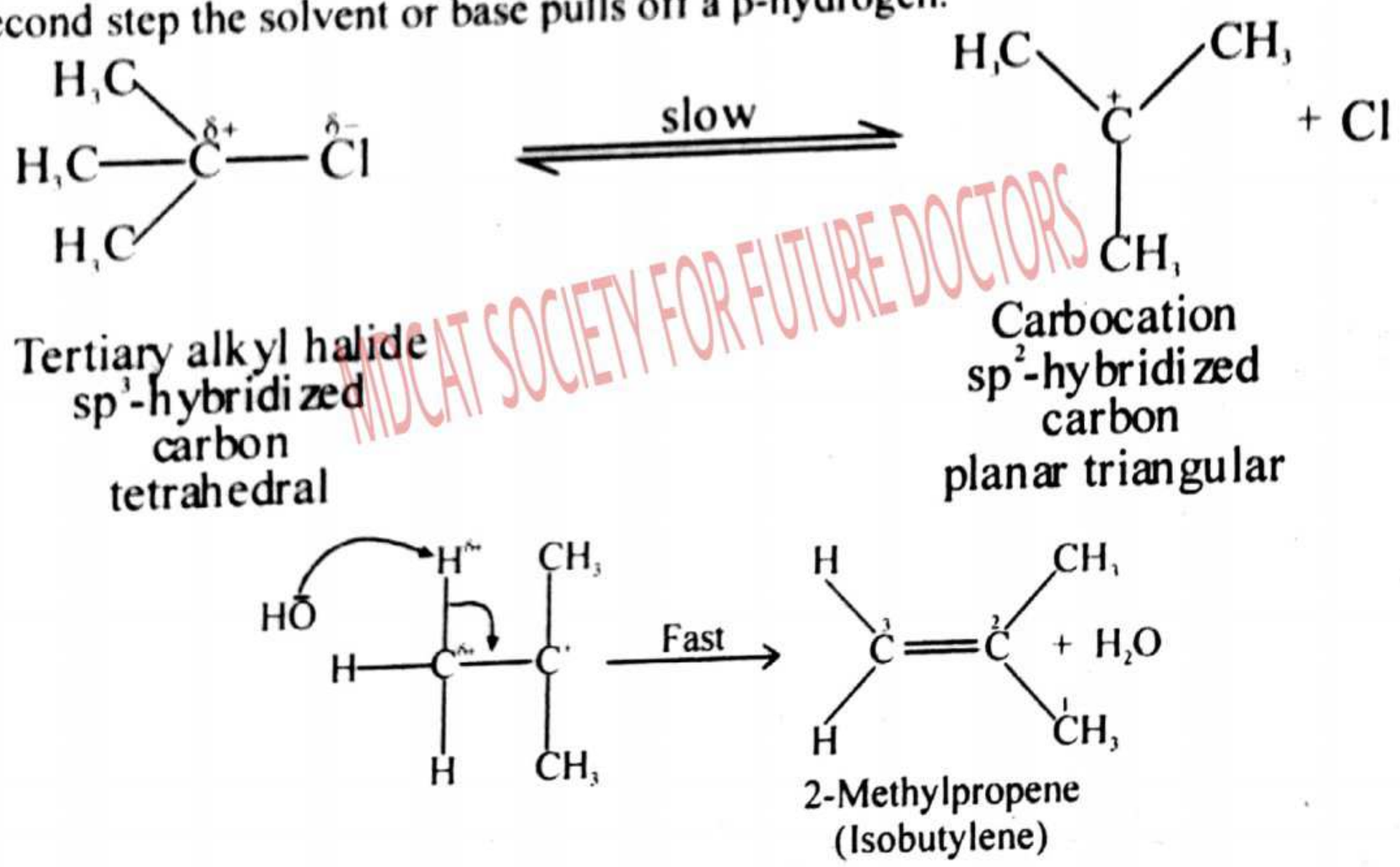


E_1 MECHANISM:

It is unimolecular two step elimination reactions.

Explanation:

The substrate undergoes slow ionization in the first step to form carbonium ion and in the second step the solvent or base pulls off a β-hydrogen.



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Molecularity:

Since only one molecule is undergoing a change in the rate determining step, i.e., first step, this is two step unimolecular elimination reactions.

First order kinetics:

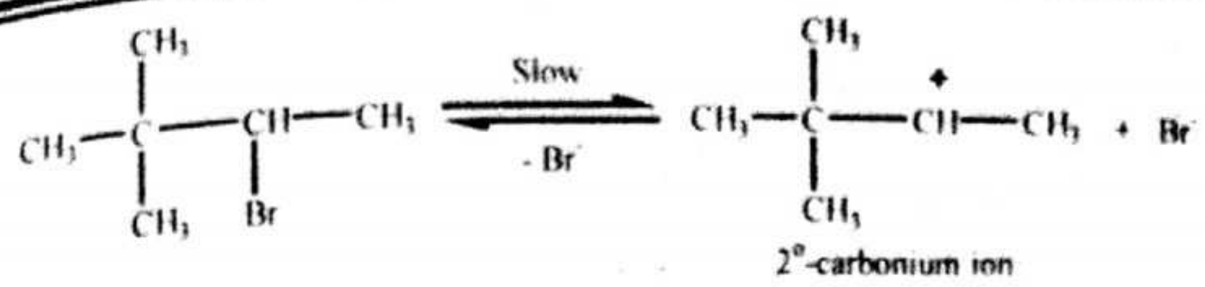
The E_1-mechanism has been supported by the study of the reaction. It follows first order kinetics, in which rate of reaction depends only on the concentration of substrate.

$$\text{Rate} = k\,[R\text{-}X]$$

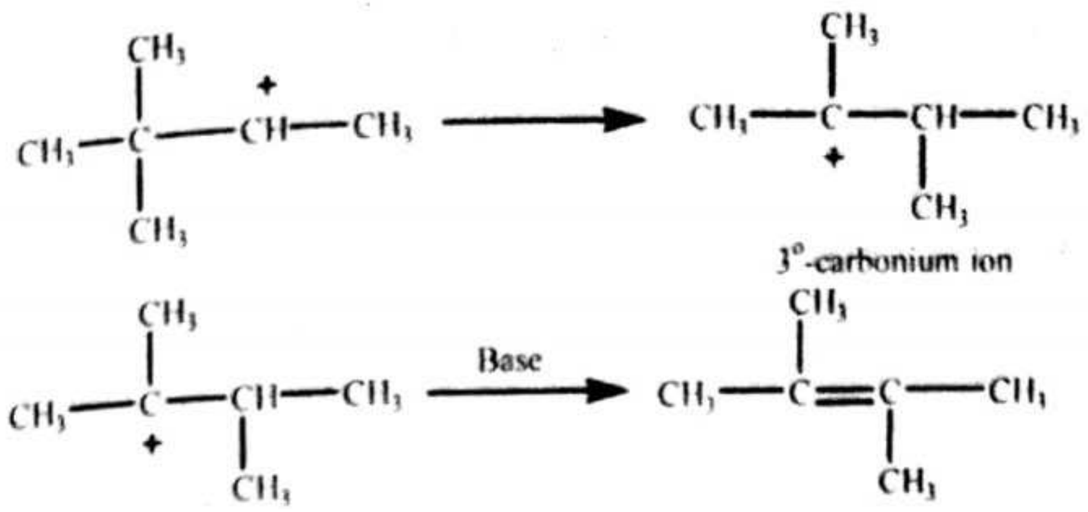
Carbonium ion:

The presence of carbonium ion as an intermediate has been indicated by the presence of more than one kind of elimination products. A relatively less stable carbonium ion rearranges to give more stable carbonium before giving elimination product.

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2°-carbonium ion

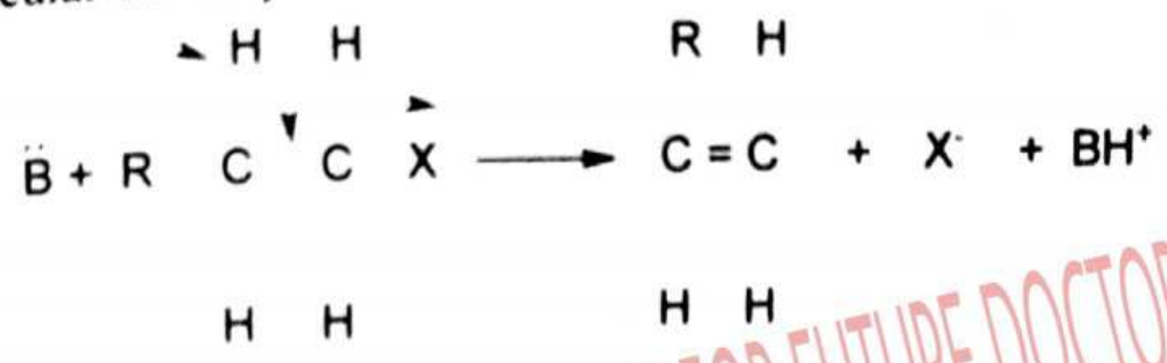


3°-carbonium ion

3°-carbonium ion

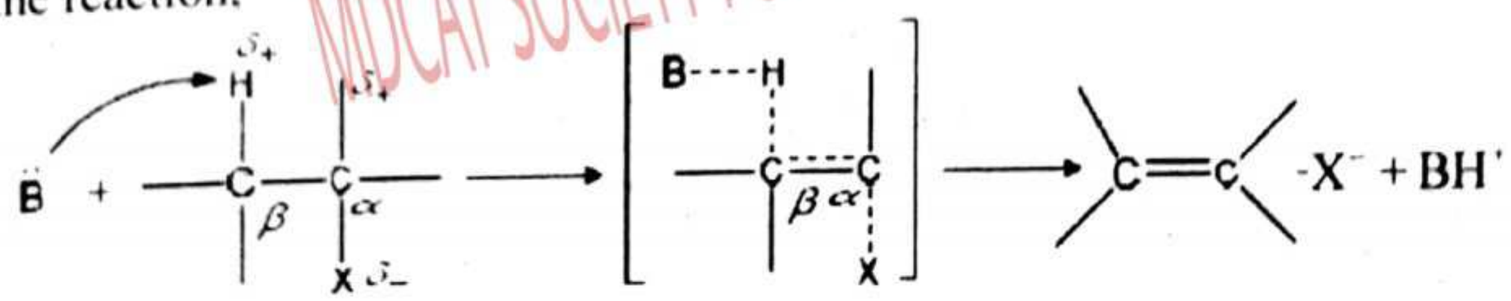
E_2 Mechanism:

It is bimolecular one step elimination reaction.



Explanation:

Consider the reaction.



The attacking base removes a proton from the β-carbon simultaneously with the formation of double bond between C_α and C_β and the loss of halide ions.

Rate determining step:

This is rate determining step because bond breaking and bond making processes are taking place simultaneously.

Molecularity:

Since two molecules are undergoing a change in transition state, it is a bimolecular one step elimination reaction.

Steps:

Thus E_2 is a one step process in which both the substrate and the base participate.

Second order kinetics:

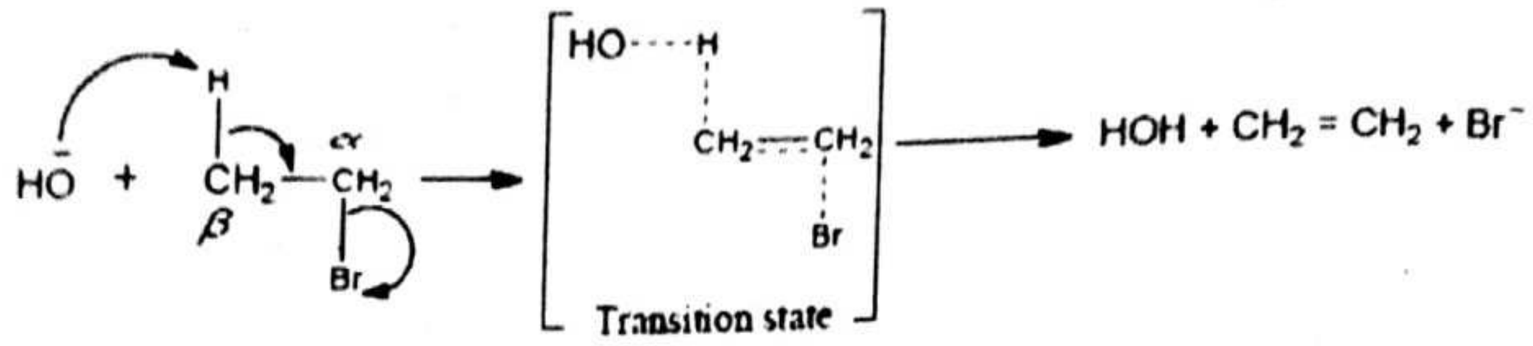
The observed rate law for E_2-reaction is

$$\text{Rate} = k\,[\text{R-X}]\,[\text{Base}]$$

The rate of E2-reaction depends upon the concentration of substrate and the base e.g., for the reaction,

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The rate of reaction follows second order kinetics.

$$\text{Rate} = k\,[CH_3\text{-}CH_2\text{-}Br]\,[OH^-]$$

Substitution versus Elimination Reactions

Though substitution and elimination reaction lead to different products, there is always a competition between them because of close resemblance in their mechanism. Since substitution is more favorable energetically it is the dominant reaction in the substitution-elimination reaction. Elimination occurs only in the presence of β- hydrogen where substitution reactions do not require this condition to be satisfied.

The following factors help to compare these two pathways:

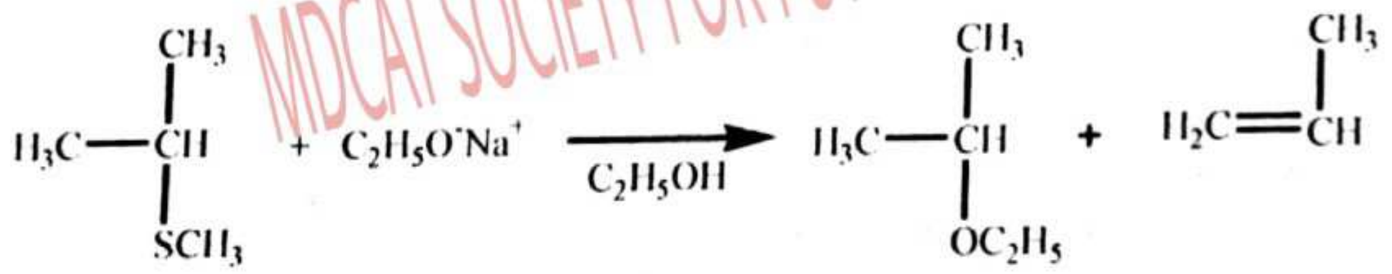
(i) Structure of Substrate:

Crowding within the substrate favours elimination over substitution because the approach of the nucleophile to α-carbon is difficult for substitution. However, the elimination is favorable because the removal of β-H atom by base from tertiary planar carbonium ion is easy.

Example:



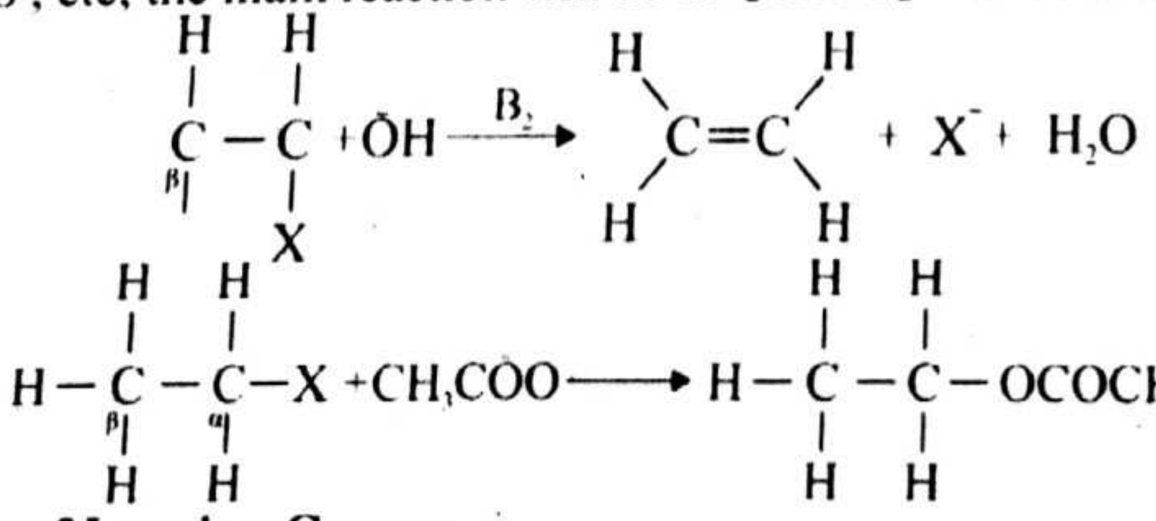
Substitution = 88% Elimination = 12%



Substitution = 39% Elimination = 61%

(ii) Nature of Base:

When the electron pair donor is a strong base, e.g., ^-OH, ^-OR etc., the dominant reaction is E_2 and SN_2 reaction is a side reaction. However, when the nucleophile is a weak base like X^-, RS^-, etc, the main reaction will be SN_2 and E_2 will be minor side reaction.



The Nature of Leaving Group:

The role of leaving groups in Elimination reactions is similar to that in substitution reactions.

In unimolecular reactions it does not affect the mechanism because both the elimination and substitution products are decided with carbonium ion.

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However, in the bimolecular reactions the nature of product greatly depends upon the nature of leaving group.

Example:

$$n\text{-}{}_{\beta}C_{18}H_{37}\text{-}X + (CH_3)_3COK \longrightarrow n\,C_{16}H_{33}\text{-}CH{=}CH_2 + n\text{-}C_{18}H_{37}OC(CH_3)_3$$

X=Br	85%	15%
X=OTS = Tosylate group	1%	99%



Nature of Solvent

Elimination is favored more than substitution by decreasing the solvent polarity. Thus alcoholic KOH affects elimination while more polar aqueous KOH is used for substitution. E_1 is favored by polar solvents like SN_1 reaction. In non-polar solvents, the reaction will follow E_2- mechanism.

Effect of Temperature

An increase in temperature will favor elimination more than substitution, because substitution reaction involve less reorganization of bonds as compared to eliminations.

Example:

$$CH_3\text{-}\underset{\underset{Br}{|}}{CH}\text{-}CH_3 + NaOH \xrightarrow{H_2O} CH_3CH{=}CH_2 + (CH_3)_2CHOH$$

(Bimolecular)

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at 45°C	53%	47%
at 100°C	64%	36%

E1 Reactions	E2 Reactions
Two steps mechanism	One step mechanism
Molecularity is one Rate α [R–X] Rate = k[R–X]	Molecularity is two Rate α [R–X] [Base] Rate = k[R–X] [Base]
Tertiary alkyl halides generally give E_1 reactions.	Primary alkyl halides generally give E_2 reactions.
Order of reaction is one.	Order of reaction is two.
The reaction is: $R\text{–}X \xrightarrow{Slow}$ carbocation + X^- Carbocation + Base $\xrightarrow{fast}$ alkene + H_2O	The reaction is: $R\text{–}X + OH^- \xrightarrow{slow}$ Alkene + H_2O + X^-

POINT TO PONDER

When alkyl halide reacts with alcoholic KOH, reaction will be elimination preferably.

$$C_2H_5\text{–}Br + KOH \xrightarrow{Alcohlic} CH_2{=}CH_2 + H_2O + KBr$$

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TOPIC-16 ALCOHOLS AND PHENOLS

COURSE CONTENTS

- Classification: Primary, Secondary and Tertiary alcohols
- Reactivity
- Phenols
- Physical properties
- Acidity
- Reactivity
- Differentiate between alcohol and phenol

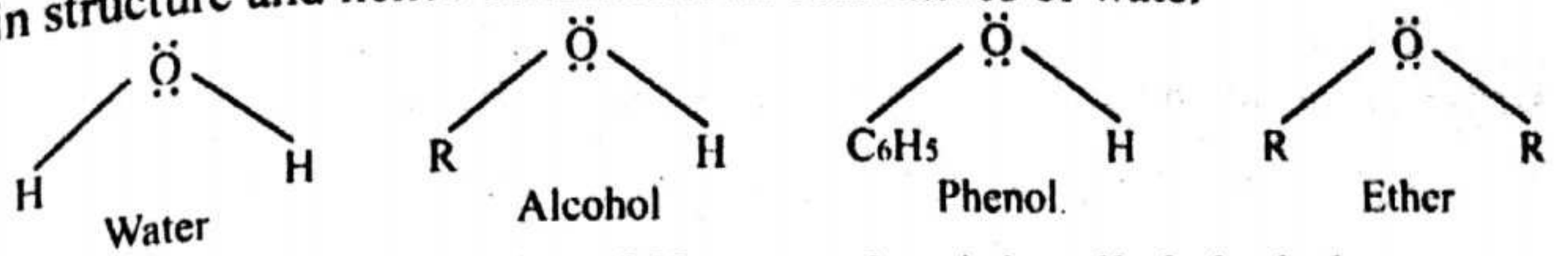
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INTRODUCTION

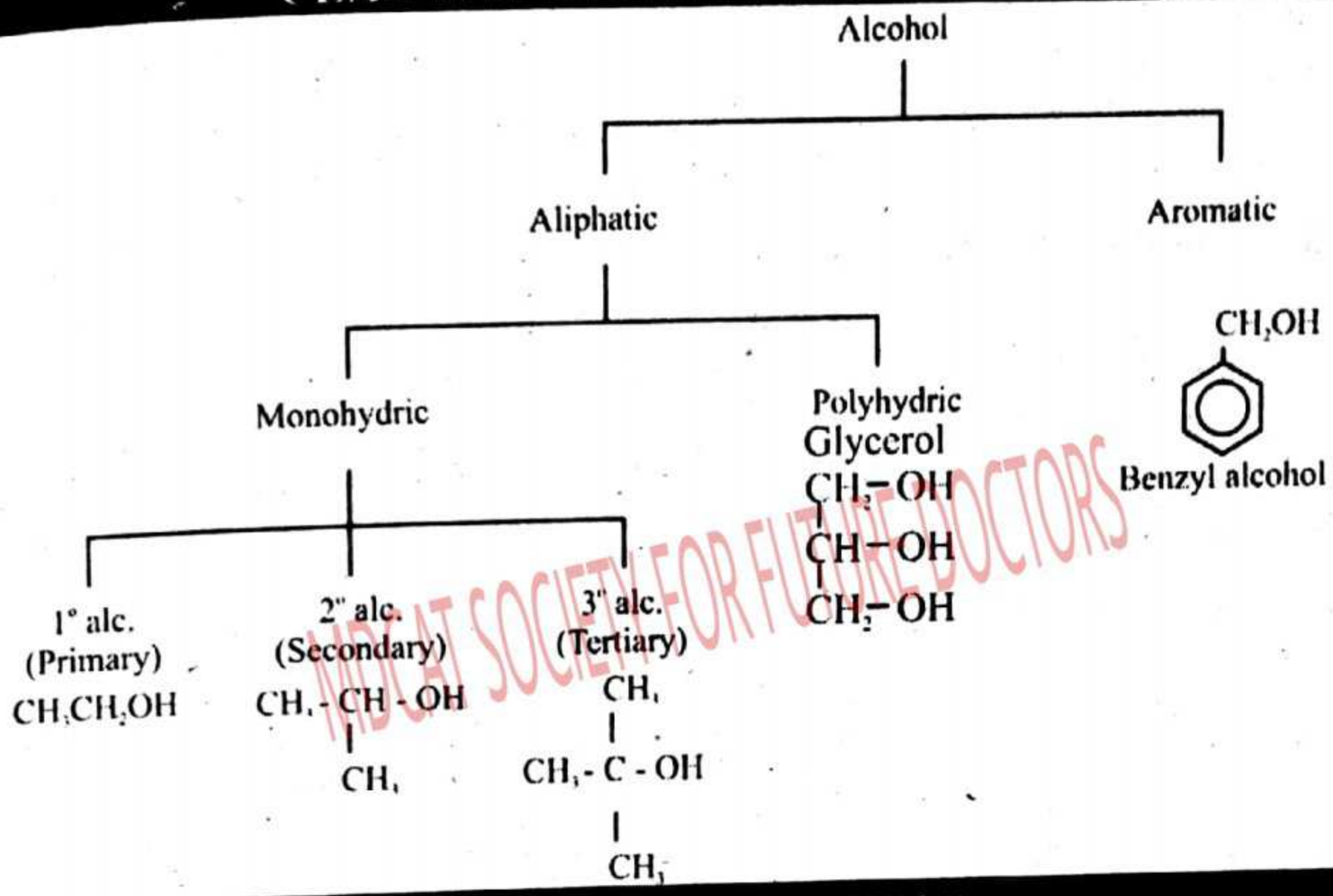
- Alcohols, phenols and ethers are classes of organic compounds which are much closer to water in structure and hence considered as derivatives of water



- When H of alkane is replaced by –OH group, then it is called alcohol.
- When the H of benzene ring is replaced by –OH group, then it is called phenol.
- The linkage between two carbon atoms through oxygen atom is called ether.

ALCOHOLS

CLASSIFICATION OF ALCOHOLS



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REACTIONS OF ALCOHOLS

Reactivity of –OH group

- Oxygen atom of the –OH group in alcohols is sp^3 hybridized
- The carbon oxygen bond (C-O) and hydrogen oxygen bond (O-H) are highly polarized.
- The negative charge is present on the oxygen atom of alcohol.

Chemical properties

- Alcohols react with other reagents in two ways
  (i) Reactions in which C-O bond breaks.
  (ii) Reactions in which O-H bond breaks.
- **The order of reactivity of alcohols when C-O bond breaks**
  Tertiary alcohol > Secondary alcohol > Primary alcohol
- **The order of reactivity of alcohols when O-H bond breaks**
  CH_3OH > Primary alcohol > Secondary alcohol > Tertiary alcohol
- Nucleophile breaks C-O bond of alcohol.
- Attacking electrophile breaks O-H bond of alcohol.

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- Catalytic oxidation of primary alcohol and secondary alcohol in presence of $K_2Cr_2O_7$ and H_2SO_4, converts them into aldehydes and ketones respectively; while same reaction of tertiary alcohol gives alkenes.
- On heating with H_2SO_4 (conc.), alcohol changes to alkene.

(i) Oxidation of alcohol:

$$C_2H_5OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - CHO + H_2O$$

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = O + H_2O$$

NOTE: Tertiary alcohols resist to oxidation instead they show elimination reaction in the presence of acidified $K_2Cr_2O_7$.

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH_2 + H_2O$$

(ii) Reactions of alcohols in which C– O bond cleavage occurs

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + HCl + POCl_3$$

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

$$C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$$

$$C_2H_5OH + NH_3 \xrightarrow{ThO_2} C_2H_5NH_2 + H_2O$$

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

(iii) Reactions of alcohols in which O–H bond cleavage occurs

$$C_2H_5 - OH + 2Na \xrightarrow{\text{Ethanol}} C_2H_5 - O^-Na^+ + H_2$$

(iv) Iodoform test:

Ethanol gives iodoform with iodine in the presence of NaOH. Formation of yellow crystals indicates that the alcohol is ethanol. Methanol does not give iodoform test

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + HCOONa + 5NaI + 5H_2O$$

$$CH_3OH + I_2 + NaOH \longrightarrow \text{No yellow ppt.}$$

(v) Esterification

It is nucleophilic substitution reaction with respect to carboxylic acid. Here –OH group of carboxylic acid is replaced by RO– (alkoxide) group of alcohol

$$C_2H_5OH + CH_3COOH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

(vi) Dehydration

Alcohols react with con. H_2SO_4 and give different products at different temperature.

(i) $C_2H_5OH \xrightarrow[180°C]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$

(ii) $2C_2H_5OH \xrightarrow[140°C]{\text{Conc. } H_2SO_4} C_2H_5 - O - C_2H_5 + H_2O$

Methanol does not produce any alkene on reaction with conc. H_2SO_4 because methanol has no β–hydrogen. Therefore, β–elimination reaction does not take place.

POINT TO PONDER

Oxygen atom of the –OH group in alcohols is sp^3 hybridized
The carbon oxygen bond (C– O) and hydrogen oxygen bond (O – H) are highly polarized.
The negative charge is present on the oxygen atom of alcohol.

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Distinction between primary, secondary, and tertiary alcohols

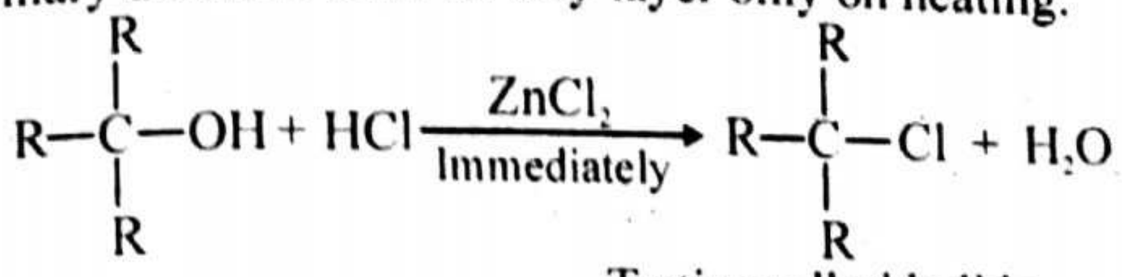
Primary, secondary, and tertiary alcohols are identified and distinguished by their reactivity with halogen acids in the presence of anhydrous $ZnCl_2$.

For example when alcohol is treated with a solution of $ZnCl_2$ in conc. HCl, then if

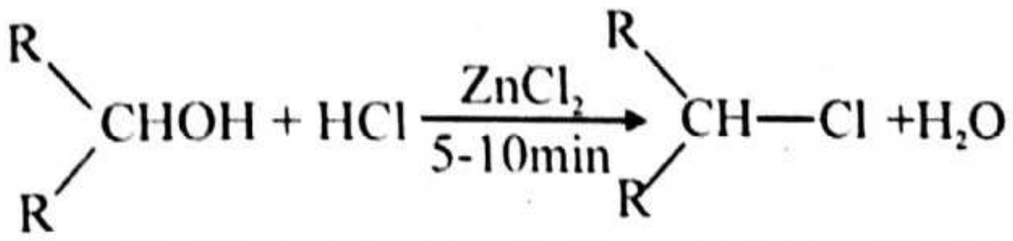
(i) Tertiary alcohol form an oily layer immediately.

(ii) Secondary alcohols forms an oily layer in five to ten minutes.

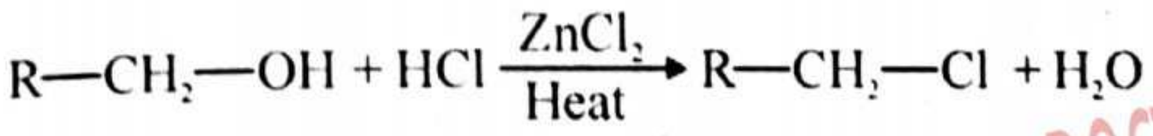
(iii) Primary alcohols form an oily layer only on heating.



Tertiary alkyl halide



Secondary alkyl halide



Primary alkyl halide

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PHENOLS

Phenol

Aromatic compounds which contain one or more –OH groups directly attached with carbon of benzene ring are called phenols.

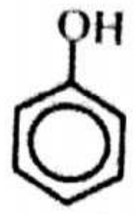
Physical properties:

- It is colorless, crystalline, deliquescent solid with characteristic smell (phenolic odour)
- Its melting point is 41°C and boiling point 182°C.
- It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5°C.
- It is poisonous and used as a disinfectant in hospitals and washrooms.

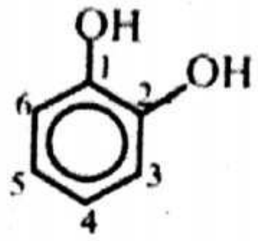
Simplest Phenol

Carbolic acid (benzenol) (C_6H_5OH) is phenol. It was first obtained from coaltar by **Runge in 1834.**

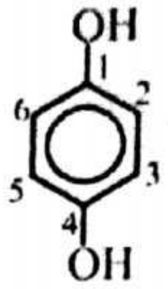
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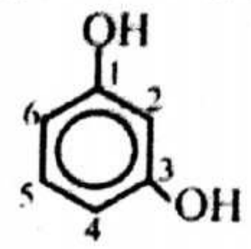
Phenol



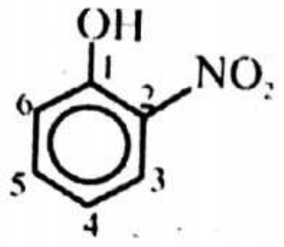
1,2-Dihydroxy benzene o-Hydroxyl phenol (catechol)



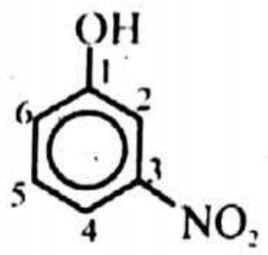
1,4-Dihydroxy benzene p-hydroxy phenol (hydroquinone)



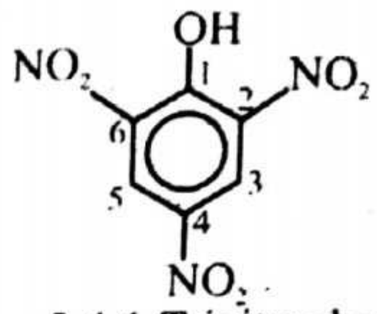
1,3-Dihydroxy benzene m-dihydroxy phenol (resorcinol)



2-Nitrophenol
o-Nitrophenol



3-Nitrophenol
m-Nitrophenol



2,4,6-Trinitrophenol
Picric acid

REACTIONS OF PHENOLS

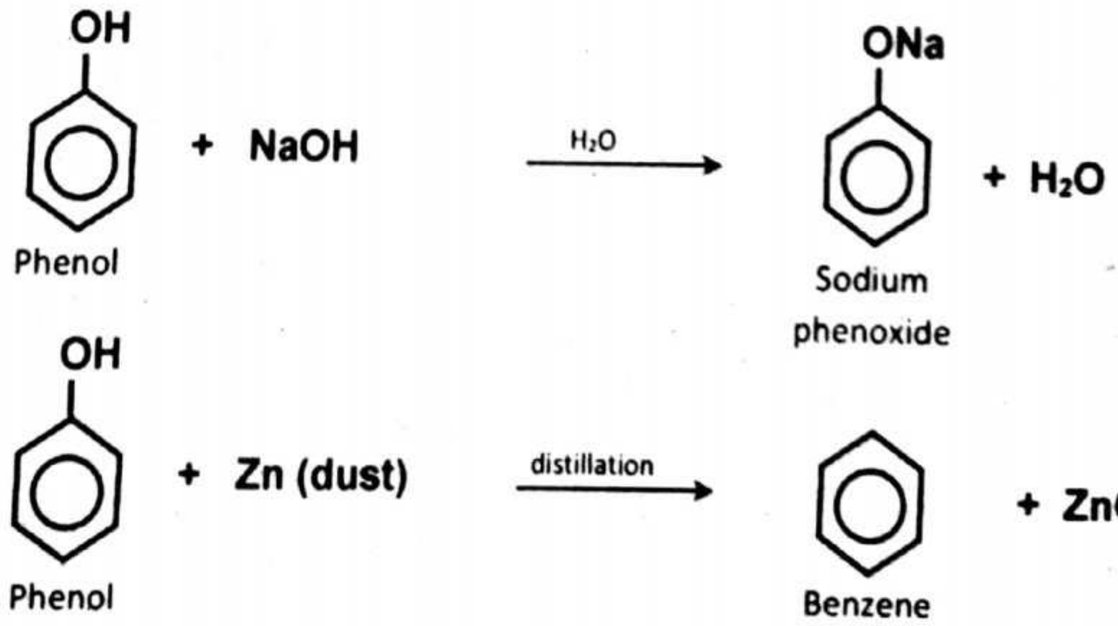
Reactions of phenol

Phenol shows two types of reactions

(i) Reaction of phenol due to –OH group

Nature of reaction	Remarks
Salt formation	Phenoxides are formed
Ester formation	Reaction takes place in basic media
Reduction with Zn	Benzene is obtained

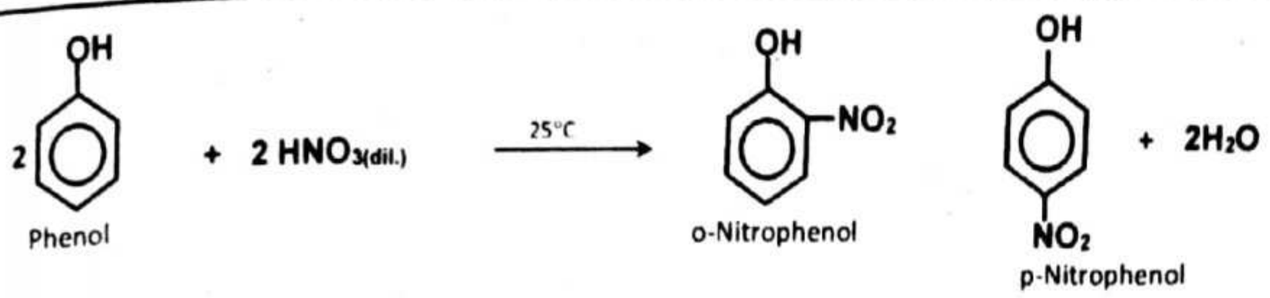
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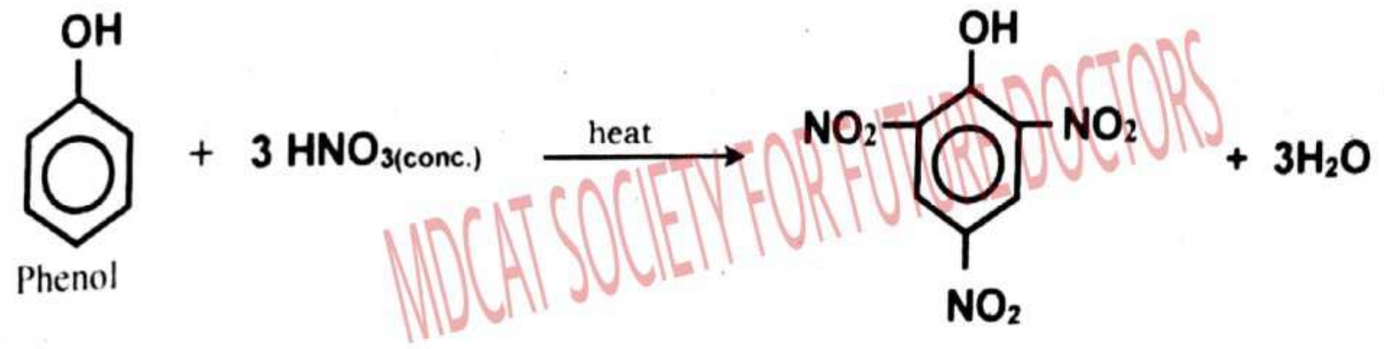


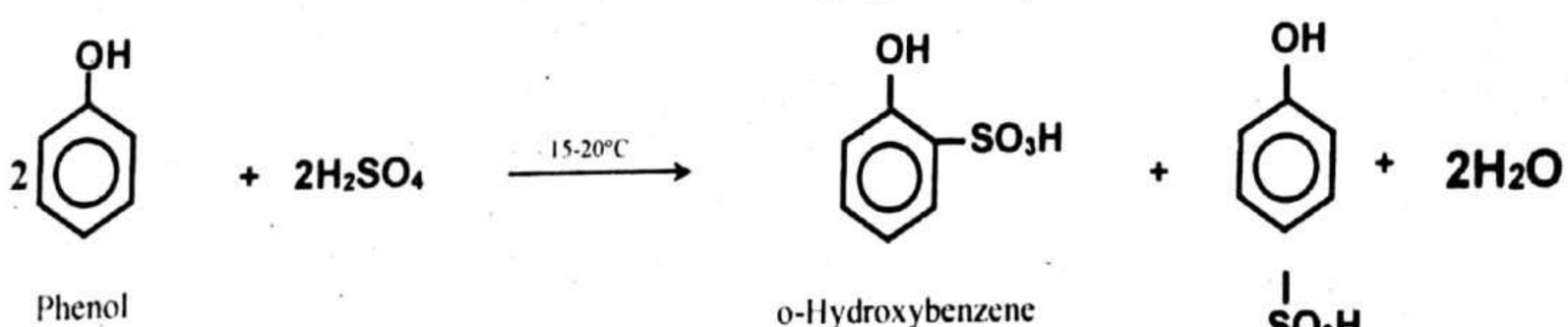
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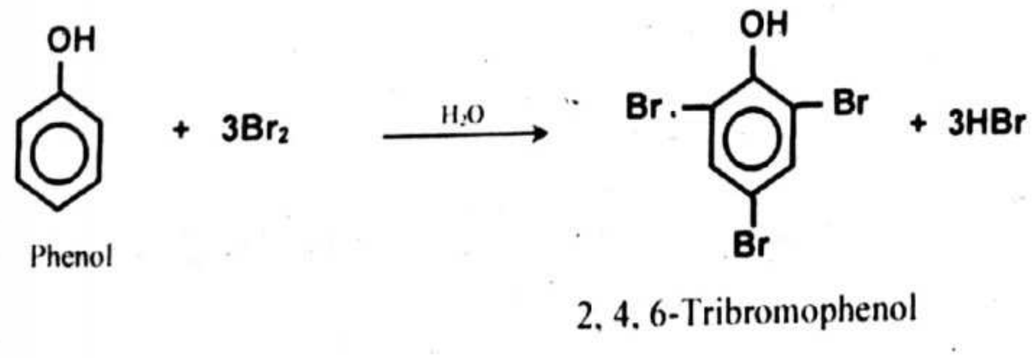
Reaction of Phenol Due to Benzene Ring

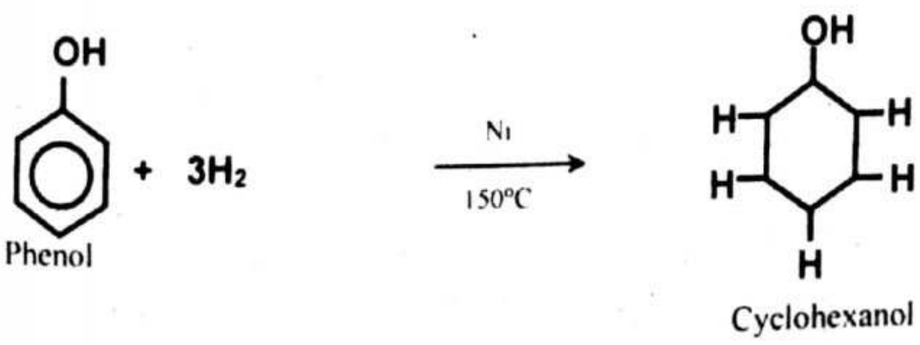
Reaction	Remarks
Nitration	▸ At room temperature, the product is a mixture of o-and p-nitrophenol with dil. HNO_3 ▸ At higher temperature, the product is picric acid with concentrated HNO_3
Sulphonation	Introduction of HSO_3^- is called sulphonation a mixture of ortho and para products at 15 to 20°C
Halogenation	White ppt. of 2,4,6-tribromophenol is obtained
Hydrogenation	Un-saturation of ring is removed
Reaction with formaldehyde	▸ This is a condensation polymerization of phenol ▸ Formaldehyde polymerizes with phenol to produces Bakelite. ▸ Bakelite is used for manufacturing of switch buttons











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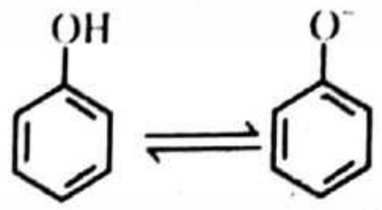
RELATIVE ACIDITY OF WATER, ETHANOL AND PHENOL

Phenol is:

- Too weak to affect the litmus paper.
- Unable to evolve CO_2 from carbonates.
- Its K_a is 1.3×10^{-10} and pKa is approximately 10.
- Acidic in nature.

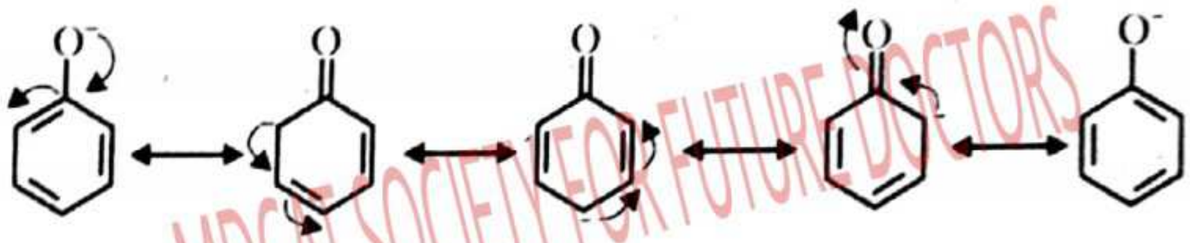
Reason

The acidic nature of phenols, as compared to alcohols, can be attributed to the formation of stable phenoxide ions after loss of proton.



Phenol Phenoxide

The phenoxide ion, thus formed is resonance stabilized.

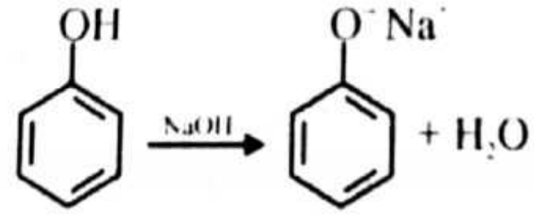


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The negative charge spreads throughout the benzene ring and is thereby dispersed. This delocalization of the charge accounts for the stability of the phenoxide ion.

Example:

Being acidic, phenol reacts with NaOH or Na metal to form salt, which shows that it is acidic in nature.



Phenol Sodium Phenoxide

Relative acidic strength of alcohol, phenol, water and carboxylic acid is as follows:

Carboxylic acid > phenol > water > alcohol

Compound	Formula	K_a (approx)	pK_a
Phenol	Ar–OH	10^{-10}	10
Alcohols	R–OH	$10^{-16} - 10^{-18}$	16–18
Carboxylic acids	R–COOH	10^{-5}	5
Water	H–OH	10^{-14}	14

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DIFFERENCE BETWEEN ALCOHOLS AND PHENOL

ALCOHOLS	PHENOLS
• The compounds in which hydroxyl group is attached to an alkyl group. (R– OH)	• The compounds in which hydroxyl group is attached to an aryl group. (Ar – OH)
• Alcohols are also called hydroxyl derivatives of alkanes	• Phenols are called hydroxyl derivatives of benzene
• The compounds in which one hydrogen of water is replaced by an alkyl group e.g $CH_3 - OH$.	• The compounds in which one hydrogen of water is replaced by an aryl group e.g.
• The general formula of alcohols is R–OH.	• The general formula of phenol is C_6H_5–OH. It is also brown as carbolic acid.
• Alcohols many be monohydric and polyhydric depending on the number of –OH groups attached.	• Phenols are not monohydric or polyhydric.
• Lower alcohols are generally colorless liquids.	• They are colorless, crystalline, deliquescent solid.
• Alcohols have a characteristic sweet smell and burning taste.	• They have characteristic phenolic occur.
• They are readily soluble in water but solubility decreases in higher alcohols.	• It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5°C.
• Alcohols react with other reagents in two ways, either in which C – O bond breaks or in which O – H bond breaks.	• Phenol react with other reagents in two ways (i) Reactions due to –OH group (ii) Reactions due to benzene ring.
• Alkomide ions have no such resonance structures.	• Phenolate have reasonance structure.
• Alcohols are less acidic. (pKa ≈16–20)	• Phenols are acidic (pKa ≈10)

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TOPIC-17 ALDEHYDES AND KETONES

COURSE CONTENTS

- Explain structure of aldehydes and ketones
- Preparation of aldehydes and ketones
- Reactivity of aldehydes and ketones and their comparison. Describe acid and base catalyzed nucleophilic addition reactions of aldehydes and ketones.
- Chemistry of aldehydes and ketones by their reduction to alcohols
- Oxidation reactions of aldehydes and ketones

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INTRODUCTION

Organic compounds containing the carbonyl functional group. $-\overset{\overset{O}{\|}}{C}-$ are called carbonyl compounds, they may be aldehydes and ketones.

Difference between aldehydes and ketones.

ALDEHYDES	KETONES
Functional Group In aldehydes, the 'C, atom of carbonyl group is directly attached at least one H–atom	In ketones the 'C, atom of carbonyl group is bonded to two carbon atoms, and so it occurs, within a chain
General formula The homologus series of aldehydes have general formula $C_nH_{2n}O$	The homologus series of ketones have general formula $C_nH_{2n}O$.
General formula structure An aldehyde may be represented by the general formula structure. $R-\overset{\overset{O}{\|}}{C}-H$	A ketone may be represented by the general formula structure $R-\overset{\overset{O}{\|}}{C}-R$
Occurrence Aldehyde groups are present in most sugars. They are main constituents of a number of essential oils used as fragrances and flavours.	Ketonic group is present in camphor and fructose.
Examples (i) $H-\overset{\overset{O}{\|}}{C}-H$ Formaldehyde (ii) $CH_3-\overset{\overset{O}{\|}}{C}-H$ Acetaldehyde	(i) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ Acetone (ii) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$ Ethyl methyl ketone

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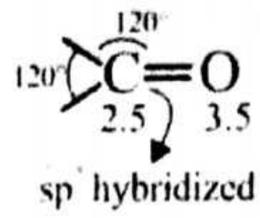
STRUCTURE OF ALDEHYDE AND KETONES

Carbonyl compounds

The organic compounds which contain carbonyl functional group ($>C=O$) in their molecules are called carbonyl compounds.

- In a carbonyl group, a carbon atom is bonded to oxygen with a double bond
- The homologous series of both aldehydes and ketones have the general formula, $C_nH_{2n}O$
- Aldehydes and Ketones are carbonyl compounds

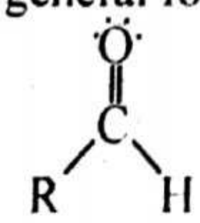
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- Due to difference in electronegative between C and O, carbonyl group is polar

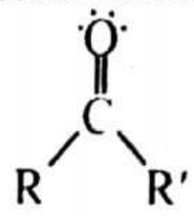
Aldehydes

- In aldehydes, the carbonyl group is bonded to at least one hydrogen atom and so it occurs at the end of the chain.
- An aldehyde can be represented by the general formula,



Ketones

- In ketones, the carbonyl group is bonded to two carbon atoms and so it occurs within a chain.
- A ketone may be represented by the general formula



Where R and R′ may be same or different but can never be H

PREPARATION OF ALDEHYDES AND KETONES

Formaldehyde

Industrial method	Laboratory method
By passing methanol vapours and air over iron oxide-molybdenum oxide or silver catalyst at 500° C	By passing methanol vapours and air over platinised asbestos or copper or silver catalyst at 300°C

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- Industrial Method

$$2CH_3OH + O_2 \xrightarrow[500°C]{FeO,\ Mo_2O_3} 2HCHO + 2H_2O$$

- Laboratory Method

$$2CH_3OH + O_2 \xrightarrow[300°C]{Pt\text{-}asbestos} 2HCHO + 2H_2O$$

$$(HCOO)_2Ca \xrightarrow{\Delta} HCHO + CaCO_3$$

POINT PONDER

A mixture of 40% formaldehyde, 8% methyl alcohol and 52% water is known as formalin.

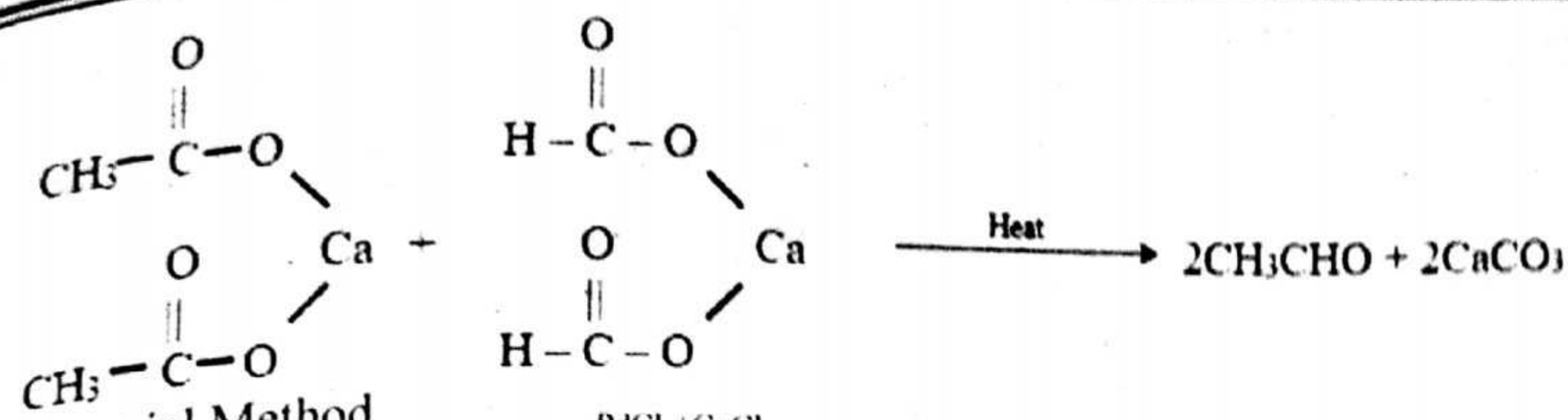
Acetaldehyde

Laboratory method	Industrial method
▸ By oxidation of ethyl alcohol with acidified sodium dichromate ▸ By dry distillation of mixture of calcium salt of formic acid and acetic acid	By oxidation of ethylene using palladium chloride catalyst with cupric chloride as promoter

- Laboratory Method

$$CH_3CH_2OH + [O] \xrightarrow[\Delta]{Na_2Cr_2O_7 + H_2SO_4} CH_3CHO + H_2O$$

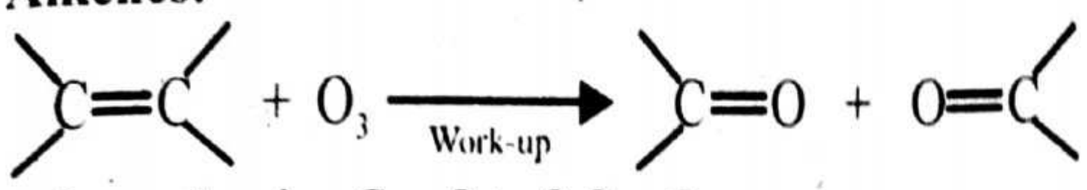
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Industrial Method

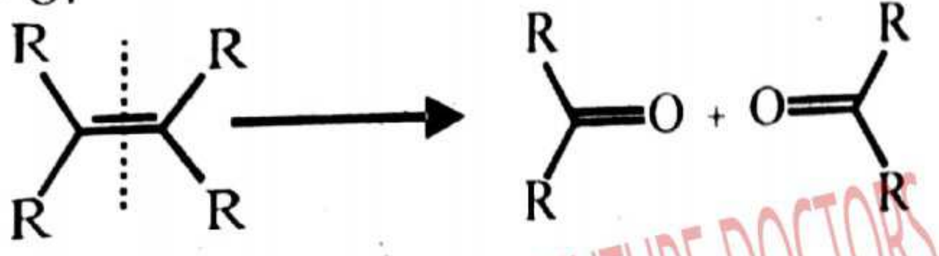
$$2CH_2{=}CH_2 + O_2 \xrightarrow[H_2O]{PdCl_2+CuCl_2} 2CH_3CHO$$

Ozonolysis of Alkenes:



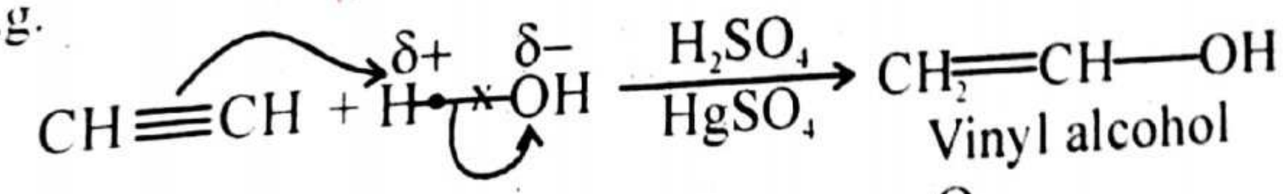
The overall transformation is: C = C to 2 C = O

This reaction is carried out in presence of ozone, O_3, followed by a reducing, in the presence of ·Zn, in acetic acid, the overall process is the cleaving of alkene in to two carbonyl compounds. If the substituents on C = C are present, they are obtained in the carbonyl C = O.



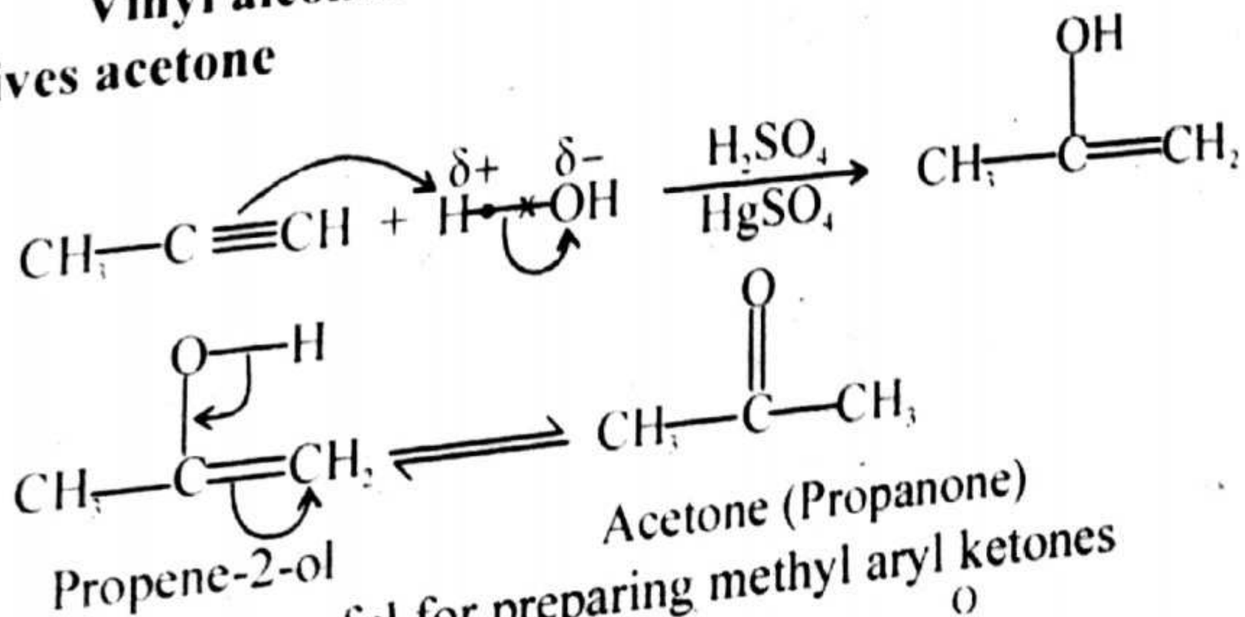
Hydration of Alkynes

Water adds on to alkynes in the presence of dil. H_2SO_4 and $HgSO_4$ to, produce an aldehyde or ketone. Enol forms as intermediate, which isomerizes in to aldehydes or ketones e.g.

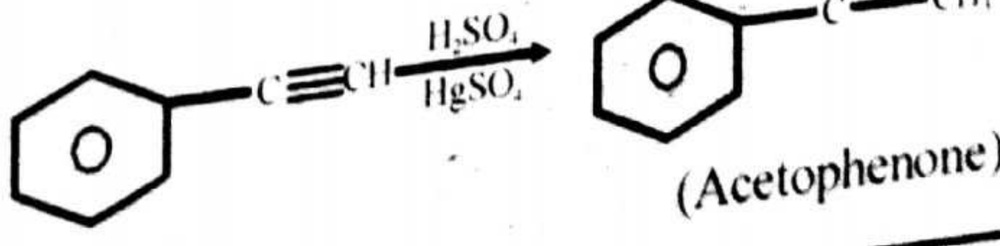


Vinyl alcohol

Propyne gives acetone



This reaction is useful for preparing methyl aryl ketones



(Acetophenone)

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Oxidation of Primary and Secondary Alcohols

Primary alcohols are oxidized to aldehydes and secondary alcohols are oxidized to ketones, when they are treated with oxidizing agents. Following oxidizing agents are used.

- Na or K dichromate solution in presence of conc. H_2SO_4. ($K_2Cr_2O_7$ or $Na_2Cr_2O_7$/conc. H_2SO_4)

Example

Primary alcohols such as butanol or Benzyl alcohols are oxidized into butanal and benzaldehyde.

$$\underset{\text{Butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[Na_2Cr_2O_7]{\text{Conc. } H_2SO_4} \underset{\text{Butanal}}{CH_3CH_2CH_2CHO}$$

Non-aqueous solvents are used to control further oxidation of products obtained.

Secondary alcohols are oxidized into ketones.

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CHOH}} \xrightarrow{[O]} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=O$$

Friedel- Craft's aceylation of benzene

The substitution of an acyl group to an organic compound in the presence of $AlCl_3$ or some other Lewis acid. The $AlCl_3$ generate acylation ion (Electrophile) which is substituted in the aromatic ring.

$$C_6H_6 + R-\underset{\displaystyle O}{\overset{\displaystyle ||}{C}}-Cl \underset{}{\overset{AlCl_3}{\rightleftharpoons}} C_6H_5COR + HCl$$

Alkylaryl ketone

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REACTIONS OF ALDEHYDES AND KETONES

Reactivity of carbonyl group

Reactivity of carbonyl group is due following reasons

- Both carbon and oxygen are sp^2 hybridized Reactivity of carbonyl group is due to the polarity of carbon and oxygen.

$$\underset{2.5}{C} = \underset{3.5}{O} \quad (\delta+ \; \delta-)$$

- Due to the presence of π-bond, it can undergo nucleophilic addition reaction.

Ketone are less reactive as compared to aldehydes because

- Electrophilic character of carbonyl carbon in ketones is less due to alkyl groups attached with carbonyl carbon which are the electron donating groups

$$H_3C-\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}-CH_3 \longleftrightarrow H_3C-\overset{\displaystyle O^-}{\overset{\displaystyle |}{C^+}}-CH_3$$

- Ketones are less reactive due to steric hinderance

Nucleophilic addition reaction

The characteristic reactions of carbonyl compounds are nucleophilic addition reactions.

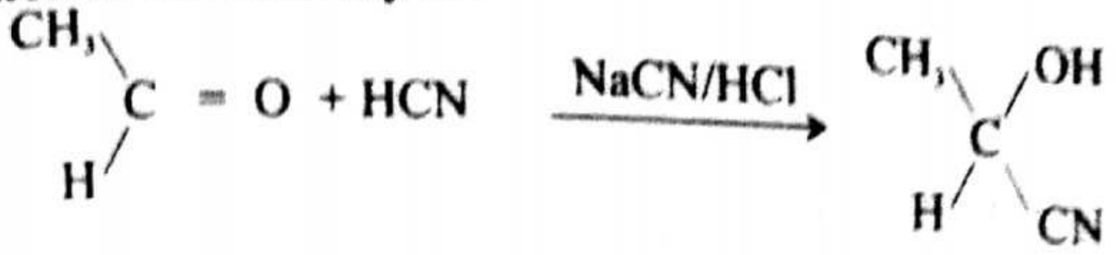
(i) Base-Catalysed Addition Reactions

- This reaction will take place with strong nucleophilic reagent
- Base reacts with reagent and releases nucleophile

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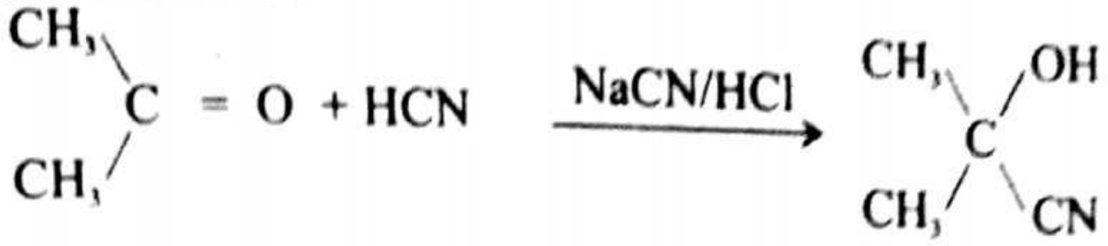
Addition of Hydrogen Cyanide

(i) Addition to Acetaldehyde:



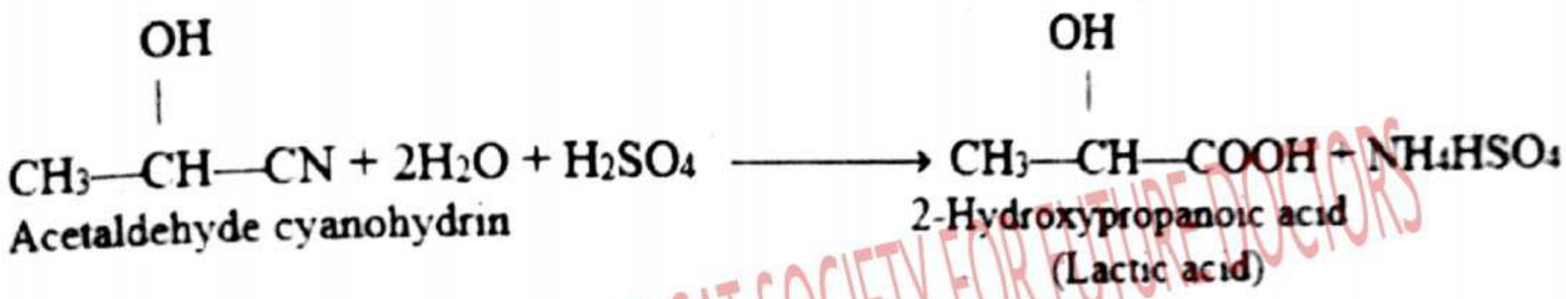
Acetaldehyde — Acetaldehyde cyanohydrin

(ii) Addition to Acetone:



Acetone — Acetone cyanohydrin

The cyano group, —C ≡ N is hydrolysed by an aqueous acid into α-hydroxy carboxylic acid through α-hydroxy acid amide.



Acetaldehyde cyanohydrin — 2-Hydroxypropanoic acid (Lactic acid)

Addition of Grignard Reagents

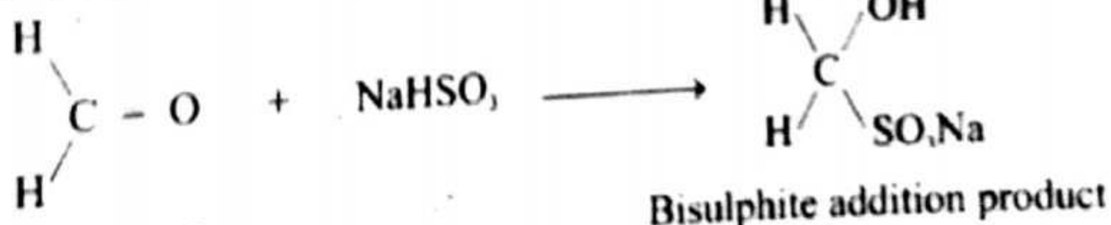
On reacting with Grignard's reagent

- Formaldehyde converts into primary alcohols
- Except formaldehyde all other aldehydes convert into secondary alcohols
- Ketones convert into tertiary alcohols

Addition of Sodium Bisulphite

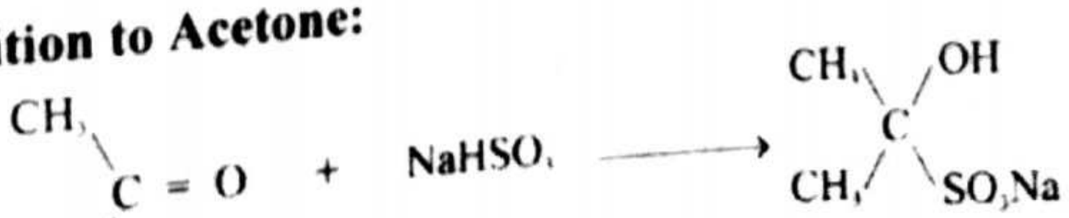
All aldehydes and only methyl ketones react with sodium bisulphite give white precipitate

(i) Addition to Formaldehyde:



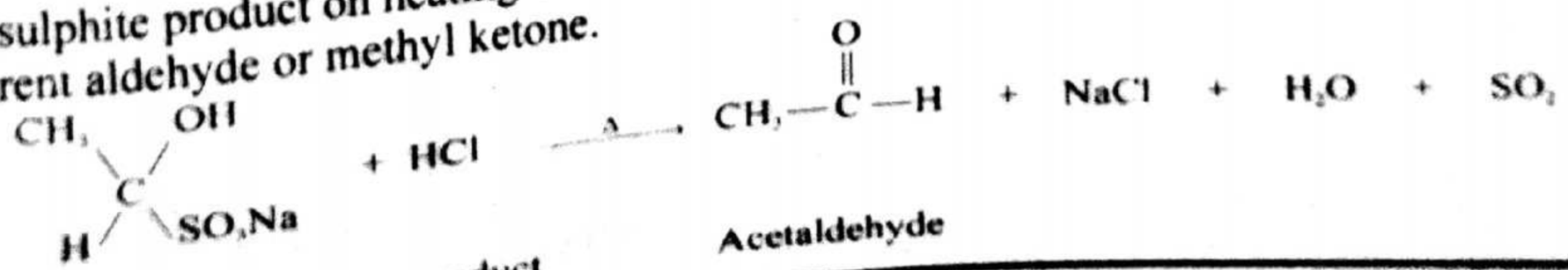
Formaldehyde — Bisulphite addition product

(ii) Addition to Acetone:



Acetone — Bisulphite addition product

Bisulphite product on heating with a dilute mineral acid (HCl or H2SO4), regenerates the parent aldehyde or methyl ketone.



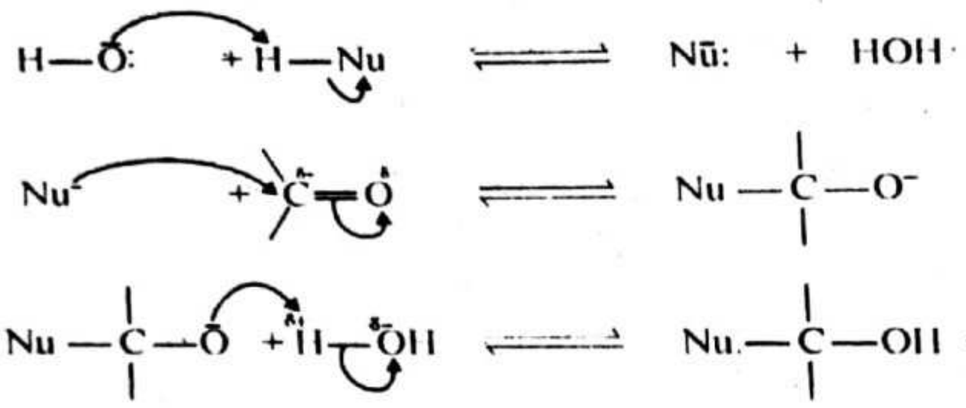
Bisulphite addition product — Acetaldehyde

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NUCLEOPHILIC ADDITION REACITON MECHANISM

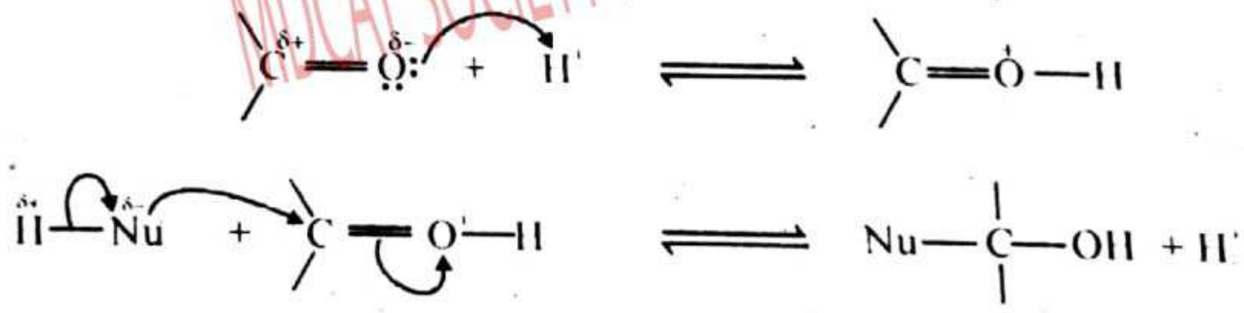
General mechanism of base-catalyzed addition reactions:

- A base-catalyzed nucleophilic addition reaction will take place with a strong nucleophilic reagent.
- The base reacts with the reagent and generates the nucleophile.
- The addition is initiated by the attack of a nucleophile on the electrophilic carbon of the carbonyl group.



General mechanism of acid-catalyzed addition reaction:

- The acid catalyzed nucleophilic addition reaction will take place with a weak nucleophilic reagent.
- The addition is initiated by the proton (H^+) liberated by the acid.
- The proton combines with the carbonyl oxygen atom and increases the electrophilic character of the carbonyl carbon.
- As a result, the attack of the weaker nucleophile on the electrophilic carbon becomes easier.



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CONDENSATION REACTIONS

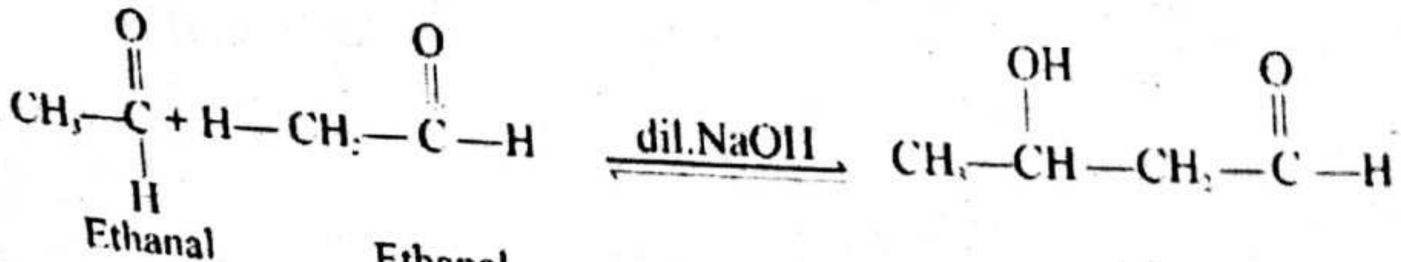
The reactions in which two molecules of the same or different compounds combine to form a new compound with or without the elimination of a small molecule like H2O or NH3, are called condensation reactions.

Aldol Condensation:

Aldehydes and ketones possessing α-hydrogen atoms react with a cold dilute solution of an alkali to form addition products known as aldols.

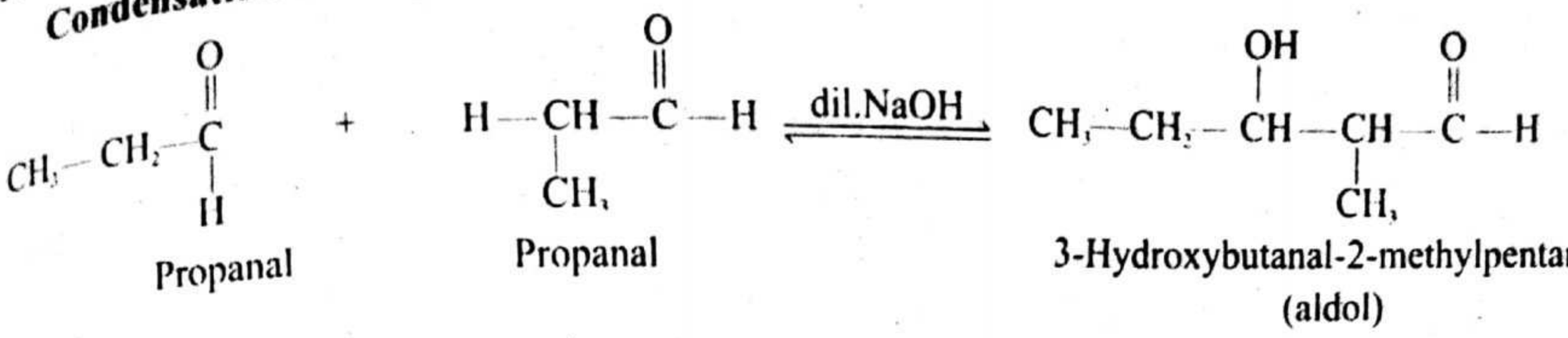
- The name aldol is given to the product because it contains both **aldehyde** and **alcohol** functional groups.
- Note that the name aldol condensation is reserved for the reaction that starts with two identical carbonyl compounds.
- Two molecules of the same carbonyl compound condense to form an aldol.

General reaction:



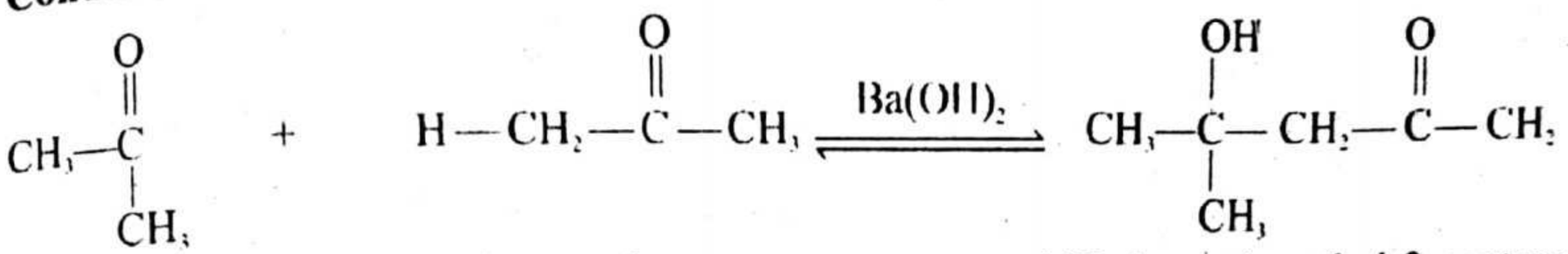
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Condensation of Propanal:



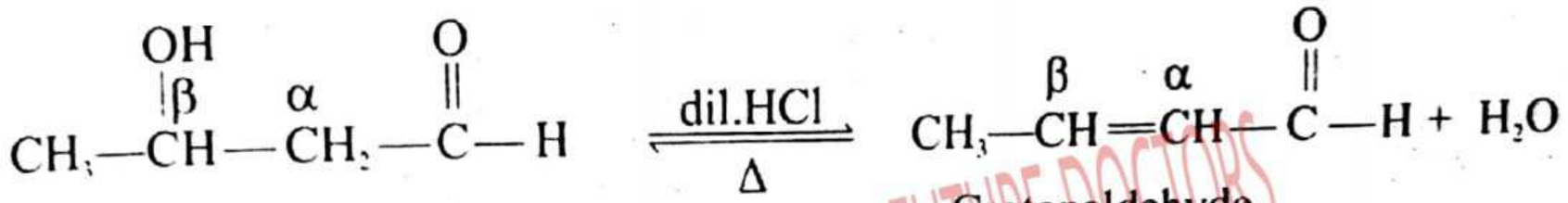
Propanal + Propanal → 3-Hydroxybutanal-2-methylpentanal (aldol)

Condensation of Propanone:



Propanal + Propanal → 4-Hydroxy-4-methyl-2-pentanone

Effect of Heat on Aldol with Dilute Acid:



3-Hydroxybutanal → Crotonaldehyde + H_2O

Cannizzaro's Reaction: (A disproportionation reaction)

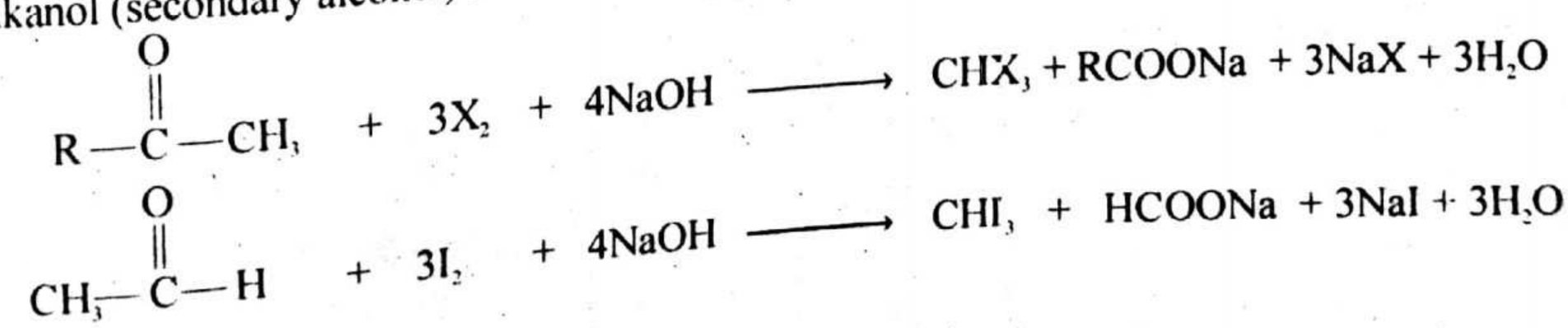
- Aldehydes that have no α-hydrogen atoms undergo cannizzaro's reaction.
- It is a disproportionation (self oxidation-reduction) reaction.
- Two molecules of the aldehyde are involved, one molecule being converted into the corresponding alcohol (the reduced product) and the other into the acid in the salt form (the oxidized product).
- The reaction is carried out with 50 percent aqueous solution of sodium hydroxide at room temperature..

$$2HCHO + NaOH \longrightarrow CH_3OH + HCOONa$$

Haloform Reaction:

Compounds that give haloform reactions are:

- Only acetaldehyde (among aldehydes)
- Methyl ketones (among ketones)
- 2-alkanol (secondary alcohol) and only ethanol (among primary alcohol)



$$R-C(=O)-CH_3 + 3X_2 + 4NaOH \longrightarrow CHX_3 + RCOONa + 3NaX + 3H_2O$$

$$CH_3-C(=O)-H + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$$

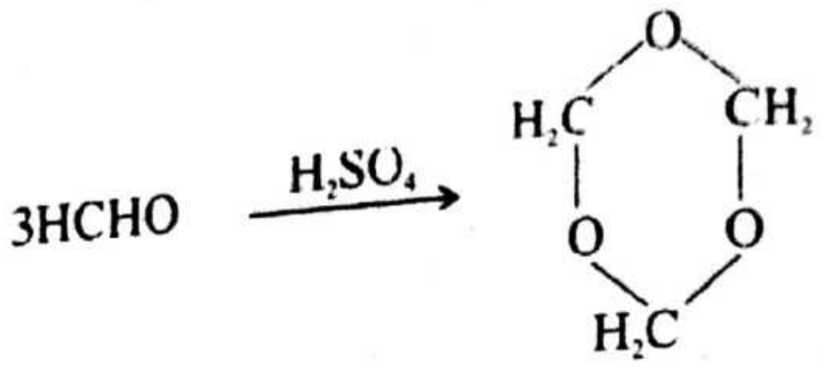
$$R-C(OH)-CH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + RCOONa + 5NaI + 5H_2O$$

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + HCOONa + 5NaI + 5H_2O$$

Acid-Catalysed Nucleophilic Addition Reactions:

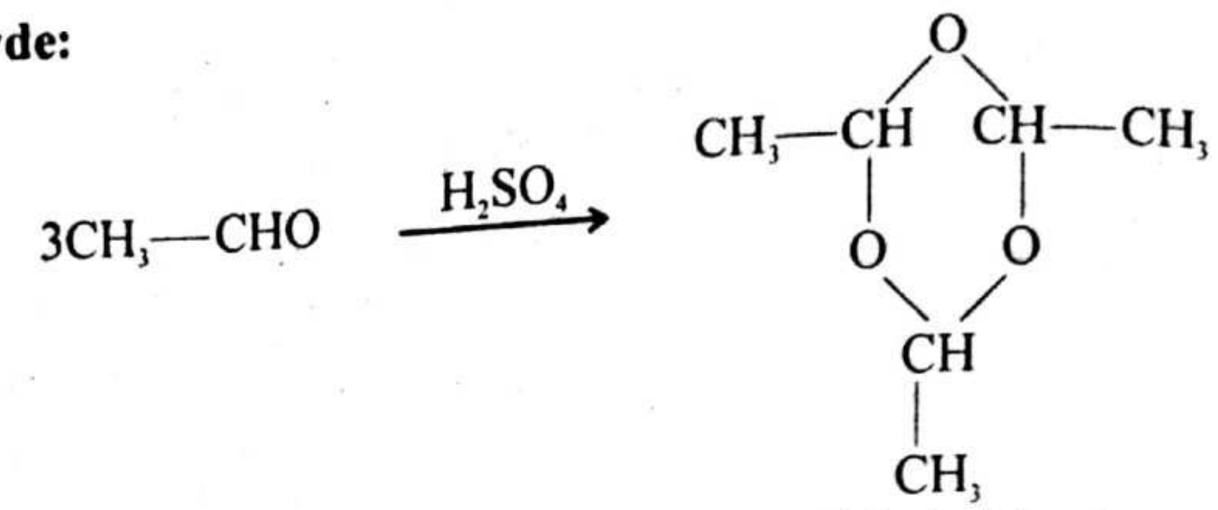
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Polymerization:
Formaldehyde



Metaformaldehyde (trimer)

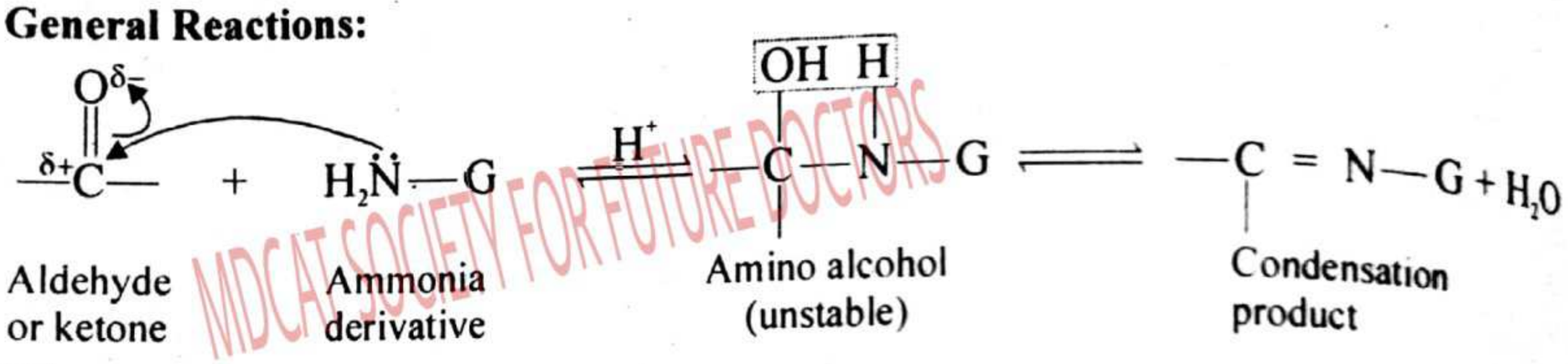
Acetaldehyde:



Paraldehyde (trimer)

Reactions of Ammonia Derivatives:

General Reactions:



Aldehyde or ketone | Ammonia derivative | Amino alcohol (unstable) | Condensation product

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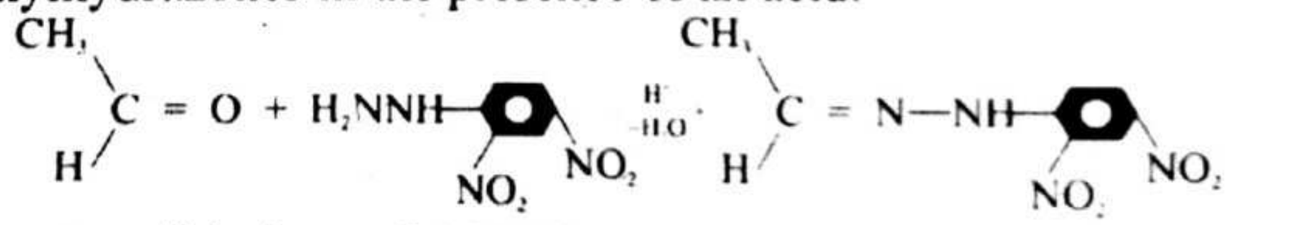
Where

$$G = \ddot{O}H, —\ddot{N}H_2, —\ddot{N}HC_6H_5, —\ddot{N}HCONH_2, \text{ etc.}$$

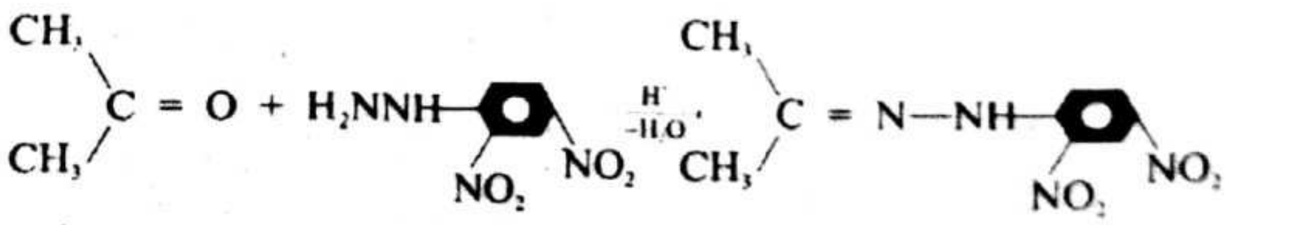
Hydroxylamine	NH_2OH
Hydrazine	NH_2NH_2
Phenyl hydrazine	$C_6H_5NHNH_2$
Semicarbazide	$NH_2NHCONH_2$
2,4-dinitrophenylhydrazine	$NH_2NHC_6H_3(NO)_2)_2$

Reaction with 2, 4-Dinitrophenyl hydrazine [2, 4-DNPH]

Aldehydes and ketones react with 2, 4-dinitrophenyhydrazine to form 2, 4-dinitrophenylhydrazones in the presence of an acid.



Acetaldehyde | 2,4-DNPH | Acetaldehyde 2,4-DNPH



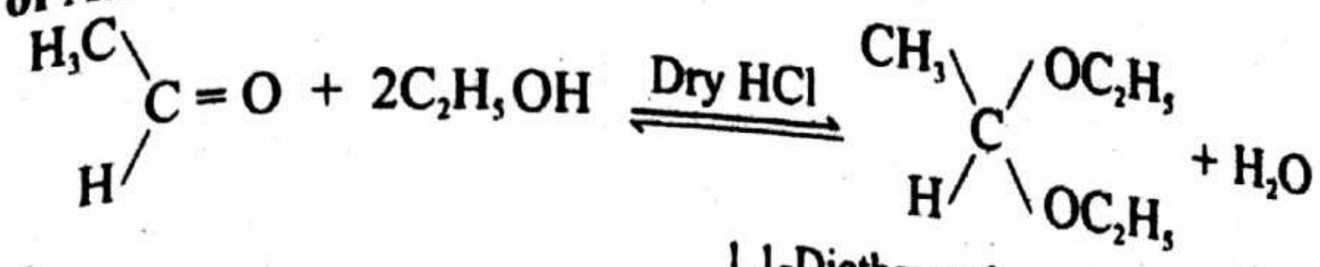
Acetone | 2,4-DNPH | Acetone 2,4-DNPH

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This reaction can be used for the identification of aldehydes and ketones because 2, 4-dinitrophenylhydrozens are usually yellow orange crystalline solids.

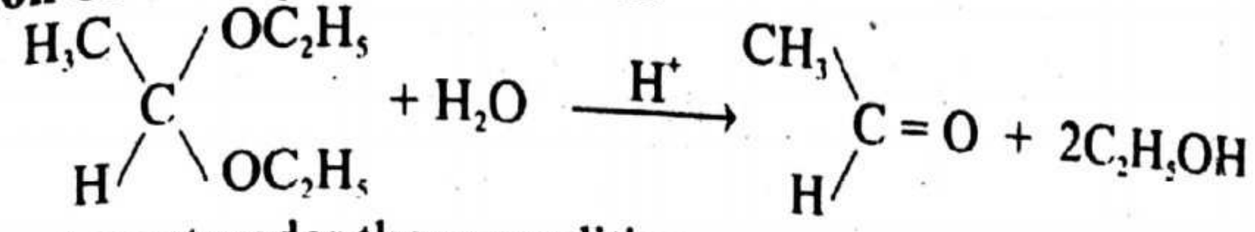
Addition of Alcohol:



1,1-Diethoxyethane (an acetal)

This reaction is used to protect the aldehyde group against alkaline oxidizing agent.

Regeneration of Aldehyde from Acetal

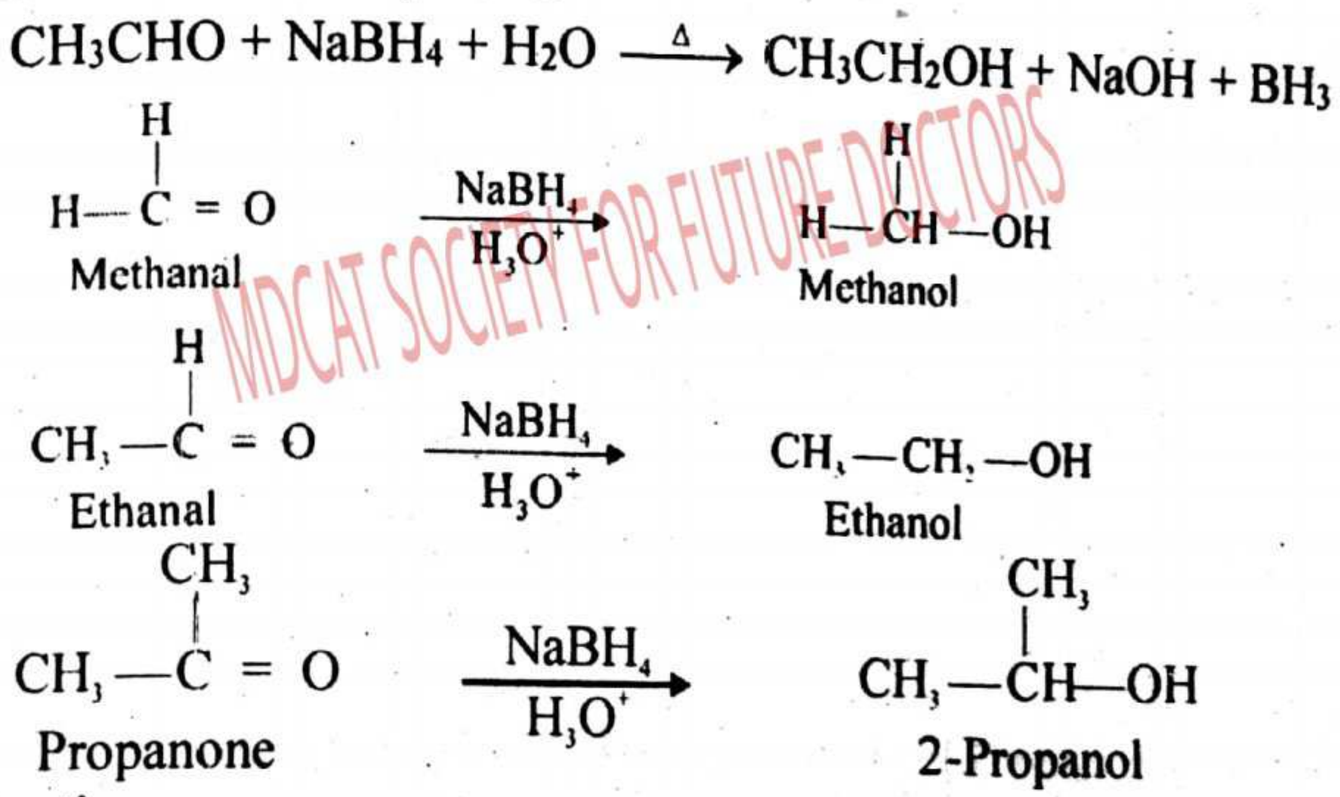


Ketones do not react under these conditions.

CHEMISTRY OF ALDEHYDES AND KETONES BY THEIR REDUCTION TO ALCOHOLS

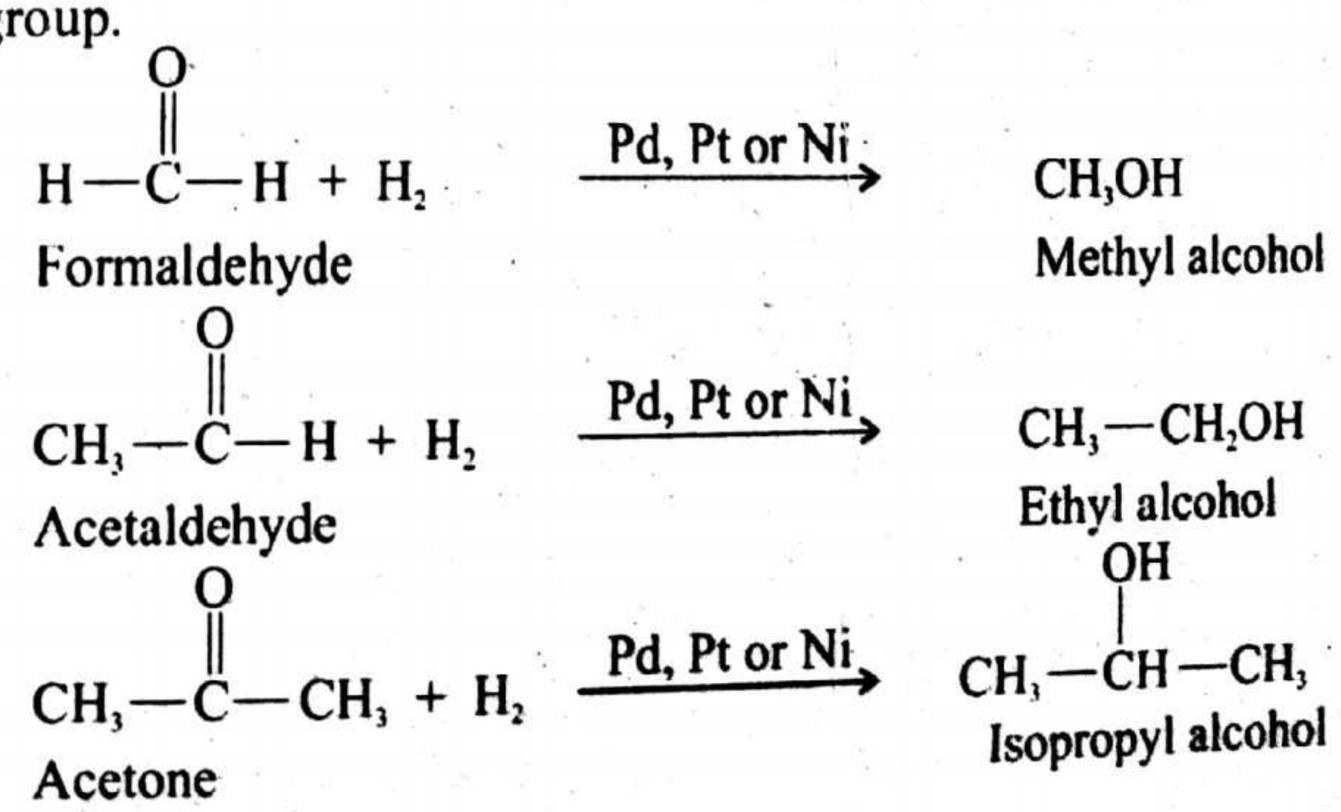
Both Aldehydes and ketones can be reduced. Aldehydes are reduced to primary alcohols whereas ketones to secondary alcohols. The carbonyl group is converted into an alcohol.

Reduction with Sodium Borohydride:



Catalytic Reduction:

Aldehydes and ketones on reduction with hydrogen in the presence of a metal catalyst like Pd, Pt or Ni form primary and secondary alcohols respectively. Hydrogen is added across the carbonyl group.



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OXIDATION REACTIONS OF ALDEHYDES AND KETONES

Oxidation of Aldehydes:

Aldehydes are easily oxidised by mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution.

- They are oxidised to carboxylic acids by strong oxidizing agents such as $K_2Cr_2O_7$ / H_2SO_4 or $KMnO_4$ / H_2SO_4 and dilute nitric acid.
- The hydrogen atom attached to the carbonyl group in aldehydes is oxidised to OH group. This is comparatively easier to oxidize.
- Hence, can be oxidized by mild oxidizing agents.

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH}$$

The carboxylic acid has the same number of carbon atoms as are present in the parent aldehyde.

Oxidation of Ketones:

Ketones do not undergo oxidation easily because they require breaking of strong carbon-carbon bond. They give no reaction with mild oxidizing agents. They are only oxidized by strong oxidizing agents such as $K_2Cr_2O_7$ / H_2SO_4, $KMnO_4/H_2SO_4$, and conc. HNO_3.

For symmetrical ketones

$$\underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + 3[O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + HCOOH$$

For unsymmetrical ketones

$$\underset{\text{Butanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3} + 3[O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Identification of carbonyl compounds

Type of reactions / Reagents	Aldehydes	Ketones
Reduction	Primary alcohols	Secondary alcohols
Oxidation	Carboxylic acid containing same number of carbon atoms	Carboxylic acid containing smaller number of carbon atoms
Reaction with Tollent's reagent	Silver(Ag) mirror	Don't give silver mirror
Reaction with Fehling's solution	Brick red ppt. of Cu_2O	Don't reduce the Fehling's solution
Rection with Benedict's solution n	Brick red precipitate of Cu_2O	They don't reduce the Benedict's solution
Polymerization	Polymerize readily	Don't polymerize
Reaction with alcohol	Acetal formation	Don't react
Reaction with sodium nitroprusside	Don't react	Wine red or orange red coloration

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TOPIC-18 CARBOXYLIC ACIDS

COURSE CONTENTS

- Classification
- Physical properties
- Preparations of carboxylic acids
- Reactivity
- Describe the chemistry of carboxylic acids by conversion to carboxylic acids derivatives
- acyl halides, acids anhydrides, esters, amides and reactions involving interconversion of these.
- Acidic strength
- Order of reactivity of derivatives

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INTRODUCTION

Carboxylic acids

Organic compounds containing –COOH as a functional group are called carboxylic acids (carb from carbonyl and oxyl from hydroxyl).

- Their general formula is R-COOH or $C_nH_{2n}O_2$
- The boiling points of carboxylic acids are relatively high due to intermolecular hydrogen bonding
- The most common carboxylic is acetic acid
- Acetic acid has strong vinegar like odour and sour taste

Nomenclature

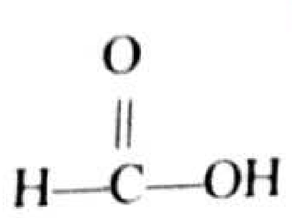
Structural Formula	Common Name	IUPAC Name
H-COOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3-CH_2-COOH	Propionic acid	Propanoic acid
CH_3-CH_2-CH_2-COOH	Butyric acid	Butanoic acid
CH_3-CHCOOH | CH_3	Iso-butyric acid	2-Methylpropanoic acid

CLASSIFICATION OF CARBOXYLIC ACIDS

- Depending upon the group (R or Ar) attached to the Carboxylic group, acids are classified as:
- **Aliphatic carboxylic acids:** Carboxylic acids in which carboxylic group (-COOH) is attached to a hydrogen or an alkyl group are called aliphatic carboxylic acids.

Example:

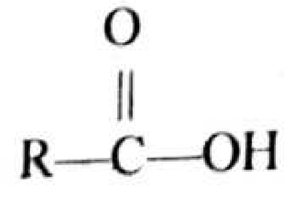
(i)

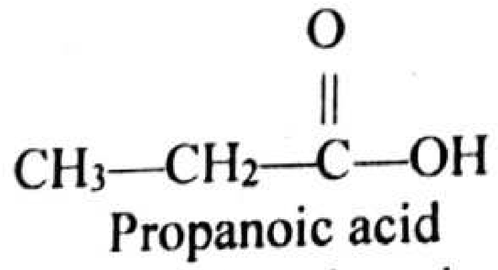


Formic acid

Ethanoic acid

or



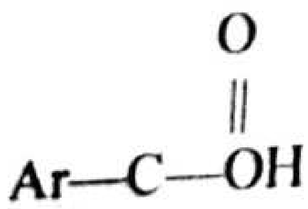


Propanoic acid

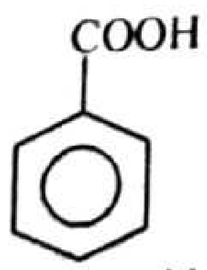
- **Aromatic carboxylic acids:** Carboxylic acids in which carboxyl group (COOH) is attached with an aryl group is called an aromatic carboxylic acid.

Example:

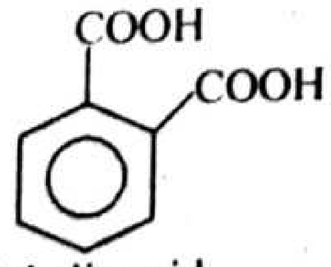
(ii)



Aromatic carboxylic acid



Benzoic acid



Phthalic acid

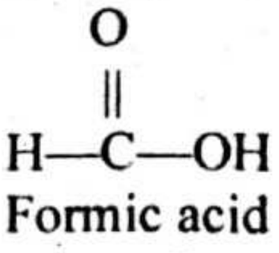
Depending upon the number of carboxyl groups in an acid, they are classified as:

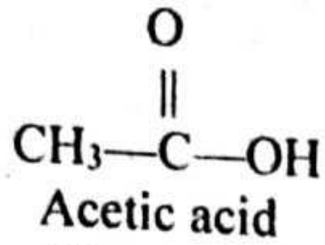
- **Monocarboxylic acids:** Carboxylic acids containing only one carboxylic group are called monocarboxylic acids.

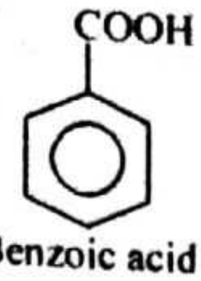
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Examples:


Formic acid

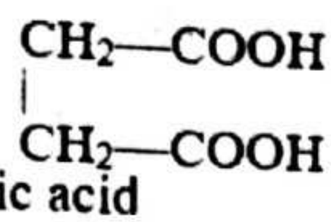

Acetic acid

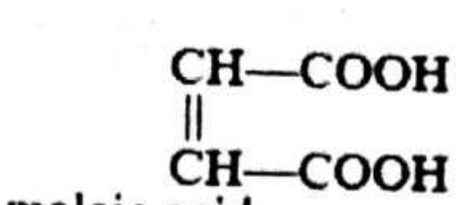

Benzoic acid

- **Dicarboxylic acids:** Carboxylic acids containing two carboxylic groups are called dicarboxylic acids.

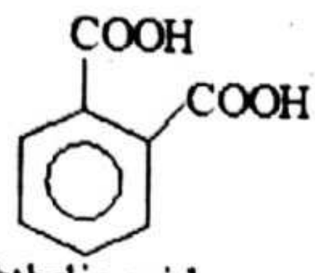
Examples:


Oxalic acid

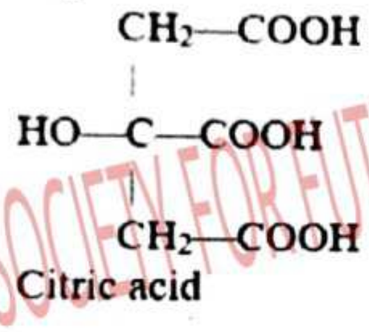

succinic acid


maleic acid


Malonic acid

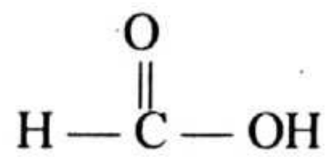
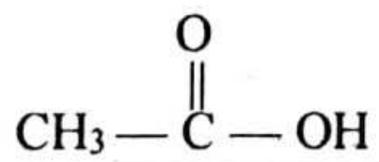
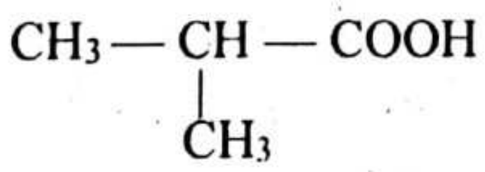

Phthalic acid

- **Polycarboxylic acids:** Carboxylic acids containing more than two carboxylic groups are called polycarboxylic acids.


Citric acid

Example:

Aliphatic mono carboxylic acid – fatty acids

Formic acid		Methanoic acid
Acetic acid		Ethanoic acid
Iso butyric acid		2-Methylpropanoic acid

Monocarboxylic acids

PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

- C_1 to C_4 have pungent smell and C_4 to C_6 have unpleasant smell.
- C_1 to C_4 are very soluble in water due to hydrogen bonding. The solubility in water decreases with the increase in molecular mass.
- The boiling points of carboxylic acids are relatively high due to intermolecular hydrogen bonding.

HCOOH	<	CH_3COOH	<	C_2H_5COOH
373K (100°C)		391K(118°C)		424K(141°C)

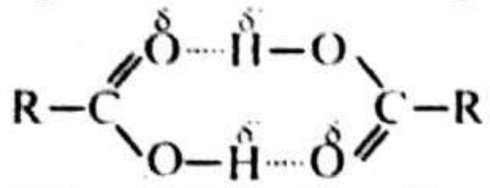
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- The melting points of carboxylic acids increase irregularly with molecular mass. The melting points of carboxylic acids containing even number of carbon atom are higher than the next lower and higher odd members.

CH_3CH_2COOH < $CH_3CH_2CH_2COOH$ > $CH_3CH_2CH_2CH_2COOH$

251K (–22°C) 267K (–6°C) 237K (–36°C)

- The molecular mass determination in non-polar solvents like benzene shows that carboxylic acids exist as cyclic dimer



Dimer of a carboxylic acid

- The pure acetic acid freezes to an ice like solid at 17°C, therefore, it is called glacial acetic acid

POINT PONDER

C_1 to C_4 have pungent smell and C_5 to C_6 have unpleasant smell.

PREPARATION OF CARBOXYLIC ACIDS

Following methods are used to prepare carboxylic acids.

Carbonation of Grignard reagent

$$R-Mg-X + CO_2 \xrightarrow{\text{Dry Ether}} R-CO-O\overset{+}{M}gX \xrightarrow[HX]{H_2O} R-COOH + MgX_2$$

Hydrolysis of nitriles

Organic compounds having cyanide group are called nitriles. Hydrolysis of an alkyl nitrile on boiling with mineral acid or alkalis yields carboxylic acids.

$$R-CN + 2H_2O \xrightarrow{HCl} R-COOH + NH_3$$

$$H_3C-C\equiv N + 2H_2O \xrightarrow{HCl} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

Oxidation of primary alcohols

$$R-CH_2-OH + [O] \xrightarrow[H_2SO_4]{KCr_2O_7} \underset{\text{Aldehyde}}{R-CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-COOH$$

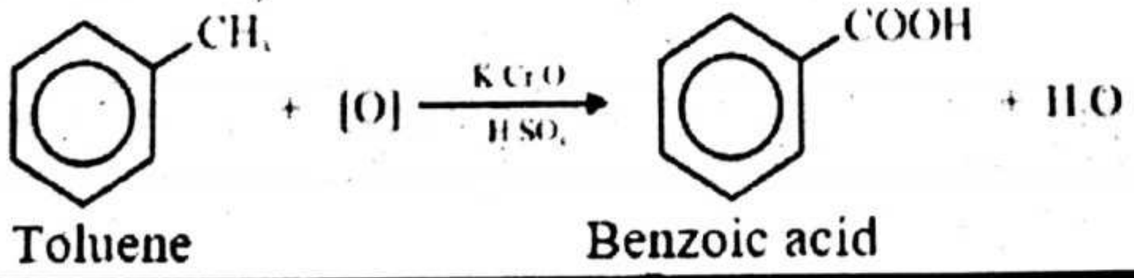
Alcohol

Oxidation of aldehydes

$$R-CHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-COOH$$

Aldehyde

Oxidation of alkyl benzene



Toluene Benzoic acid

REACTIVITY

- The carboxyl group shows the chemistry of both the carbonyl (>C=O) and the hydroxyl (–OH) groups.
- In most reactions, the carboxyl group is retained.
- However, the reactivity of these molecules is due to the presence of carbonyl group.

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REACTIONS OF CARBOXYLIC ACID

Carboxylic acids undergo the following types of reactions.

- The reaction in which hydrogen atom of the carboxyl group is involved (salt formation).
- The reaction in which OH group is replaced by another group.
- The reactions involving carboxyl group as a whole.

The reaction in which hydrogen atom of the carboxyl group is involved (salt formation).

- It is an electrophilic substitution reaction.
- In this reaction hydrogen atom of the carboxyl group is involved.
- Carboxylic acid reacts with active metals (Na, K, Ca, Mg etc.) to form their salts with the evolution of hydrogen gas.

$$2RCOOH + 2Na \longrightarrow 2RCOO^{-}Na^{+} + H_2$$

- Carboxylic acid reacts with bases (NaOH, KOH) to form salts

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

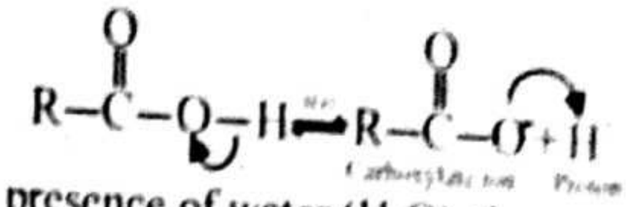
- Carboxylic acid reacts with carbonates and bicarbonates evolving carbon dioxide gas with effervescence.

$$2RCOOH + Na_2CO_3 \longrightarrow 2RCOO^{-}Na^{+} + CO_2 + H_2O$$

$$RCOOH + NaHCO_3 \longrightarrow RCOO^{-}Na^{+} + CO_2 + H_2O$$

POINT TO PONDER

Carboxylic acids are weaker acids than mineral acids. They furnish H^+ when dissolved in water.



In the presence of water (H_2O), the proton breaks away as H_3O^+ ion.

The reaction in which OH group is replaced by another group.

(i) Esterification

- It is nucleophilic substitution reaction of carboxylic acid
- In this reaction OH group of carboxyl group is replaced by alkoxide group of alcohol.
- Esterification is reversible and acid catalyzed reaction.

$$\underset{\text{Carboxylic acid}}{RCOO-H} + \underset{\text{Alcohol}}{R\text{-}OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{RCOO-R} + H_2O$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Ethylethonate}}{CH_3COOC_2H_5} + H_2O$$

- Esters have fruity smell and are used as artificial flavors.

Ester	Flavour	Ester	Flavour
Amyl acetate	Banana	Isobutyl formate	Raspberry
Benzyl acetate	Jasmine	Ethyl butyrate	Pine apple
Amyl butyrate	Apricot	Octyl acetate	Orange

(ii) Acid chloride formation (Acyl chloride)

- In this reaction OH group of carboxyl group is replaced by halo group (–X).
- This is nucleophilic substitution reaction.
- Phosphorus pentachloride (PCl_5) and thionyl chloride ($SOCl_2$) on reaction with ethanoic acid give acetyl chloride (ethanoyl chloride)

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$$

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(iii) Amide formation

- *It is nucleophilic substitution reaction.*
- *In this reaction, OH group of carboxyl group is replaced by amino group ($-NH_2$).*
- *Ethanoic acid reacts with ammonia to form ammonium acetate (intermediate) which on heating produce acetamide.*

$$RCOOH + NH_3 \longrightarrow RCOONH_4$$

$$RCOO\dot{N}H_4 \xrightarrow{\text{Heat}} RCONH_2 + H_2O$$

Reaction involving COOH group as a whole

Reduction to Alcohols:

- Carboxylic acids are reduced to primary alcohols carboxylic acids are less reactive to reduction by hydride than aldehydes, ketones or esters.
- Due to their low reactivity, carboxylic acids can only be reduced by $LiAlH_4$ and not by less reactive $NaBH_4$.

Example:

Acetic acid on reaction with Lithium aluminium hydride (LiAlH4) is reduced to ethanol (a primary alcohol).

$$R-\overset{\overset{O}{\|}}{C}-OH + 4[H] \xrightarrow[\text{ethoxyethane}]{LiAlH_4} RCH_2OH + H_2O$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + 4[H] \xrightarrow[\text{ethoxyethane}]{LiAlH_4} CH_3CH_2OH + H_2O$$

Acetic acid Ethanol

Complete Hydrogenation (Reduction to alkanes)

Carboxylic acids on reduction with HI and red phosphorous give alkanes.

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + 6HI \xrightarrow{\text{red phosphorus}} CH_3-CH_3 + 2H_2O + 3I_2$$

acetic acid ethane

In this reaction, $-COOH$ group is reduced to a $-CH_3$ group.

Decarboxylation

- Loss of carbon dioxide is called decarboxylation.
- Simple carboxylic acids rarely undergo decarboxylation.

(i) When sodium salt of carboxylic acid is strongly heated with soda lime ($NaOH + CaO$), and alkane is formed,

- The alkane formed contains one carbon less than original carboxylic acid

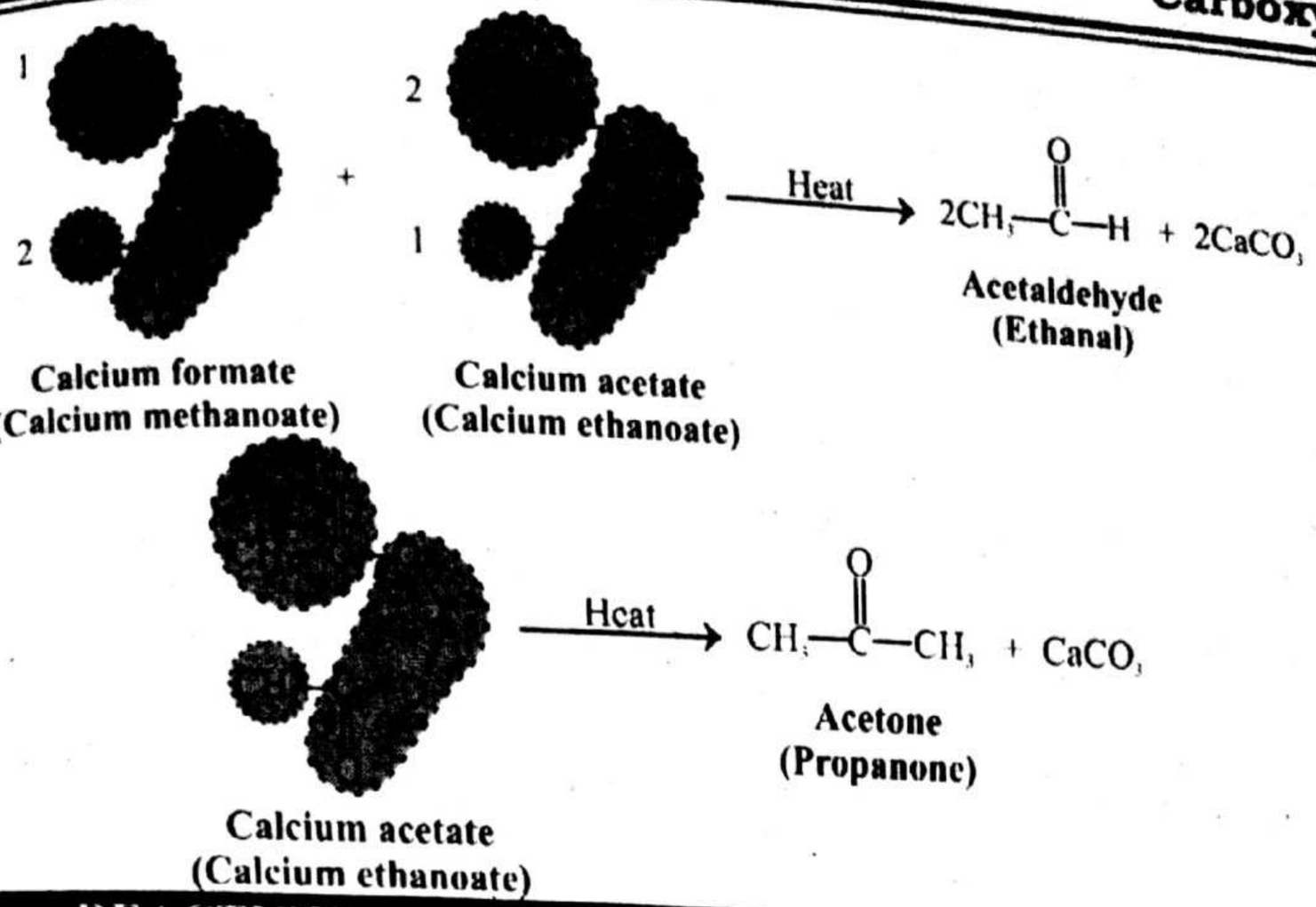
$$R-\overset{\overset{O}{\|}}{C}-O^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

$$CH_3-\overset{\overset{O}{\|}}{C}-O^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

(ii) Dry distillation of calcium slat of carboxylic acids gives aldehydes or ketone.

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REACTIONS OF CARBOXYLIC ACID DERIVATIVES

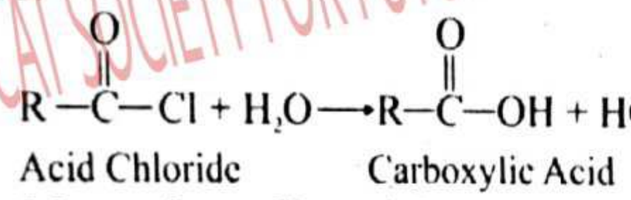
A. Reactions of Acyl Halides (Acid Halide)

Acid halides are derivatives of carboxylic caid in which (–OH) hydroxyl group has been replaced by a halogen atom.

Reactions:

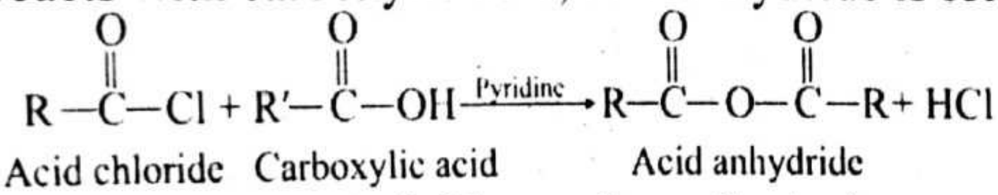
Reaction of Acid halide with water (Hydrolysis of Acid halide)

Acid chlorides react with water, often violently, to give the corresponding carboxylic acids and hydrogen chloride.



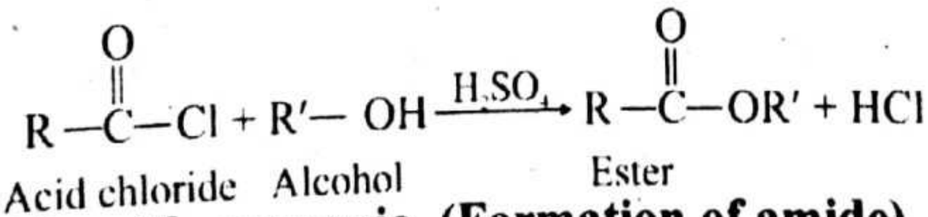
Reaction of Acid halide with carboxylic acid.

When Acid halide reacts with carboxylic acid, acid anhydride is formed.



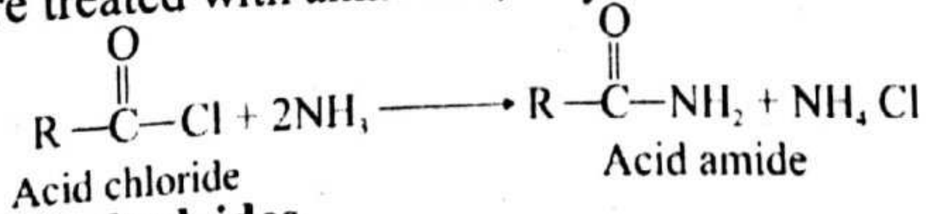
Reaction of Acid halide with alcohol (Formation of ester)

When acid halide reacts with alcohol in presence of conc. H_2SO_4 as a catalyst, ester is formed.



Reaction of acid halide with ammonia. (Formation of amide)

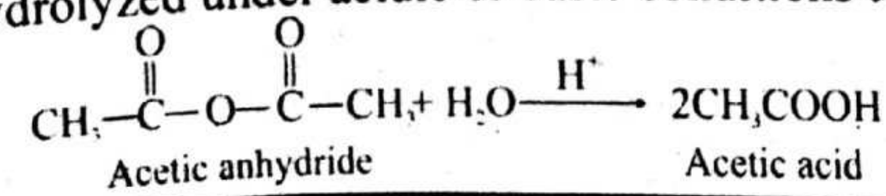
When acid halides are treated with ammonia, they form amides.



B. Reactions of Acid Anhydrides

Hydrolysis (Reaction with water)

Acid anhydrides are hydrolyzed under acidic or basic conditions to form the parent acid.

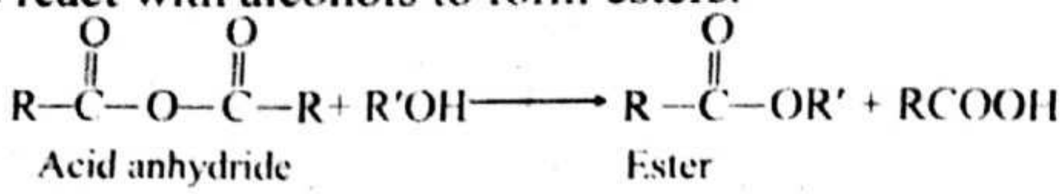


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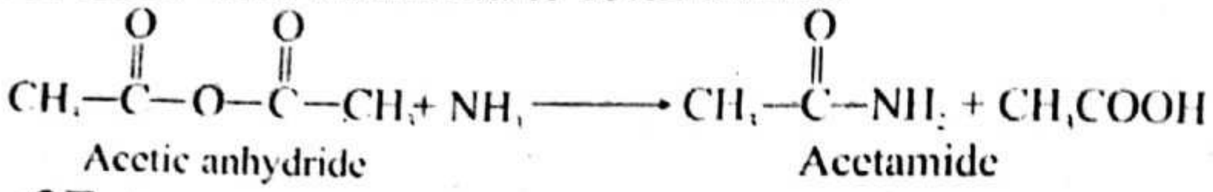
Alcoholysis

Acid anhydrides react with alcohols to form esters.



Formation of Amide

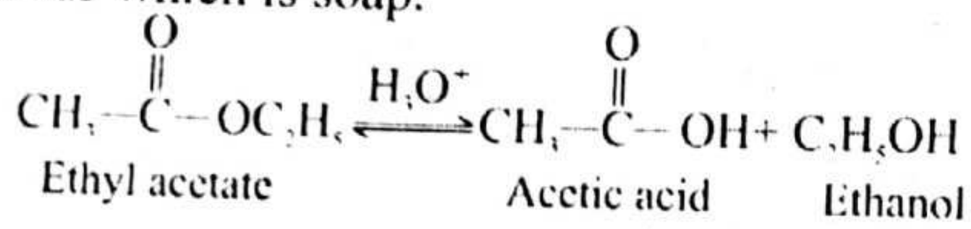
Acid anhydrides react with ammonia to form amide.

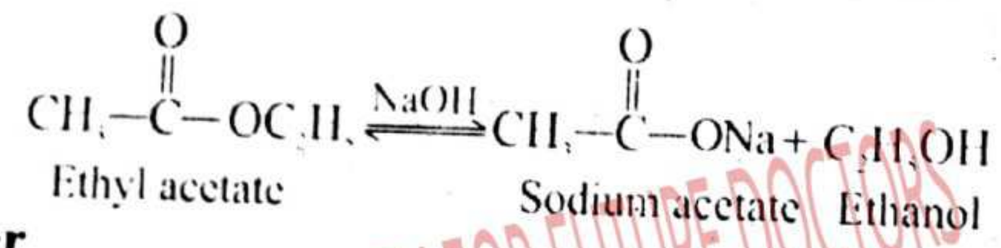


C. Reactions of Esters

Hydrolysis of Esters

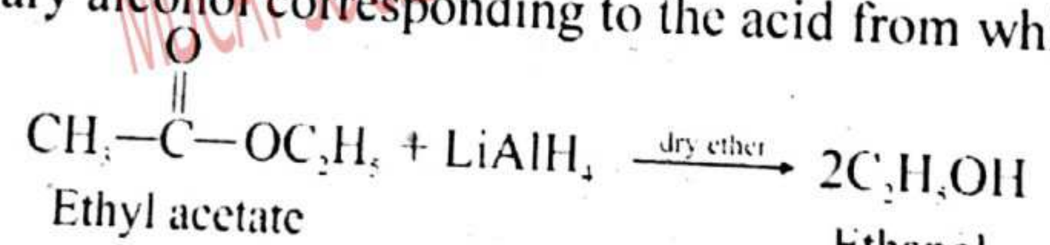
Esters can be hydrolyzed to acid and alcohol under acidic or basic conditions. Basic hydrolysis of esters is known as saponification because it leads to the formation of alkali salt of carboxylic acids which is soap.





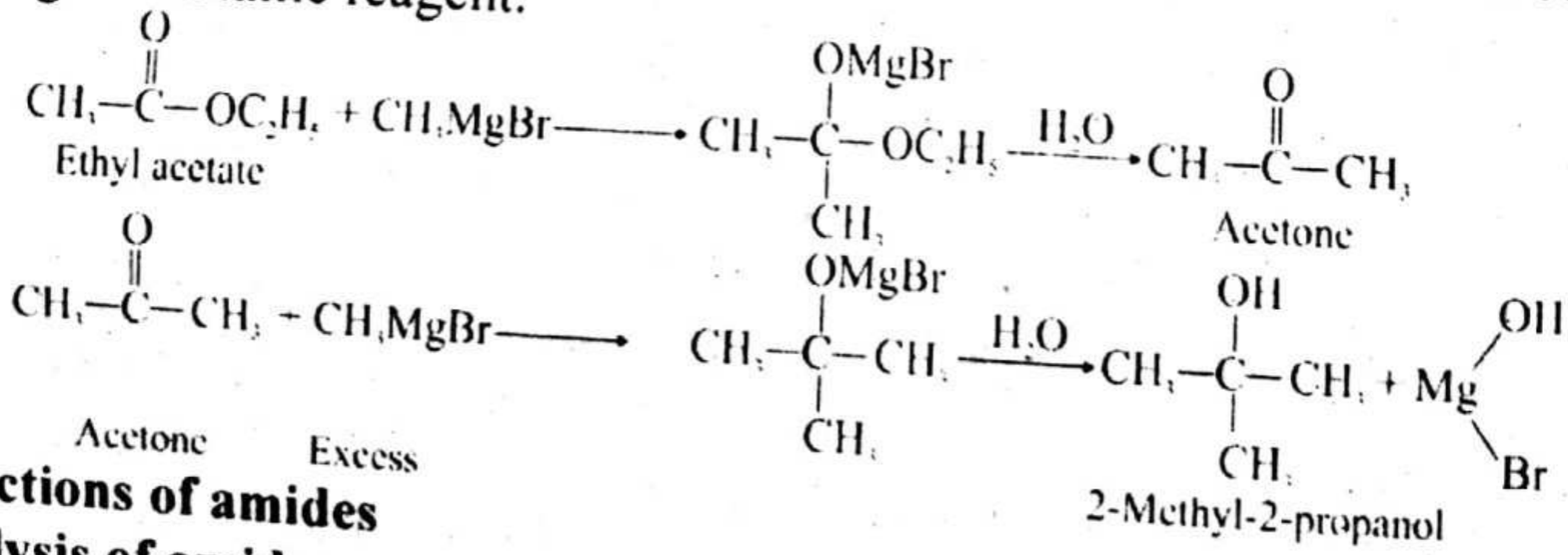
Reduction of Ester

Esters can be reduced either catalytically or using chemical reducing agents; such as LiAlH4 into primary alcohol corresponding to the acid from which it was derived.



Reactions of Grignard reagent (RMgX)With Esters

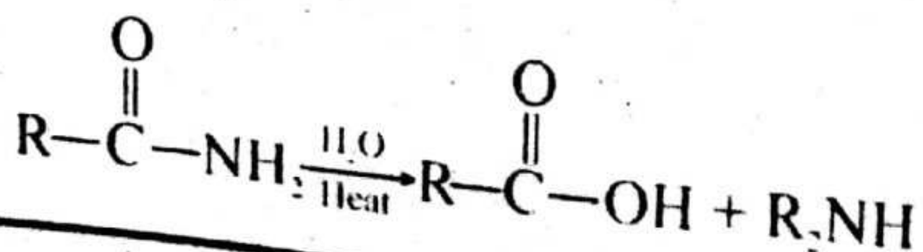
Esters (except formaldehyde) react with Grignard reagents to give tertiary alcohols. The tertiary alcohol that results contain 2 identical alkyl groups (from R in the scheme) The reaction proceeds via a ketone intermediate which then reacts with the second equivalent of the organometallic reagent.



D. Reactions of amides

Hydrolysis of amides

Amides are hydrolyzed when heated with a strong acid or a base and yield carboxylic acids and ammonia (or amines).



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Reduction of Amides

Amides can be reduced to primary amines on reduction with $LiAlH_4$

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + LiAlH_4 \longrightarrow R-CH_2-NH_2 + H_2O$$

E. Reaction of nitriles

Hydrolysis of Nitriles

Nitriles, R – C ≡ N, can be hydrolyzed to carboxylic acids, RCO_2H via the amide, $RCONH_2$ intermediate in the presence of strong acid (e.g. H_2SO_4)or strong base (e.g. NaOH) / heat.

$$R-C\equiv N \xrightarrow[\text{Heat}]{H_2O} R-\overset{\overset{O}{\|}}{C}-NH_2$$

$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\text{Heat}]{H_2O} R-\overset{\overset{O}{\|}}{C}-OH$$

Reduction of Nitriles

Nitriles can be converted to primary amines by reaction with $LiAlH_4$ (reduction agent).

General Reaction:

$$R-C\equiv N \xrightarrow[\text{Heat}]{LiAlH_4} R-CH_2-NH_2$$

Nitrile — 1°Amine

$$CH_3-C\equiv N \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$$

Methyl nitrile — Aminoethane

Reactions of RMgX with Nitriles

Grignard's reagents on reaction with alkyl nitriles give an addition product (imine salt) with on hydrolysis with dilute HCl yield ketones.

$$CH_3-Mg-Br + CH_3CN \xrightarrow{H^+} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + Mg\begin{matrix}NH_2\\Br\end{matrix}$$

Methylmagnecium bromide — Methylnitrile — Acetone

Order of reactivity of carboxylic acid derivative

Acid halide > Acid anhydride > Ester > Acid amide

ACIDIC STRENGTH

Carboxylic acids are the most acidic simple organic compounds. (pKa ≅5) but as compared with acids like HCl or H_2SO_4, they are weak acids.

Carboxylic acid	Formula	pKa
Ethanoic acid	CH_3COOH	4.7
Propanoic acid	CH_3CH_2COOH	4.9
Fluoroethanoic acid	CH_2FCOOH	2.6
Chloroethanoic acid	$CH_2ClCOOH$	2.9
Dichloroethanoic acid	$CHCl_2COOH$	1.3
Trichloroethanoic acid	CCl_3COOH	0.9
Nitroethanoic acid	O_2NCH_2COOH	1.7

- Electron withdrawing group (Cl, F, NO_2) bonded to the carbon atom next to the

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carboxylic group (COOH) make the acid stronger. Due to electron withdrawing group electron will move away from oxygen. Hence decreases charge density on oxygen atom of carboxylate ion which stabilizes the -COO^- group and makes it less likely to bond with an H^+ ion.

For example, chloroacetic acid is 100 times stronger acid than acetic acid.

- Electron donating group (alkyl) strengthens the O-H bond in the acid's -COOH group. It donates negative charge towards the -COO^- group of the carboxylate ion, making it more likely to accept an H+ ion, hence acidic strength decreases.
- For example, formic acid is more acidic than acetic acid.
- Strength of an acid is measured by pKa values. Greater the value of pKa weaker will be the acid and vice versa.

NOTE: Order of strength of acids

$$F–CH_2–COOH > Cl–CH_2–COOH > Br–CH_2–COOH > CH_3–COOH$$

- In each of the carboxylic acids, the –OH group is attached to a carbonyl C=O group, which is in turn bonded to other atoms.
- The comparison we observe here is between carboxylic acid molecules, denoted as RCOOH, and other organic molecules containing the –OH group, such as alcohols denoted as ROH (R is simply an atom or group of atoms attached to the functional group).
- The former are obviously acids whereas the latter group contains molecules which are generally extremely weak acids.
- One interesting comparison is for the acid and alcohol when R is the benzene ring ($C_6H_5–$), benzoic acid (C_6H_5COOH), has $pK_a = 4.2$, whereas phenol (C_6H_5OH) has $pK_a = 9.9$.
- Thus, the presence of the doubly bonded oxygen atom on the carbon atom adjacent to the –OH clearly increases the acidity of the molecule, and thus increases ionization of the –OH bond.
- Acidic strength order is

Carboxylic acid > Phenol > Water > Alcohol

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TOPIC-19 MACROMOLECULES

COURSE CONTENTS

- Explain the basis of classification and structure-function relationship of proteins
- Describe the role of various proteins in maintaining body functions and their nutritional importance.
- Describe the role of enzymes as biocatalysts.

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INTRODUCTION

Macromolecule
A giant molecule which is often a polymer is called macromolecule.
Polymer
A large molecule built up by the repetition of small and simple chemical units is called polymer.
Monomer
Small unit or simple molecule from which a macromolecule is formed is called monomers.

STRUCTURE OF PROTEINS

- The name protein is derived from the Greek word 'PROTEIOS' meaning of prime importance.
- Proteins are polymer of amino acids.
- Proteins upon complete hydrolysis yield amino acids.

Types of proteins

Particular	Simple protein	Conjugated protein	Derived protein
Definition	Gives only amino acid or its derivatives	Gives amino acid and prosthetic group	Contains amino acids and substances derived from simple conjugated protein
Examples	Globulins, albumins, Collagens	Lipoproteins, Phosphoproteins	Peptones, Oligopeptides, Enzyme, Proteoses, Polypeptides

STRUCTURE OF PROTEINS

The structure of a protein depends upon the spatial arrangement of polypeptide chains present in proteins. Since three spatial arrangements are possible proteins have the following four structures.

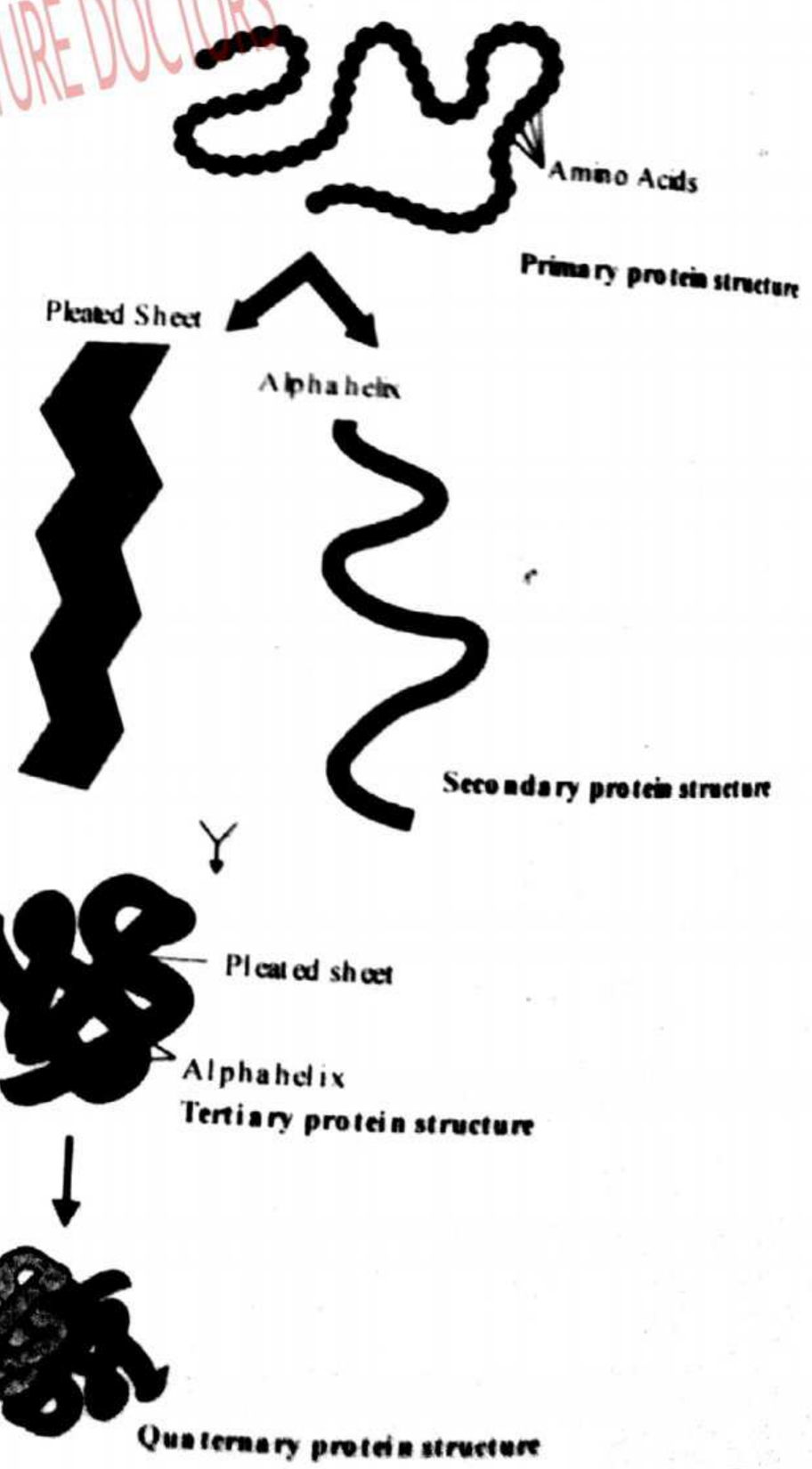
(i) Primary structure
(ii) Secondary structure
(iii) Tertiary structure
(iv) Quaternary structure

(i) The Primary structure of proteins

The sequence of amino acids in peptide chain is called primary structure. Amino acids are linked with one another though peptide bond. The arrangement of these acids is called primary structure.

(ii) The secondary structure of protein

Peptide chains may acquire spiral shape or may be present in a zig-zag manner. This coiling or zig-zagging of polypeptide is called secondary structure of protein. It is due to H-bond.



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(iii)The tertiary structure of proteins

Twisting or folding of polypeptide chains represents tertiary structure of proteins.

(iv)Quaternary Proteins

Quaternary means four. This is the fourth phase in the creation of a protein. Quaternary protein is the arrangement of multiple folded protein or coiling protein molecules in a multi-subunit complex. A variety of bonding interactions including hydrogen bonding, salt bridges, and disulfide bonds hold the various chains into a particular geometry.

Properties of proteins

Proteins are one of the four major groups of macromolecules that are found in all living organisms. These giant molecules carry out many of the vital functions needed by cells.

- Proteins are involved in such processes as food digestion, cell structure, catalysis, movement, energy manipulation and much more.
- They are complex huge associations of molecular subunits that appear impossibly difficult to understand.
- They are all built using the same construction principle. As with all macromolecules, proteins are polymers, composed of smaller subunits- the amino acids joined together in long chains.
- There are about 20-22 common amino found in most proteins. All but one of these small molecules has the same common structure, but varies in the nature of one chemical group- termed the "R-group". Amino acids are joined together in long chains called "polypeptides".

Importance of proteins

Following are the features of the protein which are considered to be very important.

- Proteins play an important role in the formation of protoplasm. Protoplasm is the essence of all form of life.
- Nucleoproteins are complex proteins and act as the carrier of heredity from one generation to the other.
- Enzymes are the biological catalyst and they are also proteins. Without enzymes life is not possible.
- Hemoglobin is a protein, it acts as carrier of oxygen.
- Some of the proteins act as hormones. They carry out the regulatory function of this body.
- Proteins have great importance in industry. The tanning of hides is an industrial process. This process is the precipitation of protein by tannic acid.
- Gelatin is obtained by heating bones, skins and tendons in water. It is used in bakery goods.
- Casein is another protein used in the manufacture of buttons and buckles.
- Proteins obtained from the soybean are used for the manufacture of plastics.

Denaturation of proteins

Denaturation of proteins can be done by:

- Heat: albumin of egg white changes into solid
- Change in pH: each enzyme has its own particular pH for action
- Oxidizing or reducing conditions

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ENZYMES AS A BIOCATALYST

Enzymes

Enzymes are biocatalysts which alter the speed of metabolic activities in the living bodies. Enzymes are complex protein molecules which are quite specific in action and sensitive to temperature and pH.

Meanings of Enzymes

Greek word En means in and Zyme means yeast.

Role of enzymes as a biocatalyst

Metabolism:

Metabolism is the set of biochemical reactions that occur in living organisms in order to maintain to life.

It is of two types

Anabolism

Anabolism includes the biochemical reactions in which larger molecules are synthesized and it is usually endothermic.

Catabolism

Catabolism includes the biochemical reactions in which larger molecules are broken down and it is usually exothermic.

Biocatalyst

Enzymes are crucial to metabolism because they act as biocatalysts up speed and regulate metabolic pathways. Enzymes are proteins that catalyze (i.e speed up) biochemical reactions and are not changed during the reaction.

Substrates and Products

The molecules at which enzymes act are called **substrates**, and enzyme converts them into different molecules, called **products**.

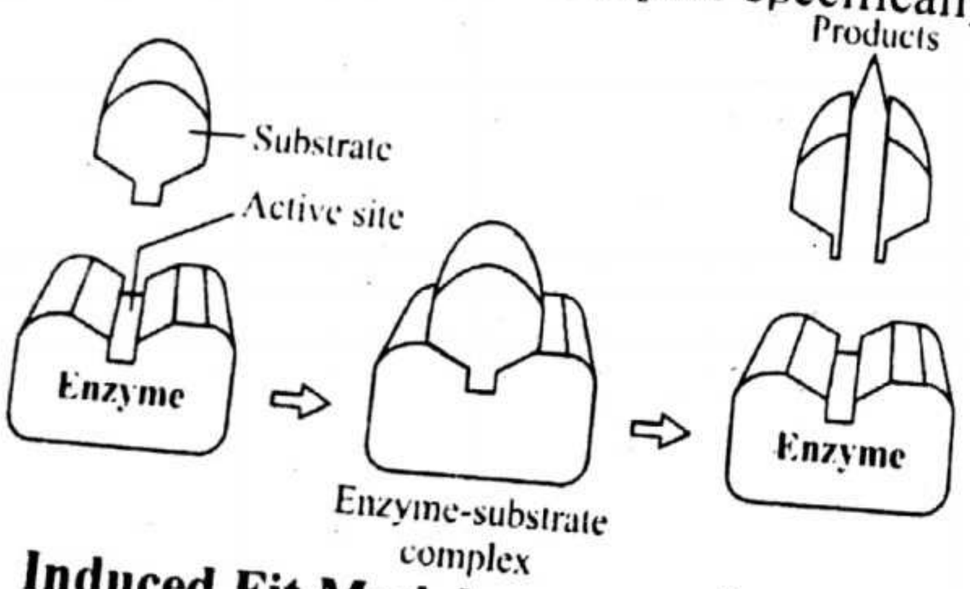
$$E+S \rightarrow E\text{-}S \text{ complex} \rightarrow E+P$$

Lock and key model

In 1894, German chemist, Emil Fischer proposed lock and key model.

According to this model, both enzyme and substrate possess specific shapes that fit exactly into one another.

This model explains enzyme specifically.

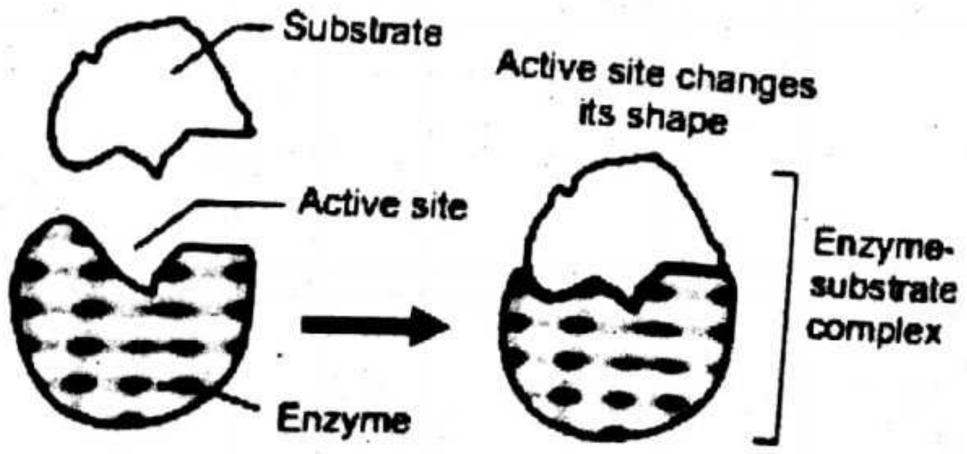


Induced Fit Model

In 1958 and American biologist Daniel Koshland suggested a modifications to lock and key model and proposed induced-fit model.

According to this model active site is not a rigid structure rather is moulded into the required shape to perform its function.

"Induced fit model" is more acceptable than "lock and key model" of enzyme action.



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Factors affecting enzyme activity

Enzymes are very sensitive to the environment in which they work. Any factor that can change the chemistry or shape of enzyme molecule, can affect its activity.

Temperature

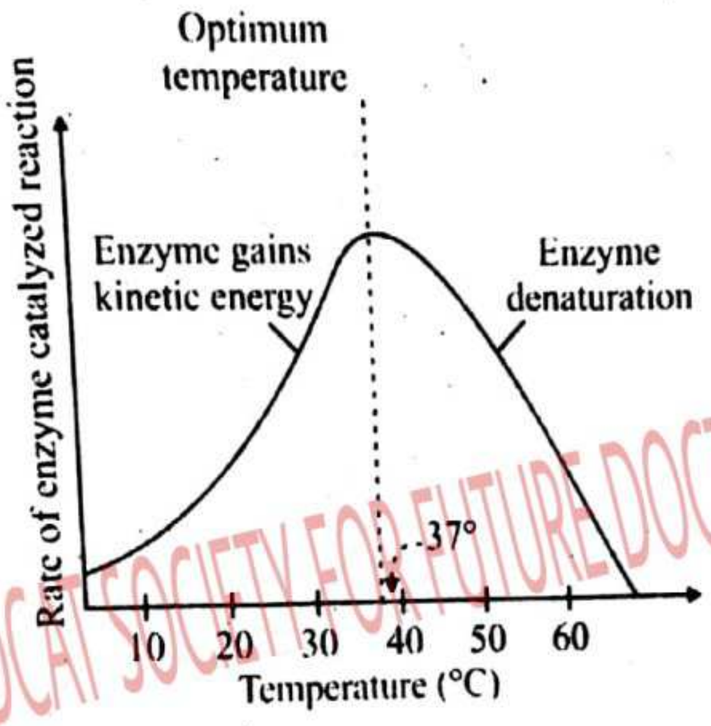
Increase in temperature speeds up the rate of enzyme catalyzed reactions, but only to a point. Every enzyme works at its maximum rate at a specific temperature called as the optimum temperature for that enzyme.

Examples:

- For most animal enzymes, optimum temperature is around body temperature (37 °C).
- ome plants enzymes such as urease has optimum temperature even up to 60 °C.

Graphical explanation:

If we plot a graph between temperature and rate or velocity of enzymatic reaction we get the curve as shown.



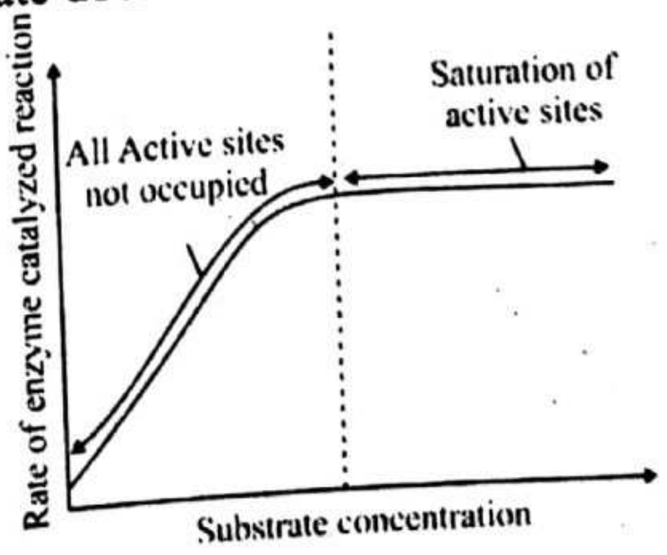
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Substrate concentration

Increase in substrate concentration, increases the rate of reaction.

If enzyme concentration is kept constant and amount of substrate in increased then rate is increased up to a limit because of the active sites of all enzymes are occupied (at high substrate concentration).

More substrate molecules do not find free active site. This state is called **saturation of active site** and reaction rate does not increase.



pH

Optimum pH:

All enzymes work at their maximum rate at narrow range of pH, called as the optimum pH. A slight change in this pH causes retardation in enzyme activity or blocks it completely. Every, enzyme has its specific optimum pH value. For example, pepsin (working in stomach) is active in acidic medium (pH=2) while trypsin (working in small intestine) shows its activity in alkaline medium (pH = 8–9).

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Inhibition of Enzyme

A molecule that binds with an enzyme and decreases its activity is known as enzyme inhibitor. Inhibition can be reversible or irreversible according to the type of interaction formed between the inhibitor and the enzyme.

Types of Inhibitors

Irreversible inhibitors	Reversible inhibitors
When the inhibitors react and form strong covalent bonds with the active sites of the enzyme, it is called irreversible inhibition. It is stable and irreversible.	The inhibition in which the activity of an enzyme is restored is called reversible inhibition. There are two types of reversible inhibition.

Competitive inhibition

A competitive inhibitor resembles the substrate. It can bind to the enzyme in the same way that the substrate does. When present in the active site the inhibitor prevents the normal substrate from binding. The effect of inhibitor is overcome by decreasing the concentration of normal substrate.

Non – competitive inhibition

A non-competitive inhibitor also reduces enzyme activity. The inhibitor usually binds at a separate binding site. It does not bind at the active site. When inhibitor binds at the second site (non-active site), it changes the shape of enzyme so that the shape of active site is changed and substrate can no longer bond to the active site.

Industrial application of enzyme

Enzymes are extensively used in different industries for fast chemical reactions. For example;

Industrial applications	Explanation
Food industry	Enzymes that break starch into simple sugars are used in the production of white bread, buns etc.
Brewing Industry	Enzymes break starch and proteins. The products are used by yeast for fermentation (to produce alcohol).
Paper Industry	Enzymes break starch to lower its viscosity that aids in making paper.
Biological detergent	Protease enzymes are used for the removal of protein stains from clothes. Amylase enzymes are used in dish washing to remove resistant starch residues.
Dairy Industry	Lipase enzymes are implemented during the production of cheese.
Starch Industry	Amylase, amyloglucosidease and Glucoamylase enzymes are used to convert starch into glucose and various syrups.
Biofuel industry	Cellulase enzymes are used to break down cellulose into sugars that can be fermented.
Contact Lense Cleaners	Protease enzymes are used to remove proteins on contact lens to prevent infections.
Rubber industry	Catalase enzymes are used to generate oxygen from peroxide to convert latex into foam rubber.
Photographic industry	Protease (Ficin) enzymes are applied to dissolve gelatin off scrap film, allowing recovery of its silver content.
Molecular biology	Restriction enzyme, DNA Ligase and polymerase enzymes are used to manipulate DNA in genetic engineering. More importantly in pharmacology, agriculture and medicine. It is also important in forensic science.

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TOPIC-20 ENVIRONMENTAL CHEMISTRY

COURSE CONTENTS

- Air Pollutants.
- Chemistry and causes of Acid Rain.
- Ozone and Chlorofluorocarbons (CFCs).

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Air pollution

The mixing of harmful substances in the atmosphere which damage the environment, human health and quality of life is called air pollution.

Main sources of air pollution:

The main sources of air pollution are as follows:

(i) Primary Pollutants:

(a) The waste products given out from chimneys of industrial units

(b) Exhaust of automobiles which may contain gases like

- Sulphur dioxide
- Sulphur trioxide
- Oxides of nitrogen
- Carbon monoxide
- Hydrocarbons
- Ammonia
- Compounds of fluorine
- Radioactive materials

(ii) Secondary Pollutants:

The primary pollutants in the atmosphere produce secondary pollutants through various reactions.

These are follows:

- Sulphuric acid
- Nitrogen monoxide (N_2O)
- Carbonic acid
- Hydrofluoric acid
- Peroxyacetyl nitrate (PAN)
- Ozone
- Aldehydes
- Ketones
- Peroxybenzol

All these compounds are toxic and their concentration in the atmosphere must be controlled.

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Some primary pollutants like carbon monoxide, oxides of nitrogen, oxides of sulphur and hydrocarbons along with their sources and adverse effects on living things have been discussed below.

(I) CARBON MONOXIDE

Sources:

(a) Natural:

Natural sources of carbon monoxide are

- Volcanic eruption
- Natural gas emission
- Oxidation of methane in the atmosphere

(b) Human Activities:

- Fuel burns in various types of transportations i.e. motor vehicles, railways, and air crafts. These sources release 75% of total carbon monoxide in the atmosphere.
- Carbon monoxide is emitted from forest fires, combustion of fossil fuel and agricultural products.

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▸ Carbon monoxide is also emitted from industries in which any type of fuel is burnt in air. These industries included iron and steel, petroleum, cement, brick kilns, paper and pulp etc.

▸ Incomplete combustion and dissociation of CO_2 at high temperature also produces CO.

Properties:

(i) It is a colourless, odourless gas.

(ii) It is soluble in water

(iii) It is three times lighter than air

(iv) It is a highly toxic gas.

(v) It causes suffocation if inhaled.

Poisoning effect of CO:

During breathing, we inhale oxygen which binds with Haemoglobin to form oxyhaemoglobin. Oxyhaemoglobin being unstable complex, decomposes to release oxygen which is used in cell activities. When CO is inhaled, it binds with haemoglobin to form carboxyhaemoglobin which is a stable complex. As a result, haemoglobin will not be available to transport oxygen for normal respiration.

Harmful effect of CO:

Exposure to high concentration of CO results in

▸ Headache ▸ Fatigue ▸ Unconsciousness

Exposure to CO for longer period eventually leads to death.

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Reversal of CO Poisoning:

The CO poisoning can be reversed by giving high pressure oxygen.

(II) NITROGEN OXIDES (NO_x)

Nitrogen gives five oxides. The gases nitric oxide, NO and nitrogen dioxide, NO_2 are frequently produced in the atmosphere. They are represented by NO_x.

Sources:

(a) Natural:

Bacterial action produces NO_x mainly NO.

(b) Human Activities:

(i) Nitrogen oxides are generally produced by combustion of fossil fuel i.e. coal, oil and natural gas

(ii) During the burning of oil in internal combustion engine, nitrogen and oxygen of air react to form NO.

$$N_2 + O_2 \xrightarrow{\text{High temperature}} 2NO$$

Nitrogen dioxide, NO_2 is produced when nitric oxide, NO, reacts with oxygen.

$$2NO + O_2 \longrightarrow 2NO_2$$

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How do the oxides of nitrogen reach the earth?

The residence time of NO and NO_2 in the atmosphere varies from **3–4 days**. Due to photochemical reactions, NO_x are converted to HNO_3 which is carried down in either rain fall or dust.

(III) SULPHUR OXIDES (SOx):

Sources:

The oxides of sulphur are sulphur dioxide SO_2 and sulphur trioxide, SO_3. They are represented by SO_x.

(a) Natural:

Most of SO_2 is produced by

- Volcanoes (67%)
- Oxidation of sulphur containing gases produced by decomposition of organic matter

(b) Human Activities:

- Combustion of coal which contains 1–9% sulphur.
- Burning of crude oil
- Burning of fossil fuel in power plants and petroleum industry.

The reactions are as follows:

$$S + O_2 \longrightarrow SO_2$$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

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Properties of SO_2 and SO_3

(i) These gases have pungent odour.

(ii) These gases are very irritant and suffocating.

Adverse Effects:

- SO_2 and SO_3 through various reactions in the atmosphere form **sulphate aerosols**. These **aerosols** cause severe respiratory troubles particularly among older people.
- SO_2 is the major source of acid deposition in the atmosphere.

(IV) HYDROCARBONS

Sources:

(a) Natural:

(i) Large quantities of hydrocarbons are emitted by different trees and plants in the atmosphere.

(ii) Paddy fields produce a significant amount of methane in the atmosphere.

(iii) Anaerobic decomposition of organic matter by bacteria in water sediments and in soils.

$$2CH_2O \xrightarrow{\text{Bacteria}} CO_2 + CH_4$$

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Residence time of methane:

The mean residence time of methane is about **3–7 years** in the atmosphere.

(b) Human Activities:

Hydrocarbons are dispersed in the atmosphere due to

- Automobiles, major source of hydrocarbons.
- Coal
- Wood
- Incinerator
- Refuse burning
- Solvent evaporators

Effect of air pollutants/polluted air on environment

Smog [Additional]

It has two types

(i) Reducing smog

- Contain higher concentration of SO_2
- It is mainly produced by combustion of coal

(ii) Oxidizing or photochemical smog

- Contain higher concentration of oxidants (e.g. O_3 etc.)
- It is produced in the presence of water droplets and chemical reactions of pollutants in the air.

Characteristics

- It is a yellowish brownish grey haze.
- It has unpleasant odour because of its gaseous component.
- The yellow colour in photochemical smog is due to the presence of nitrogen dioxide (NO_2).

The following conditions are required for the formation of smog.

- There must be sufficient NO, hydrocarbons and volatile organic compounds (VOC) emitted by the vehicular traffic.
- Sunlight, so that some of the chemical reactions may occur at a rapid rate.
- The movement of air mass must be little so that reactions are not disturbed.

POINT TO PONDER

The overall result of photochemical smog in afternoon is the built up of oxidizing agents. Such as H_2O_2, HNO_3, peroxyacetyl nitrate (PAN) and ozone in the air. PAN is an eye irritant and is also toxic to plants.

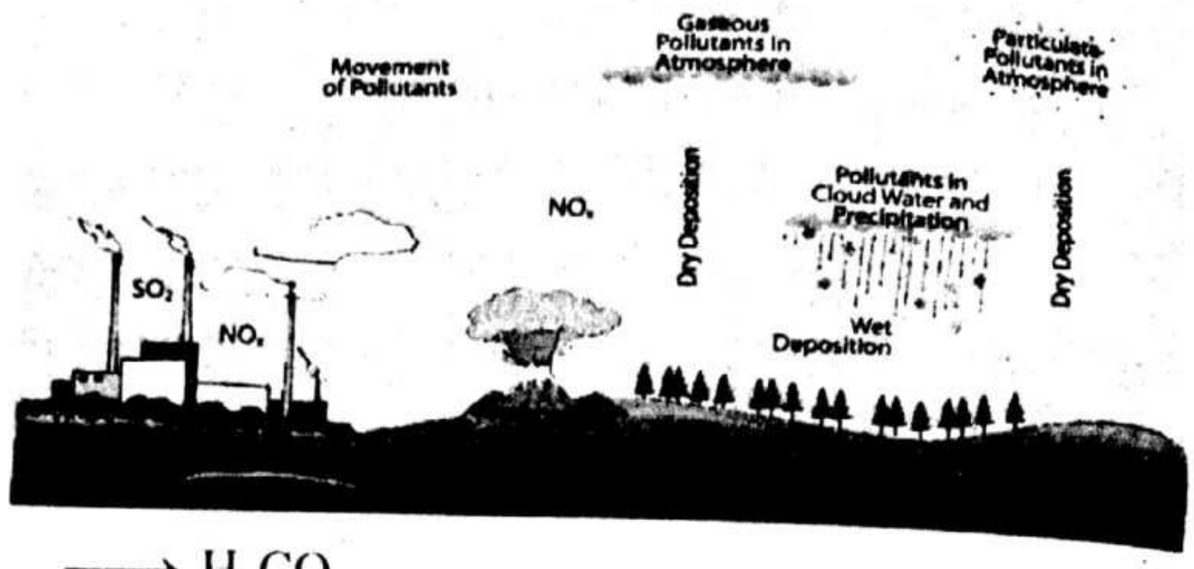
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CHEMISTRY AND CAUSES OF ACID RAIN

Discovered by Angus Smith 1650, a serious environment problem in 1950's, initially referred as precipitation, which is more acidic than natural rain

- **The pH of unpolluted rain water should be 5.6 the rain water having pH less than 5 is considered truly acidic**



$$H_2O_{(l)} + CO_{2(g)} \longrightarrow H_2CO_{3(aq)}$$

$$SO_2 + 1/2O_2 + H_2O \xrightarrow{\text{Hydrocarbons, smoke, metal oxides}} H_2SO_4$$

$$2NO_2 + H_2O + \tfrac{1}{2}O_2 \longrightarrow 2HNO_3$$

- The acid deposition includes both wet (rain, snow, fog) and dry acidic deposition.
- In some countries due to release of HCl by volcanic eruption there is temporary acid rain.

Harmful effects

ACIDIFICATION
- Rock
- Soil
- Buildings

Al, Hg, Pb, Ca — These heavy metal are the fishes. The increased concentr the gills of fishes and c

Acidification of Soil
Can leach nutrients
Damaging
- Leaves
- Plants
- Growth of forest

Damaging Building Materials
Such as
- Steel
- Paint
- Plastic
- Cement
- Masonry work
- Sculptural work especially marble and lime stone

POINT TO PONDER

Sulphur dioxide is one of the causes of acid rain. It is formed by the combustion of coal containing high sulphur contents.

OZONE AND CHLOROFLUOROCARBONS (CFCs)

Ozone is low boiling point gas and an allotrope of oxygen.

Presence

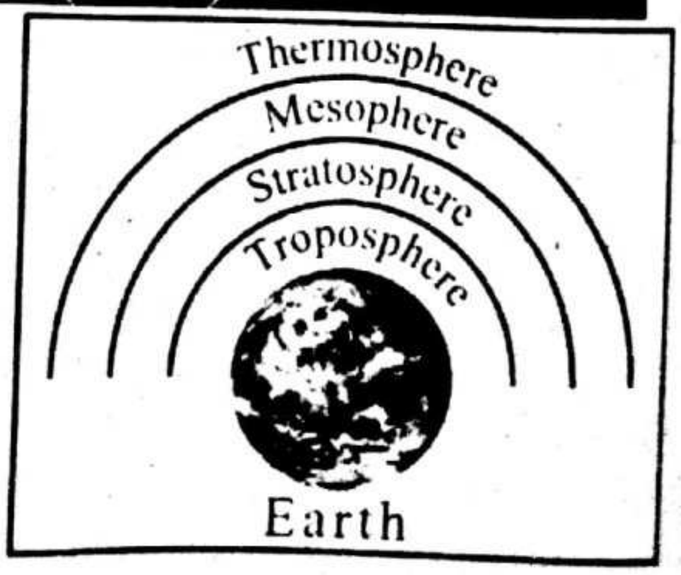
The main ozone layer exists in the stratosphere which is approximately between 15 to 40 kilometers from the earth. It is just above the troposphere which exists up to 15 kilometers from the earth.

Amount of Ozone in atmosphere

It is present in small concentrations throughout the atmosphere.

The amount of ozone in the atmosphere is expressed in **Dobson units (DU)**

The normal amount of ozone in stratosphere is about **350 DU.**



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Production

In tropical region usually in mesosphere that diffuse down in stratosphere from mesosphere.

$$O_2 \xrightarrow{\text{Dissociates}} O^{\bullet} + O^{\bullet}$$

$$O + O_2 \longrightarrow O_3$$

Function

Filter the harmful radiation of sunlight like UV.

Depletion of Ozone

- In 1980's a large hole in the ozone layer over Antarctic was discovered.
- Since mid 1970s, the thickness of the ozone layer has been decreasing over Antarctic during the spring time.
- By the mid 1980s, loss in ozone at some places over Antarctica reaches to about 50% of the total overhead amount.
- **The region in which ozone depletes substantially in every year during Sep-Nov is now termed as "ozone hole".**

Role of CFCs in Destroying Ozone

CFCs used as refrigerants in air conditioners or in aerosol sprays. CFCs diffuse from troposphere to stratosphere and form free radical due to UV radiations.

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$$CFCl_3 \xrightarrow{UV} CFCl_2^{\bullet} + Cl^{\bullet}$$

$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O \longrightarrow Cl^{\bullet} + O_2$$

A single chloride free radical can destroy up to 100,000 ozone molecules.

Effect of O_3 as Pollutant

- Health problems
- Damages eyes
- Decreases the elasticity of lung tissues
- Aggravates Asthma, Coughing and Chest Discomfort

Paints and other materials

- Attacks rubber
- Reduces durability and appearance of paint
- Causes fabric dyes to fade

POINT TO PONDER

- **Ozone is a polar molecule.**
- The ozone present in troposphere is called bad ozone. Act as a pollutant.
- The ozone present in stratosphere is called good ozone.
- However, ozone is also used in subway stations for killing bacteria, and is also as a decolourizing agent in flour industry.

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